

# **Design, Synthesis and Self-Assembly of Polymeric Building Blocks and Novel Ionic Liquids, Ionic Liquid-Based Polymers and Their Properties**

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## **ABSTRACT**

The convergence of supramolecular and polymer sciences has led to the construction of analogs of traditional covalently-constructed polymeric structures and architectures by supramolecular methods. Host-guest complexations of polymers are also possible through well-defined synthesis of polymeric building blocks, for novel supramolecular polymers.

Monotopic polymeric building blocks were synthesized by controlled radical polymerizations with a crown or paraquat initiator. The combinations of terminal and central functionalities of host and guest polymeric building blocks provided chain-extended and tri-armed homopolymers, and diblock and tri-armed copolymers.

A supramolecular graft copolymer was formed from a main-chain poly(ester crown ether) and a paraquat terminated polystyrene. This comb-like copolymer was characterized by a large viscosity increase. A four-armed polystyrene-*b*-poly(*n*-butyl methacrylate) was synthesized from a pseudorotaxane macroinitiator derived from a complex of a crown-centered polystyrene and a difunctional paraquat compound. A single peak with higher molecular weight from size exclusion chromatography proved the copolymer formation.

Supramolecular interactions enhance the ionic conductivity of semi-crystalline ionic polymers; the ionic conductivity of a C<sub>6</sub>-polyviologen and dibenzo-30-crown-10 mixture was 100 times higher than the polyviologen itself. However, ionic conductivities of amorphous polyviologens with polyethers were influenced only by glass transition temperature changes.

New imidazolium ionic liquid monomers and imidazolium based polymers were synthesized for potential applications in electroactive devices, such as actuators. Structure-property relationships for pendant imidazolium polyacrylates and main-chain imidazolium polyesters were investigated. Terminal ethyleneoxy moieties enhanced ionic

conduction 2~3 times; however, the alkyl chain length effect was negligible. For the imidazolium polyesters, higher ion conductivities result from 1) mono-imidazolium over bis-imidazolium, and 2) bis(trifluoromethanesulfonyl)imide polymers over hexafluorophosphate analogs. A semi-crystalline hexafluorophosphate polyester with C<sub>10</sub>-sebacate-C<sub>10</sub>, displayed 400-fold higher ionic conductivity than the amorphous C<sub>6</sub>-sebacate-C<sub>6</sub> analogue, suggesting the formation of a biphasic morphology in the former polyester.

New dicationic imidazolium salts have interesting features. 1,2-Bis[N-(N'-alkylimidazolium)]ethane salts stack well in the solid state and possess multiple solid-solid phase transitions. They complex with dibenzo-24-crown-8 and a dibenzo-24-crown-8 based pyridyl cryptand with  $K_a = \sim 30$  and  $360 \text{ M}^{-1}$ , respectively. Some of these dicationic imidazolium salts have low entropies of fusion, typical of plastic crystals.

These newly discovered imidazolium homopolymers have ionic conductivities up to  $10^{-4} \text{ (S cm}^{-1}\text{)}$ ; however, better properties are still required. Well-designed block copolymers should provide both good electrical and mechanical properties from bicontinuous morphologies, such ion channels.

*Dedicated to my wife Kyooyoung Kim  
and my parents, Kangryung Lee and Ransook Shin  
for support and love*

나의 처 김규영과

나의 부모님 이강룡, 신난숙님의

헌신적인 지원과 사랑에 감사드리며



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# Table of Contents

|                                                                                                                                                           |           |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------|-----------|
| <b>Chapter 1. Introduction and Dissertation Statement .....</b>                                                                                           | <b>1</b>  |
| <b>Part I: Design, Synthesis and Self-Assembly of Polymeric Building Blocks .....</b>                                                                     | <b>4</b>  |
| <b>Chapter 2. Synthesis of Rotaxanes, Cryptands and Polyrotaxanes (Literature Review)</b>                                                                 |           |
| .....                                                                                                                                                     | 4         |
| Introduction.....                                                                                                                                         | 4         |
| Synthesis of crown ethers .....                                                                                                                           | 9         |
| Cryptands .....                                                                                                                                           | 15        |
| Polypseudorotaxanes and Polyrotaxanes .....                                                                                                               | 17        |
| Prospective Research .....                                                                                                                                | 33        |
| References.....                                                                                                                                           | 36        |
| <b>Chapter 3. Synthesis of Complementary Host- and Guest-Functionalized Polymeric Building Blocks and Their Self-Assembling Behavior .....</b>            | <b>43</b> |
| Abstract.....                                                                                                                                             | 43        |
| Introduction.....                                                                                                                                         | 44        |
| Results and Discussion .....                                                                                                                              | 46        |
| Conclusions.....                                                                                                                                          | 61        |
| Experimental .....                                                                                                                                        | 61        |
| Acknowledgements.....                                                                                                                                     | 67        |
| References.....                                                                                                                                           | 67        |
| <b>Chapter 4. Supramolecular Graft Copolymer from a Crown Polyester and a Complementary Paraquat Terminated Polystyrene Guest.....</b>                    | <b>70</b> |
| Abstract.....                                                                                                                                             | 70        |
| Introduction.....                                                                                                                                         | 70        |
| Results and Discussion .....                                                                                                                              | 71        |
| Conclusions.....                                                                                                                                          | 75        |
| Acknowledgements.....                                                                                                                                     | 76        |
| References.....                                                                                                                                           | 76        |
| <b>Chapter 5. Supramolecular Four-Armed Star Copolymer (Miktoarm Star) via Host-Guest Complexation and Nitroxide Mediated Radical Polymerization.....</b> | <b>78</b> |
| Abstract.....                                                                                                                                             | 78        |

|                                                                                                                                                                 |            |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------|------------|
| Introduction.....                                                                                                                                               | 78         |
| Results and Discussion .....                                                                                                                                    | 79         |
| Conclusions.....                                                                                                                                                | 83         |
| Experimental .....                                                                                                                                              | 84         |
| Acknowledgements.....                                                                                                                                           | 85         |
| References.....                                                                                                                                                 | 85         |
| <b>Chapter 6. Rotaxane-type Hyperbranched Polymers from a Homoditopic Crown Ether<br/>Host and a Monotopic Paraquat Guest Containing a Blocking Group .....</b> | <b>89</b>  |
| Abstract.....                                                                                                                                                   | 89         |
| Introduction.....                                                                                                                                               | 90         |
| Results and Discussion .....                                                                                                                                    | 91         |
| Conclusions.....                                                                                                                                                | 104        |
| Experimental .....                                                                                                                                              | 105        |
| Acknowledgements.....                                                                                                                                           | 110        |
| References.....                                                                                                                                                 | 111        |
| <b>Chapter 7. Ion Conduction in a Semi-Crystalline Polyviologen and Its Polyether<br/>Mixtures .....</b>                                                        | <b>112</b> |
| Abstract.....                                                                                                                                                   | 112        |
| Introduction.....                                                                                                                                               | 112        |
| Results and Discussion .....                                                                                                                                    | 113        |
| Conclusions.....                                                                                                                                                | 119        |
| Experimental .....                                                                                                                                              | 120        |
| Acknowledgements.....                                                                                                                                           | 121        |
| References.....                                                                                                                                                 | 121        |
| <b>Chapter 8. Ion Conduction in Amorphous Polyviologens and Their Polyether Mixtures<br/>.....</b>                                                              | <b>123</b> |
| Abstract.....                                                                                                                                                   | 123        |
| Introduction.....                                                                                                                                               | 123        |
| Results and Discussion .....                                                                                                                                    | 124        |
| Conclusions.....                                                                                                                                                | 129        |
| Experimental .....                                                                                                                                              | 130        |
| Acknowledgements.....                                                                                                                                           | 131        |
| References.....                                                                                                                                                 | 131        |

|                                                                                                                            |            |
|----------------------------------------------------------------------------------------------------------------------------|------------|
| <b>Part II: New Ionic Liquids, Ionic Liquid-Based Polymers and Their Properties.....</b>                                   | <b>133</b> |
| <b>Chapter 9. Ionic Liquid Monomers and Ionic Polymers (Literature Review).....</b>                                        | <b>133</b> |
| Design of Polymers with Ionic Liquid Moieties.....                                                                         | 133        |
| Ionic Polymers from Ionic Liquid Monomers .....                                                                            | 138        |
| Conclusions and Prospective Research.....                                                                                  | 146        |
| References.....                                                                                                            | 148        |
| <b>Chapter 10. 1,2-Bis[N-(N'-alkylimidazolium)]ethane Salts as New Guests for Crown<br/>Ethers and Cryptands.....</b>      | <b>151</b> |
| Abstract.....                                                                                                              | 151        |
| Introduction.....                                                                                                          | 151        |
| Results and Discussion .....                                                                                               | 152        |
| Conclusions.....                                                                                                           | 157        |
| Experimental .....                                                                                                         | 158        |
| Acknowledgements.....                                                                                                      | 163        |
| Supporting Information.....                                                                                                | 164        |
| References.....                                                                                                            | 167        |
| <b>Chapter 11. Structure and Properties of N,N-Alkylene Bis(N'-alkylimidazolium) Salts<br/>.....</b>                       | <b>170</b> |
| Abstract.....                                                                                                              | 170        |
| Introduction.....                                                                                                          | 170        |
| Results and Discussion .....                                                                                               | 171        |
| Conclusions.....                                                                                                           | 181        |
| Experimental .....                                                                                                         | 181        |
| Acknowledgements.....                                                                                                      | 187        |
| Supporting Information.....                                                                                                | 188        |
| References.....                                                                                                            | 191        |
| <b>Chapter 12. 1,2-Bis[N-(N'-alkylimidazolium)]ethane Salts as a New Class of Organic<br/>Ionic Plastic Crystals .....</b> | <b>195</b> |
| Abstract.....                                                                                                              | 195        |
| Introduction.....                                                                                                          | 195        |
| Results and Discussion .....                                                                                               | 196        |
| Conclusions.....                                                                                                           | 207        |
| Acknowledgements.....                                                                                                      | 208        |
| References.....                                                                                                            | 209        |

|                                                                                                                                         |            |
|-----------------------------------------------------------------------------------------------------------------------------------------|------------|
| <b>Chapter 13. Ion Conduction in Imidazolium Acrylate Ionic Liquids and their Polymers</b>                                              | 210        |
| Abstract.....                                                                                                                           | 210        |
| Introduction.....                                                                                                                       | 210        |
| Results and Discussion .....                                                                                                            | 211        |
| Conclusions.....                                                                                                                        | 223        |
| Experimental.....                                                                                                                       | 224        |
| Acknowledgements.....                                                                                                                   | 229        |
| References.....                                                                                                                         | 230        |
| <b>Chapter 14. Synthesis of Poly(imidazolium acrylate)s and Effects of Chemical Structure on Thermal and Electrical Properties.....</b> | <b>232</b> |
| Abstract.....                                                                                                                           | 232        |
| Introduction.....                                                                                                                       | 232        |
| Results and Discussion .....                                                                                                            | 233        |
| Conclusions.....                                                                                                                        | 240        |
| Experimental.....                                                                                                                       | 241        |
| Acknowledgements.....                                                                                                                   | 247        |
| References.....                                                                                                                         | 248        |
| <b>Chapter 15. Synthesis and Properties of Imidazolium Polyesters.....</b>                                                              | <b>249</b> |
| Abstract.....                                                                                                                           | 249        |
| Introduction.....                                                                                                                       | 250        |
| Results and Discussion .....                                                                                                            | 251        |
| Conclusions.....                                                                                                                        | 263        |
| Experimental.....                                                                                                                       | 264        |
| Acknowledgements.....                                                                                                                   | 270        |
| References.....                                                                                                                         | 270        |
| <b>Chapter 16. Synthesis of Imidazolium Dienes and Precision Ionic Polyolefins .....</b>                                                | <b>272</b> |
| Abstract.....                                                                                                                           | 272        |
| Introduction.....                                                                                                                       | 272        |
| Results and Discussion .....                                                                                                            | 273        |
| Conclusions.....                                                                                                                        | 278        |
| Experimental.....                                                                                                                       | 278        |
| Acknowledgements.....                                                                                                                   | 282        |
| References.....                                                                                                                         | 283        |

|                                                      |            |
|------------------------------------------------------|------------|
| <b>Chapter 17. Conclusions and Future Work .....</b> | <b>285</b> |
| References.....                                      | 289        |

# List of Schemes

## PART I. Design, Synthesis and Self-Assembly of Polymeric Building Blocks

### Chapter 2. Synthesis of Rotaxanes, Cryptands and Polyrotaxanes (Literature Review)

|             |                                                                                                                                                                                                                                                                                                                                          |    |
|-------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Scheme 2-1  | Three different ways to synthesize a [2]rotaxane. ....                                                                                                                                                                                                                                                                                   | 5  |
| Scheme 2-2  | Synthesis of 18-crown-6 ( <b>10</b> ) from tri(ethylene glycol) and tri(ethylene glycol)ditosylate.....                                                                                                                                                                                                                                  | 9  |
| Scheme 2-3  | Synthesis of BMP32C10 derivatives containing one functional group on each aromatic ring .....                                                                                                                                                                                                                                            | 10 |
| Scheme 2-4  | Regioselective syntheses of DB24C8 derivatives: (a) cis-DB24C8 dimethyl ester <b>13</b> , (b) trans-DB24C8 dimethyl ester <b>14</b> . ....                                                                                                                                                                                               | 11 |
| Scheme 2-5  | Synthesis of novel crown ethers by Chiu group. ....                                                                                                                                                                                                                                                                                      | 12 |
| Scheme 2-6  | Synthesis of aza-18-crown-6 ( <b>19</b> ) from diethanolamine. ....                                                                                                                                                                                                                                                                      | 13 |
| Scheme 2-7  | Synthesis of thiacycrown ether by SN <sub>2</sub> cyclization. ....                                                                                                                                                                                                                                                                      | 14 |
| Scheme 2-8  | Synthesis of [2,2,2]-cryptand under high dilution. ....                                                                                                                                                                                                                                                                                  | 15 |
| Scheme 2-9  | Synthetic routes for main-chain polypseudorotaxanes and polyrotaxanes. ....                                                                                                                                                                                                                                                              | 19 |
| Scheme 2-10 | Synthetic routes for side-chain polypseudorotaxanes and polyrotaxanes.....                                                                                                                                                                                                                                                               | 20 |
| Scheme 2-11 | Synthesis of poly(azomethine)-based polyrotaxane with $\beta$ -CD by Geckeler and co-workers.....                                                                                                                                                                                                                                        | 22 |
| Scheme 2-12 | Preparation of a 1D polyrotaxane based on CB[6]. ....                                                                                                                                                                                                                                                                                    | 31 |
| Scheme 2-13 | Preparation of a polypseudorotaxane based on CB[6] and polyviologen.....                                                                                                                                                                                                                                                                 | 32 |
| Scheme 2-14 | New polypseudorotaxanes and polyrotaxanes, which will be synthesized.<br>When R = H in <b>39</b> and <b>41</b> , they are polypseudorotaxanes; when R = CAr <sub>3</sub> or CONH- <i>p</i> -C <sub>6</sub> H <sub>4</sub> CAr <sub>3</sub> , <b>39</b> and <b>41</b> are polyrotaxanes. ....                                             | 34 |
| Scheme 2-15 | Mechanically interlocked hyperbranched polymers synthesized by the Gibson group. In Scheme (a), polypseudorotaxane <b>42</b> was formed from monomer with one crown ether and two paraquats. In scheme (b), AB <sub>2</sub> type monomer was used to form a hyperbranched polypseudorotaxane <b>43</b> and polyrotaxane <b>44</b> . .... | 34 |



### **Chapter 3. Synthesis of Complementary Host- and Guest-Functionalized Polymeric Building Blocks and Their Self-Assembling Behavior**

|            |                                                                                                                                         |    |
|------------|-----------------------------------------------------------------------------------------------------------------------------------------|----|
| Scheme 3-1 | Synthesis of paraquat terminated polystyrene <b>11</b> by SFRP.....                                                                     | 46 |
| Scheme 3-2 | Synthesis of paraquat terminated PMMA <b>13</b> by ATRP.....                                                                            | 48 |
| Scheme 3-3 | Synthesis of crown ether (MPPP33C10) terminated polystyrene <b>15</b> by ATRP.<br>.....                                                 | 48 |
| Scheme 3-4 | Synthesis of crown ether (BMP32C10) centered polystyrene <b>17</b> by ATRP....                                                          | 49 |
| Scheme 3-5 | Proposed mechanism for generation of the structure <b>20</b> series from the<br>cleavage of the PMMA main chain by a rearrangement..... | 52 |
| Scheme 3-6 | Proposed mechanism for generation of the structure <b>21</b> series from the<br>cleavage of the PMMA main chain by a rearrangement..... | 52 |
| Scheme 3-7 | Proposed mechanism for generation of the structure <b>22</b> series by a McLafferty<br>type rearrangement.....                          | 54 |

### **Chapter 4. Supramolecular Graft Copolymer from a Crown Polyester and a Complementary Paraquat Terminated Polystyrene Guest**

|            |                                                                                                                                                                                                 |    |
|------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Scheme 4-1 | Schematic illustration of the formation of a supramolecular graft copolymer <b>3</b><br>from poly(ester crown ether) <b>1</b> and paraquat polystyrene guest <b>2</b> in solution.....<br>..... | 71 |
|------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|

### **Chapter 5. Supramolecular Four-Armed Star Copolymer (Miktoarm Star) via Host-Guest Complexation and Nitroxide Mediated Radical Polymerization**

|            |                                                                                                                                                                                                                                                                                            |    |
|------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Scheme 5-1 | Schematic illustration of the formation of a supramolecular polystyrene-<br>poly(butyl methacrylate) star block copolymeric [3]rotaxane <b>4</b> from a<br>pseudorotaxane complex <b>3</b> of crown centered polystyrene ( <b>1</b> ) and<br>bis(TEMPO) paraquat initiator <b>2</b> . .... | 80 |
|------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|

### **Chapter 6. Rotaxane-type Hyperbranched Polymers from a Homoditopic Crown Ether Host and a Monotopic Paraquat Guest Containing a Blocking Group**

|            |                                                                                                                                                                                                                                                                                                                                                                                                |
|------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Scheme 6-1 | Schematic illustration of two previously synthesized hyperbranched polymers<br>using self-assembly of crown ethers and paraquat derivatives: (a) a<br>supramolecular hyperbranched polymer from a covalent AB <sub>2</sub> pseudorotaxane<br>precursor containing a crown ether and two paraquat moieties, and (b) a<br>mechanically interlocked rotaxane type of hyperbranched polymer from a |
|------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

|            |                                                                                                                                                                                                                                                                                             |    |
|------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
|            | monofunctional crown ether and a difunctional paraquat via <i>in situ</i> formation of an AB <sub>2</sub> monomer. ....                                                                                                                                                                     | 90 |
| Scheme 6-2 | Schematic illustration of mechanically interlocked hyperbranched polymers from a difunctional crown ether ( <b>1</b> ) and monofunctional paraquat derivatives (m = 5, n = 6 or m, n = 10).....                                                                                             | 92 |
| Scheme 6-3 | Synthesis of paraquat carboxylic acid derivatives containing a blocking group as monofunctional guest monomers. ....                                                                                                                                                                        | 93 |
| Scheme 6-4 | Esterifications of <b>1</b> and the paraquat carboxylic derivatives <b>8</b> (or <b>9</b> ). Three basic covalent structures are possible after the esterifications: <b>1</b> , <b>12</b> and <b>14</b> (for <b>HP18</b> ), and <b>1</b> , <b>13</b> and <b>15</b> (for <b>HP19</b> ) ..... | 94 |

## **Chapter 7. Ion Conduction in a Semi-Crystalline Polyviologen and Its Polyether Mixtures**

|            |                                                  |     |
|------------|--------------------------------------------------|-----|
| Scheme 7-1 | Synthesis of polyviologen TFSI ( <b>1</b> )..... | 114 |
|------------|--------------------------------------------------|-----|

## **Chapter 8. Ion Conductions in Amorphous Polyviologens and Their Polyether Mixtures**

|            |                                                                                            |     |
|------------|--------------------------------------------------------------------------------------------|-----|
| Scheme 8-1 | Synthesis of amorphous polyviologen TFSI <b>6</b> with two different alkylene spacers..... | 124 |
|------------|--------------------------------------------------------------------------------------------|-----|

## **PART - II. New Ionic Liquids, Ionic Liquid-Based Polymers and Their Properties**

### **Chapter 10. 1,2-Bis[N-(N'-alkylimidazolium)]ethane Salts as New Guests for Crown Ethers and Cryptands**

|             |                                                           |     |
|-------------|-----------------------------------------------------------|-----|
| Scheme 10-1 | Synthesis of alkylene bis(N-alkylimidazolium) salts. .... | 152 |
|-------------|-----------------------------------------------------------|-----|

### **Chapter 11. Structure and Properties of N,N-Alkylene Bis(N'-alkylimidazolium) Salts**

|             |                                                                |     |
|-------------|----------------------------------------------------------------|-----|
| Scheme 11-1 | Synthesis of alkylene bis[N-(N'-alkylimidazolium)] salts ..... | 172 |
|-------------|----------------------------------------------------------------|-----|

### **Chapter 12. 1,2-Bis[N-(N'-alkylimidazolium)]ethane Salts as a New Class of Organic Ionic Plastic Crystals**

|             |                                                                |     |
|-------------|----------------------------------------------------------------|-----|
| Scheme 12-1 | Synthesis of alkylene bis[N-(N'-alkylimidazolium)] salts ..... | 197 |
|-------------|----------------------------------------------------------------|-----|

### **Chapter 13. Ion Conduction in Imidazolium Acrylate Ionic Liquids and their Polymers**

|             |                                                                                                                                                                                                       |     |
|-------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Scheme 13-1 | Synthesis of di(ethyleneoxy) and butyl substituted imidazolium IL monomers, effectively defining the structure of the four imidazolium monomers <b>3a</b> , <b>3b</b> , <b>3c</b> and <b>3d</b> ..... | 212 |
| Scheme 13-2 | Polymerization of the imidazolium monomers, effectively defining the structure of the four imidazolium polymers <b>4a</b> , <b>4b</b> , <b>4c</b> and <b>4d</b> .....                                 | 213 |

### **Chapter 14. Synthesis of Poly(imidazolium acrylate)s and Effect of Chemical Structure on Thermal and Electrical Properties**

|             |                                                       |     |
|-------------|-------------------------------------------------------|-----|
| Scheme 14-1 | Synthesis of imidazolium acrylate monomers. ....      | 234 |
| Scheme 14-2 | Polymerization of imidazolium acrylate monomers. .... | 234 |

### **Chapter 15. Synthesis and Properties of Imidazolium Polyesters**

|             |                                                                                                                                                                                                                                                                                                                                          |     |
|-------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Scheme 15-1 | Synthesis of 1,3-bis( $\omega$ -hydroxyalkyl)imidazolium salts. ....                                                                                                                                                                                                                                                                     | 252 |
| Scheme 15-2 | Synthesis of 1,2-bis[N-(N'-hydroxylalkylimidazolium)]ethane salts.....                                                                                                                                                                                                                                                                   | 252 |
| Scheme 15-3 | Polyesterifications of dihydroxy imidazolium salts and sebacoyl chloride. The two imidazolium units are regularly placed in <b>4a-d</b> and <b>5a-d</b> ; in other words, the distances between imidazolium units are fixed. However, the imidazolium cationic units are randomly distributed in polymers <b>4e</b> and <b>4f</b> . .... | 255 |

### **Chapter 16. Synthesis of Imidazolium Dienes and Precision Ionic Polyolefins**

|             |                                                                                                                             |     |
|-------------|-----------------------------------------------------------------------------------------------------------------------------|-----|
| Scheme 16-1 | Synthesis of ionic liquid monomers for in-chain imidazolium polymer preparation. ....                                       | 274 |
| Scheme 16-2 | Synthesis of ionic liquid monomer <b>8</b> for ionomer preparation. ....                                                    | 274 |
| Scheme 16-3 | Modified ADMET polymerization conditions for preparation of ionenes and ionomers from imidazolium based ionic liquids. .... | 275 |

# List of Figures

## PART I. Design, Synthesis and Self-Assembly of Polymeric Building Blocks

### Chapter 2. Synthesis of Rotaxanes, Cryptands and Polyrotaxanes (Literature Review)

|             |                                                                                                                                                                                                                                                                                                                  |    |
|-------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Figure 2-1  | Schematic presentation of a [2]pseudorotaxane <b>1</b> , a [2]rotaxane <b>2</b> , and a [2]catenane <b>3</b> . The number inside a bracket [ ] means the number of threading or interlocked species .....                                                                                                        | 4  |
| Figure 2-2  | An example of a [2]rotaxane <b>4</b> based on metal coordination.....                                                                                                                                                                                                                                            | 6  |
| Figure 2-3  | An example of a [2]pseudorotaxane <b>5</b> , based on hydrogen bonding interaction, and its X-ray crystal structure. ....                                                                                                                                                                                        | 6  |
| Figure 2-4  | The pH responsive rotaxanes formed by hydrogen bonding. In acidic conditions, crown ether binds the dibenzyl ammonium ion but it moves to the paraquat species in basic conditions. ....                                                                                                                         | 7  |
| Figure 2-5  | An example of [2]pseudorotaxane formation based on $\pi$ - $\pi$ stacking interactions and its X-ray crystal structure. ....                                                                                                                                                                                     | 8  |
| Figure 2-6  | Representative dibenzo-crown ethers for complexation with several guest ions . ....                                                                                                                                                                                                                              | 10 |
| Figure 2-7  | Bis(1,5-naphtho) crown ethers: 1/5DNP38C10 and 1/5DNP35C9.....                                                                                                                                                                                                                                                   | 11 |
| Figure 2-8  | An example of novel lariat ethers <b>17</b> , which have no nitrogen, and methanofullerene-crown ether <b>18</b> . ....                                                                                                                                                                                          | 12 |
| Figure 2-9  | Synthesis of diaza-18-crown-6 ( <b>20</b> ) from diacyl chloride and diamine.....                                                                                                                                                                                                                                | 13 |
| Figure 2-10 | Several heteroaromatic macrocycles containing nitrogens synthesized by the Bradshaw.....                                                                                                                                                                                                                         | 14 |
| Figure 2-11 | Several thiacycrown ethers synthesized by the Bradshaw group .....                                                                                                                                                                                                                                               | 14 |
| Figure 2-12 | Cryptands containing nitrogen atoms synthesized by the Bradshaw group.....                                                                                                                                                                                                                                       | 15 |
| Figure 2-13 | Several examples of cryptands synthesized by the Gibson group. ....                                                                                                                                                                                                                                              | 16 |
| Figure 2-14 | Solid state structure of cryptate between a BMP32C10-basedcryptatend and dimethyl paraquat.....                                                                                                                                                                                                                  | 16 |
| Figure 2-15 | Types of polypseudorotaxanes and polyrotaxanes. <b>A</b> and <b>B</b> are main-chain polypseudorotaxanes; <b>C</b> and <b>D</b> are side-chain polypseudorotaxanes; <b>E</b> , <b>F</b> , <b>G</b> , <b>H</b> and <b>I</b> are main-chain polyrotaxanes; <b>J</b> and <b>K</b> are side-chain polyrotaxanes. ... | 17 |

|             |                                                                                                                                                                                         |    |
|-------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Figure 2-16 | Necklace like polyrotaxane based on PEG and $\alpha$ -CD by Harada et al. ....                                                                                                          | 21 |
| Figure 2-17 | Poly(para-phenylenevinylene) rotaxanes by Suzuki coupling. ....                                                                                                                         | 22 |
| Figure 2-18 | (a) Cross-linked hydrolyzable hydrogels consisting of CDs and PEG chains, (b) PEG hydrogels containing CDs and Z-L-phenylalanine. ....                                                  | 23 |
| Figure 2-19 | Polypseudorotaxanes based on polyurethane by step-growth polymerization in the presence of crown ethers. ....                                                                           | 25 |
| Figure 2-20 | The number of crown ethers per repeating unit polystyrene-based polypseudorotaxane. ....                                                                                                | 26 |
| Figure 2-21 | Cross-linked polyrotaxanes via exo or endo esterification under diglyme. ....                                                                                                           | 27 |
| Figure 2-22 | The formation of linear supramolecular polymers <b>31</b> by strong interaction between crown ethers and dibenzyl ammonium cations. ....                                                | 27 |
| Figure 2-23 | The equilibrium formation of dendritic [2]-, [3]- and [4]-polypseudorotaxanes ( <b>32-34</b> ) from crown ether-functionalized dendrons and a complementary homotritopic molecule. .... | 28 |
| Figure 2-24 | The new way for fabrication of a star polymer <b>35</b> by self-assembly between a homotritopic tris(BMP32C10) and monotopic paraquat-terminated polystyrene. ....                      | 29 |
| Figure 2-25 | A new side-chain polypseudorotaxane containing crown ether rings as a part of the polymer backbone and paraquats as a guest. ....                                                       | 29 |
| Figure 2-26 | Side-chain polyrotaxanes via radical polymerization by the Takata group. ....                                                                                                           | 30 |
| Figure 2-27 | Polypseudorotaxane with cyclobis(paraquat-phenylene) as the cyclic component. ....                                                                                                      | 33 |
| Figure 2-28 | A new mechanically interlocked hyperbranched polymer from an A <sub>2</sub> B type monomer. ....                                                                                        | 35 |

### Chapter 3. Synthesis of Complementary Host- and Guest-Functionalized Polymeric Building Blocks and Their Self-Assembling Behavior

|            |                                                                                                                                                                                                                                                                                                                                                                                                                                          |    |
|------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Figure 3-1 | Cartoon representations of the formation of polymers with a terminal ( <b>1</b> ) or central pseudorotaxane unit ( <b>2</b> ), chain extension by pseudorotaxane formation from host- and guest-terminated polymers ( <b>3</b> ), 3-armed star polymers by pseudorotaxane formation ( <b>4</b> ), block copolymers by pseudorotaxane formation ( <b>5</b> ), and 3-armed block copolymers by pseudorotaxane formation ( <b>6</b> ). .... | 45 |
|------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|

|             |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |    |
|-------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Figure 3-2  | Partial MALDI-TOF mass spectrum (covering mass range 980 – 1295 Da) of paraquat terminated polystyrene <b>11</b> . Sample prepared by the D-D method in 3AQ with no added cationization agent.....                                                                                                                                                                                                                                                                                                                                                                 | 50 |
| Figure 3-3  | Partial MALDI-TOF mass spectrum (covering mass range 747 – 962 Da) of paraquat terminated PMMA <b>13</b> . Sample prepared by the D-D method in 3AQ with no added cationization agent.....                                                                                                                                                                                                                                                                                                                                                                         | 51 |
| Figure 3-4  | Partial MALDI-TOF mass spectrum (covering mass range 2700 – 2930 Da) of MPPP33C10 terminated polystyrene <b>15</b> . Sample prepared by the D-D method in dithranol with AgTFA as a cationization agent. ....                                                                                                                                                                                                                                                                                                                                                      | 53 |
| Figure 3-5  | Partial MALDI-TOF mass spectrum (covering mass range 4001 – 4305 Da) of BMP32C10 centered polystyrene <b>17</b> . Sample prepared by the D-D method in 3AQ and no added cationization agent. ....                                                                                                                                                                                                                                                                                                                                                                  | 53 |
| Figure 3-6  | Qualitative visual test of complexation: a) chloroform solutions of, from the left: paraquat terminated polystyrene <b>11</b> , paraquat terminated polystyrene <b>11</b> + DB30C10-based cryptand, <b>11</b> paraquat terminated polystyrene <b>11</b> + BMP32C10. b) From the left: crown ether centered polystyrene <b>17</b> in chloroform, crown ether centered polystyrene <b>17</b> + paraquat diol in acetone/CHCl <sub>3</sub> 1/1 and crown ether centered polystyrene <b>17</b> + paraquat terminated polystyrene <b>11</b> in CHCl <sub>3</sub> . .... | 55 |
| Figure 3-7  | ITC titration curves (top: raw data, bottom: integrated heat flow and curve fit) and calculated physical constants: a) paraquat terminated polystyrene <b>11</b> (1.03 mM) titrated with BMP32C10 (14.9 mM). b) paraquat terminated PMMA <b>13</b> (1.01 mM) titrated with BMP32C10 (14.9 mM) in CHCl <sub>3</sub> (25 °C). <i>K</i> is the association constant in M <sup>-1</sup> units and <i>H</i> is the enthalpy change in cal/mol .....                                                                                                                     | 56 |
| Figure 3-8  | Reduced viscosity of paraquat-terminated polystyrene <b>11</b> (squares), MPPP32C10 centered polystyrene <b>15</b> (triangles) and 1:1 (molar ratio) solutions of the two polymers (diamonds), in CHCl <sub>3</sub> at 25 °C .....                                                                                                                                                                                                                                                                                                                                 | 57 |
| Figure 3-9  | Reduced viscosity of paraquat-terminated polystyrene <b>11</b> (squares), BMP32C10 centered polystyrene <b>17</b> (triangles) and a 1:1 (molar ratio) solution of the two polymers (diamonds), in CHCl <sub>3</sub> at 25 °C. ....                                                                                                                                                                                                                                                                                                                                 | 57 |
| Figure 3-10 | Partial 400 MHz <sup>1</sup> H-NMR spectra of functional polystyrenes (CDCl <sub>3</sub> , 23 °C). The bottom spectrum is BMP32C10 centered polystyrene <b>17</b> and the upper                                                                                                                                                                                                                                                                                                                                                                                    |    |

|             |                                                                                                                                                                                                                                                                                                                                         |    |
|-------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
|             | spectrum is the 1:1 (molar) mixture of BMP32C10 centered polystyrene <b>17</b> and PQ terminated polystyrene <b>11</b> .....                                                                                                                                                                                                            | 58 |
| Figure 3-11 | ITC titration curve (top: raw data, bottom: integrated heat flow and curve fit) and calculated physical constants of complexation between <b>11</b> (1.03 mM) and <b>17</b> (15.0 mM) in CHCl <sub>3</sub> at 25 °C. <i>K</i> is the association constant in M <sup>-1</sup> units and <i>H</i> is the enthalpy change in cal/mol. .... | 59 |
| Figure 3-12 | Reduced viscosity of paraquat terminated PMMA <b>13</b> (squares), BMP32C10 centered polystyrene <b>15</b> (triangles), and 1:1 (molar ratio) solution of the two polymers (diamonds), in CHCl <sub>3</sub> at 25 °C.....                                                                                                               | 60 |
| Figure 3-13 | Reduced viscosity of paraquat terminated PMMA <b>13</b> (squares), BMP32C10 centered polystyrene <b>17</b> (triangles), and 1:1 (molar ratio) solution of the two polymers (diamonds), in CHCl <sub>3</sub> at 25 °C. ....                                                                                                              | 60 |

#### Chapter 4. Supramolecular Graft Copolymer from a Crown Polyester and a Complementary Paraquat Terminated Polystyrene Guest

|            |                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |    |
|------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Figure 4-1 | Reduced viscosity as a function of concentration (chloroform at 25 °C): (a) crown polyester <b>1</b> , (b) paraquat terminated polystyrene <b>2</b> , and (c) <b>1</b> and <b>2</b> (crown ether:paraquat = 1:1).....                                                                                                                                                                                                                                              | 72 |
| Figure 4-2 | DSC traces of (a) poly(ester crown ether) <b>1</b> , (b) paraquat terminated polystyrene <b>2</b> , (c) solid mixture of <b>1</b> and <b>2</b> , and (d) blend from a solution (chloroform) of <b>1</b> and <b>2</b> . The blend of polymers <b>1</b> and <b>2</b> from solution has one <i>T<sub>g</sub></i> which is even lower than the <i>T<sub>g</sub></i> s of <b>1</b> and <b>2</b> . The crown ether: paraquat is 3:1 for the (c) and (d) experiments..... | 73 |
| Figure 4-3 | SALLS images of the solution cast mixture of poly(ester crown ether) <b>1</b> and polystyryl paraquat <b>2</b> (left) and a solution cast mixture of polymer <b>1</b> and polystyrene with no functional group (right). ....                                                                                                                                                                                                                                       | 74 |
| Figure 4-4 | (a) Partial <sup>1</sup> H NMR spectra of poly(ester crown ether) <b>1</b> and graft copolymeric pseudorotaxane <b>3</b> . Ethyleneoxy protons shift upfield after formation of the graft copolymer. (b) Partial <sup>1</sup> H NMR spectra of paraquat terminated polystyrene <b>2</b> and <b>3</b> . Paraquat protons shift upfield after formation of the graft copolymer...                                                                                    | 75 |

## Chapter 5. Supramolecular Four-Armed Star Copolymer (Miktoarm Star) via Host-Guest Complexation and Nitroxide Mediated Radical Polymerization

|            |                                                                                                                                                                                                           |    |
|------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Figure 5-1 | Partial $^1\text{H}$ NMR spectra of (a) crown centered polystyrene <b>1</b> , (b) 1:1 molar mixture of <b>1</b> and <b>2</b> , and (c) paraquat initiator <b>2</b> in $\text{CDCl}_3$ (400 MHz, 23 °C)... | 81 |
| Figure 5-2 | GPC traces of crown polystyrene <b>1</b> and 4-armed star copolymer <b>4</b> (THF, 25 °C) .....                                                                                                           | 82 |
| Figure 5-3 | DSC heating scan of star polystyrene- <i>b</i> -poly(BMA) [2]rotaxane <b>4</b> (2 <sup>nd</sup> heating scan, heating rate 5 K/min, under $\text{N}_2$ ).....                                             | 83 |

## Chapter 6. Rotaxane-type Hyperbranched Polymers from a Homoditopic Crown Ether Host and a Monotopic Paraquat Guest Containing a Blocking Group

|             |                                                                                                                                                                                                                                                                                                                                                                                             |     |
|-------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Figure 6-1  | Schematic illustration of the formation of a mechanically interlocked hyperbranched polymer from an $\text{A}_2\text{B}$ semi-rotaxane precursor in this study...                                                                                                                                                                                                                           | 91  |
| Figure 6-2  | $^1\text{H}$ NMR spectra of (a) <b>1</b> , (b) <b>HP18</b> formed from <b>1</b> and <b>8</b> , and (c) <b>8</b> in $\text{CD}_3\text{CN}/\text{CDCl}_3$ 3:2 (v:v) (400 MHz, 23 °C). .....                                                                                                                                                                                                   | 96  |
| Figure 6-3  | $^1\text{H}$ NMR spectra of solutions of monomers <b>1</b> and <b>8</b> a) =1:2 molar ratio, b) 1:1 molar ratio, and c) large excess:1 molar ratio in $\text{CD}_3\text{CN}/\text{CDCl}_3$ 3:2 (v/v) (400 MHz, 23 °C).....                                                                                                                                                                  | 97  |
| Figure 6-4  | $^1\text{H}$ NMR spectra of (a) <b>1</b> , (b) <b>HP18</b> formed from <b>1</b> and <b>8</b> , and (c) <b>8</b> in $\text{DMSO}-d_6$ (400 MHz, 23 °C). .....                                                                                                                                                                                                                                | 98  |
| Figure 6-5  | Two schematic diagrams of hyperbranched polymer. There are two types of non-rotaxane crowns in structure (a) and (b). Non-rotaxane paraquat units can form taco-type complexes with the non-rotaxane crowns of other molecules. The inner rotaxanes are surrounded by many bulky species, such as other rotaxanes and blocking groups and therefore crown ether movements are limited. .... | 99  |
| Figure 6-6  | $^1\text{H}$ NMR spectra of (a) <b>1</b> , (b) <b>HP19</b> formed from <b>1</b> and <b>9</b> , and (c) <b>9</b> in $\text{CD}_3\text{CN}/\text{CDCl}_3$ 3:2 (v:v) (400 MHz, 23 °C). .....                                                                                                                                                                                                   | 100 |
| Figure 6-7. | $^1\text{H}$ NMR spectra of (a) <b>1</b> , (b) <b>HP19</b> from <b>1</b> and <b>9</b> , and (c) <b>9</b> in $\text{DMSO}-d_6$ (400 MHz, 23 °C). .....                                                                                                                                                                                                                                       | 101 |
| Figure 6-8  | Reduced viscosity of the hyperbranched polyester from <b>1</b> and <b>8</b> ( <b>HP18</b> ) as a function of concentration for solutions in THF (diamonds) and a THF solution                                                                                                                                                                                                               |     |



|             |                                                                                                                                                                                                                                |     |
|-------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
|             | of 0.0500 M tetrabutylammonium hexafluorophosphate (red squares) at 26 °C.<br>.....                                                                                                                                            | 103 |
| Figure 6-9  | Size distribution traces of <b>9</b> (long-short dash), <b>HP18</b> (red dash) and <b>HP19</b> (blue solid) by dynamic light scattering analysis. (0.020 M tetrabutylammonium hexafluorophosphate in acetonitrile, 20 °C)..... | 103 |
| Figure 6-10 | DSC traces for the esterification products from a) <b>HP18</b> (left, short spacer) and b) <b>HP19</b> (right) with heating and cooling rate 5 K/min under N <sub>2</sub> .....                                                | 104 |

## Chapter 7. Ion Conduction in a Semi-Crystalline Polyviologen and Its Polyether Mixtures

|            |                                                                                                                                                                                                                                                                                                               |     |
|------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Figure 7-1 | Partial 400 MHz <sup>1</sup> H-NMR spectra of a) polyviologen <b>1</b> and b) the solution of <b>1</b> and DB30C10 (saturated) in CD <sub>3</sub> CN/CDCl <sub>3</sub> 3:2 solvent at 23 °C. The paraquat peaks move upfield after addition of DB30C10, indicating the complexation of the two molecules..... | 114 |
| Figure 7-2 | Formation of polypseudorotaxane from <b>1</b> and DB30C10.....                                                                                                                                                                                                                                                | 115 |
| Figure 7-3 | Ionic conductivity plots of <b>1</b> (open red squares), <b>2</b> (solid red squares), <b>3</b> (green circles), <b>4</b> (purple stars), and <b>5</b> (blue triangle). .....                                                                                                                                 | 117 |
| Figure 7-4 | DSC diagram (left) of the mixture <b>2</b> (N <sub>2</sub> atmosphere, heating 5 K/min, cooling 1 K/min) and cross-polarized microscopic image (right) from a solution cast film of <b>2</b> . The microscopic image was obtained after cooling (1 K/min) from 140 °C (above melting point).....              | 118 |
| Figure 7-5 | DSC diagram (left) of mixture <b>3</b> (N <sub>2</sub> atmosphere, heating 5 K/min, cooling 1 K/min) and cross-polarized microscopic image (right) from a solution cast film of <b>3</b> . The microscopic image was obtained after cooling (1 K/min) from 140 °C (above melting point). .....                | 118 |
| Figure 7-6 | DSC diagram (left) of the mixture <b>4</b> (N <sub>2</sub> atmosphere, heating 5 K/min, cooling 1 K/min) and cross-polarized microscopic image (right) from a solution cast film of <b>4</b> . The microscopic image was obtained after cooling (1 K/min) from 140 °C (above melting point).....              | 119 |
| Figure 7-7 | DSC diagram (left) of the mixture <b>5</b> (N <sub>2</sub> atmosphere, heating 5 K/min, cooling 1 K/min) and cross-polarized microscopic image (right) from a solution cast film of <b>5</b> . The microscopic image was obtained after cooling (1 K/min) from 140 °C (above melting point).....              | 119 |

## Chapter 8. Ion Conduction in Amorphous Polyviologens and Their Polyether Mixtures

|            |                                                                                                                                                                                                                                          |
|------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Figure 8-1 | $^1\text{H}$ NMR spectra of <b>6</b> (upper) and after adding excess DB30C10 to the NMR solution (below) (400 MHz, $\text{CD}_3\text{CN}/\text{CDCl}_3$ 2:3 (v/v), 23 °C) .....125                                                       |
| Figure 8-2 | DSC diagram (upper) and TGA curve (below) of <b>6</b> . DSC was scanned with heating and cooling rates of 5 K/min with a $\text{N}_2$ stream, and TGA was observed with a heating rate of 10 K/min under $\text{N}_2$ atmosphere.....126 |
| Figure 8-3 | Ionic conductivity plots of polyviologen <b>6</b> and its mixtures.....127                                                                                                                                                               |
| Figure 8-4 | $^1\text{H}$ NMR spectrum of <b>11</b> (400 MHz, $\text{CD}_3\text{CN}/\text{CDCl}_3$ 2:3 (v/v), 23 °C). The peaks with pink arrows are from the end groups of the polymer.....128                                                       |
| Figure 8-5 | Ionic conductivity plots of <b>11</b> (open triangles) and its mixture with DB30C10 (solid triangles). .....128                                                                                                                          |
| Figure 8-6 | Ionic conductivity plots of polyviologens: semi-crystalline <b>1</b> (red squares), amorphous <b>6</b> (pink circles) and amorphous <b>11</b> (blue triangles, DP = ~5) .....129                                                         |

## PART - II. New Ionic Liquids, Ionic Liquid-Based Polymers and Their Properties

### Chapter 9. Ionic Liquid Monomers and Ionic Polymers (Literature Review)

|             |                                                                                                                                                                 |
|-------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Figure 9-1  | Synthesis of ionic liquid monomers, $[\text{AcrC}_8\text{mim}^+][\text{Cl}^-]$ and $[\text{AcrC}_{10}\text{mim}^+][\text{Cl}^-]$ by Firestone et al. ....134    |
| Figure 9-2  | Polymerizable ionic liquid monomer structures prepared by Ohno et al.....135                                                                                    |
| Figure 9-3  | Synthesis of ionic liquid type cross-linkers: acryloyl cross-linker (upper) and styryl cross-linker (below). ....135                                            |
| Figure 9-4  | Various types of zwitterionic polymerizable ionic liquids. ....136                                                                                              |
| Figure 9-5  | ROMP monomers with imidazolium ionic liquid moieties. ....136                                                                                                   |
| Figure 9-6  | Synthesis of poly(vinyl ethers) with imidazolium and pyridinium ionic pendants. ....137                                                                         |
| Figure 9-7  | Two main-chain imidazolium polymers from hydroborations .....137                                                                                                |
| Figure 9-8  | Synthesis of a main-chain imidazolium polymer used in solar panel.....138                                                                                       |
| Figure 9-9  | Homopolymer of the ionic liquid monomer with a trifluoromethanesulfonic anion and a free imidazolium cation by Teyssié et al. ....140                           |
| Figure 9-10 | Surface-initiated polymerization of ionic liquid monomer. The brushes are grown using ATRP in isopropanol/water from the initiator modified Au surface. ....141 |

|             |                                                                                                                                                                                                                                                             |     |
|-------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Figure 9-11 | Diblock copolymers of a styrene block and a polymerized ionic liquid block to form micelles in toluene.....                                                                                                                                                 | 142 |
| Figure 9-12 | Synthesis of segmented imidazolium ionens by a Menshukin reaction.....                                                                                                                                                                                      | 143 |
| Figure 9-13 | Synthesis of polymerizable ionic liquid crystalline pyridinium monomers....                                                                                                                                                                                 | 144 |
| Figure 9-14 | Illustration of layered nanostructure of ionic liquid crystalline polymer in the smectic <b>A</b> phase.....                                                                                                                                                | 144 |
| Figure 9-15 | Ionic liquid crystal monomer reported by Ohno and Kato. From this monomer, hexagonal columnar mesophase was observed on glass and ITO glass surfaces. The polymerizable end functionality provided aligned ion channels after the photopolymerization. .... | 145 |
| Figure 9-16 | Electropolymerized polymers from ionic liquid monomers of thiophene derivatives for electroactive materials. ....                                                                                                                                           | 146 |
| Figure 9-17 | Pendant imidazolium polymers (left) and main-chain imidazolium polymers with various structural factors (right).....                                                                                                                                        | 147 |
| Figure 9-18 | Main-chain poly(1,3-alkylimidazolium salt)s (left) and pendant imidazolium polyethylenes from ADMET polymerization. ....                                                                                                                                    | 148 |

## Chapter 10. 1,2-Bis[N-(N'-alkylimidazolium)]ethane Salts as New Guests for Crown Ethers and Cryptands

|              |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |     |
|--------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Figure 10-1  | Partial 400 MHz <sup>1</sup> H NMR spectra of (a) <b>2</b> (2 mM), (b) <b>2</b> + DB24C8 (1:5 molar ratio, 2 mM of <b>2</b> ), and (c) DB24C8 (10 mM) in CD <sub>3</sub> CN at 25 °C.....                                                                                                                                                                                                                                                                                                                                                                                                  | 153 |
| Figure 10-2  | Schematic diagram of complexation of <b>2</b> with DB24C8 and DB24C8-based pyridyl cryptand <b>6</b> . <sup>11</sup> .....                                                                                                                                                                                                                                                                                                                                                                                                                                                                 | 154 |
| Figure 10-3  | A capped-sticks view of the X-ray structure of <b>1</b> . PF <sub>6</sub> <sup>-</sup> anions are omitted for clarity. Ring plane/ring plane inclination of the two imidazolium rings: 0°...156                                                                                                                                                                                                                                                                                                                                                                                            |     |
| Figure 10-4  | Two capped-sticks views of the X-ray structure of <b>1</b> ·( <b>6</b> ) <sub>2</sub> : side view (left) and end view (right). There are two complexes in the unit cell and they are similar but not identical. These views are one of the complexes. PF <sub>6</sub> <sup>-</sup> anions, MeCN molecules and some hydrogens are omitted for clarity. One PF <sub>6</sub> <sup>-</sup> anion is disordered. H···O (or N) distances (Å), C-H···O (or N) angles (degrees) of : a 2.60, 165.4; b 2.89, 126; c 2.64, 138; d 2.71, 155; e 2.68, 122; f 2.79, 166; g 2.30, 135; h 2.23, 145..... | 157 |
| Figure 10-S1 | Capped-sticks views of the X-ray structure of <b>1</b> ·( <b>6</b> ) <sub>2</sub> : two sets of complex are in the asymmetric unit. <b>Set 1</b> is shown in the Fig. 4 of the main text. Two carbon                                                                                                                                                                                                                                                                                                                                                                                       |     |

atoms of a disordered ethyleneoxy arm, the  $\text{PF}_6^-$  anions, the MeCN molecules, and H-atoms not involved in hydrogen bonding are omitted for clarity. H $\cdots$ O (or N) distances (Å), C-H $\cdots$ O (or N) angles (degrees) of : (**Set 1**) **a** 2.60, 165.4; **b** 2.89, 126; **c** 2.64, 138; **d** 2.71, 155; **e** 2.68, 122; **f** 2.79, 166; **i** 2.71, 163; **j** 2.53, 138; **k** 3.04, 139; **l** 2.76, 132; **m** 2.38, 151; **n** 2.56, 152; (**Set 2**) **a'** 2.64, 160; **b'** 2.72, 132, **c'** 2.63, 138; **d'** 2.68, 162; **e'** 2.76, 122; **f'** 2.66, 169; **i'** 2.67, 172; **j'** 2.40, 134; **k'** 2.77, 129; **l'** 2.79, 125; **m'** 2.50, 160; **n'** 2.60, 146 .....164

Figure 10-S2 Ellipsoid diagram of the X-ray structure of **1**·(**6**)<sub>2</sub> with 50% probability. Two carbon atoms of one ethyleneoxy arm, one  $\text{PF}_6^-$  ion, and multiple MeCN molecules are disordered.....165

Figure 10-S3 Capped-stick X-ray crystal structures of the cryptand **6**<sup>11</sup> (left) and one of the two crystallographically independent complexes of **1**·(**6**)<sub>2</sub> (right). For the cryptand **6**, some oxygen and carbon atoms of ethyleneoxy arm are disordered. The centroid-to-centroid distance between the two catechol rings is only 6.19 Å, the atom-to-atom distance between C5 of the upper catechol and C2' of the lower one is 4.65 Å, the atom-to-atom distance between hydrogens of C5 of the upper catechol and C2 of the lower one is 4.30 Å, and the dihedral angle between the catechol rings is 20.3°. For the complex **1**·(**6**)<sub>2</sub> shown, the centroid-to-centroid distances of the phenylene and imidazolium rings are 3.6~3.9 Å and the dihedral angles of the phenylene and imidazolium planes are 12~23° (values are nearly identical for the 2nd crystallographically independent complex). Thus, the two catechol rings must move apart to complex guest **1**, and the somewhat large  $\Delta S$  of the complexation (15 cal/mol·deg) can be attributed in large part to this reorganization.....166

## Chapter 11. Structure and Properties of N,N-Alkylene Bis(N'-alkylimidazolium) Salts

Figure 11-1 Partial 400 MHz <sup>1</sup>H NMR spectra of **3Br** in D<sub>2</sub>O (upper) and acetone-*d*<sub>6</sub> (lower).....174

Figure 11-2 Partial 400 MHz <sup>1</sup>H NMR spectra of **3** ( $\text{PF}_6^-$ ,  $\text{BF}_4^-$ ,  $\text{TfO}^-$ ,  $\text{NO}_3^-$ , TFA and  $\text{Br}^-$ ) in acetone-*d*<sub>6</sub>. The chemical shift of proton H<sup>4</sup> is almost the same with various anions, but protons H<sup>2</sup> and H<sup>5</sup> resonate at different positions. **3PF<sub>6</sub>** and **3BF<sub>4</sub>** are the least ion paired, bringing the signals of protons H<sup>4</sup> and H<sup>5</sup> close to each other. **3Br** is the most ion paired; the positive charge is localized in the imidazolium ring .....175

|              |                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |     |
|--------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Figure 11-3  | Correlation of the $^1\text{H}$ chemical shift of the proton in 2-position of the imidazolium ring of <b>3</b> with the hydrogen bond acidity ( $\alpha$ ) of 1-butyl-3-methylimidazolium salts .....                                                                                                                                                                                                                                                                | 176 |
| Figure 11-4  | Two capped-sticks views of the X-ray structure of <b>1PF<sub>6</sub></b> . Hydrogens are omitted for clarity. Face-to-face stacking parameters: ring plane/ring plane inclination of the imidazolium rings in the same molecule: $0^\circ$ . Ring plane/ring plane distance and dihedral angle between imidazolium rings of different molecules within a stack: 8.66 Å, $0^\circ$ . Dihedral angle between imidazolium rings in different stacks: $67.3^\circ$ ..... | 179 |
| Figure 11-5  | Capped-sticks view of the X-ray structure of <b>1PF<sub>6</sub></b> . H $\cdots$ F distances (Å), C-H $\cdots$ F angles (degrees): <b>A</b> 2.31, 166; <b>B</b> 2.58, 137; <b>C</b> 2.78, 126; <b>D</b> 2.48, 159; <b>E</b> 2.71, 130; <b>F</b> 2.69, 164; <b>G</b> 2.66, 126; <b>H</b> 2.52, 125; <b>I</b> 2.50, 164; <b>J</b> 2.56, 112; <b>K</b> 2.60, 146; <b>L</b> 2.65, 123; <b>M</b> 2.84, 122 .....                                                          | 180 |
| Figure 11-6  | Two capped-sticks views of the X-ray structure of <b>3PF<sub>6</sub></b> . Hydrogens are omitted for clarity. Face-to-face stacking parameters: ring plane/ring plane inclination of imidazolium rings within the same molecule: $0^\circ$ . Ring plane/ring plane distance and dihedral angle between imidazolium rings of different molecules: 7.94 Å, $0^\circ$ .....                                                                                             | 180 |
| Figure 11-S1 | Ellipsoid plots of the X-ray structure of <b>1PF<sub>6</sub></b> with 50% probability .....                                                                                                                                                                                                                                                                                                                                                                          | 188 |
| Figure 11-S2 | Ellipsoid plots of the X-ray structure of <b>3PF<sub>6</sub></b> with 50% probability. All PF <sub>6</sub> anions are disordered .....                                                                                                                                                                                                                                                                                                                               | 189 |
| Figure 11-S3 | Capped-sticks view of the X-ray structure of <b>3PF<sub>6</sub></b> . H $\cdots$ F distances (Å), C-H $\cdots$ F angles (degrees): <b>A</b> 2.59, 165; <b>B</b> 2.26, 175; <b>C</b> 2.64, 175; <b>D</b> 2.29, 157; <b>E</b> 2.42, 173; <b>F</b> 2.53, 142; <b>G</b> 2.41, 142; <b>H</b> 2.55, 145; <b>I</b> 2.56, 137; <b>J</b> 2.67, 127 .....                                                                                                                      | 190 |

## Chapter 12. 1,2-Bis[N-(N'-alkylimidazolium)]ethane Salts as a New Class of Organic Ionic Plastic Crystals

|             |                                                                                                                                                                                                           |     |
|-------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Figure 12-1 | DSC diagrams of <b>3Br</b> (left) and <b>3PF<sub>6</sub></b> (right) (heating and cooling rate 5 K/min, N <sub>2</sub> ) .....                                                                            | 198 |
| Figure 12-2 | DSC diagrams of <b>6PF<sub>6</sub></b> (heating and cooling rate 5 K/min, N <sub>2</sub> ) .....                                                                                                          | 199 |
| Figure 12-3 | DSC diagrams of <b>8Br</b> (left) and <b>8PF<sub>6</sub></b> (right) (heating and cooling rate 5 K/min, N <sub>2</sub> ). Only the second and third heating traces are shown and they are identical. .... | 199 |

|              |                                                                                                                                                                                                                                                                                           |     |
|--------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Figure 12-4  | DSC diagrams of <b>9Br</b> (left) and <b>9PF<sub>6</sub></b> (right) (heating and cooling rate 5 K/min, N <sub>2</sub> ). Only the second and third heating traces are shown and they are identical                                                                                       | 200 |
| Figure 12-5  | DSC diagrams of <b>10Br</b> (left) and <b>10PF<sub>6</sub></b> (right) (heating and cooling rate 5 K/min, N <sub>2</sub> ). Only the second heating scans are shown in this figure                                                                                                        | 201 |
| Figure 12-6  | DSC diagrams of <b>11Br</b> (left) and <b>11PF<sub>6</sub></b> (right) (heating and cooling rate 5 K/min, N <sub>2</sub> ).                                                                                                                                                               | 201 |
| Figure 12-7  | The trends of melting point of bis[N-(N'-alkylimidazolium)ethane 2PF <sub>6</sub> <sup>-</sup> salts (reverse triangles), of the first T <sub>ss</sub> of Br <sup>-</sup> salts (squares), and of the first T <sub>ss</sub> of PF <sub>6</sub> <sup>-</sup> salts (triangles)             | 203 |
| Figure 12-8  | The trend of TGA 5% weight loss temperature of bis(N-alkylimidazolium)-ethane 2Br <sup>-</sup> salts (stars), and the trend of the corresponding PF <sub>6</sub> <sup>-</sup> salts (circles)                                                                                             | 204 |
| Figure 12-9  | Solid-state <sup>2</sup> H NMR spectra of <b>12</b> from 0 to 100 °C. The peak intensities (left) and the peak width (right) change as increasing temperature                                                                                                                             | 205 |
| Figure 12-10 | NMR simulation results with various time scale and two different angles (15 and 30°) of deuterium flipping motion (left) and experimental result at 0 and 100 °C (right). <sup>2</sup> H quadrupolar coupling tensor parameters used in the simulation: $e^2qQ/h = 168$ kHz, $\eta = 0$ . | 206 |
| Figure 12-11 | X-Ray powder diffraction profiles of <b>7PF<sub>6</sub></b> as a function of temperature                                                                                                                                                                                                  | 207 |

### Chapter 13. Ion Conduction in Imidazolium Acrylate Ionic Liquids and their Polymers

|             |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |     |
|-------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Figure 13-1 | Partial 400 MHz <sup>1</sup> H NMR spectra of monomer <b>3c</b> (upper) and polymer <b>4c</b> (lower) in CD <sub>3</sub> CN at 23 °C. After polymerization, the vinyl proton peaks ( <b>4</b> and <b>5</b> in the upper spectrum) disappear and <b>1</b> , <b>2</b> , <b>3</b> protons are broadened. However, the ethyleneoxy peaks ( $\alpha$ , $\beta$ , $\gamma$ , $\delta$ ) are still sharply split in the polymer (lower) spectrum, as they are in the monomer (upper) spectrum. | 214 |
| Figure 13-2 | DSC thermograms of the monomer <b>3c</b> and the polymer <b>4c</b> , showing the increase in T <sub>g</sub> on polymerization.                                                                                                                                                                                                                                                                                                                                                          | 214 |
| Figure 13-3 | Temperature dependence of ionic conductivity of (a) PF <sub>6</sub> <sup>-</sup> monomers and polymers and (b) Tf <sub>2</sub> N <sup>-</sup> monomers and polymers. Monomers (open symbols) have consistently higher conductivity than their polymers (filled symbols). Lines indicate fits to Eq. (9)                                                                                                                                                                                 | 217 |

|             |                                                                                                                                                                                                                                                                                                                                                                                                                      |     |
|-------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Figure 13-4 | Temperature dependence of conducting ion number density $p$ . The inset shows the fraction of counterions in the conducting state ( $p$ divided by the total ion concentration $p_0$ ). Monomers (open symbols) have consistently higher conducting ion content than their polymers (filled symbols). Lines are fits to Eq. (7) with the activation energy as the sole fitting parameter (listed in Table 13-4)..... | 220 |
| Figure 13-5 | Temperature dependence of conducting ion mobility for (a) $\text{PF}_6^-$ monomers and polymers and (b) $\text{Tf}_2\text{N}^-$ monomers and polymers. Monomers (open symbols) have consistently higher mobility than their polymers (filled symbols). Lines are fits to Eq. (8) with fitting parameters listed in Table 13-4.....                                                                                   | 220 |

## Chapter 14. Synthesis of Poly(imidazolium acrylate)s and Effect of Chemical Structure on Thermal and Electrical Properties

|             |                                                                                                                                                                                                                                                                                                                                                                                                      |     |
|-------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Figure 14-1 | 400 MHz $^1\text{H}$ NMR spectra of monomer <b>2c</b> and polymer <b>3c</b> (in $\text{CD}_3\text{CN}$ , 23 °C). After polymerization, vinyl proton peaks ( $\delta$ 5.7-.4) disappear and some peaks are broadened .....                                                                                                                                                                            | 235 |
| Figure 14-2 | Temperature dependence of ionic conductivities of $\text{PF}_6^-$ and $\text{Tf}_2\text{N}^-$ polymers. Lines indicate fits of Eq.(1) to the data. The inset shows ionic conductivity at room temperature as a function of glass transition temperatures of the four polymers ( <b>3b</b> (■), <b>3c</b> (●), <b>3d</b> (▲), <b>3e</b> (▼)) and two monomer ( <b>2a</b> (□) and <b>2c</b> (▽)) ..... | 238 |
| Figure 14-3 | Ionic conductivity plots of $\text{PF}_6^-$ monomer and polymer (left), and $\text{Tf}_2\text{N}^-$ monomer and polymer (right).....                                                                                                                                                                                                                                                                 | 238 |
| Figure 14-4 | Three possible distance parameters from XRD for amorphous ionic homopolymers. All the distance information is determined as an average value .....                                                                                                                                                                                                                                                   | 239 |
| Figure 14-5 | X-Ray scattering profiles of $\text{PF}_6^-$ polymers, <b>3a</b> , <b>3b</b> and <b>3d</b> . ....                                                                                                                                                                                                                                                                                                    | 240 |
| Figure 14-6 | X-Ray scattering profiles of $\text{PF}_6^-$ polymers <b>3b</b> and $\text{Tf}_2\text{N}^-$ polymers <b>3c</b> and <b>3e</b> .....                                                                                                                                                                                                                                                                   | 240 |

## Chapter 15. Synthesis and Properties of Imidazolium Polyesters

|             |                                                                                                                                 |     |
|-------------|---------------------------------------------------------------------------------------------------------------------------------|-----|
| Figure 15-1 | DSC diagrams of diols <b>2c</b> (left) and <b>3c</b> (right) ( $\text{N}_2$ atmosphere, heating and cooling rate 5 K/min). .... | 254 |
|-------------|---------------------------------------------------------------------------------------------------------------------------------|-----|

|             |                                                                                                                                                                                                                                                                                                                                                                                                                                             |     |
|-------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Figure 15-2 | $^1\text{H}$ NMR spectrum of <b>4d</b> (400 MHz, DMSO- $d_6$ , 23 °C). The big triplet ( $\delta$ 2.25) is from methylene protons next to the carbonyl moiety ( $\text{CH}_2\text{C=O}$ ) of the sebacate moiety in the repeating unit. The small triplet ( $\delta$ 2.18) is from the methylene protons next to the $\text{CO}_2\text{H}$ end group. No signal for the $\text{CH}_2\text{OH}$ end group is observed in this polyester..... | 255 |
| Figure 15-3 | a) DSC diagrams of polyester <b>5c</b> ( $\text{N}_2$ atmosphere, heating and cooling rate 5 °C/min). The first heating scan shows two $T_m$ , but the second heating scan after cooling from 200 °C shows just one $T_m$ and two $T_g$ s. b) Dynamic mechanical analysis of melt-pressed films of <b>5c</b> ( $\text{N}_2$ atmosphere, -80 ~ 60 °C with a heating rate of 3 °C/min, cantilever clip) .....                                 | 256 |
| Figure 15-4 | Ionic conductivity plots of $\text{Tf}_2\text{N}^-$ polyesters. Only polymer <b>4d</b> is crystalline and its conductivity shows significant change near $T_g$ (-45 °C or $1000/T = 4.38$ ).....                                                                                                                                                                                                                                            | 260 |
| Figure 15-5 | Ionic conductivity plots of $\text{PF}_6^-$ polyesters. Crystalline polymers <b>4c</b> and <b>4e</b> show significant change in their conductivities near $T_m$ (26 and 14 °C; $1000/T = 3.34$ and 3.48, respectively). Note, however, that semi-crystalline bis-imidazolium polyester <b>5c</b> shows significantly higher conductivity than amorphous bis-imidazolium polyester <b>5a</b> .....                                           | 260 |
| Figure 15-6 | X-ray scattering profiles of the mono-imidazolium polyesters.....                                                                                                                                                                                                                                                                                                                                                                           | 261 |
| Figure 15-7 | X-ray scattering profiles of the bis-imidazolium polyesters .....                                                                                                                                                                                                                                                                                                                                                                           | 262 |
| Figure 15-8 | 2D X-ray scattering pattern as a function of temperature for polyester <b>5c</b> at 25 °C and at 105 °C. ....                                                                                                                                                                                                                                                                                                                               | 263 |

## Chapter 16. Synthesis of Imidazolium Dienes and Precision Ionic Polyolefins

|             |                                              |     |
|-------------|----------------------------------------------|-----|
| Figure 16-1 | DSC and DMA Traces of Polymer <b>8</b> ..... | 277 |
| Figure 16-2 | DSC and DMA Traces of Polymer <b>9</b> ..... | 278 |

## Chapter 17. Conclusions and Future Work

|             |                                                                                                                                            |     |
|-------------|--------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Figure 17-1 | New supramolecular polymers from the pseudorotaxane formation from a cryptand-paraquat complexation system.....                            | 286 |
| Figure 17-2 | Supramolecular rotaxane brush copolymers from the polymerization of the pseudorotaxane macroinitiator. “I” refers an initiation site ..... | 287 |



## List of Tables

### PART I. Design, Synthesis and Self-Assembly of Polymeric Building Blocks

#### Chapter 3. Synthesis of Complementary Host- and Guest-Functionalized Polymeric Building Blocks and Their Self-Assembling Behavior

|           |                                                                                                                                           |    |
|-----------|-------------------------------------------------------------------------------------------------------------------------------------------|----|
| Table 3-1 | Molecular Weights Estimated by $^1\text{H}$ -NMR Spectroscopy and SEC for the Paraquat Terminated Polystyrenes ( <b>11</b> ) by SFRP..... | 47 |
|-----------|-------------------------------------------------------------------------------------------------------------------------------------------|----|

#### Chapter 7. Ion Conduction in a Semi-Crystalline Polyviologen and Its Polyether Mixtures

|           |                                                                    |     |
|-----------|--------------------------------------------------------------------|-----|
| Table 7-1 | Mixture Compositions of Polyviologen <b>1</b> and Polyethers ..... | 115 |
|-----------|--------------------------------------------------------------------|-----|

#### Chapter 8. Ion Conduction in Amorphous Polyviologens and Their Polyether Mixtures

|           |                                                   |     |
|-----------|---------------------------------------------------|-----|
| Table 8-1 | Blend Compositions of Polyviologen <b>6</b> ..... | 127 |
|-----------|---------------------------------------------------|-----|

### PART - II. New Ionic Liquids, Ionic Liquid-Based Polymers and Their Properties

#### Chapter 10. 1,2-Bis[N-(N'-alkylimidazolium)]ethane Salts as New Guests for Crown Ethers and Cryptands

|            |                                                                                      |     |
|------------|--------------------------------------------------------------------------------------|-----|
| Table 10-1 | ITC Results: Complexation of Imidazolium Salts by DB24C8 and Cryptand <b>6</b> ..... | 155 |
|------------|--------------------------------------------------------------------------------------|-----|

#### Chapter 11. Structure and Properties of N,N-Alkylene Bis(N'-alkylimidazolium) Salts

|            |                                                                                                 |     |
|------------|-------------------------------------------------------------------------------------------------|-----|
| Table 11-1 | Quaternization and Ion Exchange Reactions for Alkylene Bis[N-(N'-alkylimidazolium)] Salts ..... | 173 |
| Table 11-2 | Thermal Properties of the Alkylene Bis(N-alkylimidazolium) Salts.....                           | 177 |

#### Chapter 12. 1,2-Bis[N-(N'-alkylimidazolium)]ethane Salts as a New Class of Organic Ionic Plastic Crystals

|            |                                                                                            |     |
|------------|--------------------------------------------------------------------------------------------|-----|
| Table 12-1 | DSC Phase Transition Temperatures of the Alkylene Bis[N-(N'-alkylimidazolium)] Salts ..... | 202 |
|------------|--------------------------------------------------------------------------------------------|-----|

### **Chapter 13. Ion Conduction in Imidazolium Acrylate Ionic Liquids and their Polymers**

|            |                                                                                                                                               |     |
|------------|-----------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Table 13-1 | DSC and TGA Thermal Analysis of Monomers and Polymers.....                                                                                    | 215 |
| Table 13-2 | Ionic Conductivities of PF6- Monomers and Polymers.....                                                                                       | 216 |
| Table 13-3 | Ionic Conductivity of Tf2N- Monomers and Polymers .....                                                                                       | 217 |
| Table 13-4 | Parameters of the VFT Equation for Conducting Ion Mobility, Eq. (8) and the Arrhenius Equation for Conducting Ion Concentration, Eq. (7)..... | 221 |
| Table 13-5 | Fitting parameters for the temperature dependence of d.c. ionic conductivity fit to Eq. (9) .....                                             | 223 |

### **Chapter 14. Synthesis of Poly(imidazolium acrylate)s and Effect of Chemical Structure on Thermal and Electrical Properties**

|            |                                                                                  |     |
|------------|----------------------------------------------------------------------------------|-----|
| Table 14-1 | Physical Properties of $\omega$ -carboxyalkylimidazolium salts <b>1a-e</b> ..... | 234 |
| Table 14-2 | Thermal Properties of Monomer <b>2a-e</b> and Polymers <b>3a-e</b> .....         | 236 |

### **Chapter 15. Synthesis and Properties of Imidazolium Polyesters**

|            |                                                                             |     |
|------------|-----------------------------------------------------------------------------|-----|
| Table 15-1 | Properties of Dihydroxy Imidazolium Salts.....                              | 254 |
| Table 15-2 | Thermal Properties and Ionic Conductivities of Imidazolium Polyesters ..... | 259 |

## Chapter 1

### Introduction and Dissertation Statement

This dissertation includes two different central topics: “Part I: Design, Synthesis and Self-Assembly of Polymeric Building Blocks” and “Part II: Novel Ionic Liquids, Ionic Liquid-Based Polymers and Their Properties”. Exploring new self-assembling systems has been an objective of my research group (Gibson group) for more 20 years; in my time with the group (while working towards my PhD) I have expanded research endeavors by functionalizing polymeric building blocks. The second part of this dissertation, about ionic liquids and ionic polymers, was motivated by the research project “Ionic Liquid Electroactive Device (ILEAD) Multi-University Research Initiative (MURI)”, which is supported by the Army Research Office. Therefore, there are two literature review chapters in this dissertation: Chapter 2 for Part I and Chapter 9 for Part II.

In Part I Chapter 3, we discuss paraquat and crown functionalized polymeric building blocks. The polymeric building blocks reported here were synthesized by controlled radical polymerizations and many types of self-assembled structures were formed from these polymeric building blocks.

In Chapter 4, we discuss a supramolecular graft copolymer by the self-assembly of a main-chain crown ether polymer and a paraquat terminated polymer. The formation of the graft copolymer was confirmed by viscometry, proton NMR spectrometry and differential scanning calorimetry.

Synthesis and characterizations of a supramolecular four-armed star block copolymer is discussed in Chapter 5. The *in situ* formation of a macromolecular pseudorotaxane initiator is the key for the copolymer synthesis.

In Chapter 6, we discuss the synthesis and characterization of supramolecular rotaxane-type hyperbranched polymers. The structures of the monofunctional paraquat monomers are important for attaining high molecular weight hyperbranched polymers.

In Chapter 7 and 8, we discuss the ionic conductivities of polyviologens and their mixtures with polyethers. Pseudorotaxane and other complexations play an important role in bringing about the higher ionic conductivity of semi-crystalline polyviologens.

Part II is mostly about structure-property relationships of new imidazolium salts and ionic liquid-based polymers. In Chapter 10, we discuss the complexation of 1,2-bis[N-(N'-alkylimidazolium)]ethane bis(hexafluorophosphate) salts with dibenzo-24-crown-8 and a dibenzo-24-crown-8 based pyridyl cryptand.

The properties of a series of 1,2-bis[N-(N'-alkylimidazolium)]ethane salts are discussed in Chapters 11 and 12. Hydrogen bond acidity of the new imidazolium salts was investigated by proton NMR spectroscopy with different counter anions and solvents. Thermal behaviors of the new bis-imidazolium salts are also discussed and multiple solid-solid phase transitions are the main features of the bromide and hexafluorophosphate salts of 1,2-bis[N-(N'-alkylimidazolium)]ethanes.

Ionic polymers were synthesized and characterized. Pendant imidazolium polyacrylates are discussed in Chapters 13 and 14. Dielectric relaxation spectroscopy is a powerful tool for the analysis of electrical properties of the ionic polymers.

Main-chain imidazolium polymers are discussed in Chapters 15 and 16. Structure-property relationships of main-chain imidazolium polyesters were studied and we found that micro-phase separation enhanced ionic conductivity.

In this dissertation, a lot of collaborators helped me for the synthesis and characterization of new materials. Daniel Schoonover performed all the isothermal microcalorimetric (ITC) titrations and calculated physical constants for all the host-guest complexations in this dissertation. Zhenbin Niu and Dr. Carla Slebodnick helped me in growing crystals and analysis of the solid state structures of imidazolium salts and a pseudorotaxane-like complex in Chapters 10 and 11. U Hyeok Choi in Dr. Colby's group (Penn State Univ.) analyzed the electrical properties of all the imidazolium polymers by dielectric spectroscopy. Brian Aitken in Dr. Wagener's group (Univ. of Florida) is a co-author of Chapter 16 and performed ADMET polymerizations of the imidazolium dienes.

All the publications based on this dissertation are as follows:

1. Minjae Lee, Daniel V. Schoonover, Anthony P. Gies, David M. Hercules and Harry W. Gibson, Synthesis of Complementary Host- and Guest-Functionalized Polymeric Building Blocks and Their Self-Assembling Behavior, *Macromolecules*, **2009**, 42, 6483–6494. (Chapter 3)
2. Brian S. Aitken, Minjae Lee, Matthew Hunley, Harry W. Gibson, Kenneth B. Wagener, Synthesis of Precision Ionic Polyolefins Derived from Ionic Liquids, *Macromolecules*, **2010**, 43, 1699–1701. (Chapter 16)

3. Minjae Lee, Zhenbin Niu, Daniel V. Schoonover, Carla Slebodnick, Harry W. Gibson, 1,2-Bis[N-(N'-alkylimidazolium)]ethane Salts as New Guests for Crown Ethers and Cryptands, *Tetrahedron*, **2010**, 66, 7077-7082. (Chapter 10)
4. Minjae Lee, Zhenbin Niu, Carla Slebodnick, Harry W. Gibson, Structure and Properties of Alkylene Bis(N-alkylimidazolium) Salts, *J. Phys. Chem. B*, **2010**, 114, 7312–7319. (Chapter 11)
5. Minjae Lee, U Hyeok Choi, Ralph H. Colby, Harry W. Gibson, Ion Conduction in Imidazolium Acrylate Ionic Liquids and their Polymers, *Chem. Mater.* Accepted (Chapter 13)
6. Minjae Lee, U Hyeok Choi, David Salas-de la Cruz, Karen I. Winey, Ralph H. Colby and Harry W. Gibson, Imidazolium Polyesters: Structure-Property Relationships in Thermal Properties, Ionic Conductivity and Morphology, Submitted to *Adv. Funct. Mater.*
7. Minjae Lee, Daniel V. Schoonover, Zhenbin Niu and Harry W. Gibson, Supramolecular Four-Armed Star Copolymer (Miktoarm Star) via Host-Guest Complexation and Nitroxide Mediated Radical Polymerization, *Will be submitted*. (Chapter 5)

# Part I: Design, Synthesis and Self-Assembly of Polymeric Building Blocks

## Chapter 2

### Synthesis of Rotaxanes, Cryptands and Polyrotaxanes (Literature Review)

#### 1. Introduction

##### 1.1 Rotaxanes and cryptands

The word “Rotaxane” is from the Latin words ‘rota’ meaning wheel and ‘axis’ meaning axle. In chemistry, rotaxanes represent a group of compounds in which a dumbbell-shaped molecule is encircled by a macrocycle with non-covalent bonds. These mechanical bonds are responsible for the linking of the components. The properties of rotaxanes are significantly different from those of their individual components. These different features may provide the possibility of applications in nanotechnology<sup>1</sup> and material science such as smart sensors, switches or data storage.<sup>2</sup> Pseudorotaxanes are also constructed from macrocycles and linear chains, but end-capping groups do not exist. Catenanes contain two or more rings interlocked with each other (Figure 2-1).

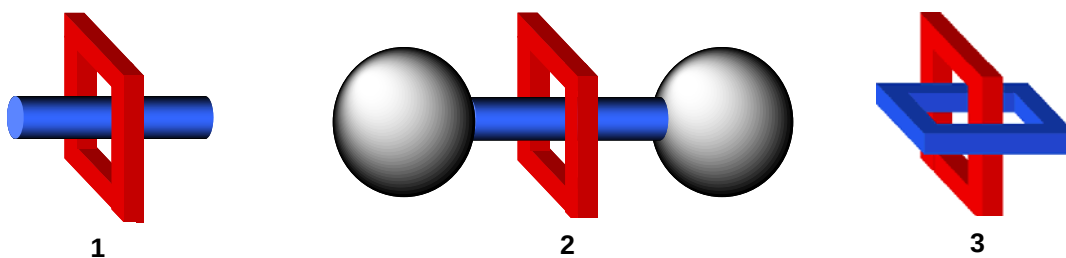


**Figure 2-1.** Schematic presentation of a [2]pseudorotaxane **1**, a [2]rotaxane **2**, and a [2]catenane **3**. The number inside a bracket [ ] means the number of threading or interlocked species.

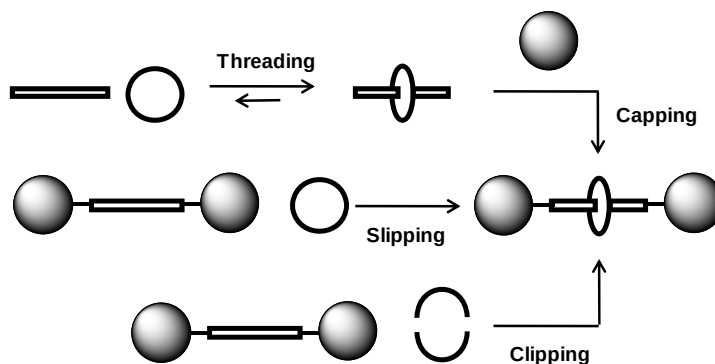
Macrocyclic structures are of special interest for designing artificial receptors: they are large (macro) and may therefore contain cavities of appropriate size and shape. Their connections allow the construction of a given architecture of specific dynamic features and arrangement of structural groups, binding sites and reactive functions. Macrobicyclic structures, which bind a

substrate in their cavity and yield inclusion complexes, cryptates, are called cryptands.<sup>3</sup> The root word crypt comes from the Latin ‘crypta’ which, in turn, comes from the Greek ‘kruptos’ meaning ‘hidden or to hide’.<sup>4</sup> In general, the complexes between cryptands and their guests require 3-dimensional recognition. Cryptands may have a bi-cyclic or tri-cyclic structure and the shapes of complexes are dependent on the place of binding sites with their guests.

## 1.2 Synthetic routes for rotaxanes

There are three different synthetic routes to prepare rotaxanes. As shown in Fig.1, rotaxanes need blocking groups to prevent dethreading. In Scheme 2-1, one route is ‘threading’ and then capping (blocking). After threading, a pseudorotaxane is formed and then blocking groups are introduced to the ends of the chain. The second route is ‘clipping’. This method is also used for the preparation of catenanes; hence, the macrocyclic structures are assembled in the presence of the end-capped thread (dumbbell). The last route, the ‘slipping’ of the cyclic molecule over the blocking group, also occurs if macrocycles and blocking groups are selected carefully. However, this reversible slippage process is quite dependent on the reaction medium and temperature (Scheme 2-1).

The first interlocked compounds were synthesized in 1960 by Wasserman.<sup>5</sup> The development of different synthetic routes since then has progressed as well as the study of various chemical structural units. Details about the synthesis of macrocyclic structures and rotaxanes will be discussed later.



**Scheme 2-1.** Three different ways to synthesize a [2]rotaxane.

## 1.3 Types of interactions in supramolecular chemistry

In contrast to molecular chemistry, which is predominantly based on the covalent bonding of atoms, supramolecular chemistry is based on intermolecular interactions, i.e. on the association of two or more building blocks, which are held together by noncovalent intermolecular bonds. Various types of interactions may be distinguished, which present different degrees of strength,

directionality, dependence on distance and angles: metal ion coordination, hydrogen bonding, van der Waals interactions, hydrophobic interactions, donor-acceptor interactions, electrostatic forces, etc. Their strengths range from weak or moderate as in hydrogen bonds, to strong or very strong for metal ion coordination. However, intermolecular forces are in general weaker than covalent bonds, so supramolecular species are thermodynamically less stable, kinetically more labile, and dynamically more flexible than chemically bonded molecules.<sup>4</sup> Rotaxanes, pseudorotaxanes and catenanes are formed by these various interactions; they are also in the supramolecular species category.

**Metal ion coordination.** In 1983, the synthesis of the first catenane was performed based on metal ion coordination by the Sauvage group. After an interlocked molecule has been synthesized, it can be demetallated and leave the two interlocked parts free to move relative to each other. This feature means that metal coordination can be used as a tool to increase the yields in the synthesis of catenane (or rotaxane) type molecules. The first rotaxane based on this approach was reported in 1991 by Gibson group.<sup>6</sup>

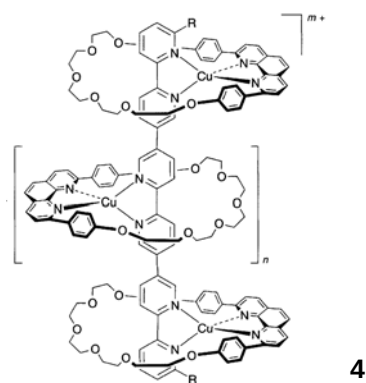


**Figure 2-2.** An example of a [2]rotaxane **4** based on metal coordination.<sup>7</sup>

For other examples of rotaxanes including metal coordination, rigid-rack multi-metallic complexes were prepared by means of Cu ions with tetrahedral coordination geometry (Figure 2-2). Their nature was confirmed by crystal structures.<sup>7</sup> The yield was very high because of the strong interactions between the metal ions and 2,2'-bipyridine ligands.

**Hydrogen bonding.** Recently, rotaxanes and catenanes have also been found in polypeptides and proteins.<sup>8, 9</sup> Although these structures might be expected to be observed only in complex biological systems, examples of synthetic rotaxanes based on hydrogen bonds have also been described. Leigh and coworkers synthesized tertiary

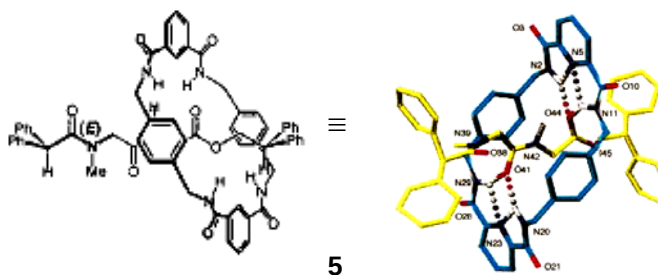


**Figure 2-3.** An example of a [2]pseudorotaxane **5**, based on hydrogen bonding interaction, and its X-ray crystal structure. (reprinted with permission from ref 10. © American Chemical Society)



amide-based rotaxanes **5** (Figure 2-3).<sup>10</sup> The structure of these rotaxanes is rigid in non-polar solvents because of the strong hydrogen bonds in the molecules. However, when they are dissolved in a polar solvent such as DMSO, the solvent can break the hydrogen bonds between the peptide and the macrocycle, leading to different conformations.

The complexes between crown ethers and dibenzylammonium ions are also formed through hydrogen bonding and donor-acceptor interactions. Since the first discovery of dibenzo-18-crown-6, numerous complexes between ammonium ions (including alkyl ammonium) and crown ethers have been studied.<sup>4</sup> The Stoddart and Gibson groups have studied the complexation between secondary ammonium ions and crown ethers in detail.<sup>11-13</sup> Hydrogen bonds are formed between the protons of the ammonium center and the polyether oxygen atoms. In Figure 2-4, the crown ether and ammonium ion complex is formed in acidic conditions by hydrogen bonding.<sup>14</sup> However, when the ammonium moiety loses the proton in basic conditions, there is no hydrogen bond between the amine and macrocycle and this crown ether ring moves to the paraquat guest because of a donor-acceptor interaction. Donor-acceptor interactions will be discussed in this section.

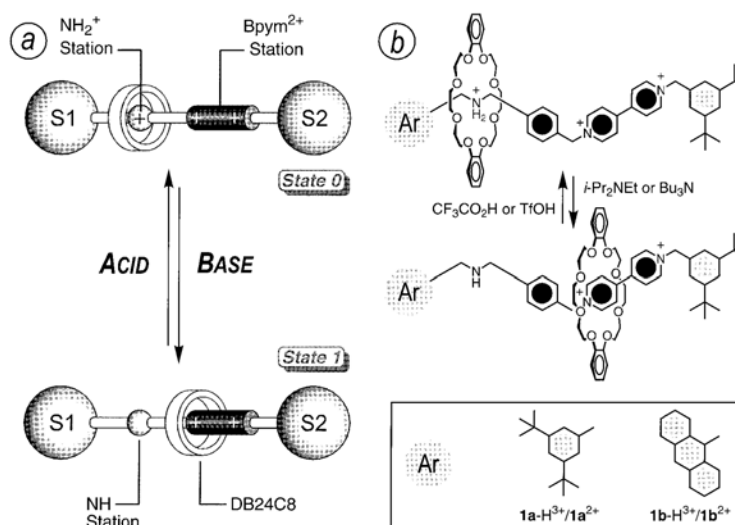


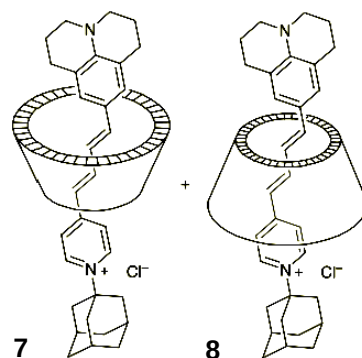
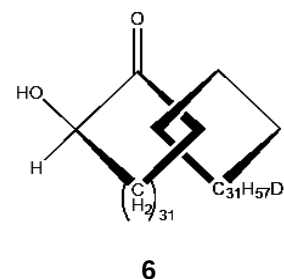
**Figure 2-4.** The pH responsive rotaxanes formed by hydrogen bonding. In acidic conditions, crown ether binds the dibenzyl ammonium ion but it moves to the paraquat species in basic conditions. (reprinted with permission from ref 14. © American Chemical Society)

**Van der Waals interactions.** The first rotaxanes and catenanes were prepared by a statistical synthetic approach, so very low yields were obtained. This outcome was very natural because the

threading of the macrocycle is entropically unfavorable. The catenane **6** was prepared in 0.1% yield.<sup>5</sup>

**Hydrophobic interactions.** Some of the best examples of rotaxanes with hydrophobic interactions are those based on cyclodextrins (CDs). The conformation of CDs is a rigid, well-defined cavity with a conical shape. They have an endo-lipophilic cavity, but are made water-soluble by the many outward-pointing OH groups.<sup>15</sup>

Examples of CD-based rotaxanes are **7** and **8**. Both aliphatic and aromatic hydrocarbon chains complex with CDs. Because of the different end groups in the dumbbell-shaped molecule and the conformation of the cyclodextrin, two isomers are obtained, which can be separated by reverse phase chromatography. The two isomers have different physical properties including different fluorescence quantum yields.<sup>16</sup>



**Donor-acceptor interactions.** Rotaxanes and catenanes presenting donor-acceptor interactions have been studied extensively by the Stoddart group. Their studies are mainly based on the combination of  $\pi$ -electron deficient bipyridinium and  $\pi$ -electron rich hydroquinone moieties.<sup>17</sup> In pseudorotaxanes, the 1,1'-dimethyl-4,4'-bipyridinium dication (dimethyl paraquat) is threaded into the crown ether. A combination of two types of interactions are present, namely hydrogen bonding between some of the polyether oxygen atoms and the  $\alpha$ -bipyridinium protons and  $\pi$ - $\pi$  stacking between the complementary aromatic units.

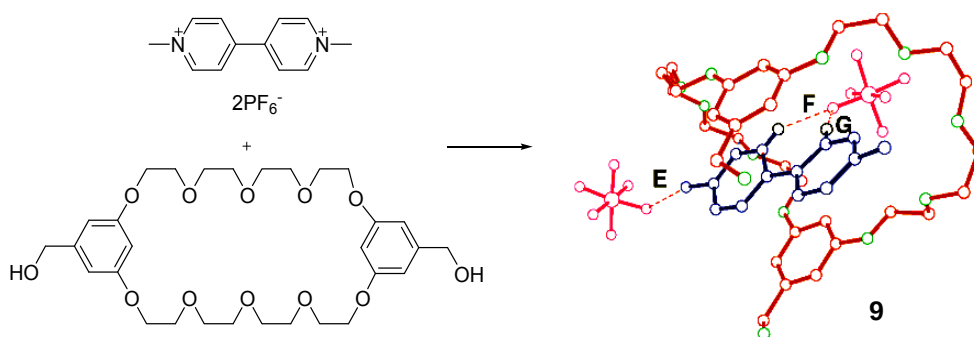


**Figure 2-5.** An example of [2]pseudorotaxane formation based on  $\pi$ - $\pi$  stacking interactions and its X-ray crystal structure. (reprinted with permission from ref. 18. © American Chemical Society)

The Gibson group has also shown unique structures derived from  $\pi$ - $\pi$  stacking interaction. The X-ray structures of complexes between bis(*m*-phenylene)-32-crown-10 (BMP32C10) and paraquat derivatives show the taco-like shape by  $\pi$ - $\pi$  stacking interactions. The three aromatic rings are parallel in the complex **9**.<sup>18, 19</sup>

## 2. Synthesis of crown ethers

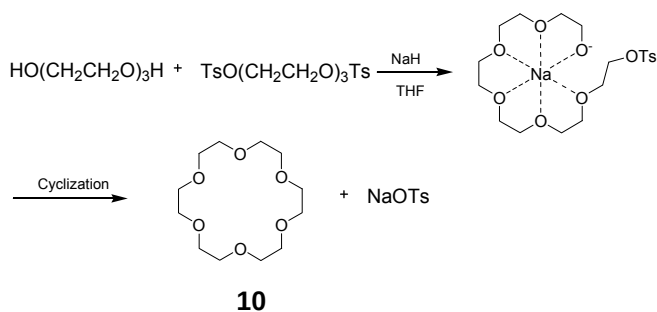
Most approaches to prepare macrocyclic rings are based on one of two synthetic strategies. The first involves simple nucleophilic substitution using one of the incipient macro-ring donor atoms as the nucleophile. This technique may be used for oxygen, sulfur, nitrogen, and other heteroatoms. The second general strategy is the formation of amide linkages followed by reduction to the saturated system. The latter approach is suitable primarily for azacrown and cryptand syntheses.

### 2.1 Crown ethers

The ethyleneoxy unit (-CH<sub>2</sub>CH<sub>2</sub>O-) is favored over other structural units to prepare the crown ethers: it is flexible, relatively strain free and commercially available. Because the inexpensive precursor, ethylene oxide, may readily be oligomerized or polymerized, precursor chemicals containing repeating ethylene oxide units are also readily available and inexpensive. This feature is why the variety of these two-carbon derivatives far exceeds the number of derivatives available for the one or three carbon units.<sup>4</sup>

Pedersen's first synthesis of dibenzo-18-crown-6 (**10**) was accomplished in reasonably concentrated solution (Scheme 2-2).<sup>20</sup> It had the special properties of high crystallinity, reasonable lipophilicity and good chemical stability. It also contains an eighteen membered ring having six donor atoms and this has proven to be unusually effective for cation complexation.

To form a cycle by nucleophilic substitution, high dilution conditions are required because non-cyclic products also



**Scheme 2-2.** Synthesis of 18-crown-6 (**10**) from tri(ethylene glycol) and tri(ethylene glycol)ditosylate

will form. In Scheme 2-2, the sodium cation has an affinity for the oxygen atoms and organizes the intermediate. Thus, the pole-dipole interactions between the sodium cation and oxygen atoms bring the ends of the reacting molecule into the proximity required for ring closure. This is why the Pedersen's first crown ether could be formed at relatively moderate concentration.<sup>4</sup>

Some phenylene crown ethers were synthesized from resorcinol residues and dibromopoly(ethylene glycol)s in 1979.<sup>21</sup> They used cesium carbonate as a base, by which the template effect worked in cyclization. To prepare the rotaxane systems, Kolchiniski et al.<sup>22</sup> and the Stoddart group<sup>11, 23</sup> studied the bis(phenylene) crown ethers (host) and ammonium ions (guest). The equilibrium constants for pseudo-rotaxane complex formation were found to be quite high for these systems, making them quite efficient for the formation of rotaxanes.<sup>11, 23</sup> The Gibson group also studied the complexation between phenylene crown ether derivatives and secondary ammonium ions.<sup>12, 24</sup> The crown ether structures are shown in Fig. 6: dibenzo-24-crown-8 (DB24C8), its asymmetric isomer (asymDB24C8), bis(*p*-phenylene)-34-crown-10 (BPP34C10) and bis(*m*-phenylene)-32-crown-10 (BMP32C10).

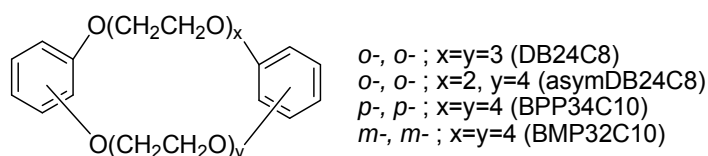
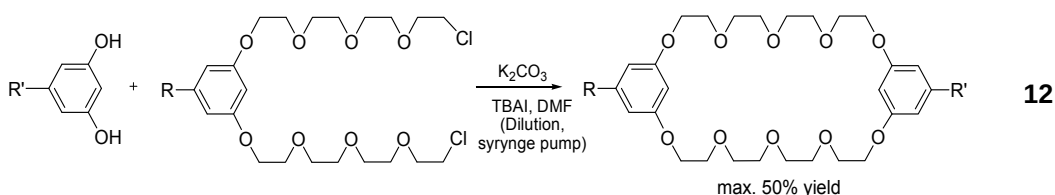
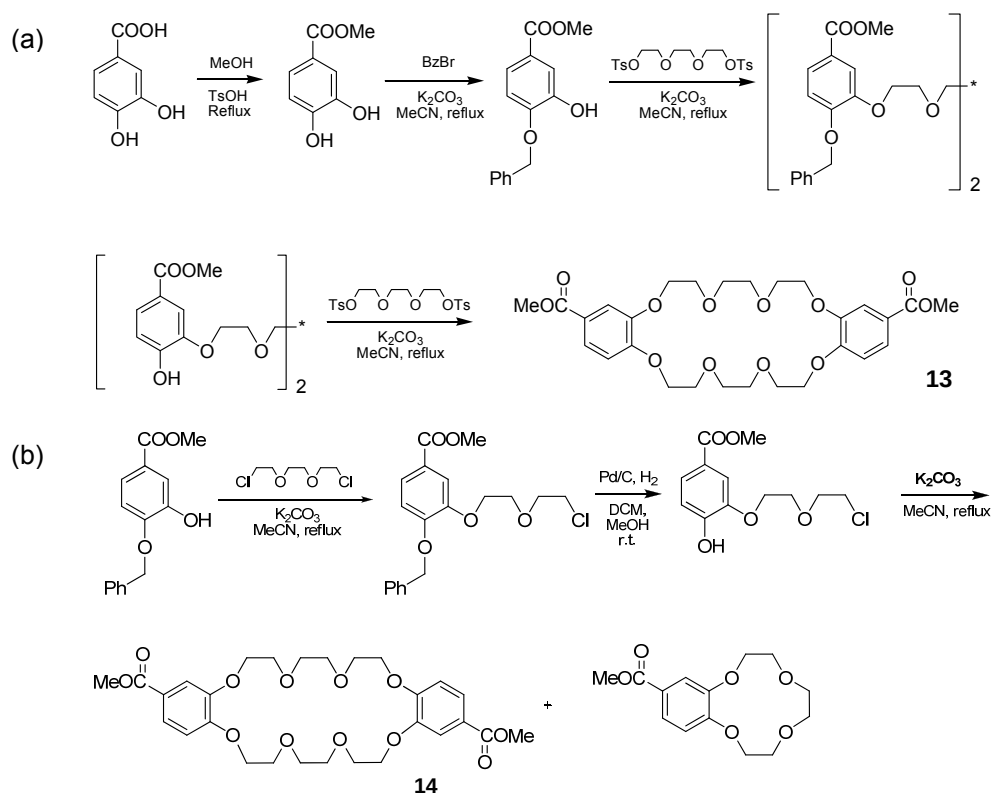


**Figure 2-6.** Representative dibenzo-crown ethers for complexation with several guest ions.

Several mono- and di-functional derivatives of bis(*m*-phenylene) crown ethers were also prepared by the Gibson group.<sup>25-29</sup> Each phenylene ring contains one functional group (R and R') such as methyl ester, hydroxymethyl and carboxylic acid. BMP32C10 derivatives 12 can be synthesized by Scheme 2-3.<sup>12</sup>



**Scheme 2-3.** Synthesis of BMP32C10 derivatives containing one functional group on each aromatic ring.



**Scheme 2-4.** Regioselective syntheses of DB24C8 derivatives: (a) *cis*-DB24C8 dimethyl ester **13**, (b) *trans*-DB24C8 dimethyl ester **14**.

Bis(1,5-naphtho) crown ethers **15** (1/5DNP38C10 or 1/5DNP35C9) were synthesized by the Stoddart group in 1987. These compounds were also used in complexation studies with several kinds of cations such as diquat or paraquat derivatives,<sup>30</sup> pyromellitic diimide and naphthadiimide (NpI).<sup>31</sup>

Novel crown ethers **16** containing *p*-xylene and di(ethylene glycol) linkers between the phenolic rings were reported by the Chiu group.<sup>32</sup> Novel lariat ethers **17**, which have no nitrogen on the ring, were synthesized. Lariat ethers are macrocyclic ethers having side arms. For example, Su and Lu synthesized three kinds of lariat ethers, which contain methoxybenzyl (*o*-, *m*-, *p*-) groups. They also studied the structural conformation of these lariat ethers by X-ray crystallography.<sup>33</sup>

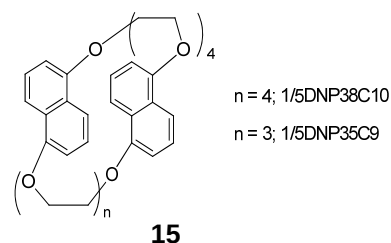
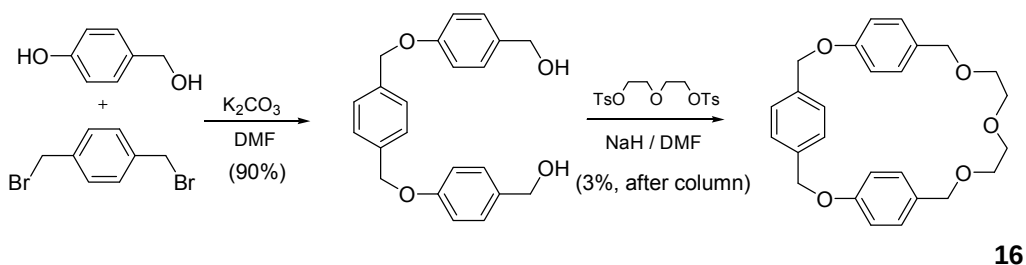


**Figure 2-7.** Bis(1,5-naphtho) crown ethers: 1/5DNP38C10 and 1/5DNP35C9.



**Scheme 2-5.** Synthesis of novel crown ethers by Chiu group.<sup>32</sup>

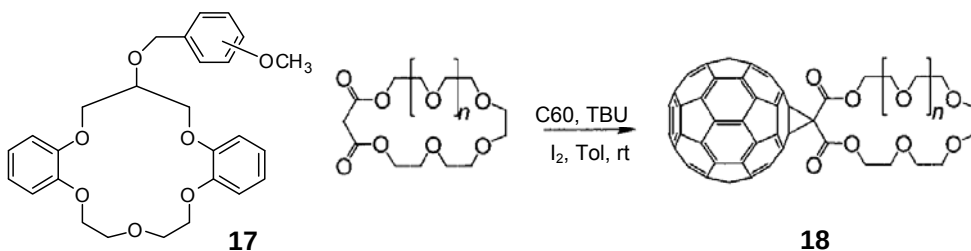


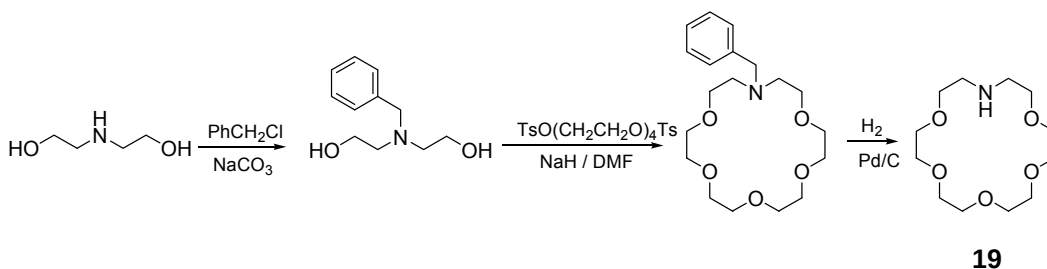
**Figure 2-8.** An example of novel lariat ethers, **17**, which have no nitrogen, and methanofullerene-crown ether **18**.<sup>34</sup>

Methanofullerenes were prepared from macrocyclic malonates by Carano et al.<sup>34</sup> They used crown ethers containing malonate units.<sup>35-37</sup> The complexation between metals and these fullerene containing macrocycles **18**, and electron paramagnetic resonance (EPR) spectroscopy of these complexes were studied in this research.<sup>34</sup>

## 2.2 Crown ethers containing nitrogen

The preparation of macrocycles containing even one nitrogen introduces a set of problems different from those encountered for the all-oxygen macrocycles. In the latter cases, the key difference was whether the oxygen nucleophile was phenoxide or alkoxide. In the case of nitrogen-containing macrocycles, we must consider if the nitrogen will be tertiary. If not, it must be protected at one stage during synthesis.

The synthesis of aza-18-crown-6 (**19**) affords an example of these protection and deprotection processes. Even though several kinds of protecting groups were used in this synthesis, the benzyl groups were preferred because they can be removed relatively easier than other protecting groups for nitrogen. Benzyl groups can be easily removed by the hydrogenolysis with noble-metal catalysts.<sup>4</sup>



**Scheme 2-6.** Synthesis of aza-18-crown-6 (**19**) from diethanolamine.<sup>4</sup>

The second important strategy for azacrown compound synthesis is to form a cyclic amide (lactam) or bis(lactam) and then to reduce it to the corresponding amine. In this approach in Fig. 9, an acid chloride is treated with a primary amine under high dilution conditions. No protecting group is required.<sup>4</sup>

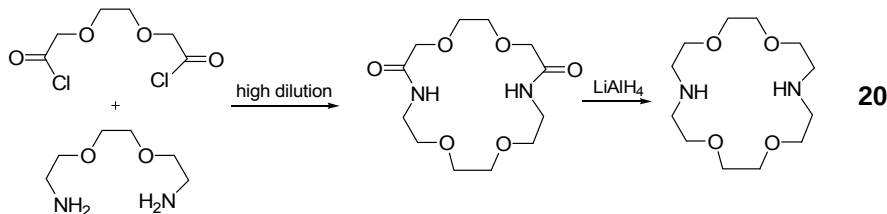


**Figure 2-9.** Synthesis of diaza-18-crown-6 (**20**) from diacyl chloride and diamine.<sup>4</sup>

The lariat ethers are represented by a large number of novel structures, prepared by many groups. The term is now applied to nearly any structures having one or more sidearms, whether or not binding is involved. The lariat ethers may be prepared in such a way that the incipient sidearm protects nitrogen during synthesis. Alternately, the readily available N-benzyl azacrown may be hydrogenolyzed to the parent and then alkylated. When the former approach is used, diethanolamine is added to the incipient sidearm in an electrophilic form. Cyclization of the N-substituted diethanolamine derivatives is accomplished in the usual way. One interesting practical problem was encountered using these two approaches. When the sidearm was longer than about three ethyleneoxy units, the substituted diethanolamine derivative was itself a good complexing agent. It bound salts so tightly that purification became quite difficult. In such cases, the parent crown was prepared and alkylated rather than using the more direct approach.

The incorporation of heteroaromatic sub-units into macrocycles is not a new concept. Many natural products which complex with metal atoms contain heteroatomic subunits. Chlorophyll and hemoglobin are two of the best known examples of natural cation-binding macrocycles. The pyridine unit is widely used in heteroaromatic macrocycles. The Bradshaw group synthesized 2,6-pyridino-18-crown-6 and its derivatives.<sup>36, 38</sup> Many diester crown ethers (**21**, **23**) have been prepared by treating an oligo(ethylene glycol) with the appropriate diacyl dichloride. In addition, transesterification has also proven to be a good method for the preparation of diestercrown ethers. Not only the pyridine unit, but also 4-pyridone (in **23**) and triazole units (in **24**) were also used in the synthesis of the macrocycles.<sup>39-41</sup>

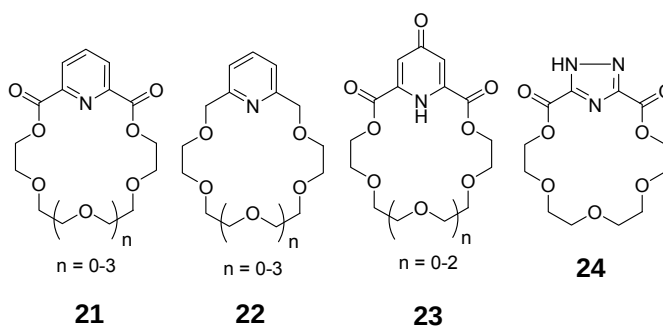


**Figure 2-10.** Several heteroaromatic macrocycles containing nitrogens synthesized by the Bradshaw

### 2.3 Crown ethers containing sulfur (thiacrown ethers)

The thiacrown ethers are similar to the crown ethers except that one or more of the polyether oxygen atoms are replaced by sulfur atoms. The various thiacrown ethers (Figure 2-11) were prepared by the Bradshaw group and thia-18-crown-6 was synthesized by Scheme 2-7.<sup>42-44</sup>

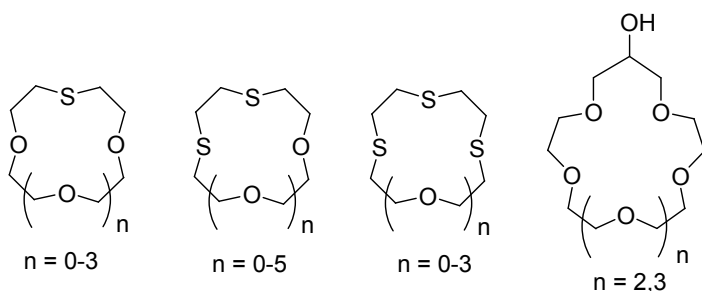
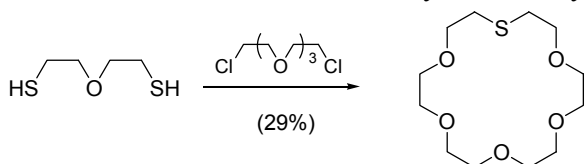


**Figure 2-11.** Several thiacrown ethers synthesized by the Bradshaw group

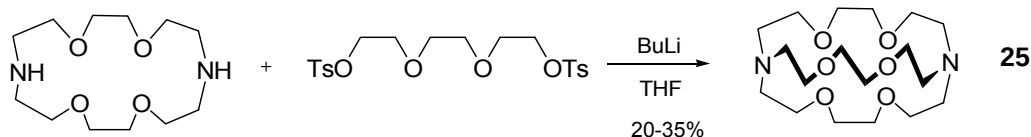


**Scheme 2-7.** Synthesis of thiacrown ether by  $S_N2$  cyclization.



### 3. Cryptands

Even though there is huge diversity in the structural class, cryptand syntheses have generally been accomplished by a strategy having two features. First, a single ring is assembled and then another strand (or two) is (are) added. The second feature of the approach is that the vast majority of synthetic reactions conducted on synthesized cryptands involve lactam formation followed by reduction. These reactions are usually conducted under high dilution conditions. [2,2,2]-Cryptand **25** was prepared by metallation on the nitrogens in 20-35% yield (Scheme 2-8).<sup>45</sup> Several cryptands containing a pyridine unit and/or azacrown ethers were also synthesized by the Bradshaw group (Fig. 12).<sup>46-50</sup>



**Scheme 2-8.** Synthesis of [2,2,2]-cryptand under high dilution.

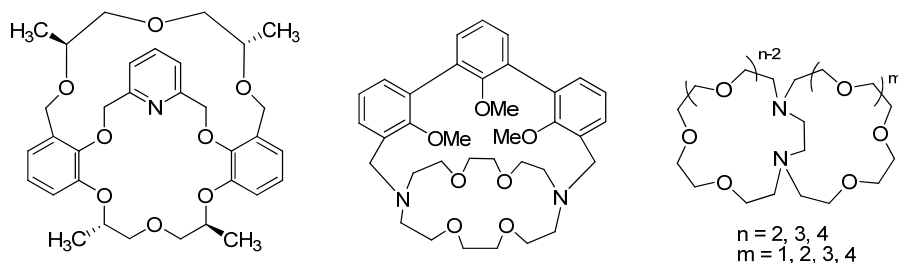


**Figure 2-12.** Cryptands containing nitrogen atoms synthesized by the Bradshaw group.

The Gibson group developed new cryptands to improve the  $K_a$  (association constant with guests such as paraquat derivatives, sec-ammonium ions, and pyridinium derivatives). X-ray diffraction results confirmed the 1:1 stoichiometry and the structures of the “pseudorotaxane”-like inclusion complex of cryptands (**26** – **28**) and paraquat derivatives.<sup>18, 51</sup>

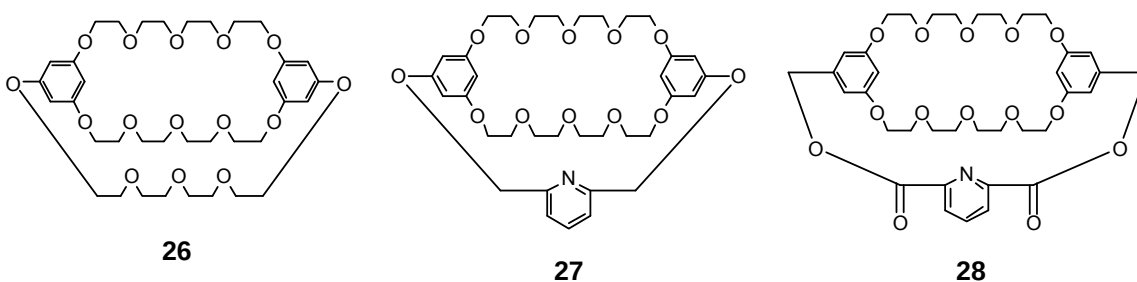
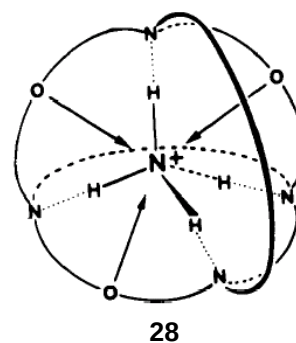


**Figure 2-13.** Several examples of cryptands synthesized by the Gibson group.

The cryptates, complexes of cryptands and proper guests ions, are very important because of their shapes. Their shapes are dependent on the macrocyclic rings and the type of guest ions. Macrobicyclic ligands with metal ions (such as [2,2,2]-cryptand) show pronounced selectivity as a function of the size complementarity between the cation and the intramolecular cavity, a feature termed spherical recognition (**28**). Selective binding of tetrahedral substrates requires



the construction of a receptor molecule with a tetrahedral recognition site. It may be achieved by positioning four suitable binding sites at the corners of a tetrahedron and linking them with six bridges. The cryptand binds a tetrahedral  $\text{NH}_4^+$ .<sup>15</sup>

The cryptate **30** between crown ether-pyridine cryptands **29** and paraquat derivatives shows that paraquat derivatives are threaded asymmetrically into the cavity of the 32-crown-10 portion of the cryptand (Fig. 14).<sup>52</sup>

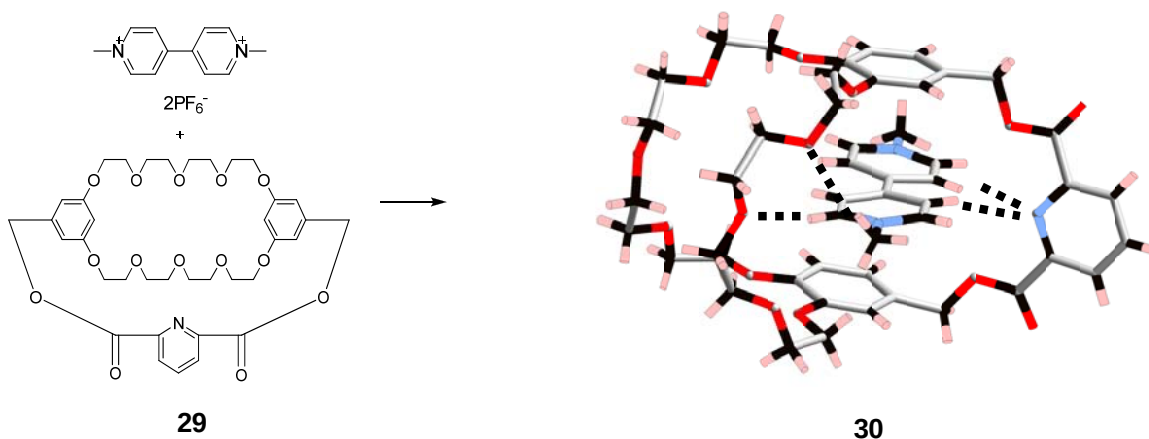


**Figure 2-14.** Solid state structure of cryptate between a BMP32C10-based cryptand and dimethyl paraquat. (reprinted with permission from ref 52. © American Chemical Society)

#### 4. Polypseudorotaxanes and Polyrotaxanes<sup>51</sup>

Polyrotaxanes (or polypseudorotaxanes) are polymers which contain rotaxane (or pseudorotaxane) moieties. Polyrotaxanes possess mechanically linked subunits, for which the connecting forces are non-covalent interactions, while typical polymers have only covalent bonds. Depending on the location of the rotaxane unit, there are two types of polyrotaxanes; main-chain polyrotaxanes and side-chain poly-rotaxanes. The main-chain polyrotaxanes are constructed with rotaxane moieties, which are located in the main chain; the side-chain polyrotaxanes contain rotaxane moieties located in the side chain.

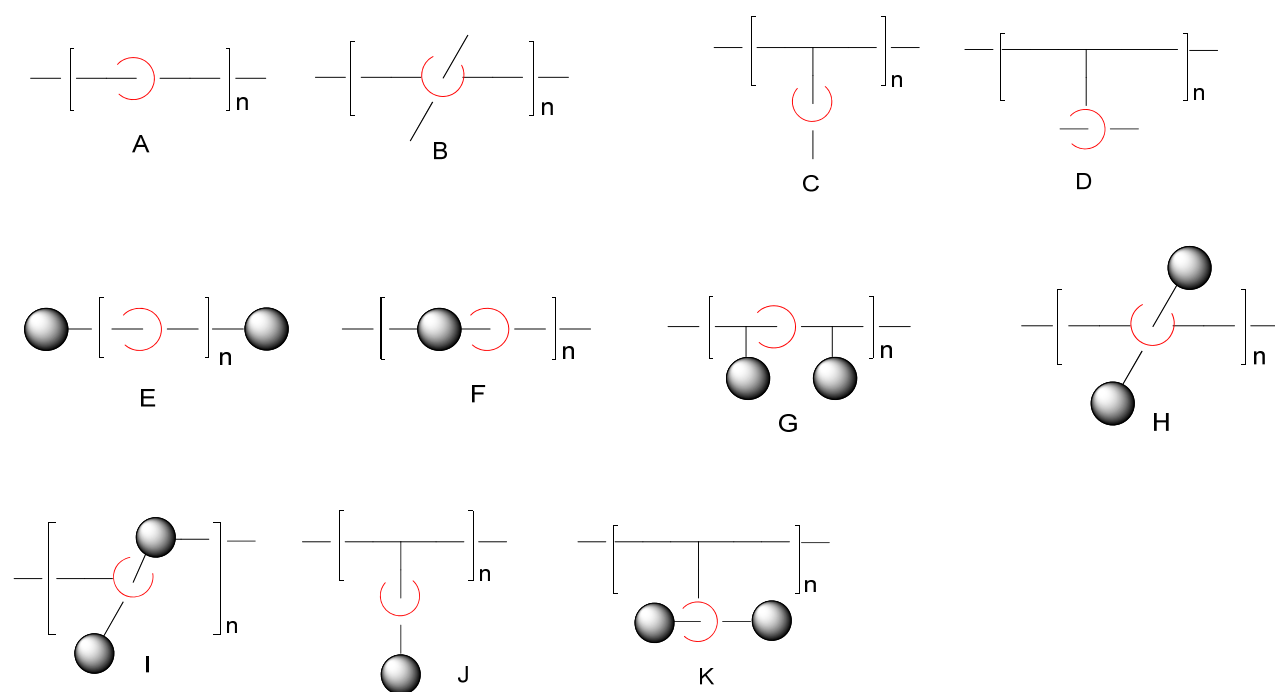


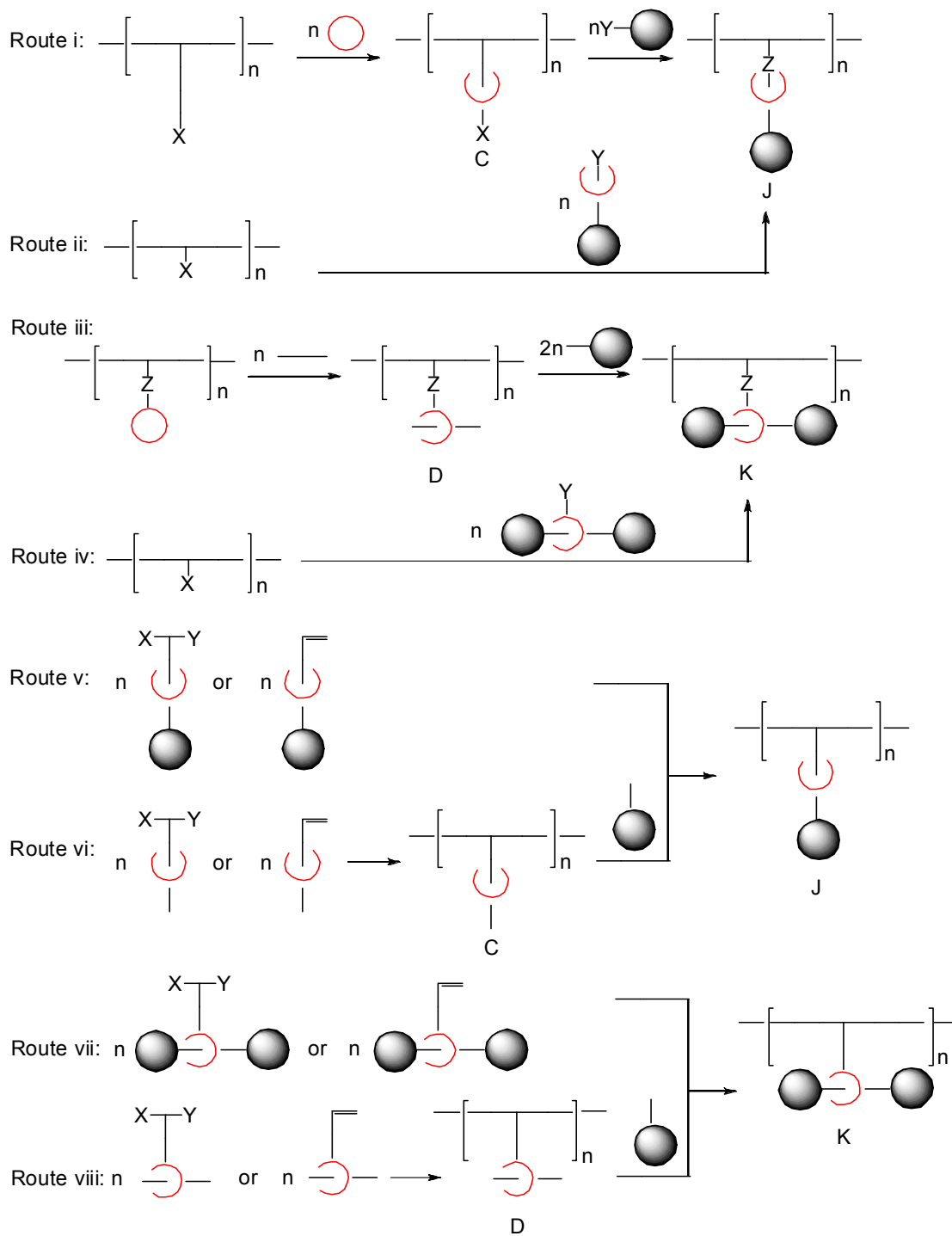
**Figure 2-15.** Types of polypseudorotaxanes and polyrotaxanes. **A** and **B** are main-chain polypseudorotaxanes; **C** and **D** are side-chain polypseudorotaxanes; **E**, **F**, **G**, **H** and **I** are main-chain polyrotaxanes; **J** and **K** are side-chain polyrotaxanes. (reprinted with permission from ref 51. © Elsevier)

#### 4.1 Synthetic routes for main-chain and side-chain polyrotaxanes

Multiple routes to make main-chain polyrotaxanes are shown in Scheme 2-9. Route I involves the polymerization of a pseudorotaxane, but route II involves only the threading of macrocycles onto the main chain of the polymer. Route III is the polymerization of a rotaxane monomer, but the bonds between the stopper and the chain are broken throughout the polymerization. Route IV involves the copolymerization between a difunctional pseudorotaxane and a difunctional stopper. Route V also involves the polymerization of the pseudorotaxane, but the difference between two pseudorotaxanes used in route I and route V is that the two functional groups are on the linear component for the former but on the cyclic component for the latter. In route IV, linear components are threaded into the macrocycles incorporated in a preformed polymer to form a polypseudorotaxane and then stoppers are introduced to produce a polyrotaxane of type F in Fig. 15. Route VII involves only the polymerization of a rotaxane monomer to produce the same type of polyrotaxane as in route VI. In route VIII, the polymerization of a difunctional rotaxane produces a slip-link polymer of type I in Fig. 15.

Side-chain polyrotaxanes can be prepared by the routes in Scheme 2-10. Macrocycles are threaded onto the side chains of an existing polymer in route ii. Then stoppers are introduced to the ends of the side chains. In route iii, macrocycles are already on the side chain of polymer, while a rotaxane containing a functionalized macrocycle reacts with polymer chain in route iv. In route vii and viii, rotaxane or pseudorotaxane monomers are prepared first and then they are polymerized. Here I review polyrotaxanes based on cyclodextrins, crown ethers, cucurbiturils, and other macrocycles.





**Scheme 2-10.** Synthetic routes for side-chain polypseudorotaxanes and polyrotaxanes. (reprinted with permission from ref 51. © Elsevier)

## 4.2 Cyclodextrin-based polyrotaxanes

Cyclodextrin (CDs) are a series of cyclic oligosaccharides of 1,4-linked d(+)-glucose units. The three most used CDs are  $\alpha$ -,  $\beta$ -,  $\gamma$ -CD and they have a cylindrical cavity with a depth of 7.0 Å and internal diameters of 4.5 Å for  $\alpha$ -CD, 7.0 Å for  $\beta$ -CD and 8.5 Å for  $\gamma$ -CD.<sup>53</sup> Since CDs have a hydrophobic interior and hydrophilic external faces, the typical linear species has two hydrophilic ends and a hydrophobic middle part to facilitate the formation of the inclusion complex with CDs. This feature is because the hydrophobic middle part inserts inside of the CDs and the hydrophilic ends stay outside of the macrocycle. A necklace-like polyrotaxane was prepared by Harada et al. They used  $\alpha$ -CD and poly(ethylene glycol) bisamine (PEG-BA) ( $M_n = 3350$ ) to synthesize the inclusion complexes and 2,4-dinitrobenzene was used as a stopper for  $\alpha$ -CD macrocycles (Fig. 16).<sup>54</sup>

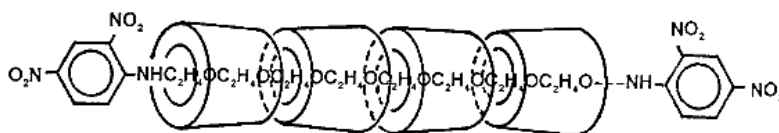
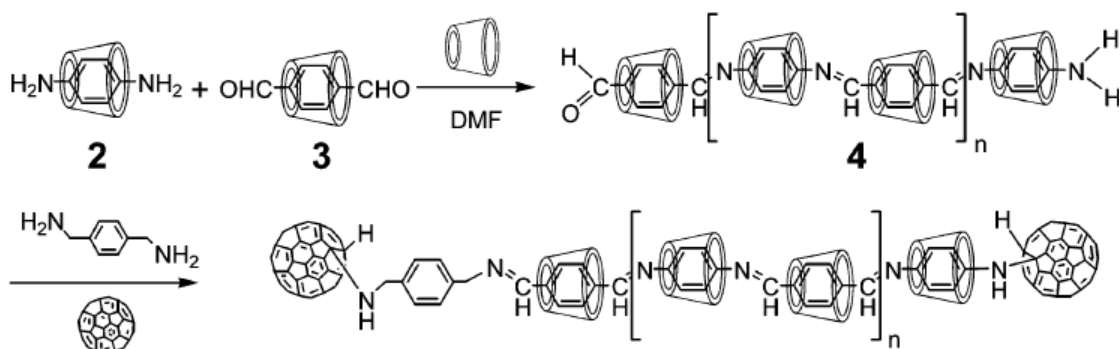


**Figure 2-16.** Necklace like polyrotaxane based on PEG and  $\alpha$ -CD by Harada et al. (reprinted with permission from ref 54. © Nature Publishing Group)

Yamaguchi et al. used route I to synthesize a polyrotaxane by reacting 3,3'-diaminobenzidine and 1,12-dodecanediol in the presence of  $\alpha$ -CD and  $\text{RuCl}(\text{PPh}_3)_3$ .<sup>55</sup> The aromatic rings incorporated along the polymer backbone are far too bulky to pass even though the relatively small cavities of the  $\alpha$ -CDs. Thus the macrocycles are trapped on the aliphatic portions of the polymer. This polyrotaxane contains a blocking group, which functions a like stopper, in every structural unit of the main chain.

Geckeler and co-workers prepared the first fullerene-terminated soluble poly(azomethine)-based polyrotaxane with  $\beta$ -CD in order to improve the solubility of the semiconducting poly(azomethine) in common organic solvents (Scheme 2-11).<sup>56</sup>



**Scheme 2-11.** Synthesis of poly(azomethine)-based polyrotaxane with  $\beta$ -CD by Geckeler and co-workers. (reprinted with permission from ref 56. © American Chemical Society)

A series of conjugated main-chain polyrotaxane insulated molecular wires was prepared by the Anderson group.<sup>57, 58</sup> The recent result showed the preparation of poly(*para*-phenylenevinylene) rotaxanes by an aqueous Suzuki coupling reaction (Fig. 2-17).

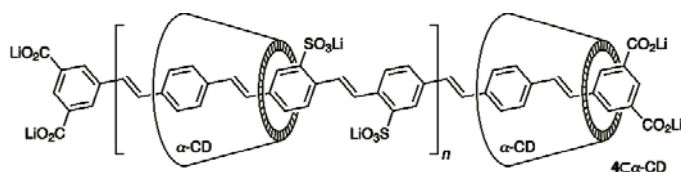


**Figure 2-17.** Poly(*para*-phenylenevinylene) rotaxanes by Suzuki coupling. (reproduced by permission from ref. 58. © The Royal Society of Chemistry)

The Yui group has prepared various CD based polypseudorotaxanes and polyrotaxanes. They mainly used PEG and poly(propylene glycol) (PPG) to prepare the polyrotaxanes. Route II (Scheme 2-9) is used to prepare biodegradable polyrotaxanes having hydrolyzable linkages at the ends of the chain.<sup>59-61</sup> This group also made a polyrotaxane in which many CDs are threaded onto a triblock copolymer of PEG and PPG end-capped with fluorescein-4-isothiocyanate. With increasing temperature, the majority of the CDs move onto the PPG block and this idea was applied as a model of stimuli-responsive molecular assemblies.<sup>62, 63</sup>

The Yui group also prepared a series of PEG hydrogels cross-linked by a hydrolyzable polyrotaxane consisting of many  $\alpha$ -CDs and a PEG chain capped with bulky end groups via ester linkages. The time to reach complete gel erosion was found to be prolonged by decreasing the polyrotaxane content and increasing the PEG/ $\alpha$ -CD ratio. This phenomenon may be due to the structural characteristic of the polyrotaxane: ester linkages may be included within the cavity of



$\alpha$ -CDs, resulting in their enhanced stability (Fig. 18).<sup>64</sup> The same type of hydrolyzable polyrotaxane was used to form a tubular structure in the hydrogel.<sup>65</sup>

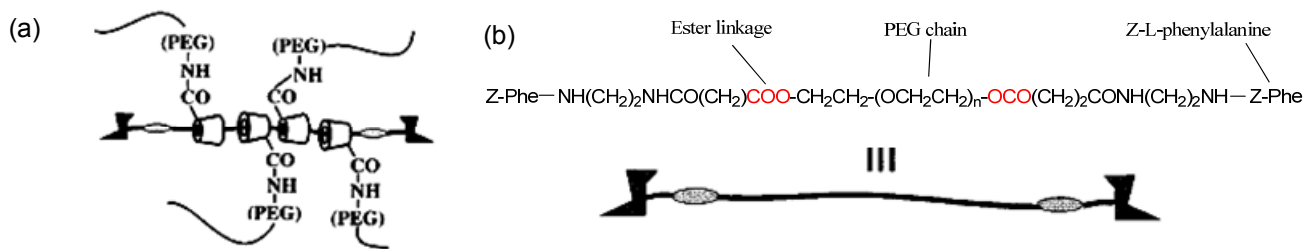


**Figure 2-18.** (a) Cross-linked hydrolyzable hydrogels consisting of CDs and PEG chains, (b) PEG hydrogels containing CDs and Z-L-phenylalanine. (reprinted with permission from ref 66. © Elsevier)

Fibroblast adhesion and proliferation on the PEG hydrogels containing of  $\alpha$ -CDs (macrocycles) and Z-L-Phe (stopper) were observed by contact angle and small light scattering measurements. It was suggested that the surface and bulk structures of the PEG hydrogels were heterogeneous. These findings suggest that the cells recognize the surface heterogeneity due to the polyrotaxane structure, and the number of cell adhesion and proliferation sites is controllable by the polyrotaxane content in feed.<sup>66</sup>

The pH responsive polypseudorotaxanes of polyethyleneimines (PEI) with various molecular weights threaded through  $\alpha$ - or  $\gamma$ -CD were also prepared. The maximum yield of the recovered polypseudorotaxane precipitates was observed at pH 11.0, whereas no complexation was observed in the pH range below 8.0 due to a protonation of the secondary amine group in PEI backbones.<sup>67</sup> The pH dependent polypseudorotaxanes of an ABA triblock copolymer consisting of PEI and PEG (PEI-block-PEG-block-PEI) with  $\alpha$ -CDs were also prepared.<sup>68</sup>

Carboxyethylester-polyrotaxanes (CEE-polyrotaxanes) with a number of CEE-modified  $\alpha$ -CDs were synthesized and the effects of the number of CEE- $\alpha$ -CDs on calcium binding and trypsin inhibition were investigated by the Yui group. The number of CEE- $\alpha$ -CDs in the CEE-polyrotaxanes can control the inhibition mechanism of trypsin activity.<sup>69</sup> The Yui group also has studied the structural effects of polyrotaxanes for biological and medicinal applications.<sup>69-73</sup>

The Yui and Stoddart groups prepared carbohydrate-displaying polyrotaxanes of CDs threaded onto linear polymer chains as dynamic multivalent neoglycoconjugates. The formation of polyrotaxanes could enhance protein-carbohydrate interactions in a dynamic multivalent way.<sup>74,75</sup>

The polypseudorotaxanes of azobenzene polyester, polyurethane and polyurea were synthesized by the Yamamoto group. The polyurethane-based polypseudorotaxanes had lower glass transition temperatures ( $T_g$ ), while the polyurea-based polyrotaxanes show higher  $T_g$ . For the former, the decrease of  $T_g$  resulted from weaker intermolecular hydrogen bonds between the urethane groups than the those of corresponding polyurethane;<sup>76</sup> for the latter the increase of  $T_g$  was due to the decrease in flexibility of the polymer chain because of the inclusion of rigid CDs onto the polyalkylene part.<sup>77</sup>

A series of CD-based polypseudorotaxanes were constructed by threading native  $\beta$ -CDs or L-tryptophan-modified  $\gamma$ -CDs onto amino-terminated PPG chains of different lengths. These polypseudorotaxanes were further assembled to form net-like supramolecular aggregates which showed not only a satisfactory water solubility, but also a good ability for capturing fullerenes in aqueous solution.<sup>78</sup>

Li et al.<sup>79-81</sup> and Nostro et al.<sup>82</sup> synthesized CD-based polypseudorotaxanes with poly(ethylene oxide) (PEO) and random or triblock copolymer of PEO and poly(propylene oxide) (PPO). They also used route II (Scheme 2-9) to prepare the polypseudorotaxanes and studied the kinetics of the threading process which was determined to be a function of the temperature and solvent composition (water, heavy water and urea). Nostro et al. also studied the effect of salts on the threading process for PPO derivatives with CDs. What emerged is that changes in the threading time are strongly dependent on the nature of both cations and anions.<sup>83</sup> Polypseudorotaxanes from poly(butylene carbonate) and CDs were synthesized by Li et al. They obtained crystalline inclusion complexes and characterized the novel polypseudorotaxanes.<sup>84</sup> Harada and co-workers reported the synthesis of the first molecular tube (MT) by cross-linking adjacent hydroxyl groups on  $\alpha$ -CDs threaded onto PEO to form a polypseudorotaxane. Hydroxyl groups on adjacent  $\alpha$ -CDs were cross-linked by epichlorohydrin.<sup>85</sup> Kim et al. prepared a well-defined three-dimensional structure of PEG and  $\alpha$ -CDs complex by crystallizing the inclusion complex. After crystallization, hexagonal fibers with 2  $\mu$ m diameter and longer than 5  $\mu$ m length were formed.<sup>86</sup>

Side-chain polyrotaxanes were reported by Ritter and co-workers.<sup>87</sup> First, 2,5-di-O-methyl  $\beta$ -CD was threaded onto a monofunctional compound to afford a semi-rotaxane. Then the semi-rotaxane was reacted with a preformed copolymer based on poly(methyl methacrylate) to derive

a side-chain polyrotaxane. Poly(ether sulfone), poly(methacrylate), and poly(acrylamide) were also used to prepare side-chain polyrotaxanes incorporating CDs by this group.<sup>88-90</sup>

A solid state synthesis to prepare rotaxanes was performed by the Otera group.<sup>91</sup> The end-capping reaction was also done in the solid state by Kihara and co-workers to prepare poly(tetrahydrofuran) (PTHF) incorporating CDs. They performed the solid-state reaction by grinding the solid polypseudorotaxanes with 4-tritylphenyl isocyanate as a blocking reagent and obtained the polyrotaxane in 24% yield.<sup>92</sup>

### 4.3 Crown ether-based polyrotaxanes

The Gibson group has actively studied the preparation of polyrotaxanes incorporating crown ether derivatives. They prepared polyester rotaxanes via statistical threading and counted the number of crown ether rings on the chain.<sup>93</sup> By carrying out step-growth polymerization in the presence of aliphatic crown ethers, main-chain polyester and polyurethane polypseudorotaxanes of Type A (Fig. 15) were prepared.<sup>94-98</sup> By using bulky monomers in step-growth polymerizations in the presence of crown ethers, polyrotaxanes of Type F were also prepared (Fig. 19).<sup>99-102</sup>

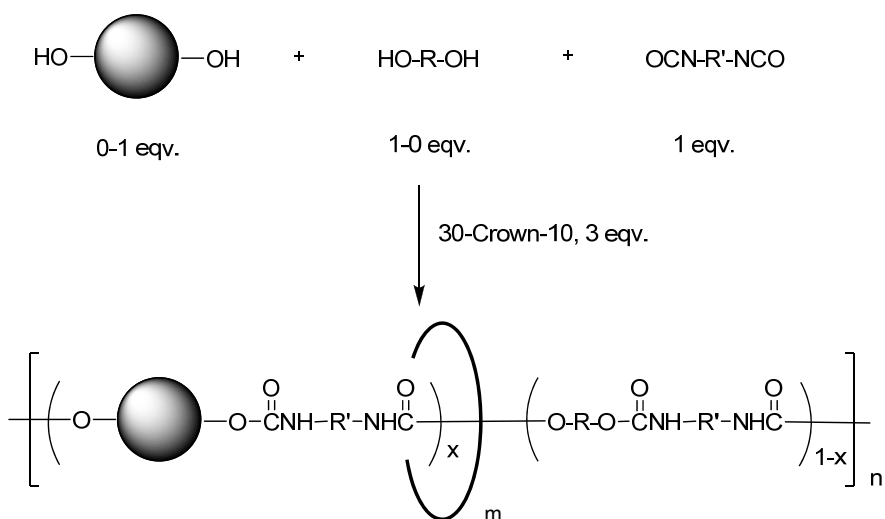


**Figure 2-19.** Polypseudorotaxanes based on polyurethane by step-growth polymerization in the presence of crown ethers.<sup>100</sup>

Polystyrene-based pseudorotaxanes (Type A) and polyrotaxanes (Type E) were synthesized by chain-growth polymerization.<sup>103-105</sup> These polyrotaxanes are examples of the statistical threading method, route I in Scheme 2-9. It was found that the m/n values (the number of

macrocycles per repeating unit) did not increase with ring size because of different threading/dethreading processes for different sized macrocycles.

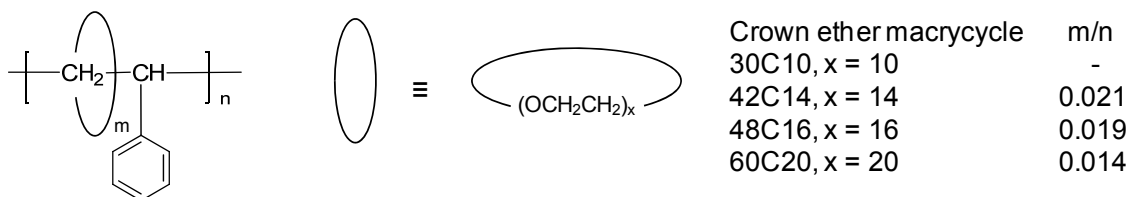


**Figure 2-20.** The number of crown ethers per repeating unit polystyrene-based polypseudorotaxane.

Difunctional blocking groups were introduced to the main-chain in order to understand the threading process (Type F in Fig. 13, route IV in Scheme 2-9). The introduction of the blocking group increases the m/n value to about 5 times that of a poly(decamethylene sebacate-30-crown-10) (30C10) rotaxane of Type A without blocking groups.<sup>99, 100, 106, 107</sup> When tetrarylmethyl blocking groups are in both the diol and diacid chloride, the m/n value increased another 3 times to reach 0.172 for 30C10.<sup>106</sup> The threading efficiency, m/n, is dependent on the blocking groups, the size of the crown ether, the ratio between the cyclic and acyclic starting materials, the interaction between crown ether and linear chain, and temperature.

More efficient polyrotaxane syntheses based on hydrogen bonding interactions between the crown ethers and the monomer and/or polymer were performed. The Gibson group studied systems in which the crown ether was functionalized and could self-associate via hydrogen bonding. As a result of such self-association, self-threading of these monomers occurs and yields mechanically branched or cross-linked polyrotaxanes (Fig. 21).<sup>108</sup> When the solvent was diglyme, the target cross-linked polyrotaxanes were formed via exo or endo esterification (including threading). However, when DMSO was used as a solvent for the esterification, only linear polymer was obtained because DMSO prevents hydrogen bonding between the hydroxyl groups and the crown ethers.

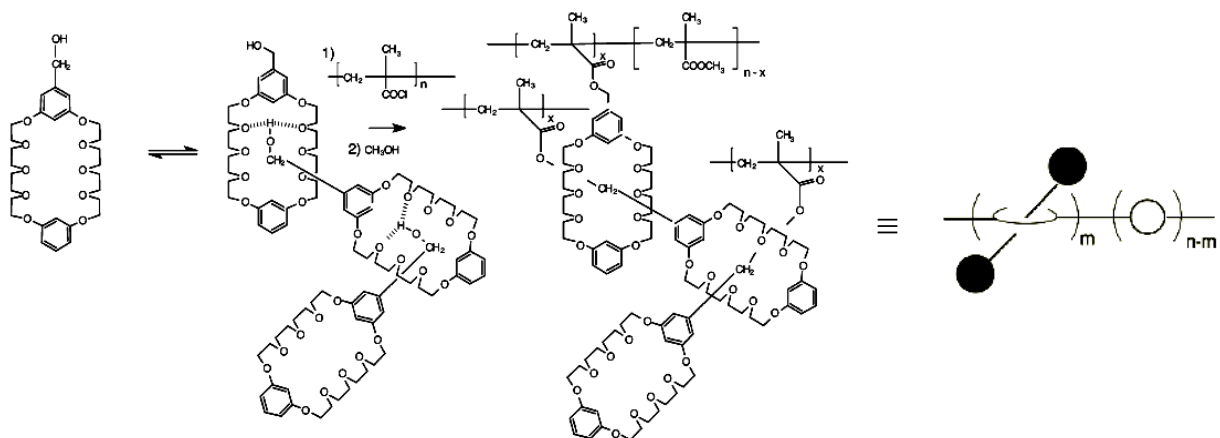


**Figure 2-21.** Cross-linked polyrotaxanes via exo or endo esterification under diglyme. (reprinted with permission from ref 108. © American Chemical Society)

In the preparation of polyamide-based polypseudorotaxanes, the Gibson group found that the threading of the crown ethers is dependent upon their cavity size and the propensity for cyclization of the polymer backbone. They also prepared polyrotaxanes and catenanes based on the same structural unit.<sup>109</sup>

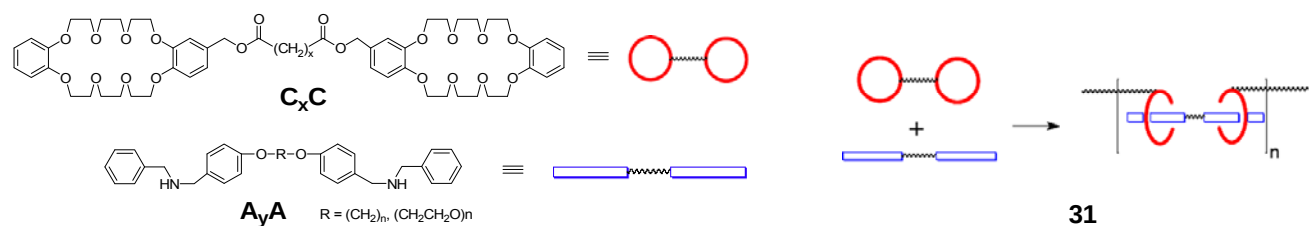


**Figure 2-22.** The formation of linear supramolecular polymers **31** by strong interaction between crown ethers and dibenzyl ammonium cations.<sup>110</sup>

The Gibson group also proposed a new model of polyrotaxanes. Self-assembly of pseudorotaxane polymers (**31**) from complementary homoditopic building blocks comprised of bis(dibenzo-24-crown-8 (DB24C8)) esters derived from the hydroxymethyl crown ether and aliphatic diacid chloride ( $C_xC$ ,  $x$  = number of methylene units in the diacid segment) and 1,10-bis-[*p*-(benzylammonio-methyl)phenoxy]alkane bis(hexafluoro-phosphate) ( $A_yA$ ,  $y$  = number of methylene unites in the linker) were studied. The linear supramolecular polymers  $lin-[C_xC \cdot A_yA]_n$  were formed and they were characterized (Fig. 22).<sup>110</sup> The linear polymer also formed as a microfiber when drawn from concentrated solution. Crown-terminated polystyrene was synthesized from a TEMPO-based free radical initiator containing DB24C8 or BMP32C10

(bis(m-phenylene)-32-crown-10). The prepared polystyrenes had narrow molecular weight distributions. Polystyrene containing DB24C8 could complex only with *sec*-ammonium cations; however, polystyrene containing BMP32C10 could complex with paraquat derivatives whose size is larger than the *sec*-ammonium cations.<sup>111</sup>

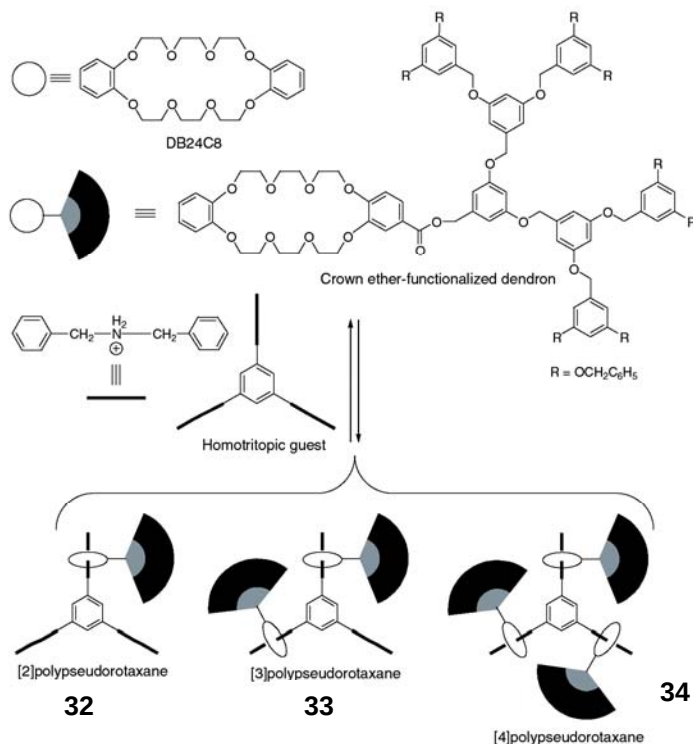


**Figure 2-23.** The equilibrium formation of dendritic [2]-, [3]- and [4]-polypseudorotaxanes (**32-34**) from crown ether-functionalized dendrons and a complementary homotritopic molecule. (reprinted with permission from ref 112. © American Chemical Society)

The Gibson group also reported dendritic [2]-, [3]-, [4]-polypseudorotaxanes from cooperative complexation between DB24C8-functionalized dendrons and a complementary homotritopic guest molecule, 1,3,5-tris[*p*-(benzylammoniomethyl)phenyl]benzene tris(hexafluorophosphate) (Fig. 23).<sup>112</sup> They prepared pH-responsive dendritic polypseudorotaxanes with BMP32C10-functionalized poly(propyleneimine) dendrimers as the cores of polypseudorotaxanes. Upon protonation of the tertiary amines in the dendritic interior, there exists an obvious “switch” in binding between unprotonated and protonated host macromolecules from an anti-cooperative regime to an independent one. Such a “switch” may be explained by rigidification of the protonated dendrimer in which the macromolecule is electrostatically forced to adopt a conformation that maximized host binding site separation.<sup>113</sup>

A new method for the fabrication of star polymers by self-assembly between a homotritopic

tris(BMP32C10) host and a complementary monotopic paraquat-terminated polystyrene guest following the same method as for formation of the dendritic pseudorotaxanes was reported (Figure 2-24).<sup>114</sup>

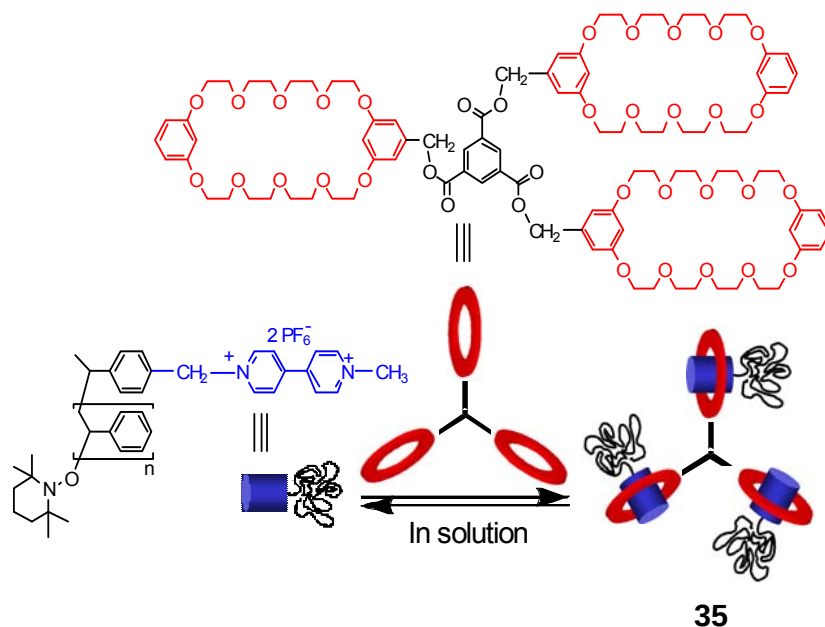


**Figure 2-24.** The new way for fabrication of a star polymer **35** by self-assembly between a homotritopic tris(BMP32C10) and monotopic paraquat-terminated polystyrene. (reprinted with permission from ref 114. © American Chemical Society)

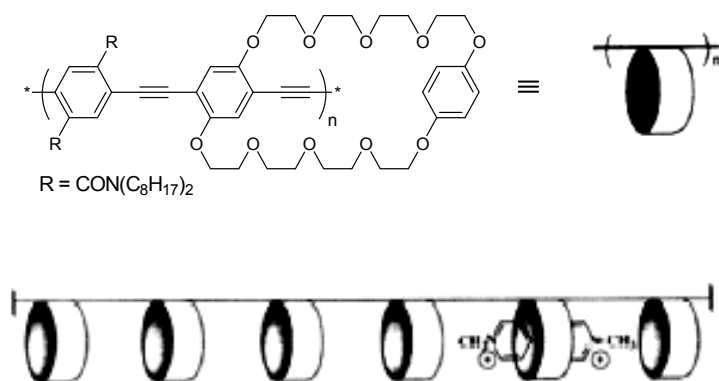


**Figure 2-25.** A new side-chain polypseudorotaxane containing crown ether rings as a part of the polymer backbone and paraquats as a guest. (reprinted with permission from ref 116. © American Chemical Society)

The Yamamoto group prepared poly(*p*-phenylenebenzimidazole)-based side chain polyrotaxanes with crown ether-metal complexes as the stoppers in DMF. The treatment of these polyrotaxanes with water caused detachment of the crown ether macrocycles and dethreading of

$\alpha$ -CDs from the side-chain.<sup>115</sup> Swager et al. synthesized a new side-chain polypseudorotaxane which is not included in Fig. 15. For these compounds, part of the cyclic component (*p*-phenylene-*m*-phenylene-32-crown-10) is a part of the polymer backbone (Figure 2-25).<sup>116, 117</sup>

The Takata group synthesized polypseudorotaxanes by radical polymerization of semi-rotaxane or pseudorotaxane monomers. They demonstrated that the radical polymerization of pseudorotaxane monomers, i.e., end-capping of pseudorotaxanes by the polymer chain during polymerization is an effective method to prepare side-chain polyrotaxanes, **36** and **37** (Fig. 26).<sup>118</sup> They also synthesized mechanically cross-linked polyrotaxanes by using the reversible thiol-disulfide interchange reaction based on dynamic covalent chemistry. The main-chain contains the crown ether ring (DB24C8) and a bis(dialkyl ammonium) salt which was linked with a disulfide bond threading into the crown ether rings. The prepared cross-linked network polymers, forming a gelled material, which had no fluidity.<sup>119</sup>

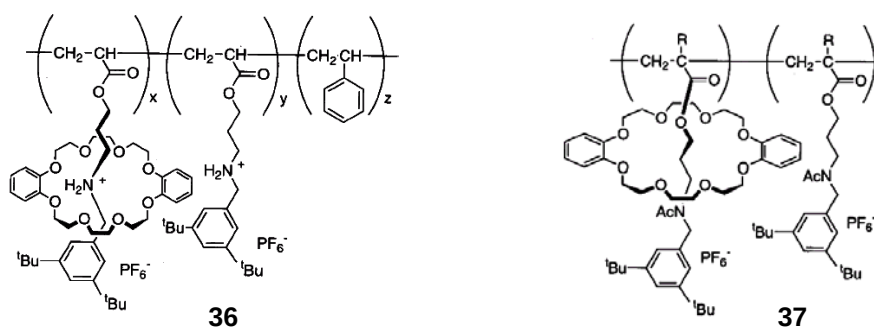


**Figure 2-26.** Side-chain polyrotaxanes via radical polymerization by the Takata group.

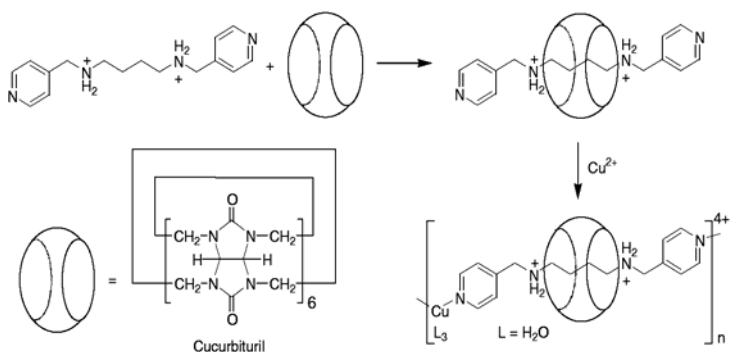
#### 4.4 Cucurbituril based polyrotaxanes<sup>51, 120</sup>

Cucurbituril (CB[6]) is a hexameric macrocyclic compound prepared from an acid-catalyzed condensation reaction of glycoluril and formaldehyde. It has a cavity of  $\sim 5.7$  Å diameter, and is accessible from the exterior by two carbonyl laced portals of  $\sim 4$  Å diameter. Although the size of the cavity is similar to that of  $\alpha$ -CD, the highly symmetrical structure with two identical openings distinguishes it from  $\alpha$ -CD. In a similar way to CDs, the hydrophobic interior of CB[6] provides a potential site for inclusion of hydrocarbon molecules. Unlike CDs, however, the polar carbonyl groups at the portals allow CB[6] to bind ions and molecules through charge-dipole and hydrogen bonding interactions. For example, CB[6] forms very stable 1:1 host-guest complexes with protonated diaminoalkanes, particularly diaminobutane and diaminopentane ( $K_a$



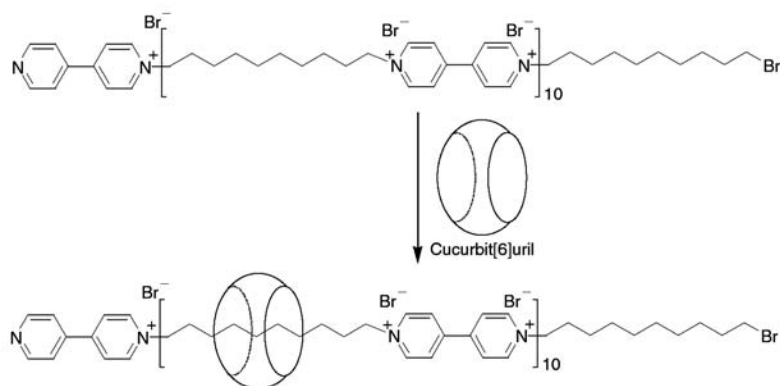
=  $\sim 105 - 106$ ), which are attributed to the strong charge–dipole interactions as well as hydrogen bonding interactions between the protonated amine groups and the portal carbonyl groups of CB[6], and the hydrophobic interactions between the internal methylene units of diaminoalkanes and the inside wall of the cavity of CB[6].<sup>120</sup>

Polypseudorotaxanes and polyrotaxanes containing CB[6] have been studied via the combination of self-assembly and coordination chemistry with transition metal ions (Scheme 2-12). The one-dimensional X-ray crystal structure of polyrotaxanes is dependent upon the geometry of transition metal complex linkers and the structure of the polypseudorotaxane itself. These polyrotaxanes may have X-ray crystal structures with zigzag, square-wave, straight-chain, and helical shapes.<sup>121-125</sup> The counter anions also play an important role in determining the solid state structures. The exchange of the counter anion produced a two-dimensional (2D) coordination polymer network.<sup>122, 126</sup> By using lanthanide transition metal ions as a linker, they also synthesized three-dimensional (3D) polyrotaxanes.<sup>127</sup>



**Scheme 2-12.** Preparation of a 1D polyrotaxane based on CB[6].

Main-chain polypseudorotaxanes containing CB[6] were synthesized by interfacial polymerization of CB[6]-spermine pseudorotaxane with various diacid chlorides such as 1,6-hexanedioyl chloride and terephthaloyl chloride. Buschmann and coworkers also prepared similar polypseudorotaxanes of polyamides and CB[6].<sup>128</sup> Characterization of the product polymers was very difficult because of their poor solubility: they dissolve only in concentrated sulfuric acid. In water-soluble main-chain polypseudorotaxanes containing CB[6] beads threaded on a polyviologen polymer, the degree of threading (number of CB[6] beads per repeating unit) could be controlled by controlling the amount of CB[6] added (Scheme 2-13).<sup>129</sup>



**Scheme 2-13.** Preparation of a polypseudorotaxane based on CB[6] and polyviologen.

Polyrotaxanes containing CB[6] macrocycles threaded on side chains were also reported by Kim and his co-workers. They used polyacrylamide and polystyrene derivatives, each repeating unit of which contains a protected diaminobutane unit as a side-chain. Deprotection of the diaminobutane units followed by threading of CB[6] on the side-chains results in the desired side-chain polypseudorotaxanes.<sup>130</sup> By using commercially available polypropyleneimine dendrimers (G1 – G5) as starting materials, the Kim group attached diaminobutane units at the ends of the dendrimers and then threaded CB[6] onto the terminals to produce pseudorotaxane terminated dendrimers. An AFM image of the G5 dendrimer on a mica surface reveals a flattened sphere with a diameter of ~15 nm and a height of ~1 nm.<sup>131</sup>

The Kim group has expanded its research to polyrotaxanes which contain other cucurbiturils, such as CB[5], CB[7], CB[8].<sup>132-134</sup> They also synthesized several types of catenane and molecular necklace supramolecules by complexation of transition metal ions as linkers and rotaxane units containing CB[6].<sup>135</sup>

#### 4.5 Polyrotaxanes based on other systems

A tetracationic cyclophane cyclobis(paraquat-phenylene) was also used as the cyclic component for polypseudorotaxanes and polyrotaxanes.<sup>136, 137</sup> High m/n values of these polypseudorotaxanes show that donor-acceptor interaction ( $\pi$ - $\pi$  stacking), charge transfer and hydrogen bonding are very efficient driving forces to form polyrotaxanes. The Tamaoki group prepared a slip-link polyrotaxane by route VIII (Scheme 2-9), but they obtained primarily a dimer or oligomers (Figure 2-27).<sup>138</sup> The self-assembly of  $\pi$ -conjugated dithiafulvene polymers

and the cyclic acceptor by a charge-transfer interaction gave polypseudorotaxanes in DMSO. After self-complexation, the effective charge-transfer interaction between the dithiafulvene unit and the cyclic acceptor afforded a highly conductive polypseudorotaxane.<sup>139</sup>

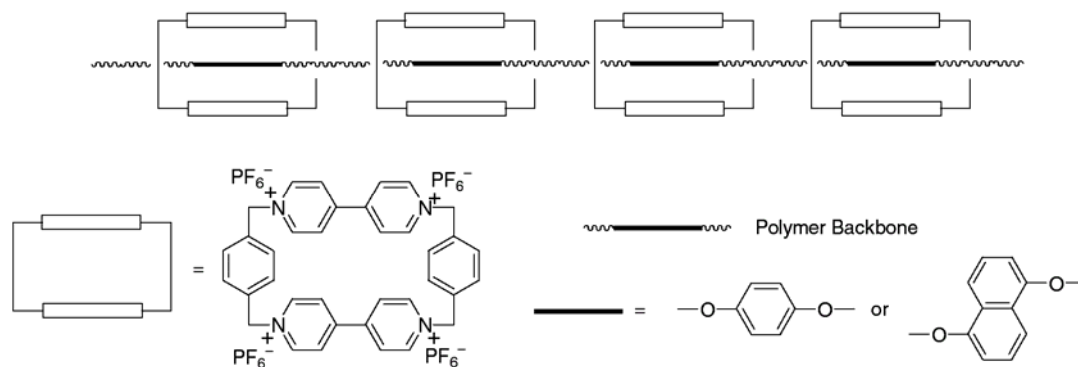


**Figure 2-27.** Polypseudorotaxane with cyclobis(paraquat-phenylene) as the cyclic component. (reprinted with permission from ref 138. © Elsevier)

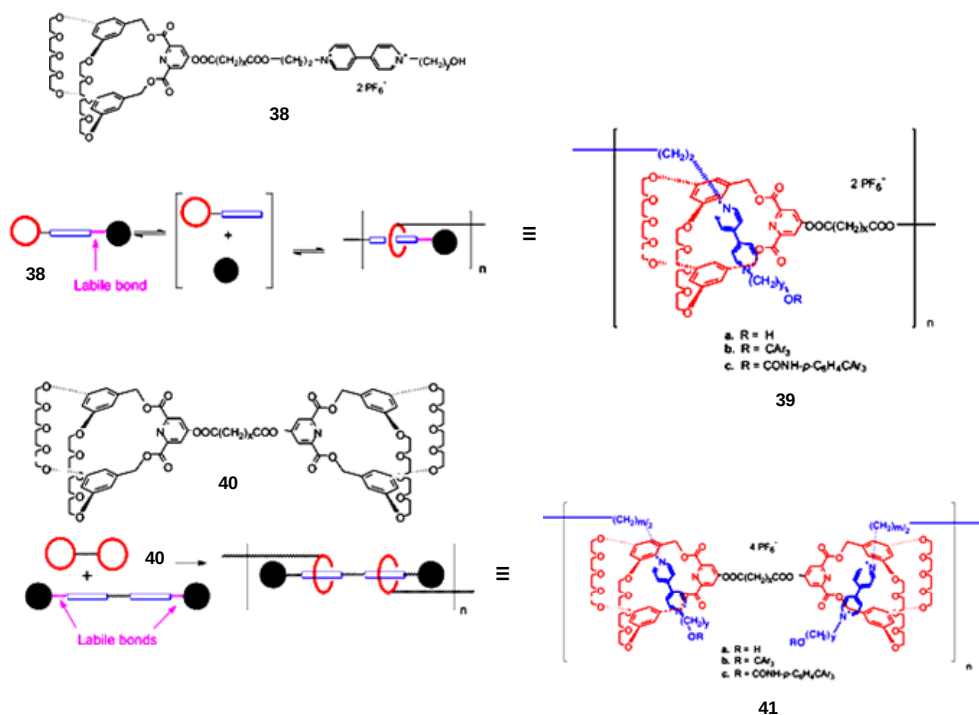
*p*-*tert*-Butylcalix[8]arene was also used for main-chain polyrotaxane with PEG as a polymer backbone. The polycondensation of *p*-*tert*-butylphenol with paraformaldehyde in the presence of PEG gave polypseudorotaxanes.<sup>140</sup>

## 5. Prospective Research

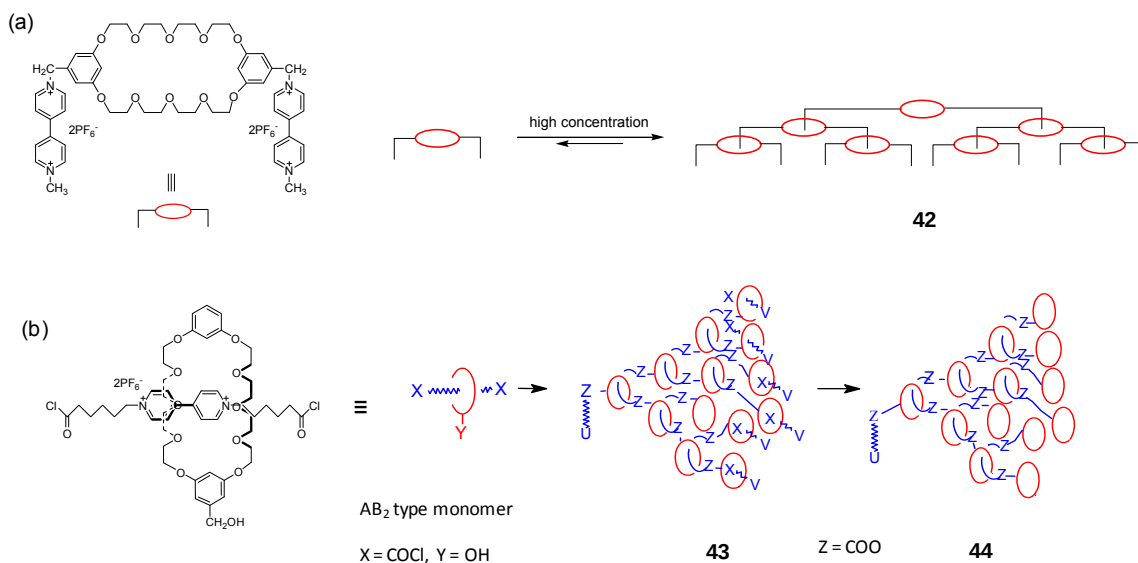
The Gibson group has shown remarkable achievement in the field of polypseudorotaxanes and polyrotaxanes constructed with crown ether macrocycles. Recently, they also synthesized novel cryptands for complexation with several guest cations.<sup>12, 13, 16, 52, 141, 142</sup> Since we have numerous examples of polyrotaxanes (and polypseudorotaxanes) and novel cryptands, new polyrotaxanes may be synthesized through the combination of these building blocks. Two polypseudorotaxane candidates, **39** and **41**, are given in Fig. 28. The monomers **38** and **40** will be prepared first. **38** can be polymerized itself and then will form the polypseudorotaxane or polyrotaxane **39**. Compound **40** containing two cryptands will form the polyrotaxane **41** with a diparaquat derivative.

A mechanically interlocked hyperbranched polymer is another type of polyrotaxane which I will study and synthesize. Huang proposed two molecules to form these hyperbranched polymers **42** and **44**; however, high molecular weight could not be achieved (Scheme 2-15).<sup>143</sup> The low molecular weight resulted because of the dethreading of pseudorotaxanes by polar solvent

washing. This result is inevitable if AB<sub>2</sub> type monomers are used to form hyperbranched rotaxane-type polymers.



**Scheme 2-14.** New polypseudorotaxanes and polyrotaxanes, which will be synthesized. When R = H in **39** and **41**, they are polypseudorotaxanes; when R = CAr<sub>3</sub> or CONH-*p*-C<sub>6</sub>H<sub>4</sub>CAr<sub>3</sub>, **39** and **41** are polyrotaxanes.



**Scheme 2-15.** Mechanically interlocked hyperbranched polymers synthesized by the Gibson group. In Scheme (a), polypseudorotaxane **42** was formed from monomer with one crown ether and two paraquats. In scheme (b), AB<sub>2</sub> type monomer was used to form a hyperbranched polypseudorotaxane **43** and polyrotaxane **44**.

New A<sub>2</sub>B type monomers which contain a blocking group in the paraquat derivatives will prevent dethreading even during washing with polar solvents, because the stopper will be placed at the ends of the polymers. The new synthesized polymers **45** will be characterized by several analytical tools, such as mass spectrometry, NMR, viscosities, thermal analysis, and microscopies.

Novel cryptands will be also synthesized and they will be applied to form various types of polypseudorotaxanes and polyrotaxanes. Various crown ethers and functionalized pyridine moieties will be used to form cryptands as building blocks. For the new cryptands, complexation studies will be also performed with guest molecules such as sec-ammonium ions, pyridinium derivatives and paraquat derivatives. To obtain the association constants for the complexations, <sup>1</sup>H-NMR will be used. If single crystals of new cryptands and complexes can be obtained, X-ray crystallography will be the most powerful tool to see their 3D structures.

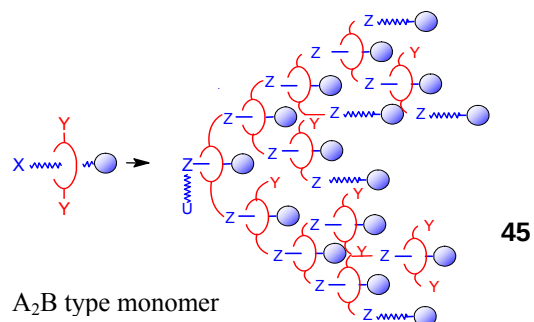


**Figure 2-28.** A new mechanically interlocked hyperbranched polymer from an A<sub>2</sub>B type monomer.

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## Chapter 3

### Synthesis of Complementary Host- and Guest-Functionalized Polymeric Building Blocks and Their Self-Assembling Behavior

#### Abstract

New polymers which incorporate paraquat or crown ether moieties as chain ends or central units were synthesized by stable free radical polymerization (SFRP) and atom transfer radical polymerization (ATRP). For SFRP, TEMPO derivatives which contain a functional unit were used as initiators. For ATRP, a copper-amine or copper-bipyridine complex was used as a catalyst with radical initiators from halide derivatives of paraquat and crown ethers. These end- or center-functionalized polymers formed pseudorotaxane complexes with complementary small molecules. They also formed reversible pseudorotaxane polymers: chain-extended, star-shaped homopolymers and block copolymers. Complexation studies to determine stoichiometry and association constants with thermodynamic parameters were performed by NMR spectroscopy and isothermal microcalorimetric (ITC) titration. The association constants of crown ether derivatives and paraquat compounds in chloroform were measured for the first time:  $K_a = 2.97 \times 10^3 \text{ M}^{-1}$  for paraquat polystyrene and bis(*m*-phenylene)-32-crown-10 and  $K_a = 4.38 \times 10^3 \text{ M}^{-1}$  for paraquat polystyrene and crown ether polystyrene. These are 4- to 6-fold higher than the association constant of the analogous small molecule host-guest system in acetone.

## Introduction

Since the synthesis and characterization of 18-crown-6 in 1967,<sup>1</sup> many crown ethers have been synthesized and their complexation behaviors have been widely studied.<sup>2</sup> Crown ethers can undergo complexation not only with metal ions, but also with rod-like cationic molecules to form threaded structures known as pseudorotaxanes and rotaxanes.<sup>3</sup> The convergence of supramolecular and polymer science has also led to the construction of analogues of traditional macromolecules by supramolecular methods. Due to their unique topological character and potential functions, these systems may lead to advancements in many applications.<sup>4</sup> Some previous examples of polymers formed by the self-assembly of the host and guest units include: dendrimers from cooperative complexation of a homotritopic guest and complementary monotopic dendron hosts,<sup>5</sup> a hyperbranched polymer from an AB<sub>2</sub> monomer,<sup>6</sup> linear polymers from self-organization of well-defined building blocks,<sup>7</sup> a supramolecular triarm star polymer from a homotritopic host and a complementary monotopic paraquat-terminated polystyrene guest,<sup>8</sup> and polymers with terminal pseudorotaxane units from polymers end-functionalized with crown ethers and small guest molecules.<sup>9</sup>

The formation of pseudorotaxanes from crown ethers and N,N'-dialkyl-4,4'-bipyridinium salts ("paraquats") was confirmed by X-ray crystallography and their association constants ( $K_a$ ) were determined by various analytical tools. The  $K_a$  of bis(*m*-phenylene)-32-crown-10 (BMP32C10) and dimethyl paraquat bis(hexafluorophosphate) was reported as 760 M<sup>-1</sup> in acetone-*d*<sub>6</sub> at ambient temperature.<sup>4a</sup> The association constants between host and guest molecules can be changed through the variation of system parameters, such as temperature, pH, solvent and impurities. In the phenylene crown ether complexes with paraquats, the main intermolecular forces for complexations are multiple hydrogen bonds, dipole-dipole and  $\pi$ -electron interactions between the host and guest. Since the complexations occur in solution, solvent effects are important. For example, protic solvents (such as methanol) interfere with the hydrogen bonding between the host and guest. Polar aprotic solvents (such as DMSO and DMF) can also lower the binding forces due to their high polarity and hydrogen bond accepting character. For this reason, higher association constants are expected in less polar solvents; however, the paraquat compounds are almost insoluble even in THF and other less polar solvents. The association constants between crown ethers and paraquat species have been measured in acetone or acetonitrile (MeCN) due to the need for a common solvent for the host and guest molecules. We

expected that the association constants of crown ethers and paraquat derivatives could be higher in solvents less polar than acetone or MeCN; however, no one has reported the association values in less polar solvents due to the poor solubilities of the paraquat compounds.

Herein, we first report pseudorotaxane formation in chloroform from paraquat-functionalized polystyrene and crown ethers (**1** in Figure 3-1) and from center-functionalized polystyrene and paraquat (**2** in Figure 3-1). From polymeric building blocks that contain a terminal crown ether or paraquat unit, chain extension (**3**) and 3-armed star polymers (**4**) were observed in solution (Figure 3-1). Diblock copolymer and 3-armed star copolymer formation from polystyrenes and PMMA with functional complementary host-guest terminal units were also tried (**5**, **6**); however they were less efficient than the polystyrene homopolymer systems. The details are discussed below.

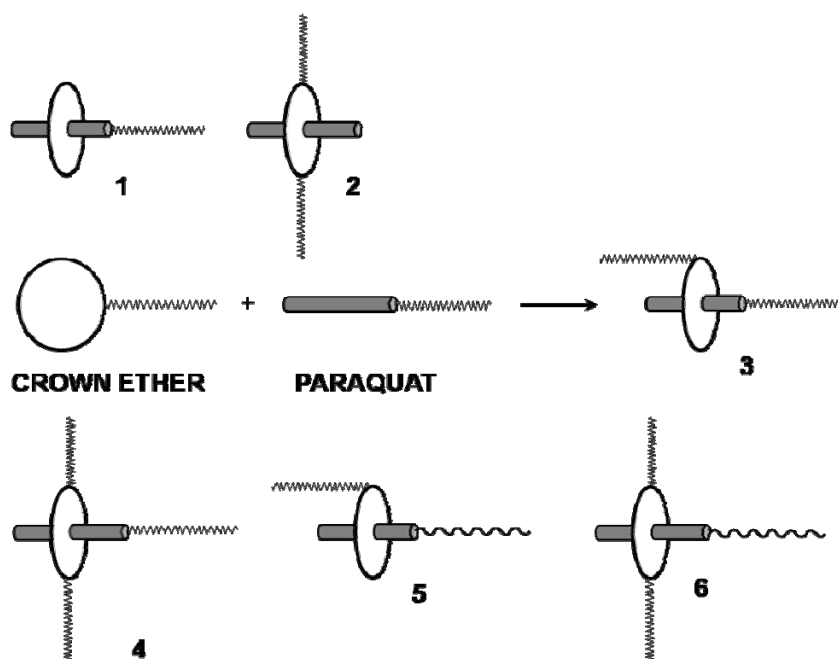
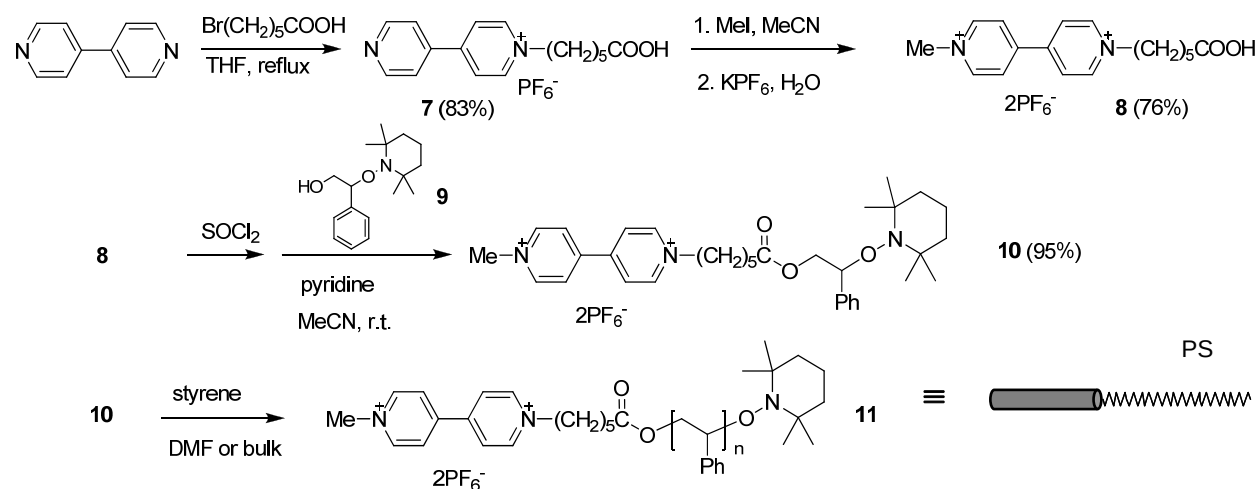


**Figure 3-1.** Cartoon representations of the formation of polymers with a terminal (**1**) or central pseudorotaxane unit (**2**), chain extension by pseudorotaxane formation from host- and guest-terminated polymers (**3**), 3-armed star polymers by pseudorotaxane formation (**4**), block copolymers by pseudorotaxane formation (**5**), and 3-armed block copolymers by pseudorotaxane formation (**6**).

## Results and Discussion

**Preparation of polymeric building blocks.** Paraquat terminated polymers were synthesized by controlled radical polymerization (CRP). For stable free radical polymerization (SFRP), a paraquat-TEMPO initiator **10** was synthesized (Scheme 3-1). In the preparation of **7** an excess of 4,4'-bipyridine was used to prevent the formation of the disubstituted bipyridinium side product. Paraquat carboxylic acid **8** was prepared by methylation of the resulting monosubstituted compound **7**. The paraquat-TEMPO initiator **10** was formed by the esterification of **8** and 2-phenyl-2-(2',2',6',6'-tetramethylpiperidine-N-oxyl)ethanol (**9**).



**Scheme 3-1.** Synthesis of paraquat terminated polystyrene **11** by SFRP.

Polystyrenes with terminal paraquat units (**11**) were synthesized with the paraquat-TEMPO initiator **10** in solution or in bulk. The reaction temperature was maintained at 120 – 130 °C for 8 to 13 hours. DMF was used as a solvent for the solution polymerization because it dissolves both polystyrene and the polar paraquat initiator **10**. The viscosity of the reaction mixture increased as the polymerization proceeded. In the bulk process the reactions were terminated when the magnetic stirrer stopped. In the first stage of the bulk polymerization, the initiator **10** was not completely soluble in styrene monomer. However, when the polymerization was completed, the initiator was completely consumed and there was no insoluble solid. Therefore, these SFRP reactions of styrene allowed good control of the molecular weight (from the ratio of the monomer and the initiator) and relatively narrow polydispersities (below 1.20) by both methods. The  $^1\text{H}$ -NMR spectrum of **11** in  $\text{CDCl}_3$  clearly shows the paraquat protons at  $\delta$  8.2 and 8.7. The

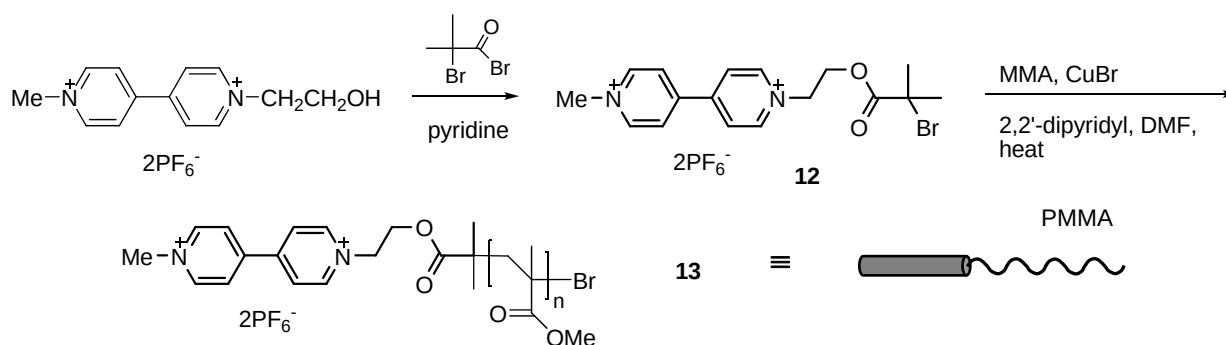


number average molecular weights calculated from integration of the NMR spectra correspond to the size exclusion chromatography (SEC) results well (THF, PS standards). (Table 3-1).

**Table 3-1.** Molecular Weights Estimated by  $^1\text{H}$ -NMR Spectroscopy and SEC for the Paraquat Terminated Polystyrenes (**11**) by SFRP.

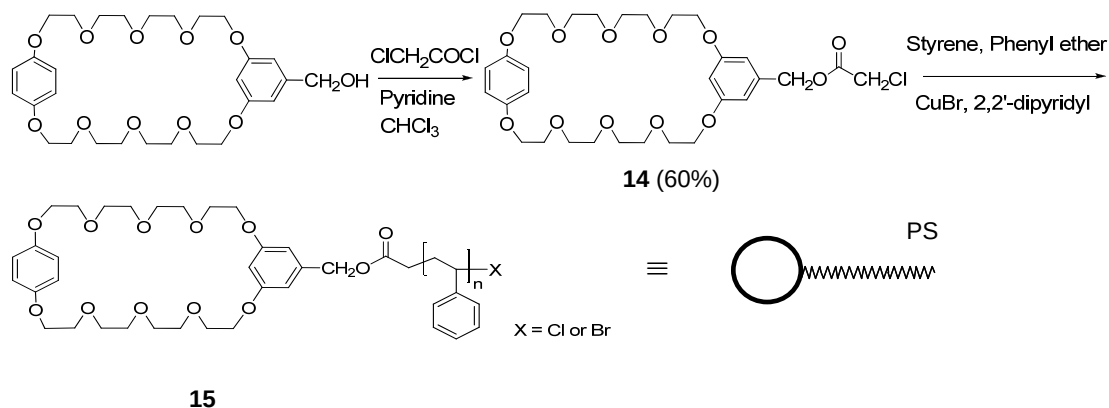
| Polymerization Method | Target $M_n$ (kDa) | $M_n$ (NMR) (kDa) | $M_n$ (SEC) (kDa) | PDI (SEC) |
|-----------------------|--------------------|-------------------|-------------------|-----------|
| SFRP, Bulk            | 31.2               | 33.7              | 31.5              | 1.19      |
| SFRP, Solution        | 31.2               | 37.5              | 31.5              | 1.07      |

A paraquat terminated poly(methyl methacrylate) (PMMA) was synthesized by ATRP. The paraquat ATRP initiator **12** was prepared by esterification of N-methyl-N'-( $\beta$ -hydroxyethyl)-4,4'-bipyridinium bis(hexafluorophosphate) with  $\alpha$ -bromoisobutyryl bromide. The ATRP of methyl methacrylate (MMA) with the initiator **12** was performed using copper(I)/2,2'-bipyridyl as catalyst in DMF at 90 °C (Scheme 3-2). The  $^1\text{H}$ -NMR spectrum of **13** in  $\text{CDCl}_3$  clearly shows the paraquat protons at  $\delta$  8.8 and 9.3. The chemical shifts of the paraquat protons are different between **11** and **13**, even though the terminal paraquat structure is same (N-methyl paraquat). The reason for the chemical shift changes must be due to the different polymer structures; hydrocarbon polystyrene and oxygen-rich PMMA. The PMMA chain induces a deshielding effect on the paraquat protons. The more polar polymer provides a local environment that is similar to acetone- $d_6$ , in which dimethyl paraquat's aromatic protons appear at 8.8 and 9.4 ppm.<sup>15a</sup> This may be ascribed to interaction (some would say hydrogen bonding) of the aromatic paraquat protons with the oxygen atom of acetone solvent or the PMMA ether and carbonyl oxygen atoms. The number average molecular weight ( $M_n$ ) was 40.7 kDa (targeted  $M_n$  10.0 kDa) and the PDI was 1.33 from SEC analysis (THF, PS standards). The molecular weight of synthesized **13** was higher than target molecular weight due to the poor solubility of copper(I)/2,2'-dipyridyl catalyst in methyl methacrylate (monomer) during the polymerization.



**Scheme 3-2.** Synthesis of paraquat terminated PMMA **13** by ATRP.

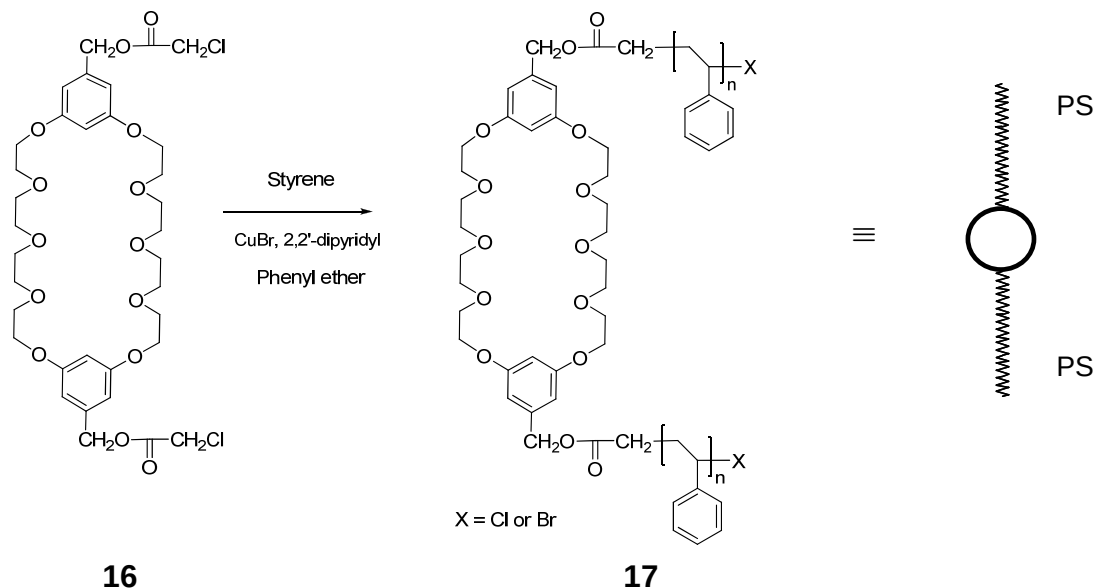
A crown ether terminated polystyrene was synthesized using the ATRP initiator **14** (Scheme 3-3). **14** was prepared by the esterification of 5-hydroxymethyl-1,3-phenylene-*p*-phenylene-33-crown-10 (MPPP33C10) with chloroacetyl chloride. In the ATRP, three equivalents of copper(I) bromide and nine equivalents of 2,2'-dipyridyl were used per initiator **14**. No polymerization occurred if only one or two equivalents of catalyst were added; we hypothesize that radical generation from the copper(I)/2,2'-dipyridyl catalyst is prevented by crown ether complexation of up to two equivalents of copper(I) ion. The number average molecular weight ( $M_n$ ) of this crown terminated polystyrene **15** was 21.4 kDa (targeted  $M_n$  = 31.3 kDa) and the PDI was 1.29 from SEC analysis (THF, PS standards).



**Scheme 3-3.** Synthesis of crown ether (MPPP33C10) terminated polystyrene **15** by ATRP.

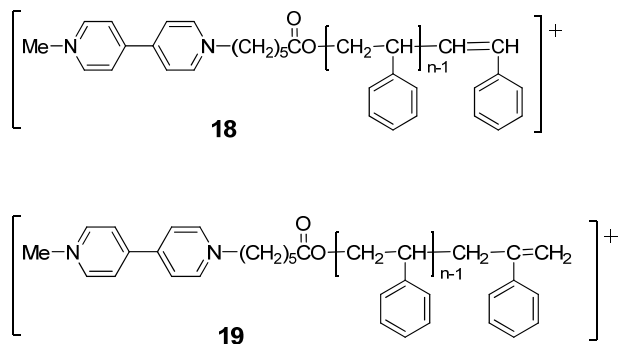
A crown ether centered polystyrene was also prepared by ATRP (Scheme 3-4) from the dichloro bis(*m*-phenylene)-32-crown-10 (BMP32C10) ATRP initiator **16**. 4 equivalents of copper(I) bromide and 12 equivalents of 2,2'-dipyridyl per initiator **16** were used in the ATRP

reaction. The number average molecular weight ( $M_n$ ) of the crown centered polystyrene **17** was 13.5 kDa (targeted  $M_n = 10.4$  kDa) and the PDI was 1.25 by SEC ( $\text{CHCl}_3$ , PS standards).



**Scheme 3-4.** Synthesis of crown ether (BMP32C10) centered polystyrene **17** by ATRP.

**MALDI-TOF Mass spectrometric analysis of the polymeric building blocks.** MALDI-TOF mass spectrometric results for the polystyrene **11** in 3-anthraquinoline are shown in Figure 3-2. The spectrum contains series of four peaks each. The sequential sets of peaks are separated by 104 mass units, corresponding to the styryl repeat unit. In the two main series of peaks after loss of a TEMPO moiety (156 Da) and hydrogen, presumably via N-hydroxytetramethylpiperidine, the paraquat end groups are clearly observed: (1) the polymer after loss of two  $\text{PF}_6$  ions (**11** –  $2\text{PF}_6$  – TEMPO – H) $^+$ , structure **18**, m/z 1010 ( $n = 7$ ), 1114 ( $n = 8$ ) and 1218 ( $n = 9$ ), and (2) the polymer after loss of a benzylidene group (**11** –  $2\text{PF}_6$  – TEMPO – H –  $\text{C}_6\text{H}_5\text{CH}$ ) $^+$ , structure **19**: m/z 1024 ( $n = 7$ ), 1128 ( $n = 8$ ), 1232 ( $n = 9$ ). The polymers with one  $\text{PF}_6$  ion are also observed but as weaker peaks: (**11** –  $\text{PF}_6$  – TEMPO – H –  $\text{C}_6\text{H}_5\text{CH}$ ) $^+$ , structure **18** +  $\text{PF}_6$ , m/z 1040 ( $n = 6$ ), 1144 ( $n = 7$ ), 1248 ( $n = 8$ ) and (**11** –  $\text{PF}_6$  – TEMPO – H) $^+$ ; structure **19** +  $\text{PF}_6$ , m/z 1054 ( $n = 6$ ), 1159 ( $n = 7$ ), 1263 ( $n = 8$ ). The loss of TEMPO in MALDI-TOF mass analysis has been already reported by Vairon et al.<sup>10</sup> In



agreement with the report of Gibson et al.,<sup>9</sup> structure **19** ( $=\text{CH}_2$  end) predominates in this high mass range over structure **18** (benzylidene end,  $=\text{CHC}_6\text{H}_5$ ). The loss of the benzylidene group is believed to occur via loss of N-benzyloxy-tetramethylpiperidine.

MALDI-TOF mass spectrometric results for paraquat terminated poly(methyl methacrylate) sample **13** in 3-anthraquinoline are shown in Figure 3-3. The sequential pairs of peaks are separated by 100 mass units, corresponding to the methyl methacrylate repeat unit. The paraquat end group is clearly observed as with the paraquat terminated polystyrene. No brominated species are observed. The series with the strongest signals correspond to structure **20** with loss of two  $\text{PF}_6$  species (presumably one as the anion and the other as  $\text{HPF}_6$ , as often observed<sup>12,13</sup>):  $m/z$  782 ( $n = 5$ ) and 882 ( $n = 6$ ). The next most prominent series of peaks are due to **21** formed by cleavage of the PMMA main chain by rearrangement:  $m/z$  838 ( $n = 5$ ) and 937 ( $n = 6$ ).

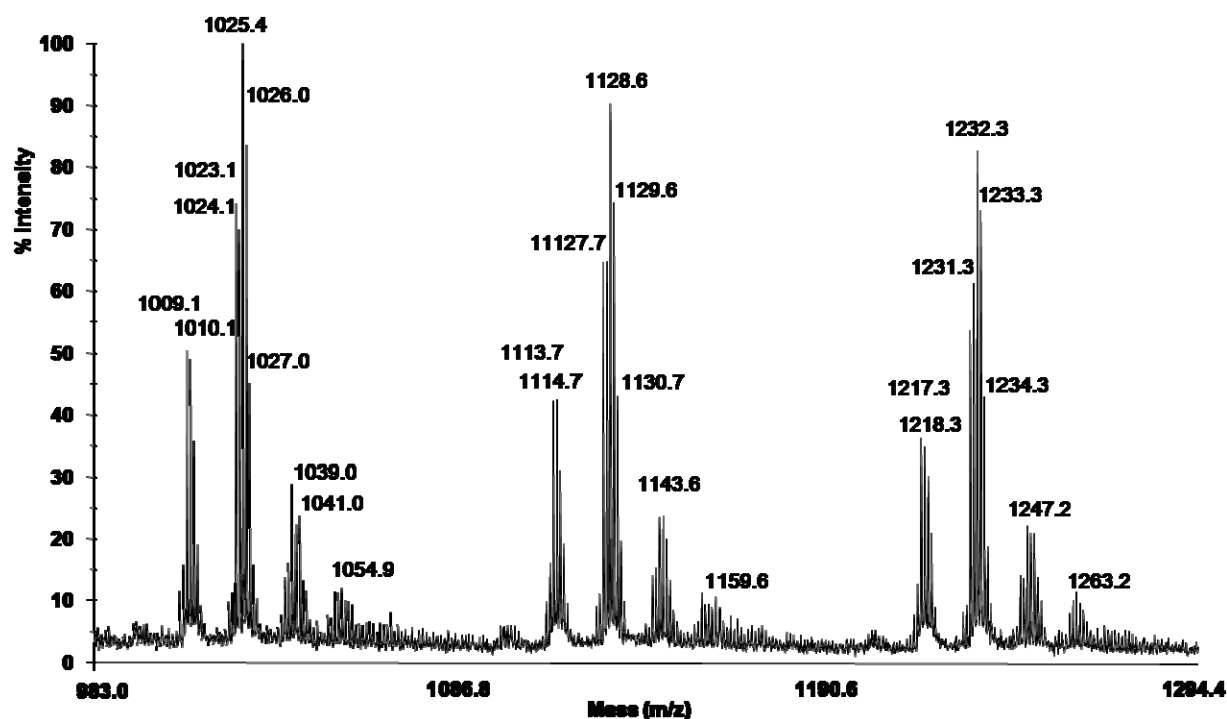


**Figure 3-2.** Partial MALDI-TOF mass spectrum (covering mass range 980 – 1295 Da) of paraquat terminated polystyrene **11**. Sample prepared by the D-D method in 3AQ with no added cationization agent.

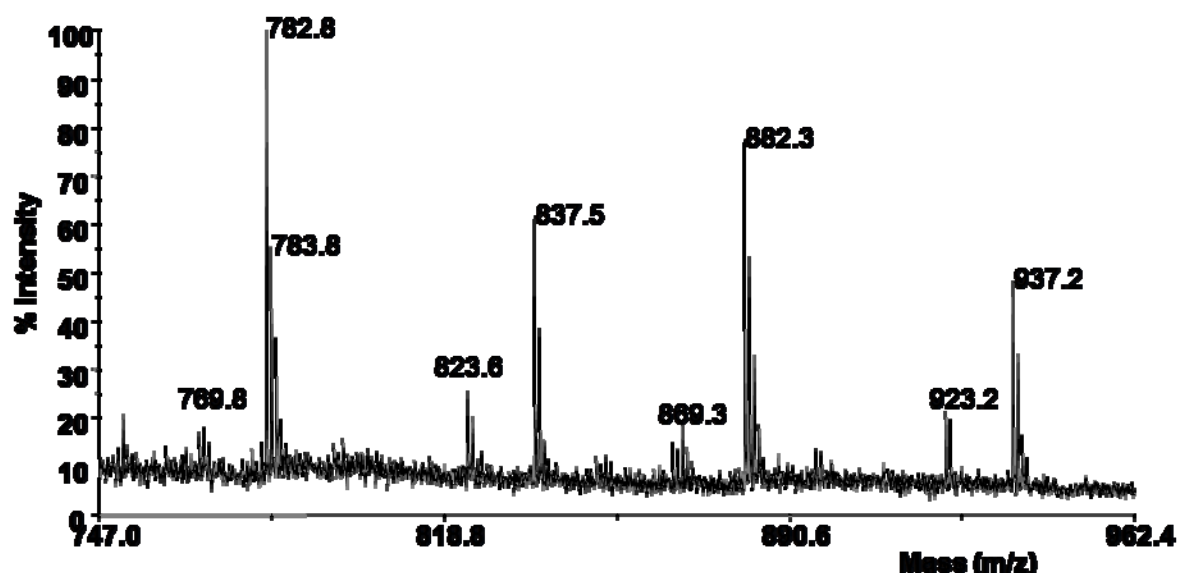
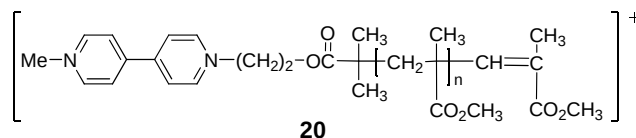
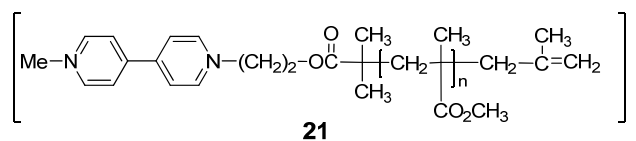


**Figure 3-3.** Partial MALDI-TOF mass spectrum (covering mass range 747 – 962 Da) of paraquat terminated PMMA **13**. Sample prepared by the D-D method in 3AQ with no added cationization agent.

The rearrangements of PMMA during mass spectrometry were reported by Scrivens et al. and they proposed the mechanisms shown in Schemes 3-5 and 3-6.<sup>11</sup> Because no cationization agent was used for this sample, we believe that only the charges are associated with the paraquat moieties of **20** and **21**. The two ways to form structure **20**, the loss of HBr from the end of **13** and the cleavage of the backbone as in Scheme 3-5, are consistent with the higher peak intensities corresponding to structure **20** vs. those corresponding to structure **21**, which can form only via the pathway shown in Scheme 3-6. The next strongest series of peaks is attributed to  $[\mathbf{21} - \text{CH}_2]^+$ :  $m/z$  824 ( $n = 5$ ) and 923 ( $n = 6$ ). The weakest series of signals is assigned to  $[\mathbf{20} - \text{CH}_2]^+$ :  $m/z$  770 ( $n = 5$ ) and 869 ( $n = 6$ ).

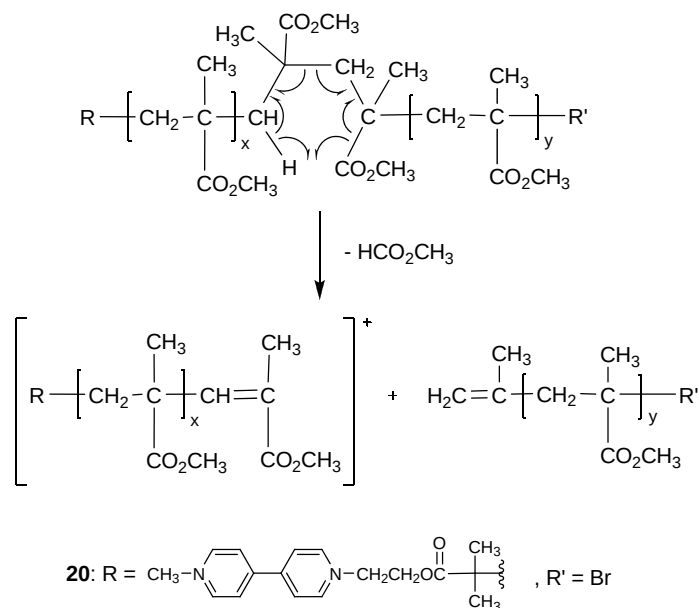


MALDI-TOF results for the crown terminated polystyrene sample **15** in dithranol and AgTFA show the existence of the end groups (Figure 3-4). The main series of peaks at  $m/z$  2708 ( $n = 25$ ), 2812

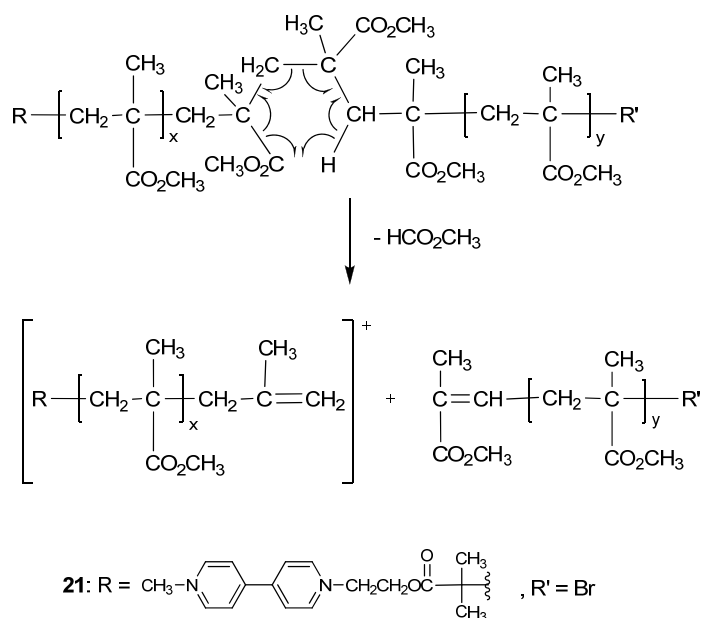


( $n = 26$ ) and 2916 ( $n = 27$ ), correspond to the silver adduct of polystyrene with no end groups (structure **22**). The loss of MPPP32C10 moiety is believed to occur via a McLafferty-type

rearrangement and cleavage one bond removed from the carbonyl group as shown in Scheme 3-7. The benzyldiene end (the other terminal group) of the structure **22** arises from loss of hydrogen chloride. In the other series of peaks, the terminal crown ether unit (MPPP33C10) and chloride are both observed as silver adducts;  $\text{Ag}^+$  is believed to be captured by the MPPP32C10 moiety (**15** +  $\text{Ag}^+$ ):  $m/z$  2726 ( $n = 19$ ) and 2830 ( $n = 20$ ).



**Scheme 3-5.** Proposed mechanism for generation of the structure **20** series from the cleavage of the PMMA main chain by a rearrangement.



**Scheme 3-6.** Proposed mechanism for generation of the structure **21** series from the cleavage of the PMMA main chain by a rearrangement.

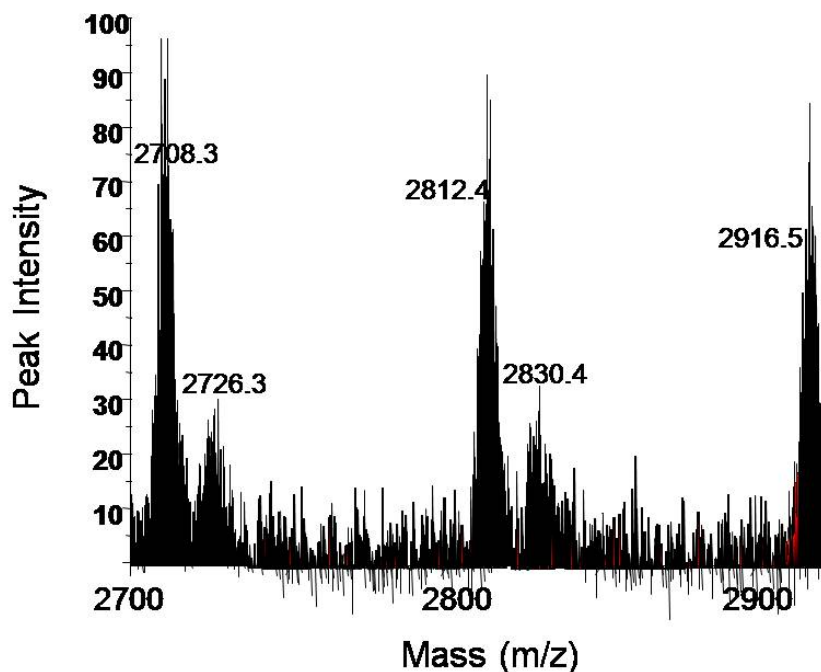


**Figure 3-4.** Partial MALDI-TOF mass spectrum (covering mass range 2700 – 2930 Da) of MPPP33C10 terminated polystyrene **15**. Sample prepared by the D-D method in dithranol with AgTFA as a cationization agent.

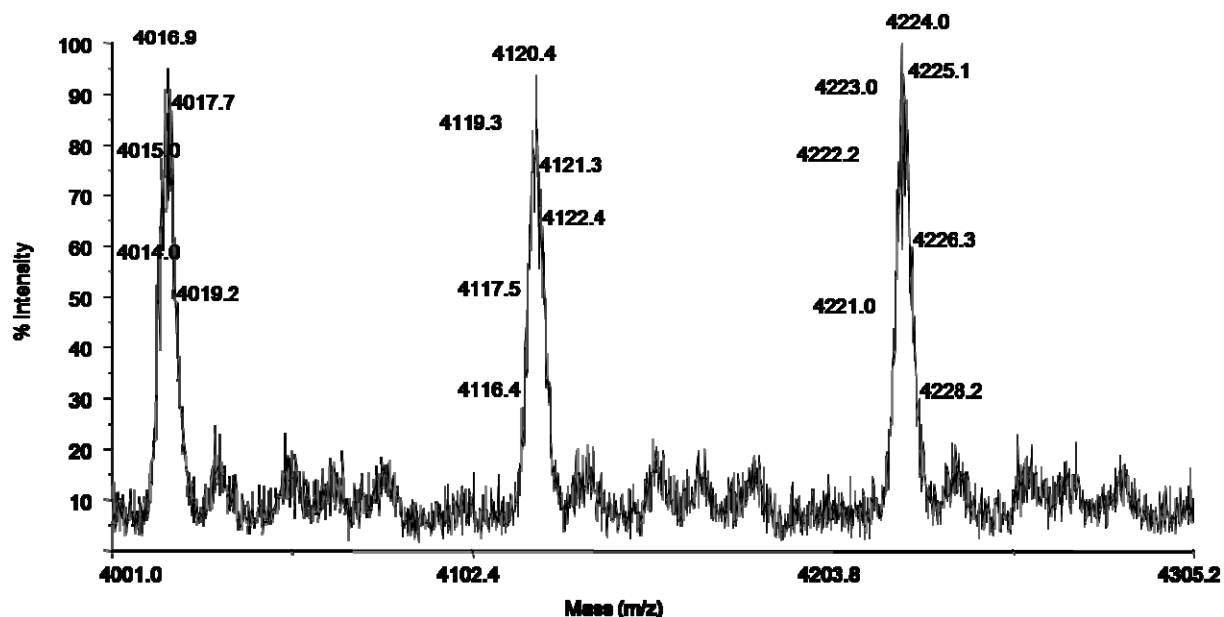
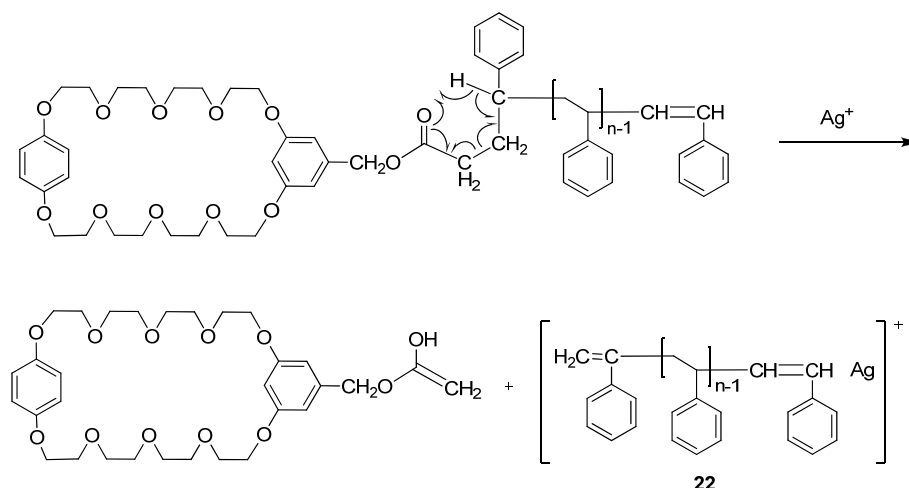
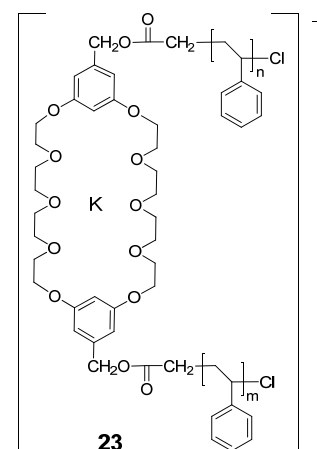


**Figure 3-5.** Partial MALDI-TOF mass spectrum (covering mass range 4001 – 4305 Da) of BMP32C10 centered polystyrene **17**. Sample prepared by the D-D method in 3AQ and no added cationization agent.



**Scheme 3-7.** Proposed mechanism for generation of the structure **22** series by a McLafferty type rearrangement.

MALDI-TOF mass spectrometric results for the crown centered polystyrene sample **17** in 3-anthraquinoline are shown in Figure 3-5. Only one series is observed and the sequential pairs of peaks are separated by 104 mass units, corresponding to the styryl repeat unit. The BMP32C10 crown ether unit and two chloride end groups are observed in the spectrum; the charge results from inclusion of potassium ions presumably captured by the crown ether rings (**23**):  $m/z$  4014 ( $n + m = 31$ ), 4118 ( $n + m = 32$ ) and 4222 ( $n + m = 33$ ). Even though the ATRP was catalyzed by copper(I) bromide, no bromide end or unsaturated terminal moiety is observed. From these results, we conclude that the chloride from the initiator was not exchanged to bromide during the ATRP, even though a different copper(I) halide (CuBr) was used as the catalyst.



In MALDI-TOF mass analysis of the paraquat terminated polymers, the paraquat moiety is clearly observed after loss of two  $\text{PF}_6$  species. Whereas the TEMPO and the bromide end groups were not detected, the structures with unsaturated ends after loss of TEMPO and bromide were observed. Interestingly for the polymers from ATRP with chloride initiators, the terminal chloride is clearly shown in the mass spectra and no unsaturated end is observed when no cationization agent was used.



**Formation of [2]pseudorotaxanes from polymers and small molecules (1 and 2 in Figure 3-1).** The binding of the host- and guest-functionalized polymers with small molecules leads to the pseudorotaxanes **1** and **2**. The complexation between host and guest molecules was visually confirmed by a color change; the yellow or yellow-orange color is due to a charge transfer interaction between the electron poor paraquat and the electron rich phenyl rings of the crown ethers.<sup>12</sup> In panel **a** of Figure 3-6, the chloroform solution of the paraquat terminated polystyrene **11** was colorless, but the solution turned yellow after addition of dibenzo-30-crown-10 (DB30C10) (right vial) or DB30C10-based cryptand<sup>13</sup> (center vial). In panel **b** of Figure 3-6, the chloroform solution of the crown ether (BMP32C10) centered polystyrene **17** was colorless (left vial). However, the color changed to yellow after addition of paraquat diol (N,N'-bis(2-hydroxyethyl)-4,4'-bipyridinium 2PF<sub>6</sub><sup>-</sup>, center vial) or the paraquat terminated polystyrene **11** (right vial). These color changes show that 1) the terminal pseudorotaxane polymers **1** were formed (panel **a**), 2) central pseudorotaxane polymer **2** was formed (panel **b**), and 3) the right vial in (panel **b**) contains a 3-armed star polymer (**4**).

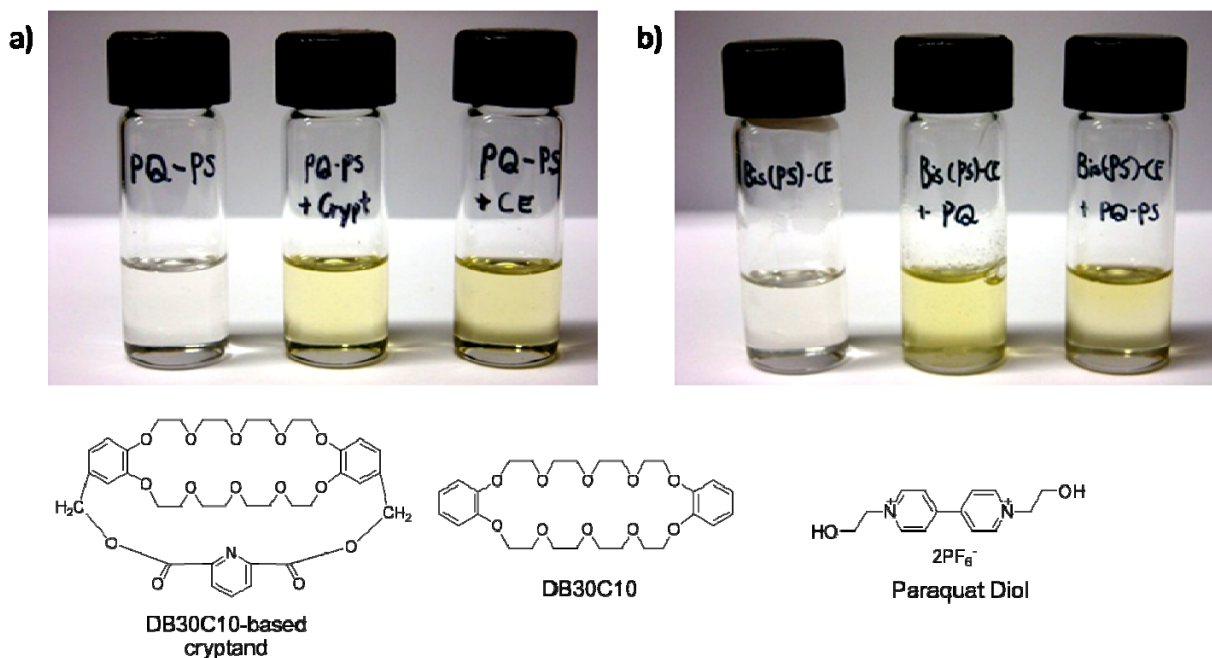


**Figure 3-6.** Qualitative visual test of complexation: a) chloroform solutions of, from the left: paraquat terminated polystyrene **11**, paraquat terminated polystyrene **11** + DB30C10-based cryptand, **11** paraquat terminated polystyrene **11** + BMP32C10. b) From the left: crown ether centered polystyrene **17** in chloroform, crown ether centered polystyrene **17** + paraquat diol in acetone/CHCl<sub>3</sub> 1/1 and crown ether centered polystyrene **17** + paraquat terminated polystyrene **11** in CHCl<sub>3</sub>.

Isothermal macrocalorimetric (ITC) titration can be used to quantify host-guest binding. The association constants between the paraquat terminated polystyrene **11** and BMP32C10, and between the paraquat terminated PMMA **13** and BMP32C10 were measured in chloroform at 25 °C:  $K_a = 2.97 (\pm 0.09) \times 10^3 \text{ M}^{-1}$  and  $K_a = 3.63 (\pm 0.10) \times 10^2 \text{ M}^{-1}$ , respectively. The association constants of paraquat and crown ether compounds in chloroform were measured for the first time; they were 4- to 6-fold higher than that of the small molecular host and guest analogs.<sup>4a</sup> As mentioned above in the introduction, the main intermolecular forces for complexations of crown ethers and paraquat derivatives are multiple hydrogen bonds, dipole-dipole and  $\pi$ -electron interactions. Because of the lower polarity of chloroform relative to acetone, the interactions are stronger than in the higher polarity acetone medium. The stronger interactions gave higher  $K_a$  values in chloroform. Surprisingly, however, the binding of the paraquat-PMMA **13** with BMP32C10 became almost 9-fold lower than that of the paraquat polystyrene **11** with BMP32C10. This decrease could be due to the interactions of the ester moieties of PMMA with the paraquat species. Perhaps one of the major interactions is hydrogen-bonding between ester oxygen atoms and the aromatic protons of the paraquat units in the relatively non-polar chloroform solution. This hypothesis is supported by the observation that the chemical shifts of paraquat terminated PMMA in  $\text{CDCl}_3$  are very similar to those of dimethyl paraquat in acetone- $d_6$ , as noted above.

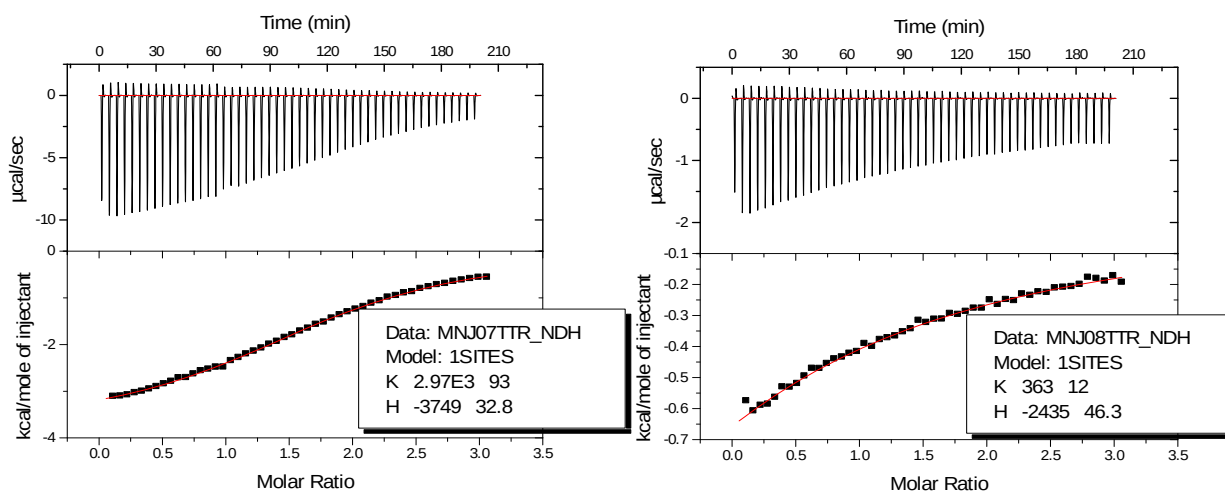


**Figure 3-7.** ITC titration curves (top: raw data, bottom: integrated heat flow and curve fit) and calculated physical constants: a) paraquat terminated polystyrene **11** (1.03 mM) titrated with BMP32C10 (14.9 mM). b) paraquat terminated PMMA **13** (1.01 mM) titrated with BMP32C10 (14.9 mM) in  $\text{CHCl}_3$  (25 °C).  $K$  is the association constant in  $\text{M}^{-1}$  units and  $H$  is the enthalpy change in cal/mol.

**Polymer-polymer binding (3, 4, 5 and 6 in Figure 3-1).** The polymer-polymer binding of the functionalized polymers was also investigated. Chain extension by self-assembly (**3** in Fig. 1) was observed by color and viscosity changes. The individual chloroform solutions of the paraquat terminated polystyrene **11** and the crown ether terminated polystyrene **15** were colorless. However, when the two polymers were dissolved in a 1:1 molar ratio in chloroform, the solution was yellow as with the other complexation systems in Figure 3-6. Viscometry provided evidence of chain extension by self-assembly in the solution (Figure 3-7). The intrinsic viscosity of the paraquat terminated polystyrene **11** was 0.270 dL/g and that of the crown ether terminated polystyrene **15** was 0.171 dL/g in chloroform. However, the intrinsic viscosity of a 1:1 molar ratio solution of the two polymers was 0.321 dL/g. This clearly demonstrates that the two polymers interact and bind to form a chain-extended larger supramolecule (**3**).

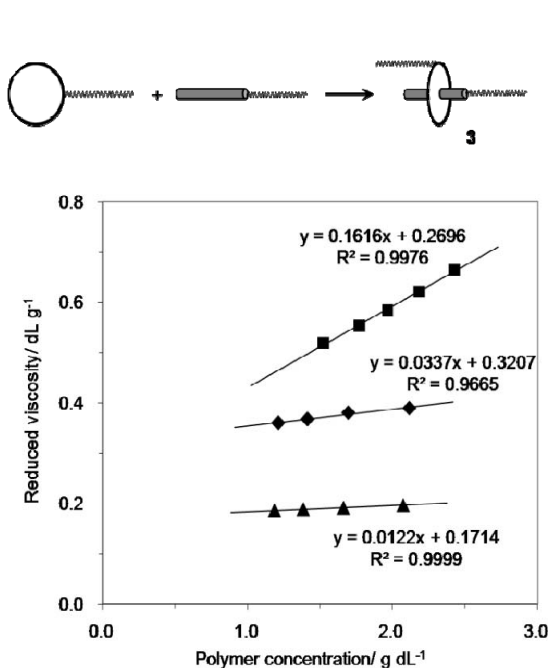


**Figure 3-8.** Reduced viscosity of paraquat-terminated polystyrene **11** (squares), MPPP32C10 centered polystyrene **15** (triangles) and 1:1 (molar ratio) solutions of the two polymers (diamonds), in CHCl<sub>3</sub> at 25 °C.

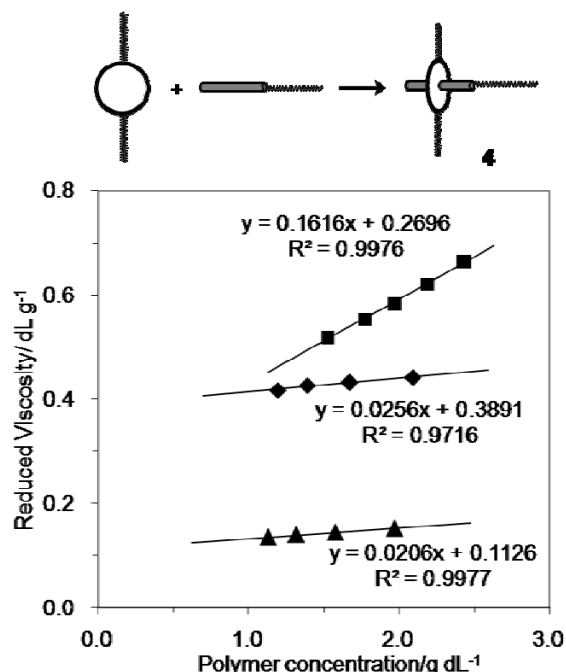


**Figure 3-9.** Reduced viscosity of paraquat-terminated polystyrene **11** (squares), BMP32C10 centered polystyrene **17** (triangles) and a 1:1 (molar ratio) solution of the two polymers (diamonds), in CHCl<sub>3</sub> at 25 °C.

A three-armed star polymer was formed from crown ether (BMP32C10) centered polystyrene **17** and the paraquat terminated polystyrene **11** in chloroform, as shown by the yellow color in panel (b) of Figure 3-6. Viscosity change also supports the formation of a star polymer formation

in solution (Figure 3-8). The intrinsic viscosity of a 1:1 molar ratio solution of the two polymers was 0.389 dL/g in chloroform; the intrinsic viscosities of the paraquat terminated polystyrene **11** and the crown ether centered polystyrene **17** were 0.270 dL/g and 0.113 dL/g, respectively. The polymer-polymer binding to form the 3-armed star polymer **4** in the solution leads to an increased hydrodynamic volume and hence the viscosity increase.

The expected complexation of the two polymers to form a star polymer was confirmed by NMR spectroscopy (Figure 3-9). The chemical shift changes of the crown ether protons of **17** in the  $^1\text{H}$ -NMR spectrum are clear evidence of the formation of the 3-armed star polymer (**4**). The ethyleneoxy protons of the uncomplexed **17** appear at  $\delta$  3.97, 3.77 and 3.64 (bottom spectrum). However, they shifted to  $\delta$  3.88, 3.73 and the upfield peak was resolved into peaks at  $\delta$  3.67 and 3.65 (upper spectrum) after adding 1 eq. of the paraquat polystyrene **11**. NMR does not easily afford a quantitative estimate of the association constant between two polymer species, because the maximum chemical shift change ( $\Delta\theta$ ) required to analyze this fast-exchange system is difficult to measure with polymeric substrates.<sup>14</sup> Nonetheless, the NMR spectroscopic results confirm that the two polymeric species are bound to each other in solution. The fast-exchange process is analogous to that observed in the binding between the small molecules BMP32C10 and dimethyl paraquat.<sup>15</sup>

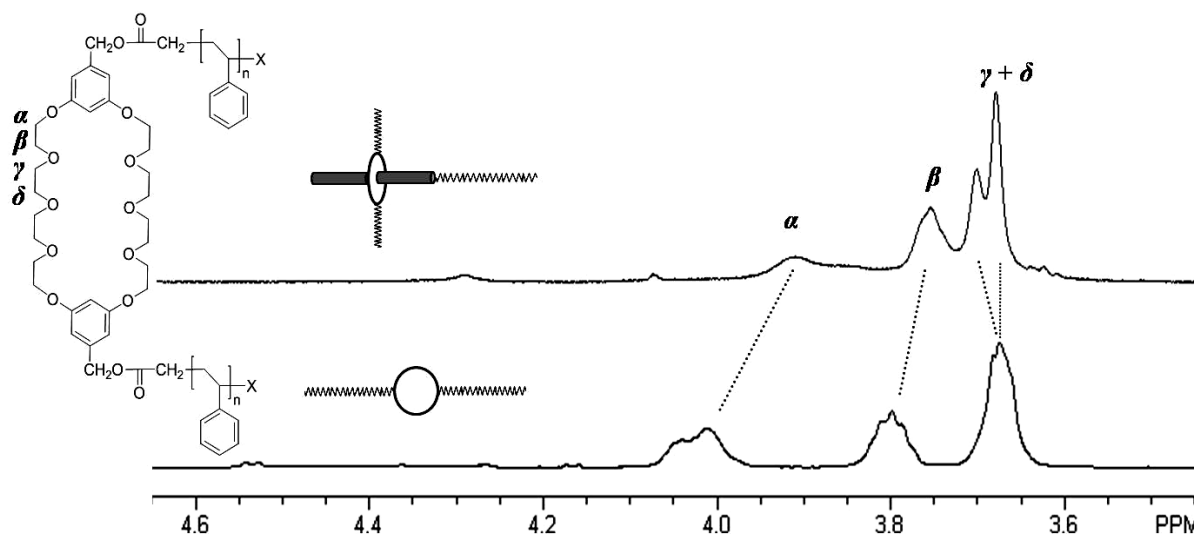


**Figure 3-10.** Partial 400 MHz  $^1\text{H}$ -NMR spectra of functional polystyrenes ( $\text{CDCl}_3$ , 23  $^\circ\text{C}$ ). The bottom spectrum is BMP32C10 centered polystyrene **17** and the upper spectrum is the 1:1 (molar) mixture of BMP32C10 centered polystyrene **17** and PQ terminated polystyrene **11**.

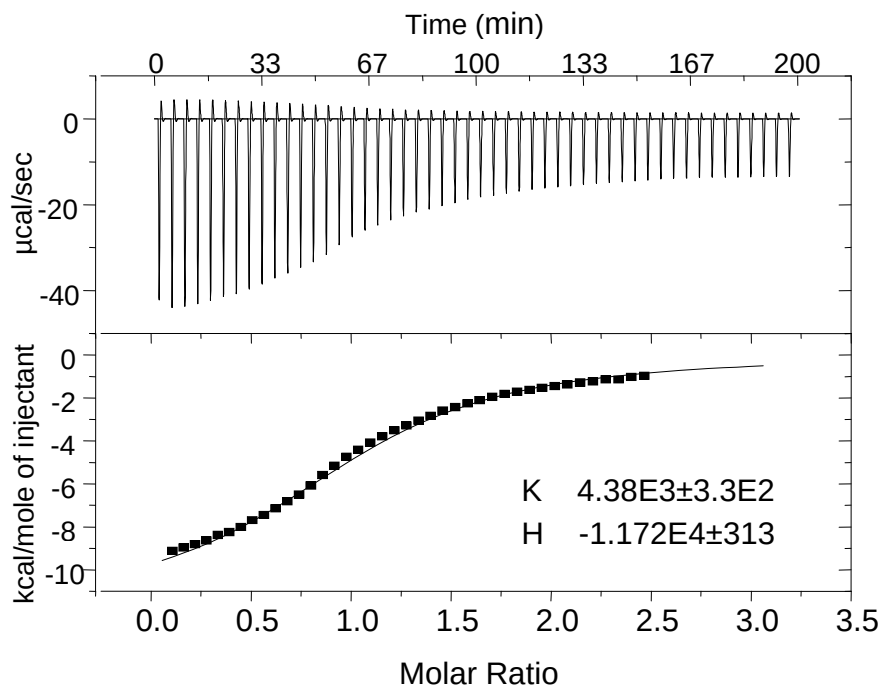


**Figure 3-11.** ITC titration curve (top: raw data, bottom: integrated heat flow and curve fit) and calculated physical constants of complexation between **11** (1.03 mM) and **17** (15.0 mM) in  $\text{CHCl}_3$  at 25 °C.  $K$  is the association constant in  $\text{M}^{-1}$  units and  $H$  is the enthalpy change in cal/mol.

However, ITC titration does afford an estimate of the association constant of this complexation (Figure 3-10). Into a chloroform solution of the paraquat polystyrene **11**, the crown ether polystyrene **17** solution was titrated and the heat flow was measured. The analysis indicates that  $K_a$  is  $4.38 (\pm 0.33) \times 10^3 \text{ M}^{-1}$  ( $\text{CHCl}_3$ , 25 °C) and 1:1 stoichiometry was observed.

Copolymer formation from the host polystyrenes **15** or **17** with the paraquat terminated PMMA **13** was investigated in the same manner. For di-block copolymer formation (**5**), the reduced viscosity plots of the individual polymers (**13** and **15**) and their 1:1 molar mixture are shown in Figure 3-11. The viscosity change was not very significant after mixing the two polymers, due to weak binding between the paraquat unit of the PMMA and the crown ether unit of the polystyrene (**13**:  $[\eta] = 0.321 \text{ dL/g}$ ; **15**:  $[\eta] = 0.171 \text{ dL/g}$ ; **13** + **15**:  $[\eta] = 0.330 \text{ dL/g}$ ). The PMMA chain seems to interfere with the interaction of the paraquat and the crown ether moieties, as noted above with **13** and BMP32C10. In the same manner as the binding of **13** and BMP32C10 and as noted above, hydrogen-bonding may occur between the ester oxygen atoms of PMMA and the paraquat units in the chloroform solution.

For three-armed copolymer formation (6), the reduced viscosity plots of the individual polymers (13 and 17) and their 1:1 mixture are shown in Figure 3-12. The viscosity change was not very significant for the same reason as the previous incomplete copolymer formation (13:  $[\eta] = 0.321$  dL/g; 17:  $[\eta] = 0.113$  dL/g; 13 + 17:  $[\eta] = 0.348$  dL/g). When a solution of the two polymers (13 and 17) was cast on a glass plate, a turbid yellow film was formed. Macro-phase separation was observed by optical microscopy.

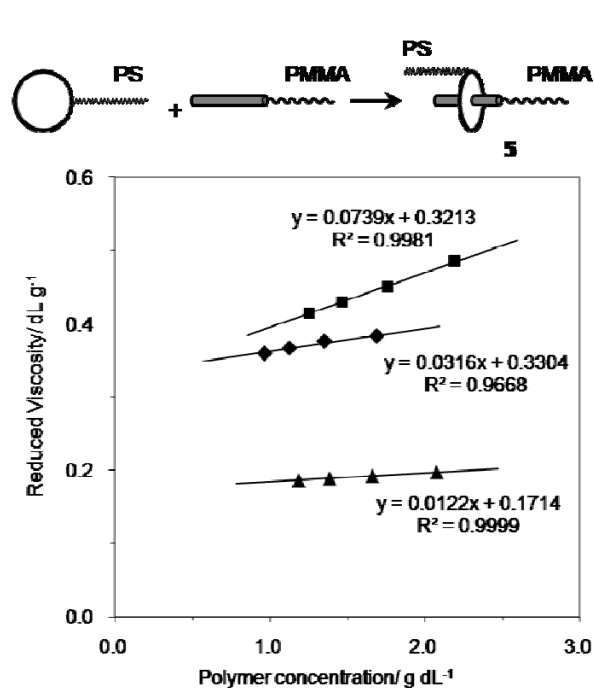


**Figure 3-12.** Reduced viscosity of paraquat terminated PMMA **13** (squares), BMP32C10 centered polystyrene **15** (triangles), and 1:1 (molar ratio) solution of the two polymers (diamonds), in CHCl<sub>3</sub> at 25 °C.

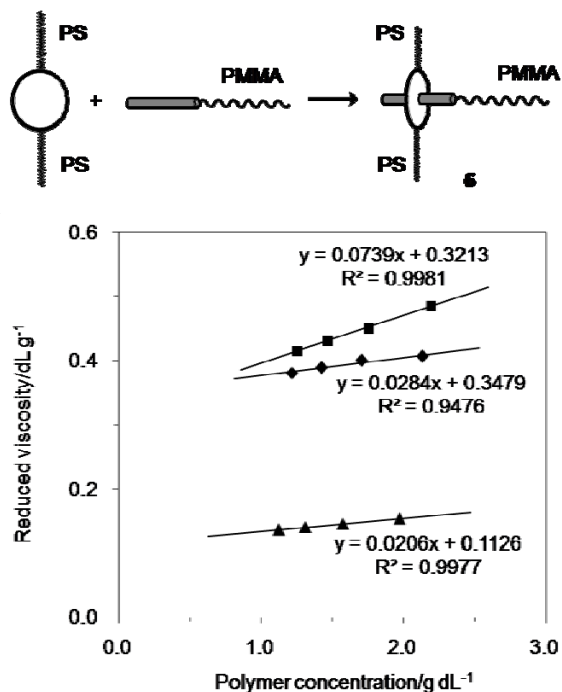


**Figure 3-13.** Reduced viscosity of paraquat terminated PMMA **13** (squares), BMP32C10 centered polystyrene **17** (triangles), and 1:1 (molar ratio) solution of the two polymers (diamonds), in CHCl<sub>3</sub> at 25 °C.

## Conclusions

Paraquat terminated polystyrenes, paraquat terminated poly(methyl methacrylate), and crown ether centered or terminated polystyrenes were synthesized by SFRP or ATRP. From these polymers, pseudorotaxane polymers (**1** and **2**), chain extended (**3**) and 3-armed star polymers (**4**) were formed by self-assembly in solution. The association constants for interaction of BMP32C10 and a DB30C10-based cryptand with the paraquat terminated polystyrene were measured in chloroform for the first time. The  $K_a$  values were 4~6 fold higher than that measured for the binding of the corresponding small molecular hosts and guest in acetone- $d_6$ . The linear and 3-armed polystyrene-PMMA copolymers (**5** and **6**) were also formed in the same way; however, the PMMA paraquat system displays lower association constants. More powerfully binding systems, such as cryptand-guest or other multivalent host-guest, with higher association constants will be required to form self-assembled polystyrene-PMMA block copolymers that have properties similar to conventional covalently bound copolymers. Overall the present results demonstrate that pseudorotaxane formation provides a unique method for reversible formation of chain extended, star and block polymers. We plan to utilize our new host systems<sup>15</sup> for these purposes in our future efforts.

## Experimental

**Isothermal microcalorimetric (ITC) titrations.** Samples of the host and guest molecules were accurately weighed into volumetric flasks and diluted to volume with solvent to yield stock solutions for titration. Titrations were run on a Microcal MCS ITC. Raw isotherm data were collected using the Microcal Observer software. Integration and fitting of the isothermal data ( $K_a$  and  $\Delta H$ ) were accomplished using Origin software with a one set of sites algorithm. The titration curve was fit using the Weisman isotherm, yielding  $\Delta H$ . The Gibb's free energy was calculated from the association constant,  $K_a$ :  $\Delta G = -RT\ln K_a$ . Then  $\Delta S$  was calculated from  $\Delta S = (\Delta H - \Delta G)/T$ .

**MALDI-TOF/TOF CID Measurements.** All samples were analyzed using a Voyager Elite DE STR MALDI-TOF MS (Applied Biosystems, Framingham, MA) equipped with a 337-nm N<sub>2</sub> laser. All spectra were obtained in the positive ion mode using an accelerating voltage of 20 kV and a laser intensity of ~ 10% greater than threshold. The grid voltage, guide wire voltage, and delay time were optimized for each spectrum to achieve the best signal-to-noise ratio. All spectra

were acquired in the reflectron mode with a mass resolution greater than 3000 fwhm; isotopic resolution was observed throughout the entire mass range detected. External mass calibration was performed using protein standards from a Sequazyme Peptide Mass Standard Kit (Applied Biosystems) and a five-point calibration method using Angiotensin I ( $m = 1296.69$  Da), ACTH (clip 1-17) ( $m = 2093.09$  Da), ACTH (clip 18-39) ( $m = 2465.20$  Da), ACTH (clip 7-38) ( $m = 3657.93$  Da) and bovine insulin ( $m = 5730.61$  Da). Internal mass calibration was subsequently performed using a PEG standard ( $M_n = 2000$ ; Polymer Source, Inc.) to yield monoisotopic masses exhibiting a mass accuracy better than  $\Delta m = \pm 0.1$  Da. The instrument was calibrated before every measurement to ensure constant experimental conditions. All samples were run in a dithranol or 3-aminoquinoline (3AQ) matrix doped with silver trifluoroacetate (AgTFA), copper (II) chloride ( $\text{CuCl}_2$ ), or with no cationization agent added ("neat"). Samples were prepared using the dried-droplet method with weight (mg) ratios of 50:10:1 (dithranol:polymer:AgTFA) in THF. After vortexing the mixture for 30 sec, 1  $\mu\text{L}$  of the mixture was pipetted on the MALDI sample plate and allowed to air dry at room temperature. MS data were processed using the Data Explorer 4.9 software supplied by the manufacturer (Applied Biosystems).

**Materials.** The preparations of the paraquat and crown ether precursors for SFRP (TEMPO derivatives) and ATRP initiators followed literature procedures.<sup>16,17</sup> Styrene (Aldrich) and methyl methacrylate (Aldrich) were filtered through basic alumina and stored under nitrogen. The monomers and dimethylformamide (DMF) were deoxygenated by nitrogen bubbling for at least 30 minutes before polymerization. Copper(I) bromide (Aldrich) was washed with glacial acetic acid, vacuum filtered, washed with absolute ethanol and dried in a vacuum oven. 2,2'-Dipyridyl was recrystallized from ethanol and dried in a vacuum oven. Acetonitrile (MeCN) for esterification reactions of acid chlorides and alcohols was distilled over calcium hydride. Pyridine was distilled over sodium hydroxide and stored under nitrogen. All other chemicals and solvents were used as received.

**N-( $\omega$ -Carboxypentyl)-4,4'-bipyridinium  $\text{PF}_6^-$  (**7**).** A solution of 4,4'-dipyridyl (9.38 g, 60 mmol) and 6-bromohexanoic acid (1.95 g, 10 mmol) in MeCN (30 mL) was refluxed for 2 days. The precipitate was filtered after cooling, and then washed with MeCN 3 times. The bromide salt was dissolved in deionized water (30 mL) and  $\text{KPF}_6$  (2.76 g, 15 mmol) was added. The precipitate was filtered and washed with deionized water twice. Drying in a vacuum oven gave an off-white crystalline solid **7** (3.45 g, 83% yield), mp 143.3–144.6 °C (dec.).  $^1\text{H-NMR}$  (400



MHz, DMSO-*d*<sub>6</sub>, 23 °C):  $\delta$  1.33 (m, 2H), 1.56 (m, 2H), 1.97 (m, 2H), 2.24 (t, *J*=7, 2H), 4.63 (t, *J*=7, 2H), 8.05 (d, *J*=7, 4H), 8.64 (d, *J*=7, 2H), 8.89 (s, 2H), 9.23 (d, *J*=7, 2H), 12.07 (br, 1H). <sup>13</sup>C-NMR (100 MHz, DMSO-*d*<sub>6</sub>, 23 °C):  $\delta$  23.8, 24.9, 30.4, 33.3, 60.3, 122.0, 125.4, 140.9, 145.3, 151.0, 152.3, 174.4. HR ESI MS: *m/z* 271.1454 ([M-PF<sub>6</sub>]<sup>+</sup>, calcd. 271.1441, error 2.9 ppm)

**N-( $\omega$ -Carboxypentyl)-N'-methyl-4,4'-bipyridinium 2PF<sub>6</sub><sup>-</sup> (8).** Into a solution of **7** (1.380 g, 2.50 mmol) in dry MeCN (10 mL), iodomethane (0.780 g, 5.5 mmol) was added at room temp. The mixture was refluxed for 3 days. After removing volatile materials, water (20 mL) and KPF<sub>6</sub> (0.55 g, 28 mmol) were added. The mixture was stirred at 60 °C for 3 hours and the precipitate was filtered, recrystallized from water twice and dried in a vacuum oven. A yellow crystalline solid, 1.100 g (76%), mp 181.1–183.3 °C (dec.), was obtained. <sup>1</sup>H-NMR (400 MHz, acetone-*d*<sub>6</sub>, 23 °C):  $\delta$  1.53 (m, 2H), 1.68 (m, 2H), 2.24 (m, 2H), 2.32 (m, 2H), 4.74 (s, 3H), 4.99 (t, *J*=8, 2H), 8.84 (m, 4H), 9.37 (d, *J*=7, 2H), 9.47 (d, *J*=7, 2H). <sup>13</sup>C-NMR (100 MHz, acetone-*d*<sub>6</sub>, 23 °C):  $\delta$  24.8, 26.1, 31.9, 33.7, 49.4, 62.9, 127.7, 128.1, 146.9, 147.8, 150.6, 150.9, 174.5. HR ESI MS: *m/z* 431.1306 ([M-PF<sub>6</sub>]<sup>+</sup>, calcd. 431.1318, error 2.8 ppm)

**N-Methyl-N'-{ $\omega$ -[(2-phenyl-2-(2',2',6',6'-tetramethylpiperidine-N-oxyl)ethoxycarbonyl]pentyl}-4,4'-bipyridinium 2PF<sub>6</sub><sup>-</sup> (10).** A mixture of **8** (0.5966 g, 1.035 mmol) and freshly distilled thionyl chloride (6 mL) was stirred at 50 °C for 12 hours under nitrogen atmosphere. After removing the excess SOCl<sub>2</sub> by vacuum distillation, the residue was rinsed with anhydrous ethyl ether 5 times. The corresponding carbonyl chloride of **8** was a dark-yellow solid; its identity was confirmed by <sup>1</sup>H-NMR. Into a solution of the carbonyl chloride in dry MeCN (15 mL), **9** (0.2871 g, 1.035 mmol) was added and then dry pyridine (0.0860 g, 1.09 mmol) was added dropwise over 10 minutes in an ice bath. After stirring for 3 days at room temp., the insoluble materials were filtered and the solvent was removed from the filtrate by rotoevaporation. The residue was dissolved in ethyl acetate (EA) (80 mL) and the solution was washed with water 3 times. The organic solution was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and the drying agent was filtered. After removing the EA by a rotoevaporator, the residual solid was washed with ethyl ether 3 times and dried in a vacuum oven at 50 °C: 0.823 g (95%) of beige (off-white) solid, mp 182.2-186.5 °C (dec.). <sup>1</sup>H-NMR (400 MHz, acetone-*d*<sub>6</sub>, 23 °C):  $\delta$  0.69 (s (br), 3H), 1.05-1.65 (m, 19H), 2.10-2.27 (m, 4H), 4.28 (m, 1H), 4.61 (m, 1H), 4.92 (t, *J*=8, 2H), 4.97 (s (br), 1H), 7.29-7.40 (m, 5H), 8.80 (m, 4H), 9.37 (d, *J*=7, 2H), 9.47 (d, *J*=7, 2H). <sup>13</sup>C-

NMR (100 MHz, acetone- $d_6$ , 23 °C):  $\delta$  17.7, 20.6, 24.7, 26.1, 31.8, 34.1, 41.1, 49.4, 60.7, 62.8, 66.3, 84.9, 127.7, 128.1, 128.7, 128.9, 146.8, 147.8, 150.6, 150.9, 173.1. HR ESI MS:  $m/z$  836.2978 ( $[M+H]^+$ , calcd. for  $[M+H]^+$  836.2974, error 0.5 ppm),  $m/z$  690.3257 ( $[M-PF_6]^+$ , calcd. 690.3254, error 0.5 ppm).

**SFRP of styrene to form 11 (bulk polymerization), target DP = 300.** A mixture of **1** (0.1298 g, 0.155 mmol) and styrene monomer (4.843 g, 46.5 mmol) was stirred at 125 °C for 15 hours. After 15 hours, the magnetic stir bar was stopped by the high viscosity. The mixture was cooled to room temp. and dissolved in chloroform (20 mL). The solution was added slowly to MeOH (450 mL) with vigorous stirring. The precipitated solid was filtered and dissolved again in 20 mL of chloroform. The solution was added to MeOH (450 mL) with vigorous stirring. The precipitated solid was dissolved in THF (15 mL) and precipitated into MeOH (450 mL). Filtration and drying in a vacuum oven gave 3.440 g (69%) of fine colorless powder. SEC:  $M_n$  = 31.5 kDa, PDI = 1.19 (THF, light scattering detector, PS standards calibration).  $^1H$ -NMR (400 MHz,  $CDCl_3$ , 22 °C):  $\delta$  1.5~2.3 (m, br), 3.96 (m, br), 4.18 (s, 3H, br), 4.38 (br), 6.6~7.3 (m, br), 8.20 (d, 4H, br), 8.67 (s, 4H, br).

**SFRP of styrene to form 11 (solution polymerization), target DP = 300.** A mixture of **10** (0.2925 g, 0.350 mmol) and styrene monomer (10.936 g, 105 mmol) in DMF (5 mL) was stirred at 125 °C for 8 hours. The mixture was cooled to room temp. and dissolved in chloroform (30 mL). The solution was added slowly to MeOH (750 mL) with vigorous stirring. The precipitated solid was filtered and then dissolved in chloroform (30 mL). The solution was added to MeOH (750 mL) with vigorous stirring. The precipitated solid was dissolved in THF (20 mL) and precipitated into MeOH (750 mL). Filtration and drying in a vacuum oven gave 9.665 g (86%) of light pink fine powder. SEC:  $M_n$  = 31.5 kDa, PDI = 1.07 (THF, light scattering detector, PS standards calibration).  $^1H$ -NMR (400 MHz,  $CDCl_3$ , 22 °C):  $\delta$  1.5~2.3 (m, br), 3.97 (br), 4.17 (s, 3H, br), 4.38 (br), 6.6~7.3 (m, br), 8.21 (d, 4H, br), 8.69 (s, 4H, br).

**N-[2-( $\alpha$ -Bromoisobutyryloxy)ethyl]-N'-methyl-4,4'-bipyridinium  $2PF_6^-$  (**12**).** Into a solution of N-(2-hydroxyethyl)-N'-methyl-4,4'-bipyridinium  $PF_6^-$   $^{13}$  (2.531 g, 5.00 mmol) and pyridine (0.475 g, 6.00 mmol) in dry MeCN (15 mL) in an ice bath,  $\alpha$ -bromoisobutyryl bromide (1.150 g, 5.00 mmol) was added by a syringe over 10 minutes. After stirring for 15 hours at room temp., the insoluble materials were removed by filtration and the solution was concentrated. The residue was dispersed in water (60 mL) and the insoluble product was filtered. After washing the filter

cake 3 times with water, drying in a vacuum oven at 50 °C gave 2.57 g (76%) of beige (off-white) crystalline solid, mp 181.9-183.7 °C (dec.). <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>, 23 °C): δ 1.85 (s, 6H), 4.43 (s, 3H), 4.72 (t, J=4, 2H), 5.08 (t, J=4, 2H), 8.75 (d, J=7, 2H), 8.85 (d, J=7, 2H), 9.28 (d, J=7, 2H), 9.42 (d, J=7, 2H). <sup>13</sup>C-NMR (100 MHz, DMSO-*d*<sub>6</sub>, 23 °C): δ 30.4, 48.5, 57.2, 59.8, 64.4, 110.0, 126.5, 126.8, 146.9, 147.1, 148.3, 149.6, 170.7. HR ESI MS: m/z 509.0427 ([M-PF<sub>6</sub>]<sup>+</sup>, calcd. 509.0423, error 0.8 ppm).

**ATRP of MMA to form 13, target DP = 100.** A mixture of **12** (0.1640 g, 0.250 mmol), CuBr (0.0360 g, 0.250 mmol), 2,2'-dipyridyl (0.1172 g, 0.75 mmol) and methyl methacrylate (2.503 g, 25.0 mmol) in DMF (2.5 g) was stirred at 90 °C for 12 hours. The mixture was cooled to room temp. and dissolved in THF (15 mL). The copper catalyst was removed through a Celite pad. The filtrate was concentrated to 3 mL and then added slowly to MeOH (60 mL) with vigorous stirring. The precipitated solid was filtered and then dissolved in chloroform (10 mL). The solution was filtered through a Celite<sup>®</sup> pad a second time to remove the green, precipitated copper catalyst. The filtrate was added slowly to MeOH (60 mL) with vigorous stirring. Filtration and drying in a vacuum oven gave 1.10 g (41%) of pale yellow powder. SEC: *M<sub>n</sub>* = 40.7 kDa, PDI = 1.33 (CHCl<sub>3</sub>, RI detector, PS standards calibration). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, 22 °C): δ 0.8-1.0 (s+s, br), 1.2 (s, br), 1.4 (m, br), 1.8-2.1 (m, br), 3.6 (s), 4.7 (m, 3H), 8.7-8.9 (m, 4H), 9.2-9.5 (m, 4H).

**5-Chloroacetoxymethyl-1,3-phenylene-*p*-phenylene-33-crown-10 (14).** Into a solution of monohydroxymethyl-MPPP33C10<sup>14</sup> (0.710 g, 1.26 mmol) and chloroacetyl chloride (0.180 g, 1.51 mmol) in dry chloroform (10 mL), triethylamine (0.152 g, 1.5 mmol) was slowly added over 10 min. in an ice bath. After the reaction mixture was stirred for 3 days at room temp., water (15 mL) was added and the mixture was extracted with chloroform (20 mL) 3 times. The combined organic layer was washed with saturated aq. NaHCO<sub>3</sub> and then water. The solution was dried over Na<sub>2</sub>SO<sub>4</sub> and the drying agent was removed by filtration. After the solvent was removed by a rotoevaporator, flash column chromatography (EA/silica-gel) gave a colorless, viscous oil 0.490 g (60%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, 22 °C): δ 3.69 (m, 16H), 3.82 (m, 8H), 4.02 (m, 8H), 4.11 (s, 2H), 5.11 (s, 2H), 6.40 (s, 1H), 6.50 (s, 2H), 6.78 (s, 4H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, 22 °C): δ 39.9, 66.6, 66.7, 67.2, 68.6, 68.7, 69.8, 69.9, 100.3, 106.0, 114.7, 135.9, 152.0, 159.1, 170.1. HR FAB MS (NBA-PEG): m/z 642.2405 (calcd. 642.2443, error 5.9 ppm).

**ATRP of polystyrene to form 15, target DP = 300.** A mixture of **14** (0.129 g, 0.20 mmol), CuBr (0.0861 g, 0.60 mmol), 2,2'-dipyridyl (0.281 g, 1.80 mmol) and styrene (6.25 g, 60 mmol) in phenyl ether (6 g) was stirred at 130 °C for 8 hours. The mixture was cooled to room temp. and then dissolved in chloroform (15 mL). The catalyst was removed by passage through a short basic alumina column. The eluent was concentrated to 10 mL volume and then slowly added to MeOH (250 mL) with vigorous stirring. The precipitated solid was filtered and dissolved in chloroform (10 mL). The chloroform solution was slowly added to MeOH (250 mL) with vigorous stirring. Filtration and drying in a vacuum oven gave 1.40 g (22%) of white powder. SEC:  $M_n$  = 21.4 kDa, PDI = 1.29 (CHCl<sub>3</sub>, RI detector, PS standards calibration). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, 22 °C):  $\delta$  1.2-2.3 (m, br), 3.67 (s, 16H), 3.79 (m, 8H), 4.01 (m, 8H), 6.3-7.4 (m, br).

**Bis(5-chloroacetoxymethyl-1,3-phenylene)-32-crown-10 (16).** Into a solution of bis(5-hydroxymethyl-1,3-phenylene)-32-crown-10<sup>14</sup> (0.579 g, 1.00 mmol) and chloroacetyl chloride (0.163 mL, 2.10 mmol) in chloroform (10 mL) in an ice bath, pyridine (0.163 mL, 2.10 mmol) was added by syringe over 30 min. After the mixture had stirred for 3 days at room temp., saturated NaHCO<sub>3</sub> solution (15 mL) was added and the product was extracted with chloroform (20 mL) 3 times. The combined organic layer was washed with 1 M HCl solution, saturated aq. NaHCO<sub>3</sub> and then water. The solution was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and the drying agent was removed by filtration. The solvent was removed by a rotoevaporator to give a colorless oil, 0.694 g (92%). The oil solidified after 1 day at room temp., mp 90.1-91.8 °C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 22 °C):  $\delta$  3.70 (m, 17H (theor. 16H)), 3.83 (t, J=4.6 Hz, 8H), 4.05 (t, J=4.6 Hz, 8H), 4.08 (s, 4H), 5.10 (s, 4H), 6.43 (t, J=2.2 Hz, 2H), 6.49 (d, J=2.2 Hz, 4H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 22 °C):  $\delta$  40.9, 67.6, 67.7, 69.6, 70.9, 101.5, 107.0, 136.9, 160.1, 167.1. HR FAB MS (NBA-PEG): m/z 748.2199 (calcd. 748.2265, error 4.5 ppm).

**ATRP of styrene to form 17, target DP = 100.** A mixture of **16** (0.209 g, 0.28 mmol), CuBr (0.160 g, 1.16 mmol), 2,2'-dipyridyl (0.545 g, 3.48 mmol) and styrene (2.91 g, 28.0 mmol) in phenyl ether (3 g) was stirred at 130 °C for 8 hours. The mixture was cooled to room temp. and dissolved in chloroform (15 mL). The catalyst was removed by passage through a short basic alumina column. The eluent was concentrated to 3 mL and then added slowly to MeOH (50 mL) with vigorous stirring. The precipitated solid was filtered and dissolved in chloroform (5 mL). The chloroform solution was added slowly to MeOH (50 mL) with vigorous stirring. Filtration

and drying in a vacuum oven gave 2.30 g (74%) of white powder. SEC:  $M_n$  = 13.5 kDa, PDI = 1.25 (CHCl<sub>3</sub>, light scattering detector, PS standards calibration). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, 22 °C):  $\delta$  1.2-2.3 (m, br), 3.67 (s, 16H), 3.80 (m, 8H), 4.01 (m, 8H), 6.3-7.4 (m, br).

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14. For fast exchange host-guest systems in proton NMR, only time-averaged peaks appear, as with our current system. In this case, the maximum chemical shift change ( $\Delta\theta$ ) is required to calculate  $K_a$  by NMR. Usually  $\Delta\theta$  can be measured by keeping the concentration of one component constant and increasing that of the other to very high values; then a plot of the chemical shift versus the inverse of the concentration of the variable component yields  $\Delta\theta$  as the zero intercept. See Tsukube, H.; Furita, H.; Odani, A.; Takeda, Y.; Kudo, Y.; Inoue, Y.; Liu, Y.; Sakamoto, H.; Kimura, K. in *Comprehensive Supramolecular Chemistry*, Atwood, J. L.; Davies, J. E. D.; MacNicol, D. D.; Vögtle, F.; exec. Eds., Pergamon, New York, vol. 8, ch. 10, pp. 425-482. However, in our systems in which both host and guests are polymeric, but contain only a single active site, there is a practical limit to how high the concentration can be before high viscosity broadens the peak too much to accurately measure the chemical shift change.
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## Chapter 4

# Supramolecular Graft Copolymer from a Crown Polyester and a Complementary Paraquat Terminated Polystyrene Guest

### Abstract

The self-assembly of the poly(ester crown ether) host containing crown ether units on its main chain and the paraquat-terminated polystyrene guest provides a new supramolecular graft copolymer based on the bis(*m*-phenylene)-32-crown-10/paraquat recognition motif for pseudorotaxane formation. The solution of the graft copolymer possesses an intrinsic viscosity almost double compared to the paraquat-terminated polystyrene. Differential scanning calorimetry showed only one glass transition of the graft copolymer, which implies the complete phase mixing occurred from the graft copolymer formation. The complete phase mixing was also confirmed by small angle laser light scattering and it showed complete mixing of two polymers by the polymer-polymer complexations. NMR chemical shift gave an evidence of the complexation of crown ether and paraquat moieties.

### Introduction

In supramolecular chemistry, the formation of pseudorotaxane and rotaxanes is a key subject, not only for better self-assembling systems but also for the expanded applications to polymeric materials due to their unique properties.<sup>1</sup> The convergence of the two areas has led to construction of analogs of traditional covalently-constructed polymeric structures and architectures by physically-bound supramolecular methods. Linear polymers were formed from self-organization of well-defined monomeric building blocks.<sup>2-5</sup> Several dendrimers were also synthesized from cooperative complexation of a homotritopic guest and complementary monotopic dendron hosts,<sup>2, 6</sup> and by other self-assembly approaches.<sup>7-12</sup> Instead of multi-step preparations for globular dendrimers, one-step formation of a hyperbranched polymer was reported by the self-assembly of an AB<sub>2</sub> monomer in concentrated solution.<sup>13</sup> A triarm star polymer was constructed from a homotritopic host and a complementary monotopic paraquat-terminated polystyrene guest by a supramolecular method in solution.<sup>14</sup> The triarm star polymer

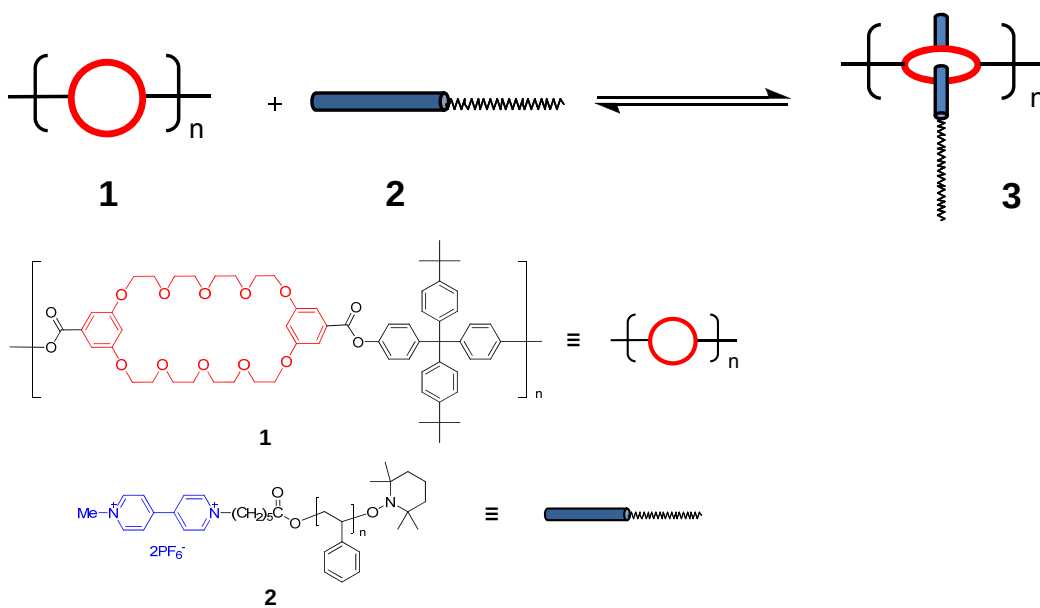


has much higher intrinsic viscosity than the individual monotopic paraquat-terminated polystyrene component. Polymers containing terminal pseudorotaxane moieties were prepared by the introduction of host or guest moieties on the polymer chain ends via controlled polymerization techniques.<sup>15</sup> Polymer-polymer binding to form supramolecular diblock copolymers was studied using host- and guest-functionalized polymeric building blocks.<sup>16, 17</sup>

Covalent comb-like graft copolymers have been widely studied.<sup>18-22</sup> Three general methods for graft copolymer synthesis are: “grafting from” reactions (polymerization of grafts from a polymer with pendant macroinitiator functionality), “grafting through” processes (homo- or copolymerization of macromonomers containing a terminal polymerizable moiety), and “grafting onto” (grafting via a preformed chain is attached to a polymer backbone).<sup>19</sup> Here we report the preparation of the first supramolecular comb-like graft copolymer based on pseudorotaxane formation.

## Results and Discussion

The self-assembly of the polyester host containing crown ether units in its main chain and the paraquat-terminated polystyrene guest provides a new supramolecular graft copolymer based on the bis(*m*-phenylene)-32-crown-10/paraquat recognition motif for pseudorotaxane formation.<sup>23-31</sup> This is a new supramolecular coupling method for fabrication of graft copolymers using noncovalent interactions.



**Scheme 4-1.** Schematic illustration of the formation of a supramolecular graft copolymer **3** from poly(ester crown ether) **1** and paraquat polystyrene guest **2** in solution.

The main-chain crown polyester host **1**<sup>32</sup> was used as a backbone of the comb-like graft copolymer. The molecular weight of **1** was determined by GPC:  $M_n = 28.5$  kDa.<sup>32</sup> The average degree of polymerization was 27; on average twenty-seven grafting sites are available on the each polyester chain. The paraquat (N,N'-substituted 4,4'-bipyridinium salt) terminated polystyrene **2** was prepared by nitroxide mediated polymerization (NMP) as previously reported.<sup>17</sup> The paraquat end-functionality was confirmed by MALDI-TOF<sup>17</sup> and ESI-TOF mass spectrometry. The molecular weight and polydispersity of **2** were analyzed by GPC:  $M_n = 31.5$  kDa and PDI = 1.07.

The formation of a graft copolymeric pseudorotaxane was confirmed by viscosity studies as shown in Figure 4-1. Solutions of crown polyester **1** and paraquat polystyrene **2** (**1:2** = 1:27 mole:mole (under GPC results), crown ether:paraquat = 1:1) possessed an intrinsic viscosity ( $[\eta] = 0.519$  dLg<sup>-1</sup>) nearly double that of paraquat terminated polystyrene **2** itself ( $[\eta] = 0.269$  dLg<sup>-1</sup>), consistent with the formation of the comb-like graft copolymer.

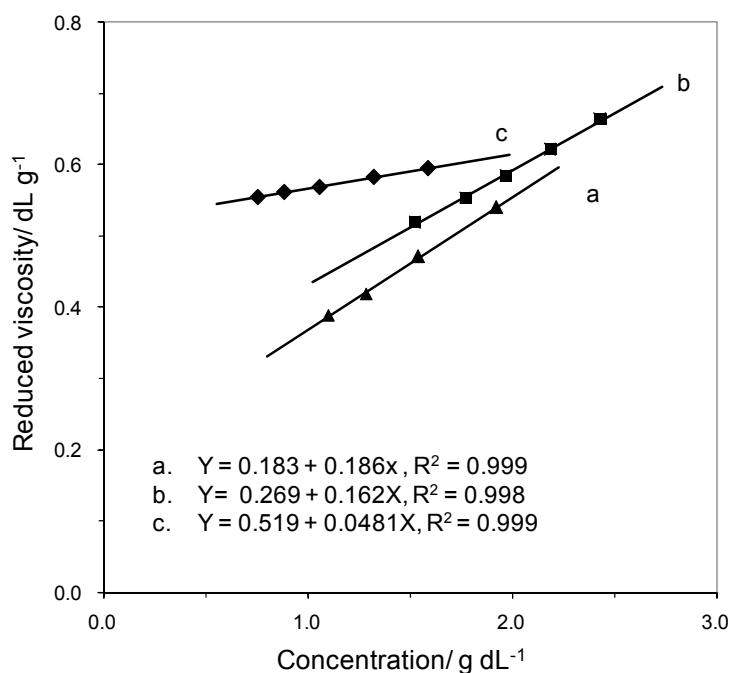


**Figure 4-1.** Reduced viscosity as a function of concentration (chloroform at 25 °C): (a) crown polyester **1**, (b) paraquat terminated polystyrene **2**, and (c) **1** and **2** (crown ether:paraquat = 1:1).

The glass transition temperatures ( $T_g$ s) gave corroborating evidence for the formation of graft copolymer **3**. The DSC heating traces of **1**, **2**, an uncomplexed solid mixture of **1** and **2**, and copolymer **3** are shown in Figure 4-2. The  $T_g$  of the crown polyester **1** is 109.3 °C and the  $T_g$  of

the paraquat polystyrene **2** is 103.4 °C. The uncomplexed solid mixture of the two components exhibits two  $T_g$ s that exactly correspond to the  $T_g$ s of the components. However, the self-assembled copolymer **3** has only one  $T_g$  (98.6 °C) and it is lower than both **1** and **2**, reflective of an increase on free volume as result of the grafting process. Mixture of **1** and **2** in solution led to the formation of the graft copolymer **3**, but mixing the polymers in the solid state did not. The DSC result from the immiscible blend of **1** and non-functionalized polystyrene ( $M_n = 28.4$  kDa, PDI = 1.5) substantiated this conclusion; the solution blend of **1** and the non-functionalized polystyrene led to a mixture with two  $T_g$ s; macroscopic phase separation occurred without the paraquat functionality. The complete miscibility of **1** and **2** is only explained by the supramolecular complexation of the two polymers to form graft copolymeric pseudorotaxane **3**.

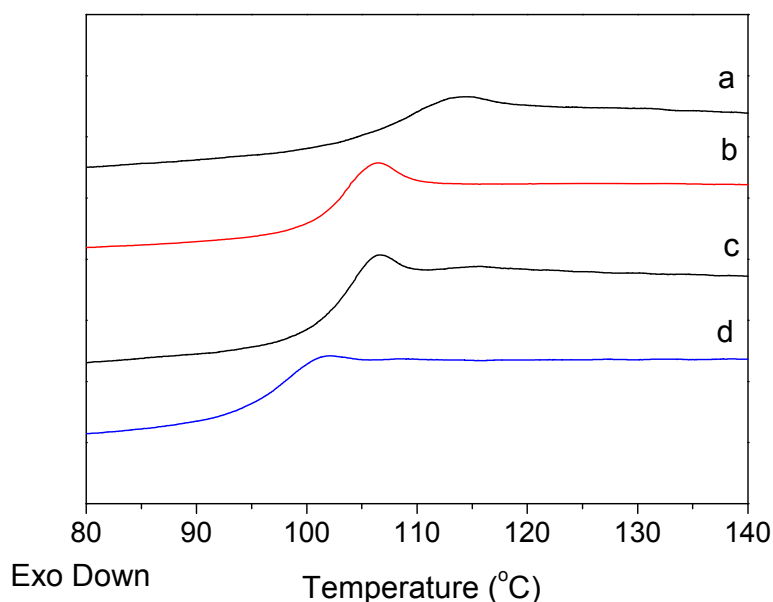


**Figure 4-2.** DSC traces of (a) poly(ester crown ether) **1**, (b) paraquat terminated polystyrene **2**, (c) solid mixture of **1** and **2**, and (d) blend from a solution (chloroform) of **1** and **2**. The blend of polymers **1** and **2** from solution has one  $T_g$  which is even lower than the  $T_g$ s of **1** and **2**. The crown ether: paraquat is 3:1 for the (c) and (d) experiments.

Optical microscopy and small angle laser light scattering (SALLS) analysis reinforce the DSC experiments. As expected, a film of the graft copolymeric pseudorotaxane **3** (crown ether: paraquat = 3:1) did not display macroscopic phase separation either by optical microscopy and SALLS. However, the blend of polyester **1** and the non-functionalized polystyrene revealed typical macroscopic phase separation.<sup>33</sup> Macro-phase separation of the blend from **1** and **2** does

not take place because of the complexation of the two species to form graft copolymer **3**. Even though this result does not indicate the complete formation of the pseudorotaxane, i. e. the extent of grafting, this new supramolecular method clearly results in compatibilization of otherwise incompatible polymers, polystyrene and the poly(ester crown ether).

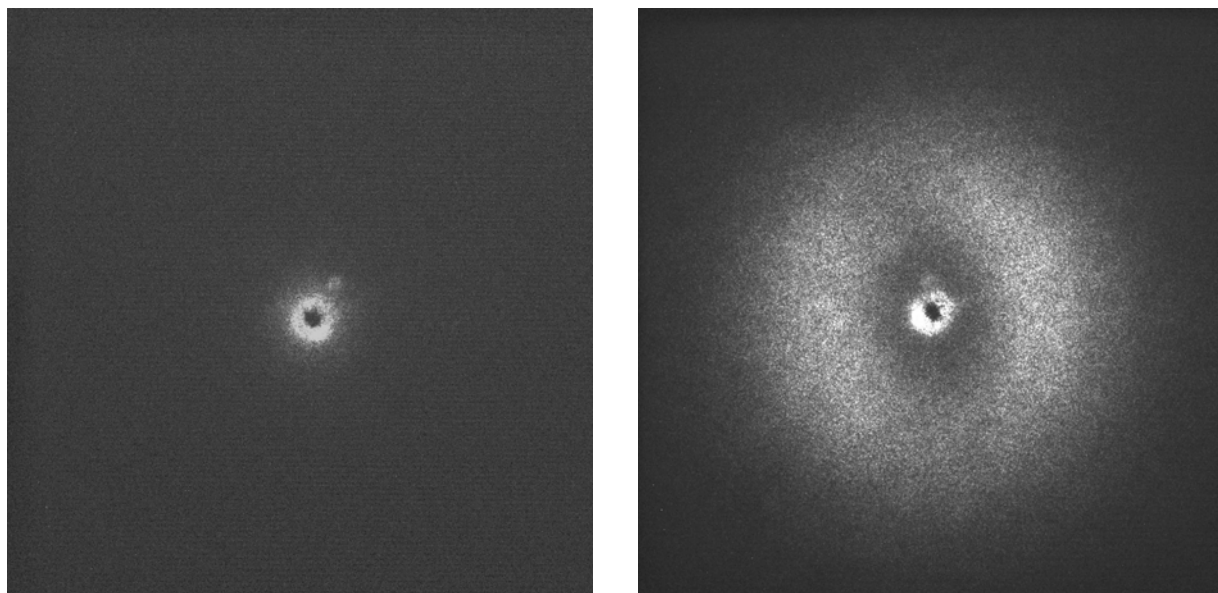


**Figure 4-3.** SALLS images of the solution cast mixture of poly(ester crown ether) **1** and polystyryl paraquat **2** (left) and a solution cast mixture of polymer **1** and polystyrene with no functional group (right).

The chemical shift changes of the crown ether protons of **1** and the paraquat protons of **2** in the  $^1\text{H}$ -NMR spectrum are further clear evidence of the formation of the graft copolymer **3** as shown in Figure 4-4. The ethyleneoxy protons of the uncomplexed **1** appear at  $\delta$  4.18, 3.86, 3.72 and 3.69. However, the first two peaks shifted to  $\delta$  4.10 and 3.83, and the last two peaks merged upon addition of paraquat terminated polystyrene **2** (crown ether: paraquat = 1:1 m/m). NMR does not easily afford a quantitative estimate of the association constant between two polymer species, because the maximum chemical shift change ( $\Delta\theta$ ) required to analyze this fast-exchange system is difficult to measure with polymeric substrates.<sup>17</sup> The fast-exchange process is analogous to that observed in the binding between the small molecules BMP32C10 and dimethyl paraquat.<sup>31</sup>

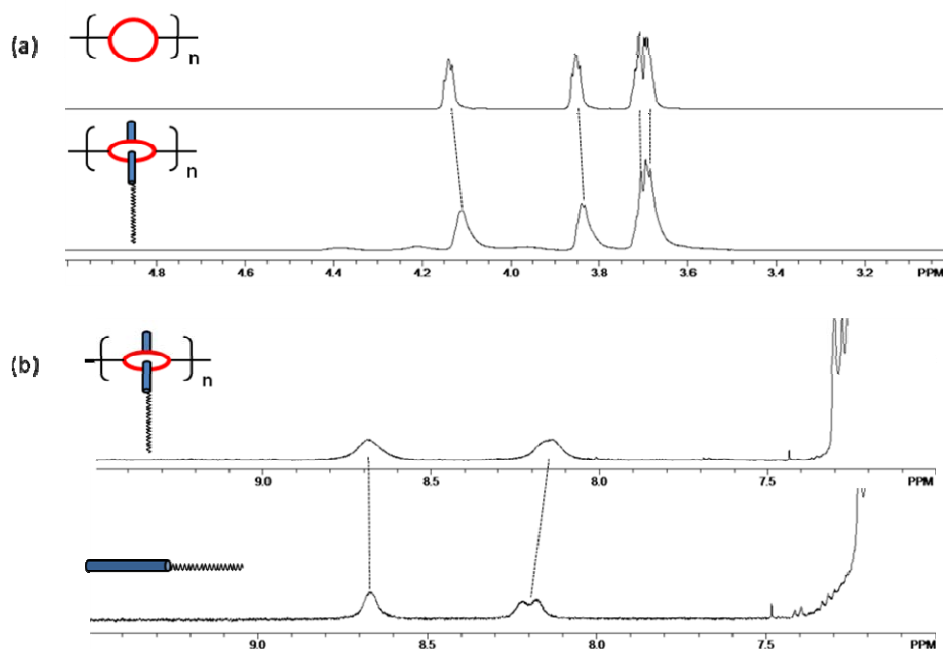


**Figure 4-4.** (a) Partial  $^1\text{H}$  NMR spectra of poly(ester crown ether) **1** and graft copolymeric pseudorotaxane **3**. Ethyleneoxy protons shift upfield after formation of the graft copolymer. (b) Partial  $^1\text{H}$  NMR spectra of paraquat terminated polystyrene **2** and **3** (400 MHz,  $\text{CDCl}_3$ , 23  $^\circ\text{C}$ ). Paraquat protons shift upfield after formation of the graft copolymer.

## Conclusions

We have reported the first supramolecular comb-like graft copolymer **3** based on pseudorotaxane formation from two polymeric building blocks, a main-chain crown ether polyester **1** and a paraquat terminated polystyrene **2**. The formation of the graft copolymer **3** was proven by a dramatic viscosity increase of solutions of the two components, the observation of a single  $T_g$  by DSC, the lack of phase separation by both optical microscopy and SALLS, and NMR chemical shift changes in solution. Introduction of appropriate blocking groups onto the paraquat units of this system after complexation will produce a mechanically interlocked comb-like graft copolymeric rotaxane. We provided one example of a physically bound supramolecular graft copolymer, and we are investigating other polymeric architectures constructed using such supramolecular approaches.

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33. Complete complexation is not necessary for phase mixing; the initially formed grafts can compatibilize other polyester-polystyrene macromolecules in the blend.

## Chapter 5

### Supramolecular Four-Armed Star Copolymer (Miktoarm Star) via Host-Guest Complexation and Nitroxide Mediated Radical Polymerization

#### Abstract

Supramolecular four-armed star copolymer was prepared from the pseudorotaxane complex of a crown centered polystyrene and a bis(2,2,6,6-tetramethylpiperidiny-1-oxyl) paraquat compound and *n*-butyl acrylate by nitroxide mediated polymerization. Solvent fractionation with dioxane/THF/MeOH removed high molecular weight homopolymer. Size exclusion chromatography gave direct evidence of the four-armed star copolymer formation by a molecular weight increase without the residual starting polystyrene. NMR spectroscopy showed the rotaxane structure of the copolymer and differential scanning calorimetry two glass transition temperatures, which correspond to polystyrene and poly(*n*-butyl acrylate).

#### Introduction

The field of supramolecular chemistry mainly consists of molecular recognition, molecular devices, and self-processing by self-assembly.<sup>1</sup> The formation of pseudorotaxane and rotaxanes is a key subject in supramolecular chemistry,<sup>2</sup> which has been expanded to polymeric materials due to their unique properties. The convergence of the two areas has led to construction of analogs of traditional polymeric structures and architectures by supramolecular methods. Some previously reported examples of macromolecules formed by the self-assembly of pseudorotaxane and rotaxane host and guest units include linear polymers from self-organization of well-defined monomeric building blocks,<sup>3-6</sup> dendrimers from cooperative complexation of a homotritopic guest and complementary monotopic dendron hosts,<sup>7</sup> dendrimers from self-assembly,<sup>8-13</sup> a hyperbranched polymer from an AB<sub>2</sub> monomer,<sup>14</sup> a triarm star polymer from a homotritopic host and a complementary monotopic paraquat-terminated polystyrene guest,<sup>15</sup> polymers with



terminal pseudorotaxane units from polymers end-functionalized with crown ethers and small guest molecules,<sup>16</sup> and supramolecular diblock copolymers from end-functionalized polymeric building blocks.<sup>17, 18</sup>

Supramolecular self-assembly of the functional polymers has been studied by our group. Host- and guest-functionalized polymeric building blocks were synthesized by nitroxide mediated polymerizations (NMP)<sup>15-17</sup> or atom transfer radical polymerizations (ATRP).<sup>18</sup> Host and guest end-functionalities included crown ether, dibenzyl ammonium and N,N-disubstituted 4,4'-bipyridinium (paraquat) salts via the initiators.

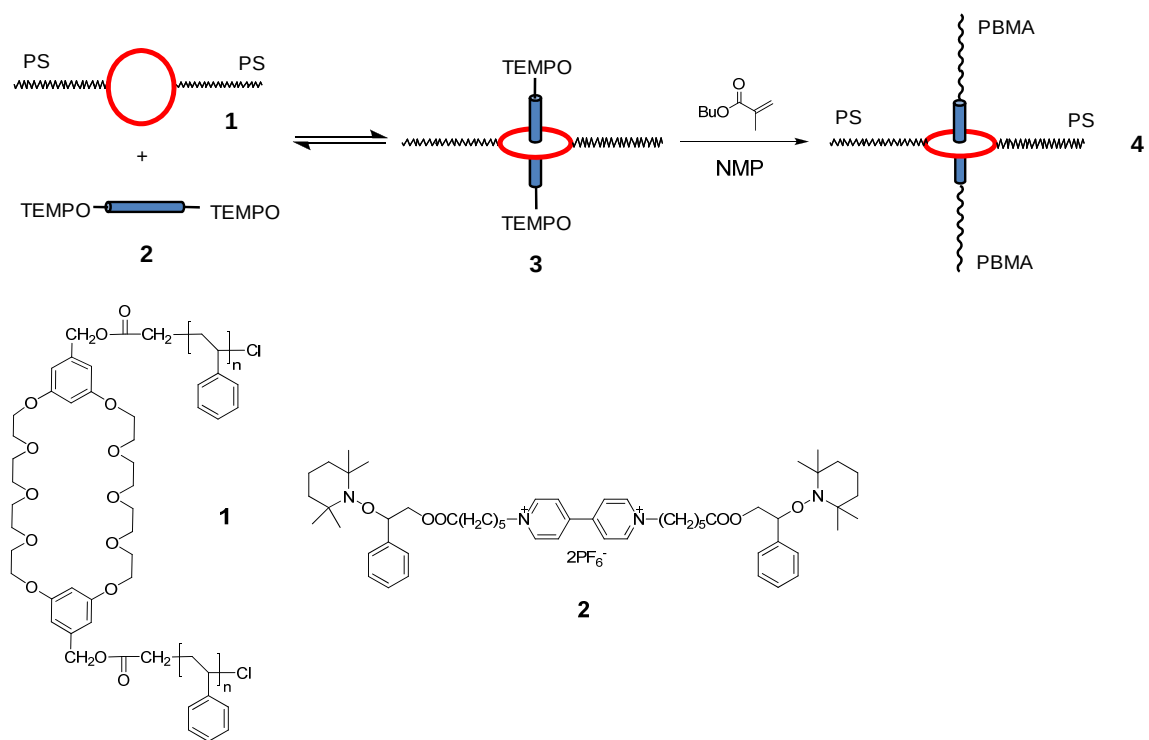
Star copolymers from controlled radical polymerizations have been generally studied by two methods. The first method, "Stars by convergent approach" starts from end-functionalized macroinitiator and then star polymers are synthesized by sequential polymerizations of divinyl monomers with a proper amount.<sup>19-21</sup> The second method, "Stars by divergent approach" uses multifunctional initiators for star polymers. The number of arms is decided by the structure of multifunctional initiators.<sup>22</sup> Here we are reporting a 4-armed star copolymer, of which the core is constructed by supramolecular interactions, and not by covalent bonds.

## Results and Discussion

The supramolecular 4-armed star copolymer was prepared by NMP from a supramolecular polymeric complex incorporating a difunctional 2,2,6,6-tetramethylpiperidine-N-oxy (TEMPO) initiator (**3**) as shown in Scheme 5-1. The crown centered polystyrene (**1**) ( $M_n = 13.1$  kDa) prepared by ATRP<sup>18</sup> was used as the host polymeric building block in this study. The bis(TEMPO) paraquat **2** prepared from the corresponding paraquat dicarboxylic acid and the hydroxy TEMPO derivative forms a pseudorotaxane complex with polystyryl crown ether **1**, as confirmed by a color change to yellow in butyl methacrylate (BMA) solution.<sup>23</sup> NMR chemical shifts also provide evidence of the complexation (Figure 5-1). The uncomplexed ethyleneoxy protons of **1** appear at  $\delta$  4.00, 3.79, and 3.67 (spectrum **a**), and the paraquat protons of **2** appear at  $\delta$  8.67 and 8.10 (spectrum **c**). However, a 1:1 molar mixture of **1** and **2** shows upfield-shifted peaks at  $\delta$  3.95, 3.76, and 3.66 (ethyleneoxy protons) and  $\delta$  8.69 and 8.05, respectively. These time averaged signal shifts are consistent with many reported complexations of paraquat derivatives with bis(*m*-phenylene)-32-crown-10<sup>24</sup> and its derivatives.<sup>25-32</sup> NMR does not easily afford a quantitative estimate of the association constant with polymeric species, because the

maximum chemical shift change ( $\Delta\theta$ ) required to analyze this fast-exchange system is difficult to measure.<sup>33</sup>

After forming the pseudorotaxane complex **3** in BMA,<sup>34</sup> the polymerization of BMA was simply initiated by heating (135 °C). After the polymerization, the supramolecular four-arm star copolymer (**4**) was obtained by precipitations from chloroform (or THF) into methanol; the GPC trace of the initial product contained a high molecular weight fraction (Figure 5-2) believed to have arisen from initiation of BMA by free, uncomplexed initiator **2** or less likely by chain transfer to monomer. The initial product was fractionated by addition of methanol to a solution in 1:1 dioxane:THF until it became slightly cloudy; filtration of the high molecular weight precipitate and evaporation of the filtrate yielded the final polyrotaxane.



**Scheme 5-1.** Schematic illustration of the formation of a supramolecular polystyrene-poly(butyl methacrylate) star block copolymeric [3]rotaxane **4** from a pseudorotaxane complex **3** of crown centered polystyrene (**1**) and bis(TEMPO) paraquat initiator **2**.

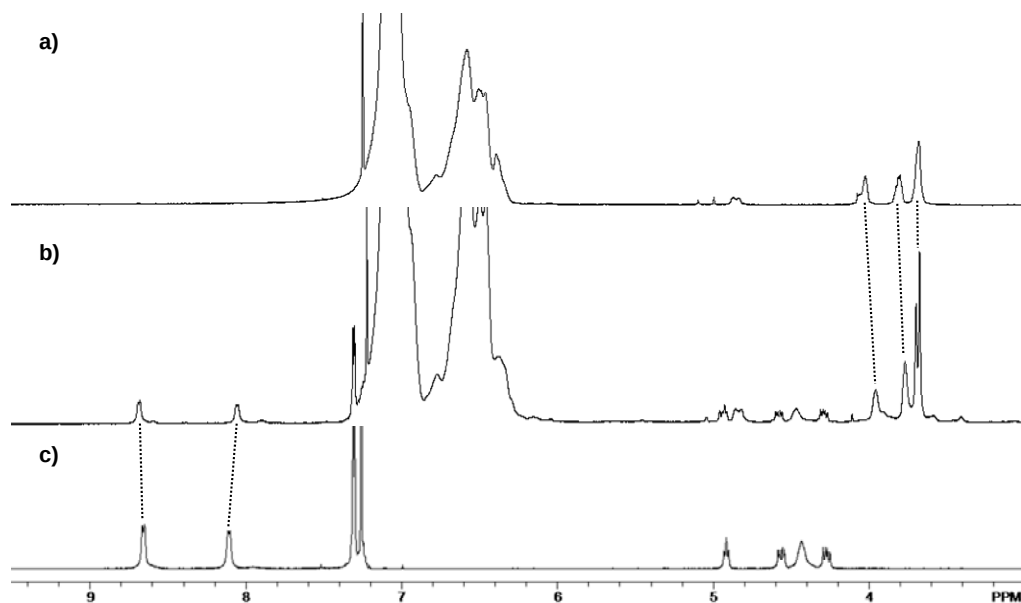


**Figure 5-1.** Partial  $^1\text{H}$  NMR spectra of (a) crown centered polystyrene **1**, (b) 1:1 molar mixture of **1** and **2**, and (c) paraquat initiator **2** in  $\text{CDCl}_3$  (400 MHz, 23  $^\circ\text{C}$ ).

The star copolymer formation was confirmed by GPC as shown in Figure 5-2. After the polymerization of BMA, the chromatogram moved to short retention time, which indicates molecular weight increase by copolymer formation. The molecular weight increase was  $\sim 9$  kDa (degree of polymerization (DP) of BMA =  $\sim 60$ ) after the polymerization of BMA: **1** ( $M_n = 13.1$  kDa, PDI = 1.25) and **4** ( $M_n = 22.5$  kDa, PDI = 1.30). In our experiences, complexes of low molar mass crown ethers and paraquat compounds are disassociated in the GPC experiment, due to separation of the equilibrated components in the column. However, in the present case, no dethreading occurred for star copolymer **4**; no peak from the starting homopolymer **1** from dethreading ( $M_n = \sim 9$  kDa) was observed. Moreover, usually bis(*m*-phenylene)-32-crown-10 complexes with paraquat derivatives have exhibited “taco structures”, which are folded,<sup>35-38</sup> in the solid state rather than pseudorotaxane structures, which involve threading of the guest unit through the cavity of the crown ether. Recently, it has been shown that paraquat complexes of bis(*m*-phenylene)-32-crown-10 can serve as efficient precursors to rotaxanes,<sup>39</sup> thus demonstrating the presence of the pseudorotaxane structure in solution.

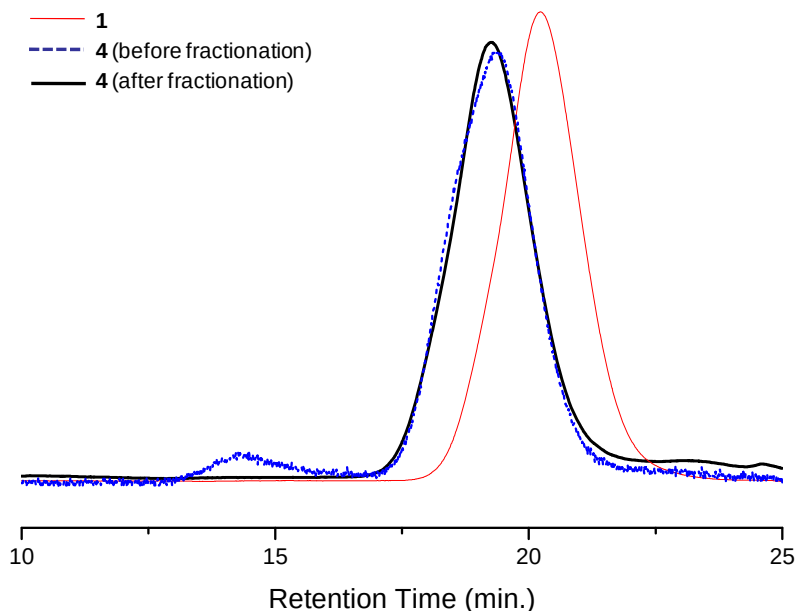


**Figure 5-2.** GPC traces of crown polystyrene **1** and 4-armed star copolymer **4** (THF, 25 °C).

The molecular weight increase was not as high as the targeted value for the BMA component ( $DP_{\text{theor}} = [M]/[\text{paraquat initiator}] = 200$ ), even after a 4-day reaction.<sup>40</sup> Polymerizations in solvents, such as DMF and N-methylpyrrolidine, did not proceed but only occurred in the neat condition.

<sup>1</sup>H NMR also provides an estimate of the molecular weight of the poly(BMA) as shown in Figure 5-2. When the integration numbers of peak at  $\delta$  3.95 (OCH<sub>2</sub> of BMA) and aromatic peak (styrene) are compared, the molecular weight ( $M_n$ ) of poly(BMA) block is 7.3 kDa, which is somewhat less than the GPC result. Star diblock copolymer formation was also confirmed by DSC as shown in Figure 5-3; **4** possesses two  $T_g$ s: 25 °C and 90 °C, which correspond poly(BMA) and polystyrene respectively.

The star copolymer contains one pseudorotaxane unit at the center. The formation of small molecule pseudorotaxanes is usually reversible and dethreading takes place in polar media. However, the GPC result for star copolymer **4** which was precipitated from DMSO to MeOH did not change the retention time. The poly(BMA) coils act as a blocking group, preventing dethreading. Therefore, we can say this star copolymer **4** is a polymeric rotaxane with polymer blocking groups.

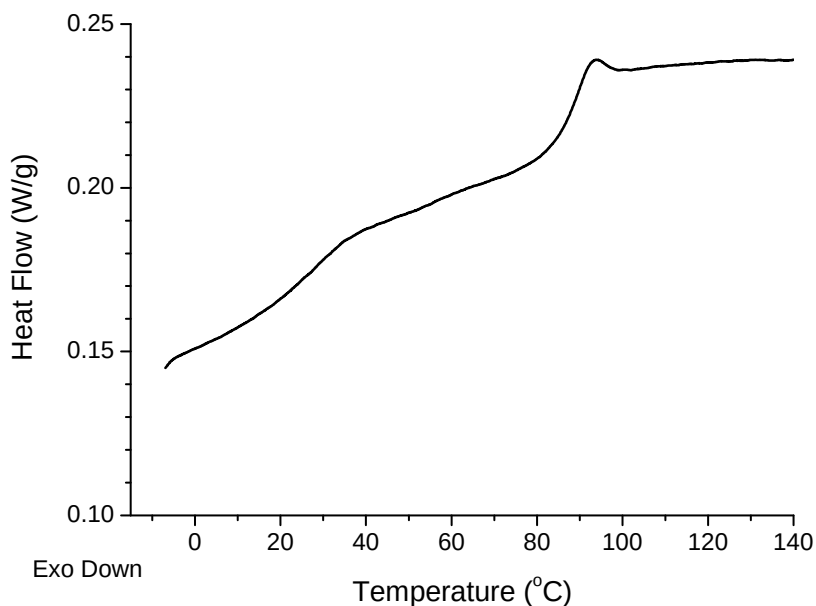


**Figure 5-3.** DSC heating scan of star polystyrene-*b*-poly(BMA) [2]rotaxane **4** (2<sup>nd</sup> heating scan, heating rate 5 K/min, under N<sub>2</sub>).

## Conclusions

A supramolecular star copolymer of polystyrene-poly(BMA) was synthesized by NMP of the complex (**3**) of the crown ether polystyrene **1** and the bis(TEMPO) paraquat initiator **2**. The two polymer blocks are bound mechanically, not with covalent bonds. This 4-armed supramolecular star copolymer was characterized by GPC, NMR and DSC. The mechanical linkage, i. e., the threaded crown unit, was not dethreaded in DMSO and during the GPC experiment, due to the poly(BMA) coils attached to the paraquat moiety. We are preparing other supramolecular copolymers from novel complexes incorporating pseudorotaxanes with various controlled radical polymerization techniques.

## Experimental

### **N,N'-Bis[5''-(2'''-TEMPO-2'''-phenylethoxycarboxy)pentyl]-4,4'-bipyridinium**

**bis(hexafluorophosphate) (2).** A mixture of N,N'-bis( $\omega$ -carboxypentyl)-4,4'-bipyridinium bis(hexafluorophosphate) (0.676 g, 1.0 mmol)<sup>S41</sup> and freshly distilled thionyl chloride (5 mL) was stirred at 50 °C for 3 days. After removing excess thionyl chloride by vacuum, the residue was dissolved in dry MeCN (5 mL). Into the solution, 2-TEMPO-2-phenylethanol<sup>S42</sup> (0.676 g, 2.4 mmol) was added and then dry pyridine (0.166 g, 21 mmol) was slowly added in an ice bath. The mixture was stirred for 3 days at rt. A precipitated salt was removed by filtration. After concentration of the filtrate, deionized water (25 mL) was added to precipitate the product. The filtered precipitate was washed with 1M HCl solution once and water 5 times. The solid product was also washed with boiling ethyl ether to remove the unreacted alcohol. Drying in a vacuum oven gave an off-white solid (0.80 g, 69%), mp 150.8-155.4 °C (dec.) <sup>1</sup>H NMR (400 MHz, acetone-*d*<sub>6</sub>, 22 °C):  $\delta$  1.10~1.97 (m, 44H), 2.17~2.34 (m, 8H), 4.48 (m, 2H), 4.66 (m, 2H), 4.98 (s, 4H), 6.10 (m(br), 2H), 7.39 (m, 8H), 7.53 (m, 2H), 8.89 (d, J=2, 4H), 9.50 (d, J=2, 4H). <sup>13</sup>C NMR (100 MHz, acetone-*d*<sub>6</sub>, 22 °C):  $\delta$  13.37, 13.43, 21.9, 22.0, 25.1, 25.2, 29.0, 29.3, 30.4, 30.5, 49.0, 50.2, 20.6, 122.2, 122.5, 123.8, 124.0, 136.0. HRMS (ESI): *m/z* 904.6094 ([M-2PF<sub>6</sub>]<sup>+</sup>, calcd. for C<sub>56</sub>H<sub>80</sub>N<sub>4</sub>O<sub>6</sub> 904.6078, error 1.8 ppm).

**Star polystyrene-poly(BMA) copolymer 4.** A solution of the crown centered polystyrene **1** (0.2700 g, 2 x 10<sup>-5</sup> mol, *M<sub>n</sub>* = 13.1 Da, PDI = 1.25)<sup>S18</sup> and **2** (0.0239 g, 2 x 10<sup>-5</sup> mol) in n-butyl methacrylate (0.5688 g, 4 mmol) was degassed by N<sub>2</sub> bubbling for 30 min at room temp. The solution was immersed in an oil bath (135 °C) and stirred for 4 days. After cooling, the polymer solution was diluted with chloroform (5 mL). The solution was added slowly to MeOH (150 mL) with vigorous stirring. The precipitated solid was filtered and dissolved in THF (5 mL). The solution was added to MeOH (150 mL) with vigorous stirring. The precipitated solid was dissolved in chloroform (5 mL) and precipitated into MeOH (450 mL). Filtration and drying in a vacuum oven gave of fine colorless powder (0.302 g). In GPC, the small broad peak in the high molecular weight region was shown and it may be from chain transfer to monomer and/or from the free uncomplexed initiator. The fractionation was performed from a solution of dioxane/THF 1:1 mixture. With vigorous stirring, MeOH was dropped to the solution with vigorous stirring until small amount of precipitate occurred. After removing the precipitate by filtration, the

solvent was removed from the filtrate solution to give pure copolymer **4**. GPC:  $M_n = 22.5$  kDa, PDI = 1.30 (THF, refractive index detector, PS standards calibration).

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33. Usually  $\Delta\theta$  can be measured by keeping the concentration of one component constant and increasing that of the other to very high values; then a plot of the chemical shift versus the inverse of the concentration of the variable component yields  $\Delta\theta$  as the zero intercept. See Tsukube, H.; Furita, H.; Odani, A.; Takeda, Y.; Kudo, Y.; Inoue, Y.; Liu, Y.; Sakamoto, H.; Kimura, K. in *Comprehensive Supramolecular Chemistry*, Atwood, J. L.; Davies, J. E. D.; MacNicol, D. D.; Vögtle, F.; exec. Eds., Pergamon, New York, vol. 8, ch. 10, pp. 425-482. However, in our systems in which both host and guest are polymeric, but contain only a single active site, there is a practical limit to how high the concentration can be before high viscosity broadens the peak too much to accurately measure the chemical shift change.
34. The concentrations of the crown ether and initiator **2** were both 21 mM. If the association constant,  $K_a$ , is greater than  $500\text{ M}^{-1}$ , complexation is essentially complete under these conditions. Note, however, the rates of homolysis and subsequent initiation of the pseudorotaxane will likely be different from those of free **2**.
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## Chapter 6

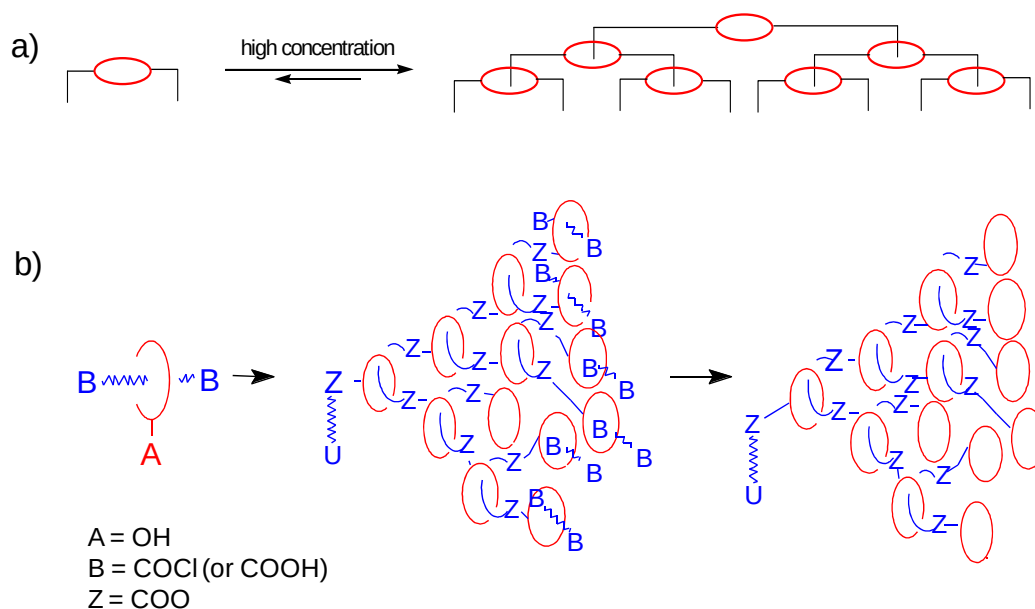
### Rotaxane-type Hyperbranched Polymers from a Homoditopic Crown Ether Host and a Monotopic Paraquat Guest Containing a Blocking Group

#### Abstract

Supramolecular rotaxane-type hyperbranched polymers were synthesized from A<sub>2</sub>B type semi-rotaxane monomers formed *in situ* via complexation of difunctional bis(m-phenylene)-32-crown-10 dimethanol and monofunctional paraquat carboxylic acid derivatives. In a proper solvent system at low temperature, the esterification was started by adding pyridine. Taco-type complexes were confirmed by proton NMR spectrometry in CD<sub>3</sub>CN/CHCl<sub>3</sub> mixture solvent, but disappeared in DMSO-*d*<sub>6</sub> by decomplexations. The fraction of paraquat units involved in taco complexes was 16 and 24% for two different hyperbranched polymers with different alkyl spacers in the paraquat monomers; the portion of taco complexes indicates the fraction of non-interlocked paraquat species in the hyperbranched polymers. NMR spectroscopy indicates the portion of rotaxanes strongly interlocked by the environment (inner rotaxanes); the polymer from the paraquat monomer with longer alkyl spacers may have a higher molecular weight because of its larger inner rotaxane portion. The molecular size increases of the hyperbranched polymers were also confirmed by size distribution analysis with dynamic light scattering and by viscometry with a solution of tetrabutylammonium hexafluorophosphate in tetrahydrofuran.

## Introduction

In polymer chemistry, supramolecular systems have been introduced to construct the same topologies as covalently bonded polymers by using the formation of pseudorotaxane and rotaxane linkages, which include mechanical bonds between macrocyclic hosts and rod-like guests. Supramolecular hyperbranched polymers have been tried by our group dating back to the 1990s; Huang et al. reported the first hyperbranched polymer by the preparation of a covalent paraquat-crown-paraquat AB<sub>2</sub> monomer and its self-assembly into a polymer (or an oligomer) in a high concentration solution.<sup>1</sup> Bhattacharjee prepared a mechanically interlocked hyperbranched polymer from a monofunctional bis(*m*-phenylene)-32-crown-10 (BMP32C10) alcohol and a paraquat diacid chloride derivative.<sup>2</sup> However, dethreading occurred during purification (an example of the dethreading is shown in the second step of Scheme 6-1b). Without any blocking groups or stoppers, dethreading from pseudorotaxanes can occur when the complexation is influenced by its environment, such as polar solvents (DMSO) or high temperatures.



**Scheme 6-1.** Schematic illustration of two previously synthesized hyperbranched polymers using self-assembly of crown ethers and paraquat derivatives: (a) a supramolecular hyperbranched polymer from a covalent AB<sub>2</sub> pseudorotaxane precursor containing a crown ether and two paraquat moieties, and (b) a mechanically interlocked rotaxane type of hyperbranched polymer from a monofunctional crown ether and a difunctional paraquat via *in situ* formation of an AB<sub>2</sub> monomer.

Here a different system, which does not allow the dethreading after interlocked structure formation because there is a blocking group in the paraquat monomer, was designed to achieve a high molecular weight supramolecular hyperbranched polymer as shown in Figure 6-1. The size of the blocking group is dependent on the size of the crown ether; the tris(*p-t*-butylphenyl)methane<sup>3</sup> moiety used in this study is capable of effectively preventing the dethreading of 25-42 membered macrocycles.<sup>4, 5</sup>

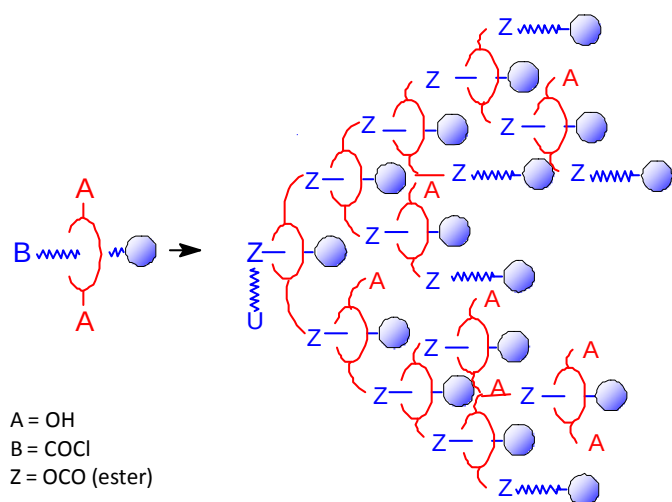
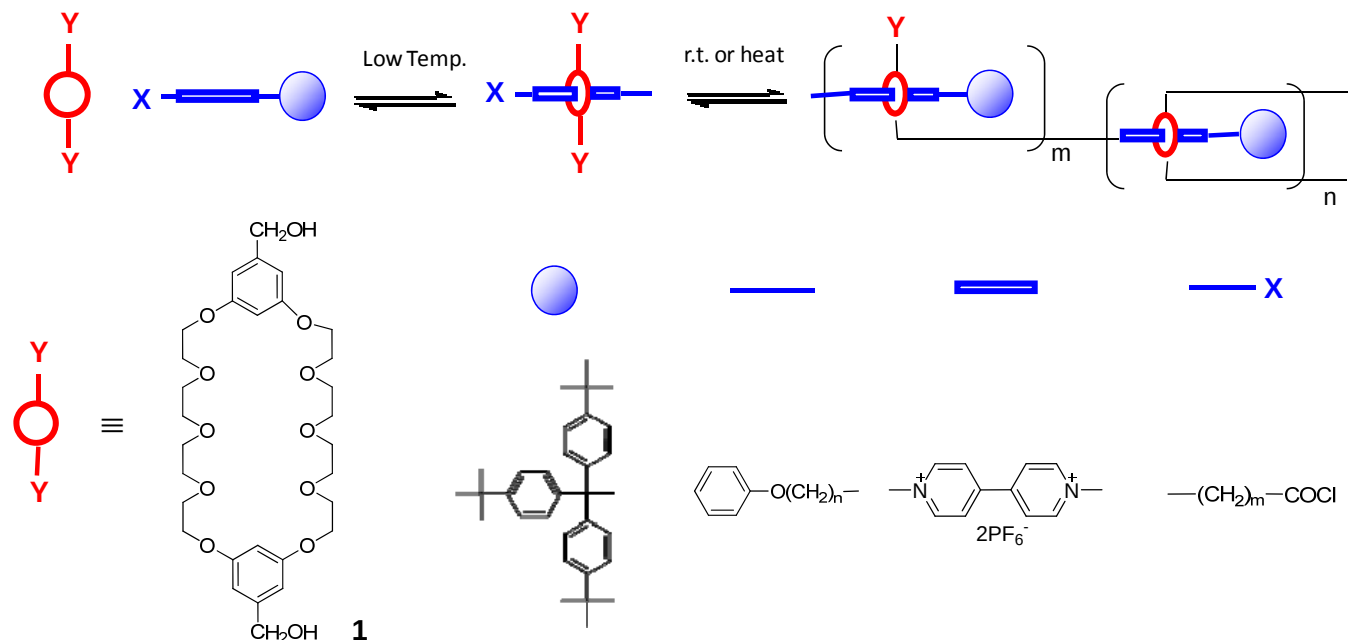


**Figure 6-1.** Schematic illustration of the formation of a mechanically interlocked hyperbranched polymer from an A<sub>2</sub>B semi-rotaxane precursor in this study.

## Results and Discussion

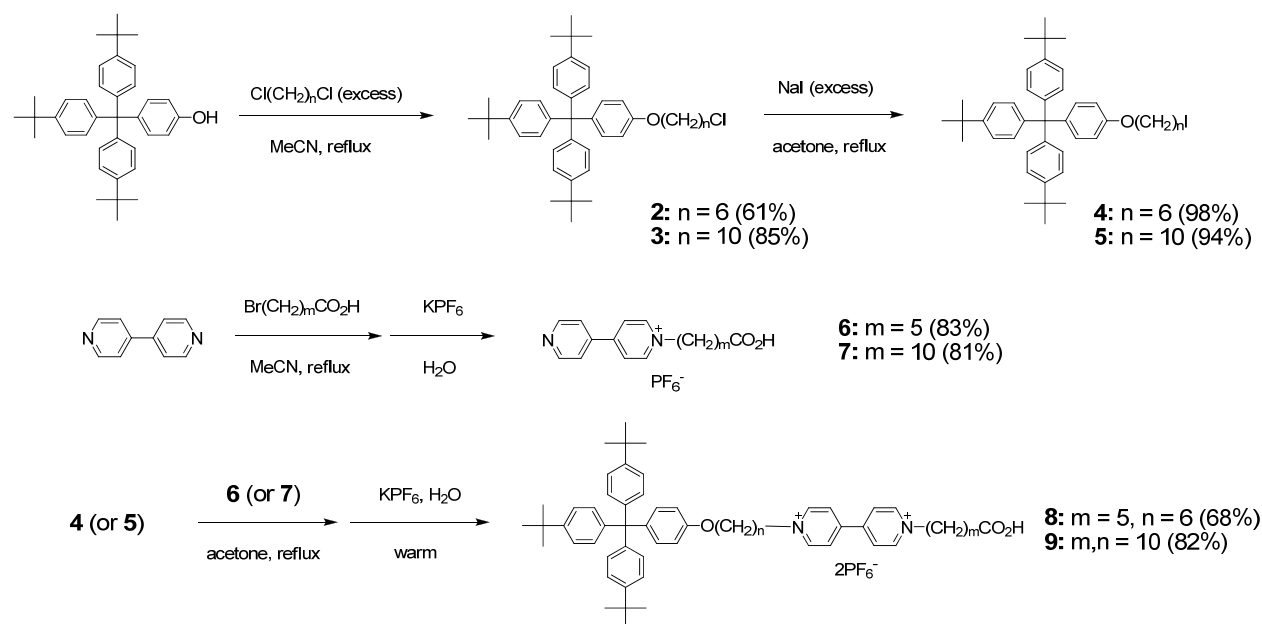
**Design and Synthesis of Monomers.** Our general synthetic strategies for preparation of mechanically interlocked hyperbranched polymers are shown in Figure 6-1. The main concept is the application of pseudorotaxane formation from functional cyclic and linear species to form a supramolecular monomer *in situ*. Tris(*p-t*-butylphenyl)methane was chosen as a blocking group<sup>3, 6</sup> for BMP32C10; it was placed on one end of the paraquat derivatives with different alkyl chain spacers. The blocking group prevents dethreading after the interlocked structure is constructed as shown in Scheme 6-2. The requirements for achieving high molecular weight products are 1) a high degree of association for formation of the threaded structure and 2) efficient polycondensation of the threaded monomer; related parameters are the association constant, the esterification temperature, and the reaction concentrations. The high degree of association is dependent on which host-guest system is used for the pseudorotaxane formation and is maximized by low temperature and high reaction concentration.



**Scheme 6-2.** Schematic illustration of mechanically interlocked hyperbranched polymers from a difunctional crown ether (**1**) and monofunctional paraquat derivatives ( $m = 5$ ,  $n = 6$  or  $m$ ,  $n = 10$ ).

The paraquat derivatives containing a blocking group were synthesized as shown in Scheme 6-2. To introduce the blocking group to the paraquat, tris(*p-t*-butylphenyl)methane derivatives<sup>3</sup> with various leaving groups (bromide, iodide and tosylate) were synthesized and then used in quaternization reactions with monosubstituted 4,4'-bipyridinium derivatives (**6** and **7**). However, only the quaternizations from alkyl iodide derivatives of tris(*p-t*-butylphenyl)methane were successful. To obtain the alkyl iodide compounds (**4** and **5**), the corresponding chloride compounds (**2** and **3**) were prepared from 4-[tris(*p-t*-butylphenyl)methyl]phenol<sup>3</sup> and excess 1, $\omega$ -dichloroalkanes with  $K_2CO_3$ . The excess dichloroalkanes were completely removed by washing with methanol. The blocking compounds **4** and **5** with terminal alkyl iodide moieties were obtained by the halide exchange reaction with an excess of NaI in acetone (the Finkelstein reaction) in high yield.

Monocarboxylalkyl 4,4'-bipyridinium salts (**6** and **7**) were prepared from excess 4,4-dipyridyl and 6-bromohexanoic acid (for **6**) or 11-bromoundecanoic acid (for **7**). The corresponding  $PF_6^-$  salts were obtained from the intermediate bromide salts by an anion exchange reaction with an aqueous  $KPF_6$  solution. The  $PF_6^-$  salts **6** and **7** were purified by a recrystallization in deionized water.

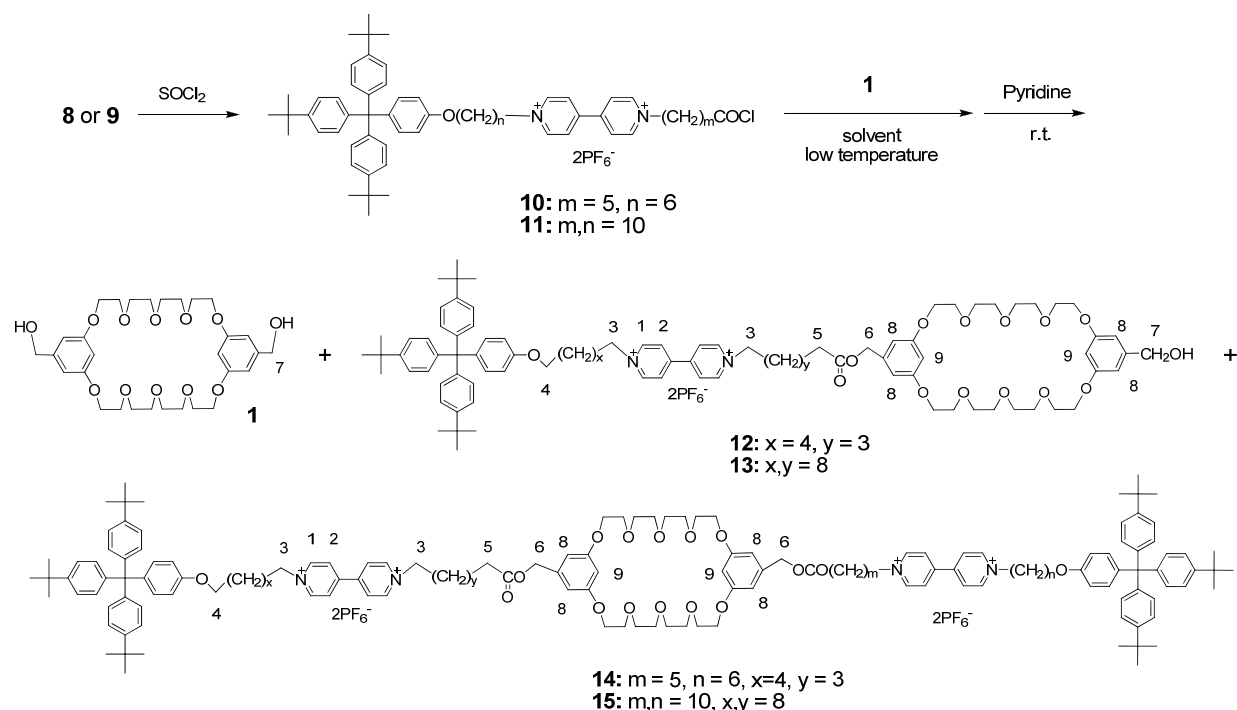


**Scheme 6-3.** Synthesis of paraquat carboxylic acid derivatives containing a blocking group as monofunctional guest monomers.

The second quaternization reactions of the paraquat derivatives (**6** or **7**) with the alkyl iodide compounds (**4** or **5**) were carried out over 2 weeks, until the reaction mixture turned deep orange (or dark purple). Even though the solubilities of **6** and **7** in MeCN were poor at the reflux temperature, the long reaction time (2 weeks) afforded the quaternized products (**8** and **9**) in good yield (>80%). The color of the reaction mixture changed to dark-orange (or purple), which implies the formation of the iodide salts that display a charge transfer band in the visible spectrum. After the reactions, the unreacted **6** (or **7**) was removed by washing with 1 M HCl. The anion exchange from iodide to  $\text{PF}_6^-$  was performed in an aqueous  $\text{KPF}_6$  solution. The  $\text{PF}_6^-$  salts were washed with boiling water to remove any residual salt. The iodide salts were dark-brown, the chloride salts were yellow, and the  $\text{PF}_6^-$  salts were pale yellow.

**Esterification for Hyperbranched Structure.** First, the chlorination of carboxylic acid **8** with  $\text{SOCl}_2$  was done to prepare the intermediate acid chloride (**10**). The formation of the carbonyl chloride was confirmed by the  $^1\text{H}$  NMR downfield chemical shift change of the methylene protons next to the carbonyl group. The esterification of BMP32C10 dimethanol (**1**) and the paraquat carbonyl chloride (**10**) was tried several times under various conditions: in different solvents and at different temperatures. Finally, the optimized solvent chosen for the esterification was benzonitrile/chloroform 1:1 (w/w) and the reaction was initiated at  $-15\text{ }^\circ\text{C}$  by

adding pyridine. The crown ether **1** was added to an equimolar solution of **10** in the mixed solvent (the solution must be clear!) and the temperature was lowered to -15 °C. The solution turned yellow-orange from the complexation of the two monomers. The esterification was performed for two weeks at room temperature. The hyperbranched polyester (**HP18**) product was purified by washing with ethyl ether to remove any unreacted crown ether **1** and several precipitations from DMSO into saturated aqueous KPF<sub>6</sub>.



**Scheme 6-4.** Esterifications of **1** and the paraquat carboxylic derivatives **8** (or **9**). Three basic covalent structures are possible after the esterifications: **1**, **12** and **14** (for **HP18**), and **1**, **13** and **15** (for **HP19**).

The esterification of **1** and **9** (for hyperbranched polyester **HP19**) was performed under same conditions except for the solvent. A mixed solvent MeCN/CHCl<sub>3</sub> (1:1 w:w) was used for reaction of these monomers, and the other reaction and work-up procedures were mostly the same as the esterification of **1** and **8**. The esterification products from the both reactions were orange-yellow solids. The mole ratio of the monomers was 1:1. Therefore, two basic covalently bonded structures of the hyperbranched polymers from the esterification are possible: **12**, **14** (for **HP18**) or **13**, **15** (for **HP19**), and possibly unreacted (only complexed) **1** as shown in Scheme 6-4.

**Characterizations of the Esterification Products.** Formation of **HP18** was clearly confirmed



by  $^1\text{H}$  NMR analysis as shown in Figure 6-2 (in  $\text{CD}_3\text{CN}/\text{CHCl}_3$  3:2 v/v). Two benzylic protons ( $\text{H}_6$  and  $\text{H}_7$ ) appeared in 1:1 integration ratio, which implies ~50% of the benzyl alcohol units reacted with the carbonyl chloride, as expected for quantitative conversion. In addition, there is no signal for the  $\text{CH}_2$  unit next to the carboxylic acid; in other words, the esterification reaction went almost quantitatively.

Crown-paraquat complexations were also confirmed by  $^1\text{H}$  NMR chemical shift changes as shown in Figure 6-2. For the paraquat protons, multiple peaks are observed after the reaction; each peak represents a paraquat unit in a different environment. For  $\text{H}_2$  protons, all the peaks shift upfield. The sharp doublet ( $\delta$  8.12) may be from taco-type BMP32C10-paraquat complexes,<sup>7-10</sup> because the sharp peak indicates a fast-exchange equilibrium between complexed and uncomplexed species. This equilibrium can occur from unthreaded crown units and non-interlocked paraquat units. The fraction of taco complexes from integration of the the sharp doublet at  $\delta$  8.12 vs. the total  $\text{H}_2$  proton signals is ~24% from. The other ~76% of paraquat units (broad peaks at  $\delta$  7.97 - 8.3) are attributable to interlocked rotaxane structures.

Figure 6-3 shows the intermediate semi-rotaxane (either taco or threaded structure) formations with different molar ratio solutions of monomers **1** and **8**. The  $\alpha$ -proton of bipyridinium ( $\text{H}_1$ ) peak of **8** did not shift as much as in the spectrum of **HP18**; however, the  $\beta$ -proton peak moved to higher field as more crown was added. The semi-rotaxane formation does not give any broad peaks; however, multiple broad peaks are exhibited by the hyperbranched polymers, not only the paraquat protons ( $\text{H}_1$  and  $\text{H}_2$ ), but also the benzylic ( $\text{H}_6$  and  $\text{H}_7$ ) and aromatic protons of the crown ether ( $\text{H}_8$  and  $\text{H}_9$ ). Therefore, the broad peaks of  $\text{H}_1$  and  $\text{H}_2$  of **HP18** are assigned to the interlocked rotaxane structures, because the peak positions of the broad  $\text{H}_2$  peak of **HP18** ( $\delta$  7.97, middle spectrum of Figure 6-2) and the  $\beta$ -proton peak with excess BMP32C10 (bottom spectrum of Figure 6-3) are almost the same.

All the crown units are incorporated in complexes in  $\text{CD}_3\text{CN}/\text{CDCl}_3$  solution, because all the aromatic protons of BMP32C10 ( $\text{H}_8$  and  $\text{H}_9$ ) shift upfield; the complexes resulted in multiple signals. The 1:2 integration ratio of signals at  $\delta$  5.41-5.80 and peaks at  $\delta$  6.04-6.14 indicates that these are due to  $\text{H}_9$  and  $\text{H}_8$ , respectively. For  $\text{H}_9$ , The broad peak at  $\delta$  5.84 may be from the interlocked rotaxanes and its fraction is ~75% of all  $\text{H}_9$ , which correspond to the paraquat protons  $\text{H}_2$  result. The peak at  $\delta$  5.46 is assigned to  $\text{H}_9$  of **12**, in which the two  $\text{H}_9$  protons are not equivalent and gives two doublets. The two peaks at  $\delta$  6.21 ( $\text{H}_8$ ) and  $\delta$  6.09 ( $\text{H}_9$ ) are assigned to

taco-type complexes because their chemical shift changes are smaller than other peaks. The fraction of taco-type complexes from these aromatic peaks is  $\sim 22\%$ , which corresponds well to the paraquat protons  $H_2$  result. The fast-exchange equilibrium between complexed and uncomplexed species gave small chemical shift changes of  $H_8$  and  $H_9$  of non-interlocked crown ethers. The aromatic rings inside the hyperbranched chains can not move quickly due to the interlocked structures and this results in broad peaks,  $\delta$  5.42, 5.84 and 6.13. This hypothesis is corroborated by the semirotaxane formation as shown in Figure 6-3. No broad peak was created from the monomer-monomer complexation (only semi-rotaxane or taco-type complex formation), which only gives simple chemical shift changes, and does cause the multiple signals observed in **HP18**. These evidences for the interlocked rotaxane structures give a direct indication for the formation of hyperbranched polyester **HP18**.

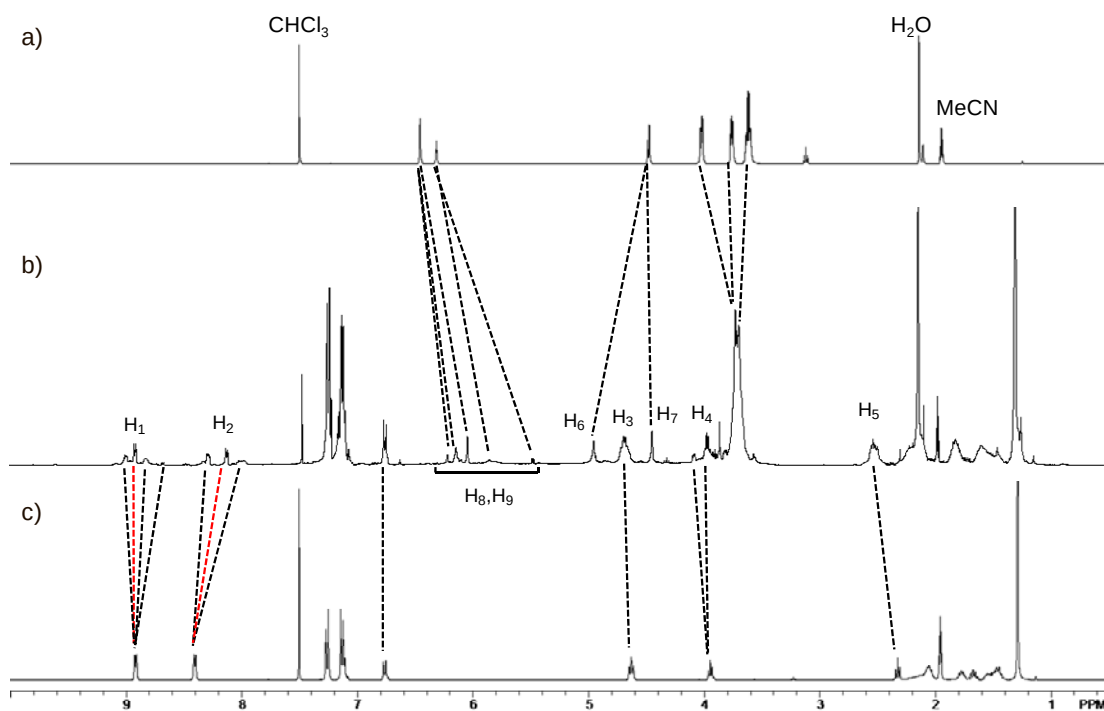


**Figure 6-2.**  $^1\text{H}$  NMR spectra of (a) **1**, (b) **HP18** formed from **1** and **8**, and (c) **8** in  $\text{CD}_3\text{CN}/\text{CDCl}_3$  3:2 (v:v) (400 MHz, 23  $^\circ\text{C}$ ).

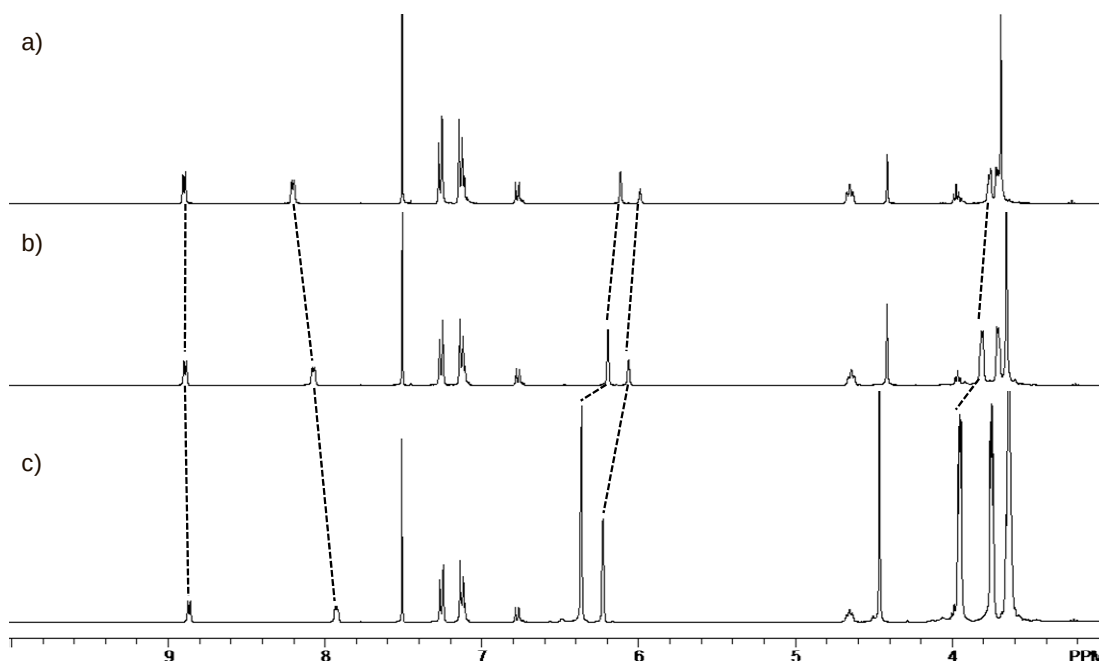


**Figure 6-3.**  $^1\text{H}$  NMR spectra of solutions of monomers **1** and **8** a) =1:2 molar ratio, b) 1:1 molar ratio, and c) large excess:1 molar ratio in  $\text{CD}_3\text{CN}/\text{CDCl}_3$  3:2 (v/v) (400 MHz, 23  $^\circ\text{C}$ ).

$^1\text{H}$  NMR spectra of **1**, **8** and **HP18** in  $\text{DMSO}-d_6$  are shown in Figure 6-4. Even though chemical shift changes in DMSO decreased for all of the protons on crown ether and paraquat units in the hyperbranched polyester, there are still some significant chemical shift changes. The remaining chemical shift changes give further direct evidence for the existence of the mechanically interlocked structure. The paraquat peaks observed at higher field in  $\text{CD}_3\text{CN}/\text{CDCl}_3$  (Figure 6-2b) still remain in  $\text{DMSO}-d_6$  (Figure 6-4b). The broad peaks at  $\delta$  7.97 ( $\text{H}_2$ ) and 8.83 ( $\text{H}_1$ ) (Figure 6-2b) appear at  $\delta$  8.57 in  $\text{DMSO}-d_6$ , even though integration numbers are smaller than the spectrum in  $\text{CD}_3\text{CN}/\text{CDCl}_3$ . These small remaining broad peaks are assigned to the inner rotaxanes as shown in Figure 6-5.

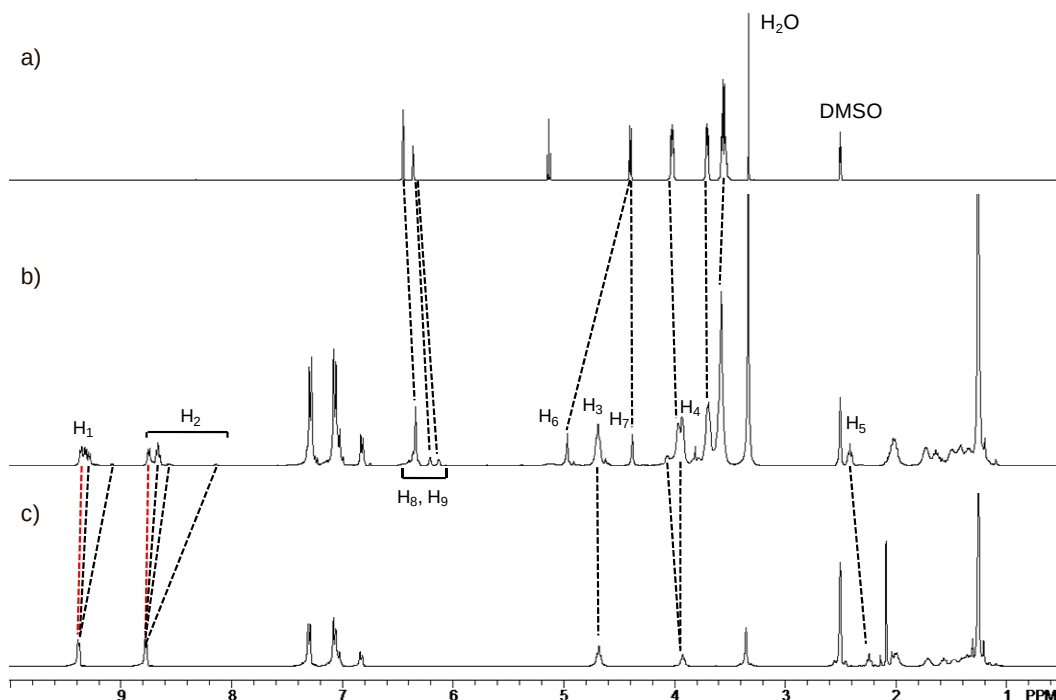


**Figure 6-4.**  $^1\text{H}$  NMR spectra of (a) **1**, (b) **HP18** formed from **1** and **8**, and (c) **8** in  $\text{DMSO-}d_6$  (400 MHz, 23  $^\circ\text{C}$ ).

The polar medium provided by DMSO prohibits the hydrogen bonding of the crown and paraquat units, and thus the crown ether units move from the paraquat sites to somewhere on the alkyl chains **12** or **14**. However, a fraction of crown ether units still strongly interact with paraquat units, and gave higher field signals at  $\delta$  9.08-9.32 ( $\text{H}_1$ ), and  $\delta$  8.14-8.67 ( $\text{H}_2$ ). The small high field signals at  $\delta$  9.08 ( $\text{H}_1$ ) and  $\delta$  8.14 ( $\text{H}_2$ ) are evidence of the existence of inner-rotaxanes in **HP18**; ~7% of rotaxane units are surrounded by other rotaxanes and blocking groups, and thus the crown ethers are tightly bound with paraquat units even in DMSO. For the aromatic protons of the crown ethers moieties, similar things are observed; the broad  $\text{H}_9$  peak ( $\delta$  5.8 in Figure 6-2b) disappears in  $\text{DMSO-}d_6$ . However, all the aromatic protons still shift upfield even in  $\text{DMSO-}d_6$ , which means a lot of crown ether molecules are threaded by the paraquat or alkyl chains of **12** or **14** and this is also a good evidence for the interlocked hyperbranched structure of **HP18**.

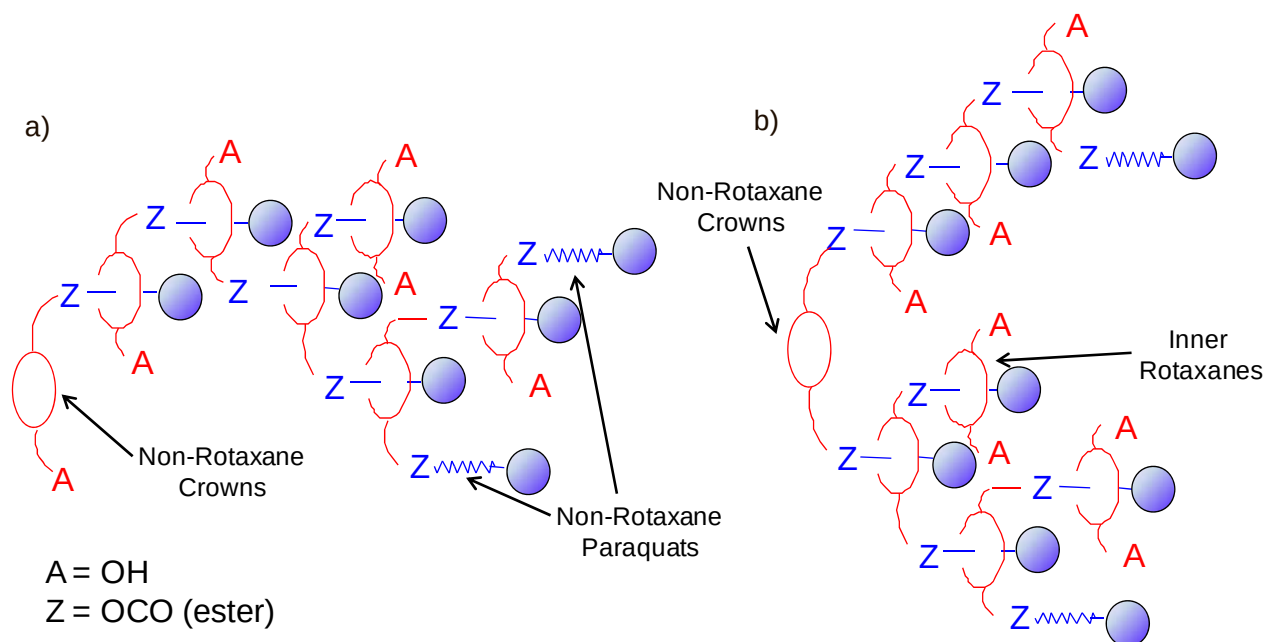


**Figure 6-5.** Two schematic diagrams of hyperbranched polymer. There are two types of non-rotaxane crowns in structure (a) and (b). Non-rotaxane paraquat units can form taco-type complexes with the non-rotaxane crowns of other molecules. The inner rotaxanes are surrounded by many bulky species, such as other rotaxanes and blocking groups and therefore crown ether movements are limited.

The NMR spectra of hyperbranched polyester **HP19** from **1** and **9** is more complicated as shown in Figure 6-6. Two benzylic protons ( $H_6$  and  $H_7$ ) appear in a 7:6 integration ratio. There is no signal for the  $CH_2$  moiety next to carboxylic acid; in other words, essentially all of the carbonyl chloride (**11**) reacted with **1** during the esterification.

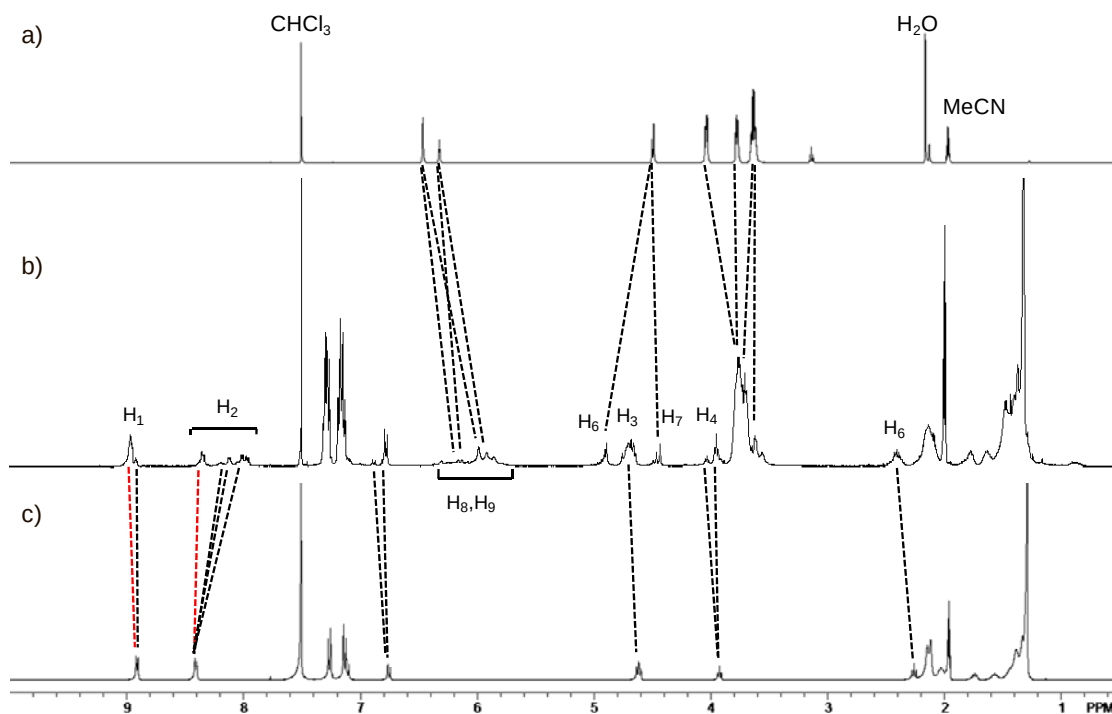


**Figure 6-6.**  $^1\text{H}$  NMR spectra of (a) **1**, (b) **HP19** formed from **1** and **9**, and (c) **9** in  $\text{CD}_3\text{CN}/\text{CDCl}_3$  3:2 (v:v) (400 MHz, 23  $^\circ\text{C}$ ).

Complexed structures in **HP19** in  $\text{CD}_3\text{CN}/\text{CDCl}_3$  were also confirmed as shown in Figure 6-6. From the integration of the doublet at  $\delta$  8.07, which is assigned to non-rotaxane paraquats (16%),  $\sim 84\%$  of paraquat units participate in the interlocked rotaxane structures in this solvent. The aromatic proton ( $\text{H}_8$  and  $\text{H}_9$ ) signals also show that almost all the crowns participate in complexation with paraquat units, because they all shift upfield. Most of the aromatic signals are broad and more upfield than  $\delta$  6.0, and more crown ethers may participate for the interlocked rotaxanes in **HP19** than in **HP18**. The signals over  $\delta$  6.09 are assigned to  $\text{H}_8$  and  $\text{H}_9$  of taco-type complexes; thus, the fraction of non-rotaxane crown ethers is calculated to be 15%, close to the  $\text{H}_2$  signals assignment result. The  $^1\text{H}$  NMR spectrum in  $\text{DMSO}-d_6$  reveals simpler signals for the paraquat protons  $\text{H}_2$  as shown in Figure 6-7. The signals at  $\delta$  9.16 ( $\text{H}_1$ ) and  $\delta$  8.48 are still in upfield in DMSO. These peaks are assigned to rotaxane units which are located in the inner part of the hyperbranched structure. The movements of the crown ether units of these inner rotaxanes are limited by their environment, such as other rotaxane units and the blocking groups. The relative integration numbers of these inner rotaxane paraquats of **HP19** ( $\sim 16\%$ ) is larger than those of **HP18** ( $\sim 7\%$ ), which means the molecular weight of **HP19** may be higher compared to

**HP18**, or alternatively that it is more highly branched. The multiple aromatic signals ( $H_8$  and  $H_9$ ) even in DMSO (Figure 6-7) indicate that a lot of crown ether units formed threaded structures in which the cyclic species are located on the alkyl-paraquat chains of **13** or **15** in hyperbranched polymer **HP19**.

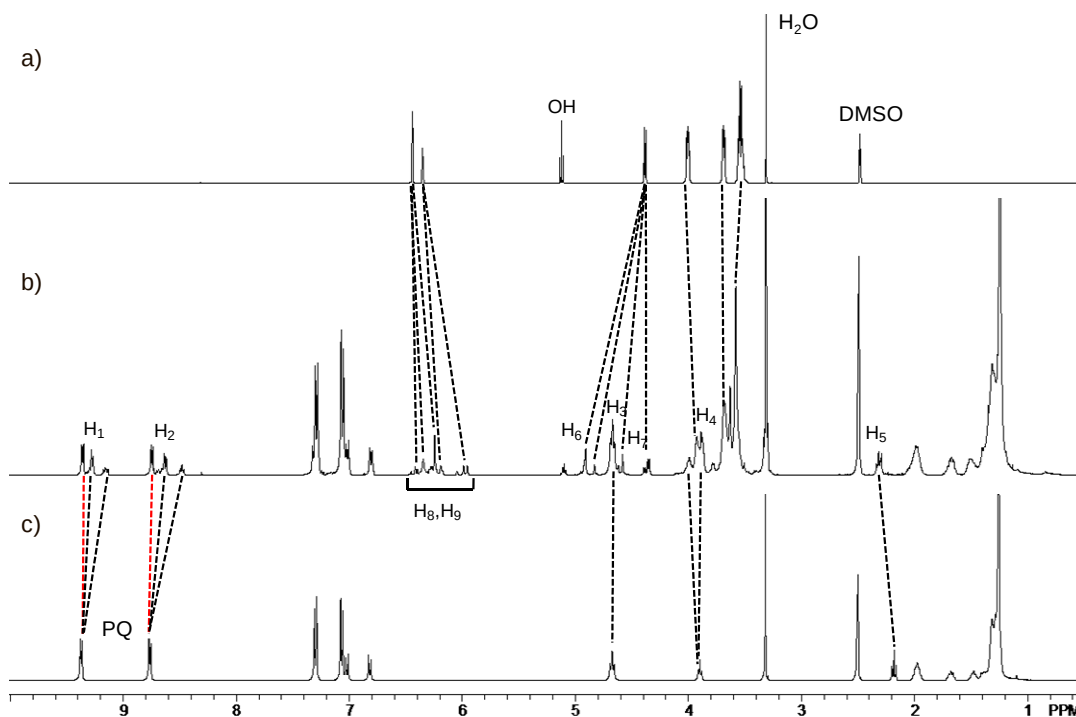


**Figure 6-7.**  $^1\text{H}$  NMR spectra of (a) **1**, (b) **HP19** from **1** and **9**, and (c) **9** in  $\text{DMSO-}d_6$  (400 MHz, 23 °C).

The benzylic peaks ( $H_6$  and  $H_7$ ) are also informative. Compared to the spectrum of **HP18**, the benzylic protons of **HP19** appear as multiple signals after the esterification. In Figure 6-7, the 1:2 integration ratio of two doublets ( $\delta$  4.35 and 4.39) shows the peaks are assigned to  $H_6$  of **1** and **13** (Scheme 6-4). The three singlets for  $H_7$  ( $\delta$  4.59, 4.63 and 4.84) are observed even in DMSO and the crown ethers may be positioned either at paraquat sites or on alkyl chains of **13** and **15**. These multiple peaks for  $H_6$  and  $H_7$  correspond to the multiple peaks for  $H_8$  even in DMSO.

In summary of the  $^1\text{H}$  NMR study, taco-type complexes were confirmed by  $H_2$  proton signals of **HP18** and **HP19**. The ratio of taco complexes is directly related to the fraction of non-rotaxane paraquat units in the hyperbranched polymers; ~24% in **HP18** and ~16% of **HP19**. However, more non-rotaxane paraquat species does not necessarily mean lower molecular

weight of the polymers; it may simply indicate a lower degree of branching. The non-rotaxane paraquat species can interact with free crowns in less polar media, but decomplexation occurs in DMSO. The simple peaks of H<sub>6</sub>, H<sub>7</sub>, H<sub>8</sub> and H<sub>9</sub> of **HP18** show that the positions of crown ether rings are limited by the short spacer alkyl chains of **12** and **14**. However, the multiple peaks of H<sub>6</sub>, H<sub>7</sub>, H<sub>8</sub> and H<sub>9</sub> of **HP18** imply the crown ether can be placed in multiple sites of the longer spacer chains of **13** and **15**.

Viscous flow is characteristic of polymer solutions. Therefore we turned to viscometry (Figure 6-8) for direct physical evidence for the formation of the mechanically interlocked hyperbranched polymers. The non-linear reduced viscosity plot of the hyperbranched polyester from **1** and **8** in THF has the typical features of traditional covalent polyelectrolytes.<sup>11</sup> In order to obtain the intrinsic viscosity, a THF solution of 0.0500 M tetrabutylammonium hexafluorophosphate was used as the solvent to screen the charges in the polymer. The intrinsic viscosity of the hyperbranched polyester was 0.054 g dL<sup>-1</sup>.<sup>12</sup> This low intrinsic viscosity value can be at least partly ascribed to the globular shape of this hyperbranched polymer,<sup>13, 14</sup> and added salt.<sup>11</sup>

The molecular weight increase of the hyperbranched polyester products was confirmed by dynamic light scattering (DLS) particle size distribution analysis of the monomer **9** and the two polyester products (Figure 6-9). To minimize aggregation, a solution of 0.020 M tetrabutylammonium hexafluorophosphate in acetonitrile was used as the solvent. The average diameter of the hyperbranched polyester from **1** and **8** is 2.3 nm and that of the polyester from **1** and **9** is 2.6 nm.<sup>15</sup> The hyperbranched polyester from longer chain monomer **9** has somewhat larger average diameter than the polyester from shorter chain monomer **8**. The hyperbranched polyester from longer chain monomer **9** may have higher molecular weight than the polyester from shorter chain monomer **8** based on this DLS size distribution result. The increased molecular sizes can be only explained by mechanically interlocked hyperbranched structures from rotaxane formation during the esterification. Quantitative molecular weight determination is still a challenge and mass spectrometry (e.g., MALDI-TOF, ESI-TOF and etc.) is another possible method to demonstrate polymer formation.



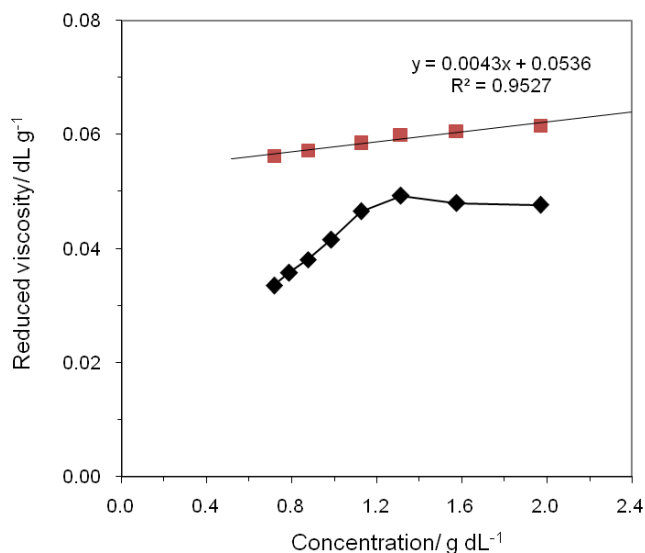


**Figure 6-8.** Reduced viscosity of the hyperbranched polyester from **1** and **8** (**HP18**) as a function of concentration for solutions in THF (diamonds) and a THF solution of 0.0500 M tetrabutylammonium hexafluorophosphate (red squares) at 26 °C.

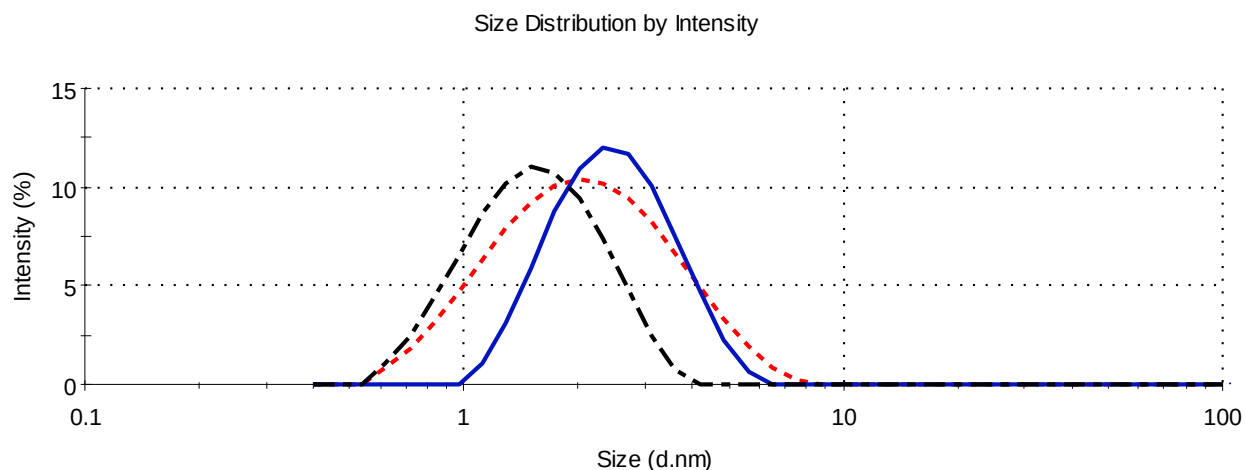


**Figure 6-9.** Size distribution traces of **9** (long-short dash), **HP18** (red dash) and **HP19** (blue solid) by dynamic light scattering analysis. (0.020 M tetrabutylammonium hexafluorophosphate in acetonitrile, 20 °C)

The DSC traces of the esterification products **HP18** and **HP19** are shown in Figure 6-10. **HP18** has an endothermic transition at 53.7 °C, presumably a melting transition, which is reversible upon cooling. **HP19** decomposed >255 °C under nitrogen, but the DSC trace does not show any transition from 0 °C to 180 °C. For reference, the melting points of **8** and **9** are over 200 °C and that of **1** is ~100 °C.

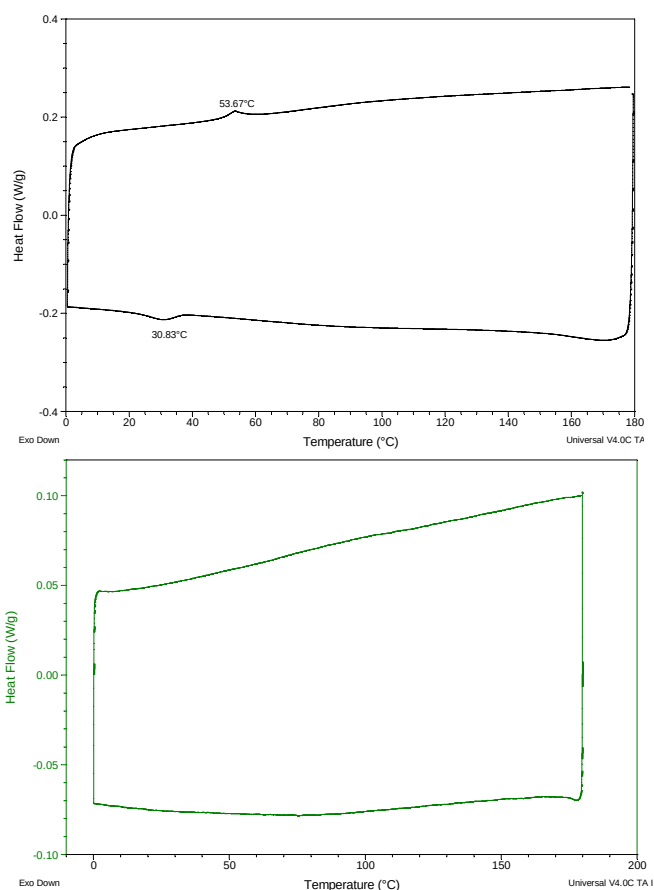


**Figure 6-10.** DSC traces for the esterification products from a) **HP18** (left, short spacer) and b) **HP19** (right) with heating and cooling rate 5 K/min under N<sub>2</sub>.

## Conclusions

Two supramolecular rotaxane-type hyperbranched polymers were synthesized by the esterification of A<sub>2</sub>B type semi-rotaxane monomers formed *in situ* via complexation of difunctional BMP32C10 dimethanol (**1**) and monofunctional paraquat acid **8** (for **HP18**) or **9** (for **HP19**). In a proper solvent system at low temperature, the esterification was started by adding pyridine. The esterification reactions were confirmed by the 1:1 ratio of benzylic protons in <sup>1</sup>H NMR spectra, one for ester units and one for unreacted alcohol moieties. In CD<sub>3</sub>CN/CDCl<sub>3</sub>, taco-type complexes were detected in <sup>1</sup>H NMR spectra, but disappeared in DMSO-*d*<sub>6</sub>. The fraction of paraquat units involved in taco complexes was 24% for **H18** and 16% for **HP19**; the portion of taco complexes indicates the fraction of non-interlocked paraquat species in the hyperbranched polymers. Some upfield NMR signals indicate the portion of rotaxanes strongly interlocked by

the environment (inner rotaxanes); the higher inner rotaxane portion in **HP19** (16%) may indicate a higher molecular weight of **HP19** compared to **HP18**. Size distribution analysis by dynamic light scattering gave molecular size increases for the hyperbranched polyesters. The average size of particles of **HP19** is larger than **HP18** and this result corresponds to the NMR experiment about the inner rotaxane portion of the hyperbranched polymers. Viscometry also gave evidence of the formation of hyperbranched structures. The intrinsic viscosity of **HP18** was measured in a solution of tetrabutylammonium hexafluorophosphate in THF. **HP18** behaves as a polyelectrolyte in THF without salt. The hyperbranched polymer **HP18** undergoes a reversible endothermic transition, presumably melting, at 54 °C as determined by DSC; however, **HP19** does not have any transitions by DSC from 0 °C to 180 °C. Both the products decomposed above 230 °C.

Well-defined molecular design and synthesis in supramolecular complexations have a lot of potential to realize polymers in supramolecular ways. The formations of supramolecular semi-rotaxanes and pseudorotaxanes are a promising research area to achieve a wide range of polymer topologies via supramolecular methods: not only hyperbranched structures as in this study, but also linear, comb-like branched and globular structures.

## Experimental

**Materials.** All solvents were HPLC or GC grade. Benzonitrile was pre-dried over  $\text{CaCl}_2$  and then distilled from  $\text{P}_2\text{O}_5$  under reduced pressure. Chloroform was pre-dried over  $\text{CaCl}_2$  and then distilled with  $\text{P}_2\text{O}_5$ . Acetonitrile was pre-dried over  $\text{K}_2\text{CO}_3$  and then distilled. NMR solvents were bought from Cambridge Isotope Laboratories and used as received. All other chemicals and solvents were used as received.

**Instruments.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained on Varian Inova 400 MHz and Unity 400 MHz spectrometers. High resolution electrospray ionization time-of-flight mass spectrometry (HR ESI TOF MS) was carried out on an Agilent 6220 Accurate Mass TOF LC/MS Spectrometer in positive ion mode. Reduced viscosity was measured in a Cannon-Ubbelohde semi-micro type viscometer (size 50). DLS size distribution analysis was carried out on a Malvern Nano ZS Zetasizer. DSC results were obtained on a TA Instrument Q2000 differential scanning calorimeter at a scan rate of 5 or 10 °C/min heating under  $\text{N}_2$  purge. TGA results were obtained on a TA Instrument Q500 Thermogravimetric Analyzer at a heating rate of 10 °C/min under  $\text{N}_2$ .

purge. Melting points were observed on a Büchi B-540 apparatus at a 2 °C/min heating rate.

**1-Chloro-6-{4'-[tris(*p*-*t*-butylphenyl)methyl]phenoxy}hexane (2).** A mixture of 4-[tris(*p*-*t*-butylphenyl)methyl]phenol<sup>3</sup> (7.97 g, 15.8 mmol) and K<sub>2</sub>CO<sub>3</sub> (6.55 g, 47.4 mmol) in 180 mL of MeCN was refluxed for 2 h. Then 1,6-dichlorohexane (12.24 g, 78.9 mmol) in MeCN (20 mL) was added at once to the reaction mixture. After 2 days at reflux, the solvent was removed by a rotoevaporator. The residue was treated with chloroform/water and then extracted with chloroform (300 mL) 3 times. After drying the combined organic layer with anhydrous Na<sub>2</sub>SO<sub>4</sub>, the drying agent was removed by filtration and the solution was concentrated to 5 mL. The solution was slowly added to MeOH (70 mL) with vigorous stirring. The insoluble product was filtered and washed with MeOH 5 times. Drying in a vacuum oven gave a colorless solid (6.01 g, 61.1%), mp 211.2 ~ 213.0 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 22 °C): δ 1.30 (s, 27H), 1.50 (t, *J* = 4, 4H), 1.80 (m, 4H), 3.55 (t, *J* = 7, 2H), 3.93 (t, *J* = 7, 2H), 6.75 (d, *J* = 8, 2H), 7.09 (m, 8H), 7.22 (d, *J* = 8, 6H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, 22 °C): δ 25.5, 26.7, 29.2, 31.4, 32.5, 34.3, 45.0, 63.0, 67.5, 112.9, 124.0, 130.2, 132.2, 139.4, 144.2, 148.26, 148.28, 156.8. HRMS (ESI): *m/z* 622.3978 ([M<sup>+</sup>+H]), calcd for C<sub>43</sub>H<sub>55</sub>ClO 622.3941, error 5.9 ppm).

**1-Chloro-10-{4'-[tris(*p*-*t*-butylphenyl)methyl]phenoxy}decane (3).**

A mixture of 4-[tris(*p*-*t*-butylphenyl)methyl]phenol (0.891 g, 1.76 mmol) and K<sub>2</sub>CO<sub>3</sub> (0.73 g, 5.3 mmol) in MeCN (15 mL) was refluxed for 2 h. Then 1,10-dichlorodecane (3.73 g, 17.6 mmol) in MeCN (5 mL) was added all at once to the reaction mixture. The mixture was refluxed for 4 days and the solvent was removed by a rotoevaporator. The residue was extracted with chloroform/water 3 times. After drying the combined organic layer over anhydrous Na<sub>2</sub>SO<sub>4</sub>, the drying agent was removed by filtration and the solution was concentrated to 5 mL. The solution was slowly added to MeOH (70 mL) with vigorous stirring. The insoluble product was filtered and then washed with MeOH 5 times. Drying in a vacuum oven gave a colorless solid **3** (1.04 g, 85%), mp 176.6 – 178.3 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 23 °C): δ 1.30 (s, 27H), 1.44 (m, 12H), 1.77 (m, 4H), 3.55 (t, *J* = 7, 2H), 3.93 (t, *J* = 7, 2H), 6.75 (d, *J* = 8, 2H), 7.08 (m, 8H), 7.22 (d, *J* = 8, 6H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, 23 °C): δ 26.1, 26.9, 28.9, 29.36, 29.39, 29.5, 31.4, 32.6, 34.3, 45.2, 63.0, 67.8, 112.9, 124.0, 130.7, 132.2, 139.4, 144.2, 148.3, 156.9. HRMS (ESI): *m/z* 678.4555 ([M<sup>+</sup>+H]), calcd for C<sub>47</sub>H<sub>63</sub>ClO 678.4567, error 1.8 ppm).

**1-Iodo 6-{4'-[Tris(*p*-*t*-butylphenyl)methyl]phenoxy}hexane (4).** A mixture of **7** (5.00 g, 8.02 mmol) and sodium iodide (12.0 g, 80.2 mmol) in dry acetone (100 mL) was refluxed for 1 day.

After removing the solvent by a rotoevaporator, the residue was partitioned in water (15 mL) and chloroform (200 mL). After collecting the chloroform layer, the aqueous phase was extracted with chloroform 3 times. After drying the combined organic layer over anhydrous Na<sub>2</sub>SO<sub>4</sub>, the drying agent was removed by filtration and the solvent was removed by a rotoevaporator. Drying the residue in a vacuum oven gave a yellow solid **4** (5.64 g, 98.4%), mp 195.2 ~ 201.0 °C (dec). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 22 °C): δ 1.30 (s, 27H), 1.48 (m, 4H), 1.81 (m, *J* = 7, 6.8 Hz, 4H), 3.20 (t, *J* = 7, 2H), 3.93 (t, *J* = 7, 2H), 6.75 (d, *J* = 7, 2H), 7.08 (m, 8H), 7.22 (d, *J* = 8, 6H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, 22 °C): δ 25.5, 29.5, 30.6, 31.5, 31.7, 33.7, 34.6, 63.4, 67.9, 113.3, 124.4, 131.1, 132.6, 139.8, 144.5, 148.6, 157.2. HRMS (ESI): *m/z* 714.3282 ([M<sup>+</sup>+H]), calcd for C<sub>43</sub>H<sub>55</sub>IO 714.3298, error 2.2 ppm).

**1-Iodo-10-{4'-[Tris(*p*-*t*-butylphenyl)methyl]phenoxy}decane (5).** A mixture of **1** (0.991 g, 1.43 mmol) and sodium iodide (2.15 g, 14.5 mmol) in dry acetone (20 mL) was refluxed for 3 days. After removing the solvent from the reaction mixture by a rotoevaporator, the residue was dispersed in water (10 mL). The aqueous phase was extracted with chloroform 3 times. After drying the combined organic layer over anhydrous Na<sub>2</sub>SO<sub>4</sub>, the drying agent was removed by filtration and the solvent was removed by a rotoevaporator. The residue was collected and dried in a vacuum oven to afford yellow solid **5** (1.033 g, 94%), mp 159.6 – 161.9 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 23 °C): δ 1.30-1.48 (m, 39H), 1.74-1.83 (m, 4H), 3.18 (t, *J* = 7, 2H), 3.92 (t, *J* = 7, 2H), 6.75 (d, *J* = 8, 2H), 7.07 (m, 8H), 7.22 (d, *J* = 8, 6H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, 23 °C): δ 7.3, 26.1, 28.5, 29.3, 29.4, 29.5, 30.4, 31.4, 33.6, 34.3, 63.0, 67.8, 112.9, 124.0, 130.7, 132.2, 139.3, 144.2, 148.3, 156.9. HRMS (ESI): *m/z* 770.3911 ([M<sup>+</sup>+H]), calcd for C<sub>47</sub>H<sub>63</sub>IO 770.3924, error 1.7 ppm).

**N-(5-Carboxypentyl)-4,4'-bipyridinium hexafluorophosphate (6).** A solution of 4,4'-dipyridyl (9.38 g, 60 mmol) and 6-bromohexanoic acid (1.95 g, 10 mmol) in MeCN (30 mL) was refluxed for 2 days. The precipitate was filtered after cooling and washed with MeCN three times. The bromide salt was dissolved in deionized water (30 mL), and KPF<sub>6</sub> (2.76 g, 15 mmol) was added. The precipitate was filtered and washed with deionized water twice. Drying in a vacuum oven gave an off-white crystalline solid **6** (3.45 g, 83% yield), mp 143.3-144.6 °C (dec). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, 23 °C): δ 1.33 (m, 2H), 1.56 (m, 2H), 1.97 (m, 2H), 2.24 (t, *J* = 7, 2H), 4.63 (t, *J* = 7, 2H), 8.05 (d, *J* = 7, 4H), 8.64 (d, *J* = 7, 2H), 8.89 (s, 2H), 9.23 (d, *J* = 7, 2H), 12.07 (br, 1H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>, 23 °C): δ 23.8, 24.9, 30.4, 33.3, 60.3, 122.0, 125.4,

140.9, 145.3, 151.0, 152.3, 174.4. HRMS (ESI):  $m/z$  271.1454 ( $[M - PF_6]^+$ , calcd for  $C_{16}H_{19}N_2O_2$  271.1441, error 2.9 ppm).

**N-(10-carboxydecyl)-4,4'-bipyridinium hexafluorophosphate (7).** A solution of 4,4'-bipyridyl (6.25 g, 40 mmol) and 11-bromoundecanoic acid (1.33 g, 5 mmol) in MeCN (20 mL) was refluxed for 2 days. After removing the solvent by a rotoevaporator, the residual bromide salt was treated with boiling THF to remove the excess 4,4'-bipyridyl. The filter cake was dispersed in deionized water (60 mL) and  $KPF_6$  (1.84 g, 10 mmol) was added with vigorous stirring. The mixture was stirred for 24 h at 60 °C and then the product was filtered with water washing. Recrystallization in deionized water gave a colorless crystalline solid (2.09 g, 81%), mp 156.0-157.4 °C.  $^1H$  NMR (400 MHz,  $CD_3CN$ , 23 °C):  $\delta$  1.24-1.35 (m, 12H), 1.55 (m, 2H), 1.99 (m, 2H), 2.26 (t,  $J = 7$ , 2H), 4.54 (t,  $J = 7$ , 2H), 7.79 (d,  $J = 7$ , 2H), 8.31 (d,  $J = 7$ , 2H), 8.76 (d,  $J = 7$ , 2H), 8.84 (dd,  $J = 7$ ,  $J = 2$ , 2H).  $^{13}C$ -NMR (100 MHz,  $CD_3CN$ , 23 °C):  $\delta$  25.6, 26.5, 29.5, 29.7, 29.9, 30.0, 31.8, 34.2, 62.5, 67.8, 122.9, 127.0, 142.4, 145.9, 152.1, 155.0, 175.4. HRMS (ESI):  $m/z$  341.2229 ( $[M-PF_6]^+$ , calcd for  $C_{21}H_{29}N_2O_2$  341.2229, error 0 ppm).

**N-(5-Carboxypentyl)-N'-(6'-{*p*-[tris(*p*-*t*-butylphenyl)methyl]phenoxy}-1-hexyl)-4,4'-bipyridinium bis(hexafluorophosphate) (8).** A mixture of **4** (1.406 g, 1.97 mmol) and **6** (1.638 g, 1.60 mmol) in MeCN (10 mL) was refluxed for 2 weeks. After removing the solvent, ethyl ether (50 mL) was added to precipitate the product. The dark-brown solid was filtered and washed with ethyl ether 4 times. The filtered solid was dispersed in 1 M HCl solution (30 mL) and then stirred for 6 h (the solid became yellow). After filtration and washing with deionized water several times, the filtered solid was dispersed in sat- $KPF_6$  solution (10 mL) with stirring overnight. The yellow precipitate was filtered and washed with plenty of water. Drying in a vacuum oven gave a pale-yellow solid (1.539 g, 68%), mp 257.9 – 261.0 °C (dec).  $^1H$  NMR (400 MHz,  $DMSO-d_6$ , 23 °C):  $\delta$  1.25-1.47 (m, 39H), 1.71 (m, 4H), 2.24 (t,  $J = 7$ , 2H), 3.92 (t,  $J = 8$ , 2H), 4.68 (t,  $J = 7$ , 4H), 6.82 (d,  $J = 7$ , 2H), 7.06 (m, 8H), 7.30 (d,  $J = 7$ , 6H), 8.77 (d,  $J = 5$ , 4H), 9.38 (d,  $J = 5$ , 2H), 12.07 (s(br), 1H).  $^{13}C$ -NMR (100 MHz,  $DMSO-d_6$ , 23 °C):  $\delta$  23.7, 24.8, 25.0, 25.1, 28.4, 30.3, 30.6, 31.0, 33.2, 33.9, 60.6, 60.7, 62.4, 66.9, 75.8, 113.2, 124.2, 126.5, 129.9, 131.3, 138.7, 143.9, 145.7, 147.6, 148.5, 156.2, 174.2. HRMS (FAB, NBA):  $m/z$  1003.5341 ( $[M-PF_6]^+$ , calcd for  $C_{59}H_{74}N_2O_3PF_6$  1003.5336, error 0.5 ppm).

**N-(10-Carboxydecyl)-N'-(10'-{*p*-[tris(*p*-*t*-butylphenyl)methyl]phenoxy}-1-decyl)-4,4'-bipyridinium bis(hexafluorophosphate) (9).** A mixture of **5** (1.009 g, 1.31 mmol) and **7** (0.780

g, 1.60 mmol) in MeCN (10 mL) was refluxed for 2 weeks. After removing the solvent, ethyl ether (50 mL) was added to precipitate the product. The dark-brown solid was filtered and washed with ethyl ether 4 times. The solid was dispersed in 1 M HCl solution (30 mL) for 6 h and then stirred for 6 h (the solid became yellow). After filtration and washing with deionized water several times, the filter cake was dispersed in sat-KPF<sub>6</sub> solution (10 mL) with stirring overnight. The ion-exchanged product was filtered and then washed with plenty of water. Drying in a vacuum oven gave a pale-yellow solid (1.375 g, 82%), mp 253.7-256.6 °C (dec). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN/CDCl<sub>3</sub> = 2:3 (v/v), 23 °C): δ 1.29-1.38 (m, 51H), 1.45 (m, 2H), 1.74 (m, 2H), 2.03 (t, *J* = 7, 2H), 2.26 (t, *J* = 8, 4H), 3.92 (t, *J* = 8, 2H), 4.62 (t, *J* = 7, 4H), 6.75 (d, *J* = 9, 2H), 7.06 (m, 8H), 7.26 (d, *J* = 9, 6H), 8.41 (d, *J* = 6, 4H), 8.91 (d, *J* = 6, 2H). <sup>13</sup>C-NMR (100 MHz, CD<sub>3</sub>CN/CDCl<sub>3</sub> = 2:3 (v/v), 23 °C): δ 25.2, 26.2, 26.3, 26.5, 29.2, 29.3, 29.5, 29.6, 29.66, 29.72, 29.76, 29.82, 31.4, 31.6, 31.7, 33.9, 34.6, 62.8, 63.5, 68.3, 78.6, 113.7, 124.8, 127.8, 130.1, 132.3, 139.9, 145.0, 146.1, 148.8, 150.3, 157.5, 174.9. HRMS (ESI): *m/z* 1129.6699 ([M-PF<sub>6</sub>]<sup>+</sup>, calcd for C<sub>68</sub>H<sub>92</sub>N<sub>2</sub>O<sub>3</sub> 1129.6750, error 5 ppm).

**Polyesterification of 1 and 8 (for repeating units 12 and 14).** A solution of 8 (0.575 g, 0.50 mmol) in SOCl<sub>2</sub> (4 mL) was stirred for 24 hour under N<sub>2</sub> atmosphere at room temperature. After removing the excess SOCl<sub>2</sub> by vacuum, dry *n*-hexane (5 mL) was added to get rid of the residual SOCl<sub>2</sub>. After completely removing the solvent by a N<sub>2</sub> stream, dry benzonitrile (1.5 mL) was added to dissolve the acid chloride 10. Using an ice-salt (NaCl) bath, the reaction temperature was lowered to -15 °C and then a solution of 1 (0.298 g, 0.50 mmol) in chloroform (1.5 mL) was added to the reaction solution. The reaction mixture was stirred for 4 h at -15 ~ -10 °C. Into the reaction solution, dry pyridine (0.40 g, 0.50 mmol) was added at -15 °C and then the ice bath was removed to raise the temperature to room temp. The reaction mixture was stirred for 2 weeks. After the solvent was removed by a rotoevaporator, ethyl ether (15 mL) was added. The precipitate was filtered and dissolved DMSO (1~2 mL). The DMSO solution was slowly added into sat-KPF<sub>6</sub> solution with vigorous stirring and the insoluble product was filtered. This reprecipitation was performed two times more. The product was washed with deionized water (several times) and ethyl ether (3 times). Drying in a vacuum oven at 70 °C gave a dark-yellow solid (0.0128 g, 82%), mp = 254.5 – 258.6 °C (dec). DSC (0 ~ 180 °C, heating rate 5 K/min, N<sub>2</sub>): unknown transition at 53.7 °C (endothermic).

**Polyesterification of 1 and 9 (for repeating units 13 and 15).** A solution of 9 (0.107 g, 0.084

mmol) in thionyl chloride (5 mL) was stirred for 24 h under N<sub>2</sub> atmosphere at room temperature. After removing the excess thionyl chloride by vacuum, dry *n*-hexane (5 mL) was added to get rid of the residual thionyl chloride. After completely removing the solvent by a N<sub>2</sub> stream, dry MeCN (1.5 mL) were added to dissolve the acid chloride **11**. Using an ice-salt (NaCl) bath, the reaction temperature was lowered to -15 °C and **1** (0.050 g, 0.084 mmol) in chloroform (1.5 mL) was added. The reaction mixture was stirred for 4 h at -15 ~ -10 °C. Into the reaction solution, dry pyridine (0.0066 mg, 0.085 mmol) was added at -15 °C and then the ice bath was removed to raise the temperature to room temp. The reaction mixture was stirred for 2 weeks. After the solvent was removed by a rotoevaporator, ethyl ether (15 mL) was added. The precipitate was filtered and dissolved DMSO (1~2 mL). The DMSO solution was slowly added into sat-KPF<sub>6</sub> solution with vigorous stirring and then insoluble product was filtered. This reprecipitation was performed two times more. The filtered product was washed with deionized water (several times) and ethyl ether (3 times). Drying in a vacuum oven at 70 °C gave a dark-yellow solid (0.0128 g, 82%). No transition on DSC (0 ~ 180 °C, N<sub>2</sub>).

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15. The average diameter of **9** is 1.6 nm in the same conditions (0.0500 M tetrabutylammonium PF<sub>6</sub><sup>-</sup> solution in acetonitrile, 20 °C).

## Chapter 7

### Ion Conduction in a Semi-Crystalline Polyviologen and Its Polyether Mixtures

#### Abstract

A polyviologen with C<sub>6</sub> spacers and bis(trifluoromethylsulfonyl)imide anions is a semi-crystalline polymer. Its mixtures with dibenzo-30-crown-10, 30-crown-10, 18-crown-6, and poly(ethylene glycol) dimethyl ether 1000 were prepared in solution and all the mixtures are also semi-crystalline materials. Their ionic conductivities were measured by dielectric relaxation spectroscopy; the room temperature ionic conductivity of the polyviologen was  $1.1 \times 10^{-9} \text{ Scm}^{-1}$ , and its mixture of 30-crown-10 was  $1.3 \times 10^{-7} \text{ Scm}^{-1}$ , over 100-fold higher than the polyviologen itself without T<sub>g</sub> drop. Pseudorotaxane formations played a role in higher conductivity, because the ionic conductivity of the mixture with 18-crown-6 showed lower ionic conductivity even with lower T<sub>g</sub>. The ring size of 18-crown-6 is too small to be threaded by the polyviologen. The other two mixtures of 30-crown-10 and poly(ethylene glycol) dimethyl ether 1000 showed  $3.4 \times 10^{-7}$  and  $2.3 \times 10^{-7} \text{ Scm}^{-1}$  respectively and lower T<sub>g</sub>s of the mixtures are the important factor for their high ionic conductivities.

#### Introduction

The field of supramolecular chemistry mainly consists of molecular recognition, molecular devices, and self-processing by self-assembly.<sup>1</sup> The formation of pseudorotaxane and rotaxanes is one of the most important subjects in the supramolecular chemistry and it has been expanded to polymeric materials due to their unique properties.<sup>2</sup> In the host-guest chemistry area, crown ethers and their recognitions to various types of guests have been well studied since the dibenzo-18-crown-6 was synthesized.<sup>3</sup>

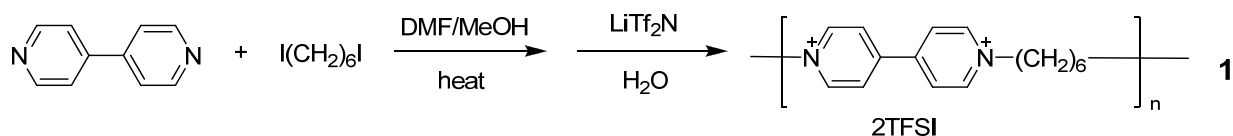
Since many of the guests for crown type hosts are ionic salts, complexation of ion-pairs must be considered. For systems which complex with ion-pairs, a less polar media should be used

over a more polar system, because polar solvents prohibit hydrogen bonding which is major factor in crown ether-type host-guest complexations. Stoddart et al.<sup>4</sup> and Gibson et al.<sup>5</sup> revealed that some pseudorotaxanes gave unique non ion-paired structures, such as the complexation between dibenzo-24-crown-8 (DB24C8) and dibenzylammonium hexafluorophosphate (PF<sub>6</sub><sup>-</sup>). The solid state structure of this complex showed that the PF<sub>6</sub> anions are placed outside of the ring; the closest distance of N<sup>+</sup> and F is 5.1 Å.<sup>4</sup> The ion pairs do not bind tightly in the usual manner in the solid state because the cavity of the host is too small to allow the anion to come close to the bound cation. In other words, the anions are separated from the cations by the complexation process in the less polar medium.<sup>5</sup> In this study, we introduced the “supramolecular non ion-paired complex” concept to electroactive materials to enhance their electrical properties. Therefore, we presume that supramolecular complexation can afford a higher free ion content and thus higher ionic conductivity, when the ionic conducting polymers contain corresponding guest units for the macrocyclic hosts.

## Results and Discussion

Polyviologens have been widely studied due to their unique electrical properties<sup>6</sup> and as a source of polypseudorotaxanes and polyrotaxanes because of their binding abilities with cucurbiturils, cyclodextrins, and crown ethers.<sup>7</sup> A polyviologen with Tf<sub>2</sub>N<sup>-</sup> anions (**1**) was prepared because Tf<sub>2</sub>N<sup>-</sup> usually gave higher conductivity in cationic polymer materials. As shown in Scheme 7-1, **1** was synthesized in two steps: quaternization polymerization to form a polyviologen halide and then an anion exchange reaction. The quaternization was done from 4,4'-dipyridyl and 1,6-diiodohexane in DMF/MeOH. The iodide salt from the quaternization was a deep purple solid and its anions were exchanged in hot water with lithium bis(trifluoromethanesulfonyl)imide (LiTf<sub>2</sub>N).

The degree of polymerization (DP) was calculated by NMR end group analysis: DP = 15 (*M<sub>n</sub>* = 12 kDa). Polyviologen **1** had a *T<sub>g</sub>* at 1.7 °C and a *T<sub>m</sub>* (broad) at 144.8 °C on DSC. The complexation of **1** and DB30C10 was qualitatively confirmed by the chemical shift change of the paraquat protons upon adding a crown ether in an NMR experiment. The peaks at  $\delta$  8.41 and 8.92 for the parent polyviologen moved to  $\delta$  8.26 and 8.89 after adding excess DB30C10 in CD<sub>3</sub>CN/CDCl<sub>3</sub> 3:2 solvent at 23 °C.



**Scheme 7-1.** Synthesis of polyviologen TFSl (**1**).

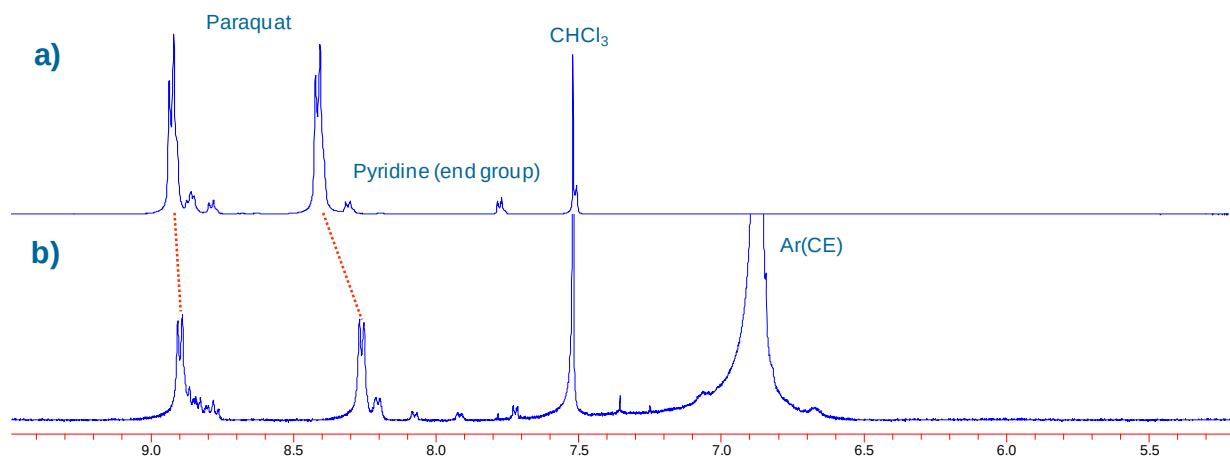


**Figure 7-1.** Partial 400 MHz  $^1\text{H}$ -NMR spectra of **a**) polyviologen **1** and **b**) the solution of **1** and DB30C10 (saturated) in  $\text{CD}_3\text{CN/CDCl}_3$  3:2 solvent at 23 °C. The paraquat peaks move upfield after addition of DB30C10, indicating the complexation of the two molecules.

Mixed solutions of the polyviologen **1** and crown ethers or poly(ethylene glycol) dimethyl ether were prepared in 1/1 acetonitrile/chloroform to confirm the non-ion pairing effect on ionic conductivity (Table 7-1: entries **2**, **3**, **4** and **5**). 50 mol% of dibenzo-30-crown-10 (DB30C10) and 30-crown-10 (30C10) were added in mixtures **2** and **3**. For 18-crown-6 and poly(ethylene glycol)-1000 (PEG) dimethyl ether, the same number of moles of ethyleneoxy units as with DB30C10 and 30C10 were added to form the mixtures **4** and **5**, thus maintaining the same ratio of paraquat and ethyleneoxy units. DB30C10 and 30C10 can allow the formation of pseudorotaxane units because they are large enough, but 18C6 is too small to be threaded by the paraquat unit and thus serves as a control.

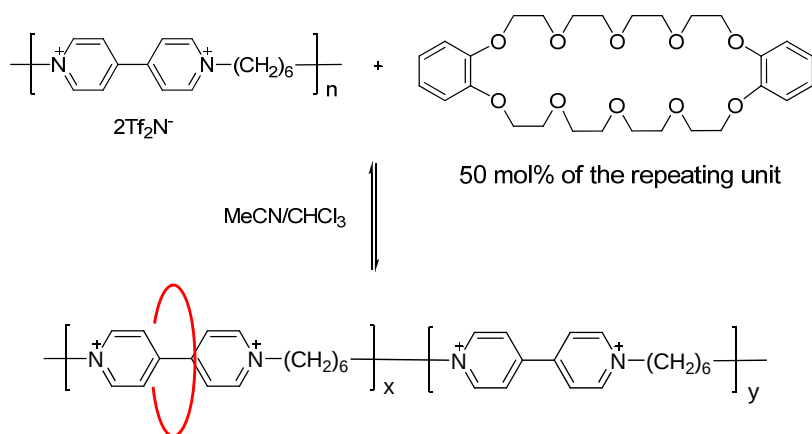


**Figure 7-2.** Formation of polypseudorotaxane from **1** and DB30C10.

**Table 7-1.** Mixture Compositions of Polyviologen **1** and Polyethers.

| Entry    | Polyviologen <b>1</b>       | Polyether                                                           | DSC Transitions (°C)*                                                                                                              |
|----------|-----------------------------|---------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------|
| <b>2</b> | 0.5412 g<br>(0.676 mmol PQ) | DB30C10<br>0.1810 g (0.337 mmol)                                    | 1 <sup>st</sup> : T <sub>g</sub> 7, T <sub>m</sub> 54, 90<br>2 <sup>nd</sup> : T <sub>g</sub> 6, no T <sub>m</sub>                 |
| <b>3</b> | 0.5614 g<br>(0.700 mmol PQ) | 30C10<br>0.1543 g (0.350 mmol)                                      | 1 <sup>st</sup> : T <sub>g</sub> = -32, T <sub>m</sub> = 87<br>2 <sup>nd</sup> : T <sub>g</sub> = -37, T <sub>m</sub> = 83         |
| <b>4</b> | 0.5410 g<br>(0.676 mmol PQ) | 18C6<br>0.1489 g (0.563 mmol)                                       | 1 <sup>st</sup> : T <sub>g</sub> = -9, T <sub>m</sub> = 47, 101<br>2 <sup>nd</sup> : T <sub>g</sub> = -7, T <sub>m</sub> = 89, 107 |
| <b>5</b> | 0.507 g<br>(0.633 mmol PQ)  | PEG dimethylether<br>M <sub>n</sub> = 1000<br>0.1360 g (0.136 mmol) | T <sub>g</sub> = -37, T <sub>m</sub> = 119.0                                                                                       |

\* DSC conditions: -80 ~ 200 °C, heating 5 K/min, cooling 1 K/min, under N<sub>2</sub> stream.

Mixture **2** (**1** and DB30C10) revealed a T<sub>g</sub> at 6 °C and T<sub>m</sub> (broad) at 50.0 and 96.0 °C on the 1<sup>st</sup> heating, but no T<sub>m</sub> during the 2<sup>nd</sup> heating. The morphologies of “before heating” and “after heating” up to 180 °C (over the melting temperature) are probably different. The 3<sup>rd</sup> and 4<sup>th</sup> heating curves showed same results as 2<sup>nd</sup> heating, only one T<sub>g</sub> and no T<sub>m</sub>. Mixtures **3** and **4** revealed different DSC results from mixture **2**; melting was observed during the 2<sup>nd</sup> heating scan after slow cooling (1 °C/min) from 180 °C. Mixture **3** showed a lower T<sub>g</sub> = -38 °C (2<sup>nd</sup> heating) and mixture **4** had T<sub>g</sub> = -7 °C (2<sup>nd</sup> heating). Because of the similar ring sizes of 30C10 and DB30C10, mixtures **2** and **3** could contain polypseudorotaxane structures. The T<sub>g</sub> of the mixture **3** was lower due to the more flexible 30C10 (mp = 25 °C) compared to DB30C10 (mp = 106 °C).

Even after the formation of the complexes, mixture **3** has more flexibility, such as rotation of the 30C10 on the polyviologen chain, which leads to a lower  $T_g$ . The  $\pi$ - $\pi$  electron interactions between paraquat and phenylene units in **2** may restrict movements and slow motions of the crown ether in the polypseudorotaxane. The relatively high  $T_g$  (-7 °C) of mixture **4** is still interesting in view of the low melting point of 18C6 (42-45 °C). Mixture **5** from poly(ethylene glycol) dimethylether ( $M_n = 1000$ ) displayed both a  $T_g$  (-37 °C) and a  $T_m$  (120 °C) which were reproduced on the 2<sup>nd</sup> and 3<sup>rd</sup> heating. The crystalline portions were observed by a cross-polarized optical microscopy for mixtures **3**, **4** and **5** after slow cooling (1 °C/min) from 150 °C (see DSC results in Supporting Information).

The ionic conductivity plots of **1** and the mixtures of **1** with the polyethers are shown in Figure 7-3. The bare polyviologen **1** has the lowest ionic conductivity up to its melting temperature (~ 140 °C), because the ions in the crystalline phase are essentially immobile. The ionic conductivity jumps up at the melting point, because the ions move more freely in the liquid state. Mixtures **2** - **5** show higher conductivities than **1**, even though the total ion concentrations were lowered by dilution with the polyethers. Two factors can contribute to the higher ionic conductivities of mixtures **2** - **5**: the  $T_g$  drop and pseudorotaxane formation, giving a higher free ion content. Interestingly the conductivity of the mixture **2** is still higher without a  $T_g$  drop. Therefore, the conductivity enhancement of **2** could be explained by the pseudorotaxane complexation of the paraquat units and DB30C10. The binding between the paraquat and DB30C10 prohibits the ionic interaction of paraquat cations and  $Tf_2N^-$  anions and as a result there are more free conducting anions in the system.

The higher ionic conduction of mixtures **3** and **5** can be explained by the decrease in  $T_g$ ; in other words, the polyethers act as plasticizers. The  $T_g$  drop leads to faster movement of the polymer chains, and then the ions can move more quickly than in polyviologen **1** which has a higher  $T_g$ . The  $T_g$  drops of **3** and **5** are the dominant factors in the lower temperature range as shown in Figure 7-4. The ionic conductivity of mixture **3** was highest in the lower temperature range (below 40 °C), but mixture **2** becomes higher above 40 °C. Mixture **4** with the smaller 18C6, which cannot be threaded by the polyviologen **1**, has lower conductivity than **2** and **3** even though the same amount of ethyleneoxy units was added. This result implies that the ring size of crown ethers are important to increase ionic conductivity and only the threaded structures (pseudorotaxanes) show higher ionic conductivity.

Interestingly, mixture 5 shows similar ionic conductivity at low temperature ( $< 40\text{ }^{\circ}\text{C}$ ) as mixture 3, but lower than mixtures 2 and 3 at high temperature. The long PEG molecules interact with the paraquat units in **1** via hydrogen bonding; this gives higher ion conduction than **1** and even than **3**. However, the interactions decrease at high temperature, due to the linear PEG chains compared to the macrocyclic crown ether rings (DB30C10 and 30C10).

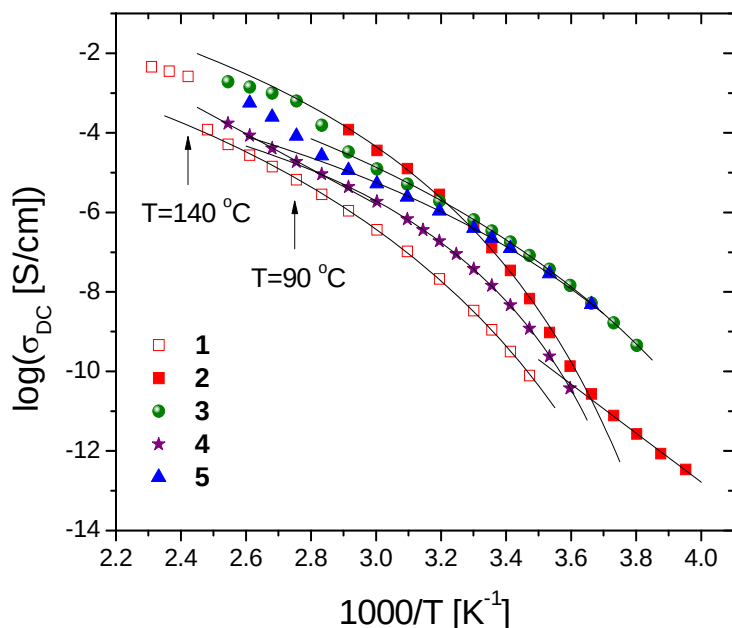


**Figure 7-3.** Ionic conductivity plots of **1** (open red squares), **2** (solid red squares), **3** (green circles), **4** (purple stars), and **5** (blue triangle).

An observation on crystallinity is important, because crystallinity may be an another important factor on ionic conductivity. Although the quantitative calculations of the crystallinities are unavailable for **1** and its mixtures, we can qualitatively assess the crystallinities by DSC and optical microscopy.

Mixture **2** develops crystallinity after slow cooling (1 K/min) from its melt phase, even though DSC does not show melting on the second heating scan. The polarized microscope picture shows crystalline portions in **2** as shown in Figure 7-5. The other blends show higher crystallinities, qualitatively, both in DSC scans and optical microscopic observations. The blend **2** shows relatively smaller crystalline portions than the other mixtures. The ionic conductivities of the mixtures could be also explained by the crystallinities. The higher ionic conductivity of **2** with no  $T_g$  drop could be rationalized by the lower extent of crystallinity, in other words, the larger amorphous fraction. If it is hypothesized that the crystalline portions consist of ionic

paraquat units, the ion movements would be slower in the crystalline portions due to their tight packing compared to the amorphous region. So the smaller crystalline fractions should afford quicker ion movement and the higher conductivity. Under this hypothesis, the higher conductivities of **3** and **5** compared to **4** result only from the  $T_g$  difference, because all three mixtures have higher crystallinity compared to **2**.

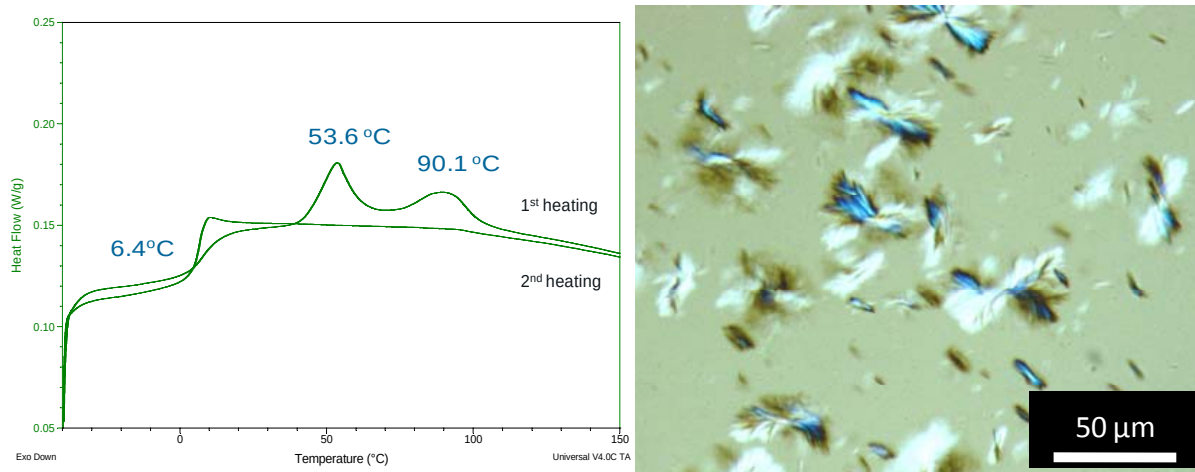


**Figure 7-4.** DSC diagram (left) of the mixture **2** ( $N_2$  atmosphere, heating 5 K/min, cooling 1 K/min) and cross-polarized microscopic image (right) from a solution cast film of **2**. The microscopic image was obtained after cooling (1 K/min) from 140 °C (above melting point).

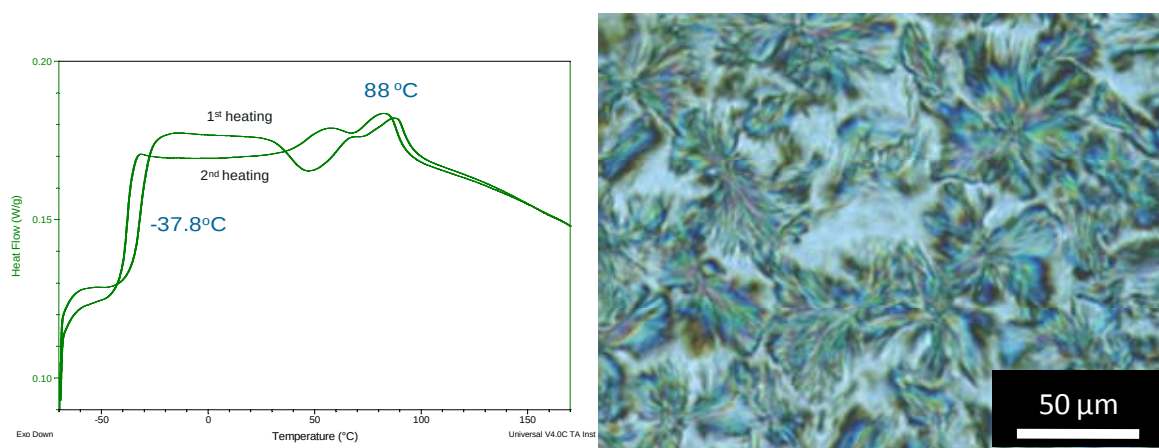


**Figure 7-5.** DSC diagram (left) of mixture **3** ( $N_2$  atmosphere, heating 5 K/min, cooling 1 K/min) and cross-polarized microscopic image (right) from a solution cast film of **3**. The microscopic image was obtained after cooling (1 K/min) from 140 °C (above melting point).



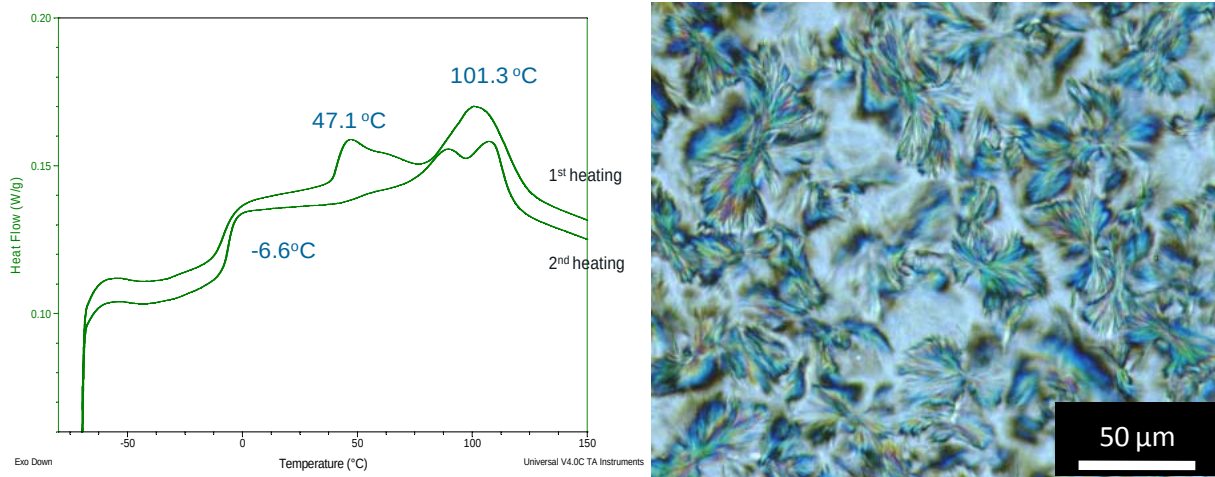


**Figure 7-6.** DSC diagram (left) of the mixture **4** ( $N_2$  atmosphere, heating 5 K/min, cooling 1 K/min) and cross-polarized microscopic image (right) from a solution cast film of **4**. The microscopic image was obtained after cooling (1 K/min) from 140 °C (above melting point).

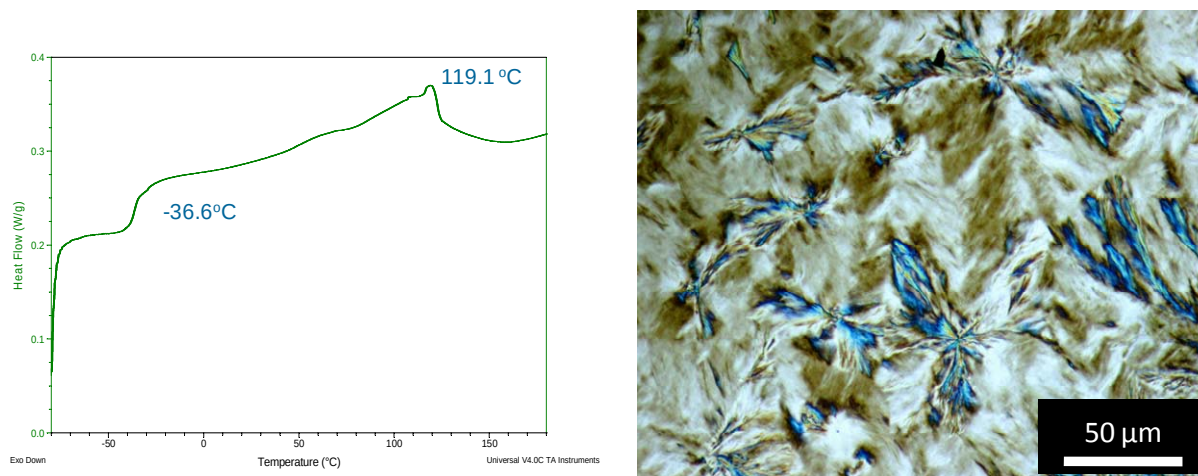


**Figure 7-7.** DSC diagram (left) of the mixture **5** ( $N_2$  atmosphere, heating 5 K/min, cooling 1 K/min) and cross-polarized microscopic image (right) from a solution cast film of **5**. The microscopic image was obtained after cooling (1 K/min) from 140 °C (above melting point).

## Conclusions

The semi-crystalline polyviologen TFSI and its mixtures with crown ethers and PEG dimethyl ether were prepared to see the effect on ionic conduction from the polypseudorotaxane formation with DB30C10 and 30C10, and hydrogen bonding interactions with 18C6 and PEG. The ethyleneoxy units were doing important job for higher ionic conductivity in this study because mixtures **2**, **3**, **4** and **5** all show higher conductivity values than bare polyviologen **1**,

even though the total ion concentrations were diluted by the non-ionic polyethers. Remarkably, the ionic conductivity increased without a  $T_g$  drop for **2** (with DB30C10). The higher conductivity of **2** may be explained by two factors: supramolecular complexation and lower crystallinity. Interestingly, mixtures **2** and **3** (30C10) had higher ionic conductivities than mixture **4**, which does not have threaded pseudorotaxane units due to the small ring size of 18C6. Also mixture **2** contains less crystalline portions than the other mixture blends, which implies that the more amorphous nature affords better ionic movement. From the idea of this study, we have known that the supramolecular complexation can be applied to control the ionic conductivity and crystallinity of ionic polymers. Therefore, a wide range of applications on electroactive materials and devices will be possible from the combinations of supramolecular concepts and electrochemical study.

## Experimental

**Instruments.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained on Varian Inova 400 MHz and Unity 400 MHz spectrometers. Differential Scanning Calorimetry (DSC) with heating (5 K/min) and cooling rates (1 K/min) on ~10 mg samples was done using a TA Instruments Q2000 differential scanning calorimeter. The thermal stabilities of these polymers were studied by TGA under  $\text{N}_2$  using a TA Instruments Q500 Thermogravimetric Analyzer at a heating rate of 10 K/min heating under  $\text{N}_2$  purge.

**Dielectric Spectroscopy.** The ionic conductivity measurements of the polymers and mixtures were performed by dielectric relaxation spectroscopy using a Novocontrol GmbH Concept 40, with 0.1 V amplitude and  $10^{-2}$  -  $10^7$  Hz frequency range. Samples were prepared for the dielectric measurements by allowing them to flow to cover a 30 mm diameter polished brass electrode at 100 °C *in vacuo* to form a puddle deeper than 50  $\mu\text{m}$  with several 50  $\mu\text{m}$  silica spacers immersed. Then a 20  $\mu\text{m}$  diameter polished brass electrode was placed on top to make a parallel plate capacitor cell which was squeezed to a gap of 50  $\mu\text{m}$  in the instrument (with precise thickness checked after dielectric measurements were complete).

**Polyviologen TFSI (1).** A solution of 4,4'-bipyridyl (1.5618 g, 10.0 mmol) and 1,6-diiodohexane (3.3797 g, 10.0 mmol) in MeOH/DMF 1:1 solvent (8 mL) was stirred for 2 days at 100 °C. After cooling to room temperature, the iodide salt was precipitated with ethyl ether (40 mL). The residue was dissolved in MeOH (10 mL) and then the product was re-precipitated with

ethyl ether (60 mL). The precipitated polymer was dissolved in water (80 mL) and LiTf<sub>2</sub>N (7.3 g, 25 mmol) was added to the solution. The mixture was stirred for 24 hours at 50 °C. The precipitated product was washed with water 3 times and then dried in a vacuum oven at 40 °C. An orange-brown candy-like material was obtained (5.20 g, 65% from monomers). Negative on the Beilstein copper/flame test. DSC (-60 ~ 200 °C, heating and cooling rate 5 K/min., N<sub>2</sub>): T<sub>g</sub> = 1.7 °C, T<sub>m</sub> = 144.8 °C (broad). TGA (heating rate 10 K/min., N<sub>2</sub>): 5% weight loss at 257.2 °C (mostly water), degradation started at 327.7 °C. DP = ~ 15 (from NMR end-group analysis).

**Acknowledgements** I thank to U Hyeok Choi and Prof. Ralph H. Colby (PSU) for the ionic conductivity measurement. This material is based upon work supported in part by the U.S. Army Research Office under grant number W911NF-07-1-0452 Ionic Liquids in Electro-Active Devices (ILEAD) MURI. We are thankful to Prof. Robert Moore (VPI&SU) for use of his microscope and kind discussions about the thermal analysis results, and to Prof. James McGrath and Timothy Long (VPI&SU) for use of their thermal analysis instruments.

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## Chapter 8

### Ion Conduction in Amorphous Polyviologens and Their Polyether Mixtures

#### Abstract

Amorphous polyviologens with bis(trifluoromethylsulfonyl)imide anions are synthesized and characterized. The amorphous morphologies were realized by a C<sub>10</sub> spacer between two paraquat units. For their ionic conductivity, they have a slope change (linear to curved) at their glass transition temperatures. The mixtures of the polyviologens with DB30C10 did not show a conductivity increase, since the T<sub>g</sub>s are almost the same as the individual polyviologens. Mixtures with 30C10 and 18C6 possessed increased ionic conductivities due to T<sub>g</sub> drops and the plot of ionic conductivity vs. T<sub>g</sub>/T reveals that the higher ionic conductivities of the mixtures can be mostly attributed to the change in T<sub>g</sub>.

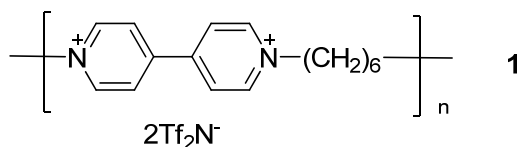
#### Introduction

1,1'-Dialkyl-4,4'-dipyridinium salts are known as viologens or paraquats.<sup>1-3</sup> Viologens were originally investigated as redox indicators in biological studies<sup>4</sup>, due to their low redox potentials and good reversibility. Additionally, some viologens have been investigated for their electrochromic properties.<sup>5-11</sup> Substituent effects on the electrochromic behavior of viologens have also been thoroughly studied.<sup>12</sup> The 1,1'-dialkyl viologens were prepared traditionally by the quaternizations of 4,4'-dipyridyl with alkyl bromides in solution or without solvent. In some cases, the quaternization was assisted by microwaves to give higher yields and shorter reaction times.<sup>13</sup>

Polyviologens are polymers of 4,4'-bipyridinium with alkylene spacers between ionic units. Polyviologens have been used as polymeric guest species in supramolecular chemistry, due to the binding abilities of the paraquat units with cucurbiturils, cyclodextrins, and crown ethers to construct polypseudorotaxanes and polyrotaxanes.<sup>14-18</sup> Furthermore, polyviologens have been

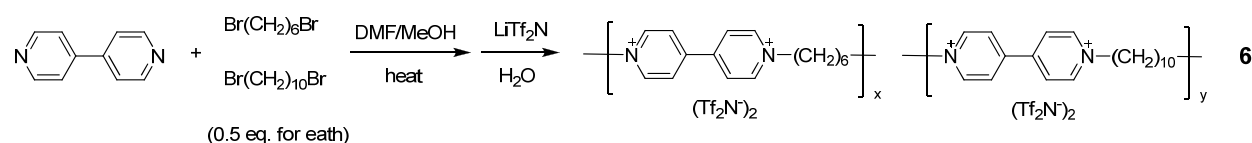
widely studied due to their unique electrical properties, such as reversible redox cycles in cyclic voltametry.<sup>19-24</sup>

In the previous chapter, a semi-crystalline polyviologen bis(trifluoromethylsulfonyl)imide ( $\text{Tf}_2\text{N}^-$  or TFSI) was prepared and we investigated its thermal properties and ionic conductivities of its mixtures with polyethers. Here we prepared two amorphous polyviologens to negate the effect of crystallinity on ionic conductivity. One polyviologen is a random copolymer which contains two alkylene spacers,  $\text{C}_6$  and  $\text{C}_{10}$ , and the other has a  $\text{C}_{10}$  spacer between paraquat units. Also we compared thermal property and ionic conductivity changes of mixtures with the same polyethers as in the earlier study with the semi-crystalline polyviologen.



## Results and Discussion

An amorphous polyviologen TFSI (**6**) was designed and synthesized according to Scheme 8-1. Two alkylene spacers,  $\text{C}_6$  and  $\text{C}_{10}$ , were used to place the ionic paraquat units in a random way. Two dibromides, 1,6-dibromohexane and 1,10-dibromodecane, were added equally (0.5 eq. of 4,4'-bipyridyl each) for the random distribution of the paraquat units. The bromide salt of the polyviologen was obtained by a precipitation using ethyl ether. Ion exchange to  $\text{Tf}_2\text{N}^-$  was done with an aqueous lithium bis(trifluoromethanesulfonyl)imide ( $\text{LiTf}_2\text{N}$ ) solution at 60 °C. Since the polyviologen TFSI (**6**) is a highly viscous material, a mechanical stirrer was used to complete the ion exchange. Complete removal of the bromide anion was confirmed by the Beilstein test with a copper/flame.



**Scheme 8-1.** Synthesis of amorphous polyviologen TFSI **6** with two different alkylene spacers.

The randomly placed spacers between paraquat units provided an amorphous morphology. The DSC diagram shows only a glass transition ( $T_g$ ) at -1 °C and no crystallinity in polyviologen **6** as shown in Figure 8-2. Thermal stability was tested by TGA and it was found to be stable up

to 330 °C (Figure 8-2); in addition to this, the 5% weight loss on TGA was seen at 370 °C under a N<sub>2</sub> atmosphere.

The molecular weight of **6** was calculated by NMR end group analysis. The degree of polymerization (DP,  $x + y$  in Scheme 8-1) is around 11, based on the integration numbers of the methylene protons of the end group at 3.36 ppm and the methylene protons attached to nitrogen of the repeating unit at 4.60 ppm. When DB30C10 was added into a solution of **6**, the complexation of **6** was qualitatively confirmed from the chemical shift changes (Figure 8-1). Quantitative analysis of this complexation was inadequate by NMR, because of the small chemical shift change even after adding an excess DB30C10.

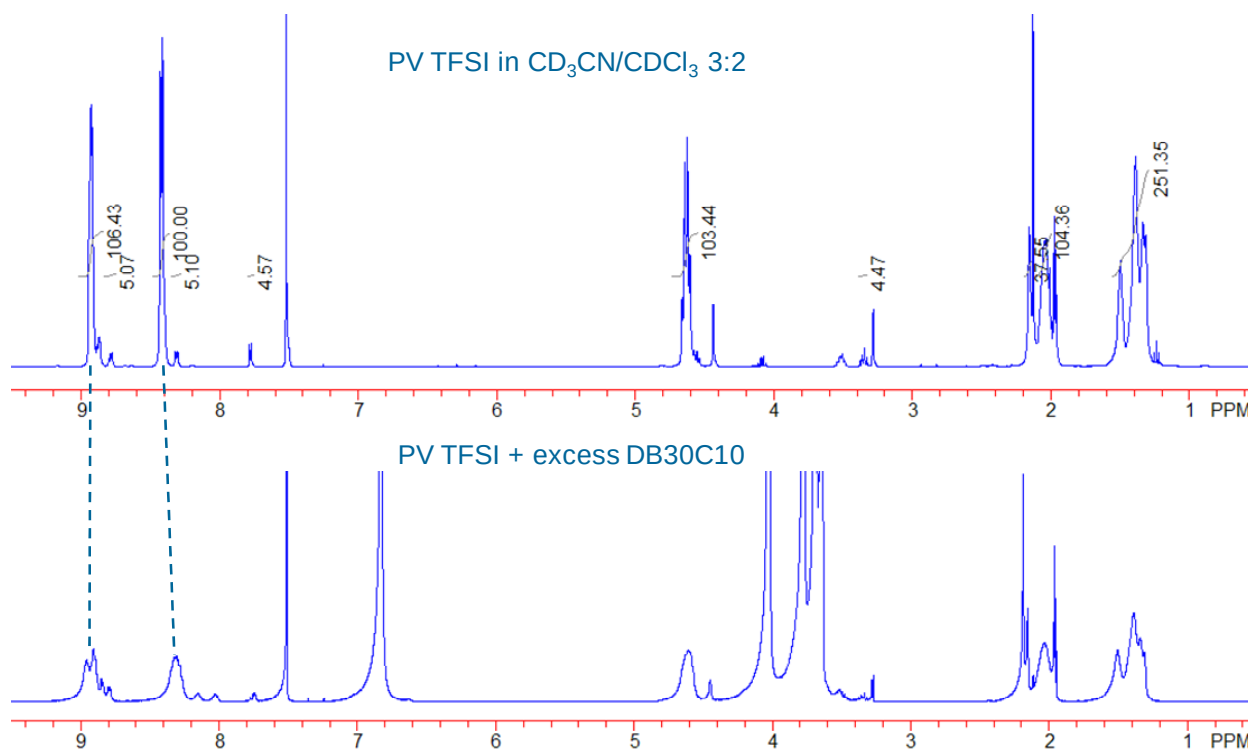


**Figure 8-1.** <sup>1</sup>H NMR spectra of **6** (upper) and after adding excess DB30C10 to the NMR solution (below) (400 MHz, CD<sub>3</sub>CN/CDCl<sub>3</sub> 2:3 (v/v), 23 °C).

As the semi-crystalline polyviologen TFSI in the previous chapter, mixtures of **6** with the same polyethers were prepared to see the conductivity changes; the mixture compositions are shown in Table 1. Since polyviologen **6** is amorphous, having only a glass transition on DSC, all the mixtures are amorphous and have only  $T_g$ . As for the earlier semi-crystalline polyviologen TFSI mixtures, the  $T_g$  of the mixture with DB30C10 (**7**) is highest and low  $T_g$ s were observed for mixture **8** (with 30C10) and **10** (with PEG 1000 dimethyl ether).

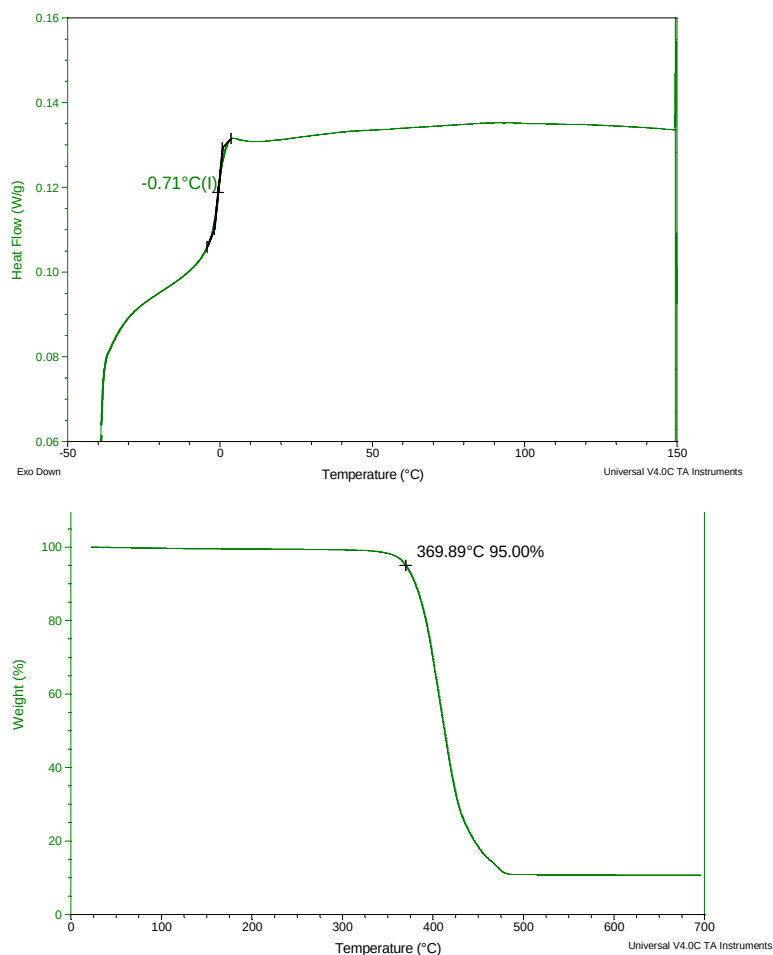


**Figure 8-2.** DSC diagram (upper) and TGA curve (below) of **6**. DSC was scanned with heating and cooling rates of 5 K/min with a N<sub>2</sub> stream, and TGA was observed with a heating rate of 10 K/min under N<sub>2</sub> atmosphere.

Ionic conductivities of the polyviologen **6** and its mixtures (**7-10**) were measured by Dielectric Relaxation Spectroscopy (DRS) (Figure 8-3). Surprisingly, there is no conductivity increase for the mixture **7**. The small T<sub>g</sub> change mirrors almost the same ionic conductivities of **6** and **7** ( $1 \times 10^{-7} \text{ Scm}^{-1}$  at rt). Two other mixtures with low T<sub>g</sub> (**8** and **10**) possess almost 50 ~ 80-fold higher ionic conductivities than **6** by itself at rt:  $5.9 \times 10^{-6} \text{ Scm}^{-1}$  (**8**) and  $8.5 \times 10^{-6} \text{ Scm}^{-1}$  (**10**). For these amorphous mixtures, ion conduction is directly dependent on T<sub>g</sub> and there seems to be less of a pseudorotaxane formation effect on ionic conductivity. This result is different from the ionic conductivity trend of the semi-crystalline polyviologen **1** and its mixtures, as shown in the previous chapter. However, this result is worthy of being applied to the ion-conducting polymers, because higher ion conduction was observed by the mixing with polyethers, even though it



results in a lower total ion concentration (diluted by polyethers). We still need more investigation on other electrical properties to find other factors that lead to ionic conductivity increases.

**Table 8-1.** Blend Compositions of Polyviologen **6**.

| Blend Entry | Polyviologen <b>6</b>       | Polyethers                                                 | DSC Transitions (°C)     |
|-------------|-----------------------------|------------------------------------------------------------|--------------------------|
| <b>7</b>    | 0.7167 g<br>(0.865 mmol PQ) | DB30C10<br>0.2321 g (0.433 mmol)                           | $T_g = -5.0$ , no $T_m$  |
| <b>8</b>    | 0.7169 g<br>(0.865 mmol PQ) | 30C10<br>0.1905 g (0.433 mmol)                             | $T_g = -30.5$ , no $T_m$ |
| <b>9</b>    | 0.7176 g<br>(0.866 mmol PQ) | 18C6<br>0.1907 g (0.722 mmol)                              | $T_g = -17.5$ , no $T_m$ |
| <b>10</b>   | 0.7183 g<br>(0.867 mmol PQ) | PEG dimethylether<br>$M_n = 1000$<br>0.1910 g (0.191 mmol) | $T_g = -33.7$ , no $T_m$ |

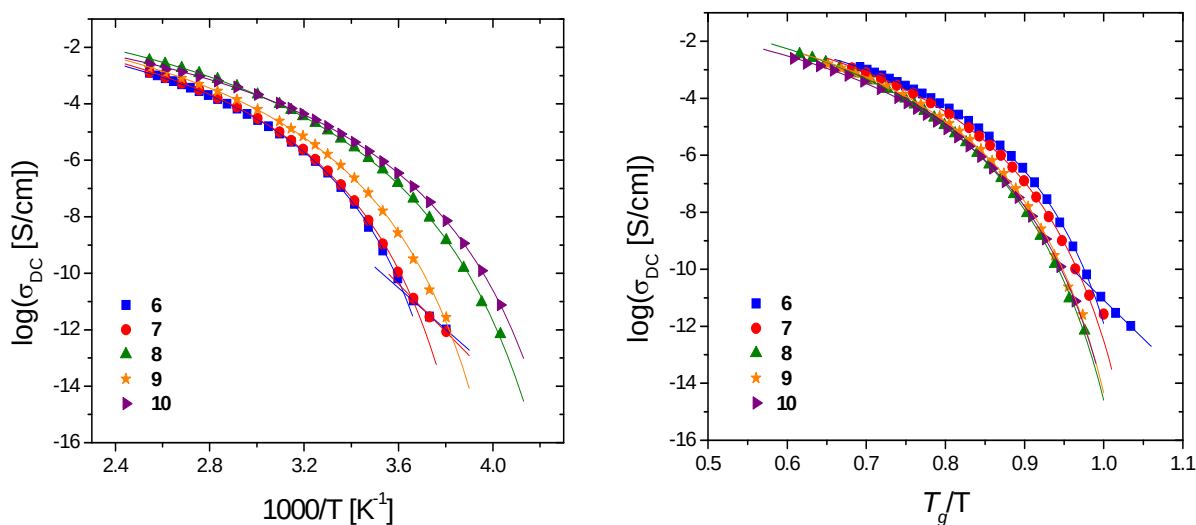
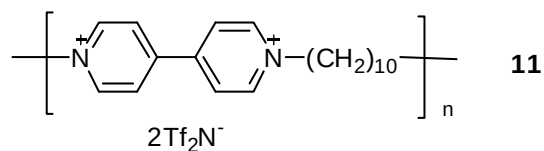


**Figure 8-3.** Ionic conductivity plots of polyviologen **6** and its mixtures.

A polyviologen with a  $C_{10}$  spacer (**11**) was synthesized and characterized also. The quaternization was performed with 4,4'-dipyridyl and 1,10-dibromodecane in methanol/DMF. The ion exchange was done under the same conditions as the other polyviologens. Polyviologen **11** reveals only a glass transition (amorphous)



from DSC and its DP is just ~5 from NMR end group analysis.

The ionic conductivities of **11** and a mixture with DB30C10 are similar throughout the temperature range (except below the  $T_g$  of **11**). This result is the same as the conductivities of **6** and its mixture **7** in Figure 8-7. Therefore, we can conclude that the pseudorotaxane formation of DB30C10 and paraquat units of the amorphous polyviologens does not significantly contribute to the conductivity.

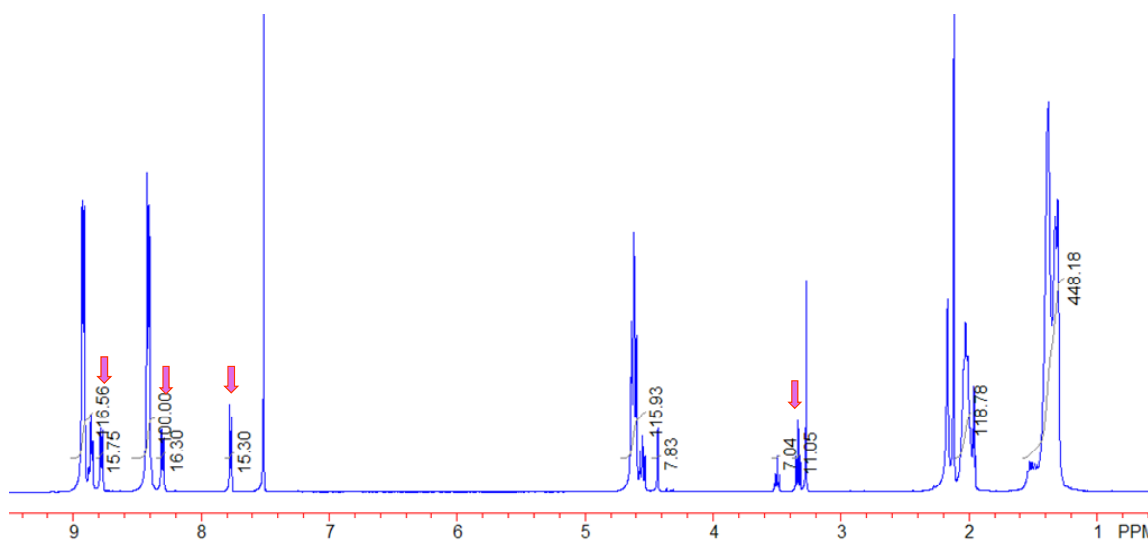


**Figure 8-4.**  $^1\text{H}$  NMR spectrum of **11** (400 MHz,  $\text{CD}_3\text{CN}/\text{CDCl}_3$  2:3 (v/v), 23 °C). The peaks with pink arrows are from the end groups of the polymer.

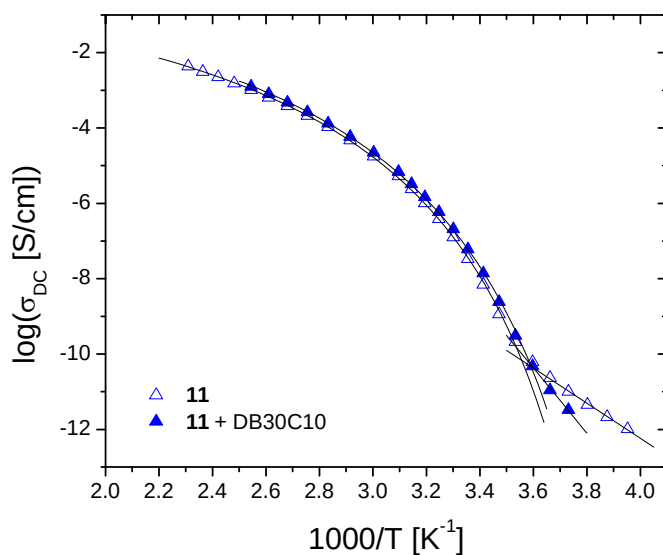


**Figure 8-5.** Ionic conductivity plots of **11** (open triangles) and its mixture with DB30C10 (solid triangles).

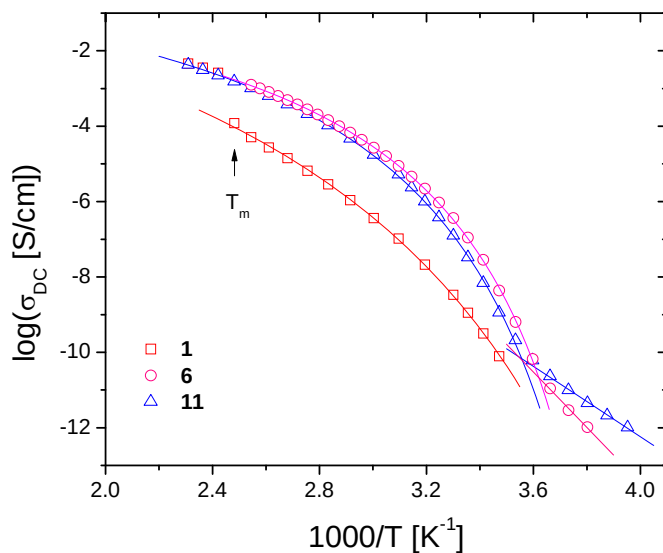


**Figure 8-6.** Ionic conductivity plots of polyviologens: semi-crystalline **1** (red squares), amorphous **6** (pink circles) and amorphous **11** (blue triangles, DP = ~5).

The ionic conductivity of amorphous polymer **6** ( $1.1 \times 10^{-7} \text{ S cm}^{-1}$ ) is 100-fold higher than that of semi-crystalline **1** ( $1.1 \times 10^{-9} \text{ S cm}^{-1}$ ) and 3-fold higher than that of amorphous polymer **11** ( $3.35 \times 10^{-8} \text{ S cm}^{-1}$ ) at room temp. Interestingly, the ionic conductivities of the three polyviologens are almost the same above the melting point of **1**. Therefore, we conclude that the crystallinity is not from the alkylene spacer, but from the ionic paraquat units, and that crystallinity from the ionic units of **1** reduces the ionic conductivity relative to the amorphous polyviologens.

## Conclusions

Two amorphous polyviologens with  $\text{Tf}_2\text{N}^-$  anions and their mixtures with polyethers were prepared. The amorphous morphologies were realized by a  $\text{C}_{10}$  spacer between two paraquat units. The amorphous morphologies were confirmed by DSC and the polyviologens are thermally stable up to  $320^\circ\text{C}$ , according to the TGA. For their ionic conductivity, they have a slope change (linear to curved) at their glass transition temperatures. The mixtures of the two polyviologens (**6** and **11**) with DB30C10 did not show a conductivity increase, since the  $T_g$ s are almost the same as the individual polyviologens. Mixtures with 30C10 and 18C6 possessed

increased ionic conductivities due to  $T_g$  drops and the plot of ionic conductivity vs.  $T_g/T$  reveals that the higher ionic conductivities of the mixtures can be mostly attributed to the change in  $T_g$ . The comparison of the three polyviologens, semi-crystalline **1** and amorphous **6** and **11**, shows that amorphous polyviologens have higher ion conductivities than semi-crystalline ones. The crystallinity from the ionic paraquat units retard ion movements below the melting point. Because many applications have been studied for the polyviologens in electrochemistry and supramolecular chemistry, this research could possibly be applied to many applications, such as electroactive devices.

## Experimental

**Polyviologen TFSI 6.** A solution of 4,4'-bipyridyl (6.2472 g, 40.0 mmol), 1,6-bromohexane (5.0303 g, 20.0 mmol) and 1,10-dibromodecane (6.0014 g, 20 mmol) in MeOH/DMF 2:1 solvent (60 mL) was refluxed for 2 days. After cooling to room temperature, the bromide salt was precipitated by ethyl ether (150 mL). The residue was dissolved in MeOH (20 mL) and then the product was re-precipitated by ethyl ether (150 mL). The precipitated polymer was dissolved in water (200 mL) and then LiTf<sub>2</sub>N (29 g, 100 mmol) was added to the solution. The mixture was stirred by a mechanical stirrer for 24 hours at 50 °C. The precipitated product was washed with water 3 times with vigorous stirring and dried in a vacuum oven at 40 °C. A dark-brown gummy material was obtained (21.20 g, 64%). Negative on a Beilstein copper/flame test. DSC (-60 ~ 200 °C, heating and cooling rate 5 K/min., N<sub>2</sub>):  $T_g$  = -0.7 °C, no  $T_m$ . TGA (heating rate 10 K/min., N<sub>2</sub>): 5% weight loss at 366.9 °C, degradation started at 340 °C. DP = ~ 11 (from NMR end-group analysis).

**Polyviologen 11.** A solution of 4,4'-bipyridyl (4.6954 g, 30.0 mmol) and 1,10-dibromodecane (9.0021 g, 30.0 mmol) in MeOH/DMF 1:4 solvent (50 mL) was stirred for 2 days at 100 °C. After cooling to room temperature, the bromide was precipitated by ethyl ether (100 mL). The residue was dissolved in MeOH (15 mL) and then the product was re-precipitated by ethyl ether (100 mL). The precipitated polymer was dispersed in water (180 mL) and then LiTf<sub>2</sub>N (30 g, 80 mmol) was added to the solution. The mixture was stirred by a mechanical stirrer for 24 hours at 50 °C. The precipitated product was washed with water 3 times and then dried in a vacuum oven at 40 °C. A light-brown very sticky (gummy) material was obtained (18.2 g, 71%). Negative on a Beilstein copper/flame test. DSC (-60 ~ 200 °C, heating and cooling rate 10 °C/min., N<sub>2</sub>):  $T_g$  = -

10.5 °C, no  $T_m$ . TGA (heating rate 10 °C/min.,  $N_2$ ): 5% weight loss at 358 °C, degradation started at 330 °C. DP = ~ 5 (from NMR end-group analysis).

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## **Part II: Novel Ionic Liquids, Ionic Liquid-Based Polymers and Their Properties**

### **Chapter 9**

#### **Ionic Liquid Monomers and Ionic Polymers (Literature Review)**

##### **1. Design of Polymers with Ionic Liquid Moieties**

Ionic liquids (ILs) have been important not only in organic chemistry but also in material science for their various attractive properties. Their low-volatility and non-flammability are really important as “Green chemicals”, their large electrochemical window is important in electrochemistry, and high ionic conductivity is important in energy technologies. Polymer scientists have given an effort to transfer these unique properties of ILs to polymeric materials. To introduce ionic liquid moieties to polymer structures, two general polymerization methods have been used: 1) chain-growth radical polymerizations of vinyl ionic liquid monomers and 2) step-growth condensation polymerization from difunctional ionic liquid monomers. To perform both polymerization methods, proper chemical structures of the monomers are desirable. For examples, the radical polymerization of terminal acryloyl imidazolium monomers gives pendant imidazolium polyacrylates and the Menshutkin quaternization of 1,4-bis(N,N'-imidazole)butane and PEG dibromide/1,12-dibromododecane gives main-chain imidazolium polymers. In addition, the properties of ionic polymers are mostly dependent on the monomer structures. Therefore, the design of ionic liquid monomers is the key part in ionic polymer synthesis to achieve proper characteristics and applications.

##### **1.1 Polymerizable ionic liquid monomers**

The representative polymerizable units introduced on the IL monomers are acrylate and methacrylate. Firestone et al. synthesized imidazolium acrylate ILs as shown in Figure 9-1.<sup>1</sup> The IL monomers contain a polymerizable acrylate unit at one end and an imidazolium ionic unit at

the other end. They investigated binary phase behaviors of the two imidazolium IL monomers with different alkyl chain length. The authors found that the monomers had mesophases and the longer ( $n=7$ , in Figure 9-1) IL monomer showed a more well-ordered structure.

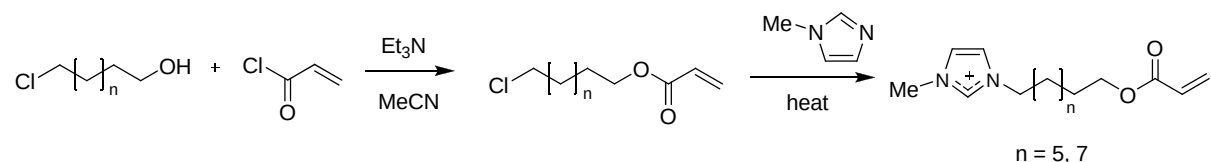


**Figure 9-1.** Synthesis of ionic liquid monomers,  $[\text{AcrC}_8\text{mim}^+][\text{Cl}^-]$  and  $[\text{AcrC}_{10}\text{mim}^+][\text{Cl}^-]$  by Firestone et al.<sup>1</sup>

1-Alkyl-3-vinylimidazolium salts are versatile polymerizable monomers. 1-Butyl-3-vinylimidazolium bromide was synthesized by a simple substitution reaction of 1-vinylimidazole and 1-bromobutane.<sup>2</sup> Quaternizations of 1-vinylimidazole and 2-methyl-1-vinylimidazole with  $n$ -alkyl iodides or with dimethyl sulfate gave the corresponding imidazolium iodide salts.<sup>3</sup> The longer chain derivatives appeared to form micelles in aqueous solution. The imidazolium iodide monomers were polymerized by a free radical pathway in aqueous solution. The ionic polymers with longer side-chain had polysoap properties. A series of 1-alkyl- (or 1-arylalkyl)- 3-vinylimidazolium IL monomer salts were reported by Helmut et al.<sup>4</sup> They synthesized various vinylimidazolium bromide IL monomers and polymerized them.

Ohno et al. have actively studied in the field of ionic liquid monomers and polymers. They have also investigated both vinyl and (meth)acryloyl polymerizable ILs. 1-Ethyl-3-vinylimidazolium bis(trifluorosulfone)imide ( $\text{Tf}_2\text{N}^-$ ) (**a** of Figure 9-2) was prepared and the effects of additional  $\text{LiTf}_2\text{N}$  on the polymerized IL were investigated.<sup>5</sup> Poly(ethylene oxide) derivatives having both acrylate and imidazolium cationic structure on their ends were prepared and polymerized (**b** of Figure 9-2).<sup>6</sup> For the monomers, the imidazolium chloride monomer showed lower conductivity than the corresponding  $\text{Tf}_2\text{N}^-$  analog and their polymers showed the same tendency. Imidazolium acrylate  $\text{Tf}_2\text{N}^-$  monomers containing various alkyl spacers were also prepared to compare the alkyl chain length effect on ionic conductivity (**c** of Figure 9-2).<sup>6-8</sup> Ohno and Nakajima reported an imidazolium cross-linking agent, which contains two imidazolium ionic moieties and two acrylate or two styrenic polymerizable units as shown in Figure 9-3.<sup>9</sup> This cross-linker provided high thermal stability when it was applied to the polymerizations of monoacryloyl polymerizable ILs (**c** of Figure 9-2) or styrene ILs (**e** of Figure 9-2).



Ohno et al. also synthesized polymerizable ILs having a phenylimidazolium group (**e** of Figure 9-2).<sup>10</sup> The styrene backbone after the polymerization did not show better ionic conductivity than the poly(1-ethyl-3-vinylimidazolium salt), but did have better film properties. New types of ionic liquid monomers were obtained by neutralization of polymerizable sulfonic acid with imidazole derivatives (**f** and **g** of Figure 9-2).<sup>11, 12</sup> Zwitterionic polymerizable ILs were also prepared as shown in Figure 9-4.<sup>13</sup> The sulfonate anion was introduced from 1-alkylimidazole and 1,3-propanesultone, the trifluoroethylsulfonimide was introduced from imidazolium sulfonyl chloride and 2,2,2-trifluoroethylamine, and the acrylimide ion was prepared from imidazolium sulfonyl chloride and acrylamide.

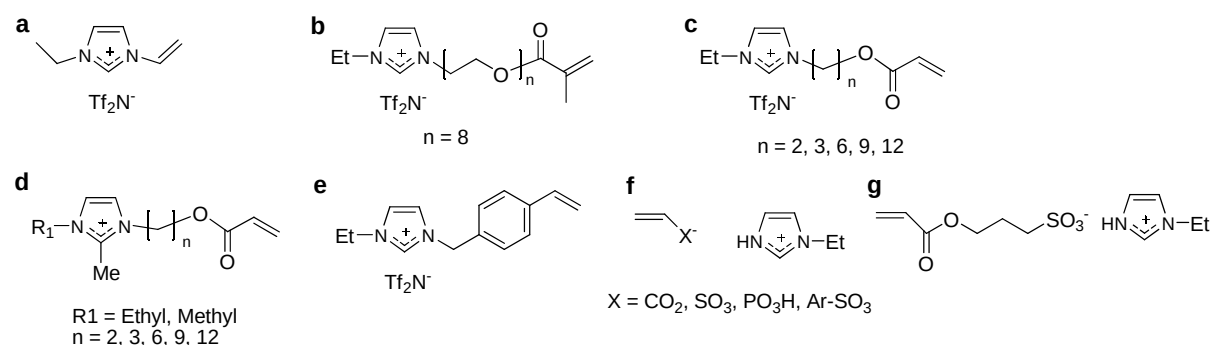


**Figure 9-2.** Polymerizable ionic liquid monomer structures prepared by Ohno et al.

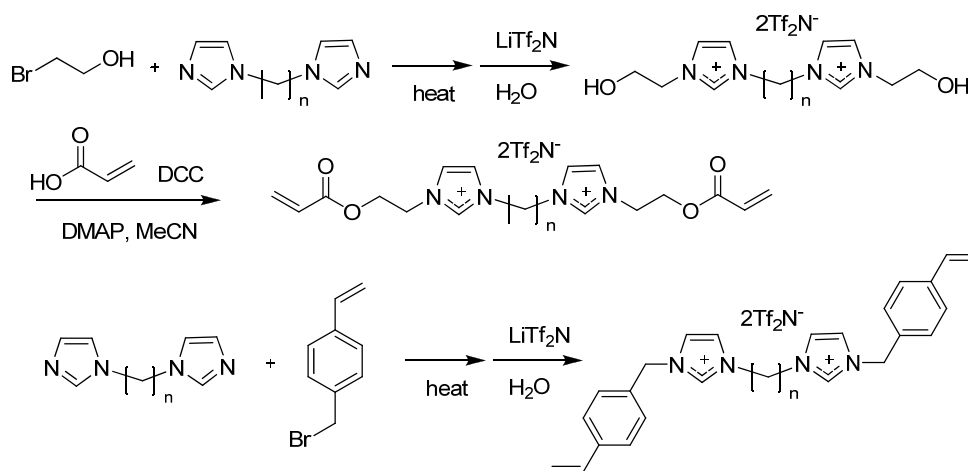


**Figure 9-3.** Synthesis of ionic liquid type cross-linkers: acryloyl cross-linker (upper) and styryl cross-linker (below).

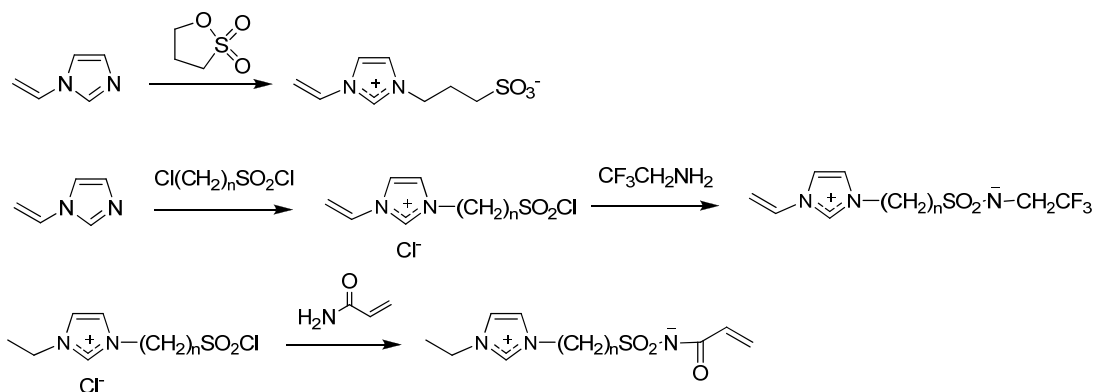


**Figure 9-4.** Various types of zwitterionic polymerizable ionic liquids.<sup>13</sup>

Imidazolium ionic liquid monomers containing a group polymerizable by ring opening metathesis reactions were also prepared. Buchmeiser et al. synthesized *exo,endo*-5-nobornene-2-yl-carboxyethyl-3-ethylimidazolium salts (**a** of Figure 9-5) as ring opening metathesis polymerization (ROMP) monomers.<sup>14</sup> As a modification of the ROMP monomer, Song et al. prepared norbornene derivatives with an imidazolium cation and a tri(ethyleneoxy) spacer (**b** of Figure 9-5).<sup>15</sup> Some ROMP polymers achieved high molecular weights, up to 180 kDa with narrow PDI (< 1.1).

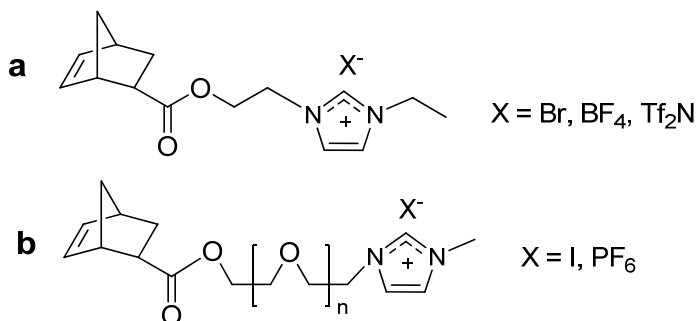


**Figure 9-5.** ROMP monomers with imidazolium ionic liquid moieties.<sup>15</sup>

## 1.2 Quaternizations of halo polymers with aromatic amines

Compared to the number of the reported polymerizable ionic liquids, a few pendant ionic polymers were synthesized by the “polymer first and quaternization next” method. Aoshima et al. reported poly(vinyl ethers) with pendant imidazolium or pyridinium salts and they investigated phase separation behaviors of the ionic polymers.<sup>16</sup> They polymerized 2-chloroethyl vinyl ether by anionic polymerization first, and then the polymer was reacted with excess 1-alkylimidazole or 4-methylpyridine in polar solvents (Figure 9-6).

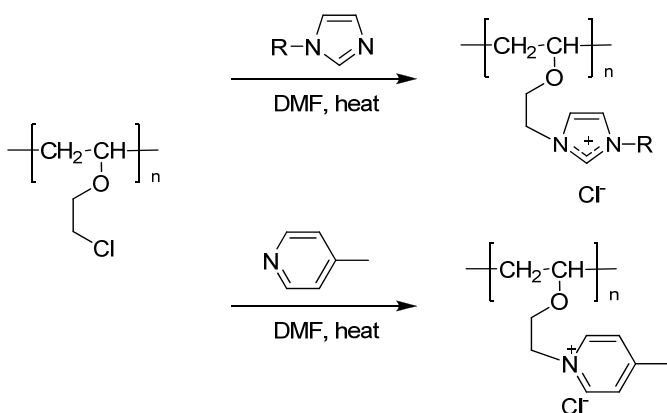


**Figure 9-6.** Synthesis of poly(vinyl ethers) with imidazolium and pyridinium ionic pendants.<sup>16</sup>

### 1.3 Difunctional ionic liquid monomers for step growth polymerization

Polymers with ionic units incorporated into the backbone are called polyionenes (or simply ionenes).<sup>17</sup> Ionenes have received increasing attention as candidates for precisely controlling the charge density in polyelectrolytes.<sup>18</sup> Ionenes are unique since the ionic sites are precisely placed along the polymer main chain; monomer design and selection provide control of total ion concentration. Some imidazolium ionenes have been reported by Ohno et al. from hydroboration polymerization of imidazolium dienes with borane compounds (RBH<sub>2</sub>).<sup>19, 20</sup> The structures of the boron polymers are shown in Figure 9-7. The polymers from hydroboration have low T<sub>gs</sub> (-60 ~ -45 °C) and good ion conduction (2~4 x 10<sup>-5</sup> S cm<sup>-1</sup>), with however relatively low molecular weight (4 – 9 kDa). The Menshutkin reaction, which involves tertiary diamines and dihalides, was used for imidazolium ionenes from alkylene bis(imidazole) and terminal diiodoalkanes as shown in Figure 9-8.<sup>21</sup> The polymers were used in quasi-solid-state solar cell fabrication, which trapped the molten salt polymer in the electrolyte phase of the cell.

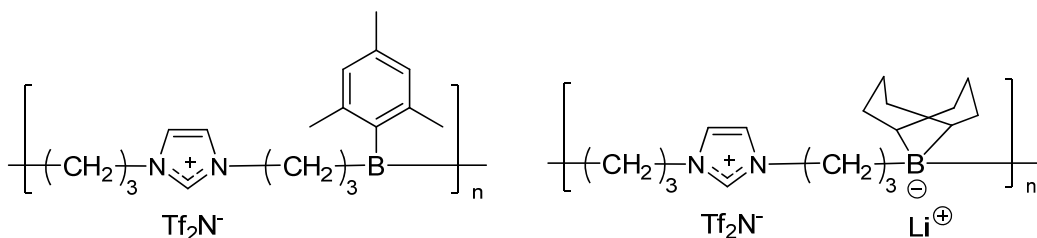


**Figure 9-7.** Two main-chain imidazolium polymers from hydroborations.<sup>19, 20</sup>

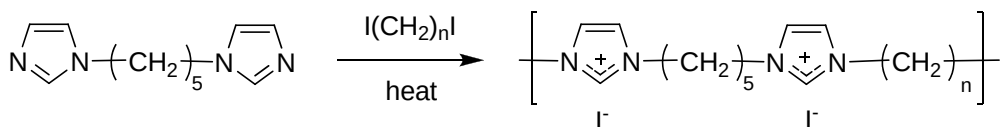


**Figure 9-8.** Synthesis of a main-chain imidazolium polymer used in solar panel.<sup>21</sup>

## 2. Ionic Polymers from Ionic Liquid Monomers

Introduction of functional groups on ionic liquids has been significant for the polymer scientists because the functionalities provided various possibilities for polymeric materials as mentioned above. Polymerization was one of the earliest chemical transformations in the studies of ionic liquids and this area has been thoroughly reviewed.<sup>22-24</sup> Also there has been a growing interest in polymers combined with ionic liquids and new types of synthetic polymers with improved mechanical properties and architectural controls.<sup>24, 25</sup> Recently polymeric functional materials based on ionic liquids were also well reviewed.<sup>26</sup>

Then why we are interested in the polymerizations of ionic liquid compounds? The major advantages of polymeric materials are improved processability, stability, flexibility, durability and controllability of micro structures. So many types of polymers have been reported during last two decades. Mostly ionic liquid homopolymers have been designed as new polyelectrolytes to achieve high ionic conductivity. However, most homopolymers of ionic liquid monomers possess  $T_g$ s and are very soft materials at room temperature. Therefore copolymerizations have been considered to enhance their mechanical properties and thermal stabilities. Also new applications have been created from the polymerized ionic liquid monomers, because their unique properties have been found either by themselves or by combinations with other materials or both.

### 2.1 Ionic homopolymers of ionic liquid monomers

Most of the monomers, which were described in the previous chapter “Design of Polymers with Ionic Liquid Moieties”, were used for ionic homopolymers by various polymerization methods. Conventional radical polymerization methods have been used for the ionic liquid monomers with (meth)acryloyl or vinyl moieties to synthesize the ionic homopolymers.

As previously mentioned, Ohno and his coworkers have intensively studied homopolymer polyelectrolytes from ionic liquid monomers. All his monomers in Figure 9-2 were polymerized

with AIBN in (or without) proper solvents. In each paper, the polymers' phase transition temperatures and ionic conductivities through various temperature ranges were reported. The ionic conductivity of poly(1-ethyl-3-vinylimidazolium tosylate) was very low ( $< 1.0 \times 10^{-10} \text{ S cm}^{-1}$ ), but an equimolar mixture of the polymer and  $\text{LiTf}_2\text{N}$  was liquid and its ionic conductivity increased to  $\sim 10^{-3} \text{ (S cm}^{-1})$ .<sup>10</sup> The polymerized imidazolium styrene monomer with  $\text{Tf}_2\text{N}^-$  (**e** of Figure 9-2) had ionic conductivity in  $\sim 10^{-5} \text{ (S cm}^{-1})$ , but no dramatic increase from mixing with  $\text{LiTf}_2\text{N}$ .<sup>10</sup>

Ohno and his coworkers have studied the effects of the pendant structure change on ionic conductivity. Their results were well summarized in the paper published in 2001.<sup>6,7</sup> First of all, they synthesized imidazolium (meth)acrylate monomers with a longer spacer and the polymerizations gave ionic long-brush polymers. The longer spacer between the polymer backbone and ionic moieties gave around 100-fold higher conductivities (from poly(1-ethyl-3-vinylimidazolium  $\text{Tf}_2\text{N}^-$ ) to poly[1-ethyl-3-(12'-acryloyldodecyl)imidazolium  $\text{Tf}_2\text{N}^-$ ] (from monomer **c** ( $n = 12$ ) in Figure 9-2). Also the ionic conductivity of the polymers increased as the pendant alkyl chain length got longer. They also studied the relationship of glass transition temperatures and ionic conductivities; lower glass transition temperature of polymers produced higher ionic conductivity.<sup>6</sup>

The ion conductive polymers from the vinyl acid monomers neutralized with 1-alkylimidazole (**e** and **f** in Figure 9-2) were also investigated.<sup>12</sup> The ionic conductivities of the neutralized monomers are  $8.7 \times 10^{-5} \sim 9.0 \times 10^{-3} \text{ S cm}^{-1}$ , and for their polymers  $1.1 \times 10^{-8} \sim 9.1 \times 10^{-4} \text{ S cm}^{-1}$ . The imidazolium vinylsulfonate monomer and polymer had the highest ionic conductivities among the neutralized analogs. From this idea, zwitterionic polymers were also synthesized (from the ionic liquid monomers in Figure 9-4).<sup>13</sup> The ionic conductivities of the polymers were similar to the previous imidazolium vinylsulfonate polymers, even though there is a higher total ion concentration in zwitterionic polymer systems. The increase in total number of ions does not give much impact on ionic conductivity, since only single ions and triple ions (e.g.  $\text{ABA}^+$ ) contribute to ion conduction but the neutral species, ion pairs and quadruple ions, have no effect on the conduction. Teyssié et al. reported high ionic conductivity ( $6.5 \times 10^{-4} \text{ S cm}^{-1}$ ) from the poly(methacrylate) with a tri(ethyleneoxy) spacer, a trifluoromethanesulfonic anion and a free imidazolium cation.<sup>27</sup>

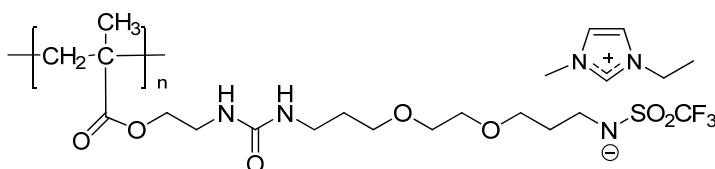


**Figure 9-9.** Homopolymer of the ionic liquid monomer with a trifluoromethanesulfonic anion and a free imidazolium cation by Teyssié et al.<sup>27</sup>

Shen et al. investigated the properties of an imidazolium acryloyl and styrene polymers. They applied the ionic polymers as membranes for CO<sub>2</sub> absorption and separation and reported that the polymerized ionic liquids possess much greater potential than ionic liquid monomers.<sup>28</sup> They also prepared 2-(1'-butylimidazolio-3'-yl)ethyl methacrylate tetrafluoroborate (BMIT) monomers in high yield. And then living/controlled radical polymerization of the imidazolium ionic liquid monomer was investigated.<sup>29</sup> Copper bromide/bromide based initiator systems polymerized BMIT very quickly with little control because of fast activation but slow deactivation. With copper chloride and chloride initiators, first-order kinetics was observed in MeCN with respect to the monomer concentration.

Liu et al. polymerized 2-(1'-butylimidazolio-3'-yl)ethyl methacrylate halides (chloride and iodide) and coated the ionic polymer on a surface.<sup>30, 31</sup> They used the polyelectrolyte as a surface modifier to modulate the interfacial resistance via conformational changes triggered by external electrolytes and solvent by ATRP<sup>30</sup> and to form a gel polymer electrolyte with suitable plasticizers (I<sub>2</sub> and polyacrylonitrile) for high ionic conductivity ( $1 \times 10^{-3} \text{ S cm}^{-1}$ ).<sup>31</sup>

Cross-linking copolymerizations also have been tried with ionic liquid cross-linkers as shown in Figure 9-2 or non-ionic cross-linkers to achieve better thermal and mechanical properties. Muldoon and Gordon reported a microparticle from a conventional aqueous suspension polymerization of water soluble ionic liquid monomer, 1-butyl-3-vinylimidazolium Tf<sub>2</sub>N<sup>-</sup>.<sup>32</sup> Dicationic N-vinylimidazolium Tf<sub>2</sub>N<sup>-</sup> was used as a cross-linker and the copolymerization gave porous polymeric micro-beads that were thermally stable up to 250 °C. From the same ionic liquid monomer, Mecerreyes et al. synthesized a water-in-oil emulsion with a non-ionic cross-linker (N,N-dimethylene bisacrylamide).<sup>33</sup> Electron microscopy provided evidence of the formation of spherical micro-emulsion particles (0.5~2.0 μm).

Micro-emulsion copolymerization of surfactant IL 1-(2-acryloyloxyundecyl)-3-methylimidazolium BF<sub>4</sub><sup>-</sup> and methacrylate in H<sub>2</sub>O/1-propanol gave a transparent gel.<sup>34</sup> The

polymer gel was transformed into a porous polymer with 0.1 M KPF<sub>6</sub> solution, and the porous polymer can be converted back into a gel by immersion in DMSO and DMF. Also these polymer gels were reconverted into porous polymers by immersion in water.

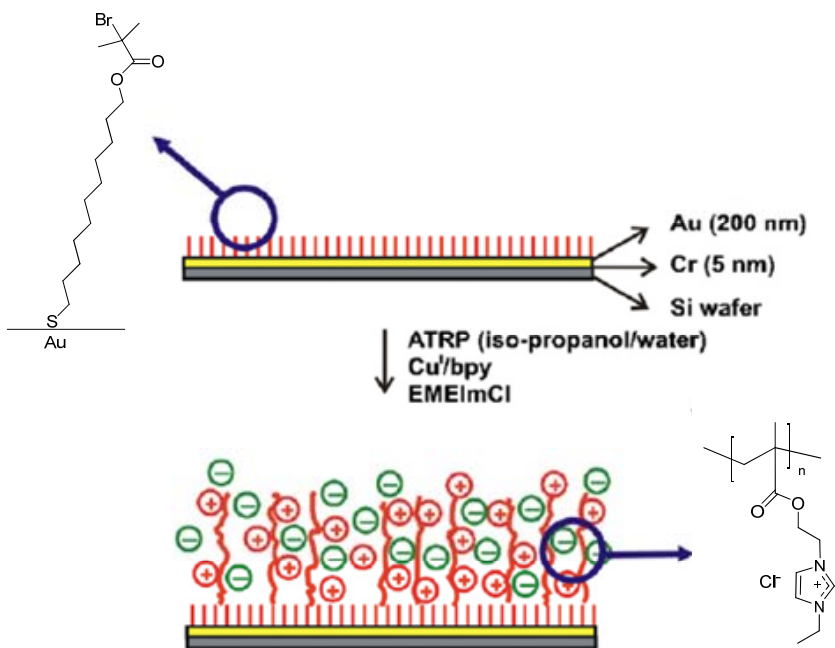


**Figure 9-10.** Surface-initiated polymerization of ionic liquid monomer. The brushes are grown using ATRP in isopropanol/water from the initiator modified Au surface (reprinted with permission from ref 30. © Elsevier).

## 2.2 Copolymers of imidazolium ionic liquids monomers

Copolymers of imidazolium monomers were first reported by Pacansky and Overberger in 1975.<sup>35</sup> They prepared random copolymers from 4(5)-vinylimidazole and 2,3-dimethyl-1-vinylimidazolium iodide. Two decades later, pendant type imidazolium organosilicon copolymers with poly(sodium styrene sulfonate) were synthesized.<sup>36</sup> These polyelectrolyte complexes dissolved in a ternary solvent system and displayed high thermal stability. The formation of the polyelectrolyte complexes decreased with increasing polyion concentration and organic solvents, but decreased with decreasing dielectric constant of the solvents. Lee and Chen reported a series of 2-hydroxyethyl methacrylate/1-vinyl-3-(3-sulfopropyl)imidazolium betaine copolymeric gels.<sup>37</sup> They investigated the influence of the amount of the zwitterionic monomer in copolymeric gels on their swelling behavior in water and various saline solutions at different temperatures and the compression strength, drug-release behavior, and crosslinking density.

Copolymerizations of ionic liquid monomers with a cross-linking agent were reported as previously mentioned in Chapter 4.1.1. Ohno et al. prepared network polymers from the same type monomers with various non-ionic cross-linkers, poly(ethylene glycol) divinyl ether and poly(ethylene glycol) di(meth)acrylate to form highly ion conductive flexible films,<sup>8</sup> up to  $1.1 \times 10^{-4} \text{ S cm}^{-1}$ . Also they prepared thermally stable polymer electrolytes from mono-functional ionic liquid monomers with dicationic ionic liquid cross-linkers.<sup>9</sup>

Just a few examples of ionic liquid monomers have been reported as components in block copolymers. Block copolymers were also synthesized. Waymouth et al. prepared a series of diblock copolymers comprising a polystyrene block and an imidazolium functionalized polystyrene block, and then characterized micelle dimensions with dynamic light scattering and small-angle neutron scattering (Figure 9-11).<sup>38</sup> They prepared diblock copolymers from styrene and chloromethylstyrene first by a nitroxide mediated polymerization (NMP) and then quaternized with 1-methylimidazole to form imidazolium ionic moieties on the second block. The preparation of a series of double hydrophilic block copolymers by sequential reversible addition fragmentation chain transfer (RAFT) polymerization of ionic liquid monomers and acrylamide or methacrylic acid was reported by Gnanou et al.<sup>39</sup> The adjustment of the hydrophilicity of the ionic liquid block by ion exchange altered the water solubility of the block copolymers, thus varying the aggregation states of the polymers from unimers to micelles.

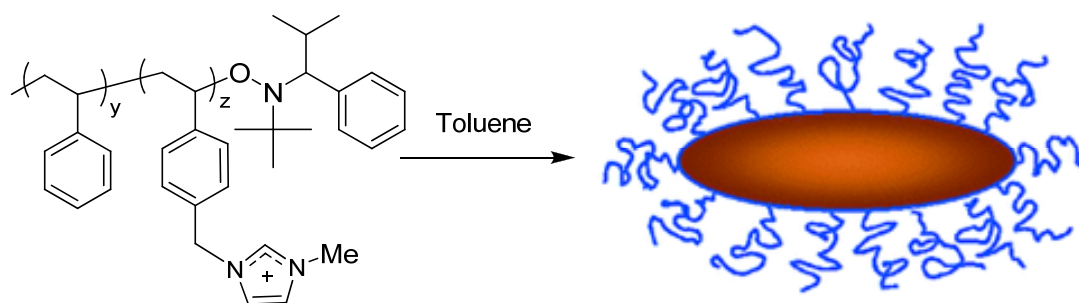


**Figure 9-11.** Diblock copolymers of a styrene block and a polymerized ionic liquid block to form micelles in toluene. (reprinted with permission from ref 38. © American Chemical Society).

Ion segmented block copolymers containing imidazolium cations are recently reported by Long et al. as shown in Figure 9-12.<sup>40</sup> They synthesized segmented imidazolium ionenes with various ionic contents from alkylene diimidazole (ionic hard segment), bromine terminated poly(tetramethylene oxide) (PTMO, non-ionic soft segment) oligomers and 1,12-



dibromododecane (to change the hard segment ratio). As the hard segment content got higher, the segmented ionenes formed tough films and were micro-phase separated with lamellar-type morphologies.

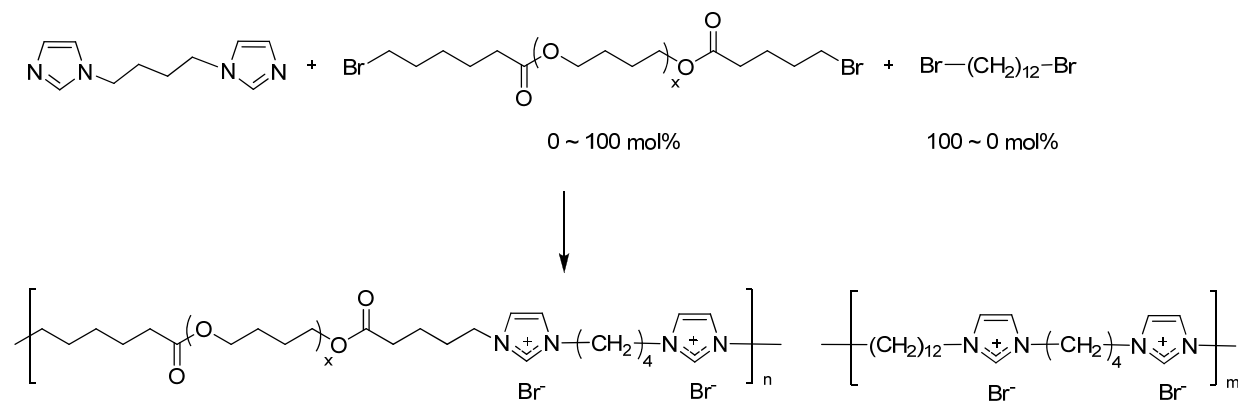


**Figure 9-12.** Synthesis of segmented imidazolium ionenes by a Menshutkin reaction.<sup>40</sup>

### 2.3 Ionic polymers with ionic liquid crystalline moieties

The self-assembly of ionic polymers into discrete nanostructures is interesting due to their various possible applications as functional materials for drug delivery, nanolithography, nanoelectronics and optoelectronics.<sup>26</sup> Liquid crystalline polymers with ionic liquid moieties have been reported to develop nanostructures with enhanced physical/electrical properties from meso-phases of the polymers. In 1995, ionic liquid crystalline polymers from linear poly(ethyleneimine) (PEI) substituted with 6-(4-methoxy-4'-biphenyloxy)hexyl bromide or 12-(4-methoxy-4'-biphenyloxy)dodecyl bromide, and quaternizations with dimethyl sulfate or hydrobromic acid were reported by Guillon et al.<sup>41</sup> A smectic **A** mesophase was identified from both completely and partially quaternized PEI derivatives. Polymers with pendant pyridinium ionic units were synthesized by Haramoto et al.<sup>42</sup> They prepared polymerizable pyridinium ionic liquid crystalline monomers as shown in Figure 9-13 and then polymerized with AIBN. The pyridinium monomers and their polymers had a smectic **A** mesophase; however, transition temperatures were much lower for the monomers. Pyrrole derivatives were also reported as liquid crystalline molecules. The polymerization of N-substituted pyrrole derivatives containing a viologen side chain via a  $\text{FeCl}_3$  method gave liquid crystalline polymers showing two smectic mesophases.<sup>43</sup>

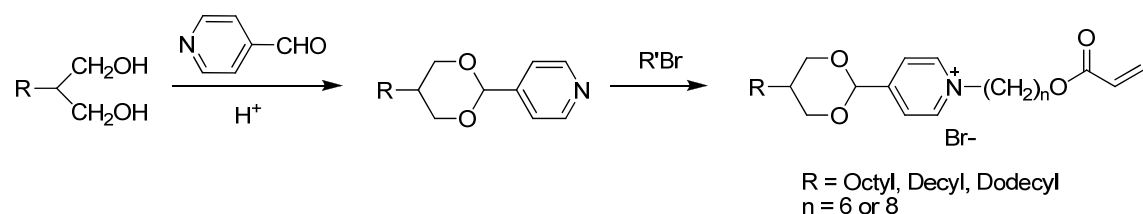


**Figure 9-13.** Synthesis of polymerizable ionic liquid crystalline pyridinium monomers.

Ohno and Kato have reported a lot of ionic liquid crystals and their anisotropic properties on surfaces. One remarkable work is that they prepared polymerizable ionic imidazolium liquid monomers containing a mesogen unit (biphenyl) and their polymers.<sup>44</sup> Oriented nanostructures of the polymers were obtained from *in situ* photopolymerization initiated by 2,2-dimethoxy-2-phenylacetophenone and UV irradiation (365 nm) in glass and ITO cells. Anisotropic ion-conduction was observed from the liquid crystalline polymers (Figure 9-14). Similar liquid crystalline polymers were reported by Koide et al.<sup>45, 46</sup> Their ionic liquid monomers also contained a biphenyl mesogen, an imidazolium moiety, and a terminal polymerizable end-group. Anisotropic ion conduction was only observed from the polymerized liquid crystalline materials.

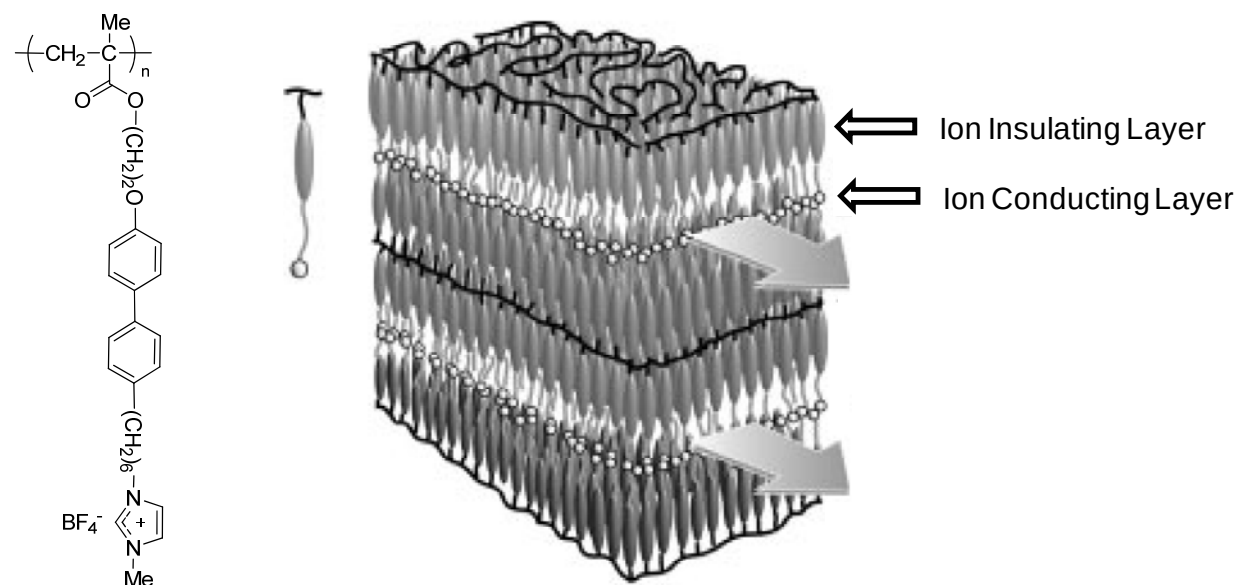


**Figure 9-14.** Illustration of layered nanostructure of ionic liquid crystalline polymer in the smectic A phase. (reprinted with permission from ref 44. © John Wiley and Sons).

Ohno and Kato also reported another type of polymerizable ionic liquid crystal to prepare polymer films containing anisotropic ion channels parallel to and perpendicular to the film surface.<sup>47</sup> The control of the direction of columns of the columnar ionic liquid crystalline

monomer (Figure 9-15) was possible on a modified glass surface (primary amine functionalized by a silane-coupling agent); the imidazolium salt self-assembled with vertical orientation to the surface and with parallel orientation to the surface by shearing. The molecular alignment after the photopolymerization gave anisotropic conductivity; the ionic conductivity was always higher for the parallel orientation of the columnar axis.

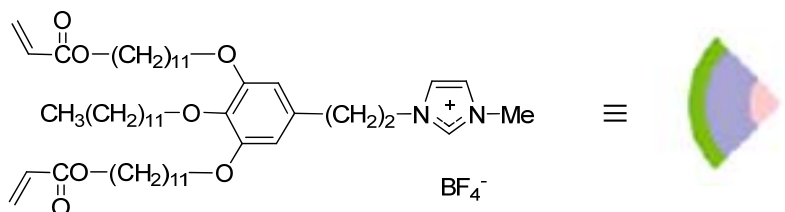


**Figure 9-15.** Ionic liquid crystal monomer reported by Ohno and Kato. From this monomer, hexagonal columnar mesophase was observed on glass and ITO glass surfaces. The polymerizable end functionality provided aligned ion channels after the photopolymerization.

## 2.4 Electroactive polymers with ionic liquid moieties

The combination of ionic transport inherent to the ionic liquids with electrical conductivity afforded by an electroactive group allows for the preparation of ionic electroactive polymers based on responsive materials applicable to bio-mimics, such as actuators or artificial muscles.<sup>48</sup> Thiophene derivatives were reported as the first electroactive materials. Naudin et al. described the synthesis of a benzylthiophene derivative bearing an imidazolium cationic unit.<sup>49</sup> After the electropolymerization of the thiophene groups, the polymer displayed both *p*- and *n*-doping redox activity. Leclerc and Ho reported an imidazolium alkoxy polythiophene and it was used as a detector for iodide anions.<sup>50</sup> Li et al. reported the synthesis of a pyrrolyl-dodecylmethylimidazolium bromide and its electropolymerization. Electropolymerization offers several advantages over chemical polymerization, including facile generation of thin polymer films on a variety of surfaces and the ability to modify and engineer surfaces with redox active molecules. The thienyl containing ionic liquid monomers for the preparation of semiconducting liquid-crystalline polymers has been reported by Firestone et al.<sup>51</sup> The thiophene moiety was appended to the terminus of the C<sub>10</sub> chain of 1-decyl-3-methylimidazolium cation. The ionic liquid monomer showed columnar hexagonal and rectangular mesophases, depending on the counterion. Moreover,  $\pi$ - $\pi$  stacking was found not only to preserve the long-range mesophase

ordering, but to also promote significant short-range ordering which can enhance low-dimensional conductivity through the columns.

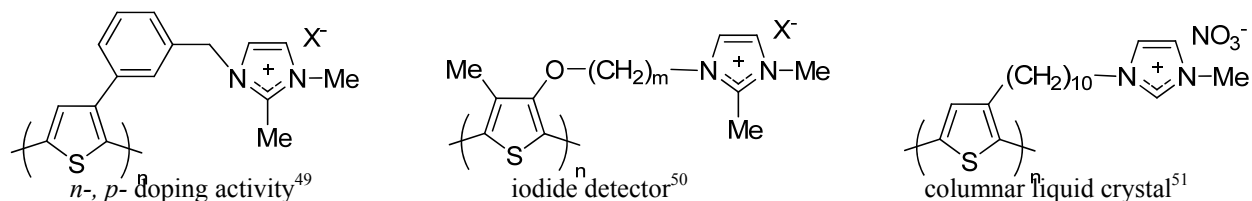


**Figure 9-16.** Electropolymerized polymers from ionic liquid monomers of thiophene derivatives for electroactive materials.

### 3. Conclusions and Prospective Research

Ionic liquids and polymers from ionic liquid monomers have become important materials in a lot of material science fields for their interesting characteristics including tunable intermolecular electrostatic interactions, thermal stability, ionic conductivity, and solubility through cation structure or facile anion exchange, leading to exquisite control over their electric, physical and electrochemical properties in combination with the advantages of polymers. Therefore, polymerized ionic liquids have provided a wide range of promising applications.

The main objective of my research is the synthesis and characterizations of ion conducting polymers, which can be applied to electroactive devices, such as artificial actuation systems. As a future work, various types of imidazolium polymers will be realized to have both high ionic conductivity and mechanical strength. To achieve high conduction polymers, understanding basis of high conductivity is most important. The structure-property relationship of the ionic polymers will be investigated with various structural factors, in either pendant or main-chain ionic polymers.

The ionic polymers containing pendant imidazolium moieties are the first candidates of my research project. The basic structure-property relationship study will be performed: the pendant chain length effect, counterion effect, difference between alkyl chains to other oxygen-rich chains, and molecular weight effects. Most highly ion conducting imidazolium polyelectrolytes contain  $\text{Tf}_2\text{N}^-$ , which is bulky and asymmetric, of low basicity. In addition, ionic polymers with other bulky ions such as  $\text{PF}_6^-$  will be synthesized to see not only ion conductivity and morphology changes, but also thermal and mechanical property differences.

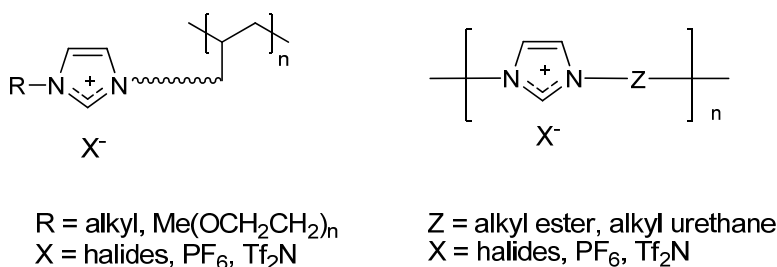


**Figure 9-17.** Pendant imidazolium polymers (left) and main-chain imidazolium polymers with various structural factors (right).

Main-chain imidazolium polymers will be also synthesized by various step-growth polymerizations from the difunctional imidazolium ionic liquids. The difunctionality will be of the **A-A** or **A-B** types. The **A-A** type monomers will be polymerized with other **B-B** type monomers by polyesterification, when **A** and **B** are hydroxy and carboxylic acid (or acid chloride) functionality or vice versa. The alkyl spacer length between the imidazolium units can be controllable from the various **B-B** type counterparts. Polyurethanes are also possible from dihydroxy imidazolium monomers and various diisocyanates. Polyurethanes from copolymerizations with poly(ethylene glycol), poly(propylene glycol), and poly(tetramethylene oxide) are also possible to form segmented main-chain imidazolium polyurethanes.

One interesting step-growth polymerization method is acyclic diene metathesis (ADMET) polymerization. ADMET polymerization is valuable in step-growth polymerization, because it can provide much higher molecular weight polymers when the proper polymerization conditions are met (catalyst, reaction temperature, pressure/vacuum, agitation, and solvent).<sup>52</sup> When imidazolium salts with terminal diene moieties are synthesized, the monomers will be polymerized by ADMET to give main-chain imidazolium polymers containing internal olefin units and further hydrogenation will give precisely defined main-chain poly(1,3-alkylimidazolium salt)s. Diene monomers with pendant imidazolium moieties will give polyethylenes with pendant imidazolium moieties from ADMET and hydrogenation.

All the synthesized imidazolium polymers will be fully characterized by various analytical tools, such as NMR, mass spectrometry, size-exclusion chromatography, thermal analysis (DSC, TGA, DMA and etc), and dielectric spectroscopy (for ionic conductivity and other electrical properties). Some ionic polymers will be applied to construct electroactive devices (actuators) as electrolytes and ion-transporting films.

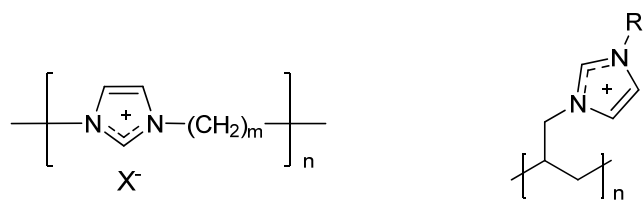


**Figure 9-18.** Main-chain poly(1,3-alkylimidazolium salt)s (left) and pendant imidazolium polyethylenes from ADMET polymerization.

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## Chapter 10

### 1,2-Bis[N-(N'-alkylimidazolium)]ethane Salts as New Guests for Crown Ethers and Cryptands

#### Abstract

1,2-Bis[N-(N'-alkylimidazolium)]ethane salts form pseudorotaxanes with crown ether and cryptand hosts. The association constants of 1,2-bis[N-(N'-butylimidazolium)]ethane bis(hexafluorophosphate) with dibenzo-24-crown-8 and a dibenzo-24-crown-8-based pyridyl cryptand were estimated as  $24 (\pm 1)$  and  $348 (\pm 30)$  M<sup>-1</sup>, respectively, in acetonitrile at 25 °C. The pseudorotaxane structure of the latter complex was confirmed by X-ray crystallography. Replacement of the ethylene spacer with propylene and butylene spacers results in  $K_a$  values an order of magnitude smaller.

#### Introduction

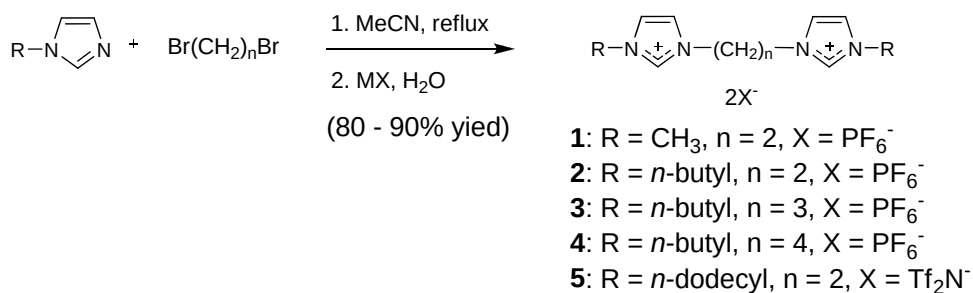
Imidazolium salts have been and are going to be significant not only in organometallic chemistry as precursors of N-heterocyclic carbenes,<sup>1</sup> but also in organic and material science areas as ionic liquids due to their unique chemical, physical and electrical properties.<sup>2</sup> For 1,3-disubstituted imidazolium ionic liquid salts, all of the protons on the imidazolium ring are quite acidic; for example the  $pK_a$  of the C2 proton is 16~24, depending on the nature of the substituents on the two imidazolium nitrogens.<sup>3</sup> The acidic protons are attractive in supramolecular chemistry, since more acidic protons provide stronger hydrogen bonds in the formation of supramolecular complexes, such as pseudorotaxanes.<sup>4</sup> 1-Alkyl-3-methylimidazolium bromides bind with cucurbit[6]uril; the binding constant depends on the number of carbons in the alkyl chain.<sup>5</sup> Schmitzer et al. reported that N,N'-disubstituted (benzyl or phenyl) methylene diimidazolium salts also act as guest molecules for various macrocycles with high association constants ( $K_a = 4200 \sim 7500$  M<sup>-1</sup>) in water:  $\beta$ -cyclodextrin, cucurbit[7]uril, and tetrapropoxy-calix[4]arene.<sup>6</sup> However, they reported lower  $K_a$  values (56 and 120 M<sup>-1</sup>) for

methylene bis[N-(N'-benzylimidazolium)] and methylene bis[N-(N'-phenylimidazolium)] bis(hexafluorophosphate)s with dibenzo-24-crown-8 (DB24C8) in CD<sub>3</sub>CN.

There is a need for structural diversity in supramolecular building blocks; discovery of new pseudorotaxane systems drives new supramolecular structures and applications. On another front, for application of imidazolium salts and other ionic liquids in electroactive actuators, ion conductivity is a key parameter.<sup>7</sup> In earlier work we demonstrated that pseudorotaxane complexes of dibenzylammonium salts with DB24C8<sup>8,9</sup> and its derivatives<sup>10</sup> are not ion paired. Similarly, we reported that the pseudorotaxane complex of N,N'-dimethyl-4,4'-bipyridinium ("paraquat" or "dimethyl viologen") 2PF<sub>6</sub><sup>-</sup> with DB24C8 likewise is not ion paired;<sup>9,11</sup> this was subsequently corroborated by other workers.<sup>12</sup> It therefore appeared to us that pseudorotaxanes derived from DB24C8 and imidazolium ionic liquids would possess a larger fraction of "free" ions than the ionic liquids themselves and thus possess enhanced performance in electroactive bending actuators. Driven by these two separate but related goals, here we report new ionic guests, alkylene 1,2-bis[N(N'-alkylimidazolium)] salts with different alkyl substituents, for complexation with crown-type host molecules. We also investigated the effect of C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub> spacers on their complexation with DB24C8.

## Results and discussion

The preparations of the imidazolium dicationic salts **1** – **5** are done in two steps (Scheme 10-1): the coupling reaction of the 1-alkylimidazole (2 molar equivalents) with a dibromoalkane (1 molar equivalent) and anion exchange in water. Non-commercial 1-hexylimidazole and 1-dodecylimidazole were prepared before quaternization.<sup>13</sup> Most of the intermediate alkylene bis[N-(N'-alkylimidazolium)] bromide salts were very hygroscopic; however, the imidazolium salts of PF<sub>6</sub><sup>-</sup> and Tf<sub>2</sub>N<sup>-</sup> salts are non-hygroscopic due to their hydrophobic anions.



**Scheme 10-1.** Synthesis of alkylene bis(N-alkylimidazolium) salts.

The complexation of **2** and DB24C8 was qualitatively observed by  $^1\text{H}$ -NMR in  $\text{CD}_3\text{CN}$ . After adding excess DB24C8 to a solution of **2** in  $\text{CD}_3\text{CN}$  at 25 °C, the imidazolium protons moved upfield. This system undergoes fast-exchange; only time-averaged signals appear in the  $^1\text{H}$  NMR spectrum (Figure 10-1). The fast-exchange in this complexation is reasonable due to the rod-like geometry of **2** which in solution probably has a *trans*-conformation predominantly, consistent with the solid-state structure of **1** (Figure 10-3). The fast exchange behavior exhibited by these systems is in contrast to the slow exchange reported for the methylene bridged bis(imidazolium) salts.<sup>6</sup>

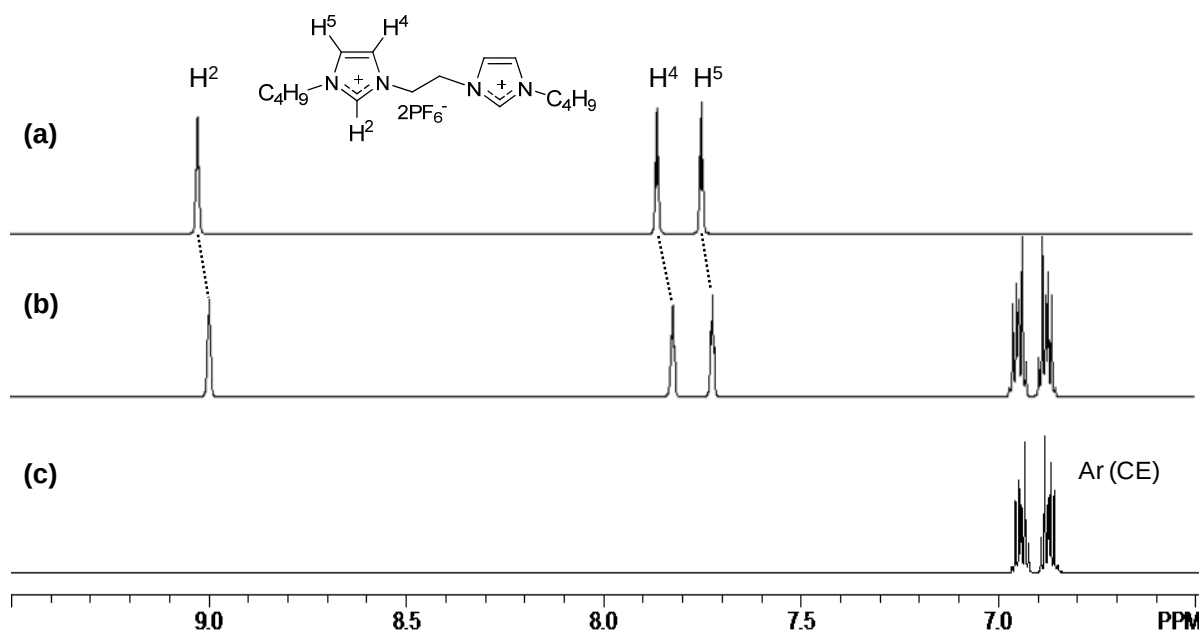


**Figure 10-1.** Partial 400 MHz  $^1\text{H}$  NMR spectra of (a) **2** (2 mM), (b) **2** + DB24C8 (1:5 molar ratio, 2 mM of **2**), and (c) DB24C8 (10 mM) in  $\text{CD}_3\text{CN}$  at 25 °C.

Isothermal microcalorimetric titration (ITC) was used to quantify the complexations of the host and guest compounds in solution. The results are summarized in Table 10-1.<sup>14</sup> All experiments were performed under ambient conditions at 25 °C. The association constants and enthalpies of N,N'-dimethyl ethylene linked **1** and N,N'-dibutyl ethylene linked **2** with DB24C8 in MeCN are similar to each other and slightly lower than the  $K_a$  ( $56\text{ M}^{-1}$ ) of bis[N-(N'-benzylimidazolium)]methane  $2\text{PF}_6^-$  with DB24C8 determined by Schmitzer et al. using a single point NMR integration,<sup>6</sup> which could be subject to significant error.<sup>8-11</sup> The two imidazolium rings of methylene bis(imidazolium) salts cannot be parallel due to the tetrahedral geometry of

the methylene spacer. In the case of the two-carbon spacer the *trans*-conformation of the ethylene unit is preferred (at room temperature, Figure 10-3). The previously reported interactions of dicationic guests, bis(pyridinium)ethane<sup>15</sup> and bis(benzimidazolium)ethane salts,<sup>16</sup> with DB24C8, are also good examples to support our idea. We predicted that the two imidazolium rings of **2** would be parallel and individually interact with the  $\pi$ -electron rich aromatic rings of DB24C8, leading to  $\pi$ -stacking interactions and higher  $K_a$  values. Contrary to our expectations based on these conformational, i. e., entropic arguments, the observed higher  $K_a$  values for the methylene<sup>6</sup> vs. the ethylene spacer can be attributed to the higher acidity of the methylene protons as a result of the two neighboring positively charged nitrogen atoms.

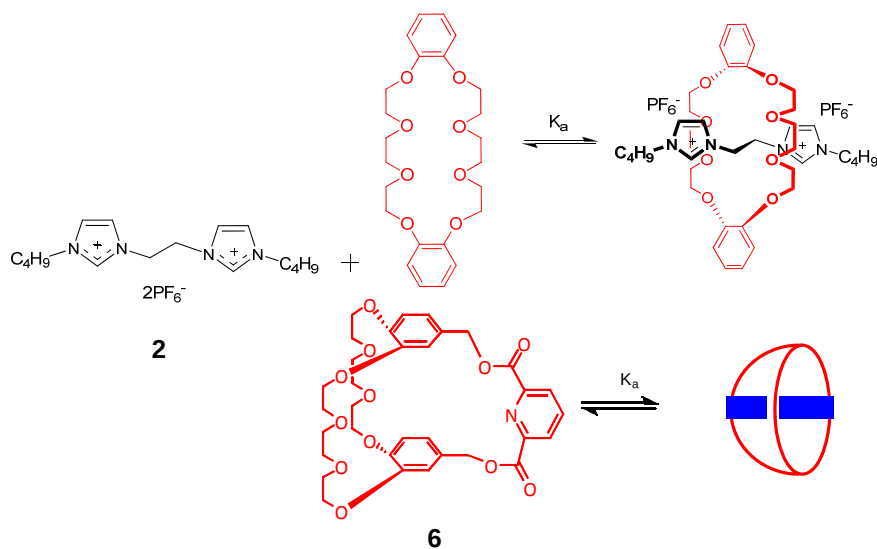


**Figure 10-2.** Schematic diagram of complexation of **2** with DB24C8 and DB24C8-based pyridyl cryptand **6**.<sup>11</sup>

The  $K_a$  values for complexations of **3** ( $C_3$  spacer) and **4** ( $C_4$  spacer) with DB24C8 are an order of magnitude smaller than those of the analogous compound with a  $C_2$  spacer (**2**). From a molecular structural viewpoint, three and four carbons between the imidazolium moieties make it less likely that both can interact with the aromatic rings of DB24C8. The spatial requirements for formation of hydrogen bonds are also less likely to be met when the two imidazolium rings are far from each other. Furthermore, only the protons of the methylene units attached to the positively charged nitrogen atoms are acidic enough to form hydrogen bonds with the crown ether oxygens; additional carbons in the spacer only increase the number of unfavorable binding conformations. Indeed the results support this analysis. The enthalpic changes for complexes of

DB24C8 with **2**, **3** and **4** are identical within experimental error; the order of magnitude decrease in  $K_a$  from the two carbon spacer to the four carbon spacer is entirely due to an increased entropic penalty for complexation, increasing from 2.0 to 5.2 to 6.8 eu, respectively.

The imidazolium salt **5** with *n*-dodecyl arms was synthesized to observe the complexation in a less polar solvent. However, the  $K_a$  of **5** and DB24C8 in CHCl<sub>3</sub> at room temperature was almost the same as the  $K_a$  of the analogous methyl analog **1** in acetonitrile. Apparently the longer terminal chains are detrimental and offset the lower polarity of the solvent. This is reflected by the fact that the enthalpy of complexation of **5** with DB24C8 is actually 2.5 times more exothermic than that of **1**, as a result of the lower polarity solvent, but **5** suffers a 7-fold larger entropic penalty, apparently due to the long alkyl side chains.

**Table 10-1.** ITC Results: Complexation of Imidazolium Salts by DB24C8 and Cryptand **6**.

| Imidazolium Salt | Macrocycle | Solvent           | $K_a$ (M <sup>-1</sup> ) <sup>a</sup> | $\Delta H$ (kcal/mol) | $-\Delta S$ (cal/mol·deg) |
|------------------|------------|-------------------|---------------------------------------|-----------------------|---------------------------|
| <b>1</b>         | DB24C8     | MeCN              | $27 \pm 3$                            | $-2.7 \pm 0.3$        | $2.3 \pm 1.1$             |
| <b>2</b>         | DB24C8     | MeCN              | $24 \pm 1$                            | $-2.5 \pm 0.1$        | $2.0 \pm 0.3$             |
| <b>3</b>         | DB24C8     | MeCN              | $4.3 \pm 0.8$                         | $-2.4 \pm 0.3$        | $5.2 \pm 1.4$             |
| <b>4</b>         | DB24C8     | MeCN              | $2.2 \pm 0.7$                         | $-2.5 \pm 0.4$        | $6.8 \pm 2.0$             |
| <b>5</b>         | DB24C8     | CHCl <sub>3</sub> | $30 \pm 1$                            | $-6.7 \pm 0.1$        | $16 \pm 1$                |
| <b>2</b>         | <b>6</b>   | MeCN              | $348 \pm 30$ <sup>b</sup>             | $-8.0 \pm 0.2$        | $15 \pm 1$                |

<sup>a</sup> All of the complexes are of 1:1 stoichiometry; other assumed stoichiometries resulted in poorer fits.

<sup>b</sup> For 1:1 assumed stoichiometry. 2:1 H:G stoichiometry yielded:  $K_a = 166 \pm 8$ ;  $\Delta H = 18.1$  kcal/mol;  $\Delta S = 50$  cal/mol·deg.

Complexation of *N*-butyl compound **2** with the DB24C8-based pyridyl cryptand **6**<sup>11</sup> was also observed by ITC. Its  $K_a$  is >10 times higher and the exothermic enthalpy change is 3.2-fold larger than the binding of **2** with DB24C8. In spite of the sizeable entropic penalty (15 eu), the larger  $K_a$  and enthalpy change are due to the presence of more binding sites on the cryptand. We tried to investigate the stoichiometry of the complex of **2** and **6** by <sup>1</sup>H NMR in CD<sub>3</sub>CN; however, to our surprise the chemical shift changes were within experimental error across a range of ratios with a total concentration of 2.2 mM.<sup>17</sup>

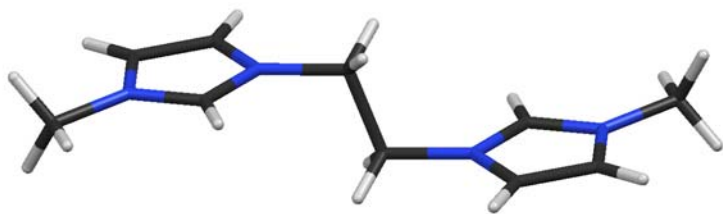
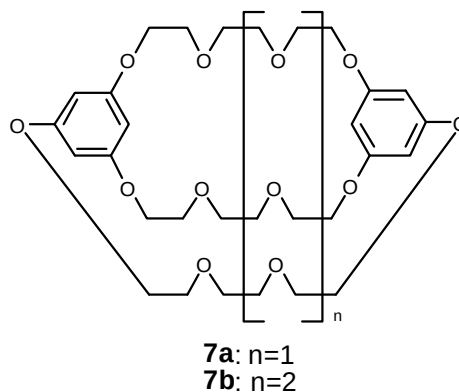


**Figure 10-3.** A capped-sticks view of the X-ray structure of **1**. PF<sub>6</sub> anions are omitted for clarity. Ring plane/ring plane inclination of the two imidazolium rings: 0°.

The formation of these complexes was also confirmed by high resolution ESI TOF mass spectrometry (see SI). A solution of **1** and DB24C8 yielded  $m/z$  785.3108, which corresponds to the 1:1 complex after loss of one PF<sub>6</sub><sup>−</sup> ion ([**1** + DB24C8 - PF<sub>6</sub>]<sup>+</sup>, calcd. for C<sub>34</sub>H<sub>48</sub>N<sub>4</sub>O<sub>8</sub>PF<sub>6</sub> 785.3114). A solution of **2** and DB24C8 yielded  $m/z$  869.4050, after loss of one PF<sub>6</sub><sup>−</sup> ion from the 1:1 complex ([**2** + DB24C8 - PF<sub>6</sub>]<sup>+</sup>, calcd. for C<sub>40</sub>H<sub>60</sub>N<sub>4</sub>O<sub>8</sub>PF<sub>6</sub> 869.4062). A solution of **5** and DB24C8 gave  $m/z$  1228.5961, corresponding to the 1:1 complex after loss of one Tf<sub>2</sub>N<sup>−</sup> anion ([**5** + DB24C8 - Tf<sub>2</sub>N]<sup>+</sup>, calcd. for C<sub>58</sub>H<sub>92</sub>F<sub>6</sub>N<sub>5</sub>O<sub>12</sub>S<sub>2</sub> 1228.6082). Solutions of cryptand **6** and the imidazolium salts also gave mass numbers corresponding to the 1:1 complexes:  $m/z$  976.3349 ([**1** + **6** - PF<sub>6</sub>]<sup>+</sup>, calcd. for C<sub>43</sub>H<sub>53</sub>N<sub>5</sub>O<sub>12</sub>PF<sub>6</sub> 976.3333) and  $m/z$  1060.4311 ([**2** + **6** - PF<sub>6</sub>]<sup>+</sup>, calcd. for C<sub>49</sub>H<sub>65</sub>N<sub>5</sub>O<sub>12</sub>PF<sub>6</sub> 1060.4281). Every host-guest solution revealed only 1:1 host/guest complex peaks, even with an excess of the host.

A crystal structure of **1**·(**6**)<sub>2</sub> (Figure 10-4) shows that the pseudorotaxane-like structure<sup>18-20</sup> in the solid state was formed from one guest **1** and two hosts **6**. This observation of different stoichiometries in solution and the solid state is consistent with several other crown ether and cryptand complexes: both cryptands **7a** and **7b** with paraquat,<sup>20</sup> DB24C8 with paraquat,<sup>11</sup> bis(*p*-xylyl)-26-crown-8 with paraquat,<sup>21</sup> DB24C8 with N,N'-dialkyl paraquats,<sup>22</sup> and DB24C8 with “diquat” (N,N'-ethylene-2,2'-bipyridinium 2PF<sub>6</sub><sup>−</sup>).<sup>23</sup>



The structure of guest **1** in the present complex (Figure 10-4) is somewhat different from the crystal structure of **1** itself (Figure 10-3); the imidazolium planes are twisted at a 44° angle, to accommodate the  $\pi$ - $\pi$  stacking with the two aromatic rings of **6**. Centroid to centroid distances of the phenylene and imidazolium rings are 3.6~3.9 Å and dihedral angles of the phenylene and

imidazolium planes are 12~23°. The catechol rings of different host molecules in the 1:2 complex are significantly tilted, which causes the twisted imidazolium rings. All of the hydrogens of **1** are hydrogen-bonded with oxygen atoms (or the nitrogen atom) of **6**. One of the imidazolium hydrogens interacts with the nitrogen atom and the other two bind with oxygens in the ethyleneoxy arms. Interestingly ester carbonyl oxygens seem to strongly interact with the ethylene protons of **1**; the H···O distances are 2.23 and 2.30 Å (**g** and **h** in Figure 10-4).

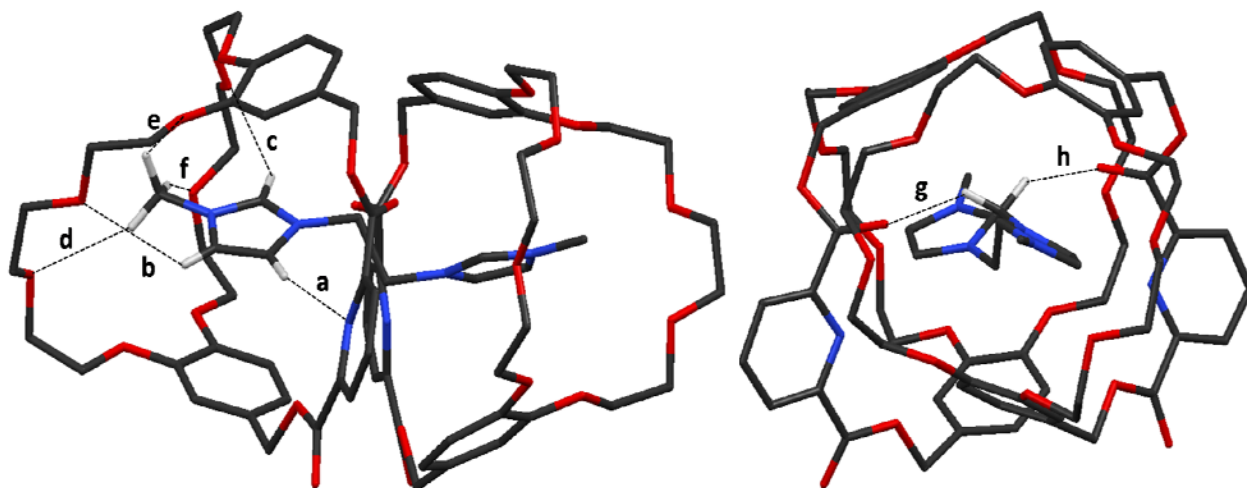


**Figure 10-4.** Two capped-sticks views of the X-ray structure of **1**·(**6**)<sub>2</sub>: side view (left) and end view (right). There are two complexes in the unit cell and they are similar but not identical. These views are one of the complexes. PF<sub>6</sub><sup>−</sup> anions, MeCN molecules and some hydrogens are omitted for clarity. One PF<sub>6</sub><sup>−</sup> anion is disordered. H···O (or N) distances (Å), C-H···O (or N) angles (degrees) of : a 2.60, 165.4; b 2.89, 126; c 2.64, 138; d 2.71, 155; e 2.68, 122; f 2.79, 166; g 2.30, 135; h 2.23, 145.

## Conclusions

The complexation of alkylene 1,2-bis[N-(N'-alkylimidazolium)] salts with DB24C8 was confirmed by <sup>1</sup>H NMR spectroscopy, mass spectrometry and ITC titrations. The association constants for pseudorotaxane (or pseudorotaxane-like complex) formation from the 1,2-bis[N-(N'-alkylimidazolium)]ethanes with DB24C8 in solution are  $K_a = 24$  to  $30 \text{ M}^{-1}$  in MeCN or CHCl<sub>3</sub> and  $K_a = 348 \text{ M}^{-1}$  in MeCN for **2** with cryptand **6**. However, alkylene bis[N-(N'-alkylimidazolium)] salts with a C<sub>3</sub> or C<sub>4</sub> spacer show weaker binding with DB24C8. The host/guest threaded structure was confirmed by the X-ray crystal structure of the 1:2 complex of **1** and **6**; every proton of the guest molecule participates in hydrogen bonding with oxygen or nitrogen atoms of the cryptand **6**. These readily accessible imidazolium salts are expected to be

valuable in the construction of larger supramolecular systems, such as polypseudorotaxanes,<sup>24</sup> and in construction of pseudorotaxane or rotaxane actuators based on ionic liquids and polyelectrolytes. Our results in these areas will be published in due course.

## Experimental

**Materials.** Dibenzo-24-crown-8 was purchased and used directly from Aldrich Chem. Co. Inc. Acetone for the quaternization reactions was dried with anhydrous CaSO<sub>4</sub> and then distilled. Acetonitrile was dried with anhydrous K<sub>2</sub>CO<sub>3</sub> and then distilled. All other chemicals and solvents were used as received.

**Instruments.** <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained on Varian Inova 400 MHz and Unity 400 MHz spectrometers. High resolution electrospray ionization time-of-flight mass spectrometry (HR ESI TOF MS) was carried out on an Agilent 6220 Accurate Mass TOF LC/MS Spectrometer in positive ion mode. Melting points were observed on a Büchi B-540 apparatus at a 2 °C/min heating rate. ITC titrations were run on a Microcal MCS ITC. Raw isotherm data were collected using the Microcal Observer software. Integration and fitting of the isothermal data (*K<sub>a</sub>* and  $\Delta H$ ) were accomplished using Origin software with a one set of sites algorithm.

**General anion exchange procedure.** Into a solution of bromide salt (1 equivalent) in deionized water, KPF<sub>6</sub> (or LiTf<sub>2</sub>N, 2-4 equivalents) was added with stirring, which continued for 1-2 hours at room temperature. The precipitate was filtered and washed with deionized water twice. Drying in a vacuum oven gave the pure imidazolium PF<sub>6</sub><sup>-</sup> (or Tf<sub>2</sub>N<sup>-</sup>) salt.

**1,2-Bis[N-(N'-methylimidazolium)]ethane bis(hexafluorophosphate) (1).** A solution of 1-methylimidazole (2.49 g, 30 mmol) and 1,2-dibromoethane (2.82 g, 15 mmol) in MeCN (20 mL) was refluxed for 3 days. The precipitate was filtered after cooling, and washed with tetrahydrofuran (THF) 3 times. Drying in a vacuum oven gave colorless crystalline bromide salt (4.54 g, 86%), mp 231.1–233.8 °C (lit. mp = 230–234 °C).<sup>25</sup> **1** was obtained by following general anion exchange procedure; from bromide salt (4.50 g), KPF<sub>6</sub> (5.52 g, 30 mmol) and deionized water (40 mL) colorless crystalline solid **1** (5.26 g, 73% based on 1,2-dibromoethane), mp 213.8–214.9 °C, was isolated. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN 23 °C):  $\delta$  3.85 (s, 6H), 4.62 (s, 4H), 7.33 (t, J=2, 2H), 7.42 (t, J=2, 2H), 8.40 (s, 2H). <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>CN, 23 °C):  $\delta$  37.2, 49.7, 123.5, 125.6, 137.6. HR ESI MS: m/z 337.1022 ([M-PF<sub>6</sub>]<sup>+</sup>, calcd. for C<sub>10</sub>H<sub>16</sub>N<sub>4</sub>PF<sub>6</sub> 337.1017, error 1.5 ppm).



**1,2-Bis[N-(N'-butylimidazolium)]ethane bis(hexafluorophosphate) (2).** The same procedure was used as for **1**. From 1-butylimidazole (6.21 g, 50 mmol) and 1,2-dibromoethane (4.69 g, 25 mmol) in MeCN (25 mL) colorless crystalline bromide salt (9.64 g, 88%), mp 166.5–168.2 °C, was produced. The anion exchange procedure was used; from the bromide salt (1.30 g, 3.0 mmol) and KPF<sub>6</sub> (1.65 g, 9 mmol) in deionized water (10 mL) colorless crystalline **2** (1.54 g, 91%), mp 181.6–182.5 °C, was isolated. <sup>1</sup>H NMR (400 MHz, acetone-*d*<sub>6</sub>, 23 °C): δ 0.94 (t, J=7, 6H), 1.33 (m, 4H), 1.78-1.85 (m, 4H), 4.14 (m, 4H), 5.04 (s, 4H), 7.39 (m, 4H), 8.42 (s, 2H). <sup>13</sup>C NMR (100 MHz, acetone-*d*<sub>6</sub>, 23 °C): δ 13.5, 19.8, 32.4, 49.9, 50.6, 123.6, 124.2, 137.5. HR ESI MS: m/z 421.1966 ([M-PF<sub>6</sub>]<sup>+</sup>, calcd. for C<sub>16</sub>H<sub>28</sub>N<sub>4</sub>PF<sub>6</sub> 421.1950, error 3.2 ppm).

**1,3-Bis[N-(N'-butylimidazolium)]propane bis(hexafluorophosphate) (3)** The same procedure was used as for **1**, except the bromide salt could not be filtered because it was a viscous oil. From 1-butylimidazole (3.73 g, 30 mmol) and 1,3-dibromopropane (3.03 g, 15 mmol) in MeCN (20 mL), a light brown viscous liquid (bromide salt, 5.81 g, 86%) was isolated. The anion exchange procedure was used; from the oily bromide salt (5.00 g, 11.1 mmol) and KPF<sub>6</sub> (6.20 g, 33 mmol) in deionized water (40 mL) colorless crystalline solid **3** (6.25 g, 97% from the bromide salt), mp 96.4–97.7 °C, resulted. <sup>1</sup>H NMR (400 MHz, acetone-*d*<sub>6</sub>, 23 °C): δ 0.94 (t, J=7, 6H), 1.38 (m, 4H), 1.94 (m, 4H), 2.74 (m, 2H), 4.36 (t, J=7, 4H), 4.55 (t, J=7, 2H), 7.81 (m, 4H), 9.12 (s, 2H). <sup>13</sup>C NMR (100 MHz, acetone-*d*<sub>6</sub>, 23 °C): δ 13.6, 20.0, 31.5, 32.6, 47.5, 50.4, 123.6, 123.9, 136.9. HR ESI MS: m/z 435.2143 ([M-PF<sub>6</sub>]<sup>+</sup>, calcd. for C<sub>17</sub>H<sub>30</sub>N<sub>4</sub>PF<sub>6</sub> 435.2112, error 7.1 ppm)

**1,4-Bis[N-(N'-butylimidazolium)]butane bis(hexafluorophosphate) (4)** The same procedure was used as for **3**; from 1-butylimidazole (3.73 g, 30 mmol) and 1,4-dibromobutane (3.24 g, 15 mmol) in MeCN (20 mL), a light brown viscous liquid (bromide salt, 5.71 g, 82%) resulted. The anion exchange procedure was used; from the oily bromide salt (5.70 g, 2.3 mmol) and KPF<sub>6</sub> (5.56 g, 30 mmol) in deionized water (40 mL) **4** was isolated as an off-white viscous liquid (7.05 g, 96% from the bromide salt), which solidified in a vacuum oven, mp 50.4–52.4 °C. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN, 23 °C): δ 0.94 (t, J=7, 6H), 1.34 (m, 4H), 1.78-1.85 (m, 8H), 2.74 (m, 4H), 4.14 (m, 8H), 7.38 (m, 4H), 8.42 (s, 2H). <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>CN, 23 °C): δ 13.7, 20.0, 27.2, 32.5, 49.8, 50.4, 123.4, 123.6, 136.3. HR ESI MS: m/z 449.2304 ([M-PF<sub>6</sub>]<sup>+</sup>, calcd. for C<sub>18</sub>H<sub>32</sub>N<sub>4</sub>PF<sub>6</sub> 449.2269, error 7.9 ppm)

**1-Dodecylimidazole.** To a solution of imidazole (6.81 g, 100 mmol) in NaOH (50%) solution (8.80 g, 110 mmol), 1-bromododecane (24.92 g, 100 mmol) and THF (30 mL) were added. The

mixture was refluxed for 3 days. After the mixture had cooled, THF was removed by a rotoevaporator. The residue was extracted with dichloromethane/water 3 times. The combined organic layer was washed with water and then dried over Na<sub>2</sub>SO<sub>4</sub>. The drying agent was filtered off and the filtrate solution was concentrated. Column chromatography through a short silica-gel column with THF gave a clear yellow oil 20.51 g (87%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 22 °C): δ 0.88 (t, J=7, 3H), 1.29 (m, 18H), 1.76 (m, J=7, 2H), 3.91 (t, J=7, 4H), 6.90 (s, 1H), 7.05 (s, 1H), 7.45 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 22 °C): δ 14.0, 22.6, 26.4, 29.0, 29.2, 29.3, 29.4, 29.5, 31.0, 31.8, 46.9, 118.6, 129.2, 136.9. The <sup>1</sup>H-NMR spectrum was exactly identical to the literature report.<sup>24</sup>

**1,2-Bis[N-(N'-dodecylimidazolium)]ethane bis[bis(trifluoromethanesulfonyl)imide] (5).** A solution of 1-dodecylimidazole (3.78 g, 16 mmol) and 1,2-dibromoethane (1.50 g, 8 mmol) in MeCN (15 mL) was refluxed for 3 days. After the mixture had cooled, the volatile materials were removed by vacuum. The residue was dispersed in THF (30 mL) and the insoluble bromide salt was filtered. The filter cake was washed with THF 3 times. Drying in a vacuum oven gave colorless crystalline solid (bromide salt, 4.54 g, 86%), mp 249.3–252.9 °C (dec). The general anion exchange procedure was used, except the mixture was stirred at 50 °C for 24 hours; from the bromide salt (2.70 g, 6.4 mmol), LiTf<sub>2</sub>N (4.32 g, 15 mmol) and deionized water (60 mL), crystalline **5** (3.89 g, 97% from the bromide salt), mp 45.5–47.7 °C, was isolated. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub> 23 °C): δ 0.87 (t, J=7, 6H), 1.25–1.31 (m (br), 36H), 1.86 (t, J=7, 4H), 4.15 (t, J=7, 4H), 4.74 (s, 4H), 7.33 (t, J=2, 2H), 7.60 (t, J=2, 2H), 8.84 (s, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 23 °C): δ 14.2, 22.8, 26.3, 29.0, 29.4, 29.5, 29.6, 29.7, 32.0, 48.5, 50.7, 123.0, 123.3, 136.0. HR ESI MS: m/z 780.3997 ([M-Tf<sub>2</sub>N]<sup>+</sup>, calcd. for C<sub>34</sub>H<sub>60</sub>F<sub>6</sub>N<sub>5</sub>O<sub>4</sub>S<sub>2</sub> 780.3985, error 0.8 ppm).

**Example of ITC Titration Methods.** Stock solutions of titrant **1** (175 mM) and **6** (6.11 mM) in MeCN were prepared using volumetric flasks. All titrations were run at 25 °C. The high gain (high sensitivity) system was used, and the reference offset was set at 50% of the maximum. During each titration, 10 injections of 2.0 μL, 20 injections of 2.5 μL, 25 injections of 3.0 μL, and 26 injections of 4.0 μL of **1** were made consecutively into the cell containing **6**. Injections were made every 180 s with a primary filter period of 2 s, and a secondary filter period of 4 s. The switch time for the filter periods was at 120 s. After the titration isotherm was recorded, the raw data were reduced using commercial software and the supplied algorithms from the manufacturer. A control titration was also completed so that the heat of dilution from the titrant

could be subtracted from the original titration isotherm. The parameters of the control titration were the same as those used in the original titration with the exception that the cell solution was replaced with pure MeCN. The control isotherm was integrated using the same method as the original titration and the energy values obtained were subtracted from the integrated point plot of the original titration. The integration data from the titrations were fit using the “One Set of Sites” model; other stoichiometries yielded unsatisfactory fits of the data.

**Crystal growing and crystallography of 1.** Colorless prisms crystallized from acetone/pentane at room temperature. The chosen crystal was centered on the goniometer of an Oxford Diffraction Gemini A Ultra diffractometer operating with MoK $\alpha$  radiation. The data collection routine, unit cell refinement, and data processing were carried out with the program CrysAlisPro.<sup>25</sup> The Laue symmetry and systematic absences were consistent with the monoclinic space groups *C2/c* and *Cc*. The centric space group *C2/c* was chosen based on the E-statistics. The structure was solved by direct methods and refined using SHELXTL NT.<sup>26</sup> The asymmetric unit of the structure comprises 0.5 crystallographically independent molecules. The final refinement model involved anisotropic displacement parameters for non-hydrogen atoms and a riding model for all hydrogen atoms.

Crystal data: prism, colorless, crystal size = 0.21 x 0.21 x 0.09 mm<sup>3</sup>, C<sub>10</sub>H<sub>16</sub>N<sub>4</sub>•2PF<sub>6</sub>, M = 482.21, wavelength = 0.71073 Å, monoclinic, space group *C2/c*, *a* = 22.186(3) Å, *b* = 6.4852(3) Å, *c* = 14.4065(13) Å,  $\alpha$  = 90°,  $\beta$  = 122.621(15)°,  $\gamma$  = 90°, *V* = 1745.8(3) Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.835 Mg/m<sup>3</sup>, *T* = 100(2) K,  $\mu$  = 0.376 mm<sup>-1</sup>, 11193 reflections collected, 2562 [*R*(int) = 0.0300] independent reflections, 2562 / 0 / 128 data / restraints / parameters, *F*(000) = 968, *R*<sub>1</sub> = 0.0358, *wR*<sub>2</sub> = 0.0780 (all data), *R*<sub>1</sub> = 0.0288, *wR*<sub>2</sub> = 0.0759 [*I* > 2 $\sigma$ (*I*)], and goodness-of-fit on *F*<sup>2</sup> = 1.051.

**Crystal growing and crystallography of 2.** Colorless plates crystallized from acetone/pentane by vapor diffusion. The chosen crystal was centered on the goniometer of an Oxford Diffraction Gemini A Ultra diffractometer operating with MoK $\alpha$  radiation. The data collection routine, unit cell refinement, and data processing were carried out with the program CrysAlisPro.<sup>27</sup> The Laue symmetry was consistent with the triclinic space group *P*-1. The structure was solved by direct methods and refined using SHELXTL NT.<sup>28</sup> The asymmetric unit of the structure comprises 0.5 crystallographically independent formula units. The final refinement model involved anisotropic displacement parameters for non-hydrogen atoms and a riding model for all hydrogen atoms. The PF<sub>6</sub> anion was modeled with 2-position disorder with relative occupancies that refined to

0.761(9) and 0.239(9). The P-F bond lengths and the F---F distances were restrained with DFIX and the anisotropic displacement parameters of the disordered fluorine atoms were restrained with SIMU.

Crystal data: plate, colorless, crystal size = 0.03 x 0.18 x 0.47 mm<sup>3</sup>, C<sub>16</sub>H<sub>28</sub>N<sub>4</sub>•2PF<sub>6</sub>, M = 566.36, wavelength = 0.71073 Å, triclinic, space group P-1, *a* = 6.5214(3) Å, *b* = 6.9156(3) Å, *c* = 13.8874(7) Å,  $\alpha$  = 97.336(4)°,  $\beta$  = 97.674(4)°,  $\gamma$  = 99.448(4)°, *V* = 605.07(5) Å<sup>3</sup>, *Z* = 1, *D<sub>c</sub>* = 1.554 Mg/m<sup>3</sup>, *T* = 100(2) K,  $\mu$  = 0.284 mm<sup>-1</sup>, 6608 reflections collected, 2795 [R(int) = 0.0338] independent reflections, 2795 / 60 / 193 data / restraints / parameters, F(000) = 290, *R*<sub>1</sub> = 0.0961, *wR*<sub>2</sub> = 0.1269 (all data), *R*<sub>1</sub> = 0.0517, *wR*<sub>2</sub> = 0.1129 [*I* > 2σ(*I*)], and goodness-of-fit on *F*<sup>2</sup> = 0.989.

**Crystal growing and crystallography of 1·(6)<sub>2</sub>.** A colorless plate of 1·(6)<sub>2</sub> was obtained in two steps. First, a 1:2 mixture of 1 and 6 was dissolved in MeCN and then the solvent was removed by evaporation in an open vial at room temperature. Then, the residue was re-dissolved in acetone and the crystal was grown by vapor diffusion of pentane into the acetone solution at room temperature. The colorless plate was centered on the goniometer of an Oxford Diffraction SuperNova diffractometer operating with CuKα radiation. The data collection routine, unit cell refinement, and data processing were carried out with the program CrysAlisPro.<sup>27</sup> The Laue symmetry and systematic absences were consistent with the monoclinic space group *P*2<sub>1</sub>/*n*. The structure was solved by direct methods and refined using SHELXTL NT.<sup>28</sup> In the final refinement model, the asymmetric unit included 4 host molecules, 2 guest salts, 7 CH<sub>3</sub>CN, an one partially occupied H<sub>2</sub>O. A 2 position disorder model was used for one PF<sub>6</sub><sup>-</sup>, 2 C-atoms in the arm of a host molecule, and one CH<sub>3</sub>CN molecule. The CH<sub>3</sub>CN is disordered across an inversion center and relative occupancies were constrained to 0.5. The relative occupancies of the remaining disordered atoms refined to 0.59 and 0.41. For steric reasons, the water molecule could only be present at the same time as the disordered PF<sub>6</sub><sup>-</sup> with occupancy 0.59; consequently, the water occupancy was tied to the PF<sub>6</sub><sup>-</sup> occupancy of 0.59. Anisotropic displacement parameters suggest additional PF<sub>6</sub><sup>-</sup> and CH<sub>3</sub>CN disorder, but attempts to model this disorder did not improve the model and were abandoned. All non-hydrogen atoms were refined anisotropically except for 2 CH<sub>3</sub>CN molecules and the partially occupied water molecule. A riding model was used for all hydrogen atoms. The H-atoms of the water molecule were not included in the refinement.

Crystal data: plate, colorless, crystal size = 0.4460 x 0.1156 x 0.0205 mm<sup>3</sup>, 2{[(C<sub>33</sub>H<sub>37</sub>NO<sub>12</sub>)<sub>2</sub>•C<sub>10</sub>H<sub>16</sub>N<sub>4</sub>][PF<sub>6</sub>]<sub>2</sub>}•7C<sub>2</sub>H<sub>3</sub>N•0.59H<sub>2</sub>O, M = 3820.97, wavelength = 1.54178 Å, monoclinic, space group *P* 2<sub>1</sub>/*n*, *a* = 30.5666(14) Å, *b* = 14.1326(5) Å, *c* = 42.0175(18) Å,  $\alpha$  = 90°,  $\beta$  = 99.972(4)°,  $\gamma$  = 90°, *V* = 17876.7(13) Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.420 Mg/m<sup>3</sup>, *T* = 100(2) K,  $\mu$  = 1.356 mm<sup>-1</sup>, 89614 reflections collected, 34633 [R(int) = 0.0563] independent reflections, 34633 / 66 / 2413 data / restraints / parameters, *F*(000) = 7984, *R*<sub>1</sub> = 0.1248, *wR*<sub>2</sub> = 0.2297 (all data), *R*<sub>1</sub> = 0.0820, *wR*<sub>2</sub> = 0.2095 [*I* > 2σ(*I*)], and goodness-of-fit on *F*<sup>2</sup> = 1.030.

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## Supporting Information

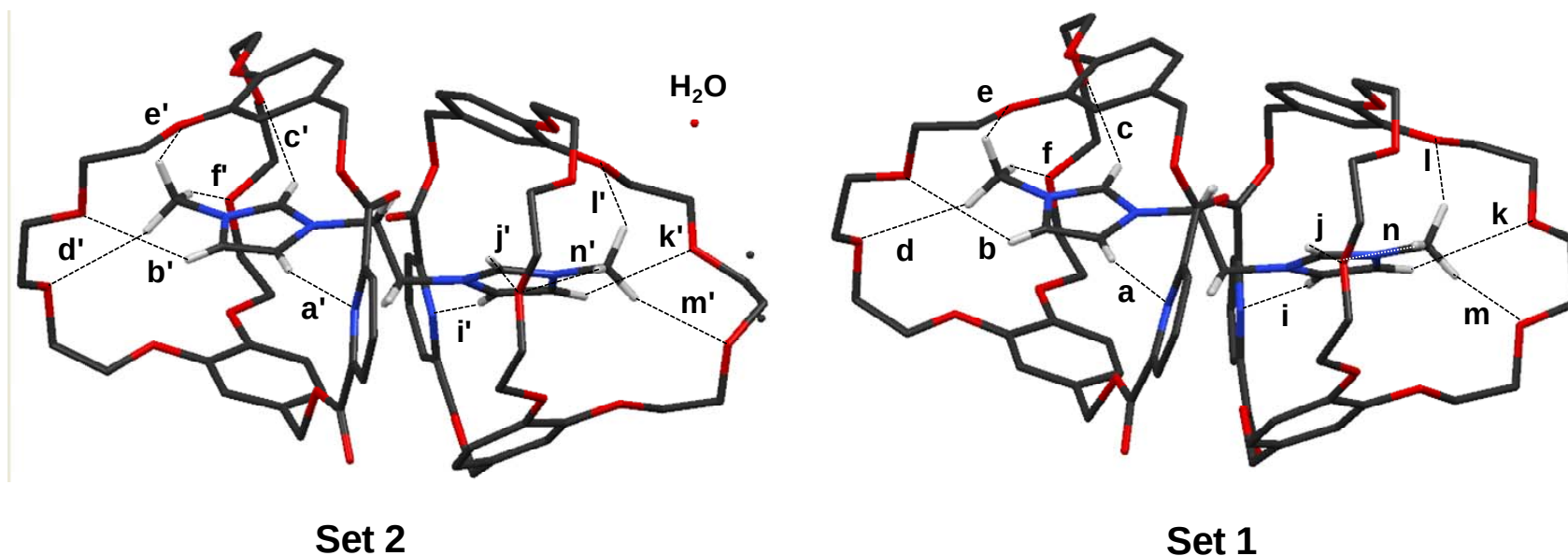


**Figure 10-S1.** Capped-sticks views of the X-ray structure of  $1 \cdot (6)_2$ : two sets of complex are in the asymmetric unit. **Set 1** is shown in the Fig. 4 of the main text. Two carbon atoms of a disordered ethyleneoxy arm, the  $\text{PF}_6^-$  anions, the MeCN molecules, and H-atoms not involved in hydrogen bonding are omitted for clarity. H $\cdots$ O (or N) distances (Å), C-H $\cdots$ O (or N) angles (degrees) of : (**Set 1**) **a** 2.60, 165.4; **b** 2.89, 126; **c** 2.64, 138; **d** 2.71, 155; **e** 2.68, 122; **f** 2.79, 166; **i** 2.71, 163; **j** 2.53, 138; **k** 3.04, 139; **l** 2.76, 132; **m** 2.38, 151; **n** 2.56, 152; (**Set 2**) **a'** 2.64, 160; **b'** 2.72, 132; **c'** 2.63, 138; **d'** 2.68, 162; **e'** 2.76, 122; **f'** 2.66, 169; **i'** 2.67, 172; **j'** 2.40, 134; **k'** 2.77, 129; **l'** 2.79, 125; **m'** 2.50, 160; **n'** 2.60, 146.

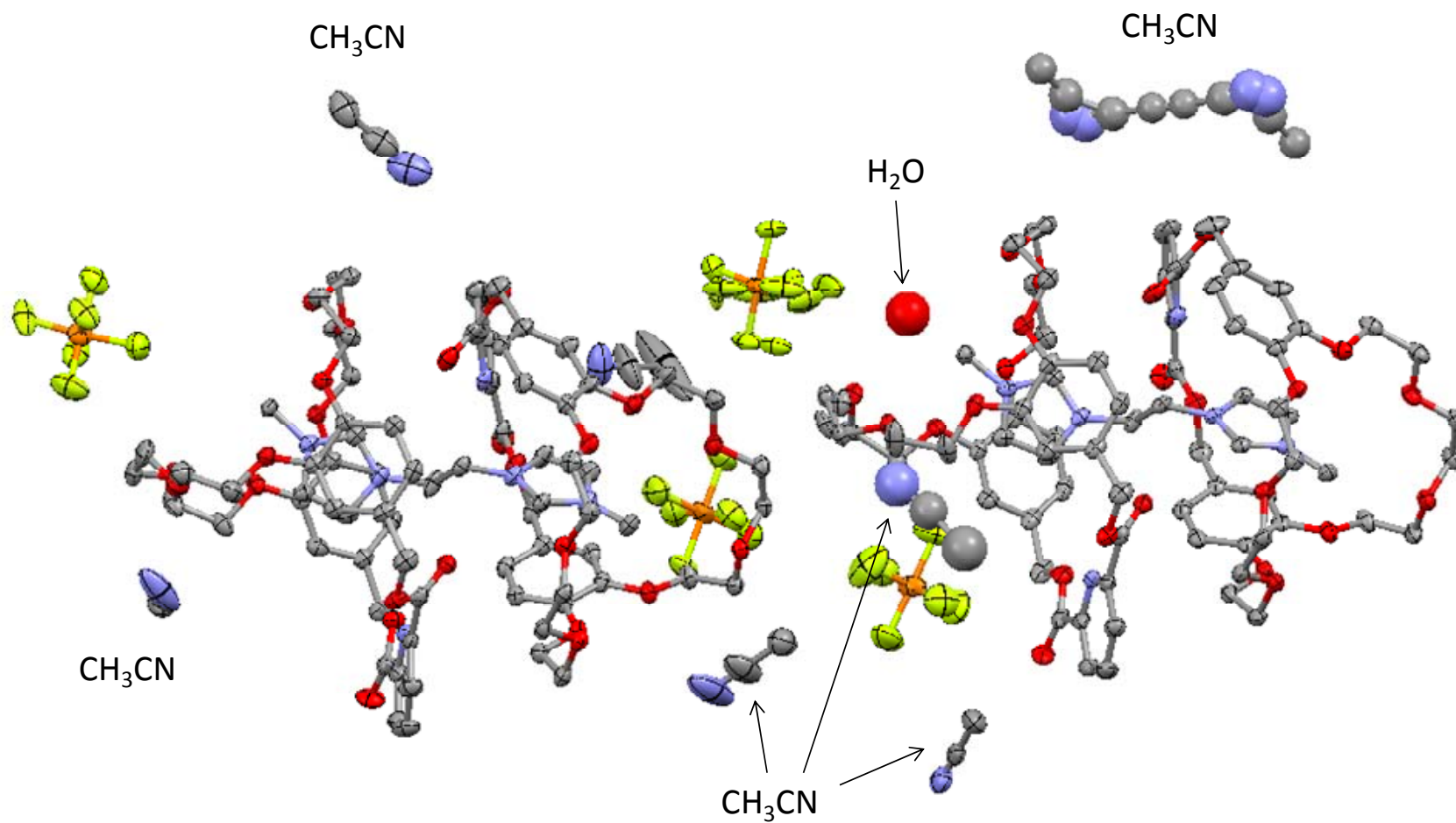


**Figure 10-S2.** Ellipsoid diagram of the X-ray structure of **1·(6)<sub>2</sub>** with 50% probability. Two carbon atoms of one ethyleneoxy arm, one PF<sub>6</sub><sup>-</sup> ion, and multiple MeCN molecules are disordered.

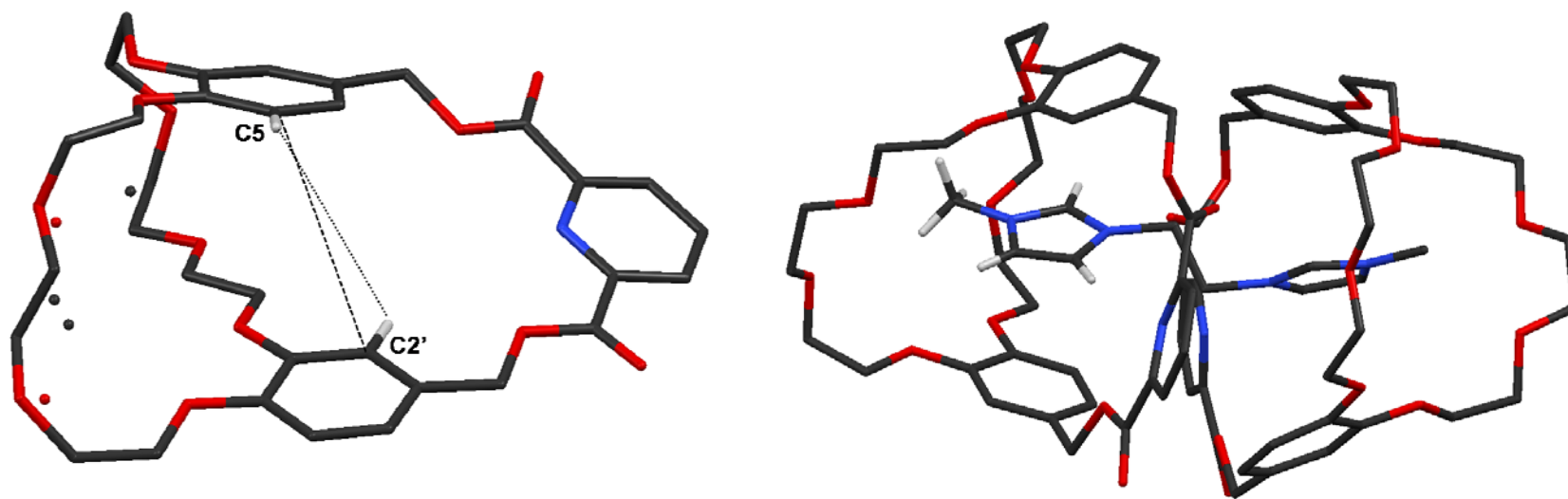


**Figure 10-S3.** Capped-stick X-ray crystal structures of the cryptand **6**<sup>11</sup> (left) and one of the two crystallographically independent complexes of **1**·(**6**)<sub>2</sub> (right). For the cryptand **6**, some oxygen and carbon atoms of ethyleneoxy arm are disordered. The centroid-to-centroid distance between the two catechol rings is only 6.19 Å, the atom-to-atom distance between C5 of the upper catechol and C2' of the lower one is 4.65 Å, the atom-to-atom distance between hydrogens of C5 of the upper catechol and C2 of the lower one is 4.30 Å, and the dihedral angle between the catechol rings is 20.3°. For the complex **1**·(**6**)<sub>2</sub> shown, the centroid-to-centroid distances of the phenylene and imidazolium rings are 3.6~3.9 Å and the dihedral angles of the phenylene and imidazolium planes are 12~23° (values are nearly identical for the 2nd crystallographically independent complex). Thus, the two catechol rings must move apart to complex guest **1**, and the somewhat large  $\Delta S$  of the complexation (15 cal/mol·deg) can be attributed in large part to this reorganization.



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## Chapter 11

### Structure and Properties of N,N-Alkylene Bis(N'-alkylimidazolium) Salts

#### Abstract

A series of N,N-alkylene bis(N'-alkylimidazolium) salts with various anions was prepared and characterized. The hydrogen bonding abilities and ion-pairing strengths of the salts in solution were varied by changing the solvent and anion. Qualitatively the extent of ion-pairing of the 1,2-bis[N-(N'-butylimidazolium)]ethane salts with different anions was determined in acetone- $d_6$  by  $^1\text{H}$  NMR spectroscopy. Thermal properties of the imidazolium salts were related to not only the nature of anions but also to the spacer length between imidazolium cations. Exceptionally high melting points of 1,2-bis[N-(N'-alkylimidazolium)]ethane bis(hexafluorophosphate)s can be explained by multiple hydrogen bonds observed in the X-ray crystal structures. Moreover a *trans*-conformation of the ethylene spacer of 1,2-bis[N-(N'-alkylimidazolium)]ethane bis(hexafluorophosphate)s allows good stacking structure in the crystals.

#### Introduction

Imidazolium salts are well-known N-heterocyclic carbene (NHC) precursors in organometallic chemistry<sup>1-11</sup> and homogeneous catalysis.<sup>12-15</sup> The formation of NHC is due to the acidic proton on the 2-position of the imidazolium unit; its  $\text{p}K_a$  is 16~24, which depends on the nature of the substituents on the two imidazolium nitrogens.<sup>16</sup> Anions of the imidazolium salts also have a strong influence on the H/D exchange reaction at the 2-position; for example, the 1-butyl-3-methyl dicyanamide salt undergoes deuterium exchange even in the absence of any base.<sup>17</sup> Transition metal complexes with bis(alkylimidazolium) salts containing a  $(\text{CH}_2)_n$  linker were studied; the length of the linker controls physical properties and effects the chelating ability.<sup>2, 5</sup>

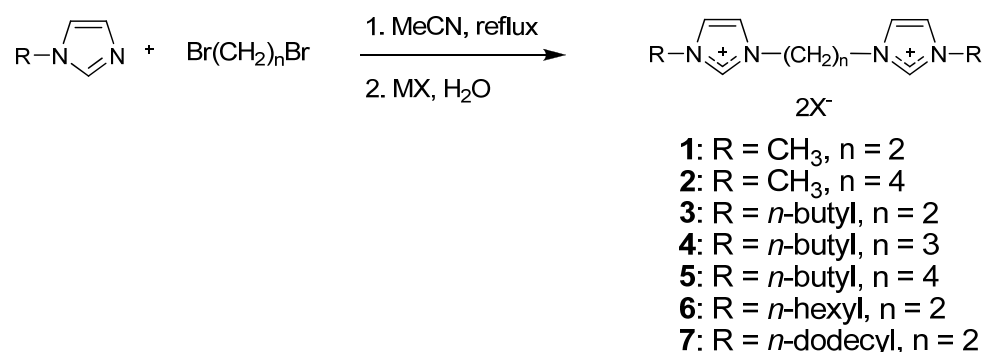
Imidazolium salts are also popular as ionic liquids (ILs), because of their unique characteristics, such as low-volatility, non-flammability, large electrochemical window, and high ionic conductivity.<sup>18-23</sup> As a result many new ILs have been synthesized and applications of ILs have been also expanded in diverse areas, such as electroactive devices.<sup>24-27</sup> Demand for new ILs with designed properties is growing due to the expansion of their applications. As one trend for new imidazolium ILs, systems with more than one imidazolium unit per molecule have been studied to obtain better properties and wider applications. Armstrong et al. studied the structure-property relationships of thermally stable dicationic ILs; the geminal imidazolium dicationic salts, in which two imidazolium units are connected by C<sub>3</sub>-C<sub>12</sub> alkyls, are more thermally stable than monoimidazolium ionic liquids.<sup>28</sup> Also the thermal properties and ionic conductivity of imidazolium dicationic di[bis(trifluoromethanesulfonyl)imide] (2Tf<sub>2</sub>N<sup>-</sup>) salts were investigated by Pitawala et al.<sup>29</sup> They compared DSC transitions and ionic conductivities of 2H- (unsubstituted at C2 of imidazolium), 2-methyl- and 2-phenyl-imidazolium dicationic salts with various spacers, with monoimidazolium Tf<sub>2</sub>N<sup>-</sup> salts. The applications of imidazolium dicationic salts were also reported; for example dicationic imidazolium iodide salts with alkylene or ethyleneoxy spacers were used in dye sensitized solar cells,<sup>30, 31</sup> and dicationic imidazolium ILs connected with fluoroalkyl, ethyleneoxy, and phenylene units were synthesized as high temperature lubricants.<sup>32, 33</sup>

However, we are surprised that no one has reported a detailed property study of dicationic imidazolium salts with an ethylene spacer. So, here we report the structure-property relationships of alkylene bis[N-(N'-alkylimidazolium)] salts with a C<sub>2</sub> (ethylene) spacer and the comparison of these salts with the analogous salts with C<sub>3</sub> and C<sub>4</sub> spacers with various lengths of N-alkyl side chains. We also studied the counterion effects on the properties. Some interesting solid-state structures were found for the imidazolium salts, which showed unique stacking patterns in X-ray crystal structures.

## Results and Discussion

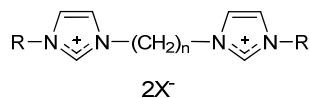
Various alkylene bis[N-(N'-alkylimidazolium)] salts were synthesized in two steps (Scheme 11-1): the coupling reaction of the 1-alkylimidazole (2 molar equivalents) with a dibromoalkane (1 molar equivalent) and anion exchange in water. Non-commercial 1-alkylimidazoles were first prepared before the quaternization; 1-hexylimidazole and 1-dodecylimidazole were prepared from imidazole and corresponding bromoalkanes with NaOH in high yields.<sup>10</sup>

Most of the alkylene N-(N'-alkylimidazolium) bromide salts were very hygroscopic; they are either crystalline solids or waxy materials. The counter anion exchange was performed in aqueous conditions with NaBF<sub>4</sub>, KPF<sub>6</sub>, or (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>NLi (denoted Tf<sub>2</sub>NLi or LiTFSI) and the resulting products (BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup> and Tf<sub>2</sub>N<sup>-</sup> salts) precipitated, as solids or liquids. The BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup> and Tf<sub>2</sub>N<sup>-</sup> salts are not hygroscopic due to their hydrophobic anions. The triflate (TfO<sup>-</sup>), nitrate and trifluoroacetate (TFA) salts were prepared from the corresponding Ag salts in water; AgBr precipitation provided the driving force to complete the ion exchange reactions. The triflate, nitrate and TFA salts are water-soluble and as hygroscopic as the bromide salts. The results of the quaternization and anion exchange reactions for the alkylene bis[N-(N'-alkylimidazolium)] salts are summarized in Table 11-1.



**Scheme 11-1.** Synthesis of alkylene bis[N-(N'-alkylimidazolium)] salts.

**Table 11-1.** Quaternization and Ion Exchange Reactions for Alkylene Bis[N-(N'-alkylimidazolium)] Salts.



| R         | n | Quaternization yield<br>(%, X = Br) | X                               | Ion exchange yield<br>(%) | Appearance        |
|-----------|---|-------------------------------------|---------------------------------|---------------------------|-------------------|
| Me        | 2 | 86                                  | PF <sub>6</sub>                 | 92                        | Crst. Solid       |
|           | 4 | 53*                                 | PF <sub>6</sub>                 | 92                        | Crst. Solid       |
|           |   |                                     | PF <sub>6</sub>                 | 91                        | Crst. Solid       |
| n-Bu      |   |                                     | BF <sub>4</sub>                 | 88                        | Crst. Solid       |
|           | 2 | 88                                  | TfO                             | 97                        | Crst. Solid       |
|           |   |                                     | NO <sub>3</sub>                 | 96                        | RTIL <sup>§</sup> |
|           |   |                                     | CF <sub>3</sub> CO <sub>2</sub> | 97                        | Yellow Solid      |
|           | 3 | 86                                  | PF <sub>6</sub>                 | 96                        | Crst. Solid       |
|           | 4 | 82                                  | PF <sub>6</sub>                 | 96                        | Sticky Solid      |
| n-Hex     |   |                                     | PF <sub>6</sub>                 | 91                        | Solid             |
|           | 2 | 87                                  | BF <sub>4</sub>                 | 88                        | RTIL <sup>§</sup> |
|           |   |                                     | Tf <sub>2</sub> N               | 90                        | RTIL <sup>§</sup> |
| n-Dodecyl | 2 | 82                                  | PF <sub>6</sub>                 | 97                        | Crst. Solid       |
|           |   |                                     | Tf <sub>2</sub> N               | 89                        | Crst. Solid       |

\* The yield was lower than other reactions due to a higher solubility of **2Br** in MeCN during the work-up procedure.

<sup>§</sup> RTIL = room temperature ionic liquid.

**<sup>1</sup>H NMR studies.** In our <sup>1</sup>H NMR studies of the new bis[N-(N'-alkylimidazolium)] salts, noteworthy chemical shift changes were observed with different solvents and counterions. The <sup>1</sup>H NMR spectra of the bromide salt of **3** (**3Br**) in D<sub>2</sub>O and acetone-*d*<sub>6</sub> are shown in Figure 11-1. The imidazolium protons appear at different positions in these solvents:  $\delta$  7.5, 7.6 and 8.9 in D<sub>2</sub>O, but  $\delta$  7.7, 8.4 and 10.4 in acetone-*d*<sub>6</sub>. The peaks of H<sup>4</sup> and H<sup>5</sup> are close to each other in D<sub>2</sub>O, but they are widely separated in acetone-*d*<sub>6</sub>. These chemical shift changes are due to the solvent properties: the better solvation of the ions in D<sub>2</sub>O vs. acetone-*d*<sub>6</sub>. This higher solvation

level isolates the bromide anions in solution and the positive charge on the resultant free cation is delocalized. As a result of the delocalization of positive charge, the chemical shifts of protons  $H^4$  and  $H^5$  are close to each other. However, poorer ion solvation in acetone- $d_6$  results in relatively tight ion pairs; therefore, the positive charge tends to localize on a specific nitrogen atom. The localized positive charge leads to different environments for protons  $H^4$  and  $H^5$  and hence their peaks occur at different positions.

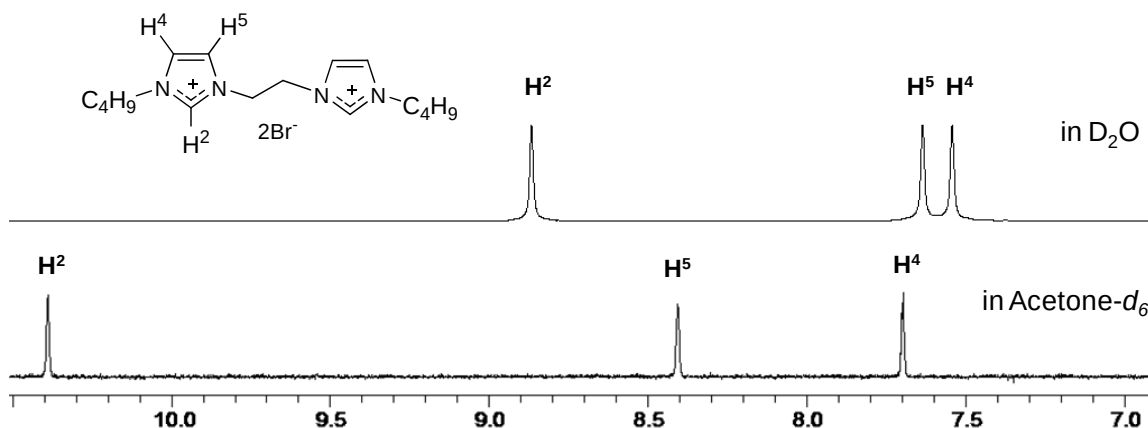


**Figure 11-1.** Partial 400 MHz  $^1\text{H}$  NMR spectra of **3Br** in  $\text{D}_2\text{O}$  (upper) and acetone- $d_6$  (lower).

The chemical shift change of proton  $H^2$  is quite large in different media:  $\delta$  8.9 ( $\text{D}_2\text{O}$ ) vs. 10.4 (acetone- $d_6$ ). This can be explained by the different solvating powers of the solvents. In  $\text{D}_2\text{O}$ , the imidazolium cations and bromide anions are well solvated and hydrogen bonding of proton  $H^2$  with the bromide anion is decreased, thus moving its signal to higher field. However, hydrogen bonding occurs in the less polar acetone- $d_6$ , in which the ions are rather tightly paired; therefore, in acetone- $d_6$  the proton  $H^2$  appears downfield. The chemical shift changes of bromide salts of (mono)imidazolium ionic liquids in different solvents were reported previously,<sup>34</sup> and those results are consistent with our study of bis(imidazolium) bromide **3Br**.

There is a counter anion effect on the chemical shifts of the imidazolium protons as shown in Figure 11-2. The hydrogen bonding abilities of the different anions influence the NMR chemical shifts. In this series, the bromide salt (**3Br**) showed the strongest hydrogen bonds and the  $\text{PF}_6^-$  and  $\text{BF}_4^-$  salts (**3PF<sub>6</sub>** and **3BF<sub>4</sub>**) showed the least hydrogen bonding in acetone- $d_6$ . The chemical shift of  $H^2$  (**a**) increased with increasing anion basicity and hydrogen bonding ability ( $\text{PF}_6^- \approx \text{BF}_4^- < \text{TfO}^- < \text{NO}_3^- < \text{Br}^-$ ).<sup>35</sup> The different ion-pairing strengths<sup>36-38</sup> of the anions were also observed from the chemical shift changes of  $H^4$  and  $H^5$ . The most ion paired salt (**3Br**) showed the largest difference in the chemical shifts of these protons, while the less ion paired salts gave



more closely spaced (**3TFA**, **3NO<sub>3</sub>**, **3BF<sub>4</sub>**, **3PF<sub>6</sub>**) or merged peaks (**3TfO**). These changes are the result of changes in the charge localization/delocalization and hydrogen bonding with the different anions.

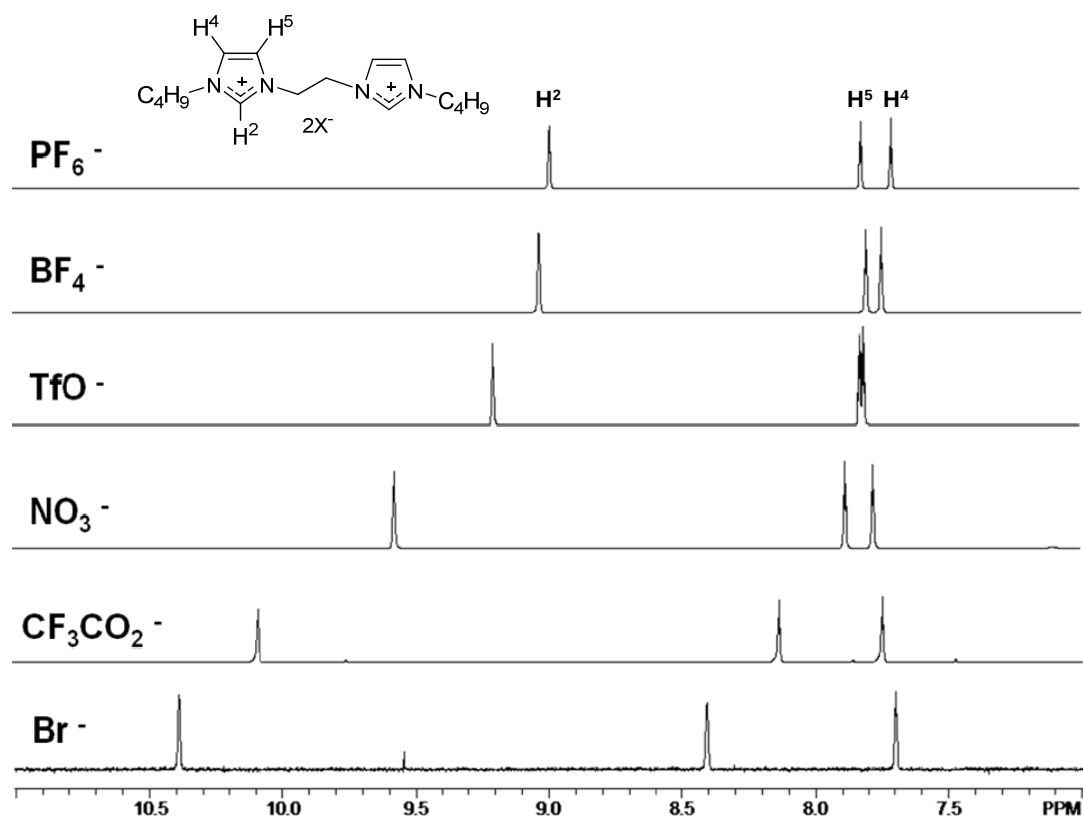


**Figure 11-2.** Partial 400 MHz  $^1\text{H}$  NMR spectra of **3** ( $\text{PF}_6^-$ ,  $\text{BF}_4^-$ ,  $\text{TfO}^-$ ,  $\text{NO}_3^-$ , TFA and  $\text{Br}^-$ ) in acetone- $d_6$ . The chemical shift of proton  $\text{H}^4$  is almost the same with various anions, but protons  $\text{H}^2$  and  $\text{H}^5$  resonate at different positions. **3PF<sub>6</sub>** and **3BF<sub>4</sub>** are the least ion paired, bringing the signals of protons  $\text{H}^4$  and  $\text{H}^5$  close to each other. **3Br** is the most ion paired; the positive charge is localized in the imidazolium ring.

The correlation of the  $^1\text{H}$  NMR chemical shifts of  $\text{H}^2$  of 1-butyl-3-methylimidazolium salts with hydrogen bonding was reported by Spange et al.<sup>39</sup> They calculated hydrogen bond acidities ( $\alpha$ ) of 1-butyl-3-methylimidazolium salts by UV/Vis spectrometry with an indicator dye as a probe. Because half of the imidazolium salts **3** corresponds to the 1-butyl-3-methylimidazolium salts, we directly adapt the  $\alpha$  values from the literature and use them to correlate the proton  $\text{H}^2$  chemical shifts (Figure 11-3). Even though the NMR spectra were taken in different solvents ( $\text{CD}_2\text{Cl}_2$  in the literature<sup>39</sup> and acetone- $d_6$  in this work), the correlation plot is similar to the literature result; the  $r^2$  of the trend line is 0.82 which is close to the literature result, 0.83. This result reflects the fact that the acidity changes through different anions are similar between the

C2 proton of the 1,2-bis[N-(N'-butylimidazolium)ethane salts **3** and that of 1-butyl-3-methylimidazolium salts.

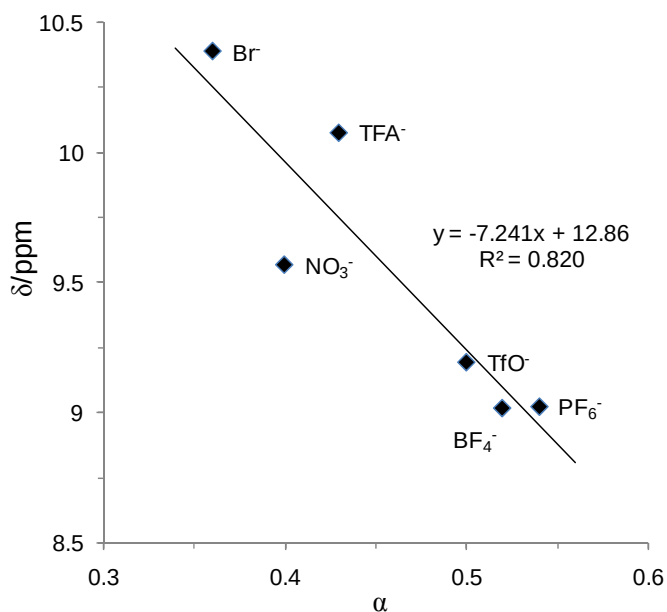


**Figure 11-3.** Correlation of the  $^1\text{H}$  chemical shift of the proton in 2-position of the imidazolium ring of **3** with the hydrogen bond acidity ( $\alpha$ ) of 1-butyl-3-methylimidazolium salts.<sup>39</sup>

**Thermal properties.** From this study, structural factors were found to affect the melting points and thermal stabilities of the alkylene bis(alkylimidazolium) salts: (1) alkyl substituent, (2) the length of the spacer between two imidazolium dications, and (3) the nature of the anion.

When we compare the melting points of the  $\text{PF}_6^-$  salts of 1,2-bis[N-(N'-alkylimidazolium)]ethanes, **7PF<sub>6</sub>**, which has  $\text{C}_{12}$  termini, has the highest melting point but decomposes upon melting. The decreasing order of melting points is: didodecyl **7PF<sub>6</sub>** > dimethyl **1PF<sub>6</sub>** > dihexyl **6PF<sub>6</sub>** > dibutyl **5PF<sub>6</sub>**. The melting points of  $\text{Br}^-$  salts with  $\text{C}_2$  spacer decrease as follows: didodecyl **7Br** > dihexyl **6Br** > dibutyl **3Br**.

**Table 11-2.** Thermal Properties of the Alkylene Bis(N-alkylimidazolium) Salts.

| Entry                  | Side Chain | Spacer         | MP (°C)*       | TGA 5% weight loss (°C) |
|------------------------|------------|----------------|----------------|-------------------------|
| <b>1PF<sub>6</sub></b> | Me         | C <sub>2</sub> | 214.3          | 304                     |
| <b>2Br</b>             | Me         | C <sub>4</sub> | 132.8          | 250                     |
| <b>2PF<sub>6</sub></b> | Me         | C <sub>4</sub> | 112.9          | 342                     |
| <b>3Br</b>             | Bu         | C <sub>2</sub> | 167.3          | 252                     |
| <b>3PF<sub>6</sub></b> | Bu         | C <sub>2</sub> | 182.0          | 273                     |
| <b>3BF<sub>4</sub></b> | Bu         | C <sub>2</sub> | 99.4           | 298                     |
| <b>3TfO</b>            | Bu         | C <sub>2</sub> | 91.6           | 331                     |
| <b>3NO<sub>3</sub></b> | Bu         | C <sub>2</sub> | - <sup>§</sup> | 161                     |
| <b>3TFA</b>            | Bu         | C <sub>2</sub> | 133.2          | 156                     |
| <b>4PF<sub>6</sub></b> | Bu         | C <sub>3</sub> | 96.1           | 326                     |
| <b>5PF<sub>6</sub></b> | Bu         | C <sub>4</sub> | 51.3           | 335                     |
| <b>6Br</b>             | Hex        | C <sub>2</sub> | 227.4 (dec.)   | 231                     |
| <b>6PF<sub>6</sub></b> | Hex        | C <sub>2</sub> | 198.2          | 239                     |
| <b>7Br</b>             | Dodecyl    | C <sub>2</sub> | 240.6 (dec.)   | 240                     |
| <b>7PF<sub>6</sub></b> | Dodecyl    | C <sub>2</sub> | 220.4 (dec.)   | 285                     |
| <b>7TFSI</b>           | Dodecyl    | C <sub>2</sub> | 46.6           | 334                     |

\* Median values from the melting (or decomposition) ranges. Melting points were observed with a Büchi B-540 apparatus at a 2 °C/min. heating rate.

<sup>§</sup> No melting point, because **3NO<sub>3</sub>** is RTIL.

The spacer length between the imidazolium cations plays an important role. The melting point of dimethyl **2PF<sub>6</sub>** with a C<sub>4</sub> spacer is 100° lower than the melting point of dimethyl **1PF<sub>6</sub>** with a C<sub>2</sub> spacer. Similarly dibutyl **3PF<sub>6</sub>** with a C<sub>2</sub> spacer melts 86° higher than dibutyl **4PF<sub>6</sub>** with a C<sub>3</sub> spacer and 131° higher than dibutyl **5PF<sub>6</sub>** with a C<sub>4</sub> spacer. These results are consistent with the literature.

To see the effect of the anions, the bis(imidazolium)ethanes were compared. The melting points increased in the following order: **3TfO** < **3BF<sub>4</sub>** < **3TFA** < **3Br** < **3PF<sub>6</sub>**. (**3NO<sub>3</sub>** falls below all of these because it is an RTIL). This order is somewhat different from previously reported systems with longer spacers (C<sub>3</sub> to C<sub>12</sub>) between the imidazolium units; in these systems the melting points of the bromide salts were usually higher than the PF<sub>6</sub><sup>-</sup> salts.<sup>28</sup>

The thermal stabilities of the alkylene bis(N-alkylimidazolium) salts were investigated by thermal gravimetric analysis (TGA) in N<sub>2</sub> atmosphere. All the imidazolium salts evinced one step degradation; the 5% weight loss temperatures are shown in Table 11-2. For the 1,2-bis(alkylimidazolium)ethane PF<sub>6</sub> salts the thermal stabilities are in the following order: dimethyl **1PF<sub>6</sub>** > dibutyl **3PF<sub>6</sub>** > > didodecyl **7PF<sub>6</sub>** > dihexyl **6PF<sub>6</sub>**. The Br<sup>-</sup> salts showed a similar order: dibutyl **3Br** > didodecyl **7Br** > dihexyl **6Br**.

The thermal stability was also affected by the spacer length. For the salts with methyl arms, **2PF<sub>6</sub>** with a C<sub>4</sub> spacer has better thermal stability than **1PF<sub>6</sub>** with a C<sub>2</sub> spacer. The dibutyl analogs behave similarly. In the dibutyl series: **5PF<sub>6</sub>** with a C<sub>4</sub> spacer > **4PF<sub>6</sub>** with a C<sub>3</sub> spacer > **3PF<sub>6</sub>** with a C<sub>2</sub> spacer. The literature reported that bis(1-methylimidazolium) 2Tf<sub>2</sub>N<sup>-</sup> with a C<sub>9</sub> spacer started to decompose at ~330 °C,<sup>28</sup> which is slightly higher compared to the degradation of dibutyl **5PF<sub>6</sub>** with a C<sub>4</sub> spacer and didodecyl **7TFSI** with a C<sub>2</sub> spacer.

The nature of the anion greatly influences the thermal stabilities of the salts of dibutyl **3** with a C<sub>2</sub> spacer. The thermal stability is in the following order: **3TfO** > **3BF<sub>4</sub>** > **3PF<sub>6</sub>** > **3Br** > **3NO<sub>3</sub>** > **3TFA**. This thermal stability order is almost the same order as the basicity of anions; the more basic TFA<sup>-</sup> and NO<sub>3</sub><sup>-</sup> salts degrade at relatively low temperatures. However, the imidazolium salts containing less basic counterions show good thermal stabilities.

**Solid state structures of 1PF<sub>6</sub>, 3PF<sub>6</sub>.** Crystals of **1PF<sub>6</sub>** and **3PF<sub>6</sub>** were obtained by vapor diffusion methods. The crystal structure of **1PF<sub>6</sub>**<sup>42</sup> (Figure 11-4) reveals that the planar imidazolium rings are parallel in each molecule. There are two sets of stacks in the unit cell; the imidazolium rings are arranged at an angle of 67.3° to one another in the two stacks, i.e., a herringbone structure. Surprisingly every proton of **1PF<sub>6</sub>** is within hydrogen bonding distance of a fluorine atom of PF<sub>6</sub><sup>-</sup> anions (Figure 11-5). The H...F distances are in the range of 2.31 – 2.69 Å. The shortest H...F distance is **A** (2.31 Å) for the most acidic proton, H<sup>2</sup>, of the imidazolium cation.

The crystal structure of dibutyl **3PF<sub>6</sub>**<sup>45</sup> (Figure 11-6) contains only one type of stacking; that is, the structure is of higher symmetry than **1PF<sub>6</sub>**. The two imidazolium rings of the molecule are exactly parallel. The two imidazolium ring planes of neighboring molecules are also exactly parallel. There are also many apparent hydrogen bonds in the solid state. The shortest H...F distance is 2.26 Å for H<sup>2</sup> and the C-H...F angle is 175°. The H...F distances for H<sup>3</sup> and H<sup>4</sup> are 2.23 and 2.42 Å, respectively. The H...F distances for the ethylene protons are 2.41 and 2.52 Å.

We can rationalize the high melting points of the  $\text{PF}_6^-$  salts with  $\text{C}_2$  spacers from the solid state structures. Due to the octahedral geometry of the  $\text{PF}_6^-$  anion, two or three fluorine atoms are bound to one cation and the other three are bound to the neighboring cations (Figure 11-5); in this way each cation is linked to its neighbors. The lower melting points of  $\text{BF}_4^-$  (tetrahedral) and TFSI (asymmetric) salts are probably due to weaker and fewer hydrogen bonds provided by these lower symmetry anions.

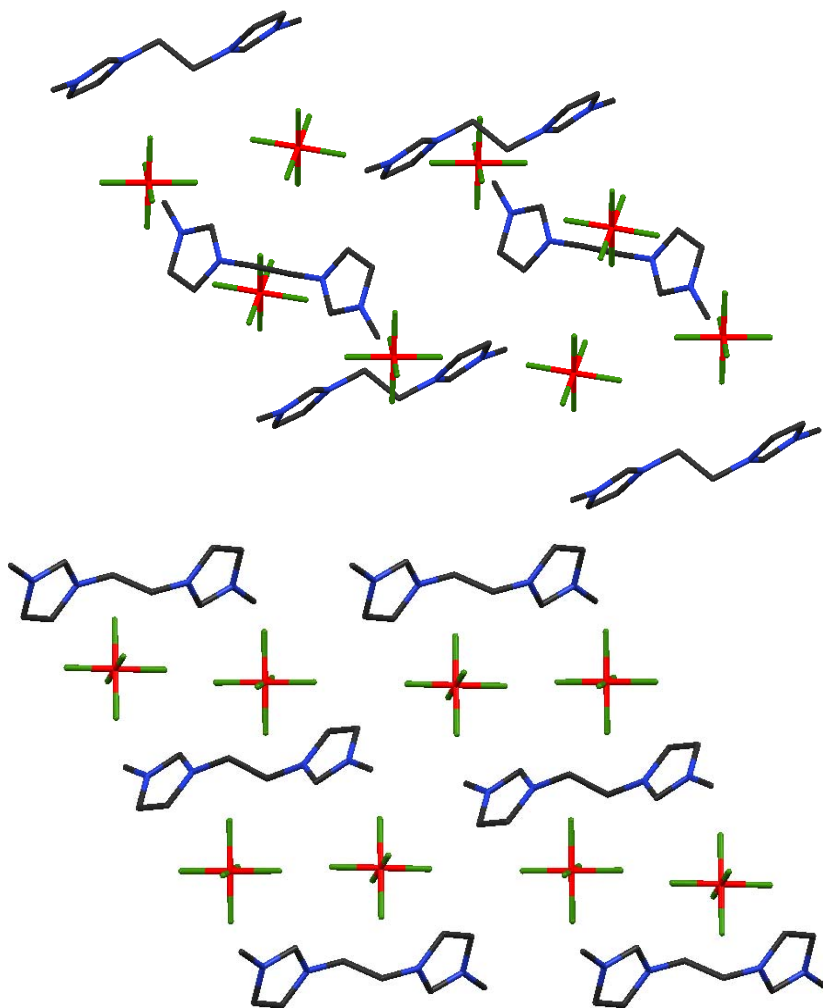


**Figure 11-4.** Two capped-sticks views of the X-ray structure of **1PF<sub>6</sub>**. Hydrogens are omitted for clarity. Face-to-face stacking parameters: ring plane/ring plane inclination of the imidazolium rings in the same molecule: 0°. Ring plane/ring plane distance and dihedral angle between imidazolium rings of different molecules within a stack: 8.66 Å, 0°. Dihedral angle between imidazolium rings in different stacks: 67.3°.

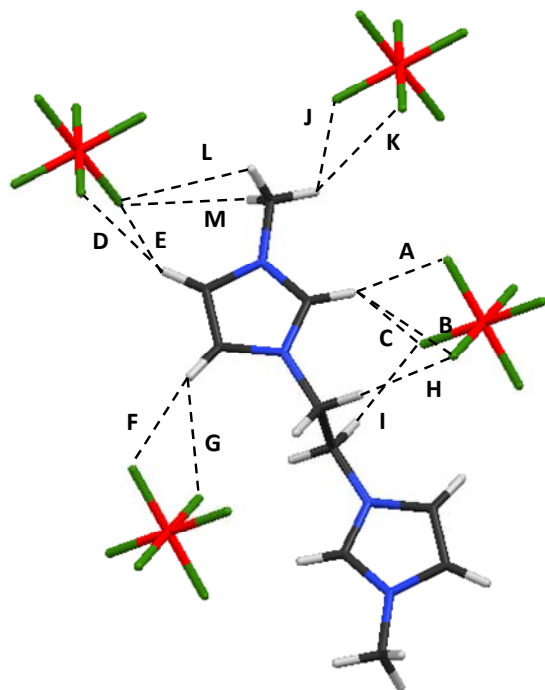


**Figure 11-5.** Capped-sticks view of the X-ray structure of **1PF<sub>6</sub>**. H...F distances (Å), C-H...F angles (degrees): **A** 2.31, 166; **B** 2.58, 137; **C** 2.78, 126; **D** 2.48, 159; **E** 2.71, 130; **F** 2.69, 164; **G** 2.66, 126; **H** 2.52, 125; **I** 2.50, 164; **J** 2.56, 112; **K** 2.60, 146; **L** 2.65, 123; **M** 2.84, 122.

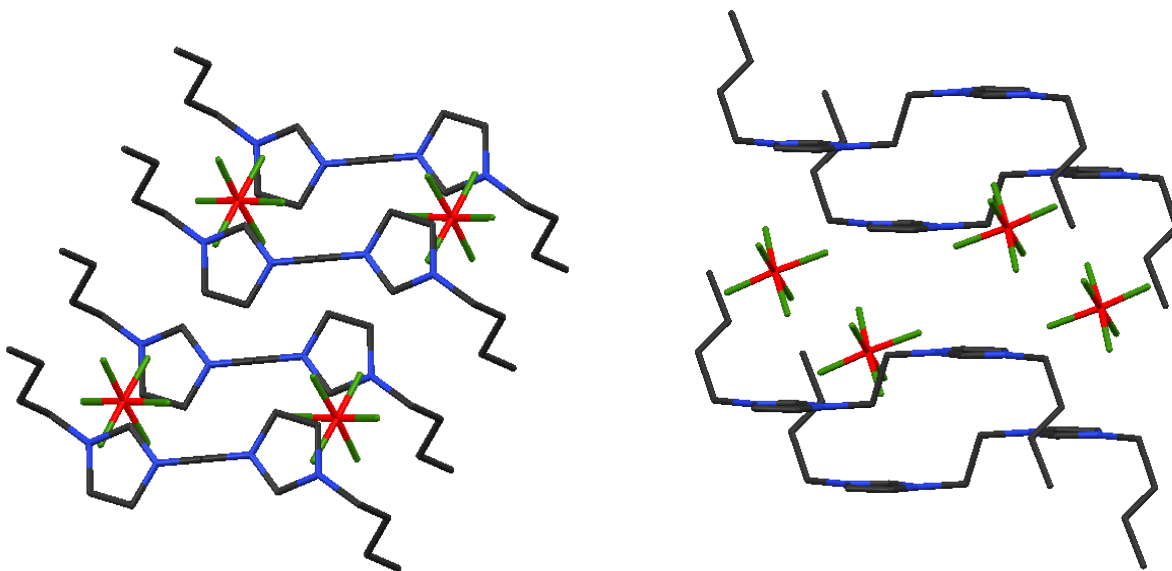


**Figure 11-6.** Two capped-sticks views of the X-ray structure of **3PF<sub>6</sub>**. Hydrogens are omitted for clarity. Face-to-face stacking parameters: ring plane/ring plane inclination of imidazolium rings within the same molecule: 0°. Ring plane/ring plane distance and dihedral angle between imidazolium rings of different molecules: 7.94 Å, 0°.

## Conclusions

A series of alkylene bis[N-(N'-alkylimidazolium)] salts with various anions was prepared in high yields. The hydrogen bonding and ion-pairing of the salts in solution were characterized by  $^1\text{H}$ -NMR. Chemical shift changes of the C2 proton result from changes in solvent and anion. For the bromide salts, the hydrogen bonding of  $\text{H}^2$  with the counterion was more pronounced in acetone- $d_6$  than in  $\text{D}_2\text{O}$ . The hydrogen bonding ability was also related to the basicity of the anion ( $\text{Br}^- > \text{TFA}^- > \text{NO}_3^- > \text{TfO}^- \geq \text{BF}_4^- \approx \text{PF}_6^-$ ). Thermal properties of the salts were investigated by their melting points and TGA. The spacers affect the melting points and thermal stabilities. The  $\text{C}_2$  spacer salts show higher melting points and low thermal stabilities than  $\text{C}_3$  and  $\text{C}_4$  spacer analogs. The length of alkyl side arms does have a significant effect on the thermal properties. Also, the effect of the anions is significant. Better thermal stability was shown with the less nucleophilic anions:  $\text{TfO}^- > \text{BF}_4^- > \text{PF}_6^- > \text{Br}^- > \text{NO}_3^- > \text{TFA}^-$ . The  $\text{PF}_6^-$  salts of 1,2-bis[N-(N'-alkylimidazolium)]ethane surprisingly possess high melting points; this is attributed to the multiple hydrogen bonds of the imidazolium units with fluorine atoms of  $\text{PF}_6^-$ , as directly observed in X-ray crystal structures. The two imidazolium rings in the same molecule are parallel due to the *trans*-conformation of the ethylene spacer. The multiple hydrogen bonds and the *trans*-conformation also provide well ordered stacks in their X-ray crystal structures.

## Experimental

**Materials.** Acetone for the quaternization reactions was dried with anhydrous  $\text{CaSO}_4$  and then distilled. Acetonitrile (MeCN) was dried with anhydrous  $\text{K}_2\text{CO}_3$  and then distilled. All other chemicals and solvents were used as received.

**Instruments.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained on Varian Inova 400 MHz and Unity 400 MHz spectrometers. High resolution electrospray ionization time-of-flight mass spectrometry (HR ESI TOF MS) was carried out on an Agilent 6220 Accurate Mass TOF LC/MS Spectrometer in positive ion mode. DSC results were obtained on a TA Instrument Q2000 differential scanning calorimeter at a scan rate of 5 or 10  $^\circ\text{C}/\text{min}$  heating under  $\text{N}_2$  purge. TGA results were obtained on a TA Instrument Q500 Thermogravimetric Analyzer at a heating rate of 10  $^\circ\text{C}/\text{min}$  under  $\text{N}_2$  purge. Melting points were observed on a Büchi B-540 apparatus at a 2  $^\circ\text{C}/\text{min}$  heating rate.

**General anion exchange procedure A.** Into a solution of bromide salt (1 equivalent) in deionized water,  $\text{KPF}_6$  (or  $\text{NaBF}_4$  or  $\text{LiTf}_2\text{N}$ , 2-4 equivalents) was added with stirring, which

continued for 1-2 hours at room temperature. The precipitate was filtered and washed with deionized water twice. Drying in a vacuum oven gave the pure imidazolium PF<sub>6</sub><sup>-</sup> (or BF<sub>4</sub><sup>-</sup> or Tf<sub>2</sub>N<sup>-</sup>) salt.

**General anion exchange procedure B.** Into a solution of bromide salt (1 equivalent) in deionized water, AgTfO (or AgNO<sub>3</sub> or AgTFA, 2.06 equivalents) was added with stirring, which continued for 3-4 hours at 50 °C. Insoluble AgBr was removed by filtration and the water in the filtrate was removed under vacuum. Further drying in a vacuum oven gave the corresponding TfO<sup>-</sup> (or NO<sub>3</sub><sup>-</sup> or TFA<sup>-</sup>) salt.

**1,2-Bis[N-(N'-methylimidazolium)]ethane salts (1Br and 1PF<sub>6</sub>)** A solution of 1-methylimidazole (2.49 g, 30 mmol) and 1,2-dibromoethane (2.82 g, 15 mmol) in MeCN (20 mL) was refluxed for 3 days. The precipitate was filtered after cooling, and washed with tetrahydrofuran (THF) 3 times. Drying in a vacuum oven gave colorless crystalline **1Br** (4.54 g, 86%), mp 231.1–233.8 °C (lit. mp = 230–234 °C).<sup>4</sup> **1PF<sub>6</sub>** was obtained by following general anion exchange procedure A; from **1Br** (4.50 g), KPF<sub>6</sub> (5.52 g, 30 mmol) and deionized water (40 mL) colorless crystalline solid **1PF<sub>6</sub>** (5.26 g, 73% based on 1,2-dibromoethane), mp 213.8–214.9 °C, was isolated. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN, 23 °C): δ 3.85 (s, 6H), 4.62 (s, 4H), 7.33 (t, J=2, 2H), 7.42 (t, J=2, 2H), 8.40 (s, 2H). <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>CN, 23 °C): δ 37.2, 49.7, 123.5, 125.6, 137.6. HRMS (ESI): m/z 337.1022 ([M-PF<sub>6</sub>]<sup>+</sup>, calcd for C<sub>10</sub>H<sub>16</sub>N<sub>4</sub>PF<sub>6</sub> 337.1017, error 1.5 ppm).

**1,4-Bis[N-(N'-methylimidazolium)]butane salts (2Br and 2PF<sub>6</sub>)** The same procedure was used as for **1Br**. 1-Methylimidazole (2.46 g, 30 mmol) and 1,4-dibromobutane (3.24 g, 15 mmol) in MeCN (20 mL) produced colorless crystalline **2Br** (3.04 g, 53%), mp 131.7–133.8 °C. <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O, 23 °C): δ 1.89 (m, 4H), 3.88 (s, 6H), 4.23 (m, 4H), 7.43 (t, J=2, 2H), 7.46 (t, J=2, 2H), 8.72 (s, 2H). The <sup>1</sup>H NMR spectrum was identical to that in the literature.<sup>40</sup> **2PF<sub>6</sub>** was obtained by following the general anion exchange procedure A; from **2Br** (2.10 g, 5.5 mmol), KPF<sub>6</sub> (3.04 g, 16.5 mmol) and deionized water (40 mL) colorless crystalline **2PF<sub>6</sub>** (2.59 g, 92% from **2Br**), mp 111.7–114.2 °C, resulted. <sup>1</sup>H NMR (400 MHz, acetone-*d*<sub>6</sub>, 23 °C): δ 2.05 (t, J=7, 4H), 4.01 (s, 6H), 4.41 (s, 4H), 7.66 (t, J=2, 2H), 7.68 (t, J=2, 2H), 8.86 (s, 2H). <sup>13</sup>C NMR (100 MHz, acetone-*d*<sub>6</sub>, 23 °C): δ 26.7, 35.9, 49.0, 122.6, 124.2, 136.7. HRMS (ESI): m/z calcd 365.1344 ([M-PF<sub>6</sub>]<sup>+</sup>, calcd for C<sub>12</sub>H<sub>20</sub>N<sub>4</sub>PF<sub>6</sub> 365.1330, error 3.8 ppm).

**1,2-Bis[N-(N'-butylimidazolium)]ethane dibromide (3Br).** The same procedure was used as for **1Br**. From 1-butylimidazole (6.21 g, 50 mmol) and 1,2-dibromoethane (4.69 g, 25 mmol) in



MeCN (25 mL) colorless crystalline **3Br** (9.64 g, 88%), mp 166.5–168.2 °C, was produced. <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O, 23 °C): δ 0.90 (t, J=7, 6H), 1.25 (m, 4H), 1.83 (m, 4H), 4.22 (t, J=7, 4H), 4.80 (s, 4H), 7.52 (t, J=2, 2H), 7.62 (t, J=2, 2H), 8.85 (s, 2H). The <sup>1</sup>H NMR result corresponds to the literature spectrum (in CDCl<sub>3</sub>).<sup>5</sup> HRMS (ESI): m/z 355.1508 ([M-Br]<sup>+</sup>, calcd for C<sub>16</sub>H<sub>28</sub>N<sub>4</sub>Br 355.1497, error 3.1 ppm).

**1,2-Bis[N-(N'-butylimidazolium)]ethane bis(hexafluorophosphate) (3PF<sub>6</sub>).** Anion exchange procedure A was used; from **3Br** (1.30 g, 3.0 mmol) and KPF<sub>6</sub> (1.65 g, 9 mmol) in deionized water (10 mL) colorless crystalline **3PF<sub>6</sub>** (1.54 g, 91%), mp 181.6–182.5 °C, was isolated. <sup>1</sup>H NMR (400 MHz, acetone-*d*<sub>6</sub>, 23 °C): δ 0.94 (t, J=7, 6H), 1.33 (m, 4H), 1.78–1.85 (m, 4H), 4.14 (m, 4H), 5.04 (s, 4H), 7.39 (m, 4H), 8.42 (s, 2H). <sup>13</sup>C NMR (100 MHz, acetone-*d*<sub>6</sub>, 23 °C): δ 13.5, 19.8, 32.4, 49.9, 50.6, 123.6, 124.2, 137.5. HRMS (ESI): m/z 421.1966 ([M-PF<sub>6</sub>]<sup>+</sup>, calcd for C<sub>16</sub>H<sub>28</sub>N<sub>4</sub>PF<sub>6</sub> 421.1950, error 3.2 ppm).

**1,2-Bis[N-(N'-butylimidazolium)]ethane bis(tetrafluoroborate) (3BF<sub>4</sub>).** Anion exchange procedure A was used; from **3Br** (1.0 g, 2.3 mmol) and NaBF<sub>4</sub> (0.55 g, 5 mmol) in deionized water (10 mL) colorless crystalline **3BF<sub>4</sub>** (0.91 g, 88%), mp 98.6–100.1 °C, was isolated. <sup>1</sup>H NMR (400 MHz, acetone-*d*<sub>6</sub>, 23 °C): δ 0.94 (t, J=7, 6H), 1.36 (m, 4H), 1.92 (m, 4H), 4.34 (t, J=7, 4H), 4.97 (s, 4H), 7.74 (t, J=2, 2H), 7.80 (t, J=2, 2H), 9.02 (s, 2H). <sup>13</sup>C NMR (100 MHz, acetone-*d*<sub>6</sub>, 23 °C): δ 13.7, 20.0, 32.4, 49.7, 50.5, 123.8, 124.1, 137.7. HRMS (ESI): m/z 363.2363 ([M-BF<sub>4</sub>]<sup>+</sup>, calcd for C<sub>16</sub>H<sub>28</sub>N<sub>4</sub>BF<sub>4</sub> 363.2343, found (error 5.5 ppm).

**1,2-Bis[N-(N'-butylimidazolium)]ethane bis(triflate) (3TfO).** Anion exchange procedure B was used; from **3Br** (0.30 g, 0.69 mmol) and AgTfO (0.364 g, 1.42 mmol) in deionized water (15 mL) colorless solid **3TfO** (0.384 g, 97%), mp 90.1–93.2 °C, resulted. <sup>1</sup>H NMR (400 MHz, acetone-*d*<sub>6</sub>, 23 °C): δ 0.94 (t, J=7, 6H), 1.38 (m, 4H), 1.92 (m, 4H), 4.35 (t, J=7, 4H), 5.03 (s, 4H), 7.82 (m, 4H), 9.20 (t, J=2, 2H). <sup>13</sup>C NMR (100 MHz, acetone-*d*<sub>6</sub>, 23 °C): δ 13.6, 20.0, 32.5, 49.8, 50.5, 123.9, 124.1, 137.8. HRMS (ESI): m/z 425.1845 ([M-TfO]<sup>+</sup>, calcd for C<sub>17</sub>H<sub>28</sub>F<sub>3</sub>N<sub>4</sub>O<sub>3</sub>S 425.1834; error 2.6 ppm).

**1,2-Bis[N-(N'-butylimidazolium)]ethane bis(nitrate) (3NO<sub>3</sub>).** Anion exchange procedure B was used; from **3Br** (0.30 g, 0.69 mmol) and AgNO<sub>3</sub> (0.234 g, 1.42 mmol) in deionized water (15 mL) **3NO<sub>3</sub>** was isolated as a colorless viscous liquid (0.277 g, 97%). <sup>1</sup>H NMR (400 MHz, acetone-*d*<sub>6</sub>, 23 °C): δ 0.94 (t, J=7, 6H), 1.35 (m, 4H), 1.91 (m, 4H), 4.35 (t, J=7, 4H), 5.02 (s, 4H), 7.78 (t, J=2, 2H), 7.89 (t, J=2, 2H), 9.57 (t, J=2, 2H). <sup>13</sup>C NMR (100 MHz, acetone-*d*<sub>6</sub>,

23 °C):  $\delta$  13.7, 20.0, 32.5, 49.8, 50.4, 123.8, 124.0, 138.6. HRMS (ESI):  $m/z$  338.2203 ( $[M-NO_3]^+$ , calcd for  $C_{16}H_{28}N_5O_3$  338.2192, error 3.3 ppm).

**1,2-Bis[N-(N'-butylimidazolium)]ethane bis(trifluoroacetate) (3TFA).** Anion exchange procedure B was used; from **3Br** (0.30 g, 0.69 mmol) and AgTFA (0.348 g, 1.42 mmol) in deionized water (15 mL) yellow crystalline **3TFA** (0.348 g, 91%), mp 131.7–134.6 °C, resulted.  $^1H$  NMR (400 MHz, acetone- $d_6$ , 23 °C):  $\delta$  0.93 (t,  $J=7$ , 6H), 1.33 (m, 4H), 1.91 (m, 4H), 4.32 (t,  $J=7$ , 4H), 5.12 (s, 4H), 7.75 (t,  $J=2$ , 2H), 8.14 (t,  $J=2$ , 2H), 10.09 (t,  $J=2$ , 2H).  $^{13}C$  NMR (100 MHz, acetone- $d_6$ , 23 °C):  $\delta$  13.6, 19.9, 32.5, 49.2, 50.3, 123.3, 124.3, 139.1. HRMS (ESI):  $m/z$  389.2173 ( $[M-CF_3CO_2]^+$ , calcd for  $C_{18}H_{28}F_3N_4O_2$  389.2164, error 2.3 ppm).

**1,3-Bis[N-(N'-butylimidazolium)]propane bis(hexafluorophosphate) (4PF<sub>6</sub>)** The same procedure was used as for **1Br**, except the product could not be filtered because it was a viscous oil. From 1-butylimidazole (3.73 g, 30 mmol) and 1,3-dibromopropane (3.03 g, 15 mmol) in MeCN (20 mL), a light brown viscous liquid **4Br** (5.81 g, 86%) was isolated.  $^1H$  NMR (400 MHz, D<sub>2</sub>O, 23 °C):  $\delta$  0.92 (t,  $J=7$ , 6H), 1.31 (m, 4H), 1.84 (m, 4H), 2.54 (m, 2H), 4.20 (t,  $J=7$ , 4H), 4.33 (t,  $J=7$ , 2H), 7.53 (m, 4H), 8.86 (s, 2H). Anion exchange procedure A was used for **4PF<sub>6</sub>**; from **4Br** (5.00 g, 11.1 mmol) and **KPF<sub>6</sub>** (6.20 g, 33 mmol) in deionized water (40 mL) colorless crystalline solid **4PF<sub>6</sub>** (6.25 g, 97% from **4Br**), mp 96.4–97.7 °C, resulted.  $^1H$  NMR (400 MHz, acetone- $d_6$ , 23 °C):  $\delta$  0.94 (t,  $J=7$ , 6H), 1.38 (m, 4H), 1.94 (m, 4H), 2.74 (m, 2H), 4.36 (t,  $J=7$ , 4H), 4.55 (t,  $J=7$ , 2H), 7.81 (m, 4H), 9.12 (s, 2H).  $^{13}C$  NMR (100 MHz, acetone- $d_6$ , 23 °C):  $\delta$  13.6, 20.0, 31.5, 32.6, 47.5, 50.4, 123.6, 123.9, 136.9. HRMS (ESI):  $m/z$  435.2143 ( $[M-PF_6]^+$ , calcd for  $C_{17}H_{30}N_4PF_6$  435.2112, error 7.1 ppm)

**1,4-Bis[N-(N'-butylimidazolium)]butane bis(hexafluorophosphate) (5PF<sub>6</sub>)** The same procedure was used as for **4Br**; from 1-butylimidazole (3.73 g, 30 mmol) and 1,4-dibromobutane (3.24 g, 15 mmol) in MeCN (20 mL), **5Br** was obtained as a light brown viscous liquid (5.71 g, 82%). Anion exchange procedure A was used for **5PF<sub>6</sub>**; from **5Br** (5.70 g, 2.3 mmol) and **KPF<sub>6</sub>** (5.56 g, 30 mmol) in deionized water (40 mL) **5PF<sub>6</sub>** was isolated as an off-white viscous liquid (7.05 g, 96% from **5Br**), which solidified in a vacuum oven, mp 50.4–52.4 °C.  $^1H$  NMR (400 MHz, CD<sub>3</sub>CN, 23 °C):  $\delta$  0.94 (t,  $J=7$ , 6H), 1.34 (m, 4H), 1.78–1.85 (m, 8H), 2.74 (m, 4H), 4.14 (m, 8H), 7.38 (m, 4H), 8.42 (s, 2H).  $^{13}C$  NMR (100 MHz, CD<sub>3</sub>CN, 23 °C):  $\delta$  13.7, 20.0, 27.2, 32.5, 49.8, 50.4, 123.4, 123.6, 136.3. HRMS (ESI):  $m/z$  449.2304 ( $[M-PF_6]^+$ , calcd for  $C_{18}H_{32}N_4PF_6$  449.2269, error 7.9 ppm)

**1-Hexylimidazole.** To a solution of imidazole (1.361 g, 20 mmol) in NaOH (50%) solution (0.19 g, 24 mmol), 1-bromohexane (3.31 g, 20 mmol) and THF (15 mL) were added. The mixture was refluxed for 3 days. After the mixture had cooled to room temperature, THF was removed by a rotoevaporator. The residue was extracted with dichloromethane/water 3 times. The combined organic layer was washed with water and then dried over Na<sub>2</sub>SO<sub>4</sub>. The drying agent was filtered off and the filtrate solution was concentrated. Drying in a vacuum oven gave yellow oily product, 2.64 g (87%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 22 °C): δ 0.88 (t, J=7, 3H), 1.29 (s (br), 6H), 1.77 (m, 2H), 3.92 (t, J=7, 2H), 6.90 (s, 1H), 7.05 (s, 1H), 7.46 (s, 1H). The <sup>1</sup>H-NMR spectrum was exactly identical to the literature result.<sup>41</sup>

**1,2-Bis[N-(N'-hexylimidazolium)]ethane dibromide (6Br).** The same procedure was used as for **1Br**. From 1-hexylimidazole (1.52 g, 10 mmol) and 1,2-dibromoethane (0.940 g, 5 mmol) in MeCN (10 mL), colorless crystalline **6Br** (2.14 g, 87%) was isolated, mp 225.5–229.3 °C (dec.). <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O, 23 °C): δ 0.71 (t, J=7, 6H), 1.12 (m, 12H), 1.68 (m, J=7, 4H), 4.04 (t, J=8, 4H), 4.79 (overlapped with solvent residual peak), 7.34 (s, 2H), 7.45 (s, 2H), 8.68 (s, 2H). <sup>13</sup>C NMR (100 MHz, D<sub>2</sub>O, 23 °C): δ 13.4, 21.9, 25.1, 29.0, 30.4, 49.0, 50.2, 123.8, 124.0, 136.0. HRMS (ESI): m/z 411.2132 ([M-Br]<sup>+</sup>, calcd for C<sub>20</sub>H<sub>36</sub>N<sub>4</sub>Br 411.2123, error 2.2 ppm).

**1,2-Bis[N-(N'-hexylimidazolium)]ethane bis(tetrafluoroborate) (6BF<sub>4</sub>).** Anion exchange procedure A was used; the precipitated oil was washed with water 5 times and then dried in a vacuum oven. From **6Br** (1.0 g, 2.0 mmol) and NaBF<sub>4</sub> (0.66 g, 6 mmol) in deionized water (10 mL) **6BF<sub>4</sub>** was isolated as a colorless viscous material (0.80 g, 78%). <sup>1</sup>H NMR (400 MHz, acetone-*d*<sub>6</sub>, 23 °C): δ 0.87 (t, J=7, 6H), 1.33 (m, 12H), 1.97 (m, J=7, 4H), 4.33 (t, J=8, 4H), 4.94 (s, 4H), 7.72 (s, 2H), 7.76 (s, 2H), 9.00 (s, 2H). <sup>13</sup>C NMR (100 MHz, acetone-*d*<sub>6</sub>, 22 °C): δ 14.1, 22.9, 26.3, 30.3, 31.8, 49.9, 50.8, 123.6, 124.1, 137.1. HRMS (ESI): m/z 419.2991 ([M-BF<sub>4</sub>]<sup>+</sup>, calcd for C<sub>20</sub>H<sub>36</sub>N<sub>4</sub>BF<sub>4</sub> 419.2969, error 5.2 ppm).

**1,2-Bis[N-(N'-hexylimidazolium)]ethane bis(hexafluorophosphate) (6PF<sub>6</sub>).** Anion exchange procedure A was used; from **6Br** (0.630 g, 1.3 mmol) and KPF<sub>6</sub> (0.56 g, 3.0 mmol) in deionized water (5 mL) colorless crystalline **6PF<sub>6</sub>** (0.810 g, 91%), mp 197.5–198.8 °C, was isolated. <sup>1</sup>H NMR (400 MHz, acetone-*d*<sub>6</sub>, 22 °C): δ 0.87 (t, J=7, 6H), 1.33 (m, 12H), 1.94 (m, J=7, 4H), 4.34 (t, J=8, 4H), 5.01 (s, 4H), 7.74 (s, 2H), 7.87 (s, 2H), 9.04 (s, 2H). <sup>13</sup>C NMR (100 MHz, acetone-*d*<sub>6</sub>, 22 °C): δ 14.1, 23.0, 26.4, 30.5, 31.8, 49.9, 50.8, 123.7, 124.3, 137.3. HRMS (ESI): m/z 477.2603 ([M-PF<sub>6</sub>]<sup>+</sup>, calcd for C<sub>20</sub>H<sub>36</sub>N<sub>4</sub>PF<sub>6</sub> 477.2582, error 4.4 ppm).

**1,2-Bis[N-(N'-hexylimidazolium)]ethane bis[bis(trifluoromethanesulfonyl)imide] (6TFSI).**

The same procedure was used as for **6BF<sub>4</sub>**. From **6Br** (0.492 g, 1.0 mmol) and LiTf<sub>2</sub>N (0.86 g, 3.0 mmol) in deionized water (5 mL), **6TFSI** was isolated as a colorless viscous oil (0.810 g, 91%). <sup>1</sup>H NMR (400 MHz, acetone-*d*<sub>6</sub>, 22 °C): δ 0.87 (t, J=7, 6H), 1.32 (m, 12H), 1.97 (m, J=7, 4H), 4.36 (t, J=8, 4H), 5.08 (s, 4H), 7.73 (s, 2H), 7.96 (s, 2H), 9.11 (s, 2H). <sup>13</sup>C NMR (100 MHz, acetone-*d*<sub>6</sub>, 22 °C): δ 14.1, 23.0, 26.3, 30.4, 31.7, 49.8, 50.7, 123.6, 124.2, 137.3. HRMS (ESI): m/z 612.2155 ([M-Tf<sub>2</sub>N]<sup>+</sup>, calcd for C<sub>22</sub>H<sub>36</sub>F<sub>6</sub>N<sub>5</sub>O<sub>4</sub>S<sub>2</sub> 612.2113, error 4.2 ppm).

**1-Dodecylimidazole.** To a solution of imidazole (6.81 g, 100 mmol) in NaOH (50%) solution (8.80 g, 110 mmol), 1-bromododecane (24.92 g, 100 mmol) and THF (30 mL) were added. The mixture was refluxed for 3 days. After the mixture had cooled, THF was removed on a rotoevaporator. The residue was extracted with dichloromethane/water 3 times. The combined organic layer was washed with water and then dried over Na<sub>2</sub>SO<sub>4</sub>. The drying agent was filtered off and the filtrate solution was concentrated. Column chromatography through a short silica-gel column with THF gave a clear yellow oil (20.51 g, 87%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 22 °C): δ 0.88 (t, J=7, 3H), 1.29 (m, 18H), 1.76 (m, J=7, 2H), 3.91 (t, J=7, 4H), 6.90 (s, 1H), 7.05 (s, 1H), 7.45 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 22 °C): δ 14.0, 22.6, 26.4, 29.0, 29.2, 29.3, 29.4, 29.5, 31.0, 31.8, 46.9, 118.6, 129.2, 136.9. The <sup>1</sup>H-NMR spectrum was exactly identical to the literature result.<sup>41</sup>

**1,2-Bis[N-(N'-dodecylimidazolium)]ethane salts (7Br, 7PF<sub>6</sub> and 7TFSI)** A solution of 1-dodecylimidazole (3.78 g, 16 mmol) and 1,2-dibromoethane (1.50 g, 8 mmol) in MeCN (15 mL) was refluxed for 3 days. After the mixture had cooled, the volatile materials were removed by vacuum. The residue was dispersed in THF (30 mL) and the insoluble bromide salt was filtered. The filter cake was washed with THF 3 times. Drying in a vacuum oven gave colorless crystalline solid **7Br** (4.54 g, 86%), mp 249.3–252.9 °C (dec). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, 23 °C): δ 0.86 (t, J=7, 6H), 1.25 (m (br), 36H), 1.74 (t, J=7, 4H), 4.13 (t, J=7, 4H), 4.71 (s, 4H), 7.69 (s, 2H), 7.85 (s, 2H), 9.15 (s, 2H). HRMS (ESI): m/z 499.4739 ([M-H-2Br]<sup>+</sup>, calcd for C<sub>32</sub>H<sub>59</sub>N<sub>4</sub> 499.4740, error 0.2 ppm), m/z 250.7419 ([M-2Br+H]<sup>2+</sup>, calcd for half mass of C<sub>32</sub>H<sub>60</sub>N<sub>4</sub> 250.7443, error 9.4 ppm). **7PF<sub>6</sub>** was obtained by following general anion exchange procedure A, except the mixture was stirred at 50 °C for 24 hours; from **7Br** (2.00 g, 3.03 mmol), KPF<sub>6</sub> (1.56 g, 8.5 mmol) and deionized water (60 mL) colorless solid **7PF<sub>6</sub>** (2.33 g, 97%), mp 217.4–223.0 °C (dec), was isolated. <sup>1</sup>H NMR (400 MHz, acetone-*d*<sub>6</sub>, 23 °C): δ 0.87 (t, J=7, 6H), 1.27–1.36 (m (br), 36H), 1.95 (t, J=7, 4H), 4.35 (t, J=7, 4H), 5.03 (s, 4H), 7.73 (t, J=2, 2H), 7.85

(t, J=2, 2H), 9.03 (s, 2H).  $^{13}\text{C}$  NMR (100 MHz, acetone- $d_6$ , 23 °C):  $\delta$  14.3, 23.3, 26.8, 29.7, 30.0, 30.1, 30.30, 30.35, 30.36, 32.6, 50.1, 50.9, 123.8, 124.4, 137.4. HRMS (ESI): m/z 645.4465 ( $[\text{M-PF}_6]^+$ , calcd for  $\text{C}_{32}\text{H}_{60}\text{N}_4\text{PF}_6$  645.4460, error 0.8 ppm). For **7TFSI**, the same procedure was used as for **7PF<sub>6</sub>**. From **7Br** (2.70 g, 6.4 mmol),  $\text{LiTf}_2\text{N}$  (4.32 g, 15 mmol) and deionized water (60 mL), crystalline **7TFSI** (3.89 g, 97% from **7Br**), mp 45.5-47.7 °C, was isolated.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 23 °C):  $\delta$  0.87 (t, J=7, 6H), 1.25-1.31 (m (br), 36H), 1.86 (t, J=7, 4H), 4.15 (t, J=7, 4H), 4.74 (s, 4H), 7.33 (t, J=2, 2H), 7.60 (t, J=2, 2H), 8.84 (s, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 23 °C):  $\delta$  14.2, 22.8, 26.3, 29.0, 29.4, 29.5, 29.6, 29.7, 32.0, 48.5, 50.7, 123.0, 123.3, 136.0. HRMS (ESI): m/z 780.3997 ( $[\text{M-Tf}_2\text{N}]^+$ , calcd for  $\text{C}_{34}\text{H}_{60}\text{F}_6\text{N}_5\text{O}_4\text{S}_2$  780.3985, error 0.8 ppm).

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## Supporting Information

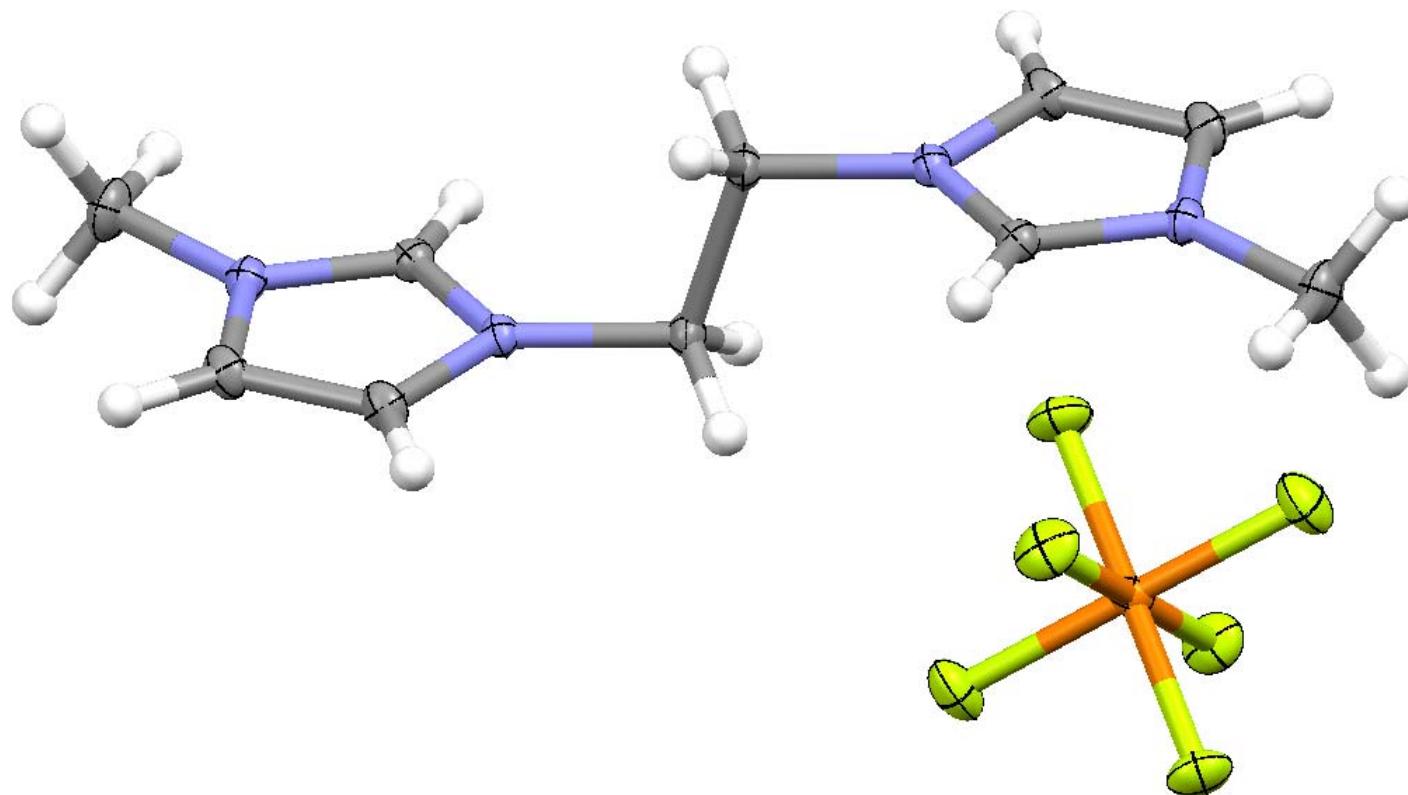


**Figure 11-S1.** Ellipsoid plots of the X-ray structure of **1PF<sub>6</sub>** with 50% probability.

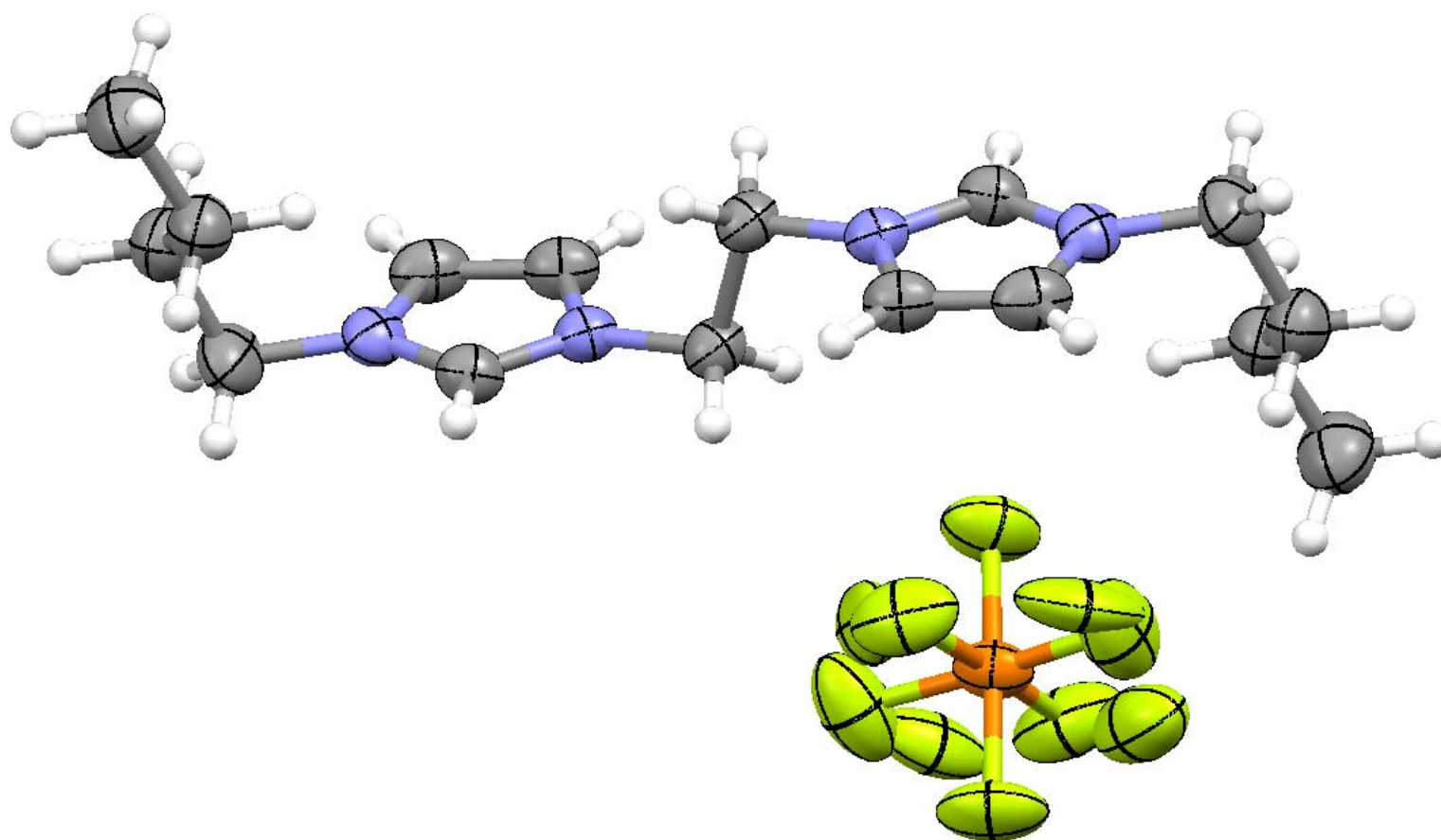


**Figure 11-S2.** Ellipsoid plots of the X-ray structure of **3PF<sub>6</sub>** with 50% probability. All PF<sub>6</sub> anions are disordered.

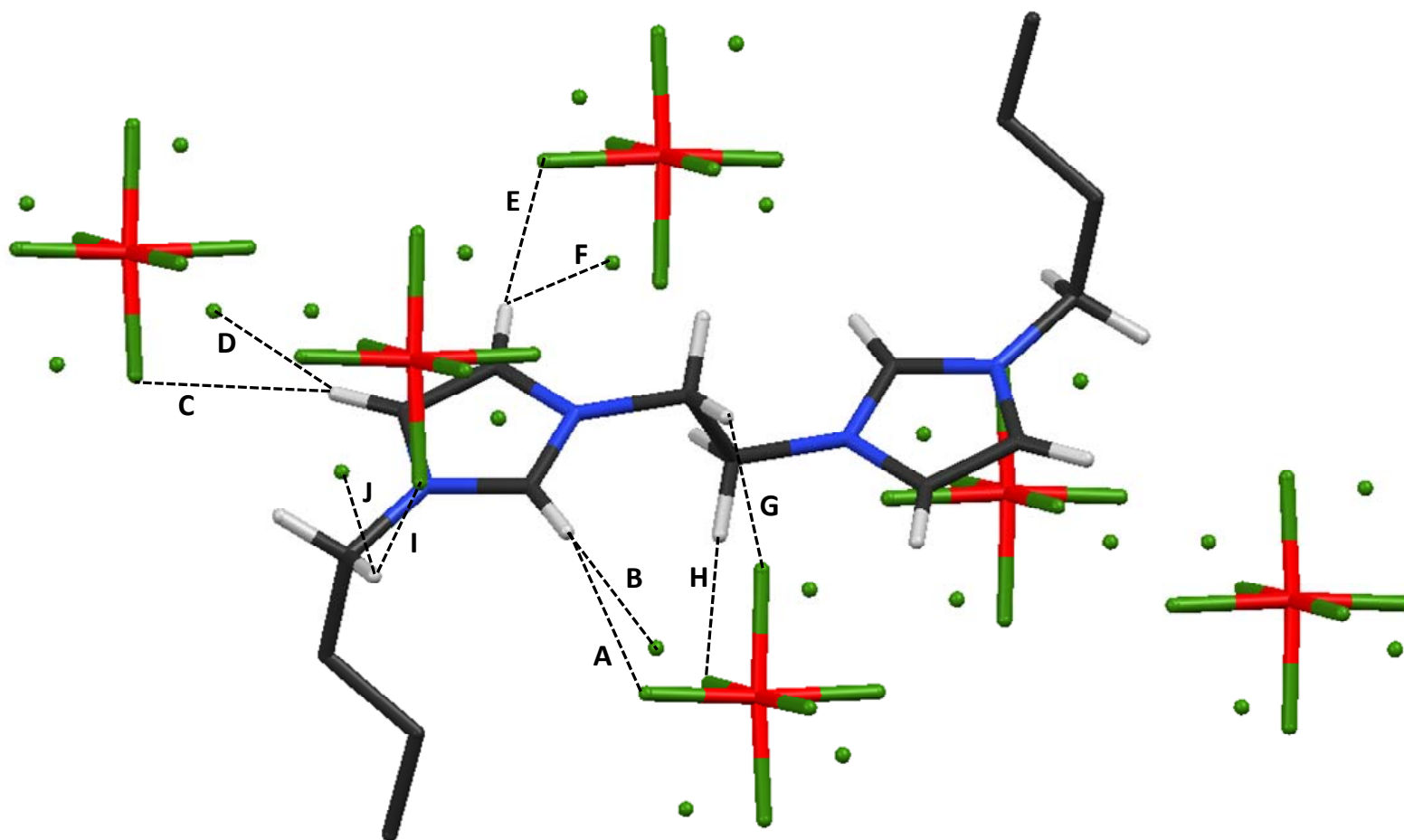


**Figure 11-S3.** Capped-sticks view of the X-ray structure of 3PF<sub>6</sub>. H···F distances (Å), C-H···F angles (degrees): **A** 2.59, 165; **B** 2.26, 175; **C** 2.64, 175; **D** 2.29, 157; **E** 2.42, 173; **F** 2.53, 142; **G** 2.41, 142; **H** 2.55, 145; **I** 2.56, 137; **J** 2.67, 127.



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42. Colorless prisms crystallized from acetone/pentane at room temperature. The chosen crystal was centered on the goniometer of an Oxford Diffraction Gemini A Ultra

diffractometer operating with MoK $\alpha$  radiation. The data collection routine, unit cell refinement, and data processing were carried out with the program CrysAlisPro.<sup>43</sup> The Laue symmetry and systematic absences were consistent with the monoclinic space groups *C2/c* and *Cc*. The centric space group *C2/c* was chosen based on the E-statistics. The structure was solved by direct methods and refined using SHELXTL NT.<sup>44</sup> The asymmetric unit of the structure comprises 0.5 crystallographically independent molecules. The final refinement model involved anisotropic displacement parameters for non-hydrogen atoms and a riding model for all hydrogen atoms.

Crystal data: prism, colorless, crystal size = 0.21 x 0.21 x 0.09 mm<sup>3</sup>, C<sub>10</sub>H<sub>16</sub>N<sub>4</sub>•2PF<sub>6</sub>, M = 482.21, wavelength = 0.71073 Å, monoclinic, space group *C2/c*, *a* = 22.186(3) Å, *b* = 6.4852(3) Å, *c* = 14.4065(13) Å,  $\alpha$  = 90°,  $\beta$  = 122.621(15)°,  $\gamma$  = 90°, *V* = 1745.8(3) Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.835 Mg/m<sup>3</sup>, *T* = 100(2) K,  $\mu$  = 0.376 mm<sup>-1</sup>, 11193 reflections collected, 2562 [R(int) = 0.0300] independent reflections, 2562 / 0 / 128 data / restraints / parameters, *F*(000) = 968, *R*<sub>1</sub> = 0.0358, *wR*<sub>2</sub> = 0.0780 (all data), *R*<sub>1</sub> = 0.0288, *wR*<sub>2</sub> = 0.0759 [*I* > 2 $\sigma$ (*I*)], and goodness-of-fit on *F*<sup>2</sup> = 1.051.

43. CrysAlisPro v171.33.51, Oxford Diffraction: Wroclaw, Poland, 2009

44. G. M. Sheldrick, *Acta Cryst.* 2008, **A64**, 112-122.

45. Colorless plates crystallized from acetone/pentane by vapor diffusion. The chosen crystal was centered on the goniometer of an Oxford Diffraction Gemini A Ultra diffractometer operating with MoK $\alpha$  radiation. The data collection routine, unit cell refinement, and data processing were carried out with the program CrysAlisPro.<sup>43</sup> The Laue symmetry was consistent with the triclinic space group *P*-1. The structure was solved by direct methods and refined using SHELXTL NT.<sup>44</sup> The asymmetric unit of the structure comprises 0.5 crystallographically independent formula units. The final refinement model involved anisotropic displacement parameters for non-hydrogen atoms and a riding model for all hydrogen atoms. The PF<sub>6</sub> anion was modeled with 2-position disorder with relative occupancies that refined to 0.761(9) and 0.239(9). The P-F bond lengths and the F---F distances were restrained with DFIX and the anisotropic displacement parameters of the disordered fluorine atoms were restrained with SIMU.

Crystal data: plate, colorless, crystal size = 0.03 x 0.18 x 0.47 mm<sup>3</sup>, C<sub>16</sub>H<sub>28</sub>N<sub>4</sub>•2PF<sub>6</sub>, M = 566.36, wavelength = 0.71073 Å, triclinic, space group *P*-1, *a* = 6.5214(3) Å, *b* = 6.9156(3) Å, *c* = 13.8874(7) Å,  $\alpha$  = 97.336(4)°,  $\beta$  = 97.674(4)°,  $\gamma$  = 99.448(4)°, *V* = 605.07(5) Å<sup>3</sup>, *Z* =

1,  $D_c = 1.554 \text{ Mg/m}^3$ ,  $T = 100(2) \text{ K}$ ,  $\mu = 0.284 \text{ mm}^{-1}$ , 6608 reflections collected, 2795 [R(int) = 0.0338] independent reflections, 2795 / 60 / 193 data / restraints / parameters,  $F(000) = 290$ ,  $R_1 = 0.0961$ ,  $wR_2 = 0.1269$  (all data),  $R_1 = 0.0517$ ,  $wR_2 = 0.1129$  [ $I > 2\sigma(I)$ ], and goodness-of-fit on  $F^2 = 0.989$ .

## Chapter 12

### 1,2-Bis[N-(N'-alkylimidazolium)]ethane Salts as a New Class of Organic Ionic Plastic Crystals

#### Abstract

A new class of organic ionic plastic crystals was found from dicationic imidazolium salts. A series of alkylene 1,2-bis[N-(N'-alkylimidazolium)] salts with Br<sup>-</sup> and PF<sub>6</sub><sup>-</sup> anions was prepared and most of 1,2-bis[N-(N'-alkylimidazolium)]ethane salts show multiple solid-solid phase transitions. The salts with a longer spacer (C<sub>3</sub> or C<sub>4</sub>) do not show any solid-solid transitions. The PF<sub>6</sub><sup>-</sup> salts with C<sub>10</sub> and C<sub>12</sub> are “organic ionic plastic crystals” by the Timmermans’ definition because they have low  $\Delta S_f$  (11 J K<sup>-1</sup> mol<sup>-1</sup> for C<sub>10</sub> and 12 J K<sup>-1</sup> mol<sup>-1</sup> for C<sub>12</sub> side armed compounds). The melting point of the PF<sub>6</sub><sup>-</sup> salts gradually increases from C<sub>4</sub> to C<sub>10</sub> side armed compounds. The thermal degradations of the salts with *n*-hexyl side arms occur at the lowest temperatures in both Br<sup>-</sup> and PF<sub>6</sub><sup>-</sup> cases; the thermal stabilities increases as the side chain length gets longer up to C<sub>10</sub>.

#### Introduction

Organic ionic plastic crystals are attractive materials as their novel physical properties and potential applications are realized: highly conductive solid state electrolytes. The applications are getting wider: electroactive devices such as fuel cells, batteries and solar cells.<sup>1</sup> Plastic crystals were described in detail by Timmermans; typically molecular plastic crystalline materials have a low entropy of melting,  $\Delta S_f < 20 \text{ J K}^{-1} \text{ mol}^{-1}$ .<sup>2</sup> Plastic crystals have long range order but short-range disorder, which typically are from rotational motions of the molecules.<sup>3,4</sup> It is very difficult to predict which ionic materials will have plastic crystalline behaviors; however, McFarlane et al. found that cation structure is most important in determining plasticity after comparison of a range of organic ionic plastic crystals.<sup>3</sup>

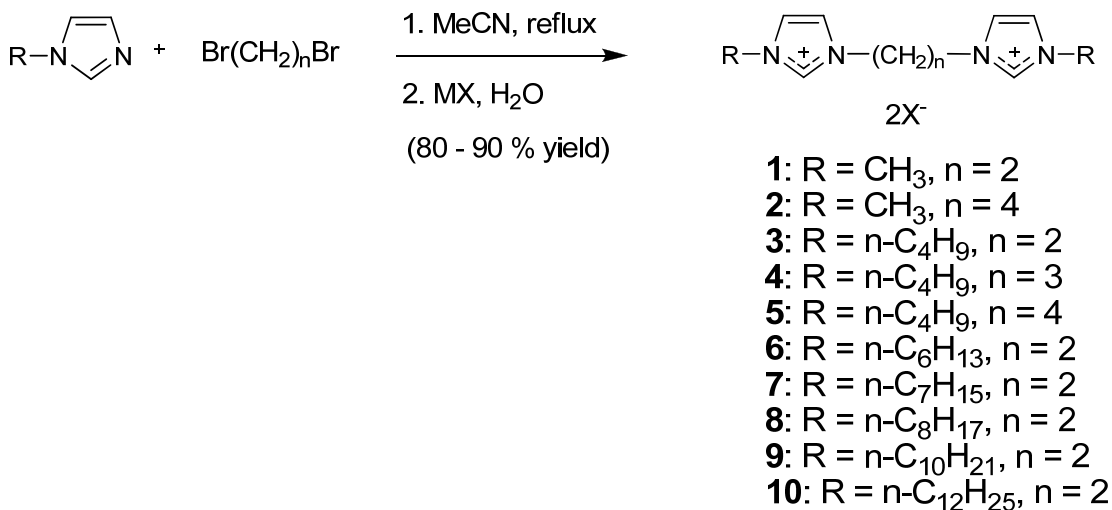
Tetraethylammonium dicyanamide ([Et<sub>4</sub>N][DCA]) has a highly conducting plastic crystal phase that spans room temp. and its  $\Delta S_f$  is  $4 \pm 0.5 \text{ J K}^{-1} \text{ mol}^{-1}$ , which is one of the lowest known.<sup>5</sup> Pyrrolidinium salts with different alkyl substituents and a wide range of anions show plastic crystal behaviors. N-Methyl-N-alkylpyrrolidinium salts were studied by MacFarlane et al.<sup>6-11</sup> Some of the salts are room temperature ionic liquids (RTILs). MacFarlane and Forsyth have studied organic plastic crystals and ionic liquids enthusiastically and they characterize materials with various analytical tools: DSC, TGA, X-ray diffraction (XRD), NMR, impedance spectrometry (for conductivity), Raman spectroscopy (for rotational properties), and cyclic voltammetry (for electrical properties).<sup>1, 4</sup> However, it is hard to find plastic crystals of imidazolium salts up to now. MacFarlane studied some imidazolium salts to compare their electrical properties with other organic ionic plastic crystals, but the imidazolium salts they studied did not show any solid-solid phase transition.

In the previous chapter we discussed structure-property relationships of the bis(N-alkylimidazolium) salts with various lengths of side arms and lengths of alkylene spacers between imidazolium units. For the thermal properties, melting points and thermal decomposition temperatures were discussed vs. structure. Surprisingly, we found multiple thermal transitions for the bis(N-alkylimidazolium) salts by DSC. For example, bis[N-(N'-hexylimidazolium)ethane 2PF<sub>6</sub><sup>-</sup>] shows 4 endothermic peaks (including a melting point) during heating and the transitions are perfectly reproducible. Thus, we are reporting the preparation of novel dicationic imidazolium plastic crystals with different side-arm lengths and their thermal properties.

## Results and Discussion

**Synthesis of Alkylene Bis(N-alkylimidazolium) Salts.** Various alkylene bis[N-(N'-alkylimidazolium)] salts were synthesized in two steps (Scheme 12-1): the coupling quaternization reaction of the 1-alkylimidazole (2 molar equivalents) with a dibromoalkane (1 molar equivalent) and anion exchange in water. Non-commercial 1-alkylimidazoles were prepared; 1-hexyl-, 1-heptyl-, 1-octyl-, 1-decyl-, and 1-dodecylimidazole were prepared from imidazole and the corresponding bromoalkanes with NaOH in high yields.<sup>12</sup> Most of the alkylene N-(N'-alkylimidazolium) bromide salts were very hygroscopic; they are either crystalline solids or waxy materials. The counter anion exchange reactions were performed in aqueous conditions with KPF<sub>6</sub>. The reaction mixture was heated to 60 °C, if the bromide salt was

not soluble at room temperature. The completion of the ion exchange reactions was confirmed by the Beilstein (copper/flare) test for each sample. All the imidazolium PF<sub>6</sub><sup>-</sup> salts are colorless crystalline solids at room temp, except **5PF<sub>6</sub>**, which is a pale-yellow sticky material.



**Scheme 12-1.** Synthesis of alkylene bis[N-(N'-alkylimidazolium)] salts.

**Thermal Analysis – Phase Behavior.** The phase transitions and thermal decompositions (TGA) of the newly synthesized imidazolium salts are summarized in Table 12-1. Generally, all the bis(N-alkylimidazolium) salts with an ethylene (C2) spacer and PF<sub>6</sub><sup>-</sup> (or Br<sup>-</sup>) have one or more solid-solid transitions on DSC. And all the transitions were reversible, unless the salts were thermally decomposed; the transition peaks were also clearly shown on cooling scans.

**1PF<sub>6</sub>** (methyl side arms) shows an endothermic peak at 199 °C before melting. The molar entropy of fusion ( $\Delta S_f$ ) is 64 J K<sup>-1</sup> mol<sup>-1</sup> and it is somewhat larger than typical plastic crystals (20 J K<sup>-1</sup> mol<sup>-1</sup> from Timmermans' definition). **2PF<sub>6</sub>** with a C<sub>4</sub> spacer does not have a T<sub>ss</sub>, but only has a T<sub>m</sub> at 113 °C. For the salts with *n*-butyl side arms, **3Br** has two solid-solid transitions at 46 and 163 °C. It has a small heat absorption at T<sub>m</sub> and it could be an ionic plastic crystal, but  $\Delta S_f$  is hard to calculate from the heating scan, because the two transitions (T<sub>ss</sub> and T<sub>m</sub>) are too close to integrate the T<sub>m</sub> at 165 °C. Its T<sub>m</sub> is visually confirmed by a melting point apparatus (167 °C, a median value). If the exothermic peak during the cooling was used,  $\Delta S_f$  is 2.2 J K<sup>-1</sup> mol<sup>-1</sup>, which could be the lowest known value. **3PF<sub>6</sub>** has one T<sub>ss</sub> (solid-solid transition temperature) at 24 °C, a broad endothermic peak.  $\Delta S_f$  of **3PF<sub>6</sub>** is 49 J K<sup>-1</sup> mol<sup>-1</sup> and it is still larger than typical plastic crystals. As I reported in the previous chapter, the solid-state structures of **1PF<sub>6</sub>** and **3PF<sub>6</sub>** are quite different; there are two sets of stack for **1PF<sub>6</sub>** but **3PF<sub>6</sub>** has only one set. These different

types of stacking may be a clue for the solid-solid transitions, but no evidence has been found for this. **3BF<sub>4</sub>** is relatively soft material compared to other crystalline bis-imidazolium salts, and it has  $T_g$  at -31 °C and an exothermic crystallization peak at 36 °C before the melting point.

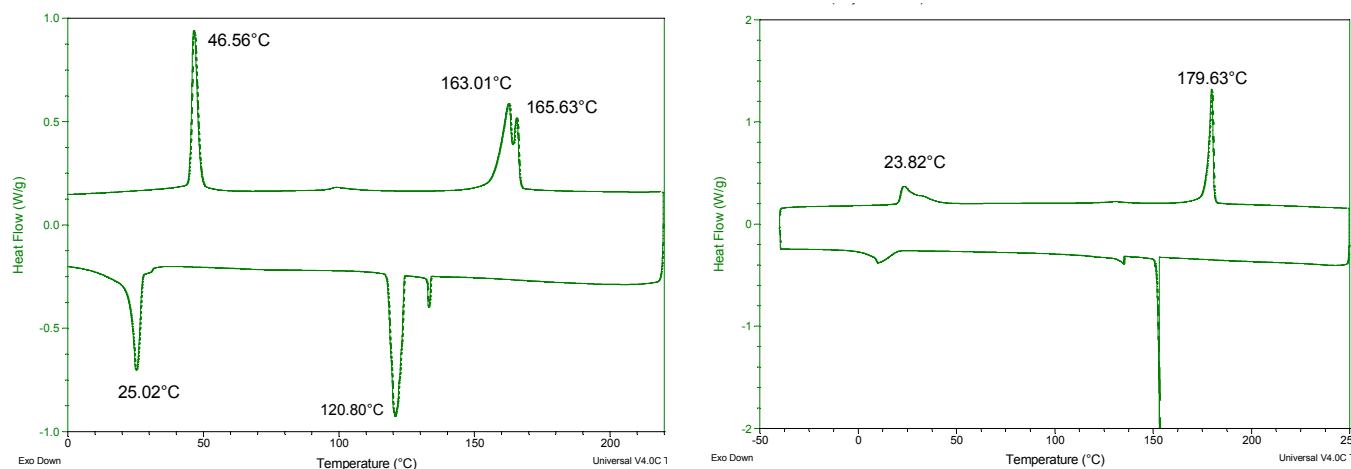


**Figure 12-1.** DSC diagrams of **3Br** (left) and **3PF<sub>6</sub>** (right) (heating and cooling rate 5 K/min, N<sub>2</sub>).

For the salts with *n*-hexyl side arms, both **6Br** and **6PF<sub>6</sub>** show three solid-solid transitions. Interestingly, the first transition of **6PF<sub>6</sub>** is below room temperature, 9.5 °C and then two more endothermic peaks appear at 78.8 and 79.8 °C in heating. These three transitions are also reproducible in cooling at 2.4, 76.3 and 78.3 °C, respectively. The three transitions have different heat absorptions, but surprisingly the first transition at 9.5 °C has a quite large heat absorption, even though no visual difference could not be found between the two phases (colorless crystalline).  $\Delta S_f$  of **6PF<sub>6</sub>** is still large, 44 J K<sup>-1</sup> mol<sup>-1</sup>. **7Br** and **7PF<sub>6</sub>** with a C<sub>3</sub> spacer possess glass transitions and melting points, but do not have  $T_{ss}$ . So the structures of bis(*N*-alkylimidazolium) salts with a C<sub>3</sub> or C<sub>4</sub> spacer do not promote solid-solid transitions.

The imidazolium salts with *n*-heptyl side arms (**8Br** and **8PF<sub>6</sub>**) are also interesting. **8Br** has four solid-solid transitions and all they are reproducible as shown in Figure 12-2. The second and third heating traces of the samples are identical and the phase transitions during cooling are quite symmetric compared to the heating traces.  $\Delta S_f$  of **8PF<sub>6</sub>** is still large, 41 J K<sup>-1</sup> mol<sup>-1</sup> but close to the  $\Delta S_f$  of *N*-methyl-*N*-alkylpyrrolidinium bis(trifluoromethanesulfone)imide salts (38-43 J K<sup>-1</sup> mol<sup>-1</sup>).<sup>6</sup>



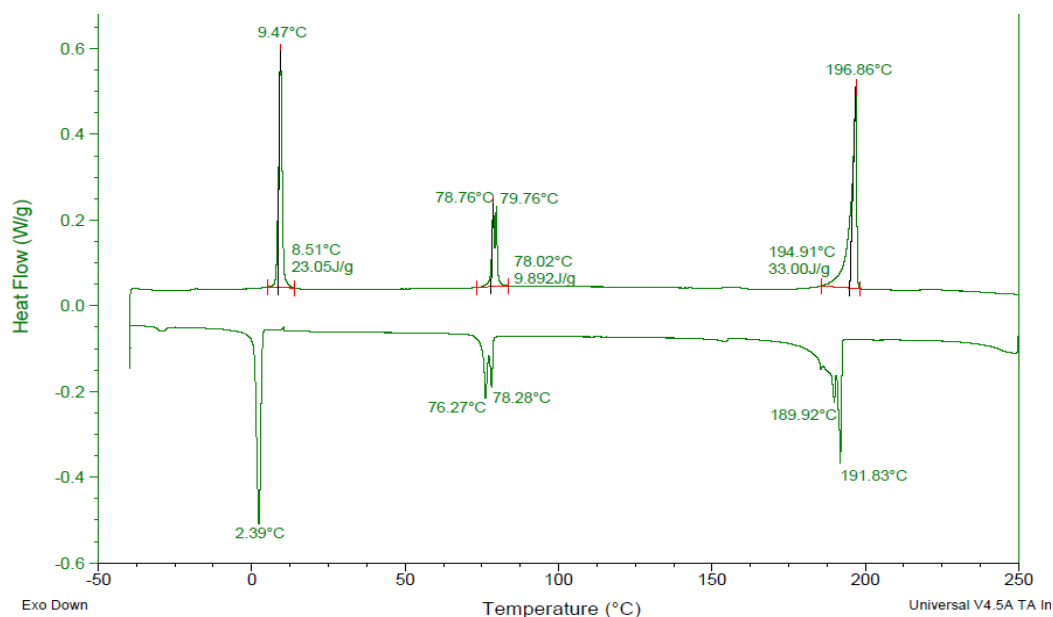


**Figure 12-2.** DSC diagrams of **6PF<sub>6</sub>** (heating and cooling rate 5 K/min, N<sub>2</sub>).

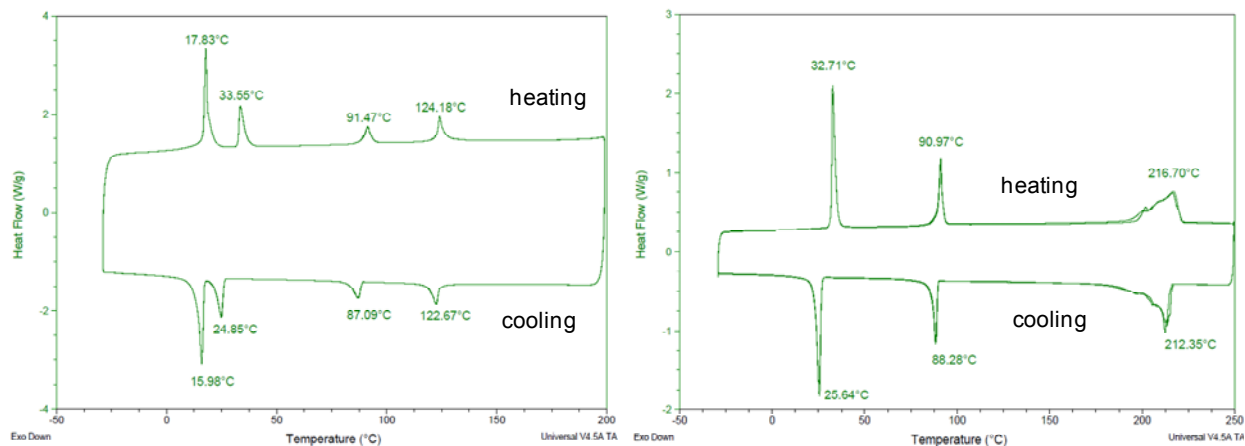


**Figure 12-3.** DSC diagrams of **8Br** (left) and **8PF<sub>6</sub>** (right) (heating and cooling rate 5 K/min, N<sub>2</sub>). Only the second and third heating traces are shown and they are identical.

The imidazolium salts with *n*-octyl side arms (**9Br** and **9PF<sub>6</sub>**) also shows multiple solid-solid transitions. **9Br** has three  $T_{ss}$ : 6, 127 and 135 °C. The heat absorption at 127 °C is tiny compared to the other transitions, but still it is observed during the cooling and the next heating scans. Its  $T_m$  is not clearly observed because of its low decomposition temperature. Decomposition of **9Br** started at 235 °C from TGA. **9PF<sub>6</sub>** has two clear solid-solid transitions at low temperatures: 44 and 70 °C.  $T_m$  of **9PF<sub>6</sub>** is 236 °C and  $\Delta S_f$  is 36 J K<sup>-1</sup> mol<sup>-1</sup>.

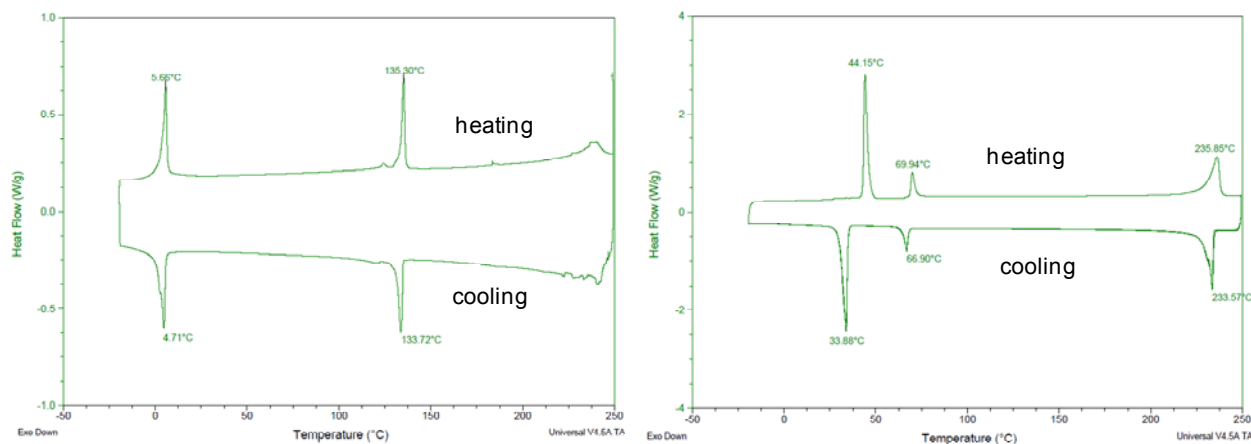


**Figure 12-4.** DSC diagrams of **9Br** (left) and **9PF<sub>6</sub>** (right) (heating and cooling rate 5 K/min, N<sub>2</sub>). Only the second and third heating traces are shown and they are identical.

The imidazolium salts with *n*-decyl side arms (**10Br** and **10PF<sub>6</sub>**) also shows multiple solid-solid transitions. Both salts have two  $T_{ss}$ s before melting or decomposition. The first transition of **10Br** is close to room temp (33 °C). The melting point may be ~240 °C, but it's very close to the decomposition temperature and it is hard to calculate  $\Delta S_f$ . The DSC trace of **10PF<sub>6</sub>** looks more like typical a ionic plastic crystal; two big transition peaks before melting point and small heat absorption at  $T_m$  (249 °C), which is close to the decomposition temperature.  $\Delta S_f$  of **10PF<sub>6</sub>** is 11 J K<sup>-1</sup> mol<sup>-1</sup> from the DSC result, which is typical value of organic ionic plastic crystals, even though the integration of  $T_m$  is not clear due to the decomposition (249 °C) very close to the transition.

The imidazolium salts with *n*-dodecyl side arms (**11Br** and **11PF<sub>6</sub>**) are similar to compounds **10**. **11Br** has two  $T_{ss}$ s and decomposed before melting and its first and second transitions are slightly higher than **10Br**. **11PF<sub>6</sub>** has also two solid-solid transitions and also has  $T_m$  at 247 °C.  $\Delta S_f$  of **11PF<sub>6</sub>** is 12 J K<sup>-1</sup> mol<sup>-1</sup> from the DSC result and **11PF<sub>6</sub>** is also an ionic plastic crystal.

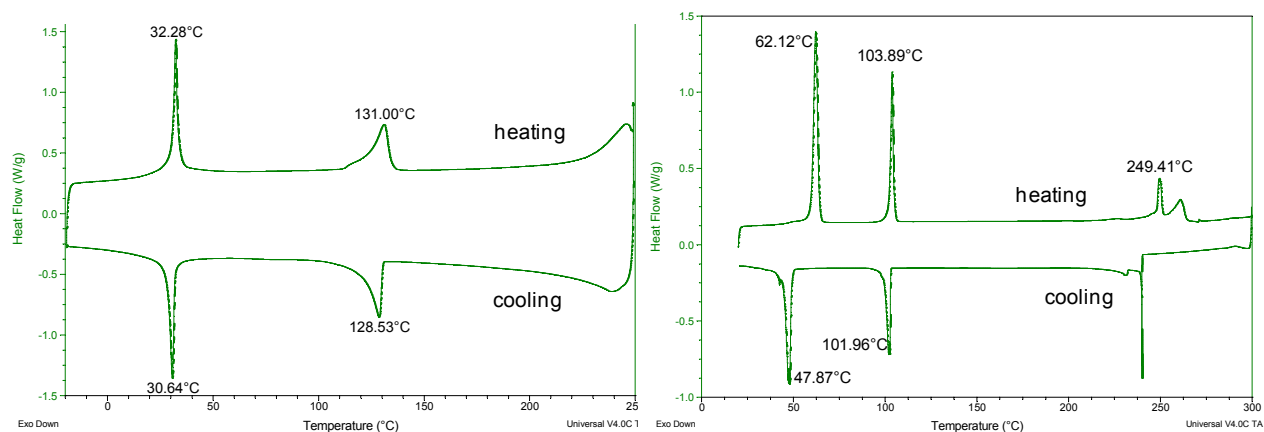


**Figure 12-5.** DSC diagrams of **10Br** (left) and **10PF<sub>6</sub>** (right) (heating and cooling rate 5 K/min, N<sub>2</sub>). Only the second heating scans are shown in this figure.

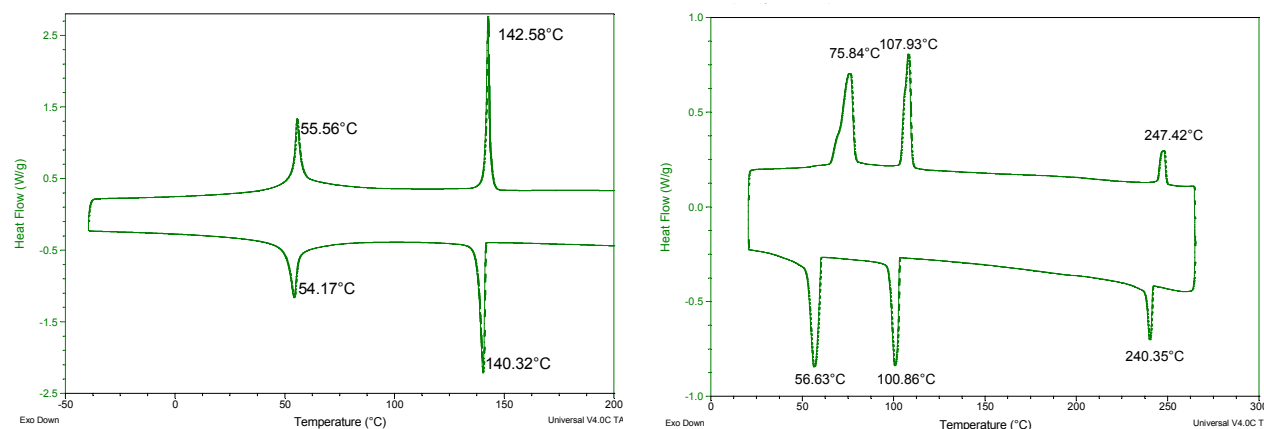


**Figure 12-6.** DSC diagrams of **11Br** (left) and **11PF<sub>6</sub>** (right) (heating and cooling rate 5 K/min, N<sub>2</sub>).

In summary of the DSC phase behavior, the solid-solid transitions occurred only for the bis(N-alkylimidazolium)ethane moieties with either Br<sup>−</sup> and PF<sub>6</sub><sup>−</sup> anions. The salts with a longer spacer have no T<sub>ss</sub>. Even though we tested just one such anion, the bisimidazolium salt with BF<sub>4</sub><sup>−</sup> does not show T<sub>ss</sub> either. The bisimidazolium PF<sub>6</sub><sup>−</sup> salts with C<sub>10</sub> and C<sub>12</sub> (**10PF<sub>6</sub>** and **11PF<sub>6</sub>**) can be called “organic plastic crystals” from the Timmermans’ definition based on the  $\Delta S_f$  value; however, **11PF<sub>6</sub>** needs more investigation to obtain accurate entropy of fusion. One of the bromide salts, **3Br** with butyl side arms may be a true ionic plastic crystal, because its heat absorption (or emission during cooling) at T<sub>m</sub> is quite small.

**Table 12-1.** DSC Phase Transition Temperatures of the Alkylene Bis[N-(N'-alkylimidazolium)] Salts.

$R-N\text{---}N(CH_2)_n\text{---}N\text{---}N-R$   
 $2X^-$

| Entry                   | Side-Arm          | Spacer         | DSC Transitions (°C) <sup>a</sup> |                 |                 |                 |                 | T <sub>m</sub>   | $\Delta S_f$ (±10%)<br>(J K <sup>-1</sup> mol <sup>-1</sup> ) | TGA 5%<br>weight loss<br>(°C) |
|-------------------------|-------------------|----------------|-----------------------------------|-----------------|-----------------|-----------------|-----------------|------------------|---------------------------------------------------------------|-------------------------------|
|                         |                   |                | T <sub>g</sub>                    | T <sub>ss</sub> | T <sub>ss</sub> | T <sub>ss</sub> | T <sub>ss</sub> |                  |                                                               |                               |
| <b>1PF<sub>6</sub></b>  | Me                | C <sub>2</sub> | -                                 | -               | -               | -               | 199             | 215              | 64                                                            | 304                           |
| <b>2PF<sub>6</sub></b>  | Me                | C <sub>4</sub> | -                                 | -               | -               | -               | -               | 113              |                                                               | 342                           |
| <b>3Br</b>              | <i>n</i> -Bu      | C <sub>2</sub> | -                                 | -               | -               | 47              | 163             | 167              | 2.2 <sup>b</sup>                                              | 252                           |
| <b>3PF<sub>6</sub></b>  | <i>n</i> -Bu      | C <sub>2</sub> | -                                 | -               | -               | -               | 24              | 179              | 49                                                            | 273                           |
| <b>3BF<sub>4</sub></b>  | <i>n</i> -Bu      | C <sub>2</sub> | -31                               | 36 <sup>c</sup> | -               | -               | -               | 95               |                                                               | 298                           |
| <b>4PF<sub>6</sub></b>  | <i>n</i> -Bu      | C <sub>3</sub> | -                                 | -               | -               | -               | -               | 95               |                                                               | 326                           |
| <b>5PF<sub>6</sub></b>  | <i>n</i> -Bu      | C <sub>4</sub> | -                                 | -               | -               | -               | -               | 49 <sup>d</sup>  |                                                               | 335                           |
| <b>6Br</b>              | <i>n</i> -Hex     | C <sub>2</sub> | -                                 | -               | 110             | 136             | 174             | N/A <sup>e</sup> |                                                               | 231                           |
| <b>6PF<sub>6</sub></b>  | <i>n</i> -Hex     | C <sub>2</sub> | -                                 | -               | 9               | 79              | 80              | 197              | 44                                                            | 239                           |
| <b>7Br</b>              | <i>n</i> -Hex     | C <sub>3</sub> | -38                               | -               | -               | -               | -               | 104              |                                                               | 242                           |
| <b>7PF<sub>6</sub></b>  | <i>n</i> -Hex     | C <sub>3</sub> | -48                               | -               | -               | -               | -               | 83               |                                                               | 330                           |
| <b>8Br</b>              | <i>n</i> -Heptyl  | C <sub>2</sub> | -                                 | 18              | 34              | 91              | 124             | N/A <sup>e</sup> |                                                               | 241                           |
| <b>8PF<sub>6</sub></b>  | <i>n</i> -Heptyl  | C <sub>2</sub> | -                                 | -               | -               | 33              | 91              | 217              | 41                                                            | 268                           |
| <b>9Br</b>              | <i>n</i> -Octyl   | C <sub>2</sub> | -                                 | -               | 6               | 127             | 135             | N/A <sup>e</sup> |                                                               | 245                           |
| <b>9PF<sub>6</sub></b>  | <i>n</i> -Octyl   | C <sub>2</sub> | -                                 | -               | -               | 44              | 70              | 236              | 36                                                            | 283                           |
| <b>10Br</b>             | <i>n</i> -Decyl   | C <sub>2</sub> | -                                 | -               | -               | 33              | 131             | N/A <sup>e</sup> |                                                               | 248                           |
| <b>10PF<sub>6</sub></b> | <i>n</i> -Decyl   | C <sub>2</sub> | -                                 | -               | -               | 62              | 104             | 249 <sup>f</sup> | 11                                                            | 295                           |
| <b>11Br</b>             | <i>n</i> -Dodecyl | C <sub>2</sub> | -                                 | -               | -               | 56              | 143             | N/A <sup>e</sup> |                                                               | 240                           |
| <b>11PF<sub>6</sub></b> | <i>n</i> -Dodecyl | C <sub>2</sub> | -                                 | -               | -               | 73              | 106             | 247              | 12                                                            | 285                           |

<sup>a</sup> All the transitions from the second heating scan. <sup>b</sup> From cooling scan. <sup>c</sup> Exothermic crystallization.

<sup>d</sup> First heating scan result. <sup>e</sup> Decomposed before melting

<sup>f</sup> It is not clear that the endothermic peak is T<sub>m</sub>, because it's too close to its decomposition temperature.

**Thermal Analysis – Thermal Stability.** Figure 12-7 shows the trends of melting point of the  $\text{PF}_6^-$  salts with the different side arms ( $\text{C}_2$  spacer). The melting points decrease from methyl to butyl, but increase up to decyl ( $\text{C}_{10}$ ) side arms. The trend of the first  $T_{\text{ss}}$  of  $\text{PF}_6^-$  salts ( $\text{C}_2$  spacer) is similar to the melting point changes with increasing side-arm length. For a trend of  $\text{Br}^-$  salts ( $\text{C}_2$  spacer),  $T_{\text{ss}}$  of **6Br** is highest and increases from  $\text{C}_8$  to  $\text{C}_{12}$ .

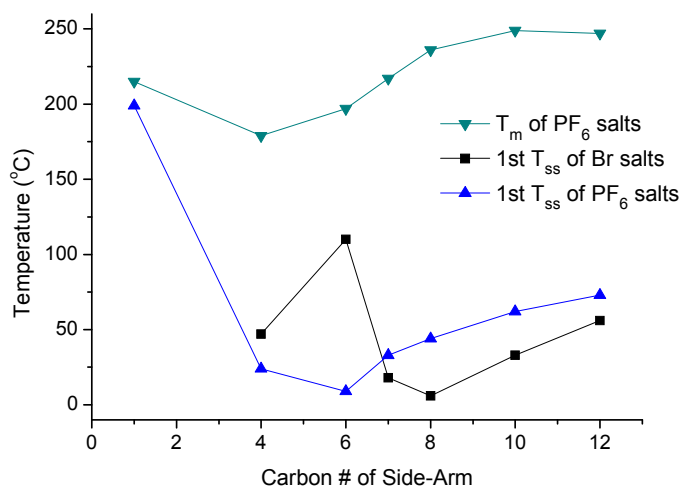


**Figure 12-7.** The trends of melting point of bis[N-(N'-alkylimidazolium)ethane  $2\text{PF}_6^-$  salts (reverse triangles), of the first  $T_{\text{ss}}$  of  $\text{Br}^-$  salts (squares), and of the first  $T_{\text{ss}}$  of  $\text{PF}_6^-$  salts (triangles).

Thermal decomposition temperatures were measured by TGA 5% weight loss points (under  $\text{N}_2$ ). The general trend of  $\text{Br}^-$  salts and  $\text{PF}_6^-$  salts were already discussed in the previous chapter and correspond to the Table 12-1 results. The  $\text{Br}^-$  salts decomposed in the range of 230 - 250 °C and the  $\text{PF}_6^-$  salts decomposed in a wider range: 239 – 340 °C. The trends of the thermal decomposition temperature (TGA 5% weight loss) are shown in Figure 12-8. For the both anions,  $\text{C}_6$  side-arm analogs are least thermally stable and the thermal stability increases up to the  $\text{C}_{10}$  side-arm imidazolium salts.

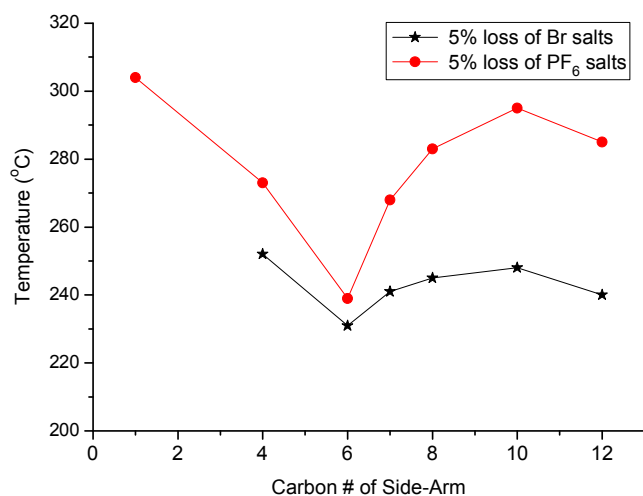
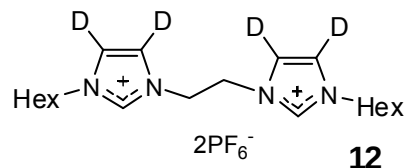


**Figure 12-8.** The trend of TGA 5% weight loss temperature of bis(N-alkylimidazolium)ethane  $2\text{Br}^-$  salts (stars), and the trend of the corresponding  $\text{PF}_6^-$  salts (circles).

**NMR Study.**  $^2\text{H}$  NMR experiment was performed for the deuterated analog of **7** $\text{PF}_6$ . Deuterium exchange reaction was done with  $\text{NaOD}$  in  $\text{D}_2\text{O}$  and the product was precipitated by aqueous saturated  $\text{KPF}_6$  in solution. The deuterium exchange was occurred at the 4- and 5- positions of the imidazolium rings as shown in structure **12**. The 2-position was also deuterated during the reaction, but was quickly protonated during treatment with  $\text{KPF}_6$  solution. Figure 12-9 shows the  $^2\text{H}$  NMR spectra at different temperatures, from 0 to 100 °C. Each signal is a doublet due to the different environments of C4 and C5 deuteriums. For the full spectra (the left series of Figure 12-9), the peak intensities change with increasing temperature; the intensities of three center peaks are different at low temperature, but almost the same at 100 °C. The peak width also gets narrower as temperature increases. The changes in peak intensity and peak width imply changes of the motions of the deuterium atoms.



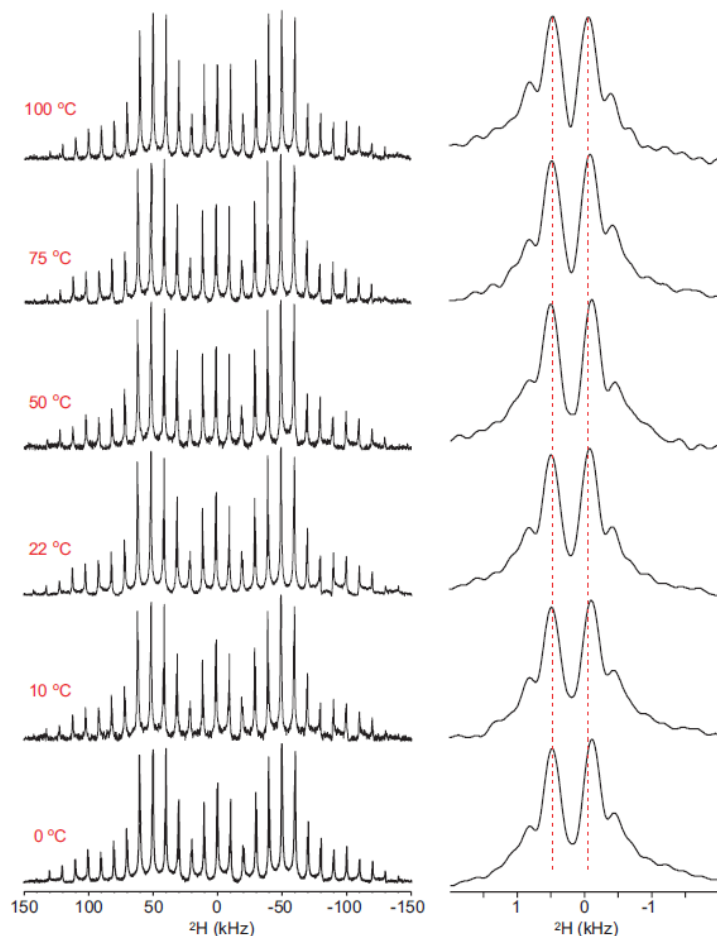


**Figure 12-9.** Solid-state  $^2\text{H}$  NMR spectra of **12** from 0 to 100 °C. The peak intensities (left) and the peak width (right) change as increasing temperature.

The comparison of the simulation results of the deuterium motion and actual spectra suggests the actual motion frequency and angles ( $\beta$  in Figure 12-10). The simulation results were calculated in 100 ns to sec. time scale for the deuterium flipping motion rate and the flipping angles (15 and 30 degree). The frequency of the flipping motion is within the 1 – 10 ms time scale, when the experimental results are compared with the simulation results. Moreover, the flipping angle gets wider as the temperature increases, because the experimental spectrum at 0 °C is similar to the simulation result of  $\beta = 15^\circ$ , but the experimental spectra at 100 °C is similar to the simulation result of  $\beta = 30^\circ$ .

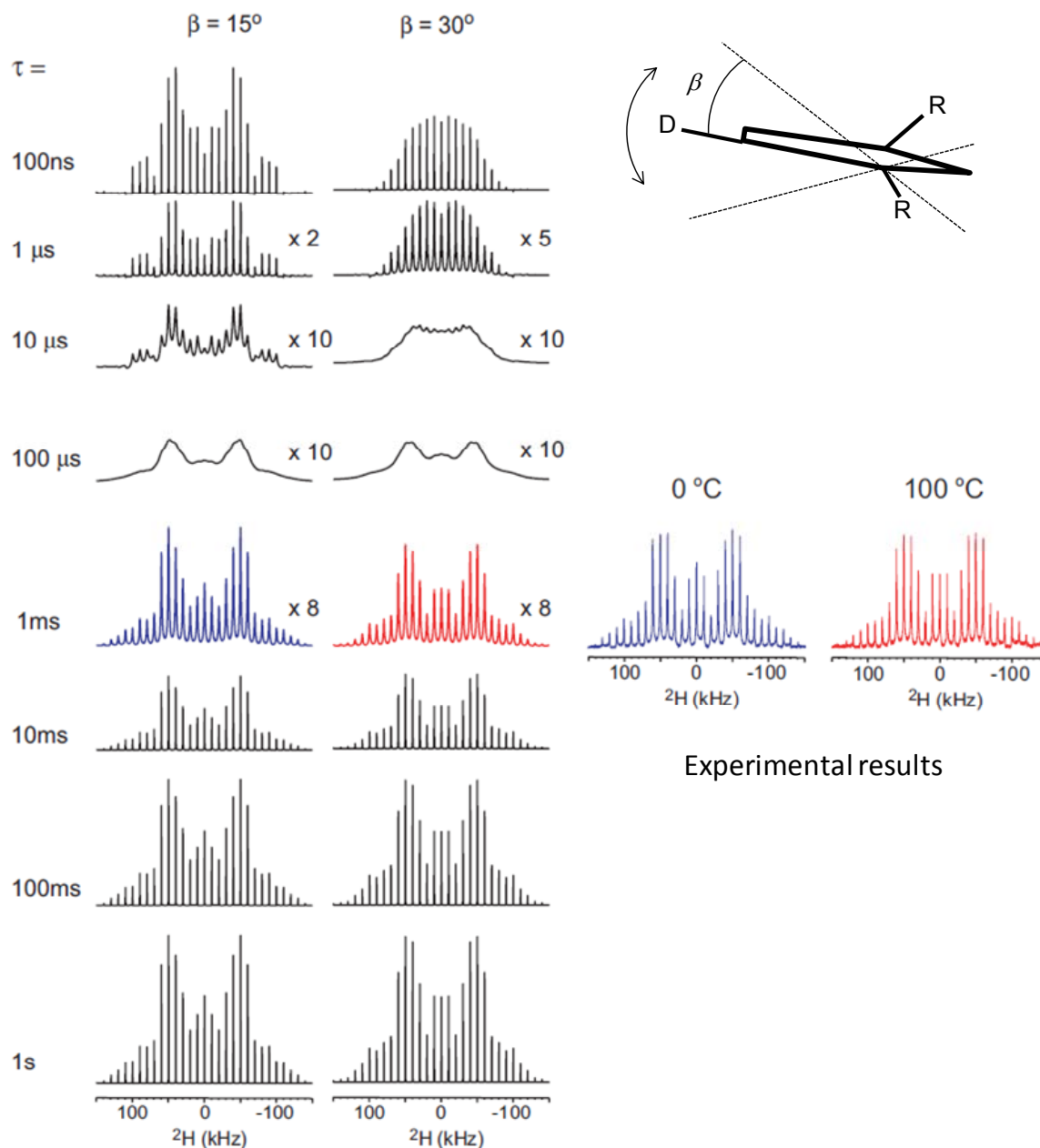


**Figure 12-10.** NMR simulation results with various time scale and two different angles (15 and  $30^\circ$ ) of deuterium flipping motion (left) and experimental result at 0 and  $100^\circ\text{C}$  (right).  $^2\text{H}$  quadrupolar coupling tensor parameters used in the simulation:  $e^2qQ/h = 168 \text{ kHz}$ ,  $\eta = 0$ .

The solid state  $^2\text{H}$  NMR experiments and simulation give some idea of the motions of the molecule as temperature increases; however, they do not provide direct evidence of the structural changes at the two solid-solid transition temperatures, 9 and  $80^\circ\text{C}$ . The peak intensities and the peak width do not show a significant change at those temperatures. More investigations on the



$^2\text{H}$  spectra will be necessary; and also phosphorus and fluorine NMR studies may be helpful to identify the structures of the each phase.

**X-Ray Diffraction (XRD).** X-Ray diffraction analysis of **7PF<sub>6</sub>** clearly indicates that the materials experiences structural changes at the first solid-solid transition ( $T_{ss} = 9\text{ }^\circ\text{C}$ ) as shown in Figure 12-11. Above the  $T_{ss}$  ( $9\text{ }^\circ\text{C}$ ), the XRD peaks clearly change; some peaks dramatically are decreased and some new ones are created. Even though the molecule **7PF<sub>6</sub>** is symmetrical, many peaks are shown in XRD. The peak intensity changes and some new peaks above the  $T_{ss}$  may give some structural information, however the detailed structural changes have not solved yet. High temperature XRD will be helpful to determine the structure change at the high temperature.

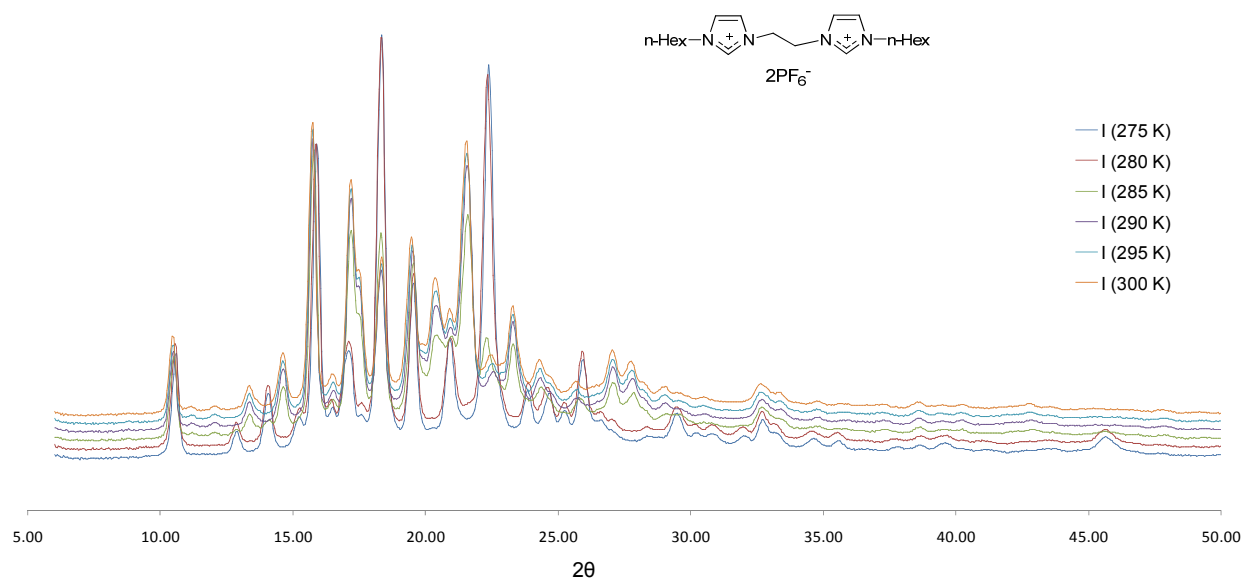


**Figure 12-11.** X-Ray powder diffraction profiles of **7PF<sub>6</sub>** as a function of temperature.

## Conclusions

A series of alkylene 1,2-bis[N-(N'-alkylimidazolium)] salts with  $\text{Br}^-$  and  $\text{PF}_6^-$  anions was prepared to investigate solid-solid phase transitions. Solid-solid transitions occurred only for the series with bis[N-(N'-alkylimidazolium)]ethane moieties. The salts with a longer spacer ( $\text{C}_3$  or  $\text{C}_4$ ) do not show any solid-solid transitions. **3BF<sub>4</sub>** does not display  $T_{ss}$  either, but has a  $T_g$  and an exothermic crystallization peak. The  $\text{PF}_6^-$  salts with  $\text{C}_{10}$  and  $\text{C}_{12}$  may be “organic ionic plastic crystals” by the Timmermans’ definition because they have low  $\Delta S_f$  ( $11\text{ J K}^{-1}\text{ mol}^{-1}$  for **10PF<sub>6</sub>** and  $12\text{ J K}^{-1}\text{ mol}^{-1}$  for **11PF<sub>6</sub>**). Also **3Br** with butyl side arms possess quite small fusion entropy and it may also be an interesting material in an ionic plastic crystal study region. Melting points and TGA thermal stabilities of the 1,2-bis[N-(N'-alkylimidazolium)]ethane salts with  $\text{Br}^-$  and

$\text{PF}_6^-$  were also investigated with different lengths of side-arm. The melting point of the  $\text{PF}_6^-$  salts gradually increases from  $\text{C}_4$  to  $\text{C}_{10}$ . The thermal degradations of the salts with *n*-hexyl side arms occur at the lowest temperatures in both  $\text{Br}^-$  and  $\text{PF}_6^-$  cases; the thermal stabilities increases as the side chain length gets longer up to  $\text{C}_{10}$ .

The discovery of a new class of organic ionic plastic crystals in this study may be important, because there is no good example of an imidazolium plastic crystal. This new cationic structure may be expanded to the research of many combinations of cations and anions for preparation of new ionic plastic crystalline materials.

**Acknowledgement** We are grateful to Prof. Sungsool Wi for the solid-state NMR analysis and simulations, and Dr. Carla Slebodnick for X-ray powder diffraction analysis. This material is based upon work supported in part by the U.S. Army Research Office under grant number W911NF-07-1-0452, Ionic Liquids in Electro-Active Devices (ILEAD) MURI. We thank for the funding sources to upgrade the Bruker 300 MHz solid state NMR (NSF CHE-0541764) and to purchase the Oxford Diffraction SuperNova X-ray diffractometer (NSF CHE-0131128).

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## Chapter 13

### Ion Conduction in Imidazolium Acrylate Ionic Liquids and their Polymers

#### Abstract

Polymerizable imidazolium acrylates and their polymers with pendant imidazolium cations were synthesized with two ionic liquid counter-anions and characterized using calorimetry and dielectric spectroscopy. After polymerization, the ionic polymers containing a diethyleneoxy unit as an N-substituent on the imidazolium cation shows higher ionic conductivity than the analogous N-*n*-butyl polymer. Using a physical model of electrode polarization, we separate the conductivity of single-ion conductors into number density of conducting ions  $p$  and their mobility  $\mu$ . The monomers invariably show higher conducting ion number density, owing to one ion being part of the polymer, but  $p$  is insensitive to the N-substituent. In contrast, the diethyleneoxy N-substituent imparts higher mobility than the *n*-butyl N-substituent, for both monomers and polymers, owing to a lower binding energy between the imidazolium and the counter-anions and *not* directly reflected in glass transition temperature.

#### Introduction

For the last few decades, the impact of ionic liquids (ILs) on chemical and material sciences has evolved from “green chemicals” in organic reactions to functional integration into electromechanical devices and high-performance membranes.<sup>1</sup> ILs have been studied widely because of their unique characteristics, such as low-volatility, non-flammability, large electrochemical window, and high ionic conductivity.<sup>2-11</sup>

Polymerizable ionic liquid monomers and their polymers have been studied for use as high performance single-ion-conducting membranes. Polymerizations of 1-alkyl-3-vinylimidazolium salts and their conducting properties were studied by Ohno and his coworkers.<sup>12</sup> They also changed the pendant structures of polymers by introduction of polymerizable (meth)acrylate moieties; imidazolium units placed at the end of longer brush pendant chains afforded higher

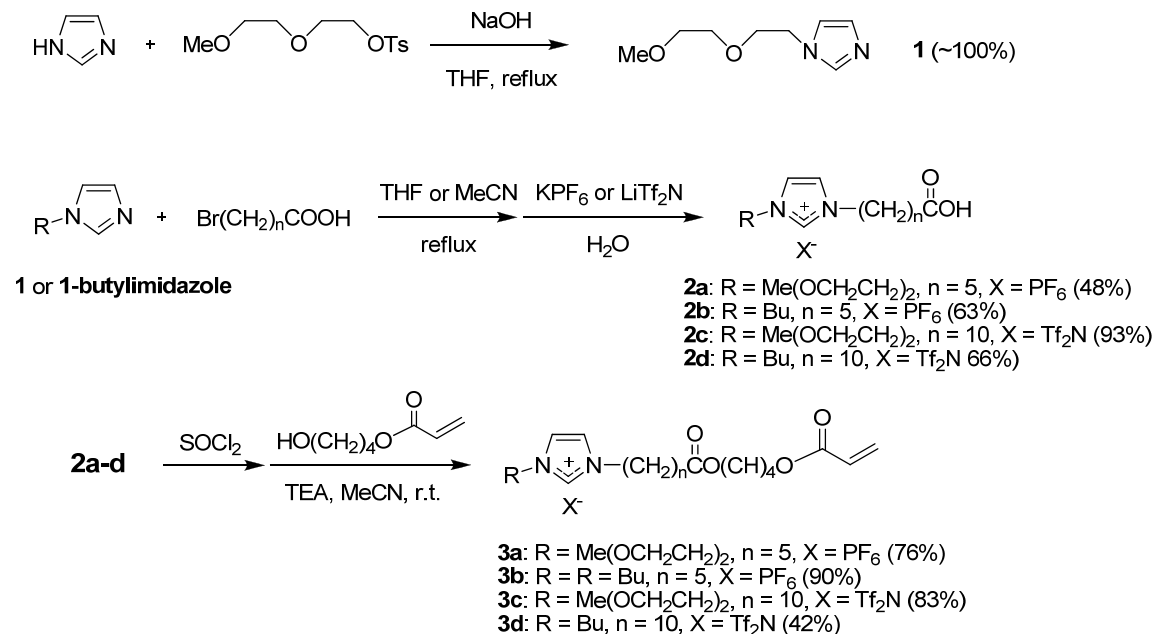
conductivities than shorter brush polymers.<sup>13,14</sup> Polystyrenes with phenylimidazolium groups were also studied by Ohno et al. In some cases, the polymer-lithium salt composites showed higher conductivities than the polymers by themselves, and the ionic conductivity increased upon addition of up to 1 equivalent of lithium salt per ionic unit.<sup>15</sup> A new class of ionic liquid monomers, which were formed by neutralization of long chain acids and N-monoalkylimidazoles, was also prepared and their polymerizations were studied.<sup>16,17</sup> Solution properties of polymerized ionic liquid monomers and electrospun fibers from the polymers were observed by Elabd et al.<sup>18</sup> They also studied the effect of random copolymer compositions from imidazolium methacrylate and hexyl acrylate on ion conduction.<sup>19</sup> The properties of liquid crystalline imidazolium polymers have also been reported.<sup>20-23</sup> The anisotropic conductivities were observed from homeotropic one-dimensional alignment and photopolymerization of ionic liquid crystals on modified glass surfaces.<sup>23</sup>

Herein, we synthesized new polymerizable acrylate monomers with ionic imidazolium units. We polymerized those monomers using free radical methods and studied both monomers and polymers using DSC to measure the glass transition temperature  $T_g$  and dielectric spectroscopy. In addition to conductivity and dielectric constant of these monomers and polymers, we analyze the macroscopic electrode polarization at lower frequencies in dielectric measurements to determine the number density of conducting ions and their mobility,<sup>24-27</sup> which has recently been utilized with great success for single-ion conductors above  $T_g$ .<sup>28-30</sup>

## Results and Discussion

**Synthesis** The monomers were constructed in three parts: polymerizable acrylate moiety, alkylene spacer connected via an ester linkage and a N-substituted imidazolium ionic group with hexafluorophosphate ( $\text{PF}_6^-$ ) and bis(trifluoromethanesulfonyl)imide ( $\text{Tf}_2\text{N}^-$ ) anions. The imidazolium acrylate monomers were synthesized as shown in Scheme 13-1. Diethyleneoxy units were introduced to the imidazole ring using tosylated di(ethylene glycol) monomethyl ether under basic conditions in the first step; the end of the ethyleneoxy unit was capped as a methyl ether to avoid hydrogen bonding effects by a hydroxyl group. The quaternization reactions of the 1-substituted imidazoles with 6-bromohexanoic acid and 11-bromoundecanoic acid and ion exchange gave carboxy terminated imidazolium salts **2a** and **2c**, respectively. The quaternization reactions were performed in acetonitrile (MeCN) under reflux for several days. The ion exchange reactions from bromide to  $\text{PF}_6^-$  or  $\text{Tf}_2\text{N}^-$  were done in aqueous conditions with

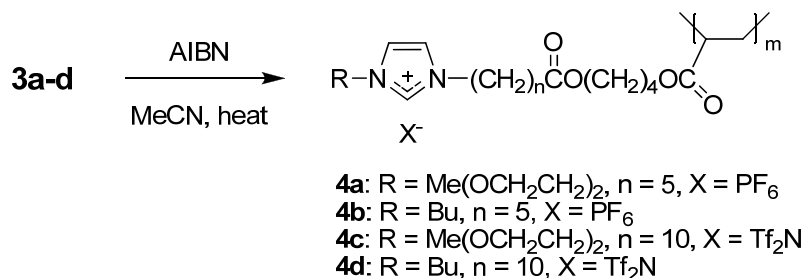
KPF<sub>6</sub> or LiTf<sub>2</sub>N. The resulting precipitated salts were washed with deionized water several times and dried *in vacuo* for 2 days or longer with heat. The absence of bromide residue was confirmed by the Beilstein halide test<sup>31</sup> or treatment with silver nitrate solution. N-*n*-Butyl substituted imidazolium carboxylic acids **2b** (PF<sub>6</sub><sup>-</sup> salt) and **2d** (Tf<sub>2</sub>N<sup>-</sup>) were prepared similarly from 1-butylimidazole. The carboxy imidazolium salts **2a-d** are room temperature ionic liquids (RTILs).



**Scheme 13-1.** Synthesis of di(ethyleneoxy) and butyl substituted imidazolium IL monomers, effectively defining the structure of the four imidazolium monomers **3a**, **3b**, **3c** and **3d**.

The polymerizable acrylate unit was introduced by esterification of the carboxy imidazolium salts with 4-hydroxybutyl acrylate. After conversion of the carboxylic acid to the corresponding carbonyl chloride with thionyl chloride, it was reacted with 4-hydroxybutyl acrylate and triethylamine in dry MeCN. The PF<sub>6</sub><sup>-</sup> monomers (**3a** and **3b**) were purified by several reprecipitations from the good solvent acetone into poor solvent THF (or ethyl ether) and washing with deionized water. The Tf<sub>2</sub>N<sup>-</sup> monomers (**3c** and **3d**) were purified by extraction with ethyl acetate (EA)/water and washing with ethyl ether to remove unreacted nonpolar reactants. All the monomers **3a-d** are RTILs and they are less viscous than the precursor imidazolium carboxylic acids; they have low T<sub>gs</sub> (Table 13-1).

The radical polymerizations of the monomers were performed with 2,2'-azobisisobutyronitrile (AIBN) in degassed MeCN at 65 °C. The product polymers were purified by precipitation with EA, which is a good solvent only for the monomers. The polymers were also washed with deionized water several times to remove water soluble impurities and dried *in vacuo* for several days at 60 °C. <sup>1</sup>H-NMR spectroscopy showed complete conversion into the homopolymers; the vinyl protons of the monomers ( $\delta$  5.8, 6.2, and 6.4) disappeared after the polymerizations were completed (Figure 13-1). The polymers also exhibited some peak broadening. The CH<sub>2</sub> protons that are close to the polymer backbone were broadened, whereas the ethyleneoxy (or butyl) protons which are well removed from the polymer backbone still appear as sharply split signals. Carbon-carbon bond rotation is much faster in the alkyl chains which are far from the polymer backbone and therefore those proton signals remained sharp.



**Scheme 13-2.** Polymerization of the imidazolium monomers, effectively defining the structure of the four imidazolium polymers **4a**, **4b**, **4c** and **4d**.

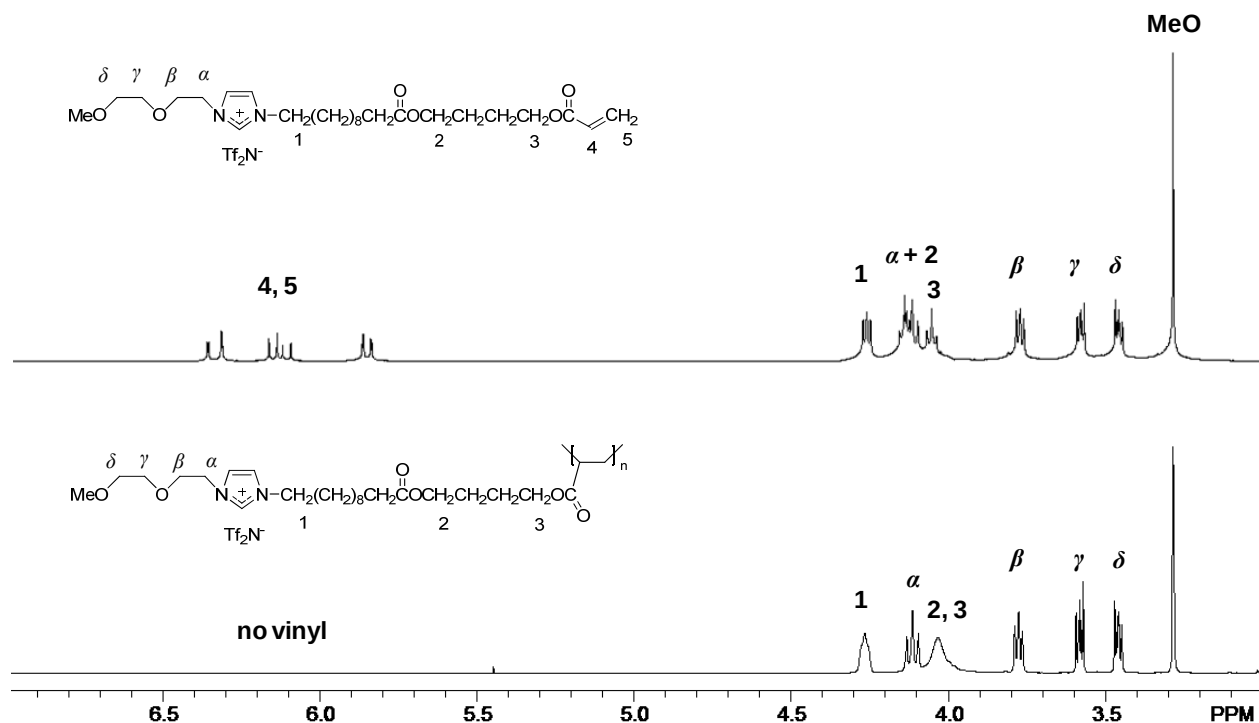


**Figure 13-1.** Partial 400 MHz  $^1\text{H}$  NMR spectra of monomer **3c** (upper) and polymer **4c** (lower) in  $\text{CD}_3\text{CN}$  at  $23^\circ\text{C}$ . After polymerization, the vinyl proton peaks (4 and 5 in the upper spectrum) disappear and 1, 2, 3 protons are broadened. However, the ethyleneoxy peaks ( $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ ) are still sharply split in the polymer (lower) spectrum, as they are in the monomer (upper) spectrum.

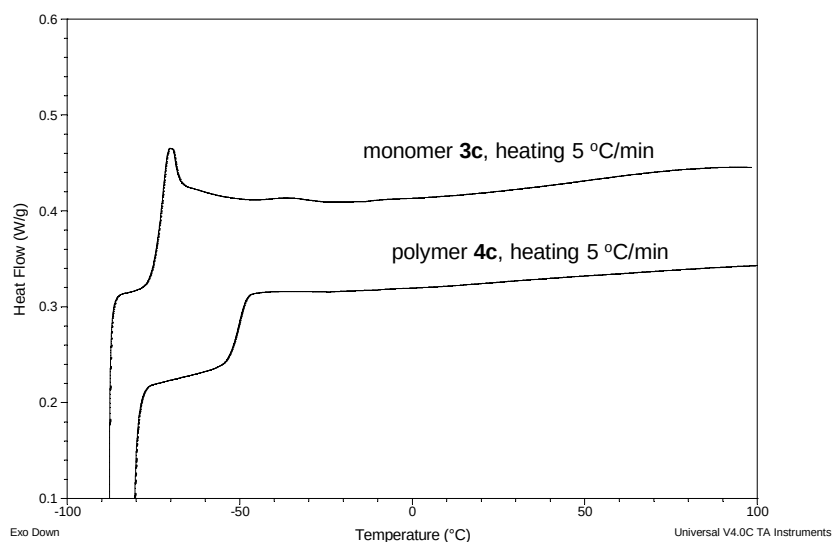


**Figure 13-2.** DSC thermograms of the monomer **3c** and the polymer **4c**, showing the increase in  $T_g$  on polymerization.



**Table 13-1.** DSC and TGA Thermal Analysis of Monomers and Polymers

| Monomers  | T <sub>g</sub> (°C, DSC) | Polymers  | T <sub>g</sub> (°C, DSC) | TGA (°C)<br>5% w/w loss | ΔT <sub>g</sub> (K) |
|-----------|--------------------------|-----------|--------------------------|-------------------------|---------------------|
| <b>3a</b> | -49                      | <b>4a</b> | -23                      | 326                     | 26                  |
| <b>3b</b> | -39                      | <b>4b</b> | -18                      | 334                     | 21                  |
| <b>3c</b> | -70                      | <b>4c</b> | -43                      | 318                     | 27                  |
| <b>3d</b> | -69                      | <b>4d</b> | -50                      | 382                     | 19                  |

**Thermal Analysis.** Differential Scanning Calorimetry (DSC) with heating and cooling rates of 10 K/min on ~10 mg samples was done using a TA Instrument Q2000 differential scanning calorimeter. The T<sub>g</sub> values of the polymers are 20-40 K higher than those of the corresponding monomers, as reported in Table 13-1. The new imidazolium pendant homopolymers are amorphous; the polymers do not display crystallization or melting in the temperature range of -80 ~ 200 °C by DSC. Replacing PF<sub>6</sub><sup>-</sup> with Tf<sub>2</sub>N<sup>-</sup> consistently lowered T<sub>g</sub>. Monomers have T<sub>g</sub> 21-30 K lower with Tf<sub>2</sub>N<sup>-</sup>; polymers have T<sub>g</sub> 20-32 K lower with Tf<sub>2</sub>N<sup>-</sup>. The Tf<sub>2</sub>N<sup>-</sup> counterion has previously been seen to act as a plasticizer for imidazolium ionic liquids and their polymers.<sup>18</sup> The thermal stabilities of these polymers were studied by TGA under N<sub>2</sub> using a TA Instrument Q500 Thermogravimetric Analyzer. A significant anion effect on thermal stability occurs only in the polymers with a butyl substituent; TGA 5% weight loss of **4d** (Tf<sub>2</sub>N<sup>-</sup>) takes place at 382 °C, but at 334 °C in **4b** (PF<sub>6</sub><sup>-</sup>). The N-diethyleneoxy polymers do not show much difference; the TGA 5% weight loss of **4a** (PF<sub>6</sub><sup>-</sup>) is 326 °C and that of **4c** (Tf<sub>2</sub>N<sup>-</sup>) is 318 °C. The lower thermal stability of the ethyleneoxy polymers vs. the butyl polymers is due to the presence of the more labile C-O-C bonds.

**Dielectric Spectroscopy.** The ionic conductivity measurements of the monomer and polymer liquids were performed by dielectric spectroscopy using a Novocontrol GmbH Concept 40, with 0.1 V amplitude and 10<sup>-2</sup> - 10<sup>7</sup> Hz frequency range. Samples were prepared for the dielectric measurements by allowing them to flow to cover a 30 mm diameter polished brass electrode at 100 °C *in vacuo* to form a puddle deeper than 50 μm with 50 μm silica spacers immersed. Then a 15 mm diameter polished brass electrode was placed on top to make a parallel plate capacitor cell which was squeezed to a gap of 50 μm in the instrument (with precise thickness checked

after dielectric measurements were complete). Each sample was annealed in the Novocontrol at 120 °C in a heated stream of nitrogen for 1 hour prior to measurements. Data were collected in isothermal frequency sweeps from 120 °C to near  $T_g$ .

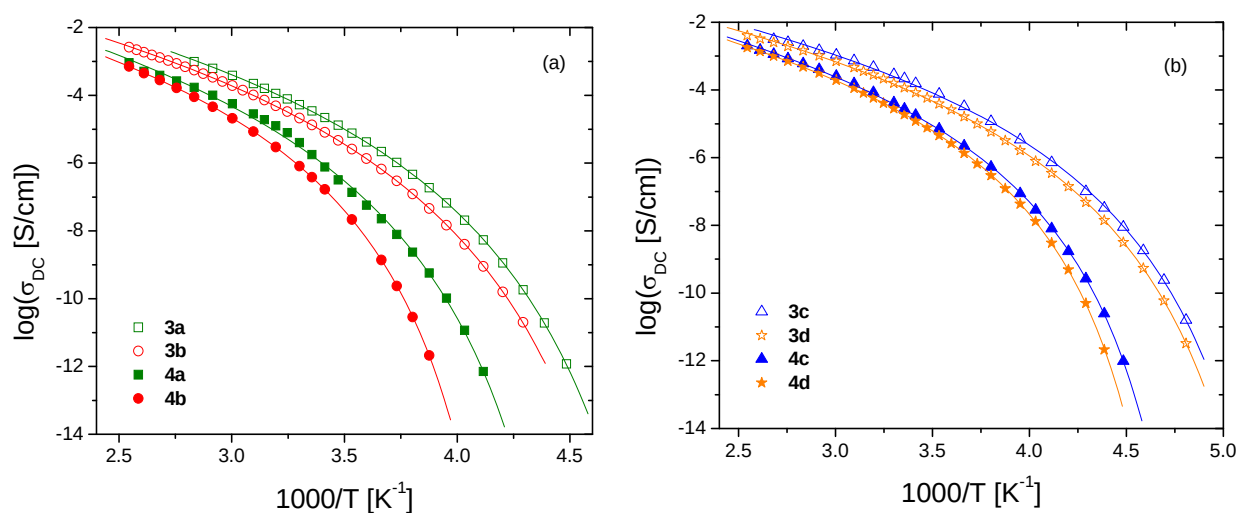
**Ionic Conductivity.** As expected, ionic conductivities are lower for the polymers than the monomers (Tables 13-2 and 13-3). The decreased ionic conductivity in the polymers can be mostly explained by the decrease in the segmental motion in the polymer relative to the monomer reflected in a change in  $T_g$ .<sup>13</sup> There is also a significant effect from the diethyleneoxy vs. the butyl terminal N-substituents on ionic conductivity for  $PF_6^-$  monomers and polymers. The room temperature ionic conductivity of the ethyleneoxy monomer **3a** ( $3.5 \times 10^{-5} \text{ Scm}^{-1}$ ) is higher than that of butyl substituted monomer **3b** ( $1.3 \times 10^{-5} \text{ Scm}^{-1}$ ). After polymerization, the conductivity of the ethyleneoxy substituted polymer **4a** ( $1.8 \times 10^{-6} \text{ Scm}^{-1}$ ) is almost 5-fold higher than the butyl substituted polymer **4b** ( $3.9 \times 10^{-7} \text{ Scm}^{-1}$ ). For the  $Tf_2N^-$  polymers, the room temperature ionic conductivity of ethyleneoxy substituted **4c** ( $2.8 \times 10^{-5} \text{ Scm}^{-1}$ ) is 50% higher than butyl substituted polymer **4d** ( $1.8 \times 10^{-5} \text{ Scm}^{-1}$ ). The diethyleneoxy units on the imidazolium cation afford a higher ionic conductivity at low temperature, but a negligible effect at high temperature, relative to the butyl substituted system as shown in Figure 13-3. Ohno observed with brush imidazolium  $Tf_2N^-$  polymers that dodecyl spacers possessed slightly higher ionic conductivity than the ethyleneoxy  $[(CH_2CH_2O)_8]$  containing polymer.<sup>14</sup> The spacers of his polymers were placed between the polymer backbone and the imidazolium. However, in our polymer the diethyleneoxy substituent, which is placed far from the polymer backbone, plays a more important role in the ion conduction at room temperature.

**Table 13-2.** Ionic Conductivities of  $PF_6^-$  Monomers and Polymers

| Compound  | 25 °C Conductivity ( $\text{Scm}^{-1}$ ) |
|-----------|------------------------------------------|
| <b>3a</b> | $3.5 \times 10^{-5}$                     |
| <b>3b</b> | $1.3 \times 10^{-5}$                     |
| <b>4a</b> | $1.8 \times 10^{-6}$                     |
| <b>4b</b> | $3.9 \times 10^{-7}$                     |

**Table 13-3.** Ionic Conductivity of  $\text{Tf}_2\text{N}^-$  Monomers and Polymers.

| Compound  | 25 °C Conductivity ( $\text{Scm}^{-1}$ ) |
|-----------|------------------------------------------|
| <b>3c</b> | $2.2 \times 10^{-4}$                     |
| <b>3d</b> | $1.2 \times 10^{-4}$                     |
| <b>4c</b> | $2.8 \times 10^{-5}$                     |
| <b>4d</b> | $1.8 \times 10^{-5}$                     |

**Figure 13-3.** Temperature dependence of ionic conductivity of (a)  $\text{PF}_6^-$  monomers and polymers and (b)  $\text{Tf}_2\text{N}^-$  monomers and polymers. Monomers (open symbols) have consistently higher conductivity than their polymers (filled symbols). Lines indicate fits to Eq. (9).

**Electrode Polarization Analysis.** In order to better understand the conduction mechanism, it is necessary to distinguish whether the increase in ionic conductivity is due to a larger fraction of conducting ions or to an increase in ion mobility, since ionic conductivity is the product of charge  $e$ , number density of conducting ions  $p$  and their mobility  $\mu$ .

$$\sigma_{DC} = ep\mu \quad (1)$$

A physical model of electrode polarization (EP) makes it possible to separate ionic conductivity into the contributions of conducting ion concentration and ion mobility<sup>24-27</sup> as has recently been done for other single-ion conductors above  $T_g$ .<sup>28-30</sup> Electrode polarization occurs

at low frequencies, where the transporting ions have sufficient time to polarize at the blocking electrodes during the cycle. That polarization manifests itself in (1) an increase in the effective capacitance of the cell (increasing the dielectric constant) and (2) a decrease in the in-phase part of the conductivity, as the polarizing ions reduce the field experienced by the transporting ions. The natural time scale for conduction is the time where counterion motion becomes diffusive

$$\tau_{\sigma} \equiv \frac{\varepsilon_s \varepsilon_0}{\sigma_{DC}} \quad (2)$$

where  $\varepsilon_s$  is the static relative permittivity of the sample,  $\varepsilon_0$  is the permittivity of vacuum and  $\sigma_{DC}$  is the d.c. conductivity, evaluated from a roughly 3-decade frequency range where the in-phase part of the conductivity  $\sigma'(\omega) = \varepsilon''(\omega) \varepsilon_0 \omega$  is independent of frequency and discussed in the previous section. At low frequencies the conducting ions start to polarize at the electrodes and fully polarize at the electrode polarization time scale

$$\tau_{EP} \equiv \frac{\varepsilon_{EP} \varepsilon_0}{\sigma_{DC}} \quad (3)$$

where  $\varepsilon_{EP}$  is the (considerably larger) effective permittivity after the electrode polarization is complete. The Macdonald/Coelho model<sup>24-28</sup> treats electrode polarization as a simple Debye relaxation with loss tangent.

$$\tan \delta = \frac{\omega \tau_{EP}}{1 + \omega^2 \tau_{\sigma} \tau_{EP}} \quad (4)$$

In practice, the loss tangent associated with electrode polarization is fit to Eq. (4) to determine the electrode polarization time  $\tau_{EP}$  and the conductivity time  $\tau_{\sigma}$ . The Macdonald/Coelho model then determines the number density of conducting ions  $p$  and their mobility  $\mu$  from  $\tau_{EP}$

$$p = \frac{1}{\pi l_B L^2} \left( \frac{\tau_{EP}}{\tau_{\sigma}} \right)^2 \quad (5)$$

$$\mu = \frac{e L^2 \tau_{\sigma}}{4 \tau_{EP}^2 k T} \quad (6)$$

where  $l_B \equiv e^2 / (4 \pi \varepsilon_s \varepsilon_0 k T)$  is the Bjerrum length,  $L$  is the spacing between electrodes,  $e$  is the elementary charge,  $k$  is the Boltzmann constant and  $T$  is absolute temperature.

**Conducting Ion Content.** The temperature dependence of the number density of conducting ions  $p$  calculated from Eq. (5) is plotted as shown in Figure 13-4 for the polymerizable ionic liquid acrylate monomers (open symbols) and their polymers (filled symbols) and the fraction of ions participating in conduction ( $p/p_0$  where  $p_0$  is the total anion number density) is shown in the Figure 13-4 inset. The temperature dependence of conducting ion concentration for these monomers and polymers is well described by an Arrhenius equation

$$p = p_0 \exp\left(-\frac{E_a}{RT}\right) \quad (7)$$

where  $p_0$  is the total anion concentration (all anions are in conducting states at all times as  $T \rightarrow \infty$ ) here estimated from density determined by the group contribution method<sup>32</sup> and  $E_a$  is an activation energy for conducting ions. The activation energy of the conducting ions in these materials is an effective experimental measure of the binding energy of an ion pair (the electrostatic attraction between cation and anion, mediated by the environment). The activation energies determined by fitting the data in Figure 13-4 to Eq. (7) are listed in Table 13-4. The inset in Figure 13-4 indicates that the fraction of ions in a conducting state at any instant in time is quite low, of order 0.1 % of the ion being in conducting at reasonable temperatures, similar to observations on other single-ion conducting ionomers with sulfonate ions bound to the chain and alkali metal counterions.<sup>28-30</sup> Interestingly, the monomers (**3a**, **3b**, **3c**, and **3d**) have somewhat higher conducting ion concentration than the polymers (**4a**, **4b**, **4c**, and **4d**). Part of the reason for that is the monomers are similar to conventional ionic liquids, with two ions participating in conduction. The activation energy is  $E_a = 15.6$  kJ/mol for both  $\text{PF}_6^-$  monomers (**3a** and **3b**) and  $E_a = 14.2$  kJ/mol for both  $\text{Tf}_2\text{N}^-$  monomers (**3c** and **3d**). Both of these activation energies increase by about 25% on polymerization, as the  $\text{PF}_6^-$  polymers (**4a** and **4b**) have  $E_a = 19.5$  kJ/mol and the  $\text{Tf}_2\text{N}^-$  polymers (**4c** and **4d**) have  $E_a = 17.8$  kJ/mol. The lower activation energy in  $\text{Tf}_2\text{N}^-$  monomers and polymers indicates a lower binding energy of the larger  $\text{Tf}_2\text{N}^-$  ions to the imidazolium ions compared to the  $\text{PF}_6^-$  ions.<sup>11</sup>

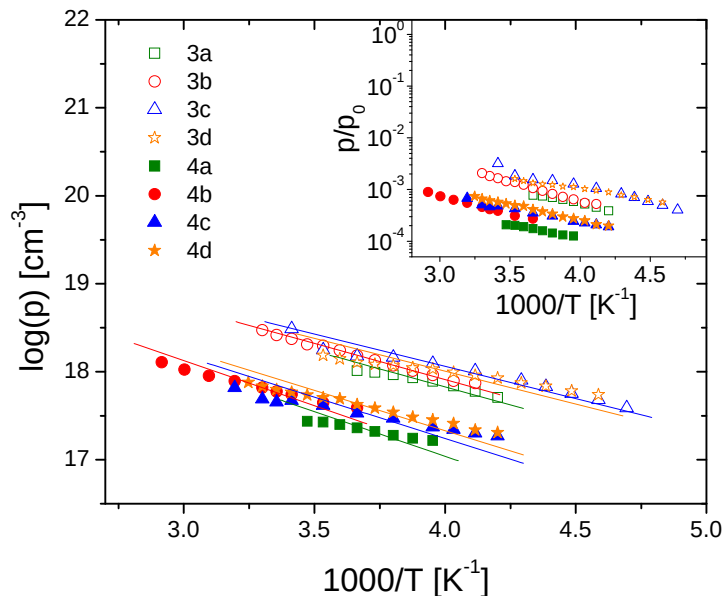


**Figure 13-4.** Temperature dependence of conducting ion number density  $p$ . The inset shows the fraction of counterions in the conducting state ( $p$  divided by the total ion concentration  $p_0$ ). Monomers (open symbols) have consistently higher conducting ion content than their polymers (filled symbols). Lines are fits to Eq. (7) with the activation energy as the sole fitting parameter (listed in Table 13-4).

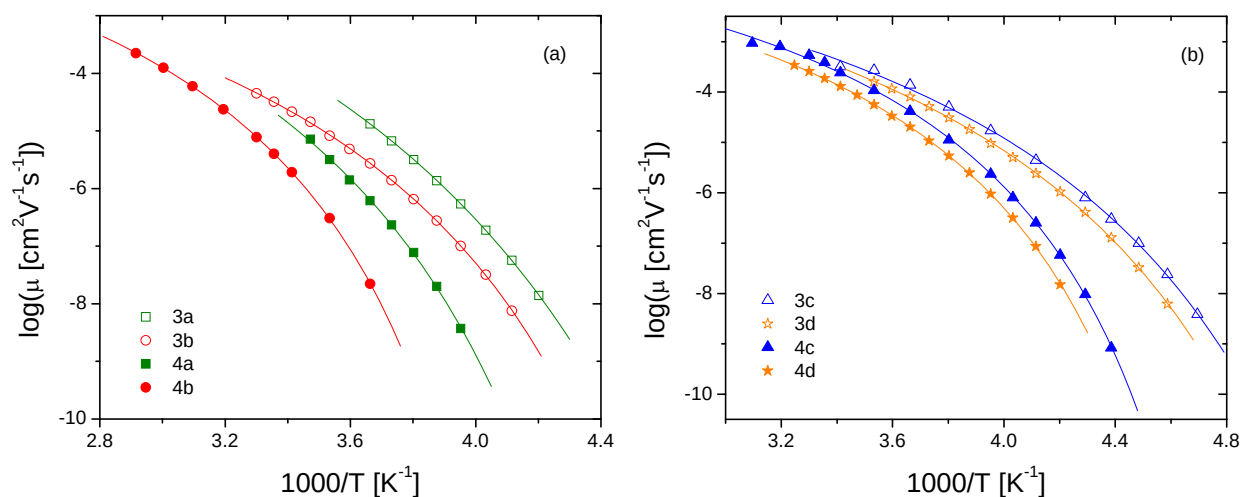


**Figure 13-5.** Temperature dependence of conducting ion mobility for (a)  $\text{PF}_6^-$  monomers and polymers and (b)  $\text{Tf}_2\text{N}^-$  monomers and polymers. Monomers (open symbols) have consistently higher mobility than their polymers (filled symbols). Lines are fits to Eq. (8) with fitting parameters listed in Table 13-4.

**Table 13-4.** Parameters of the VFT Equation for Conducting Ion Mobility, Eq. (8) and the Arrhenius Equation for Conducting Ion Concentration, Eq. (7).

| Compound  | Conducting ion mobility                                            |           |              |                    | Conducting ion concentration       |                   |
|-----------|--------------------------------------------------------------------|-----------|--------------|--------------------|------------------------------------|-------------------|
|           | $\log \mu_{\infty}$<br>( $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ ) | $D_{\mu}$ | $T_0$<br>(K) | $T_g - T_0$<br>(K) | $\log p_0$<br>( $\text{cm}^{-3}$ ) | $E_a$<br>(kJ/mol) |
| <b>3a</b> | 0.8                                                                | 3.3       | 172          | 52                 | 21.1                               | 15.5              |
| <b>3b</b> | -0.9                                                               | 2.1       | 188          | 46                 | 21.2                               | 15.7              |
| <b>3c</b> | -0.3                                                               | 2.4       | 164          | 39                 | 21.0                               | 14.1              |
| <b>3d</b> | -0.3                                                               | 2.4       | 167          | 37                 | 21.0                               | 14.3              |
| <b>4a</b> | -0.1                                                               | 2.3       | 197          | 53                 | 21.1                               | 19.4              |
| <b>4b</b> | -0.6                                                               | 1.7       | 221          | 34                 | 21.2                               | 19.6              |
| <b>4c</b> | -0.5                                                               | 1.7       | 191          | 39                 | 21.0                               | 18.0              |
| <b>4d</b> | -0.7                                                               | 1.7       | 193          | 30                 | 21.0                               | 17.6              |

**Mobility of the Conducting Ions.** The ion mobility determined from the EP model is displayed in Figure 13-5 vs. inverse temperature. We fit these data to the Vogel-Fulcher-Tammann (VFT) equation

$$\mu = \mu_{\infty} \exp\left(-\frac{D_{\mu}T_0}{T - T_0}\right) \quad (8)$$

where  $\mu_{\infty}$  is the ion mobility as  $T \rightarrow \infty$ ,  $D_{\mu}$  is the so-called strength parameter related to the divergence from Arrhenius temperature dependence, and  $T_0$  is the Vogel temperature where the free volume extrapolates to zero. The fit parameters  $\mu_{\infty}$ ,  $D_{\mu}$ , and  $T_0$  are given in Table 13-4. The VFT dependence of ion mobility reflects the coupling of segmental motion of polymer backbone and ion motion. Like ionic conductivity, the ion mobility of the ethyleneoxy substituted monomers (**3a** and **3c**) and polymers (**4a** and **4c**) is higher than the butyl substituted monomers (**3b** and **3d**) and polymers (**4b** and **4d**) (Figure 13-5). Watanabe and co-workers<sup>33,34</sup> showed that the conductivity/diffusion of ionic liquids deviates from the Nernst-Einstein approximation, indicating that the effective number of ions available for conduction is reduced through formation of ion pairs having a zero net charge, that still contribute to diffusion. Hence,

it is a reasonable assumption that under the influence of electrostatic interaction counterions interacting with ion pairs might form triple ions which contribute to the conductivity. The fact that the imidazolium cations are attached to the polymer chain suggests that the  $\text{PF}_6^-$  and  $\text{Tf}_2\text{N}^-$  anions, assisted by the activated motion of the polymer host, could exchange themselves between one ion pair and a neighboring one. In other words, the mobility will result from not only the segmental motion but also an energy barrier for anion hopping. The enhanced ion mobility in the ethyleneoxy substituted monomers and polymers, therefore, may be interpreted as simply lowering this barrier. The ether-functionalized imidazolium cations have an energetic preference for the gauche conformation that allows interactions between the ether oxygen atoms and the hydrogen atoms of the imidazolium ring.<sup>35</sup> The  $\text{H-O}_{\text{ether}}$  interactions also result in a reduction of cation-anion pair dissociation energy (effectively stabilizing the cation separated from its anion) which results in a lower energy barrier for anion hopping. This more rapid dynamics of ionic liquids with ether groups is also observed in viscosity<sup>36,37</sup> and ion-diffusion coefficients.<sup>38</sup> On the other hand, the difference in ion mobility between the ethyleneoxy and the butyl substituted  $\text{Tf}_2\text{N}^-$  polymers is smaller than that of  $\text{PF}_6^-$  polymers. This is likely caused by the  $\text{Tf}_2\text{N}^-$  counterions being better plasticizers (lowering  $T_g$ ) than the considerably smaller  $\text{PF}_6^-$  counterions.

On the basis of both ion mobility and conducting ion concentration, we can determine the temperature dependence of ionic conductivity by combining Eq. (1) with Eqs. (7) and (8);

$$\sigma = ep\mu = ep_{\infty}\mu_{\infty} \exp\left(-\frac{D_{\sigma}T_0}{T-T_0}\right) \exp\left(-\frac{E_a}{RT}\right) \quad (9)$$

$E_a$  was fixed to the activation energy determined by fitting conducting ion content to Eq. (7). As a result, we observe that a value of  $T_0$  obtained using Eq. (9) in Table 13-5 is slightly higher than using Eq. (8) in Table 13-4. Conductivity is measured over a considerably wider temperature range than mobility, since EP can only be analyzed over a smaller T-range, and in particular, since conductivity is always measured closer to  $T_g$  than mobility, the  $D$  and  $T_0$  values from fitting conductivity data to Eq. (9), listed in Table 13-5, are more reliable. This result also points out that larger  $T_g - T_0$  always goes with larger  $D$  and that both suggest lower fragility.



**Table 13-5.** Fitting parameters for the temperature dependence of d.c. ionic conductivity fit to Eq. (9).

| Compound  | Ionic conductivity                        |                   |              |              |                    |
|-----------|-------------------------------------------|-------------------|--------------|--------------|--------------------|
|           | $\log(ep_{\infty}\mu_{\infty})$<br>(S/cm) | $E_a$<br>(kJ/mol) | $D_{\sigma}$ | $T_0$<br>(K) | $T_g - T_0$<br>(K) |
| <b>3a</b> | 1.6                                       | 15.5              | 2.0          | 185          | 39                 |
| <b>3b</b> | 1.5                                       | 15.7              | 2.1          | 187          | 47                 |
| <b>3c</b> | 1.0                                       | 14.1              | 1.6          | 174          | 29                 |
| <b>3d</b> | 0.9                                       | 14.3              | 1.6          | 175          | 29                 |
| <b>4a</b> | 1.6                                       | 19.4              | 1.9          | 203          | 47                 |
| <b>4b</b> | 1.4                                       | 19.6              | 1.6          | 221          | 34                 |
| <b>4c</b> | 1.1                                       | 18.0              | 1.3          | 194          | 36                 |
| <b>4d</b> | 0.9                                       | 17.6              | 1.3          | 198          | 25                 |

## Conclusion

Two new polymerizable ionic liquid imidazolium acrylate monomers and their corresponding polymers, which contain either a *n*-butyl or a diethyleneoxy substituent on imidazolium unit, have been synthesized and their properties characterized. The introduction of diethyleneoxy vs. *n*-butyl units on the imidazolium cation affected the thermal and electrical properties of the polymers. The effect is clearly shown in room temperature conductivity; the ionic conductivity of ethyleneoxy substituted **4a** is 5 times higher than that of the butyl polymer **4b**; likewise that of ethyleneoxy substituted **4c** is 50% higher than the butyl polymer **4d**.

A physical model of EP makes it possible for ionic conductivity to be separated into (1) conducting ion number density and (2) conducting ion mobility. The reduction in cation-anion interactions due to the ether tail leads to the higher mobility of the ethyleneoxy substituted imidazolium monomers and polymers, and increased conductivity. Beyond the conductivity time scale  $\tau_{\sigma}$  counterion motion becomes diffusive, with all counterions contributing equally to ion conduction. Even though electrode polarization occurs on a much longer time scale, the conducting ion content evaluated from the EP model is the number density of ions in a conducting state in any snapshot, which sets the boundary condition for the solution of the

Poisson-Boltzmann equation. For this reason, only a small fraction of total ions is in a conducting ion at any given instant in time, in these materials and in other ionomers.

## Experimental

**Instruments.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained on Varian Inova 400 MHz and Unity 400 MHz spectrometers. High resolution electrospray ionization time-of-flight mass spectrometry (HR ESI TOF MS) was carried out on an Agilent 6220 Accurate Mass TOF LC/MS Spectrometer in positive ion mode. Differential Scanning Calorimetry (DSC) with heating and cooling rates of 5 or 10 K/min on ~10 mg samples was done using a TA Instrument Q2000 differential scanning calorimeter. The thermal stabilities of these polymers were studied by TGA under  $\text{N}_2$  using a TA Instrument Q500 Thermogravimetric Analyzer at a heating rate of 10 K/min heating under  $\text{N}_2$  purge.

**Dielectric Spectroscopy.** The ionic conductivity measurements of the monomer and polymer liquids were performed by dielectric spectroscopy using a Novocontrol GmbH Concept 40, with 0.1 V amplitude and  $10^{-2}$  -  $10^7$  Hz frequency range. Samples were prepared for the dielectric measurements by allowing them to flow to cover a 30 mm diameter polished brass electrode at 100 °C *in vacuo* to form a puddle deeper than 50  $\mu\text{m}$  with several 50  $\mu\text{m}$  silica spacers immersed. Then a 15 mm diameter polished brass electrode was placed on top to make a parallel plate capacitor cell which was squeezed to a gap of 50  $\mu\text{m}$  in the instrument (with precise thickness checked after dielectric measurements were complete). Each sample was annealed in the Novocontrol at 120 °C in a heated stream of nitrogen for 1 hour prior to measurements. Data were collected in isothermal frequency sweeps from 120 °C to near  $T_g$ .

**Materials.** 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from chloroform below 40 °C and dried in a vacuum oven and stored in a freezer (<-10 °C). Acetonitrile (MeCN) for polymerizations was distilled over calcium hydride. All other chemicals and solvents were used as received.

**1-[2'-(2''-Methoxyethoxy)ethyl]imidazole (1).** To a mixture of imidazole (2.042 g, 30 mmol), NaOH 50% solution (2.88 g, 30 mmol) in THF (35 mL), 2-(2'-methoxyethoxy)ethyl *p*-toluenesulfonate (8.23 g, 30 mmol) was added. The reaction mixture was refluxed for 2 days. After cooling and removing all solvents under vacuum, the product was extracted 3 times with  $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$ . The combined organic layer was washed with water and then dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The drying agent was removed by filtration and the solvent was removed by

rotoevaporator. A yellow liquid (5.22 g, 100%) was obtained after drying in a N<sub>2</sub> stream. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, 23 °C): δ 3.37 (s, 3H), 3.51 (m, 2H), 3.57 (m, 2H), 3.74 (t, J=5, 2H), 4.12 (t, J=5, 2H), 6.99 (s, 1H), 7.04 (s, 1H), 7.53 (s, 1H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, 23 °C): δ 46.9, 59.0, 70.5, 70.6, 71.7, 119.3, 129.1, 137.4. The <sup>1</sup>H-NMR spectra data are exactly the same as reported in the literature.<sup>39</sup>

**1-[2'-(2''-Methoxyethoxy)ethyl]-3-(ω-carboxypentyl)imidazolium PF<sub>6</sub><sup>-</sup> (2a).** A solution of **1** (2.553 g, 15 mmol) and 6-bromohexanoic acid (2.926 g, 15 mmol) in THF (15 mL) was refluxed for 3 days. After the reaction mixture was cooled to room temp., the THF was decanted off and the residue was washed with THF and ethyl ether 3 times each. The bromide salt was dissolved in water (15 mL) and KPF<sub>6</sub> (3.04 g, 17 mmol) was added. The mixture was stirred for 1 hour at room temp. The precipitated oily product was washed with ethyl ether 5 times. Drying in a vacuum oven gave a yellow viscous liquid 3.10 g (48%). <sup>1</sup>H-NMR (400 MHz, acetone-*d*<sub>6</sub>, 23 °C): δ 1.42 (m, 2H), 1.64 (m, 2H), 2.00 (m, 2H), 2.31 (m, 2H), 3.30 (s, 3H), 3.49 (m, 2H), 3.65 (m, 2H), 3.92 (tt, J=5, 2H), 4.40 (t, J=7, 2H), 4.53 (t, J=5, 2H), 7.78 (m, 2H), 9.07 (s, 1H). <sup>13</sup>C-NMR (100 MHz, acetone-*d*<sub>6</sub>, 23 °C): δ 25.4, 26.6, 29.5, 29.8, 29.95, 30.02, 30.1, 30.5, 34.5, 50.7, 50.9, 69.5, 70.6, 72.1, 123.4, 124.7, 136.7, 176.2. HR MS: m/z 285.1801 ([M-PF<sub>6</sub>]<sup>+</sup>, calcd. for C<sub>14</sub>H<sub>25</sub>N<sub>2</sub>O<sub>4</sub> 285.1814, error 4.6 ppm).

**1-Butyl-3-(5'-carboxypentyl)imidazolium PF<sub>6</sub><sup>-</sup> (2b).** A mixture of N-butylimidazole (5.92 g, 47.7 mmol) and 6-bromohexanoic acid (9.30 g, 47.7 mmol) in THF (40 mL) was refluxed for 3 days. After the reaction mixture was cooled to room temperature, the THF was decanted off and the residue was washed with THF 3 times. The residual yellow viscous oil was dissolved in deionized water (80 mL) and then KPF<sub>6</sub> (10.12 g, 55 mmol) was added. The mixture was stirred for 24 hours at room temperature. After decanting off the upper aqueous layer, the residual oily product was washed with deionized water 3 times. Drying in a vacuum oven gave a pale-yellow viscous liquid (11.57 g, 63%). DSC (N<sub>2</sub>, -80 ~ 200 °C, heating and cooling rate 5 °C): T<sub>g</sub> = -39.3 °C (2<sup>nd</sup> cycle), no other transition found. <sup>1</sup>H-NMR (400 MHz, acetone-*d*<sub>6</sub>, 23 °C): δ 0.95 (t, J=8, 3H), 1.40 (m, 4H), 1.65 (m, 4H), 1.97 (m, 4H), 2.32 (t, J=8, 2H), 4.36 (q, J=8, 1H), 7.77 (m, 2H), 9.03 (s, 1H). <sup>13</sup>C-NMR (100 MHz, acetone-*d*<sub>6</sub>, 23 °C): δ 13.6, 20.0, 24.7, 26.1, 30.3, 30.6, 32.6, 33.8, 50.3, 123.5, 136.7, 174.7. HR ESI MS: m/z 239.1746 ([M-PF<sub>6</sub>]<sup>+</sup>, calcd. for C<sub>13</sub>H<sub>23</sub>N<sub>2</sub>O<sub>2</sub> 239.1754, error 3.3 ppm).

**1-[2'-(2''-Methoxyethoxy)ethyl]-3-(10'''-carboxydecyl)imidazolium Tf<sub>2</sub>N<sup>-</sup> (2c).** A mixture of **1** (5.11 g, 31 mmol) and 11-bromoundecanoic acid (8.22 g, 31 mmol) in MeCN (60 mL) was

refluxed for 4 days. After the MeCN was removed by vacuum, ethyl ether (120 mL) was added with stirring. The precipitated bromide salt was filtered and then washed with ethyl ether 3 times. The filtered solid was dissolved in deionized water (300 mL) and LiTf<sub>2</sub>N (10 g, 35 mmol) was added. The mixture was stirred for 24 hours at 50 °C. After decanting off the upper aqueous layer, the precipitated oil was washed with deionized water 3 times. Drying in a vacuum oven gave a yellow-brown viscous liquid (18.22 g, 93%). DSC (N<sub>2</sub>, -80 ~ 200 °C, heating and cooling rate 5 °C): T<sub>g</sub> = -63 °C, no other transition found. <sup>1</sup>H-NMR (400 MHz, CD<sub>3</sub>CN, 23 °C): δ 1.28(m, 12H), 1.55 (m, 2H), 1.82 (m, 4H), 2.26 (t, J=7, 2H), 3.29 (s, 3H), 3.46 (t, J=5, 2H), 3.58 (t, J=5, 2H), 3.78 (t, J=5, 2H), 4.12 (t, J=7, 2H), 4.27 (t, J=5, 2H), 7.38 (s, 1H), 7.42 (s, 1H), 8.52 (s, 1H). <sup>13</sup>C-NMR (100 MHz, CD<sub>3</sub>CN, 23 °C): δ 25.6, 26.6, 29.5, 29.7, 29.91, 29.95, 29.97, 30.5, 34.2, 50.5, 50.6, 69.1, 70.8, 72.4, 123.0, 124.0, 136.8, 175.6. HR MS: m/z 355.2606 ([M-Tf<sub>2</sub>N]<sup>+</sup>, calcd. for C<sub>19</sub>H<sub>35</sub>N<sub>2</sub>O<sub>4</sub> 355.2597, error 2.7 ppm).

**1-Butyl-3-(10'-carboxydecyl)imidazolium Tf<sub>2</sub>N<sup>-</sup> (2d).** A mixture of N-butyylimidazole (6.21 g, 50 mmol) and 11-bromoundecanoic acid (13.97 g, 50.0 mmol) in THF (120 mL) was refluxed for 4 days. After the reaction mixture was cooled to room temp., the precipitated bromide salt was filtered and then washed with cold THF 3 times. The filtered solid was dissolved in deionized water (100 mL) and LiTf<sub>2</sub>N (15.6 g, 55 mmol) was added. The mixture was stirred for 24 hours at 50 °C. After decanting off the upper aqueous layer, the precipitated oil was washed with deionized water and ethyl ether 3 times each. Drying in a vacuum oven gave a yellow viscous liquid (19.4 g, 66%). DSC (N<sub>2</sub>, -80 ~ 200 °C, heating and cooling rate 5 °C): T<sub>g</sub> = -55 °C, no other transition found. <sup>1</sup>H-NMR (400 MHz, acetone-*d*<sub>6</sub>, 23 °C): δ 0.95 (t, J=7, 3H), 1.30-1.40 (m, 14H), 1.58 (m, 2H), 1.97 (m, 4H), 2.27 (t, J=7, 2H), 4.38 (t, J=7, 2H), 7.81 (s, 2H), 9.14 (s, 1H). <sup>13</sup>C-NMR (100 MHz, acetone-*d*<sub>6</sub>, 23 °C): δ 13.7, 20.0, 25.7, 26.7, 29.6, 30.0, 30.7, 32.7, 34.3, 50.3, 50.6, 123.6, 136.7, 174.9. HR MS: m/z 309.2527 ([M-Tf<sub>2</sub>N]<sup>+</sup>, calcd. for C<sub>18</sub>H<sub>33</sub>N<sub>2</sub>O<sub>2</sub> 309.2537, error 3.2 ppm).

**1-{ω-[1'''-(4'''-Acryloyloxy)butoxy]carbonylpentyl}-3-[2'-(2''-methoxyethoxy)ethyl]imidazolium PF<sub>6</sub><sup>-</sup> (3a).** A solution of **2a** (2.043 g, 4.75 mmol) in freshly distilled SOCl<sub>2</sub> (5 mL) was stirred for 24 hours at room temperature under N<sub>2</sub> atmosphere. After removing the excess SOCl<sub>2</sub> under vacuum, the residue was washed with anhydrous ethyl ether 5 times and then dried by N<sub>2</sub> stream. The residue was dissolved in dry MeCN (5 mL), and 4-hydroxybutyl acrylate (0.822 g, 5.70 mmol) was added. Into the reaction mixture in an ice bath, triethylamine (0.484 g, 4.76 mmol) was slowly added. The reaction mixture was stirred for 24 hours at room

temperature. After water (10 mL) was added, the product was extracted 3 times with EA and then the combined organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The drying agent was removed by filtration and the solvent was removed by a rotoevaporator. The product was rinsed with ethyl ether 5 times with vigorous stirring and then dried in a  $\text{N}_2$  stream. A yellow viscous liquid (2.02 g, 76.4%) was obtained after drying. DSC (-80 ~ 60 °C, heating and cooling rate 10 °C/min.,  $\text{N}_2$ ):  $T_g$  = -49 °C, no other transition found.  $^1\text{H}$ -NMR (400 MHz, acetone- $d_6$ , 23 °C):  $\delta$  1.42 (m, 2H), 1.61-1.76 (m, 6H), 2.00 (m, 2H), 2.33 (m, 2H), 3.30 (s, 3H), 3.49 (m, 2H), 3.65 (m, 2H), 3.93 (t,  $J=5$ , 2H), 4.10 (m, 2H), 4.17 (m, 2H), 4.41 (t,  $J=7$ , 2H), 4.54 (t,  $J=5$ , 2H), 5.89 (dd,  $J=10$  (cis),  $J=2$  (gem.), 1H), 6.15 (dd,  $J=17$  (trans),  $J=10$  (cis), 1H), 6.35 (dd,  $J=17$  (trans),  $J=2$  (gem.), 1H), 7.82 (m, 2H), 9.12 (s, 1H).  $^{13}\text{C}$ -NMR (100 MHz, acetone- $d_6$ , 23 °C): 24.8, 26.0, 26.1, 26.2, 30.4, 34.2, 50.3, 50.5, 58.8, 64.3, 64.6, 69.3, 70.8, 72.4. HR ESI MS:  $m/z$  411.2534 ( $[\text{M-PF}_6]^+$ , calcd. for  $\text{C}_{21}\text{H}_{35}\text{N}_2\text{O}_6$  411.2495, error 9.4 ppm).

**1- $\{\omega$ -[1'-(4'-Acryloyloxy)butoxy]carbonylpentyl}-3-butyliimidazolium  $\text{PF}_6^-$  (3b).** A solution of **2b** (1.78 g, 4.6 mmol) in freshly distilled  $\text{SOCl}_2$  (5 mL) was stirred for 24 hours at room temperature under  $\text{N}_2$  atmosphere. After removing the excess  $\text{SOCl}_2$  by vacuum, the residue was washed with anhydrous ethyl ether 5 times and then dried by a  $\text{N}_2$  stream. The residue was dissolved in dry MeCN (5 mL), and then 4-hydroxybutyl acrylate (0.801 g, 5.6 mmol) was added. Into the reaction mixture in an ice bath, triethylamine (0.468 g, 4.6 mmol) was slowly added. The reaction mixture was stirred for 24 hours at room temp. After water (20 mL) was added, the product was extracted 3 times with EA and then the combined organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The drying agent was removed by filtration and the solvent was removed by a rotoevaporator. The product was rinsed with ethyl ether 5 times with vigorous stirring. Drying in a vacuum oven at room temperature gave a brown viscous liquid (2.13 g, 90%). DSC (-80 ~ 60 °C, heating and cooling rate 5 °C/min.,  $\text{N}_2$ ):  $T_g$  = -58 °C, no other transition found.  $^1\text{H}$ -NMR (400 MHz, acetone- $d_6$ , 23 °C):  $\delta$  0.95 (t,  $J=7$ , 3H), 1.40 (m, 4H), 1.63-1.74 (m, 6H), 1.92-2.05 (m, 4H), 2.33 (t,  $J=7$ , 2H), 4.08-4.19 (m, 4H), 4.38 (m, 4H), 5.89 (dd,  $J=10$  (cis),  $J=2$  (gem.), 1H), 6.16 (dd,  $J=17$  (trans),  $J=10$  (cis), 1H), 6.35 (dd,  $J=17$  (trans),  $J=2$  (gem.), 1H), 7.80 (s, 2H), 9.09 (s, 1H).  $^{13}\text{C}$ -NMR (100 MHz, acetone- $d_6$ , 23 °C):  $\delta$  13.7, 20.0, 24.8, 26.0, 26.1, 26.2, 30.3, 32.7, 34.1, 50.33, 50.34, 64.3, 64.6, 123.6, 129.5, 131.1, 136.8, 166.4, 173.5. HR ESI MS:  $m/z$  365.2428 ( $[\text{M-PF}_6]^+$ , calcd. for  $\text{C}_{20}\text{H}_{35}\text{N}_2\text{O}_4$  365.2435, error 1.9 ppm).

**1-{ $\omega$ -[1'''-(4'''-Acryloyloxy)butoxy]carbonyldecyl}-3-[2'-(2''-methoxyethoxy)ethyl]**

**imidazolium Tf<sub>2</sub>N<sup>-</sup> (3c).** A solution of **2c** (6.92 g, 10.9 mmol) in freshly distilled SOCl<sub>2</sub> (15 mL) was stirred for 24 hours at room temperature under N<sub>2</sub> atmosphere. After removing the excess SOCl<sub>2</sub> under vacuum, the residue was washed with anhydrous ethyl ether 5 times and then dried by N<sub>2</sub> stream. The residue was dissolved in dry MeCN (5 mL), and 4-hydroxybutyl acrylate (1.81 g, 12.4 mmol) was added. Into the reaction mixture in an ice bath, triethylamine (1.26 g, 12.5 mmol) was slowly added. The reaction mixture was stirred for 24 hours at room temperature. After water (10 mL) was added, the product was extracted 3 times with EA and then the combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The drying agent was removed by filtration and the solvent was removed by a rotoevaporator. The product was rinsed with ethyl ether 5 times with vigorous stirring and then dried in a N<sub>2</sub> stream. A yellow viscous liquid (6.88 g, 83%) was obtained after drying. DSC (-80 ~ 60 °C, heating and cooling rate 10 °C/min., N<sub>2</sub>): T<sub>g</sub> = -70 °C, no other transition found. <sup>1</sup>H-NMR (400 MHz, CD<sub>3</sub>CN, 23 °C):  $\delta$  1.31 (m, 2H), 1.58 (m, 2H), 1.72 (m, 4H), 1.85 (m, 2H), 2.29 (t, J=7, 2H), 3.31 (s, 3H), 3.49 (m, 2H), 3.61 (m, 2H), 3.80 (t, J=5, 2H), 4.10 (m, 2H), 4.06-4.18 (m, 6H), 4.29 (t, J=5, 2H), 5.87 (dd, J=10 (cis), J=2 (gem.), 1H), 6.36 (dd, J=17 (trans), J=10 (cis), 1H), 6.35 (dd, J=17 (trans), J=2 (gem.), 1H), 7.42 (m, 2H), 8.54 (s, 1H). <sup>13</sup>C-NMR (100 MHz, acetone-*d*<sub>6</sub>, 23 °C): 25.7, 26.1, 26.7, 29.5, 29.7, 29.8, 29.9, 29.98, 30.00, 30.5, 34.8, 50.5, 50.6, 59.0, 64.4, 64.9, 69.1, 70.9, 72.4, 123.0, 124.0, 129.5, 131.3, 136.8, 166.9, 174.4. HR ESI MS: m/z 481.3307 ([M-Tf<sub>2</sub>N]<sup>+</sup>, calcd. for C<sub>26</sub>H<sub>45</sub>N<sub>2</sub>O<sub>6</sub> 481.3278, error 6.0 ppm).

**1-{ $\omega$ -[1'-(4'-Acryloyloxy)butoxy]carbonyldecyl}-3-butylimidazolium Tf<sub>2</sub>N<sup>-</sup> (3d).** A solution of **2d** (6.150 g, 10.4 mmol) in freshly distilled SOCl<sub>2</sub> (12 mL) was stirred for 24 hours at room temperature under N<sub>2</sub> atmosphere. After removing the excess SOCl<sub>2</sub> under vacuum, the residue was washed with anhydrous ethyl ether 5 times and then dried by a N<sub>2</sub> stream. The residue was dissolved in dry MeCN (20 mL), and 4-hydroxybutyl acrylate (1.656 g, 10.9 mmol) was added. Into the reaction mixture in an ice bath, triethylamine (1.052 g, 10.4 mmol) was slowly added. The reaction mixture was stirred for 24 hours at room temp. After water (20 mL) was added, the product was extracted 3 times with EA and then the combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The drying agent was removed by filtration and the solvent was removed by a rotoevaporator. The product was rinsed with ethyl ether 5 times with vigorous stirring. Drying in a vacuum oven at room temp gave a yellow viscous oil (3.16 g, 42%). DSC (-80 ~ 60 °C, heating and cooling rate 5 °C/min., N<sub>2</sub>): T<sub>g</sub> = -69 °C, no other transition found. <sup>1</sup>H-NMR (400

MHz, CD<sub>3</sub>CN, 23 °C):  $\delta$  0.94 (t, J=7, 3H), 1.28 (m, 16H), 1.56 (m, 2H), 1.69 (m, 2H), 1.81 (m, 4H), 2.27 (t, J=7, 2H), 4.10-4.16 (m, 8H), 5.84 (dd, J=10 (cis), J=2 (gem.), 1H), 6.13 (dd, J=17 (trans), J=10 (cis), 1H), 6.34 (dd, J=17 (trans), J=2 (gem.), 1H), 7.38 (ss, 2H), 8.43 (s, 1H). <sup>13</sup>C-NMR (100 MHz, CD<sub>3</sub>CN, 23 °C):  $\delta$  13.6, 20.0, 25.7, 26.0, 26.1, 26.7, 29.5, 29.7, 29.9, 29.96, 29.98, 30.4, 32.5, 34.8, 50.3, 50.6, 64.4, 64.9, 123.4, 129.5, 131.3, 136.1, 174.4. HR ESI MS: m/z 435.3246 ([M-Tf<sub>2</sub>N]<sup>+</sup>, calcd. for C<sub>25</sub>H<sub>43</sub>N<sub>2</sub>O<sub>4</sub> 435.3223, error 2.5 ppm).

**Radical polymerizations of imidazolium acrylate monomers.** A solution of the imidazolium acrylate monomer and AIBN (2 mol% of the monomer) in degassed MeCN was bubbled with N<sub>2</sub> for 30 min. The solution was stirred for 24 hours at 65 °C. After removing MeCN under vacuum, the residue was stirred with EA. Reprecipitation from acetone into EA was performed 5 times and the precipitated polymer was washed with deionized water twice. Drying in a vacuum oven at 60 °C gave highly viscous materials.

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## Chapter 14

### Synthesis of Poly(imidazolium acrylate)s and Effects of Chemical Structure on Thermal and Electrical Properties

#### Abstract

Alkylimidazolium acrylate salts were synthesized as ionic liquid monomers. These monomers are room temperature ionic liquids (RTILs) and have low  $T_g$ s ( $< -40\text{ }^{\circ}\text{C}$ ). The monomers were polymerized with AIBN (1-2 mol%) in solution. The resultant poly(alkylimidazolium acrylate)s have low  $T_g$ s ( $< -15\text{ }^{\circ}\text{C}$ ) and are thermally stable (5% weight loss  $> 250\text{ }^{\circ}\text{C}$ ). The transport properties were investigated by dielectric relaxation spectroscopy (DRS). The room temperature ionic conductivities of the monomers were on the order of  $10^{-2}$  to  $10^{-3}\text{ S cm}^{-1}$ , and the conductivities of polymers were on the order of  $10^{-4}$  to  $10^{-7}\text{ S cm}^{-1}$ . Structure and property relationship were investigated thermally and electrically;  $\text{Tf}_2\text{N}^-$  polymers have lower glass transition temperature, better thermal stability and higher ionic conductivities than the  $\text{PF}_6^-$  polymers. The longer pendant polymers show slightly lower  $T_g$ , but no difference in ionic conductivity. X-ray scattering profiles provided three distances information: backbone-to-backbone, salt-to-salt and backbone-to-backbone distance. Average distance of backbone-to-backbone increases as the pendant chain gets longer, and the average salt-to-salt distance is larger for  $\text{Tf}_2\text{N}^-$  polymers than  $\text{PF}_6^-$  analogues. The average pendant-to-pendant distance of the polymers is maintained even though the pendant structure changes.

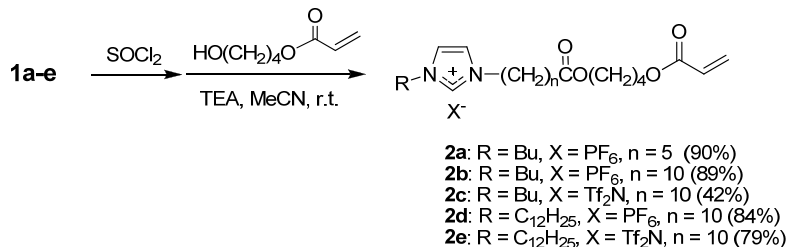
#### Introduction

Polymerizable ionic liquid monomers and their polymers have been studied due to the need for unique thermal/electrical properties of ionic liquids combined with the mechanical properties of polymeric materials. As I mentioned in Chapter 8 and Chapter 12, polymerizable groups were introduced to traditional ionic liquid moieties and then polymeric ionic materials were prepared by various polymerization methods. Ohno and his coworkers studied structure-ionic conductivity relationships of homopolymers with pendant

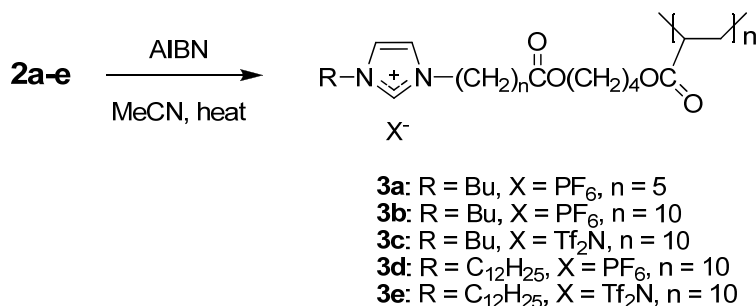
imidazolium moieties. The polymers in which the imidazolium unit was placed at the end of longer side chains gave higher conductivities.<sup>1, 2</sup> They also compared the pendant spacer structure's effect: alkyl vs. ethyleneoxy chain. The brush imidazolium Tf<sub>2</sub>N<sup>-</sup> polymers with dodecyl spacers possessed slightly higher ionic conductivity than the octa(ethyleneoxy) [(CH<sub>2</sub>CH<sub>2</sub>O)<sub>8</sub>] containing polymer. However, the imidazolium polymers containing ethyleneoxy units at the end of the pendant showed higher conductivities than the butyl substituted polymer, as reported in the previous chapter (Chapter 10). Herein, we synthesized acrylate monomers with imidazolium ionic liquid units with different of spacer lengths and counterions. Inhibitors have been usually used during imidazolium (meth)acrylate-family monomer synthesis,<sup>3,4</sup> because the monomers can be easily auto-polymerized even by contacting air at room temperature. In this study, 4-hydroxybutyl acrylate was as a starting material to make the monomer to prevent self-polymerization of the monomers. The polymers from the imidazolium acrylate monomers were prepared by a conventional radical polymerization. Physical and electrical properties were investigated upon changing the pendant structure of the ionic polymers in this study and the results will be discussed below.

## Results and Discussion

**Synthesis.** The quaternization reactions of 1-alkylimidazoles and  $\omega$ -bromoalkanoic acids followed by ion exchange gave carboxy terminated imidazolium salts **1a-e** (Scheme 14-1). The quaternization reactions were performed in tetrahydrofuran (THF) (or acetonitrile (MeCN)) under reflux conditions for several days. The ion exchanges from the bromide salts to the hexafluorophosphate (PF<sub>6</sub><sup>-</sup>) or bis(trifluoromethanesulfonyl)imide (Tf<sub>2</sub>N<sup>-</sup>) salts were done under aqueous condition with KPF<sub>6</sub> or LiTf<sub>2</sub>N, respectively, and the resulting products precipitated. To confirm the complete removal of the halide ions, a Beilstein halide test test<sup>5</sup> or treatment with silver nitrate solution was performed before the next reaction. The imidazolium salts **1a-e** are room temperature ionic liquids (RTILs) with low glass transition temperatures ( $\leq -40$  °C) except for **1d** which has a long dodecyl alkyl chain. The thermal stabilities of Tf<sub>2</sub>N<sup>-</sup> salts are better than that of PF<sub>6</sub><sup>-</sup> salts as judged by TGA (**1b** vs. **1c** and **1d** vs. **1e**).



**Scheme 14-1.** Synthesis of imidazolium acrylate monomers.



**Scheme 14-2.** Polymerization of imidazolium acrylate monomers.

**Table 14-1.** Physical Properties of  $\omega$ -carboxyalkylimidazolium salts **1a-e**.

|           | Phase<br>(at 25 °C) | Color        | Transitions (DSC)             |                              | TGA (°C)<br>5% w/w loss |
|-----------|---------------------|--------------|-------------------------------|------------------------------|-------------------------|
|           |                     |              | T <sub>g</sub> (°C)           | T <sub>m</sub> (°C)          |                         |
| <b>1a</b> | Liquid              | Yellow       | -39                           | -                            | 254                     |
| <b>1b</b> | Liquid              | Yellow       | -42                           | -                            | 289                     |
| <b>1c</b> | Liquid              | Yellow       | -54                           | -                            | 352                     |
| <b>1d</b> | Solid               | Light yellow | -20<br>(2 <sup>nd</sup> scan) | 44<br>(2 <sup>nd</sup> scan) | 243                     |
| <b>1e</b> | Liquid              | Pale Yellow  | -57<br>(2 <sup>nd</sup> scan) | 0<br>(1 <sup>st</sup> scan)  | 291                     |

The polymerizable acrylate unit was introduced by the esterification of **1a-e** with 4-hydroxybutyl acrylate. After the chlorination of the carboxylic acids to the corresponding carbonyl chlorides with thionyl chloride, 4-hydroxybutyl acrylate and triethyl amine were added in dry MeCN. The imidazolium acrylate monomers **2a-e** are RTILs, but less viscous

than **1a-e**. They are soluble in acetone, MeCN, dimethyl formamide (DMF) and sometimes in ethyl acetate (EA), but not soluble in water. The phase transitions of the monomers are shown in Table 14-2. All monomers have only  $T_g$ , except **2d** has only  $T_m$ . The melting of **2d** may be from the long dodecyl chain and symmetric  $PF_6^-$  anions. The same structure with  $Tf_2N^-$  has only a low  $T_g$  ( $-70\text{ }^\circ\text{C}$ ) on DSC. There is an anion effect on  $T_g$ ; the  $T_g$  of the  $PF_6^-$  anion monomers (**2b**) is lower than that of monomers with  $Tf_2N^-$  (**2c**). From TGA, the imidazolium acrylate monomers were thermally stable up to  $250\text{ }^\circ\text{C}$  under  $N_2$  atmosphere. One-step degradation in TGA was shown for all ionic liquid monomers **2a-e**, as in the thermal decomposition of most small organic molecules. However, a self-polymerization occurred with some monomers when they were stored at room temperature being exposed to air. To prevent the self-polymerization, all monomers were stored in a freezer ( $< 0\text{ }^\circ\text{C}$ ) after packing with dry  $N_2$ .

The radical polymerization of the monomers was done with 2,2'-azobisisobutyronitrile (AIBN) in MeCN. MeCN was degassed before the polymerizations for at least 1 hour by  $N_2$  bubbling. The polymerization temperature was maintained at  $65\text{ }^\circ\text{C}$ . The product polymers were purified by precipitation from EA which is a good solvent for the monomers **2a-e**, but doesn't dissolve the polymers **3a-e**. The polymers were also washed with deionized water several times to remove water soluble impurities. The residual water was removed by vacuum with heating for several days. The water contents of the polymers were simply checked by  $^1\text{H-NMR}$  spectroscopy.

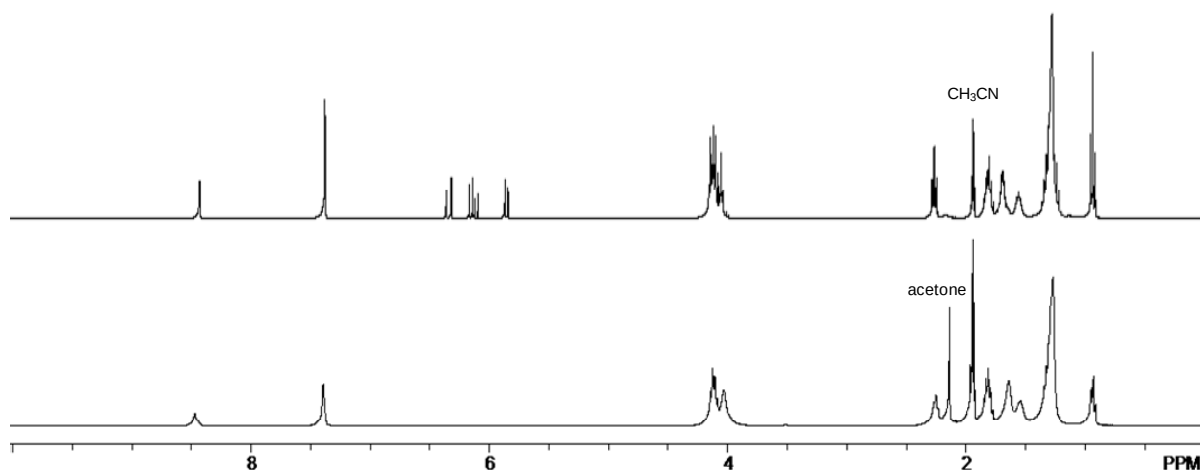


**Figure 14-1.** 400 MHz  $^1\text{H}$  NMR spectra of monomer **2c** and polymer **3c** (in  $CD_3CN$ ,  $23\text{ }^\circ\text{C}$ ). After polymerization, vinyl proton peaks ( $\delta$  5.7-.4) disappear and some peaks are broadened.

The polymerizations were confirmed by a precipitation an aliquot from the reaction mixture with ethyl acetate . In addition, spectroscopic methods gave quantitative information about the polymerization reactions. In the comparison of  $^1\text{H}$ -NMR spectra between monomers and polymers the vinyl protons of the monomers disappeared in the purified polymers (Figure 14-1). The polymers also exhibited some peak broadening. The  $\text{CH}_2$  protons that are close to the polymer backbone were broadened after the polymerization, whereas the alkyl protons which are well removed from the polymer backbone still appear as sharp signals. The carbon-carbon bond rotation is much faster in the alkyl chains which are far from the polymer backbone and they remained sharp. The glass transition temperature changes are also evidence for the polymerizations. The  $T_g$ s of the polymers are 20 – 40 degree higher than those of the corresponding monomers (Table 14-2).

**Table 14-2.** Thermal Properties of Monomer **2a-e** and Polymers **3a-e**.

| Monomers  | $T_g$ ( $^{\circ}\text{C}$ ) | Polymers  | $T_g$ ( $^{\circ}\text{C}$ ) | TGA ( $^{\circ}\text{C}$ )<br>5% w/w loss |
|-----------|------------------------------|-----------|------------------------------|-------------------------------------------|
| <b>2a</b> | -58                          | <b>3a</b> | -18                          | 334                                       |
| <b>2b</b> | -62                          | <b>3b</b> | -17                          | 341                                       |
| <b>2c</b> | -69                          | <b>3c</b> | -43                          | 382                                       |
| <b>2d</b> | $T_m = -24^*$                | <b>3d</b> | -29                          | 340                                       |
| <b>2e</b> | -70                          | <b>3e</b> | -47                          | 336                                       |

\* No  $T_g$  in the range of  $-80 \sim 200$   $^{\circ}\text{C}$  by DSC.

**Thermal Properties.** The relationship between the imidazolium pendant structures and thermal properties of the polymers was investigated by DSC and TGA (Table 14-2). The polymers **3a-e** are amorphous (no crystallization or melting) in the temperature range of  $-80 \sim 200$   $^{\circ}\text{C}$ . The nature of the anions affects the  $T_g$ s of polymers; the polymers with  $\text{PF}_6^-$  anions have higher  $T_g$  than those with  $\text{TF}_2\text{N}^-$  anions (**3b** vs. **3c** and **3d** vs. **3e**). The thermal stabilities of the polymers **3a-e** were good up to 280  $^{\circ}\text{C}$ . There is also an anion effect on the thermal stability; the  $\text{TF}_2\text{N}^-$  anion polymer (**3c**) has better thermal stability than **3b** with  $\text{PF}_6^-$ , when the polymers **3b** and **3c** are compared. However, polymers with a long dodecyl chain do not show much difference (**3d** and **3e**). The thermal degradations of the polymers were one step, which means that the ionic imidazolium units were stable up to the degradation temperature

of the polyacrylate backbone.

**Ionic Conductivity.** To understand the influence of anions and the length of the tail on ionic conductivity, the temperature dependence of d.c. conductivity shown in Figure 14-2 was evaluated over a roughly 3-decade frequency range where the in-phase part of the conductivity  $\sigma'(\omega) = \varepsilon''(\omega)\varepsilon_0\omega$  is independent of frequency. With increasing temperature the d.c. conductivity increases exponentially for all samples. We fit the dependence of conductivity on temperature by combining a Vogel-Fulcher-Tammann (VFT) equation and an Arrhenius equation

$$\sigma_{DC} = e\mu p = e\mu_{\infty}p_{\infty} \exp\left(-\frac{DT_0}{T-T_0}\right) \exp\left(-\frac{E_a}{RT}\right), \quad (1)$$

where  $e$ ,  $\mu$ , and  $p$  are the elementary electric charge, the conducting ion mobility, and the number density of conducting ions, respectively.  $\mu_{\infty}$  and  $p_{\infty}$  refer to the ionic mobility and the conducting ion concentration as  $T \rightarrow \infty$ , and  $D$ ,  $T_0$ , and  $E_a$  mean the so-called strength parameter related to the divergence from Arrhenius temperature dependence, the Vogel temperature where the free volume is zero, and an activation energy for conducting ions. The well-described ionic conductivity with Eq. (1) indicates that there is strong coupling between polymer relaxation and macroscopic ion motion.

The inset in Figure 14-2 shows the strong correlation between ionic conductivity and  $T_g$  for these materials. The monomers with lower  $T_g$  show higher ionic conductivities than polymers with higher  $T_g$ s. There is also a significant effect from different anions on ionic conductivity for these polymers. Due to the suppression of the  $T_g$ , the larger  $\text{Tf}_2\text{N}^-$  anion results in an increase in ionic conductivity of its polymers (**3c** and **3e**) by approximately 2 orders magnitude at room temperature, compared to  $\text{PF}_6^-$  polymers (**3b** and **3d**). However, an effect from the dodecyl vs. butyl tail on ionic conductivity is more subtle, that is, polymers with shorter tail (**3b** and **3c**) showed slightly higher ionic conductivity above room temperature in spite of having higher  $T_g$  as shown in Figure 14-3. The higher conductivity of the short butyl substituted polymers may be from 1) higher total ion contents compare due to the lower molecular weight of butyl compare to dodecyl and 2) segmental motions of the neutral longer dodecyl substituent might prevent the ion movement. Further electrical and relaxation studies will yield detailed information that may explain the conductivity difference of the polymers.

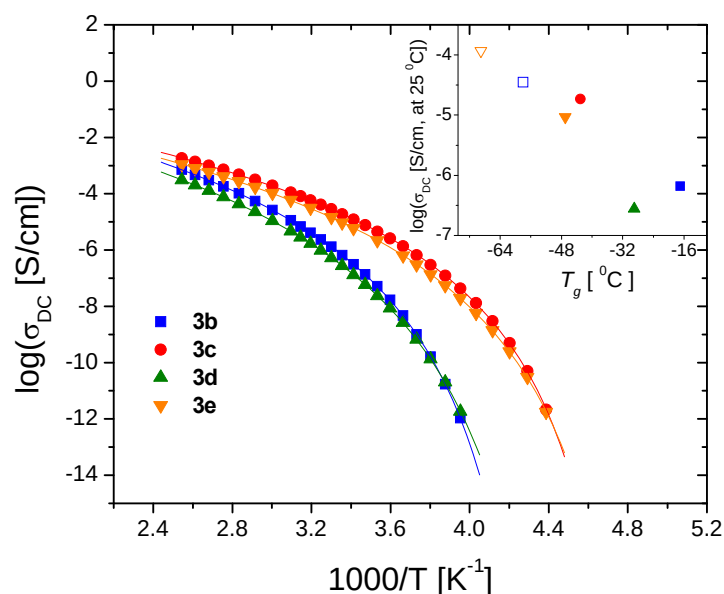


**Figure 14-2.** Temperature dependence of ionic conductivities of  $\text{PF}_6^-$  and  $\text{Tf}_2\text{N}^-$  polymers. Lines indicate fits of Eq.(1) to the data. The inset shows ionic conductivity at room temperature as a function of glass transition temperatures of the four polymers (**3b** (■), **3c**(●), **3d**(▲), **3e**(▼)) and two monomer (**2a**(□) and **2c**(▼)).

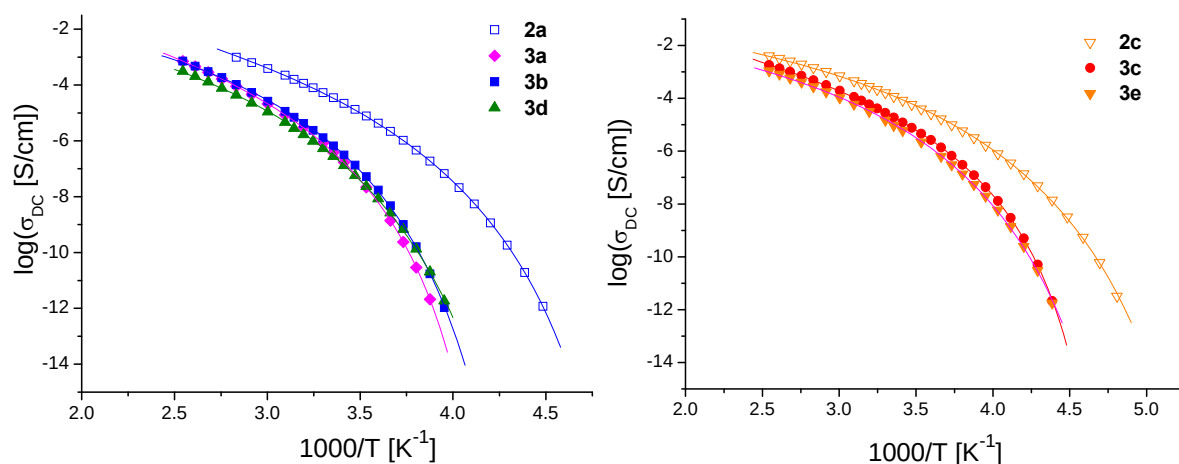


**Figure 14-3.** Ionic conductivity plots of  $\text{PF}_6^-$  monomer and polymer (left), and  $\text{Tf}_2\text{N}^-$  monomer and polymer (right).

**X-Ray Scattering Analysis.** X-Ray scattering (XRS) is one of the most powerful methods to study polymer morphology. For amorphous pendant ionic homopolymers, three distance parameters can be determined by XRS experiments: average distances of backbone-to-backbone, salt-to-salt and pendant-to-pendant as the diagram shown in Figure 14-4. As we



expected, these three major peaks were detected by XRS and each peak was assigned for a series of the synthesized polymers.

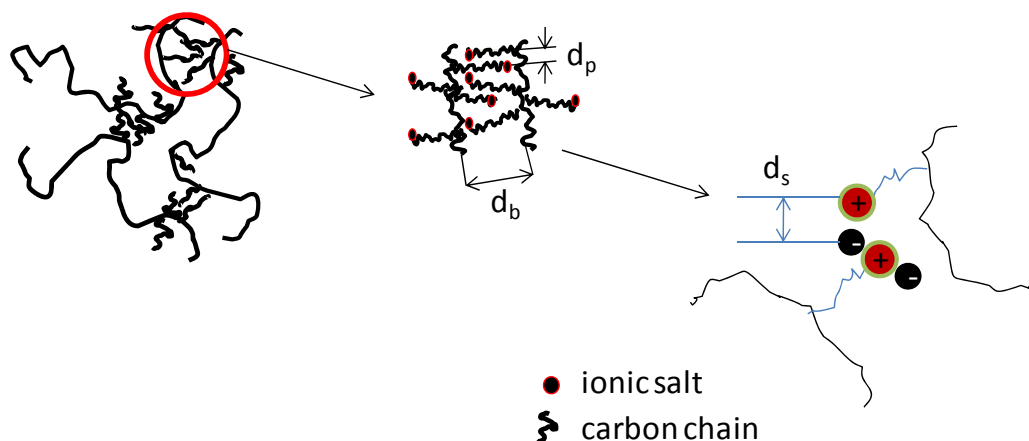


**Figure 14-4.** Three possible distance parameters from XRD for amorphous ionic homopolymers. All the distance information is determined as an average value.

The XRD scattering profiles of the  $\text{PF}_6^-$  polymers are shown in Figure 14-5. The largest  $q$  ( $\sim 12$ ) and small mounds at  $q = 9$  refer pendant-to-pendant distance and salt-to-salt distance, respectively, because they don't change with different length of pendant within the same class of the homopolymers, **3a**, **3b** and **3d**. The peaks with the smallest  $q$  represent the backbone-to-backbone distance of the homopolymers; this  $q$  value decreases as the pendant length increases. The same peak assignment was also applied to the XRS results from  $\text{Tf}_2\text{N}^-$  polymers. Figure 14-6 shows the XRD scattering profiles of  $\text{PF}_6^-$  polymer **3b** and  $\text{Tf}_2\text{N}^-$  polymers **3c** and **3e**. For **3b** and **3c**, the average pendant-to-pendant distance does not change significantly from the peaks with the largest  $q$ , even though the counter anion size gets bigger from  $\text{PF}_6^-$  to  $\text{Tf}_2\text{N}^-$ . However, the salt-to-salt distance increases, and the backbone-to-backbone distance still remains constant because the pendant length does not change. The backbone-to-backbone distance only changes as the length of a pendant chain increases, from the result of **3c** and **3e**.

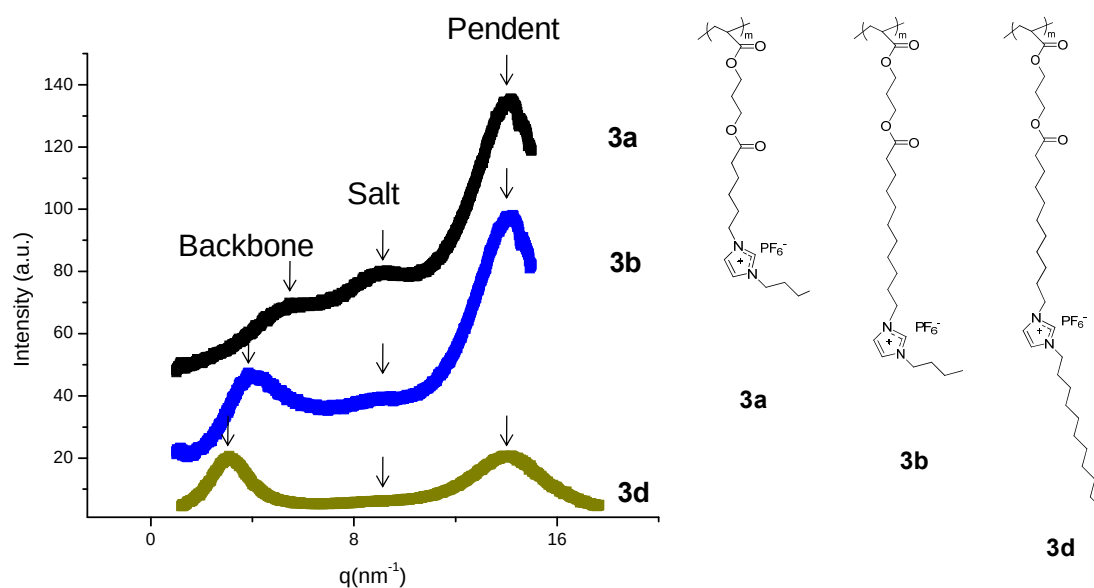


**Figure 14-5.** X-Ray scattering profiles of  $\text{PF}_6^-$  polymers, **3a**, **3b** and **3d**.

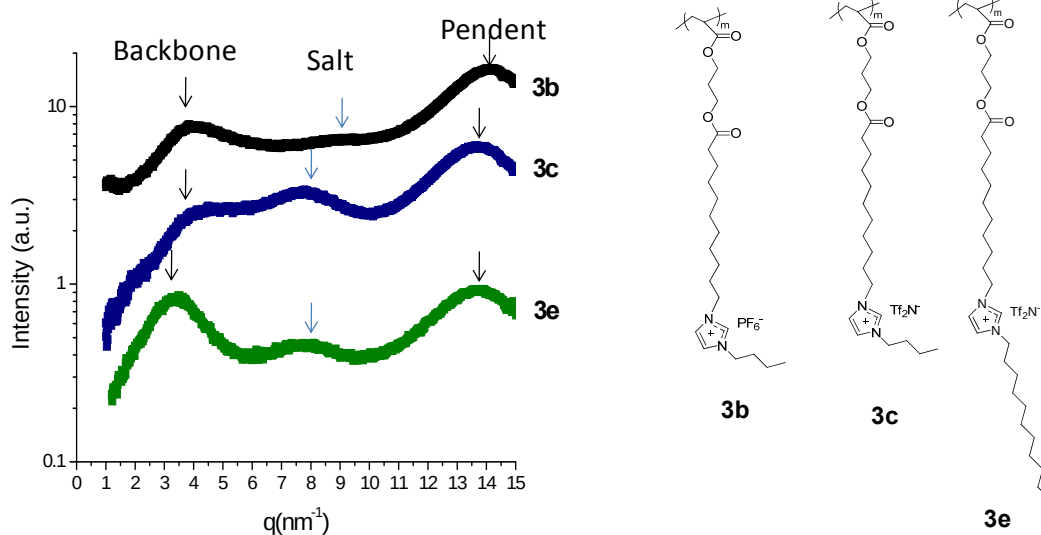


**Figure 14-6.** X-Ray scattering profiles of  $\text{PF}_6^-$  polymers **3b** and  $\text{Tf}_2\text{N}^-$  polymers **3c** and **3e**.

## Conclusions

As new RTILs, various mono-carboxy imidazolium salts were prepared and converted to N-alkylimidazolium acrylate salts as polymerizable RTIL monomers. The imidazolium acrylate monomers were polymerized by a conventional radical pathway. The effect of counterions is clearly observed in the glass transition temperature and ionic conductivity;  $\text{Tf}_2\text{N}^-$  polymers with lower  $T_g$  have higher ionic conductivity than  $\text{PF}_6^-$  polymers. The ionic

conductivity is also strongly coupled with segmental motion of polymer chain as indicated by the observation of VFT dependence. There are three peaks from X-ray scattering experiments and they are assigned as the average pendant-to-pendant distance, salt-to-salt distance and backbone-to-backbone distance of the amorphous polymers. The average backbone-to-backbone distance increases as the pendant chain gets longer, and the average salt-to-salt distance is larger for  $\text{Tf}_2\text{N}^-$  polymers than  $\text{PF}_6^-$  analogs. The average pendant-to-pendant distance of the polymers is maintained regardless of the different pendant structures, because the polymers are all acrylates.

## Experimental

**Materials.** Acetonitrile was dried over anhydrous  $\text{K}_2\text{CO}_3$  and then distilled. All other chemicals and solvents were used as received.

**Spectroscopic and thermal characterizations.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained on Varian Inova 400 MHz and Unity 400 MHz spectrometers. High resolution electrospray ionization time-of-flight mass spectrometry (HR ESI TOF MS)) was carried out on an Agilent 6220 Accurate Mass TOF LC/MS Spectrometer in positive ion mode. Differential Scanning Calorimetry (DSC) with heating and cooling rates of 5 or 10 K/min on  $\sim 10$  mg samples was done using a TA Instrument Q2000 differential scanning calorimeter. The thermal stabilities of these polymers were studied by TGA under  $\text{N}_2$  using a TA Instrument Q500 Thermogravimetric Analyzer at a heating rate of 10 K/min heating under  $\text{N}_2$  purge.

**Measurement of Ionic Conductivities of Monomers and Polymers.** The ionic conductivity measurements of the monomers and polymers were performed by dielectric spectroscopy using a Novocontrol GmbH Concept 40, with 0.1 V amplitude and  $10^{-2}$  -  $10^7$  Hz frequency range. Samples were prepared for the dielectric measurements by allowing them to flow to cover a 30 mm diameter polished brass electrode at 100  $^\circ\text{C}$  *in vacuo* to form a puddle deeper than 50  $\mu\text{m}$  with several 50  $\mu\text{m}$  silica spacers immersed. Then a 15 mm diameter polished brass electrode was placed on top to make a parallel plate capacitor cell which was squeezed to a gap of 50  $\mu\text{m}$  in the instrument (with precise thickness checked after dielectric measurements were complete). Each sample was annealed in the Novocontrol at 120  $^\circ\text{C}$  in a heated stream of nitrogen for 1 hour prior to measurements. Data were collected in isothermal frequency sweeps from 120  $^\circ\text{C}$  to near  $T_g$ .

**Materials.** 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from chloroform below 40  $^\circ\text{C}$  and dried in a vacuum oven and stored in a freezer ( $< -10$   $^\circ\text{C}$ ). Acetonitrile (MeCN) for

polymerizations was distilled over calcium hydride. All other chemicals and solvents were used as received.

**1-Dodecylimidazole.** To a solution of imidazole (6.81 g, 100 mmol) in NaOH (50%) solution (8.80 g, 110 mmol), 1-bromododecane (24.92 g, 100 mmol) and THF (30 mL) were added. The mixture was refluxed for 3 days. After the mixture had cooled, THF was removed by a rotoevaporator. The residue was extracted by dichloromethane/water 3 times. The combined organic layer was washed with water and then dried over Na<sub>2</sub>SO<sub>4</sub>. The drying agent was filtered off and the filtrate solution was concentrated. Column chromatography through a short silica-gel column with THF gave a clear yellow oil 20.51 g (86.8%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 22 °C): δ 0.88 (t, *J*=7, 3H), 1.29 (m, 18H), 1.76 (m, *J*=7, 2H), 3.91 (t, *J*=7, 4H), 6.90 (s, 1H), 7.05 (s, 1H), 7.45 (s, 1H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, 22 °C): δ 14.0, 22.6, 26.4, 29.0, 29.2, 29.3, 29.4, 29.5, 31.0, 31.8, 46.9, 118.6, 129.2, 136.9. The <sup>1</sup>H-NMR spectrum was exactly identical to the literature reported.<sup>6</sup>

**1-Butyl-3-(5'-carboxypentyl)imidazolium PF<sub>6</sub><sup>-</sup> (1a).** A mixture of N-butyylimidazole (5.92 g, 47.7 mmol) and 6-bromohexanoic acid (9.30 g, 47.7 mmol) in THF (40 mL) was refluxed for 3 days. After the reaction mixture was cooled to room temperature, the THF was decanted and the residue was washed with THF 3 times. The residual yellow viscous oil was dissolved in deionized water (80 mL) and KPF<sub>6</sub> (10.12 g, 55 mmol) was added. The mixture was stirred for 24 hours at room temperature. After decanting the upper aqueous layer, the residual oily product was washed with deionized water 3 times. Drying in a vacuum oven gave pale-yellow viscous liquid (11.57 g, 63%). DSC (N<sub>2</sub>, -80 ~ 200 °C, heating and cooling rate 5 °C): T<sub>g</sub> = -39.3 °C (2<sup>nd</sup> cycle), no other transition found. <sup>1</sup>H-NMR (400 MHz, acetone-*d*<sub>6</sub>, 23 °C): δ 0.95 (t, *J*=8, 3H), 1.40 (m, 4H), 1.65 (m, 4H), 1.97 (m, 4H), 2.32 (t, *J*=8, 2H), 4.36 (q, *J*=8, 1H), 7.77 (m, 2H), 9.03 (s, 1H). <sup>13</sup>C-NMR (100 MHz, acetone-*d*<sub>6</sub>, 23 °C): δ 13.6, 20.0, 24.7, 26.1, 30.3, 30.6, 32.6, 33.8, 50.3, 123.5, 136.7, 174.7. HRMS (ESI): *m/z* 239.1746 ([M-PF<sub>6</sub>]<sup>+</sup>, calcd. 239.1754, error 3.3 ppm).

**1-Butyl-3-(10'-carboxydecyl)imidazolium PF<sub>6</sub><sup>-</sup> (1b).** A mixture of N-butyylimidazole (6.21 g, 50.0 mmol) and 11-bromoundecanoic acid (13.97 g, 50.0 mmol) in THF (60 mL) was refluxed for 4 days. After the reaction mixture was cooled to room temp., the precipitated bromide salt was filtered and then washed with cold THF 3 times. The residual brown solid was dissolved in deionized water (100 mL) and KPF<sub>6</sub> (10.12 g, 55 mmol) was added. The mixture was stirred for 24 hours at 50 °C. After decanting the upper aqueous layer, the residual oil was washed with deionized water and ethyl ether 3 times each. Drying in a

vacuum oven gave yellow viscous liquid (16.58 g, 73.1%). DSC (N<sub>2</sub>, -80 ~ 200 °C, heating and cooling rate 5 °C): T<sub>g</sub> = -42.2 °C (2<sup>nd</sup> cycle), no other transition found. <sup>1</sup>H-NMR (400 MHz, acetone-*d*<sub>6</sub>, 23 °C): δ 0.95 (t, *J*=8, 3H), 1.34-1.41 (m, 14H), 1.58 (m, 2H), 1.96 (m, 4H), 2.27 (t, *J*=8, 2H), 4.38 (t, *J*=8, 2H), 7.80 (s, 2H), 9.10 (s, 1H). <sup>13</sup>C-NMR (100 MHz, acetone-*d*<sub>6</sub>, 23 °C): δ 13.8, 20.0, 25.6, 26.7, 29.6, 29.7, 29.9, 29.96, 29.98, 30.7, 32.6, 34.2, 50.3, 50.6, 119.39 (t, <sup>1</sup>*J*=319, CF<sub>3</sub>), 123.6, 136.8, 174.9. HRMS (ESI): *m/z* 309.2564 ([M-PF<sub>6</sub>]<sup>+</sup>, calcd. 309.2537, error 8.7 ppm).

**1-Butyl-3-(10'-carboxydecyl)imidazolium Tf<sub>2</sub>N<sup>-</sup> (1c).** A mixture of N-butylimidazole (6.21 g, 50.0 mmol) and 11-bromoundecanoic acid (13.97 g, 50.0 mmol) in THF (120 mL) was refluxed for 4 days. After the reaction mixture was cooled to room temp., the precipitated bromide salt was filtered and washed with cold THF 3 times. The filtered solid was dissolved in deionized water (100 mL) and LiTf<sub>2</sub>N (15.6 g, 55 mmol) was added. The mixture was stirred for 24 hours at 50 °C. After decanting the upper aqueous layer, the precipitated oil was washed with ethyl ether 3 times. The oily product was dissolved in EA (100 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>. After removing the drying agent by filtration, solvent evaporation and drying in a vacuum oven gave a yellow viscous liquid (19.4 g, 66%). DSC (N<sub>2</sub>, -80 ~ 200 °C, heating and cooling rate 5 °C): T<sub>g</sub> = -55 °C, no other transition found. <sup>1</sup>H-NMR (400 MHz, acetone-*d*<sub>6</sub>, 23 °C): δ 0.95 (t, *J*=7, 3H), 1.30-1.40 (m, 14H), 1.58 (m, 2H), 1.97 (m, 4H), 2.27 (t, *J*=7, 2H), 4.38 (t, *J*=7, 2H), 7.81 (s, 2H), 9.14 (s, 1H). <sup>13</sup>C-NMR (100 MHz, acetone-*d*<sub>6</sub>, 23 °C): δ 13.7, 20.0, 25.7, 26.7, 29.6, 30.0, 30.7, 32.7, 34.3, 50.3, 50.6, 123.6, 136.7, 174.9. HRMS (ESI): *m/z* 309.2527 ([M-Tf<sub>2</sub>N]<sup>+</sup>, calcd. 309.2537, error 3.2 ppm).

**1-Dodecyl-3-(10'-carboxydecyl)imidazolium PF<sub>6</sub><sup>-</sup> (1d).** A mixture of N-dodecylimidazole (4.73 g, 20.0 mmol) and 11-bromoundecanoic acid (5.30 g, 20.0 mmol) in MeCN (15 mL) was refluxed for 4 days. After the reaction mixture was cooled to room temperature, the MeCN was removed by a rotoevaporator. Ethyl ether (80 mL) was added to solidify the residual bromide salt. The precipitate was filtered and washed with ethyl ether 3 times. The colorless crystalline solid (9.02 g, 90%) was obtained after drying in air. The bromide salt (3.55 g, 7.08 mmol) was dispersed in deionized water (200 mL) and KPF<sub>6</sub> (2.76 g, 15 mmol) was added. The mixture was stirred for 24 hours at 50 °C. After decanting the upper aqueous layer, the residual oil was washed with deionized water and ethyl ether 3 times each. Drying in a vacuum oven gave a light-yellow viscous liquid (3.95 g, 98% from bromide salt). The product was solidified at room temperature after several days. DSC (N<sub>2</sub>, -80 ~ 200 °C,

heating and cooling rate 5 °C):  $T_g = -20.3$  °C,  $T_m = 44$  °C (2<sup>nd</sup> heating scan). <sup>1</sup>H-NMR (400 MHz, acetone-*d*<sub>6</sub>, 22 °C):  $\delta$  0.83 (t,  $J=7$ , 3H), 1.24-1.35 (m, 32H), 1.55 (m, 2H), 1.94 (m, 4H), 2.24 (t,  $J=7$ , 4H), 4.37 (t,  $J=7$ , 2H), 7.79 (s, 2H), 9.10 (s, 1H). <sup>13</sup>C-NMR (100 MHz, acetone-*d*<sub>6</sub>, 22 °C):  $\delta$  14.3, 14.5, 20.8, 23.3, 25.7, 26.6, 26.7, 26.8, 29.6, 29.8, 30.0, 30.1, 30.3, 30.7, 32.6, 34.1, 50.6, 60.5, 123.6, 136.7, 174.7. HRMS (ESI):  $m/z$  421.3805 ([M-PF<sub>6</sub>]<sup>+</sup>, calcd. 421.3794, error 2.6 ppm).

**1-Dodecyl-3-(10'-carboxydecyl)imidazolium Tf<sub>2</sub>N<sup>-</sup> (1e).** From the previous experiment, the bromide salt (5.48 g, 11.0 mmol) was dispersed in deionized water (200 mL) and LiTf<sub>2</sub>N (4.58 g, 16 mmol) was added. The mixture was stirred for 24 hours at 50 °C. After decanting the upper aqueous layer, the residual oil was washed with deionized water and ethyl ether 3 times each. Drying in a vacuum oven gave a light-yellow viscous liquid (7.65 g, 99% from the bromide salt). DSC (N<sub>2</sub>, -80 ~ 200 °C, heating and cooling rate 5 °C):  $T_m = 0$  °C (1<sup>st</sup> heating scan)  $T_g = -57$  °C (2<sup>nd</sup> heating scan), no other transition found. <sup>1</sup>H-NMR (400 MHz, acetone-*d*<sub>6</sub>, 22 °C):  $\delta$  0.84 (t,  $J=7$ , 3H), 1.24-1.33 (m, 32H), 1.54 (m, 2H), 1.94 (m, 4H), 2.23 (t,  $J=7$ , 4H), 4.35 (t,  $J=7$ , 2H), 7.79 (s, 2H), 9.11 (s, 1H), 10.32 (s (br), 1H). <sup>13</sup>C-NMR (100 MHz, acetone-*d*<sub>6</sub>, 22 °C):  $\delta$  14.3, 14.4, 20.8, 23.3, 25.6, 26.6, 26.7, 26.8, 29.6, 29.8, 30.0, 30.1, 30.3, 30.7, 32.6, 34.1, 50.5, 60.5, 123.4, 136.6, 174.6. HRMS (ESI):  $m/z$  421.3806 ([M-Tf<sub>2</sub>N]<sup>+</sup>, calcd. 421.3794, error 2.8 ppm).

**1-{ $\omega$ -[1'-(4''-Acryloyloxy)butoxy]carbonylpentyl}-3-butylimidazolium PF<sub>6</sub><sup>-</sup> (2a).** A solution of **1a** (1.78 g, 4.6 mmol) in freshly distilled SOCl<sub>2</sub> (5 mL) was stirred for 24 hours at room temp. under N<sub>2</sub> atmosphere. After removing the excess SOCl<sub>2</sub> by vacuum, the residue was washed with anhydrous ethyl ether 5 times and dried by N<sub>2</sub> stream. The residue (acid chloride of **1a**) was dissolved in dry MeCN (5 mL), and then 4-hydroxybutyl acrylate (0.801 g, 5.6 mmol) was added. Into the reaction mixture, triethylamine (0.468 g, 4.6 mmol) was slowly added in an ice bath. The reaction mixture was stirred for 24 hours at room temp. After water (20 mL) was added, the product was extracted 3 times with EA and the combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The drying agent was removed by filtration and the solvent of the filtrate was removed by a rotoevaporator. The product was rinsed with ethyl ether 5 times with vigorous stirring. Drying in a vacuum oven at room temp gave a brown viscous liquid (2.13 g, 90%). DSC (-80 ~ 60 °C, heating and cooling rate 5 °C/min., N<sub>2</sub>):  $T_g = -58$  °C, no other transition found. <sup>1</sup>H-NMR (400 MHz, acetone-*d*<sub>6</sub>, 22 °C):  $\delta$  0.95 (t,  $J=7$ , 3H), 1.40 (m, 4H), 1.63-1.74 (m, 6H), 1.92-2.05 (m, 4H), 2.33 (t,  $J=7$ , 2H), 4.08-4.19 (m, 4H), 4.38 (m, 4H), 5.89 (dd,  $J=10$  (*cis*),  $J=2$  (*gem.*), 1H), 6.16 (dd,  $J=17$  (*trans*),  $J=10$

(*cis*), 1H), 6.35 (dd,  $J=17$  (*trans*),  $J=2$  (*gem.*), 1H), 7.80 (s, 2H), 9.09 (s, 1H).  $^{13}\text{C}$ -NMR (100 MHz, acetone- $d_6$ , 23 °C):  $\delta$  13.7, 20.0, 24.8, 26.0, 26.1, 26.2, 30.3, 32.7, 34.1, 50.33, 50.34, 64.3, 64.6, 123.6, 129.5, 131.1, 136.8, 166.4, 173.5. HRMS (ESI): 365.2428 ( $[\text{M-PF}_6]^+$ , cald. 365.2435, error 1.9 ppm).

**1-{ $\omega$ -[1'-(4''-Acryloyloxy)butoxy]carbonyldecyl}-3-butyliimidazolium PF<sub>6</sub><sup>-</sup> (2b).** A solution of **1b** (2.98 g, 6.56 mmol) in freshly distilled SOCl<sub>2</sub> (8 mL) was stirred for 24 hours at room temp. under N<sub>2</sub> atmosphere. After removing the excess SOCl<sub>2</sub> by vacuum, the residue was washed with anhydrous ethyl ether 5 times and then dried by an N<sub>2</sub> stream. The residue (acid chloride of **1b**) was dissolved in dry MeCN (5 mL), and 4-hydroxybutyl acrylate (1.229 g, 8.53 mmol) was added. Into the reaction mixture, triethylamine (0.665 g, 6.56 mmol) was slowly added in an ice bath. The reaction mixture was stirred for 24 hours at room temp. After water (20 mL) was added, the product was extracted 3 times with EA and the combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The drying agent was removed by filtration and the solvent of the filtrate was removed by a rotoevaporator. The product was rinsed with ethyl ether 5 times with vigorous stirring. Drying in a vacuum oven at room temp gave a brown viscous liquid (3.40 g, 89%). DSC (-80 ~ 60 °C, heating and cooling rate 5 °C/min., N<sub>2</sub>): T<sub>g</sub> = -62 °C, no other transition found.  $^1\text{H}$ -NMR (400 MHz, acetone- $d_6$ , 22 °C):  $\delta$  0.95 (t,  $J=8$ , 3H), 1.30-1.42 (m, 20H), 1.58 (m, 2H), 1.73 (m, 4H), 1.97 (m, 4H), 2.29 (t,  $J=7$ , 2H), 4.10 (t,  $J=7$ , 2H), 4.18 (t,  $J=7$ , 2H), 4.39 (m, 4H), 5.88 (dd,  $J=10$  (*cis*),  $J=2$  (*gem.*), 1H), 6.15 (dd,  $J=17$  (*trans*),  $J=10$  (*cis*), 1H), 6.35 (dd,  $J=17$  (*trans*),  $J=2$  (*gem.*), 1H), 7.82 (s, 2H), 9.12 (s, 1H).  $^{13}\text{C}$ -NMR (100 MHz, acetone- $d_6$ , 22 °C):  $\delta$  13.7, 20.0, 24.9, 26.0, 26.1, 26.2, 29.5, 29.8, 29.9, 30.01, 30.04, 30.4, 32.5, 34.1, 50.3, 50.4, 64.3, 64.7, 123.4, 129.5, 131.1, 136.6, 173.4. HRMS (ESI): 435.3255 ( $[\text{M-PF}_6]^+$ , cald. 435.3223, error 7.4 ppm).

**N-Butyl-N'-{ $\omega$ -[1-(4-acryloyloxy)butoxy]carbonyldecyl}imidazolium Tf<sub>2</sub>N<sup>-</sup> (2c).** A solution of **1c** (6.150 g, 10.4 mmol) in freshly distilled SOCl<sub>2</sub> (12 mL) was stirred for 24 hours at room temp. under N<sub>2</sub> atmosphere. After removing the excess SOCl<sub>2</sub> by vacuum, the residue was washed with anhydrous ethyl ether 5 times and dried by an N<sub>2</sub> stream. The residue (acid chloride of **1c**) was dissolved in dry MeCN (20 mL), and then 4-hydroxybutyl acrylate (1.656 g, 10.9 mmol) was added. Into the reaction mixture, triethylamine (1.052 g, 10.4 mmol) was slowly added in an ice bath. The reaction mixture was stirred for 24 hours at room temp. After water (20 mL) was added, the product was extracted 3 times with EA and the combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The drying agent was removed by filtration and the solvent of the filtrate was removed by a rotoevaporator. The

product was rinsed with ethyl ether 5 times with vigorous stirring. Drying in a vacuum oven at room temp gave a yellow viscous oil (3.16 g, 42%). DSC (-80 ~ 60 °C, heating and cooling rate 5 °C/min., N<sub>2</sub>): T<sub>g</sub> = -69 °C, no other transition found. <sup>1</sup>H-NMR (400 MHz, CD<sub>3</sub>CN, 22 °C): δ 0.94 (t, *J*=7, 3H), 1.28 (m, 16H), 1.56 (m, 2H), 1.69 (m, 2H), 1.81 (m, 4H), 2.27 (t, *J*=7, 2H), 4.10-4.16 (m, 8H), 5.84 (dd, *J*=10 (*cis*), *J*=2 (*gem.*), 1H), 6.13 (dd, *J*=17 (*trans*), *J*=10 (*cis*), 1H), 6.34 (dd, *J*=17 (*trans*), *J*=2 (*gem.*), 1H), 7.38 (ss, 2H), 8.43 (s, 1H). <sup>13</sup>C-NMR (100 MHz, CD<sub>3</sub>CN, 22 °C): δ 13.6, 20.0, 25.7, 26.0, 26.1, 26.7, 29.5, 29.7, 29.9, 29.96, 29.98, 30.4, 32.5, 34.8, 50.3, 50.6, 64.4, 64.9, 123.4, 129.5, 131.3, 136.1, 174.4. HRMS (ESI): 435.3246 ([M-Tf<sub>2</sub>N]<sup>+</sup>, cald. 435.3223, error 5.3 ppm).

**1-{ω-[1'-(4''-Acryloyloxy)butoxy]carbonyldecyl}-3-dodecylimidazolium PF<sub>6</sub><sup>-</sup> (2d).** A solution of **1d** (2.94 g, 5.2 mmol) in freshly distilled SOCl<sub>2</sub> (10 mL) was stirred for 24 hours at room temp. under N<sub>2</sub>. After removing the excess SOCl<sub>2</sub> by vacuum, the residue was washed with anhydrous ethyl ether 5 times and dried by an N<sub>2</sub> stream. The residue (acid chloride of **1d**) was dissolved in dry MeCN (10 mL), and 4-hydroxybutyl acrylate (0.823 g, 5.7 mmol) was added. Into the reaction mixture, triethylamine (0.578 g, 5.7 mmol) was slowly added in an ice bath. The reaction mixture was stirred for 24 hours at room temp. After water (20 mL) was added, the product was extracted 3 times with EA and the combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The drying agent was removed by filtration and the solvent was removed by a rotoevaporator. The product was rinsed with ethyl ether 5 times with vigorous stirring. Drying in a vacuum oven at room temperature gave a brown viscous liquid (3.33 g, 84%). DSC (-80 ~ 60 °C, heating and cooling rate 5 °C/min., N<sub>2</sub>): T<sub>m</sub> = -24 °C, no other transition found. <sup>1</sup>H-NMR (400 MHz, CD<sub>3</sub>CN, 22 °C): δ 0.89 (t, *J*=8, 3H), 1.28 (m, 30H), 1.57 (m, 2H), 1.70 (m, 4H), 1.83 (m, 4H), 2.28 (t, *J*=8, 2H), 4.11 (m, 8H), 5.87 (dd, *J*=10 (*cis*), *J*=2 (*gem.*), 1H), 6.15 (dd, *J*=17 (*trans*), *J*=10 (*cis*), 1H), 6.34 (dd, *J*=17 (*trans*), *J*=2 (*gem.*), 1H), 7.39 (s, 2H), 8.44 (s, 1H). <sup>13</sup>C-NMR (100 MHz, CD<sub>3</sub>CN 22 °C): δ 13.7, 20.0, 24.9, 26.0, 26.1, 26.2, 29.5, 29.8, 29.9, 30.01, 30.04, 30.4, 32.5, 34.1, 50.3, 50.4, 64.3, 64.7, 123.4, 129.5, 131.1, 136.6, 173.4. HRMS (ESI): 435.3255 ([M-PF<sub>6</sub>]<sup>+</sup>, cald. 435.3223, error 7.4 ppm).

**1-{ω-[1'-(4'-acryloyloxy)butoxy]carbonyldecyl}-3-dodecylimidazolium Tf<sub>2</sub>N<sup>-</sup> (2e).** A solution of **1e** (5.31 g, 7.5 mmol) in freshly distilled SOCl<sub>2</sub> (12 mL) was stirred for 24 hours at room temp. under N<sub>2</sub> atmosphere. After removing the excess SOCl<sub>2</sub> by vacuum, the residue was washed with anhydrous ethyl ether 5 times and dried by an N<sub>2</sub> stream. The residue (acid chloride of **1e**) was dissolved in dry MeCN (20 mL), and 4-hydroxybutyl acrylate (1.20 g, 8.3



mmol) was added. Into the reaction mixture, triethylamine (0.839 g, 8.3 mmol) was slowly added in an ice bath. The reaction mixture was stirred for 24 hours at room temp. After water (20 mL) was added, the product was extracted 3 times with EA and the combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The drying agent was removed by filtration and the solvent was removed by a rotoevaporator. The product was rinsed with ethyl ether 5 times with vigorous stirring. Drying in a vacuum oven at room temp gave a yellow viscous oil (4.88 g, 79%). DSC (-80 ~ 60 °C, heating and cooling rate 5 °C/min., N<sub>2</sub>): T<sub>g</sub> = -70 °C, no other transition found. <sup>1</sup>H-NMR (400 MHz, CD<sub>3</sub>CN, 22 °C): δ 0.88 (t, *J*=7, 3H), 1.27 (m, 30H), 1.56 (m, 2H), 1.69 (m, 2H), 1.82 (m, 4H), 2.27 (t, *J*=7, 2H), 4.11 (m, 8H), 5.85 (dd, *J*=10 (*cis*), *J*=2 (*gem.*), 1H), 6.13 (dd, *J*=17 (*trans*), *J*=10 (*cis*), 1H), 6.34 (dd, *J*=17 (*trans*), *J*=2 (*gem.*), 1H), 7.38 (ss, 2H), 8.43 (s, 1H). <sup>13</sup>C-NMR (100 MHz, CD<sub>3</sub>CN, 22 °C): δ 13.6, 20.1, 25.7, 26.0, 26.1, 26.7, 29.5, 29.7, 29.9, 29.96, 29.98, 30.4, 32.5, 34.8, 50.3, 50.6, 64.4, 64.9, 123.4, 129.5, 131.3, 136.1, 174.4. HRMS (ESI): 435.3246 ([M-Tf<sub>2</sub>N]<sup>+</sup>, calcd. 435.3223, error 5.3 ppm).

**Radical polymerizations of imidazolium acrylate monomers.** A solution of the imidazolium acrylate monomer and AIBN (2 mol% of the monomer) in degassed MeCN was bubbled with N<sub>2</sub> for 30 min. The solution was stirred for 24 hours at 65 °C. After removing MeCN under vacuum, the residue was stirred with EA. Reprecipitation from acetone into EA was performed 5 times and the precipitated polymer was washed with deionized water twice. Drying in a vacuum oven at 60 °C gave highly viscous materials.

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5. The Beilstein test was done as follows. A copper wire was heated in a burner flame until there was no further coloration of the flame. The wire was allowed to cool slightly, then dipped into the monomer and again heated in the flame. A green flash is indicative of halide ions, whereas pure  $\text{BF}_4^-$  and  $\text{PF}_6^-$  salts give orange or red colors.
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## Chapter 15

### Synthesis and Properties of Imidazolium Polyesters

#### Abstract

New bis( $\omega$ -hydroxyalkyl)imidazolium and 1,2-bis[N-( $\omega$ -hydroxyalkyl)imidazolium]ethane salts were synthesized and characterized; most of the salts are room temperature ionic liquids. These hydroxyl end-functionalized ionic liquids were polymerized with sebacoyl chloride, yielding polyesters containing imidazolium cations embedded in the main-chain. Polyesters with a repeating unit of mono-imidazolium- $C_{10}$ -sebacate- $C_{10}$  with either hexafluorophosphate or bis(trifluoromethanesulfonyl)imide, mono-imidazolium- $C_{10}$ -sebacate- $C_6$ , and 1,2-bis(imidazolium)ethane- $C_{10}$ -sebacate- $C_{10}$  hexafluoro-phosphate are semi-crystalline. The difference between the amorphous and semi-crystalline polyesters was also clearly shown in X-ray scattering results. The other imidazolium polyesters are amorphous. Room temperature ionic conductivities of the mono-imidazolium polyesters ( $4 \times 10^{-6} \sim 3 \times 10^{-5} \text{ S cm}^{-1}$ ) are higher than the corresponding bis-imidazolium polyesters ( $4 \times 10^{-9} \sim 2 \times 10^{-6} \text{ S cm}^{-1}$ ), even though the bis-imidazolium polyesters have higher ion concentrations. Counterions affect ionic conduction significantly; all bis(trifluoromethanesulfonyl)imide polymers had higher ionic conductivities than the hexafluorophosphate analogues. Interestingly, a semi-crystalline hexafluorophosphate polyester, 1,2-bis(imidazolium)ethane- $C_{10}$ -sebacate- $C_{10}$ , displayed almost 400-fold higher ionic conductivity than the 1,2-bis(imidazolium)ethane- $C_6$ -sebacate- $C_6$  analogue, suggesting the incorporation of “ion channels” in the biphasic structure of the former polyester.

## Introduction

The number of papers and patents on ionic liquids (ILs) has exploded in the last two decades,<sup>1</sup> although the first ionic liquid was reported in 1888.<sup>2</sup> The term “ionic liquid” refers to a salt melting below 100 °C; many room temperature ionic liquids (RTILs) with melting points below room temperature have been synthesized. ILs have been widely studied because of their unique characteristics, such as low-volatility, non-flammability, high ionic conductivity, and large electrochemical windows.<sup>3-10</sup> Therefore, the impact of ILs on material sciences has increased to functional integration into electromechanical devices and high-performance membranes.<sup>10, 11</sup>

The introduction of polymerizable units onto ILs and their polymerizations have aimed to achieve enhanced stability, flexibility with durability, and improved control over meso-to nano-structures.<sup>12</sup> Generally two common polymerizable groups has been examined: (meth)acryloyl or vinyl groups. Ohno and his co-workers have investigated both acryloyl and vinyl polymerizable ILs and tried to achieve high ionic conductivity after polymerization.<sup>13-21</sup> The room temperature ionic conductivity of the polymeric materials decreased 20 ~ 100-fold relative to the monomers due to the decreased segmental motion in the polymers.<sup>18</sup> However, no molecular weights were reported for their polymers, because the conventional molecular weight determination methods, such as size exclusion chromatography (SEC), are difficult for ionic polymers, since they aggregate in solution.

Ammonium polyionenes (ionenes), which are polymers containing quaternary nitrogen atoms in the polymer main chain, have been also studied.<sup>22</sup> Ionenes have received increasing attention as candidates for precisely controlling the charge density in polyelectrolytes.<sup>23</sup> Ionenes are unique since the ionic sites are precisely placed along the polymer main chain; monomer design and selection provide control of total ion concentration. However, just a few main-chain imidazolium polyionenes have been reported, compared to pendant imidazolium polymers.<sup>10</sup> Some imidazolium ionenes have been reported by Ohno et al. from hydroboration polymerization of imidazolium dienes with borane compounds (RBH<sub>2</sub>).<sup>24, 25</sup> The polymers from hydroboration have low T<sub>g</sub>s (-60 ~ -45 °C) and good ion conduction (2~4 x 10<sup>-5</sup> S cm<sup>-1</sup>), with however relatively low molecular weights (4 – 9 kDa). The Menshutkin reaction, which involves tertiary diamines and dihalides, was used for imidazolium ionenes from alkylene bis(imidazole)s and terminal diiodoalkanes.<sup>26</sup> The polymers were used in quasi-solid-state solar cell fabrication,

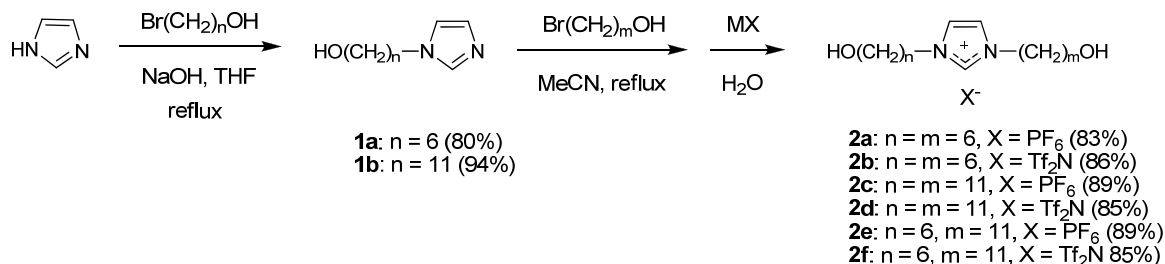
which trapped the molten salt polymer in the electrolyte phase of the cell.

We recently reported preparation of imidazolium-containing  $\alpha,\omega$ -dienes and their polymerization via acyclic diene metathesis (ADMET).<sup>27</sup> This step growth approach yields polymers with regularly spaced imidazolium moieties in the polymer backbones. Our aim was to produce biphasic materials that provided good mechanical integrity combined with ionic conduction for use in actuators and other electroactive devices.

In the present effort new terminal dihydroxy imidazolium ionic liquids were prepared as monomers for main-chain imidazolium ionic polyesters with the same goal in mind. Two kinds of the imidazolium salts were prepared: mono-imidazolium and 1,2-bis(imidazolium)ethane (bis-imidazolium) salts. Most of these dihydroxy imidazolium salts with  $\text{PF}_6^-$  or  $\text{Tf}_2\text{N}^-$  counterions are RTILs. The new hydroxyl terminated ionic liquids were thermally characterized by DSC and TGA. The polyesterifications were performed with the dihydroxy imidazolium salts and sebacoyl chloride. The synthesis and characterization of the dihydroxy imidazolium monomers and the imidazolium polyesters are discussed below.

## Results and Discussion

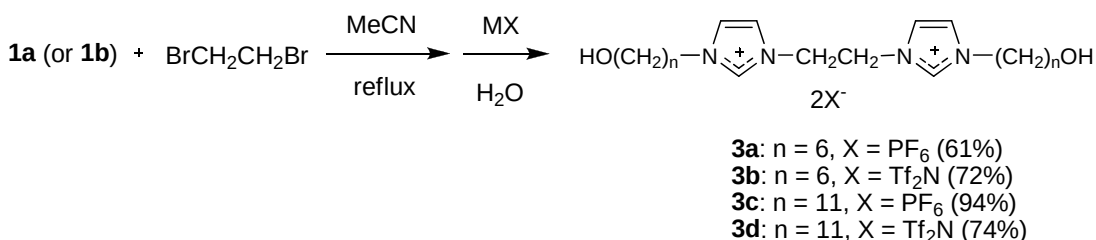
**Dihydroxy Imidazolium Salts.** New dihydroxy imidazolium salts were prepared as difunctional monomers for polyesterification. The imidazolium ionic liquid monomers were generally synthesized in three steps: first substitution, then quaternization and finally metathetic ion exchange (Scheme 15-1).  $\text{C}_6$  and  $\text{C}_{11}$  alkyl spacers were introduced from 6-bromo-1-hexanol and 11-bromo-1-undecanol, respectively. Both bromoalkanols are commercially available, but 6-bromo-1-hexanol was prepared in our lab because it is exorbitantly expensive. Partial bromination of 1,6-hexanediol was done by following a reported procedure.<sup>28</sup> 1-( $\omega$ -Hydroxyalkyl)imidazoles were prepared from imidazole and 6-bromo-1-hexanol or 11-bromo-1-undecanol with NaOH in tetrahydrofuran (THF) under reflux (Scheme 15-1).



**Scheme 15-1.** Synthesis of 1,3-bis( $\omega$ -hydroxyalkyl)imidazolium salts.

The second step for the mono-imidazolium salts, quaternization of 1-substituted imidazoles (**1a** and **1b**) with 6-bromo-1-hexanol and 11-bromo-1-undecanol, gave the imidazolium bromide salts first. Some bromide salts are RTILs, but some are white crystalline solids at room temperature. All bromide salts were purified by washing with THF or ethyl ether to remove starting materials. Anion exchange reactions were performed with a slight excess of  $\text{KPF}_6$  or  $\text{LiTf}_2\text{N}$  in aqueous conditions. The mixtures were warmed to 60 °C, if the bromide salts were not completely soluble in water at room temperature. All water insoluble  $\text{PF}_6^-$  or  $\text{Tf}_2\text{N}^-$  salts were washed with deionized water several times to remove the excess metal salts. Symmetric compounds (**2a-d**) were prepared from the same bromoalkanol, and asymmetric compounds (**2e** and **2f**) were formed from the different bromoalkanols (Scheme 15-1).

Dihydroxy bis-imidazolium salts were prepared as shown in Scheme 15-2. The coupling reactions (quaternization) were performed on the 1-substituted imidazole (**1a** or **1b**) and 1,2-dibromoethane in acetonitrile (MeCN) under reflux. The anion exchange reactions were also done in aqueous conditions and the mixtures were heated if necessary. Only symmetric bis-imidazolium monomers were prepared. The ethylene spacer between the imidazolium units was selected because 1,2-bis(imidazolium)ethane bis(hexafluorophosphate) units showed good stacking in solid-state structures.<sup>29</sup> The imidazolium stacking structure may form ion channels or lead to micro-phase separation when specific conditions are met.



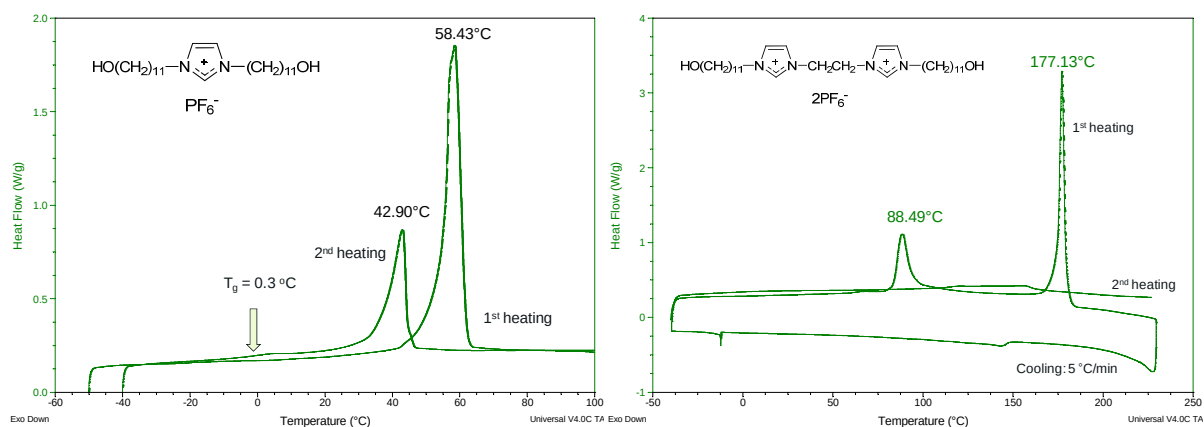
**Scheme 15-2.** Synthesis of 1,2-bis[N-(N'-hydroxylalkylimidazolium)]ethane salts.

The thermal properties of the dihydroxy imidazolium salts are summarized in Table 15-1. **3a** is an interesting material; it has both a glass transition and a melting point and it appears as a solid/liquid mixed phase at room temperature, since the melting point is close to room temperature. Only two dihydroxy imidazolium salts, **2c** and **3c**, are solids at room temperature. The DSC traces of **2c** and **3c** are shown in Figure 15-1. For mono-imidazolium salt **2c**, the first heating exhibits just one endothermic peak ( $T_m = 58\text{ }^{\circ}\text{C}$ ), but the second heating displays a glass transition at  $0.3\text{ }^{\circ}\text{C}$  and an endothermic peak ( $T_m = 43\text{ }^{\circ}\text{C}$ ). After heating above  $T_m$ , the amorphous portion was created from the long side chains, and it remained even after the most part of the material was crystallized. This created amorphous region shows a glass transition at  $0.3\text{ }^{\circ}\text{C}$ , and  $T_m$  is lower than the first heating scan due to the amorphous phase. The amorphous-crystalline phase separation of **2c** occurred from the first heating scan, as annealing gives clear phase separations of block-copolymers. The DSC trace of bis-imidazolium salt **3c** is more interesting; the first heating reveals two endothermic peaks ( $T_m = 88, 177\text{ }^{\circ}\text{C}$ ), but no significant transition during the second heating scan after a cooling from  $225\text{ }^{\circ}\text{C}$  (cooling rate =  $5\text{ K/min}$ ). This result is not from the decomposition, because no weight loss was found up to  $240\text{ }^{\circ}\text{C}$  on TGA. TGA 5% weight loss of **3c** is  $277\text{ }^{\circ}\text{C}$ . No transition in the second heating may be due to the highly viscous liquid **3c** above its melting point ( $177\text{ }^{\circ}\text{C}$ ), and the viscous material might not have a chance to be crystallized. Except for the three salts mentioned above, the other imidazolium salts are RTILs that exhibit low  $T_g$ s.

The thermal stability of the dihydroxy imidazolium salts was investigated as 5% weight loss by TGA. As is usual for ionic liquids, the  $\text{Tf}_2\text{N}^-$  salts possess better thermal stabilities than the  $\text{PF}_6^-$  salts, because  $\text{PF}_6^-$  is thought to be more nucleophilic than  $\text{Tf}_2\text{N}^-$ . For the imidazolium salts with the same anion, the mono-imidazolium salts are more stable than the bisimidazolium salts, due to the weaker structure of the 1,2-bis(imidazolium)ethane.

**Table 15-1.** Properties of Dihydroxy Imidazolium Salts.

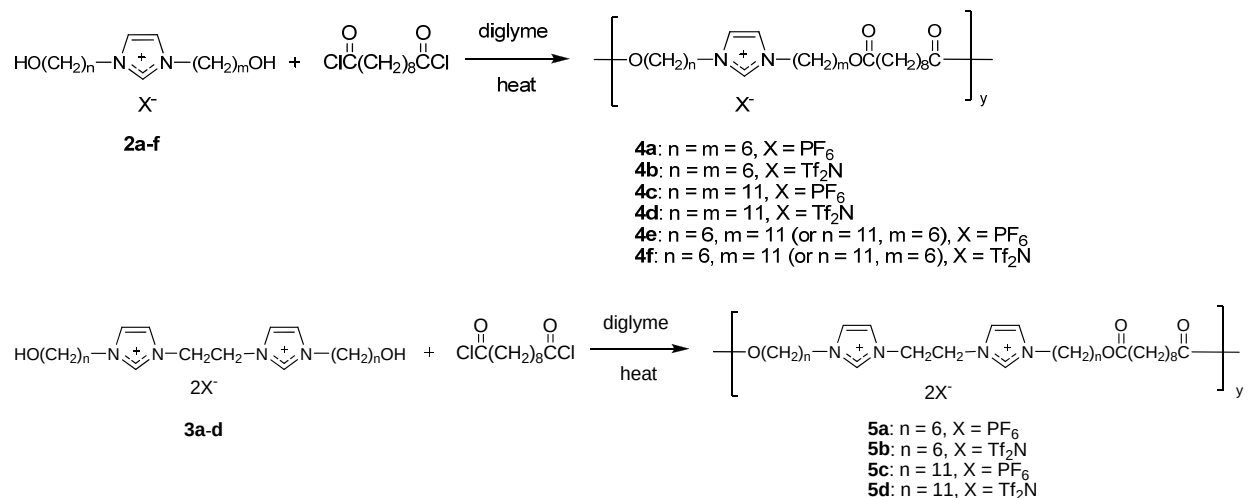
|           | Appearance   | DSC Transitions<br>(°C)       | TGA (°C)<br>5% weight loss |
|-----------|--------------|-------------------------------|----------------------------|
| <b>2a</b> | RTIL         | $T_g = -48.8$                 | 236                        |
| <b>2b</b> | RTIL         | $T_g = -61.9$                 | 321                        |
| <b>2c</b> | Cr. Solid    | $T_g = 0.3$<br>$T_m = 42.9$   | 281                        |
| <b>2d</b> | RTIL         | $T_g = -59.7$                 | 382                        |
| <b>2e</b> | RTIL         | $T_g = -48.8$                 | 291                        |
| <b>2f</b> | RTIL         | $T_g = -52.5$                 | 365                        |
| <b>3a</b> | Solid/Liquid | $T_g = -56.7$<br>$T_m = 33.7$ | 250                        |
| <b>3b</b> | RTIL         | $T_g = -46.1$                 | 366                        |
| <b>3c</b> | Cr. Solid    | $T_m = 177.1$                 | 277                        |
| <b>3d</b> | RTIL         | $T_g = -43.5$                 | 372                        |

**Figure 15-1.** DSC diagrams of diols **2c** (left) and **3c** (right) ( $N_2$  atmosphere, heating and cooling rate 5 K/min).

**Polyesterification and Thermal Properties.** Polyesterification reactions of the dihydroxy imidazolium salts and sebacoyl chloride were performed in diglyme at 150 °C under inert gas atmosphere ( $N_2$  or argon). Diglyme was chosen as a polymerization solvent because it dissolves both monomers and polymers at high temperature. During the polymerizations, by-product HCl



gas evolved due to the high temperature. HCl gas evolution was confirmed by pH paper placed at the end of the gas vent. After the polymerizations were completed, the products were purified by acetone/THF precipitation at least 3 times. The residual monomer and the reaction solvent were removed during these precipitations. A small amount of deionized water was added to hydrolyze any acid chloride moieties during the precipitations and the precipitated polymers were washed with deionized water again before vacuum drying.



**Scheme 15-3.** Polyesterifications of dihydroxy imidazolium salts and sebacoyl chloride. The two imidazolium units are regularly placed in **4a-d** and **5a-d**; in other words, the distances between imidazolium units are fixed. However, the imidazolium cationic units are randomly distributed in polymers **4e** and **4f**.

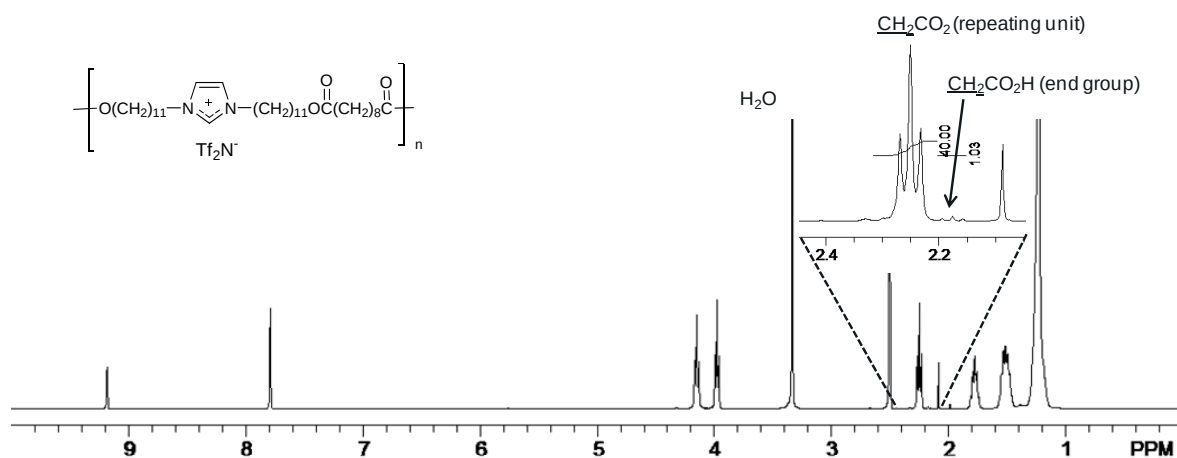


**Figure 15-2.**  $^1\text{H}$  NMR spectrum of **4d** (400 MHz,  $\text{DMSO-}d_6$ , 23 °C). The big triplet ( $\delta$  2.25) is from methylene protons next to the carbonyl moiety ( $\text{CH}_2\text{C=O}$ ) of the sebacate moiety in the repeating unit. The small triplet ( $\delta$  2.18) is from the methylene protons next to the  $\text{CO}_2\text{H}$  end group. No signal for the  $\text{CH}_2\text{OH}$  end group is observed in this polyester.

The imidazolium polyesters are mostly IL-like materials, although they are highly viscous at room temperature. Interestingly, the  $\text{PF}_6^-$  polyesters are opaque whether they are liquids or tough resins. However, all  $\text{Tf}_2\text{N}^-$  polyesters are transparent and clear. The crystallinity of the polymers can affect opaqueness; however, some opaque  $\text{PF}_6^-$  polymers (**4a** and **5a**) show no melting or crystallization on DSC. Most of the imidazolium polyesters are soluble in polar aprotic solvents, such as acetone, MeCN, DMF and DMSO, except for tough resin **5c**. The solubility of **5c** was really not good in most organic solvents-only slightly soluble in DMSO. Dimethylacetamide (DMAC) and N-methylpyrrolidinone (NMP) did not dissolve **5c**, but gave a swollen resin.

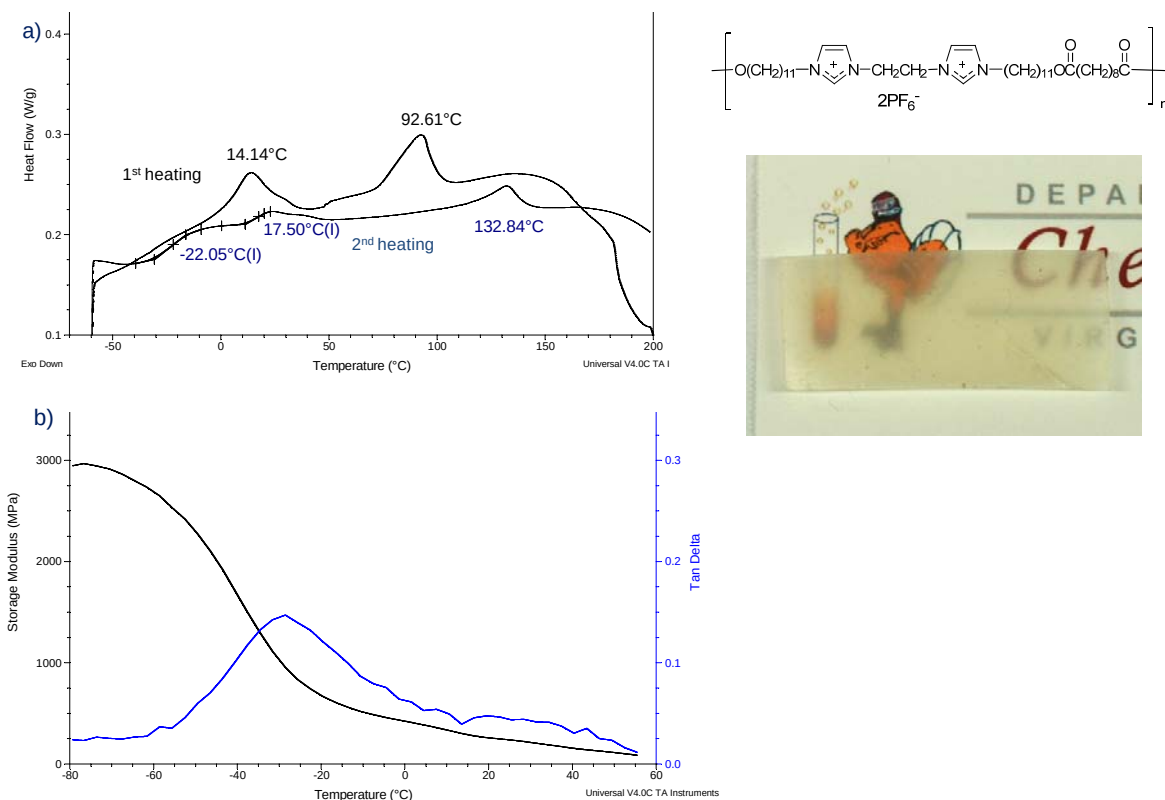


**Figure 15-3.** a) DSC diagrams of polyester **5c** ( $\text{N}_2$  atmosphere, heating and cooling rate  $5^\circ\text{C}/\text{min}$ ). The first heating scan shows two  $T_m$ , but the second heating scan after cooling from  $200^\circ\text{C}$  shows just one  $T_m$  and two  $T_g$ s. b) Dynamic mechanical analysis of melt-pressed films of **5c** ( $\text{N}_2$  atmosphere,  $-80 \sim 60^\circ\text{C}$  with a heating rate of  $3^\circ\text{C}/\text{min}$ , cantilever clip).

The imidazolium polyesters were characterized by  $^1\text{H}$  NMR spectroscopy. A triplet at  $\delta$  2.25 is from the methylene protons next to carbonyl moieties as shown in Figure 15-2. Number average molecular weights ( $M_n$ ) of the polymers were calculated by end-group analysis. Since two kinds of end groups were possible; the average degree of polymerization ( $\overline{DP}$ ) was calculated from the integration number of methylene protons next to carbonyl groups ( $\delta$  2.25)

and the summation of integration numbers of methylene protons next to carboxylic acid ( $\delta$  2.18) and hydroxyl groups ( $\sim \delta$  3.5).

Due to their low melting points and low  $T_g$ s, films were not easily formed from the imidazolium polyesters. A film was made from **5c** by melt-pressing at 150 °C. The film was opaque and sticky under heat. Semi-crystalline **5c** has two  $T_m$ s (14 and 93 °C) during the first heating scan in DSC. However, the second heating scan after cooling from 200 °C contains two  $T_g$ s (-22 and -17 °C) and one  $T_m$  (133 °C) (Figure 15-2a). This is due to the different morphologies before and after annealing the polymer. Heating above its melting point provided micro-phase separation of crystalline and amorphous phase to show  $T_g$ s and  $T_m$ . The film from the melt-pressing shows same DSC trace as the second heating scan. Thermomechanical behavior was probed using dynamic mechanical analysis (DMA) with the melt-pressed film of **5c**. The DMA trace of **5c**, however, did not show a sharp transition around the  $T_m$  or  $T_g$  detected by DSC, but rather a gradual transition with no clear onset. The film of **5c** actually elongated significantly during the run, making it hard to draw conclusions about the crystallinity or ionic aggregate breakup. The storage modulus was low (<500 MPa) even at -20 °C. After heating to 60 °C, the film was very sticky and was torn very easily with a small force. The low storage modulus probably results from the low molecular weight of the polymer, which in turn is a consequence of its low solubility.

Of the  $Tf_2N^-$  polymers, only mono-imidazolium polymer **4d**, which has the longest spacer ( $C_{11}$ -sebacate- $C_{11}$ ), is crystalline,  $T_m = -21$  °C. All the other  $Tf_2N^-$  polyesters display only  $T_g$ s at low temperature. They are also highly viscous materials and transparent at room temperature. Three  $PF_6^-$  polymers were crystalline as demonstrated by DSC. Mono-imidazolium polyester **4c** containing the  $C_{11}$ -sebacate- $C_{11}$  spacer exhibits  $T_m = 26$  °C and no  $T_g$ , while **4e** containing the random  $C_6$ -sebacate- $C_{11}$  spacer exhibits  $T_m = 14$  °C and no  $T_g$ . Both polymers are adhesive-like, highly sticky materials and opaque at room temperature.

The repeating-unit structural effects can be also considered for the thermal properties. First of all, the nature of anions affects the  $T_g$  (or  $T_m$ ) of the imidazolium polyesters. For the same polymer backbone structure (in both mono- and bis-imidazolium polyesters),  $Tf_2N^-$  polymers have lower  $T_g$  and  $T_m$  than  $PF_6^-$  analogs. The difference in glass transitions is more significant for the bis-imidazolium polymers. The spacer length between two imidazolium (either mono- or bis-) units is also important; all polyesters with a short spacer ( $C_6$ -sebacate- $C_6$ ) are amorphous with

either  $\text{PF}_6^-$  or  $\text{Tf}_2\text{N}^-$  counterion. The  $\text{C}_6$ -sebacate- $\text{C}_6$  chains do not seem to be long enough to allow good packing for crystallinity. **4f** (mono-imidazolium, randomly distributed  $\text{C}_{11}$ -sebacate- $\text{C}_6$ ) as expected is amorphous. **5d** (bis-imidazolium,  $\text{C}_{11}$ -sebacate- $\text{C}_{11}$ ) in spite of the long spacers is amorphous, perhaps due to the big and asymmetric  $\text{Tf}_2\text{N}^-$  anions. Only mono-imidazolium **4d** ( $\text{C}_{11}$ -sebacate- $\text{C}_{11}$ ) shows crystallinity among the  $\text{Tf}_2\text{N}^-$  polymers as described previously. The lack of crystallinity of bis-imidazolium analog **5d** may be due to the higher anion concentration in the neat state compared to **4d** (mono-imidazolium); it may hinder the crystallization of the linear aliphatic chains.

Thermal stabilities of the polymers were compared by thermal gravimetric analysis (TGA). All  $\text{Tf}_2\text{N}^-$  polymers show better thermal stabilities than  $\text{PF}_6^-$  analogs. TGA 5% weight loss values of **4d** and **4f** are over 400 °C. The better thermal stabilities of  $\text{Tf}_2\text{N}^-$  polymers result from the lower basicity of  $\text{Tf}_2\text{N}^-$  than  $\text{PF}_6^-$ . Interestingly, mono-imidazolium polyesters have better thermal stabilities than the bis-imidazolium polymers (**4a/5a**, **4b/5b** and **4d/5d**). This may be due to higher anion (possible nucleophile) concentrations of the bis-imidazolium polymers and/or weaker nature of N,N'-imidazolium-ethylene-imidazolium structure against the nucleophiles at high temperature.

**Ionic conductivity.** Ionic conductivities of the imidazolium polyesters were measured by dielectric resonance spectroscopy. The liquid-like samples were placed between two electrodes with silica spacers which control the sample thickness. The ionic conductivities of  $\text{Tf}_2\text{N}^-$  polymers are around 10 to 500-fold higher than  $\text{PF}_6^-$  analogs at room temperature, while at 100 °C the conductivities of are higher by 5 ~ 50 times.

For the  $\text{Tf}_2\text{N}^-$  polymers, the ionic conductivities are affected by the monomer structure, but are not dependent on the molecular weight up to 33 kDa. The mono-imidazolium  $\text{Tf}_2\text{N}^-$  polymers are almost the same in ionic conductivity, but their molecular weights are different: **4b** (11 kDa), **4d** (33 kDa), and **4e** (26 kDa). The bis-imidazolium  $\text{Tf}_2\text{N}^-$  polymers (**5b** and **5d**) have lower ionic conductivities than mono-imidazolium analogs, even though they have almost double the number of anions at the same weight. We hypothesize that the bis(imidazolium)ethane cationic structure binds anions more tightly and forms stronger ionic aggregates in the polymers. Only one crystalline  $\text{Tf}_2\text{N}^-$  polymer (**4d**) shows a critical change in conductivity at its  $T_m$  (cyan tilted triangle in Figure 15-3) and this behavior is due to the dramatic increase in ionic mobility above the melting point.

**Table 15-2.** Thermal Properties and Ionic Conductivities of Imidazolium Polyesters

| Polymer   | Appearance             | T <sub>g</sub> (°C)                                     | TGA (°C)<br>5% weight loss | M <sub>n</sub> (NMR)*<br>(kDa) | Room<br>Temperature<br>$\sigma$ (S cm <sup>-1</sup> ) |
|-----------|------------------------|---------------------------------------------------------|----------------------------|--------------------------------|-------------------------------------------------------|
| <b>4a</b> | Opaque<br>Viscous Oil  | -45                                                     | 303                        | 6                              | 2.0 x 10 <sup>-6</sup>                                |
| <b>4b</b> | Clear<br>Viscous Oil   | -50                                                     | 381                        | 11                             | 3.1 x 10 <sup>-5</sup>                                |
| <b>4c</b> | Opaque<br>Tough Gum    | T <sub>m</sub> = 26                                     | 290                        | 44                             | 3.1 x 10 <sup>-7</sup>                                |
| <b>4d</b> | Clear<br>Viscous Oil   | T <sub>g</sub> = -45.5<br>T <sub>m</sub> = -21.2        | 411                        | 33                             | 2.4 x 10 <sup>-5</sup>                                |
| <b>4e</b> | Opaque<br>Gum          | T <sub>m</sub> = 14                                     | 323                        | 13                             | 1.1 x 10 <sup>-6</sup>                                |
| <b>4f</b> | Clear<br>Viscous Oil   | -63                                                     | 407                        | 26                             | 3.2 x 10 <sup>-5</sup>                                |
| <b>5a</b> | Opaque<br>Highly Visc. | -2                                                      | 276                        | 7                              | 4.3 x 10 <sup>-9</sup>                                |
| <b>5b</b> | Clear<br>Viscous Oil   | -37                                                     | 367                        | 21                             | 7.8 x 10 <sup>-6</sup>                                |
| <b>5c</b> | Opaque<br>Tough Resin  | T <sub>g</sub> = -20.1, -17.5<br>T <sub>m</sub> = 132.8 | 290                        | -                              | 1.6 x 10 <sup>-6</sup>                                |
| <b>5d</b> | Clear<br>Viscous Oil   | -36                                                     | 305                        | 33                             | 3.5 x 10 <sup>-6</sup>                                |

\* Number average molecular weights were calculated by the end-group analysis from proton NMR spectra of imidazolium polymers.

The ionic conductivities of the PF<sub>6</sub><sup>-</sup> polymers are more complicated. Among the mono-imidazolium polymers (**4a**, **4c**, and **4e**), an amorphous one (**4a**) shows the highest conductivity and a crystalline polymer (**4c**) has the lowest conductivity at room temperature. This result is common; usually amorphous polymers possess higher ion mobilities. The conductivity plots of **4c** and **4e** change from linear to curved above their melting points. The amorphous bis-imidazolium polymer **5a** shows the lowest conductivity of all imidazolium polyesters both at room temperature and above. The low conductivity of **5a** may be due to its relatively higher T<sub>g</sub> (-2 °C). Surprisingly, the semi-crystalline film of **5c** shows exceptionally higher conductivity than **5a**, almost 400 times at room temperature. Even though it needs more investigation to explain the higher conductivity of **5c** compared to **5a**, the 1,2-bis(imidazolium)ethane unit may form a

well stacked micro-structure to enhance the ionic conductivity by forming ion channels. Thermal properties, molecular weight and room temperature ionic conductivities of all polymers are summarized in Table 15-2.

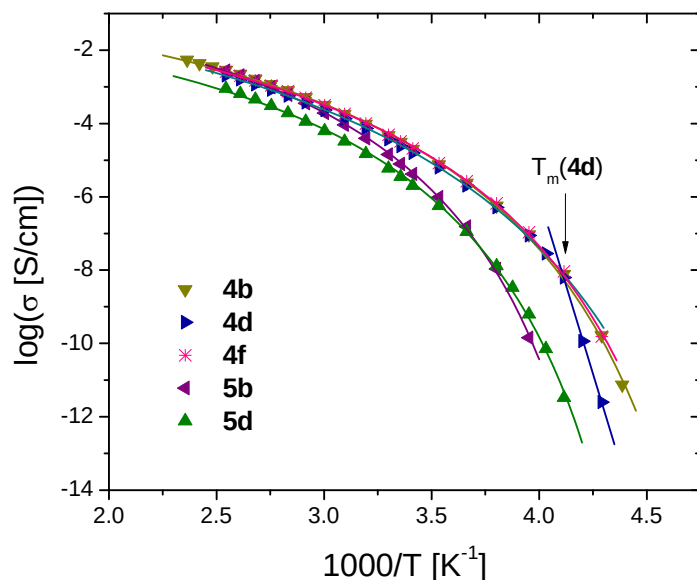


**Figure 15-4.** Ionic conductivity plots of  $\text{Tf}_2\text{N}^-$  polyesters. Only polymer **4d** is crystalline and its conductivity shows significant change near  $T_g$  ( $-45^\circ\text{C}$  or  $1000/T = 4.38$ ).

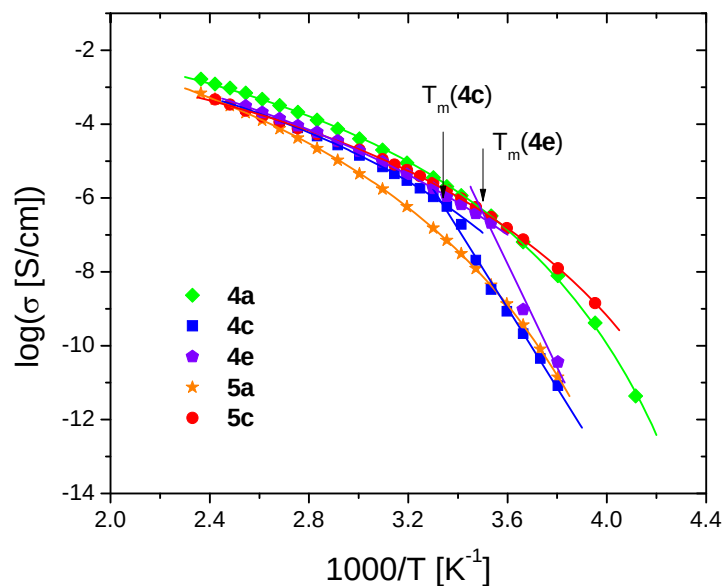


**Figure 15-5.** Ionic conductivity plots of  $\text{PF}_6^-$  polyesters. Crystalline polymers **4c** and **4e** show significant change in their conductivities near  $T_m$  ( $26$  and  $14^\circ\text{C}$ ;  $1000/T = 3.34$  and  $3.48$ , respectively). Note, however, that semi-crystalline bis-imidazolium polyester **5c** shows significantly higher conductivity than amorphous bis-imidazolium polyester **5a**.

**X-Ray scattering study.** Figure 15-6 shows the X-ray scattering profile for two kinds of the mono-imidazolium polyesters, presented as a function of alkyl spacer chain length and counterion. The X-ray scattering profiles for the mono-imidazolium  $\text{PF}_6^-$  polyesters show that **4a** is amorphous (only 3 peaks) while **4c** and **4e** are semi-crystalline (multiple peaks) at room temperature. As the alkyl chain length for the two terminal groups increases, the material changes from amorphous to crystalline at room temperature. These results are exactly consistent with the previously discussed DSC results.

The X-ray scattering profiles for the  $\text{Tf}_2\text{N}^-$  polyesters show that all the mono-imidazolium  $\text{Tf}_2\text{N}^-$  polyesters are in the amorphous state near room temperature. The scattering profile reveals three distinct scattering peaks at  $q \sim 14.1, 8.13$  and  $3.0 \text{ nm}^{-1}$ . The peaks of amorphous  $\text{PF}_6^-$  polyester **4a** are also same. The most striking result is that the crest for the scattering peak at  $q \sim 3.0 \text{ nm}^{-1}$  increases as the alkyl chain length of the two terminal groups increases. The former suggest an increase in order as the alkyl chain increases. The structure and size of the counterion  $\text{Tf}_2\text{N}^-$  is preventing crystallization.

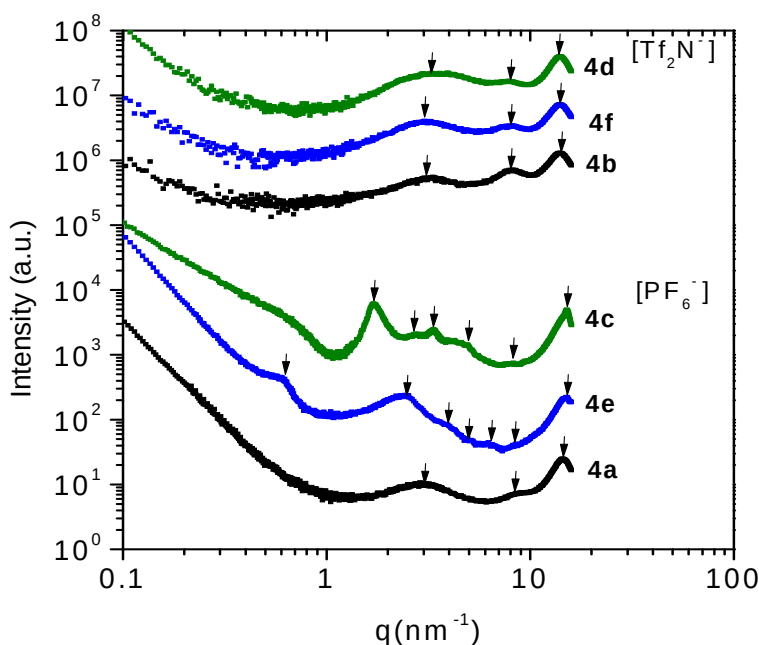


**Figure 15-6.** X-ray scattering profiles of the mono-imidazolium polyesters.

The X-ray scattering profiles of the bis-imidazolium polyesters reveal the same patterns as

the mono-imidazolium polyesters as shown in Figure 15-7. The semi-crystalline **5a** displays multiple peaks in the profile; however, three distinct scattering peaks appear at  $q \sim 14.1$ ,  $8.13$  and  $3.0 \text{ nm}^{-1}$  for the amorphous **5b** and **5d**. Also the intensity of the peak at  $q \sim 3.0 \text{ nm}^{-1}$  increases as the alkyl spacer is lengthened. The  $q$  values of the peaks of the amorphous polyesters are almost the same regardless of whether they are mono- or bis-imidazolium and counter ion type. In addition, the semi-crystalline hexafluorophosphate polyester, 1,2-bis(imidazolium)ethane- $\text{C}_{11}$ -sebacate- $\text{C}_{11}$  (**5c**), displayed anisotropic X-ray scattering pattern upon heating to  $105^\circ\text{C}$  different from that of the 1,2-bis(imidazolium)ethane- $\text{C}_6$ -sebacate- $\text{C}_6$  (**5a**) analogue, suggesting the specific morphologies of the former polyester in the biphasic structures of the former polyester. Figure 15-8 shows the 2D X-ray scattering pattern as a function of temperature for polyester **5c**. The imidazolium stacking structure may lead to a micro-phase separation alignment when specific conditions are met.

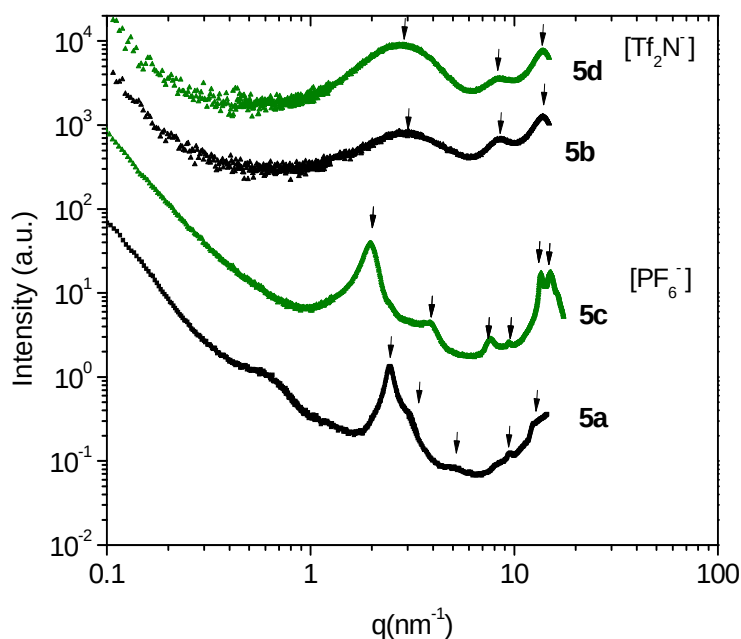


**Figure 15-7.** X-ray scattering profiles of the bis-imidazolium polyesters.



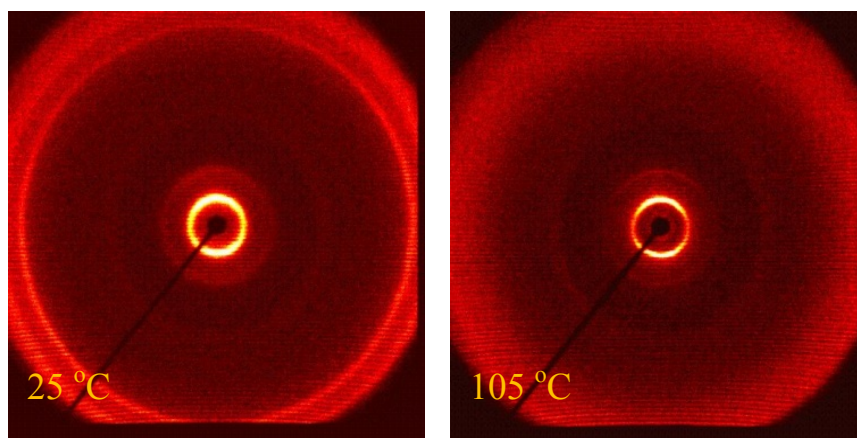


**Figure 15-8.** 2D X-ray scattering pattern as a function of temperature for polyester **5c** at 25 °C and at 105 °C.

## Conclusions

A series of dihydroxy mono- and bis-imidazolium ionic liquid monomers was prepared and characterized. The polyesterifications of the dihydroxy monomers and sebacoyl chloride were performed at high temperature and the polymers were characterized by NMR, DSC and TGA. **5c** formed a film by melt-pressing and the film was characterized by DMA. Generally the polyesters with short spacers are amorphous with both  $\text{PF}_6^-$  and  $\text{Tf}_2\text{N}^-$  counterions. The polyesters with  $\text{C}_{11}$ -sebacate- $\text{C}_{11}$  spacers between two imidazolium units are semi-crystalline, except **5d** with a higher concentration of asymmetric  $\text{Tf}_2\text{N}^-$  ions. The bis(imidazolium) polyesters have higher  $T_g$  and/or  $T_m$  than their mono-imidazolium analogues. The thermal stabilities of mono-imidazolium polymers are better than the bis-imidazolium analogs, and  $\text{Tf}_2\text{N}^-$  polymers are better than  $\text{PF}_6^-$  analogs. The ionic conductivity of  $\text{Tf}_2\text{N}^-$  polymers is higher than the  $\text{PF}_6^-$  salts. For the  $\text{Tf}_2\text{N}^-$  polymers, mono-imidazolium polyesters have higher ionic conductivities than bis-imidazolium analogs. The semi-crystalline bis-imidazolium polyester **5c** shows significantly higher conductivity than **5a**, even though it has high  $T_m$ , indicating a phase separated morphology. The semi-crystalline and amorphous natures of the imidazolium polyesters were also confirmed by X-ray scattering analysis. Multiple peaks are observed in the plots of intensity vs.  $q$  ( $\text{nm}^{-1}$ ) for the semi-crystalline polymers, while the same peak positions appear for the amorphous polyesters regardless of their structures. The peak intensity increase of the crystalline polyesters may reveal

micro-phase separation even though a full assignment of the X-ray scattering peaks would be necessary in the future to confirm this hypothesis.

## Experimental

**Spectroscopic and thermal characterizations.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained on Varian Inova 400 MHz and Unity 400 MHz spectrometers. High resolution electrospray ionization time-of-flight mass spectrometry (HR ESI TOF MS) was carried out on an Agilent 6220 Accurate Mass TOF LC/MS Spectrometer in positive mode. High resolution fast-atom-bombardment mass spectrometry (HR FAB MS) was carried out on a JEOL Model HX 110. DSC results were obtained on a TA Instrument Q2000 differential scanning calorimeter at a scan rate of 5 or 10 K/min heating and cooling under  $\text{N}_2$  atmosphere. TGA results were obtained on a TA Instrument Q500 Thermogravimetric Analyzer at a heating rate of 10 K/min under a  $\text{N}_2$  stream.

**Ionic conductivity measurements.** Ionic conductivity was measured on a Novocontrol GmbH Concept 40 broadband dielectric spectrometer. Samples for dielectric relaxation spectroscopic measurements were placed on a brass electrode and dried in a vacuum oven at 60 °C for 24 h, after which a second brass electrode was placed on top of the sample. Silica spacers were used to control the sample thickness at 50  $\mu\text{m}$ . Frequency sweeps were performed isothermally from 10 MHz to 0.01 Hz over a range of temperature. In order to minimize the amount of water in the samples and to avoid a change in water content during the experiment, the samples were initially held at 120 °C for 1 h, and the measurements were performed during subsequent cooling under a flow of dry  $\text{N}_2$ .

**X-Ray scattering.** X-ray scattering was performed with the multi-angle X-ray scattering system (MAXS) at the University of Pennsylvania. The MAXS system generates Cu K X-ray from a Nonius FR 591 rotating-anode operated at 40 kKV and 85 mA. The bright, highly collimated beam was obtained via Osmic Max-Flux optics and pinhole collimation in an integral vacuum system. The scattering data were collected using a Brukers Hi Star two-dimensional detector with a sample to detector distance of 11, 54, and 150 cm. Rubbery homopolymer samples were inserted into 1 mm glass capillaries with the exception the semi-crystalline hexafluorophosphate polyester, 1,2-bis(imidazolium)ethane- $\text{C}_{11}$ -sebacate- $\text{C}_{11}$  (**5c**) which was tested as a film. Patterns were collected for 30 min at a sample to detector distance of 11 cm, 45 minutes at 54 cm and 60 minutes at 150 cm. Using Datasqueeze software, the 2-D scattering patterns were

azimuthally integrated to yield intensity versus scattering angle, intensity corrected for primary beam intensity, and background scattering was subtracted but not corrected for sample density. The intensity reported is not the absolute intensity and, thus, is thus reported in arbitrary units (a.u.). Scattering profiles were also collected for the polyester 1,2-bis(imidazolium)ethane-C11-sebacate-C11 at different temperatures using a Linkham HFS91 temperature controller which controls temperature to better than 0.1 °C. Temperature samples were heated at 10 °C/min and isothermally held for 10 min before collecting data for 30 min.

**Materials.** Acetonitrile (MeCN) as a reaction solvent was distilled over calcium hydride. Diglyme for polyesterifications was pre-dried over NaOH pellets and then distilled over calcium hydride. Sebacoyl chloride was vacuum distilled and stored in a calcium chloride desiccator. All other chemicals and solvents were used as received.

**1-(6'-Hydroxyhexyl)imidazole (1a).** To a solution of imidazole (6.81 g, 100 mmol) in NaOH solution (50%, 9.00 g, 110 mmol), 6-bromo-1-hexanol (20.58 g, 110 mmol) and THF (150 mL) were added. The mixture was refluxed for 3 days. After the mixture had cooled, THF was removed by a rotoevaporator. The residue was extracted with dichloromethane/water 3 times. The combined organic layer was washed with water and dried over Na<sub>2</sub>SO<sub>4</sub>. The drying agent was filtered and the filtrate was concentrated. Column chromatography through a short silica-gel column with ethyl ether and ethyl acetate gave a clear yellow oil (13.40 g, 80%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, 22 °C):  $\delta$  1.27-1.43 (m, 4H), 1.56 (m, 2H), 1.79 (m, 4H), 3.62 (t, *J*=7, 2H), 3.93 (t, *J*=7, 2H), 6.90 (s, 1H), 7.04 (s, 1H), 7.45 (s, 1H). The <sup>1</sup>H-NMR spectrum was identical to the literature result.<sup>30</sup>

**1-(11'-Hydroxyundecyl)imidazole (1b).** To a solution of imidazole (3.40 g, 50 mmol) in NaOH solution (50%, 4.50 g, 55 mmol), 11-bromo-1-undecanol (12.56 g, 50 mmol) and THF (40 mL) were added. The mixture was refluxed for 3 days. After the mixture had cooled, THF was removed by a rotoevaporator. The residue was extracted with dichloromethane/water 3 times. The combined organic layer was washed with water and dried over Na<sub>2</sub>SO<sub>4</sub>. The drying agent was filtered and the filtrate was concentrated. Column chromatography through a short silica-gel column with ethyl ether and THF gave a colorless solid (11.22 g, 94%), mp 54.5 – 55.8 °C (no literature value). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, 22 °C):  $\delta$  1.28 (m, 12H), 1.56 (m, 2H), 1.77 (m, 4H), 3.64 (t, *J*=7, 2H), 3.92 (t, *J*=7, 2H), 6.90 (s, 1H), 7.05 (s, 1H), 7.46 (s, 1H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, 22 °C):  $\delta$  25.7, 26.4, 28.9, 29.3, 29.4, 29.5, 31.0, 32.8, 47.0, 62.8, 118.8, 129.3,

137.0. The  $^1\text{H}$ -NMR spectra were identical to the literature result.<sup>31</sup>

**1,3-Bis(6'-hydroxy-1'-hexyl)imidazolium hexafluorophosphate (2a).** A solution of **1a** (6.73 g, 40 mmol) and 6-bromo-1-hexanol (7.60 g, 42 mmol) in dry MeCN (25 mL) was refluxed for 3 days. After the reaction, the MeCN was removed by a rotoevaporator. The residual bromide salt was washed with THF 5 times and then dried in a vacuum oven. The bromide salt (3.50 g, 10 mmol) was dissolved in water (50 mL) and  $\text{KPF}_6$  (2.8 g, 15 mmol) was added to the solution with vigorous stirring. After decanting off the upper aqueous layer, the residual viscous liquid was washed with deionized water 5 times. Drying in a vacuum oven gave a pale-yellow viscous liquid (3.43g, 83%). DSC:  $T_g = -48.8\text{ }^\circ\text{C}$ , no  $T_m$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ ,  $22\text{ }^\circ\text{C}$ ):  $\delta$  1.35 (m, 8H), 1.47 (m, 4H), 1.84 (m, 4H), 3.35 (m, 2H), 3.47 (t,  $J=6$ , 4H), 4.11 (t,  $J=7$ , 4H), 7.37 (s, 2H), 8.43 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{CN}$ ,  $22\text{ }^\circ\text{C}$ ):  $\delta$  25.2, 25.6, 30.0, 32.5, 50.0, 61.7, 121.9, 134.9. HRMS (ESI):  $m/z$  269.2244 ( $[\text{M-PF}_6]^+$ , calcd. for  $\text{C}_{15}\text{H}_{29}\text{N}_2\text{O}_2$  269.2229, error 5.7 ppm).

**1,3-Bis(6'-hydroxy-1'-hexyl)imidazolium bis(trifluoromethanesulfonyl)imide (2b).** From the previous experiment, the bromide salt (3.50 g, 10 mmol) was dissolved in water (50 mL) and  $\text{LiTf}_2\text{N}$  (4.3 g, 15 mmol) was added with vigorous stirring. After decanting off the upper aqueous layer, the residual viscous liquid was washed with deionized water 5 times. Drying in a vacuum oven gave a yellow viscous liquid (4.72g, 86%). DSC:  $T_g = -61.9\text{ }^\circ\text{C}$ , no  $T_m$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ ,  $22\text{ }^\circ\text{C}$ ):  $\delta$  1.33 (m, 8H), 1.47 (m, 4H), 1.84 (m, 4H), 3.35 (m, 1H (theor. 2H)), 3.47 (t,  $J=6$ , 4H), 4.11 (t,  $J=7$ , 4H), 7.38 (s, 2H), 8.44 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{CN}$ ,  $22\text{ }^\circ\text{C}$ ):  $\delta$  25.2, 25.8, 29.8, 32.4, 50.1, 62.0, 122.7, 135.4. HRMS (ESI):  $m/z$  269.2241 ( $[\text{M-Tf}_2\text{N}]^+$ , calcd. for  $\text{C}_{15}\text{H}_{29}\text{N}_2\text{O}_2$  269.2229, error 4.3 ppm).

**1,3-Bis(11'-hydroxy-1'-undecyl)imidazolium hexafluorophosphate (2c).** A solution of **1b** (1.03 g, 4.3 mmol) and 11-bromo-1-undecanol (1.10 g, 4.4 mmol) in dry MeCN (15 mL) was refluxed for 3 days. After the reaction, the MeCN was removed by a rotoevaporator. The residual bromide salt was dispersed in THF (25 mL) and stirred for 10 min. The bromide salt was filtered and washed with THF 3 times. The filter cake was dispersed in water (80 mL).  $\text{KPF}_6$  (1.5 g, 8 mmol) was added and the mixture was stirred for 24 h at  $50\text{ }^\circ\text{C}$ . After cooling to room temperature, the precipitated solid was filtered and washed with deionized water 3 times. Drying in a vacuum oven gave a white crystalline solid (2.13g, 89%). DSC:  $T_m = 62.4\text{ }^\circ\text{C}$  (first heating),

no  $T_g$ .  $^1\text{H}$  NMR (400 MHz, acetone- $d_6$ , 22 °C):  $\delta$  1.29-1.36 (m, 28H), 1.49 (m, 4H), 1.97 (m, 4H), 3.44 (s (br), 2H), 3.52 (t,  $J=6$ , 4H), 4.37 (t,  $J=7$ , 4H), 7.79 (s, 2H), 9.07 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz, acetone- $d_6$ , 22 °C):  $\delta$  26.6, 26.8, 29.6, 30.1, 30.16, 30.21, 30.7, 33.7, 50.5, 62.4, 123.6, 136.7. HRMS (ESI):  $m/z$  409.3814 ( $[\text{M-PF}_6]^+$ , calcd. for  $\text{C}_{25}\text{H}_{49}\text{N}_2\text{O}_2$  409.3794, error 4.8 ppm).

**1,3-Bis(11'-hydroxy-1'-undecyl)imidazolium bis(trifluoromethanesulfonyl)imide (2d).** A solution of **1b** (0.905 g, 3.8 mmol) and 11-bromo-1-undecanol (0.950 g, 3.8 mmol) in dry MeCN (10 mL) was refluxed for 3 days. After the reaction, the MeCN was removed by a rotoevaporator. The residual bromide salt was dispersed in THF (25 mL) and stirred for 10 min. The bromide salt was filtered and washed with THF 3 times. The filter cake was dispersed in water (100 mL).  $\text{LiTf}_2\text{N}$  (1.5 g, 5.2 mmol) was added and the mixture was stirred for 24 hours at 50 °C. After cooling to room temperature, the product was extracted with dichloromethane/ $\text{H}_2\text{O}$  3 times. The combined organic layer was washed with deionized water and then dried over  $\text{Na}_2\text{SO}_4$ . The drying agent was filtered and the filtrate was concentrated by a rotoevaporator. Drying in a vacuum oven gave a pale-yellow viscous liquid (2.20g, 85%). DSC:  $T_g = -59.7$  °C, no  $T_m$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ , 22 °C):  $\delta$  1.29-1.50 (m, 32H), 1.97 (m, 4H), 3.45 (t,  $J=6$ , 4H), 4.11 (t,  $J=7$ , 4H), 7.38 (s, 2H), 8.44 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{CN}$ , 22 °C): 26.6, 26.7, 29.6, 30.1, 30.15, 30.20, 30.3, 30.5, 33.6, 50.6, 62.6, 123.4, 136.1. HRMS (ESI):  $m/z$  409.3808 ( $[\text{M-Tf}_2\text{N}]^+$ , calcd. for  $\text{C}_{25}\text{H}_{49}\text{N}_2\text{O}_2$  409.3794, error 3.5 ppm).

**1-(6'-Hydroxy-1'-hexyl)-3-(11''-hydroxy-1''-undecyl)imidazolium hexafluorophosphate (2e).** A solution of **1a** (3.37 g, 20 mmol) and 11-bromo-1-undecanol (4.28 g, 21 mmol) in dry MeCN (30 mL) was refluxed for 3 days. After the reaction, the MeCN was removed by a rotoevaporator. The residual bromide salt was washed with THF 3 times and dried in a vacuum oven. The bromide salt (2.52 g, 7.0 mmol) was dispersed in water (100 mL) and  $\text{KPF}_6$  (1.9 g, 10 mmol) was added with vigorous stirring. The upper water layer was decanted and the precipitated oil was washed with deionized water 3 times. Drying in a vacuum oven gave a pale-yellow viscous oil (3.00 g, 89%). DSC:  $T_g = -48.8$  °C, no  $T_m$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ , 22 °C):  $\delta$  1.28-1.48 (m, 22H), 1.97 (m, 4H), 3.47 (m, 4H), 4.11 (m, 4H), 7.38 (s, 2H), 8.44 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{CN}$ , 22 °C):  $\delta$  25.9, 26.5, 26.6, 26.7, 29.5, 30.0, 30.1, 30.2, 30.3, 30.46, 30.50, 33.2, 33.6, 50.5, 50.6, 62.3, 62.6, 123.4, 136.1. HRMS (ESI):  $m/z$  339.3034 ( $[\text{M-PF}_6]^+$ , calcd.

for  $C_{20}H_{39}N_2O_2$  339.3012, error 6.5 ppm).

**1-(6'-Hydroxy-1'-hexyl)-3-(11''-hydroxy-1''-undecyl)imidazolium**

**bis(trifluoromethanesulfonyl)imide (2f).** From the previous experiment, the bromide salt (2.52 g, 7.0 mmol) was dispersed in water (100 mL) and  $LiTf_2N$  (2.9 g, 10 mmol) was added with vigorous stirring. The upper water layer was decanted and the precipitated oil was washed with deionized water 3 times. Drying in a vacuum oven gave a colorless (pale-yellow) liquid (3.70 g, 85%). DSC:  $T_g = -52.5\text{ }^{\circ}C$ , no  $T_m$ .  $^1H$  NMR (400 MHz,  $CD_3CN$ ,  $22\text{ }^{\circ}C$ ):  $\delta$  1.28-1.48 (m, 22H), 1.97 (m, 4H), 3.47 (m, 4H), 4.11 (m, 4H), 7.38 (s, 2H), 8.44 (s, 1H).  $^{13}C$  NMR (100 MHz,  $CD_3CN$ ,  $22\text{ }^{\circ}C$ ):  $\delta$  25.8, 26.5, 26.6, 26.7, 29.5, 30.08, 30.12, 30.2, 30.3, 30.46, 30.50, 33.3, 33.8, 50.5, 50.6, 62.2, 62.5, 123.5, 136.1. HRMS (ESI):  $m/z$  339.3044 ( $[M-PF_6]^+$ , calcd. for  $C_{20}H_{39}N_2O_2$  339.3012, error 9.4 ppm).

**1,2-Bis[N,N'-(6''-hydroxy-1''-hexyl)imidazolium]ethane bis(hexafluorophosphate) (3a).** A solution of **1a** (3.365 g, 20 mmol) and 1,2-dibromoethane (1.877 g, 10 mmol) in dry MeCN (15 mL) was refluxed for 3 days. After the reaction, the bromide salt was filtered and washed with THF 3 times. The filter cake was dissolved in water (25 mL).  $KPF_6$  (4.6 g, 25 mmol) was added to the solution with vigorous stirring. After decanting off the upper water layer, the residue was washed with deionized water 3 times. Drying in a vacuum oven gave a pale-yellow gummy material (4.00g, 61%). DSC:  $T_g = -56.7\text{ }^{\circ}C$ ,  $T_m = 33.7\text{ }^{\circ}C$ .  $^1H$  NMR (400 MHz, acetone- $d_6$ ,  $22\text{ }^{\circ}C$ ):  $\delta$  1.36-1.52 (m, 12H), 1.95 (m, 4H), 3.52 (t,  $J=6$ , 4H), 4.35 (t,  $J=7$ , 4H), 5.02 (s, 4H), 7.72 (s, 2H), 7.84 (s, 2H), 9.04 (s, 2H).  $^{13}C$  NMR (100 MHz, acetone- $d_6$ ,  $22\text{ }^{\circ}C$ ):  $\delta$  26.5, 26.7, 30.6, 33.6, 50.0, 50.8, 62.3, 123.7, 124.3, 137.3. HRMS (FAB, NBA-PEG):  $m/z$  509.2479 ( $[M-PF_6]^+$ , calcd. for  $C_{20}H_{36}N_4O_2PF_6$  509.2475, error 0.8 ppm).

**1,2-Bis[N,N'-(6''-hydroxy-1''-hexyl)imidazolium]ethane**

**bis[bis(trifluoromethanesulfonyl)imide] (3b).** A solution of **1a** (3.365 g, 20 mmol) and 1,2-dibromoethane (1.877 g, 10 mmol) in dry MeCN (15 mL) was refluxed for 3 days. After the reaction, the bromide salt was filtered and washed with THF 3 times. The filter cake was dissolved in water (25 mL).  $LiTf_2N$  (7.1 g, 25 mmol) was added to the solution with vigorous stirring. After decanting off the upper aqueous layer, the residue was washed with deionized water 3 times. Drying in a vacuum oven gave a pale-yellow viscous liquid (6.68 g, 72%). DSC:  $T_g = -46.1\text{ }^{\circ}C$ , no  $T_m$ .  $^1H$  NMR (400 MHz,  $CD_3CN$ ,  $22\text{ }^{\circ}C$ ):  $\delta$  1.28-1.50 (m, 12H), 1.82 (m,

4H), 3.48 (t,  $J=6$ , 4H), 4.12 (t,  $J=7$ , 4H), 4.56 (s, 4H), 7.30 (s, 2H), 7.44 (s, 2H), 8.39 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{CN}$ , 22 °C):  $\delta$  25.9, 26.5, 30.5, 33.2, 49.6, 50.9, 62.3, 123.5, 124.3, 136.8. HRMS (ESI):  $m/z$  644.2029 ( $[\text{M-Tf}_2\text{N}]^+$ , calcd. for  $\text{C}_{22}\text{H}_{36}\text{F}_6\text{N}_5\text{O}_6\text{S}_2$  644.2011, error 2.8 ppm).

**1,2-Bis[N,N'-(11"-hydroxy-1"-undecyl)imidazolium]ethane bis(hexafluorophosphate) (3c)** A solution of **1b** (7.15 g, 30 mmol) and 1,2-dibromoethane (2.81 g, 15 mmol) in dry MeCN (25 mL) was refluxed for 3 days. After cooling to room temperature, the bromide salt was filtered and washed with THF 3 times and dried: 9.32 g (94%). The bromide salt (2.50 g, 3.8 mmol) was dispersed in deionized water (100 mL) and  $\text{KPF}_6$  (1.73 g, 9.4 mmol) was added. The mixture was stirred for 24 h at 50 °C. After cooling to room temperature, the precipitated solid was filtered and washed with deionized water 3 times. Drying in a vacuum oven gave a white crystalline solid (3.00 g, 100% from the bromide salt). DSC:  $T_m$  = 88.5, 177.1 (two endothermic peaks), no  $T_g$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ , 22 °C):  $\delta$  1.29 (s(br), 28H), 1.46 (m, 4H), 1.80 (m, 4H), 2.47 (t,  $J=5$ , 2H), 3.46 (q,  $J=6$ , 4H), 4.11 (t,  $J=7$ , 4H), 4.57 (s, 4H), 7.31 (s, 2H), 7.42 (s, 2H), 8.36 (s, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{CN}$ , 22 °C):  $\delta$  26.6, 26.7, 29.6, 30.1, 30.16, 30.21, 30.3, 30.7, 33.7, 49.8, 50.5, 62.4, 123.5, 124.3, 137.0. HRMS (ESI):  $m/z$  649.4058 ( $[\text{M-PF}_6]^+$ , calcd. for  $\text{C}_{30}\text{H}_{56}\text{N}_4\text{O}_2\text{PF}_6$  649.4045, error 2.0 ppm).

**1,2-Bis[N,N'-(11"-hydroxy-1"-undecyl)imidazolium]ethane**

**bis[bis(trifluoromethanesulfonyl)imide] (3d).** From the previous experiment, the bromide salt (2.50 g, 3.8 mmol) was dispersed in deionized water (100 mL) and  $\text{LiTf}_2\text{N}$  (7.1 g, 25 mmol) was added with vigorous stirring. The mixture was stirred for 24 h at 50 °C. After cooling to room temperature, the upper aqueous layer was decanted off and the product was extracted with ethyl acetate/water 3 times. The combined organic layer was washed with deionized water and dried over  $\text{Na}_2\text{SO}_4$ . The drying agent was filtered and the filtrate was concentrated by a rotoevaporator. Drying in a vacuum oven gave a pale-yellow viscous liquid (3.27 g, 82% from the bromide salt). DSC:  $T_g$  = -43.5 °C, no  $T_m$ .  $^1\text{H}$  NMR (400 MHz, acetone- $d_6$ , 22 °C):  $\delta$  1.28-1.52 (m, 32H), 1.95 (m, 4H), 2.94 (s(br), 2H), 3.52 (t,  $J=6$ , 4H), 4.36 (t,  $J=7$ , 4H), 5.08 (s, 4H), 7.78 (s, 2H), 7.89 (s, 2H), 9.12 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{CN}$ , 22 °C):  $\delta$  25.8, 25.9, 29.2, 29.3, 29.4, 29.8, 32.8, 49.2, 50.0, 61.5, 122.9, 123.5, 136.5. HRMS (ESI):  $m/z$  784.3586 ( $[\text{M-Tf}_2\text{N}]^+$ , calcd. for  $\text{C}_{32}\text{H}_{56}\text{F}_6\text{N}_5\text{O}_6\text{S}_2$  784.3571, error 1.9 ppm).

**General procedure for polyesterifications.** A mixture of dihydroxy imidazolium salt (1.000

eq.) and sebacoyl chloride (1.000 eq.) in dried diglyme (same weight as monomers) was stirred at 150 °C for 1-3 days under N<sub>2</sub>. The polymerization was deemed complete when HCl gas was not evolved over a 30 min period (detected by pH paper). After cooling the mixture to room temperature, ethyl acetate (or THF) was added to precipitate the polymerized product. After removing the upper non-solvent layer by decanting, the residue was dissolved in acetone (or other good solvent such as MeCN and DMF). Ethyl acetate (or THF) was added to precipitate the polymer again. This precipitation step was repeated at least 3 times. The precipitated polymer was washed with deionized water 3 times. Drying in a vacuum oven at 70 °C gave highly viscous imidazolium polyesters. The molecular weights of the synthesized polymers were analyzed by comparing integration numbers of repeating unit protons and the end group protons.

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## Chapter 16

### Synthesis of Imidazolium Dienes and Precision Ionic Polyolefins

#### Abstract

New regio-regular imidazolium ionene and ionomer polyolefins were synthesized by acyclic diene metathesis polymerization from imidazolium diene ionic liquids. The in-chain ionene is remarkably viscous beyond its rubbery plateau, whereas the pendant-chain ionomer is semicrystalline in nature.

#### Introduction

Ionomers, ionenes, and polymer gels impregnated with IL's have become the focus of intense research in the field of high performance materials and ion conductive matrices.<sup>1,2</sup> Work over several decades has shown that factors such as the degree of ionic clustering, crystallinity, and other morphological characteristics play roles in the properties of these materials.<sup>2-5</sup> While these features have been studied in varying degrees for *random* ionomers and well defined ionenes, fundamental studies of the former have been limited by an inherent lack of control over the repeat unit.<sup>2,3,5,6</sup>

For example, consider the complexities of partially neutralized poly(ethylene-co-methacrylic acid) or poly(ethylene-co-acrylic acid) which can display up to four, often thermally contiguous, mechanical relaxations. These relaxations likely result from three contributing factors: multiple amorphous phases, a distribution of crystal thicknesses due to the statistical incorporation of co-monomers, and devitrification of ionic domains.<sup>3,7</sup> The situation is less complicated for amorphous ionomers, but they too contain responses from ion-depleted segments as well as devitrification of ion-rich regions.<sup>2,8</sup>

Devising a reliable synthetic pathway to precision ionomers, those containing perfectly regular repeat units, allows us to fine tune the interplay between dispersion forces which govern

polymer crystallization and Coulombic attraction which regulates formation of clusters and multiplets, thus providing us the opportunity to markedly deconvolute experimental data. Ion conductivity is also of interest in ionic polymers.<sup>4,5,6a</sup> Prior research from our laboratory suggests the possibility of inducing formation of channel like ion-rich regions between lamella in highly interactive precision polymers;<sup>9</sup> these materials may also be valuable as unique conduction matrices.

Herein we report the use of acyclic diene metathesis polymerization to synthesize ionic polyolefins derived from ionic liquid (IL) monomers. New imidazolium based ionomers and ionenes with perfectly regular repeat units are the result. Precision placement of the ionic group either in the polymer backbone or pendant to it generates significant variance in mechanical performance.

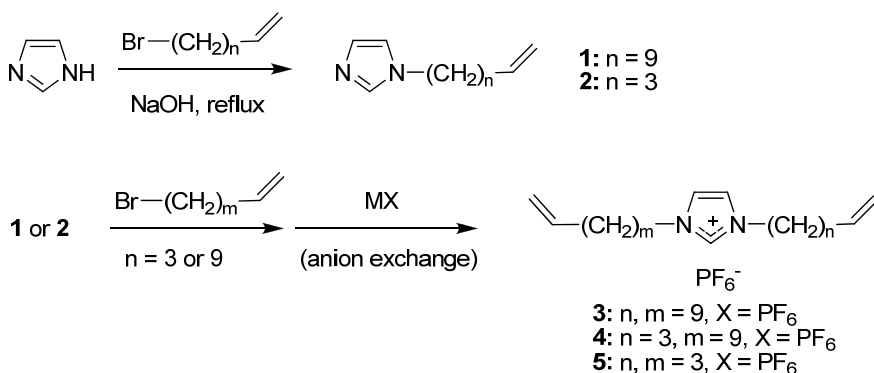
## Results and Discussion

Preparation of ADMET polymers requires that only two criteria be met: the monomer must contain an alpha-omega diene, and it, as well as any trace impurities, must not poison the catalyst. Although catalysts with varying functional group tolerances are available, the underlying theme is the exclusion of Brønsted acids or nucleophiles.<sup>10</sup> Further, the design of suitable ionomer synthons requires that either of two possible polymer synthesis routes be employed: postfunctionalization (ionization) of the polymer or polymerization of an ionic monomer. The latter path is preferred for precision polyolefin synthesis since it does not necessitate quantitative conversion in a postpolymerization modification.

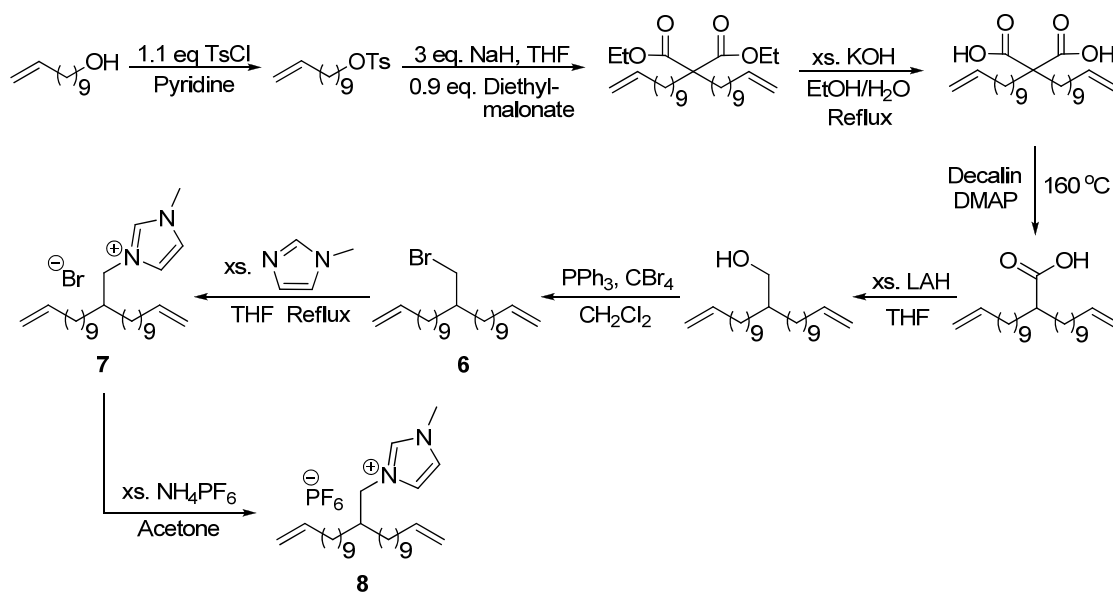
Metathesis polycondensation of a fully ionic monomer carries a new challenge, in that most ionic molecules are solids with melting points well above room temperature and/or are insoluble in organic solvents. Our approach to circumvent this problem is simply to prepare ionic monomers that are, themselves, liquids thus allowing for bulk polymerization. The imidazolium hexafluorophosphate salts are appealing as they are less-nucleophilic.

**Synthesis of Diene Monomers.** Scheme 16-1 displays the chemistry used to generate IL dienes for in-chain imidazolium polymers from commercially available starting materials. The imidazole derivatives **1** and **2** were prepared first in basic condition in high yield (>85%). The

quaternization reactions were performed in acetonitrile (MeCN) and bromide salts are usually hygroscopic. Ion exchange of the bromide salts to  $\text{PF}_6^-$  salts were done in aqueous condition for **4** and **5**, however in dry acetone for **3**, due to the poor solubility of the bromide salt precursor of **3**.



**Scheme 16-1.** Synthesis of ionic liquid monomers for in-chain imidazolium polymer preparation.

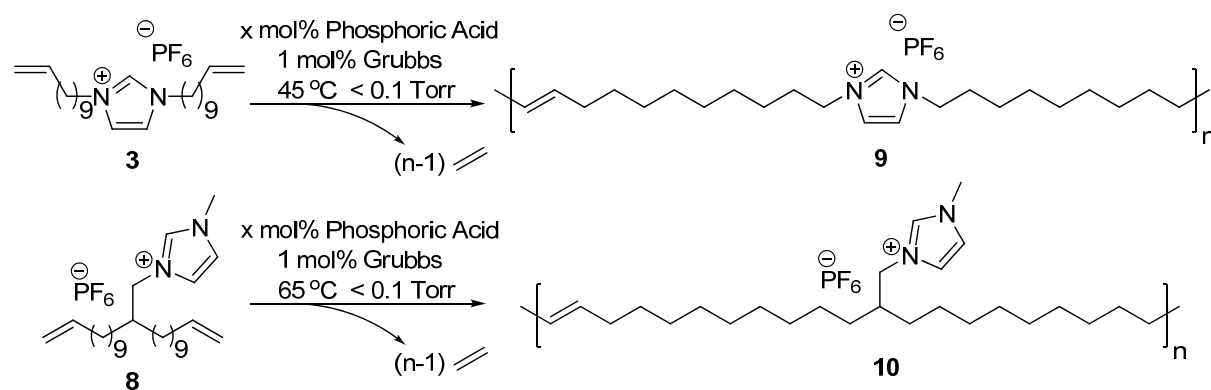


**Scheme 16-2.** Synthesis of ionic liquid monomer **8** for ionomer preparation.

The synthesis of pendant imidazolium diene **8** was more complicate as shown in Scheme 16-2. The overall isolated yield was 16%. As the quaternization for **5**, the quaternization of the bromide salt **7** to  $\text{PF}_6^-$  salt **8** was done in dry acetone, because of the poor solubility of **7** in water. As catalyst poisoning can be a problem, purity was thoroughly assessed. In both cases, no

bromide ion was detected by the Beilstein copper-flame test after anion exchange and the final products passed elemental analysis (**3**: theory: C, 57.90; H, 8.75; N, 5.40. Found: C, 57.76; H, 8.79; N, 5.39. **8**: theory: C, 59.98; H, 9.17; N, 5.0; Found: C, 60.02; H, 9.30; N: 4.93.)

**ADMET Polymerizations and Characterizations.** The ADMET polymerizations of the synthesized monomers were tried in various conditions, however, we only obtained polymeric materials from **3** and **8**.



**Scheme 16-3.** Modified ADMET polymerization conditions for preparation of ionenes and ionomers from imidazolium based ionic liquids.

The first attempt to polymerize **3** using standard ADMET conditions (bulk polymerization using Grubbs' first or second generation catalyst under high vacuum at 45 °C) yielded oligomers, apparently due to catalyst inhibition. While ethylene generation was initially observed in the form of vigorous bubbling, polymerization eventually slowed and olefin isomerization ensued regardless of whether Grubbs I or II was employed.

Ondruschka and coworkers encountered a similar situation during cross metathesis in imidazolium-based IL's, reporting that contamination by trace quantities of N-alkyl-imidazole was sufficient to decrease the reaction rate while simultaneously increasing catalyst death and olefin isomerization rates.<sup>11</sup> Additionally, Schanz and P'Pool observed that while ROMP with Grubbs I or II could be completely inhibited with catalytic amounts of N-alkyl imidazoles, full restoration of catalytic activity was achieved after addition of phosphoric acid to protonate the inhibitor.<sup>12</sup> Grubbs and coworkers also have found that, even in the absence of inhibitors, addition of catalytic quantities of Brönsted acids can increase the rate of catalyst initiation and turnover frequency by enhancing tricyclohexyl phosphine dissociation.<sup>13</sup>

At first we did not believe we were dealing with the aforementioned catalyst poisoning problem. Electrospray ionization MS, as well as  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra for **3**, showed no evidence of N-alkyl-imidazole contamination, and elemental analysis agreed with the theoretical values. However, further mass spectral data collected by atmospheric pressure chemical ionization, which selectively detects semi-volatile compounds, combined with HPLC MS, qualitatively indicated the presence of trace quantities of imidazole **1**. This observation led us to investigate the use of phosphoric acid as in Schanz and P'Pool's work. The concentration of acid was varied from 1 to 25 mol% with respect to monomer (Scheme 16-3); olefin isomerization was effectively halted with the addition of 10 mol% acid; higher concentrations of  $\text{H}_3\text{PO}_4$  accelerated catalyst death, as indicated by the formation of brown precipitates.

With the issues of isomerization and catalyst death addressed, driving polycondensation beyond oligomerization became a matter of enhancing removal of ethylene from the highly viscous polymerizing mass. Typically ADMET chemistry has been accomplished using magnetic agitation; however, in this case, powerful interchain interactions between ionic moieties results in a rapid viscosity increase; magnetic stirring becomes impossible even at low conversions.

We constructed a small scale high vacuum mechanical stirring apparatus capable of continuously spreading the polymerization matrix as a thin film, thereby maximizing the rate of ethylene removal under vacuum. Polymerization of monomer **3** (Scheme 16-3) proceeded rapidly using this device, generating polymer **9**; 10 mol% phosphoric acid/Grubbs I led to high conversion overnight as indicated by complete conversion of terminal olefin groups to internal olefins according to  $^1\text{H}$  NMR.

Analysis of polymer **9** by DSC and TGA reveals a  $T_g$  at  $-3\text{ }^\circ\text{C}$  with no melting transition up to  $200\text{ }^\circ\text{C}$ , near the onset of thermal decomposition. Powerful interchain interactions in this precision ionene **9** preclude GPC measurements; persistent aggregation was observed in all solvents tested (hexane, toluene, diethyl ether, chloroform, THF, methylene chloride, 1,2-dichlorobenzene, acetone, DMF, DMSO, methanol, water, and DMF-LiCl solutions), as indicated by multi-modality of dynamic light scattering (DLS) results. Nonetheless, NMR measurements (endgroups vanish) assure the formation of high polymer as do its mechanical properties.

Polymerization of pendant IL monomer **8** (Scheme 16-3) to polymer **10** was achieved using similar conditions, except that the reactor was heated to  $65\text{ }^\circ\text{C}$  for melt polymerization.

Conversion was completed easily, as indicated by disappearance of the terminal olefin according to  $^1\text{H}$  NMR. DSC analysis reveals a  $T_g$  at 5 °C and a  $T_m$  at 65 °C, quite different from ionene **9**. Polymer **9** is amorphous and tough, while polymer **10** is semicrystalline. As before, a high degree of interchain aggregation in organic solvents was observed, again precluding GPC measurements.

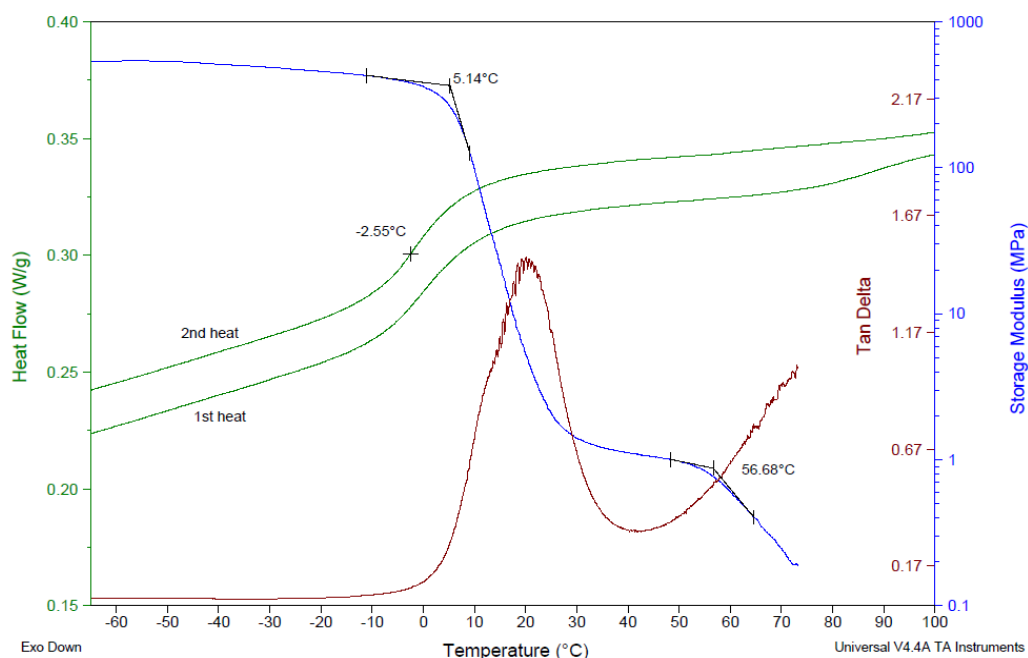


**Figure 16-1.** DSC and DMA Traces of Polymer **8**.

Dynamic mechanical Analysis (DMA) data was collected on melt pressed films, information which clearly distinguishes the mechanical differences between the in-chain material and the pendant polymer. Ionene **9** displayed the onset of a glass transition at 5 °C, consistent with the DSC result ( $T_g = -3$  °C, no  $T_m$ ), followed by a rubbery plateau out to 55 °C. The plateau is attributed to ionic aggregates while the second transition at 55 °C is believed to correspond to their dissociation. The DMA of ionomer **10**, however, did not show a sharp glass transition but rather a gradual relaxation with no clear onset. A peak in tan delta appears near 60 °C, close to the measured  $T_m$ . This rather broad relaxation is concomitant with what appears to be either strain-induced or cold crystallization, immediately followed by liquefaction due to aggregate dissociation, regardless of the heating rate.

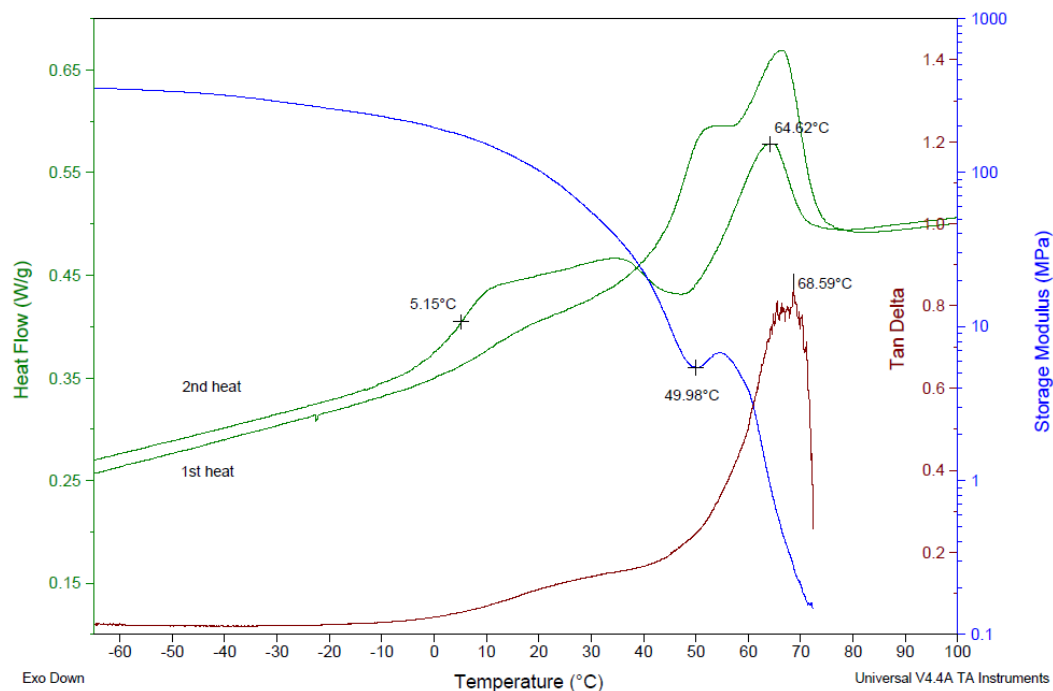


**Figure 16-2.** DSC and DMA Traces of Polymer **9**.

## Conclusions

These new regioregular ioene and ionomer polyolefins appear to exhibit an unprecedented degree of interchain interaction between precisely placed functionalities, a hypothesis supported by persistent aggregation of the polymers in a wide variety of organic solvents, combined with their mechanical behavior in both the solid and liquid state. The in-chain polymer **9** is remarkably viscous beyond its rubbery plateau, whereas the pendant-chain polymer **10** is semicrystalline in nature. Detailed solid-state structural and morphological analysis is underway to better understand the behavior of this new class of ionomer/ionenes, to include a systematic study of the relationship between precision ionomer/ionene structure and ion conduction.

## Experimental

**Materials and Methods.** All materials were purchased from Aldrich and used as received, unless noted otherwise. Acetone was dried with anhydrous  $\text{CaSO}_4$  and then distilled. Methylene Chloride and Tetrahydrofuran (THF) was obtained from an MBraun solvent purification system. Grubbs' first and second generation ruthenium catalysts, bis(tricyclohexylphosphine)benzylidene



ruthenium(IV)dichloride and Ruthenium, [1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene] dichloro (phenylmethylene) (tricyclohexylphosphine) respectively, were generous gifts from Materia, Inc.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained on Varian Inova 400 MHz, Unity 400 MHz, and Mercury 300 MHz spectrometers. High resolution fast atom bombardment mass spectrometry (HR FAB MS) was carried out on a JEOL model HZ110 dual-focusing mass spectrometer using xenon gas for ionization. Atmospheric pressure chemical ionization mass spectra were acquired using a ThermoFinnigan LCQ. HPLC/MS was carried out using an Agilent 1100 series HPLC equipped with a Waters Atlantis dC18 (2.1 x 150mm; 3 $\mu\text{m}$ ; no guard column) column and a ThermoFinnigan LCQ (+)ESI mass spec detector. 0.3% acetic acid/water was used as the mobile phase. DSC results were obtained on a TA Instruments Q1000 from -150 to 150  $^{\circ}\text{C}$  at a scan rate of 10  $^{\circ}\text{C}/\text{min}$  under an  $\text{N}_2$  purge. TGA results were obtained on a TA instruments Q5000 at a scan rate of 50  $^{\circ}\text{C}/\text{min}$  under an  $\text{N}_2$  purge. DMA of melt pressed films was performed using a TA Instruments Q800 DMA in tensile geometry from -70 to 75  $^{\circ}\text{C}$  at a heating rate 3  $^{\circ}\text{C}/\text{min}$ . The films of **8** and **9** were melt-pressed between two Teflon sheets at 100  $^{\circ}\text{C}$  by applying a 10 kg-force for 30 seconds, releasing the pressure, and repeating twice. The dimensions of the films for DMA were 8.30 mm X 6.88 mm X 0.30 mm (**8**) and 16.27 mm X 7.70 mm X 0.18 mm (**9**).

**N,N'-Bis(undecen-10-yl)imidazolium hexafluorophosphate (3).** To a solution of imidazole (2.723 g, 40 mmol) in NaOH (50% solution, 3.5 g, 44 mmol), 11-bromo-1-undecene (9.33 g, 40 mmol) and THF (20 mL) was added and the mixture was refluxed for 2 days. After the mixture cooled, THF was removed with a rotoevaporator. The residue was extracted with dichloromethane/water 3 times. The combined organic layer was washed with water and then dried over  $\text{Na}_2\text{SO}_4$ . The drying agent was filtered and the filtrate was concentrated. The resultant crude **1** (8.85 g, ~100%, a yellow oil) was used directly in the next reaction. A solution of crude **1** and 11-bromo-1-undecene (9.33 g, 40 mmol) in THF (40 mL) was heated at reflux for 4 days. After the mixture cooled, THF was removed with a rotoevaporator. The residue was washed with diethylether 5 times and then dried in a vacuum oven. The bromide salt was viscous oil (18.13 g, 99%) with MP 27  $^{\circ}\text{C}$  (DSC).  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$  23  $^{\circ}\text{C}$ ):  $\delta$  1.26-1.40 (m, 24H), 1.93 (m, 4H), 2.03 (m, 4H), 4.37 (t,  $J=8$ , 4H), 4.95 (m, 4H), 5.80 (m, 2H), 7.49 (d,  $J=1$ , 2H), 10.55 (s, 1H).  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ , 23  $^{\circ}\text{C}$ ):  $\delta$  26.3, 28.86, 28.99, 29.3, 30.3, 31.0, 33.8, 50.1, 114.2, 122.0, 137.2, 139.1. HR FAB MS (NBA-PEG):  $m/z$  373.3579 ( $[\text{M}-\text{Br}]^+$ , calcd. 373.3583,

error 1.1 ppm). Into a solution of the bromide salt (6.40 g, 14.1 mmol) in dry acetone (20 mL),  $\text{NH}_4\text{PF}_6$  (2.42 g, 14.8 mmol) was added. The mixture was stirred for 24 hours at room temperature, after which the precipitate was filtered. The filtrate was concentrated and the residue was dissolved in chloroform (40 mL). The solution was washed with water twice then dried with anhydrous  $\text{Na}_2\text{SO}_4$ . The drying agent was filtered and the solution was concentrated with a rotoevaporator. Drying in a vacuum oven (50 °C) gave RTIL **3** (6.90 g, 94%) as a brown semisolid, mp 28 °C (DSC).  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ , 23 °C):  $\delta$  1.27-1.38 (m, 24H), 1.87 (m, 4H), 2.03 (m, 4H), 4.16 (t,  $J=8$ , 4H), 4.94 (m, 4H), 5.80 (m, 2H), 7.33 (d,  $J=1$ , 2H), 8.57 (s, 1H).  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ , 23 °C):  $\delta$  26.1, 28.8, 29.0, 29.23, 29.25, 29.9, 33.7, 50.1, 114.1, 122.2, 135.1, 139.1. HR FAB MS (NBA-PEG):  $m/z$  373.3582 ( $[\text{M-PF}_6]^+$ , calcd. 373.3583, error 0.2 ppm). Elemental Anal.: found C, 57.76; H, 8.79; N, 5.39.; calcd.  $\text{C}_{25}\text{H}_{45}\text{N}_2\text{PF}_6$ : C, 57.90; H, 8.75; N, 5.40; P, 5.97; F, 21.98

**N-(Penten-1-yl)-N'-(undecen-1-yl)imidazolium hexafluorophosphate (4).** Same procedure as the synthesis procedure for **2**, except 5-bromo-1-pentene (9.33 g, 40 mmol) was used. **2** (8.85 g, ~100%, a yellow oil) was used directly in the next reaction. A solution of **2** (2.30 g, 17 mmol) and 11-bromo-1-undecene (3.94 g, 17 mmol) in THF (10 mL) was refluxed for 4 days. After the mixture cooled, THF was removed with a rotoevaporator. The residue was washed with diethylether 5 times. The residual bromide salt was dispersed in aqueous  $\text{KPF}_6$  solution (3.2 g in deionized water (50 mL)) and the mixture was stirred overnight at room temp. The bottom layer was washed with deionized water 5 times and then dried in a vacuum oven at 60 °C for 3 days. A yellow oil (6.00 g, 82% from **2**) was obtained.  $^1\text{H}$ -NMR (400 MHz, acetone- $d_6$ , 23 °C):  $\delta$  1.29-1.40 (m, 12H), 1.95-1.22 (m, 8H), 4.38 (t,  $J=8$ , 4H), 4.98 (m, 4H), 5.82 (m, 2H), 7.79 (d,  $J=2$ , 2H), 9.07 (s, 1H).  $^{13}\text{C}$ -NMR (100 MHz, acetone- $d_6$ , 23 °C):  $\delta$  26.8, 29.6, 29.72, 29.74, 30.7, 30.9, 34.4, 50.0, 50.6, 114.7, 116.2, 123.58, 123.62, 136.8, 137.7, 139.8. HRMS (ESI):  $m/z$  289.2641 ( $[\text{M-PF}_6]^+$ , calcd. for  $\text{C}_{19}\text{H}_{33}\text{N}_2$  289.2638, error 1.0 ppm).

**N,N'-Bis(penten-1-yl)imidazolium hexafluorophosphate (5).** A solution of **2** (2.30 g, 17 mmol) from previous procedure and 5-bromo-1-pentene (2.52 g, 17 mmol) in THF (10 mL) was refluxed for 4 days. After the mixture cooled, THF was removed with a rotoevaporator. The residue was washed with diethylether 5 times. The residual bromide salt was dispersed in aqueous  $\text{KPF}_6$  solution (3.2 g in deionized water (50 mL)) and the mixture was stirred overnight at room temp. The bottom layer was washed with deionized water 5 times and then dried in a vacuum

oven at 60 °C for 3 days. A yellow oil (5.04 g, 85% from **2**) was obtained. <sup>1</sup>H-NMR (400 MHz, acetone-*d*<sub>6</sub>, 23 °C): δ 2.04-2.19 (m, 8H), 4.38 (t, *J*=8, 4H), 5.01 (m, 4H), 5.82 (m, 2H), 7.79 (d, *J*=2, 2H), 9.01 (s, 1H). <sup>13</sup>C-NMR (100 MHz, acetone-*d*<sub>6</sub>, 23 °C): δ 29.7, 30.9, 50.0, 116.2, 123.6, 136.8, 137.7. HRMS (ESI): *m/z* 205.1716 ([M-PF<sub>6</sub>]<sup>+</sup>, calcd. for C<sub>13</sub>H<sub>21</sub>N<sub>2</sub> 205.1705, error 5.4 ppm).

**1-methyl-3-(2-(undec-10-en-1-yl)tridec-12-en-1-yl)-1H-imidazol-3-ium bromide (7).** To a solution of 2-(undec-10-en-1-yl)tridec-12-en-1-yl **6**<sup>14</sup> (2 g, 4.84 mmol) in THF (6 mL) was added 450 mg of N-methyl-imidazole and the mixture was refluxed for 48 hours. After cooling, the THF was removed by rotary evaporation and the excess N-methyl-imidazole was removed by heating in a vacuum oven for 24 hours at 80 °C to give **11** (2.38 g, 99%) as a pale yellow solid. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ 1.15-1.40 (m, 32H), 1.83 (m, 1H), 2.02 (q, 4H), 3.92 (s, 3H), 4.02 (d, 2H), 4.94 (m, 4H), 5.80 (m, 2H), 7.20 (t, 1H), 7.54 (t, 1H), 10.47 (s, 1H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): δ 26.8, 29.2, 29.3, 29.7, 29.8, 30.0, 32.77, 34.01, 34.03, 39.7, 39.9, 114.3, 121.9, 123.4, 139.41, 139.44. HRMS (ESI): *m/z* 415.4064 ([M-Br]<sup>+</sup>, calcd. for C<sub>28</sub>H<sub>51</sub>N<sub>2</sub> 415.4047, error 4.1 ppm).

**1-methyl-3-(2-(undec-10-en-1-yl)tridec-12-en-1-yl)-1H-imidazol-3-ium**

**hexafluorophosphate (8).** Into a solution of **8** (2.38 g, 4.79 mmol) in dry acetone (20 mL), NH<sub>4</sub>PF<sub>6</sub> (861 mg, 5.28 mmol) was added. The mixture was stirred for 24 hours at room temperature, after which the precipitate was filtered. The filtrate was concentrated and the residue was dissolved in chloroform (40 mL). The solution was washed with water twice and then dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The drying agent was filtered and the solution was concentrated with a rotoevaporator. Drying in a vacuum oven (70 °C) gave **12** (2.56 g, 95%) as a pale yellow solid. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ 1.17-1.42 (m, 32H), 1.84 (m, 1H), 2.03 (q, 4H), 3.93 (s, 3H), 4.03 (d, 2H), 4.94 (m, 4H), 5.80 (m, 2H), 7.20 (t, 1H), 7.31 (t, 1H), 8.49 (s, 1H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): δ 26.3, 29.2, 29.3, 29.7, 29.8, 30.0, 30.9, 34.0, 36.6, 39.0, 54.2, 114.3, 122.5, 123.9, 136.6, 139.4. HRMS (ESI): *m/z* 415.4044 ([M-PF<sub>6</sub>]<sup>+</sup>, calcd. for C<sub>28</sub>H<sub>51</sub>N<sub>2</sub> 415.4047, error 0.7 ppm). Elemental Anal. Calcd C<sub>28</sub>H<sub>51</sub>N<sub>2</sub>PF<sub>6</sub> C, 59.98; H, 9.17; N, 5.0; P, 5.52; F, 20.33 Found: C, 60.02; H, 9.30; N, 4.93

**Polymer 8.** To the flat bottomed reactor described in the body of this publication, **5** (1 g, 1.93 mmol) was added under strong argon flow. The reactor was then heated to 45 °C, evacuated, and left to stir for 1 hour to remove any trace oxygen. After cooling, the reaction vessel was

transferred to an argon filled glove box and Grubbs' first generation catalyst (15 mg, 18.2  $\mu\text{mol}$ ), as well as 85% phosphoric acid (12.5  $\mu\text{L}$ , 183  $\mu\text{mol}$ ), was added. The reaction vessel was immediately removed from the glove box, placed into the reactor, and heated to 45  $^{\circ}\text{C}$  under vacuum ( $<0.1$  Torr). Rapid mechanical stirring of the polymerization matrix as a thin film on the reactor bottom was initiated. As viscosity increased, stirring was gradually slowed until solidification occurred, at which point polymerization was terminated by adding dimethyl sulfoxide (DMSO) to dissolve the polymer and precipitate the catalyst. After all precipitates settled, the polymer solution was decanted and the DMSO was evaporated in vacuo to give **8**, (890 mg, 94%).  $^1\text{H}$ -NMR (300 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  1.22 (s, 24H), 1.77 (s, 4H), 1.91 (s, 4H), 4.13 (s, 4H), 5.34 (s, 2H), 7.77 (s, 2H), 9.16 (s, 1H).  $^{13}\text{C}$ -NMR could not be collected, presumably due to short spin-lattice relaxation times.

**Polymer 9.** Identical procedures as those used to prepare polymer **7** were used here except that the reactor was heated to 65  $^{\circ}\text{C}$  to allow for melt polymerization. Polymerization of **7** (1 g, 1.78 mmol) yielded **9** (900 mg, 95%).  $^1\text{H}$ -NMR (300 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  1.21 (s, 32H), 1.75-1.95 (m, 5H), 3.83 (s, 3H), 4.05 (s, 2H), 5.33 (s, 2H), 7.69 (s, 2H), 9.07 (s, 1H).  $^{13}\text{C}$ -NMR could not be collected, presumably due to short spin-lattice relaxation times.

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## Chapter 17

### Conclusions and Future Work

Two main research topics were presented in this dissertation: 1) supramolecular host-guest interactions of polymeric building blocks and other systems and 2) synthesis and properties of new ionic liquid monomers and ionic liquid-based polymers. Some merged subjects were also studied, such as new imidazolium guest molecules for the complexations of crowns and cryptands, and the pseudorotaxane formation effects on electrical properties of polyviologens and their mixtures with polyethers.

The supramolecular polymers from the polymeric building blocks constituted various types of polymer structures, which have been already synthesized by covalent bonds. The host and guest functionalized polymeric building blocks were synthesized by controlled radical polymerizations with crown or paraquat initiators. Crown or paraquat terminated polymers were made from monofunctional initiators, and crown or paraquat centered polymers were prepared from difunctional initiators. The combinations of terminal and central functionalities of host- and guest-functionalized polymeric building blocks provided chain-extended polymers, tri-armed star homo and copolymers, diblock copolymers, graft copolymers and diblock four-armed copolymers. The new polymeric building blocks and supramolecular polymers were characterized by NMR spectroscopy, Mass spectrometry, viscometry and ITC.

A chain extended system was formed from an MPPP33C10 terminated polystyrene (host) and a paraquat terminated polystyrene (guest) in solution. A tri-armed star homopolymer was prepared from a BMP32C10 centered polystyrene and a paraquat terminated polystyrene. The association constant between these host and guest polystyrenes was measured by ITC:  $K_a = 4.4 \times 10^3 \text{ M}^{-1}$  in chloroform at room temperature, which is the highest value in crown-paraquat systems. Diblock and three-armed copolymers of crown polystyrenes and paraquat terminated PMMA were also synthesized; however, these systems were not very efficient for block copolymer formations, due to the weak interactions between paraquat moieties and PMMA building blocks.

A supramolecular graft copolymer was formed from a main-chain poly(ester crown ether) and a paraquat terminated polystyrene. Pseudorotaxane formation on multiple crown sites of the polyester gave a comb-like copolymer. One  $T_g$  and no macro phase separation of the copolymer implied the formation of the graft copolymer by DSC and SALLS. A four-armed block copolymer was synthesized by a nitroxide mediated polymerization of *n*-butyl methacrylate with a pseudorotaxane macroinitiator from the complex of crown-centered polystyrene and a difunctional paraquat initiator. The copolymer formation was confirmed by a single peak on GPC; the copolymer had two glass transitions, which corresponded to polystyrene and poly(BMA). The studies on polymeric building blocks presented here may stimulate further studies for new supramolecular polymers. First of all, the use of cryptand-paraquat host-guest systems<sup>1</sup> will be extremely useful because of their strong binding forces. The cryptand-paraquat systems are also applicable to various types of supramolecular copolymers, which I already studied in this dissertation. For examples, a chain extension system is illustrated in Figure 1a and a new chain extender from bis-cryptand compounds is also possible as shown in Figure 1b. The only a disadvantage in this system is the low yield in synthesis of functional cryptands.

One other example of new supramolecular polymers is to use controlled radical polymerization after formation of pseudorotaxanes. Figure 2 shows new brush polymers from a poly(ester crown ether) and a difunctional guest initiator. This brush copolymer does not allow the dethreading after the polymerization because the new polymer coils will act as blocking groups for the crown ethers.

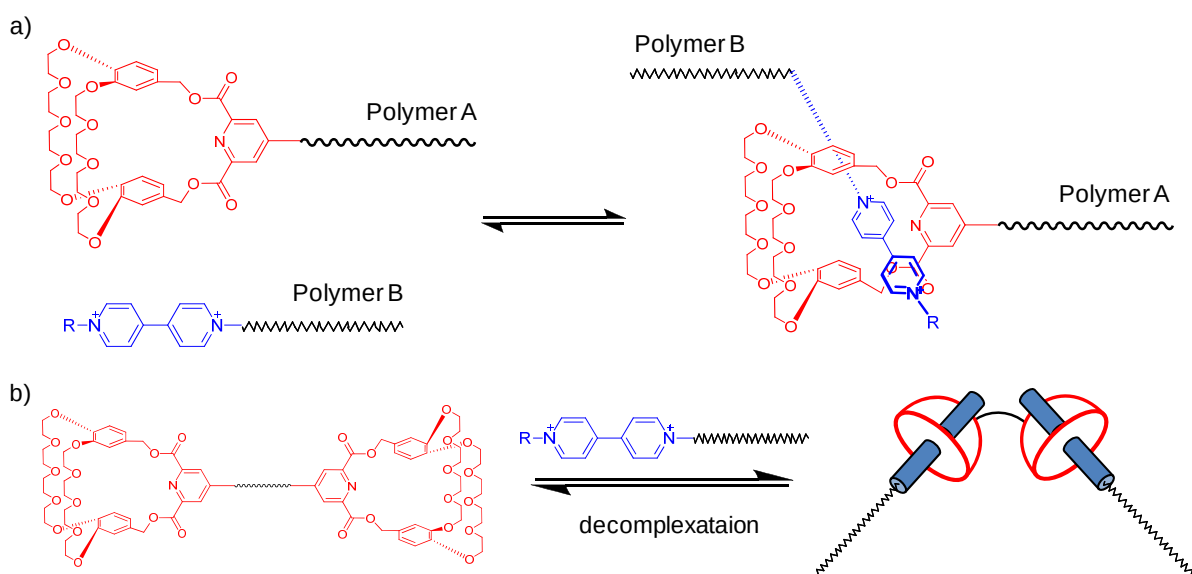


**Figure 17-1.** New supramolecular polymers from the pseudorotaxane formation from a cryptand-paraquat complexation system.



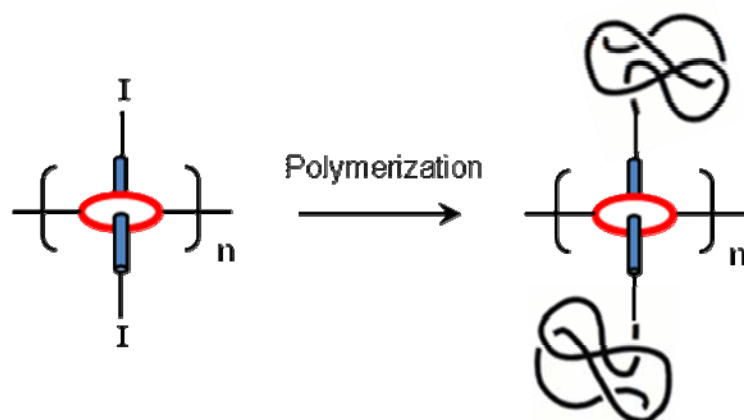


**Figure 17-2.** Supramolecular rotaxane brush copolymers from the polymerization of the pseudorotaxane macroinitiator. “I” refers an initiation site.

Ion conduction for ionic polymers is an important feature for electroactive polymers. In this dissertation, I found that supramolecular interactions can enhance the ionic conductivity of semi-crystalline ionic polymers. The supramolecular interactions between a semi-crystalline polyviologen TFSI and polyethers increased the ionic conductivity just by mixing the two components. The mixtures with larger crown ethers showed higher ionic conductivities than a mixture with small 18C6. However, the ionic conductivities of an amorphous polyviologen and its mixtures of polyethers were affected only by glass transition temperature changes. The amorphous polyviologen mixtures with lower  $T_g$  have higher ionic conductivities.

New imidazolium ionic liquids and imidazolium based polymers were synthesized for the potential applications to electroactive devices, such as mechanical actuators. Two types of imidazolium based polymers were designed and synthesized: pendant imidazolium acrylate homopolymers and main-chain imidazolium polyesters and polyolefins.

Structure-property relationships were investigated for the pendant imidazolium homopolymers from imidazolium acrylate monomers with different substituents on imidazolium ring, counter anions, and length of alkyl spacers. Interestingly, ethyleneoxy units placed as terminal units on the pendant enhanced ionic conductivity due to the higher ion mobility, which is different from Ohno’s results.<sup>2</sup>

Structure-property relationships were also investigated for the series of dicationic alkyl imidazolium salts and dihydroxy imidazolium ionic liquids. The latter difunctional ionic liquids were used as monomers for main-chain imidazolium polyesters. Three structural factors were considered in the polymer design, 1) length of the alkyl spacer, 2) the ionic

segment structure (mono- vs. bis-imidazolium), and 3) the nature of counter anions. The length of alkyl spacers changed crystallinities of the polyesters; a long alkyl spacer provided crystallinity. The ionic conductivities of mono-imidazolium polyesters were generally higher than bis-imidazolium analogs. One semi-crystalline imidazolium polyester has a biphasic structure, which was confirmed by DSC, DRS and XRS. The phase separation of ionic and non-ionic domains provided higher ion conductivity.

A series of new dicationic imidazolium salts were synthesized and characterized. We found that 1,2-bis[N-(N'-alkylimidazolium)]ethane moieties show a good stacking in the solid state and also show multiple solid-solid phase transitions. The 1,2-bis[N-(N'-alkylimidazolium)]ethane salts with *n*-butyl (Br<sup>-</sup>), *n*-decyl (PF<sub>6</sub><sup>-</sup>) and *n*-dodecyl (PF<sub>6</sub><sup>-</sup>) possess low entropies of fusion, and therefore appear to be a new class of organic ionic plastic crystals. 1,2-Bis[N-(N'-alkylimidazolium)]ethane salts also act as guests for supramolecular complexation with dibenzo-24-crown-8 and a dibenzo-24-crown-8 based pyridyl cryptand with  $K_a = \sim 30$  and  $360 \text{ M}^{-1}$ , respectively, in acetonitrile. The host/guest threaded pseudorotaxane-like structure was confirmed by an X-ray crystal structure of the complex from 1,2-bis[N-(N'-methylimidazolium)]ethane 2PF<sub>6</sub><sup>-</sup> and dibenzo-24-crown-8 based pyridyl cryptand.<sup>3</sup>

As future work for electroactive polymers (EAP), the most important research topic is development of new ion-transporting polymers combining high ionic conductivity and tough mechanical strength. Design and synthesis of block copolymers are the best candidates in this stage, because many types of homopolymers from polymerizable ionic liquids have been studied in this dissertation. The first approach to di- or tri-block copolymers from imidazolium vinyl monomers and other neutral monomers will be achieved by controlled radical polymerization. For example, difunctional macroinitiators can be prepared first from the difunctional initiator, and a sequential polymerization with next monomer will provide tri-block copolymers containing ionic and neutral blocks. As well-studied for neutral block copolymers, many types of morphologies will be possible from the ionic-neutral block copolymers. Also specific bicontinuous morphologies will provide high ionic conductivity through the ionic domains as well as physical toughness from the neutral domain.

I studied only imidazolium ionic liquids in this dissertation, because there are many advantages in imidazolium structures for the various functionalities. However, there are many other types of ionic liquids, which can be applied to polymer materials. For example there are the recently reported triazole ionic liquids.<sup>4</sup> 1,2,3-Triazole moieties are well-known as the

product of the azide/alkyne ‘click’ reaction (Huisten 1,3-dipolar cycloaddition). Various functionalities can be introduced in these new ionic liquids via the click reaction.

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