

**PART I: SYNTHESIS AND RING OPENING POLYMERIZATION OF
MACROCYCLIC MONOMERS FOR PRODUCTION OF ENGINEERING
THERMOPLASTICS**

PART II: SYNTHESIS OF POLYROTAXANES

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PART I: SYNTHESIS AND RING OPENING POLYMERIZATION OF MACROCYCLIC MONOMERS FOR PRODUCTION OF ENGINEERING THERMOPLASTICS

PART II: SYNTHESIS OF POLYROTAXANES

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(Abstract)

Part I: Single sized, pure arylene ether macrocycles ranging from 30 to 60 atom ring sizes were synthesized in good yields (up to 83%) by the two component method under high dilution conditions. These macrocycles have unsymmetric structures containing sulfone/ketone or sulfone/phosphine oxide functional groups and have relatively low melting points. The melt ROP of the single sized macrocycles to form poly(arylene ether)s exhibits two stage characteristics: the first stage is very fast, driven by the large entropy difference between cyclics and linears; the second stage is very slow and is diffusion controlled due to the high viscosity created in the first stage reaction. The latter stage leads to incomplete polymerization at the low initiator concentrations (1-3 mol%). At high initiator concentrations (5-7 mol%), 100% conversion is reached due to improved initiator distribution in macrocycles; however, this reduces molecular weights of the polymers. The molecular weight is found to build up very rapidly, independent of conversion, reaction time and type of initiator. The ROP is initiated by CsF and alkali phenoxides. The efficiency of the alkali counterion is generally in the order of $\text{Cs}^+ > \text{K}^+ > \text{Na}^+$, while a phenoxide initiator is more efficient than a fluoride initiator. It is also found that the Cs counterion leads to highest degree of crosslinking. The ROP of cyclic oligomeric mixtures is also reported for comparison; the study shows that the molecular weight depends on time and conversion, and that the conversion is sensitive to the content of linear impurities and the average ring size of cyclic mixtures.

Part II: Polyrotaxanes are novel polymeric materials comprised of linear polymer molecules and threaded macrocycles with no covalent bond between the two components. With potential movements of the cyclic component and judicious combinations of the two components of different properties, these materials have brought interesting changes of physical properties, such as morphology, crystallinity, solubility, viscosity, etc. In this part of the dissertation, a new family of polyrotaxanes with poly(arylene ether)s as backbones and crown ethers as cyclic components are described. These include linear poly(arylene ether) based polyrotaxanes and hyperbranched poly(ether ether ketone) based polyrotaxanes; both are synthesized via aromatic nucleophilic substitution reactions. Preliminary studies show that these polymers exhibit great enhancement of solubility. The polymers form emulsions in water and methanol which are normally non-solvents for the poly(arylene ether) backbones. In some cases, they are even soluble in water to form a clear solution. The attempted syntheses of polyrotaxanes using aromatic macrocycles described in Part I was not successful, with no indication of threading.

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Part One

Synthesis and Ring Opening Polymerization of Macrocyclic Monomers for Production of Engineering Thermoplastics

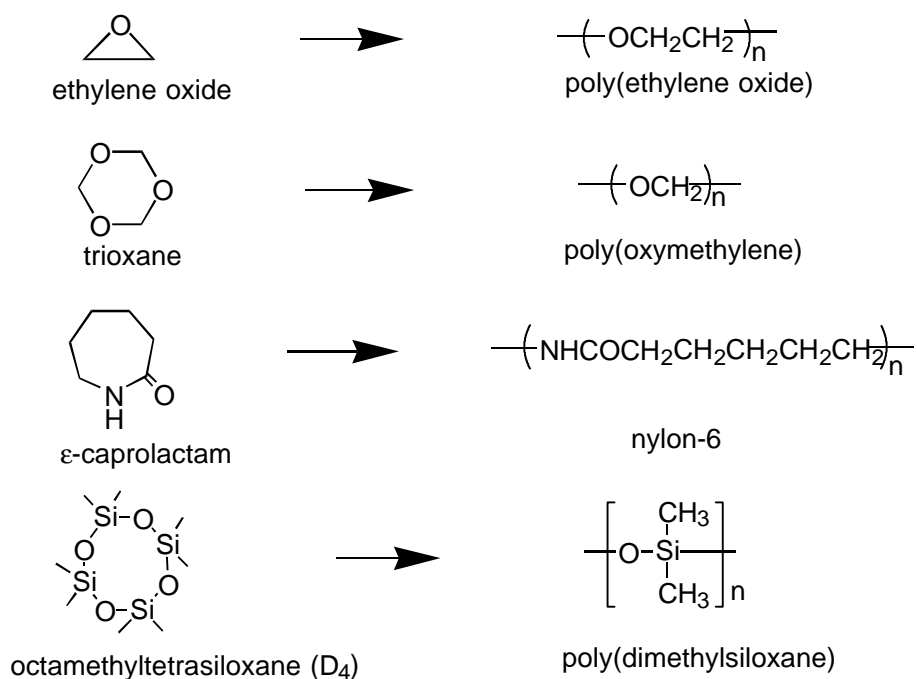
Chapter 1

Literature Review

1.1 Introduction

Ring opening polymerization (ROP) is an important polymerization technique, along with other step and chain polymerization techniques, for production of polymers. Studies of ROP have been active areas of industrial and academic research.¹ This polymerization technique has provided a number of commercially important materials. Scheme 1.1 illustrates some of those examples.

Scheme 1.1



A wide variety of aliphatic cyclic monomers have been successfully polymerized by the ring opening polymerization. This includes cyclic esters (lactones), amines, sulfides, olefins, cyclotriphosphazenes, *etc.*, besides those mentioned in Scheme 1.1. The polymerizability of a cyclic monomer depends on both thermodynamic and kinetic factors. Kinetically, polymerization requires that there be an available mechanism for the ring to open and undergo reaction. The presence of a heteroatom in the ring provides a site for nucleophilic or electrophilic attack by an initiator species, resulting in initiation and subsequent propagation by ring opening. The most important factor that one may often deal with, however, is the thermodynamic factor, that is, the

¹ (a) Ivin, K. J.; Saegusa, T. ed. *Ring-Opening Polymerization*, Elsevier Applied Science, London, 1984, Vols. 1-3. (b) McGrath, J. E. ed. *Ring-Opening Polymerization: Kinetics, Mechanisms, and Synthesis*, American Chemical Society, Washington, DC, 1985. (c) Brunelle, D. J. ed. *Ring-Opening Polymerization / Mechanisms, Catalysis, Structure, Utility*, Hanser Publisher, 1993.

relative stabilities of the cyclic monomer. Small rings, such as 3- and 4-membered rings, are highly strained and, accordingly, have a large exothermic enthalpy associated with the ring opening. In these cases, enthalpy is the major factor in determining the free energy of polymerization. The large enthalpy (negative) ensures that the equilibrium between monomer and product favors the product. By contrast, less strained medium rings, such as 5- to 9-membered rings, are certainly less favorable, because the enthalpy now is smaller, about equal to the entropy (both are negative), and the free energy becomes less negative accordingly. Polymerization is no longer favorable above some temperature (the ceiling temperature) where the free energy becomes positive. For very large rings (entropy is positive), such as oligomeric rings discussed later, the ring opening is nearly thermoneutral, and polymerization is basically driven by the entropy.^{1c}

With development of synthetic techniques for cyclic monomers, the ring opening polymerization technique has recently been introduced for production of engineering thermoplastics, aiming at alleviating the difficulty in processing these materials. Engineering thermoplastics are those plastics which maintain dimensional stability and most mechanical properties above 100°C and below 0°C.² Plastics falling within the scope of this definition include acetal resins, nylons (or aliphatic polyamides), polyimides, polyetherimides, polyesters, polycarbonates, polyethers, polysulfones, polyketones, polysulfide polymers and others. Since these polymers, except acetals and nylons, tend to contain aromatic rings in order to increase the thermal stability and chain stiffness, they typically have high melt viscosity. Although conventional plastics processing techniques, such as injection molding, blow molding and extrusion as well as thermoforming are commonly used for processing these materials, high temperatures and high pressures are normally required in the processing, as is considerable expertise.³ Poor processibility increases costs and limits applications and developments of advanced engineering thermoplastics. Since the inherent advantage of ROP is the transformation of low molecular weight cyclic precursors to high molecular weight polymers without formation of any byproducts, ROP in the melt allows the use of reactive processing techniques in which cyclic monomer is directly polymerized into final objects by extrusion or molding. This process features low viscosity and thus much more facile than processing high viscosity, high molecular weight engineering thermoplastics. The technique also opens up the possibility of applications currently restricted to high molecular weight polymers due to their high melt viscosities. In particular, ROP would be very useful in fabrication of fiber-reinforced thermoplastic composites for the fiber wetting should be improved with low molecular weight cyclics.^{4,5,6}

² Clagett, D. C. in Kroschwitz, J. I. ed. *Encyclopedia of Polymer Science and Engineering*, 2nd ed., John Wiley & Sons, Inc., 1984, Vol 6, pp94-131.

³ *Thermoplastics* in Juran, R. ed. *Modern Plastics Encyclopedia*, McGraw-Hill, Inc., New York, 1991, pp19-139.

⁴ Brunelle, D. J.; Boden, E. P.; Shannon, T. G. *J. Am. Chem. Soc.*, **1990**, *112*, 2399.

⁵ Mullins, M. J.; Woo, E. P.; Murray, D. J.; Bishop, M. T. *Chemtech*, **1993** August, 25.

⁶ Colquhoun, H. M.; Dudman, C. C.; Thomas, M.; Mahoney, C. A.; Williams, D. J. *J. Chem. Soc., Chem. Commun.*, **1990**, 336.

The application of ROP technique in the preparation of engineering thermoplastics relies on the availability of corresponding aromatic cyclic monomers. Thus, the synthesis of the cyclic monomers has been the major subject in this field. Since bisphenol-A based cyclooligomeric carbonate was first successfully made by Brunelle et al. in 1989,⁷ much progress has been made in the development of cyclic monomers for preparation of engineering thermoplastics. In the following sections, recent research activities in this field are reviewed.

1.2 Aromatic macrocycles

It has been well known that cyclic species are frequently obtained in a sizable amount in the preparation of high molecular weight condensation polymers.⁸ For example, cyclic species of various ring sizes in poly(phenylene sulfide) (PPS)⁹, poly(ether ether ketone) (PEEK)¹⁰, and bisphenol-A based polycarbonate¹¹ have been isolated from their parent polymers. Deliberate synthesis of cyclics in high yields uses high dilution conditions¹² under which cyclization is favorable but the formation of linear macromolecules is unfavorable, because the former is a first order intramolecular reaction, whereas the latter is a second order intermolecular reaction. The formation of cyclics under high dilution conditions is often assisted by the rigid group effect, cesium effect, and template effect.¹² Two approaches can be employed to achieve high dilution conditions.¹³ In the batch-wise method, the reactant is added at the beginning of the reaction to a large volume of solvent. To save solvent, the second method, known as the pseudo-high dilution technique or the influx procedure, features a slow addition of the reactant to a relatively small volume of solvent, resulting a low stationary concentration of reactant. The slower the feed rate, the lower this stationary concentration and consequently the higher the yield of cyclics. The choice of the feed rate is very much dependent on the reactivity of reactant. With a more reactive species, a faster feed rate can be applied while a high degree of dilution can still be achieved. The high dilution principle, especially the pseudo-high dilution procedure, has been well applied to synthesis of various types of aromatic macrocycles in high yields in recent years.

1.2.1 Cyclic Carbonates

The first aromatic macrocycle prepared in high yield was bisphenol-A based cyclic carbonate oligomeric mixtures reported by Brunelle et al. of General Electric Co. in 1989.^{7,14} Through proper choice of chemistry and reaction conditions, they found that aromatic cyclic

⁷ Brunelle, D. J.; Evans, T. L.; Shannon, T. G.; Boden, E. P.; Stewart, K. R.; Fontana, L. P.; Bonauto, D. K. *Am. Chem. Soc. Div. Polym. Chem. Polym. Preprints*, **1989**, 30(2),569-570.

⁸ Maravigna, P.; Montaudo, G. in Allen, G.; Bevington, J. C. ed. *Comprehensive Polymer Science*, 1st ed., Pergamon Press, 1989, Vol 5, Chapter 5, p 63.

⁹ Montaudo, G.; Puglisi, C.; Scamporrino, E.; Vitalini, D. *Macromolecules* **1986**, 19, 2157.

¹⁰ Jonas, A.; Legras, R. *Macromolecules* **1993**, 26, 2674.

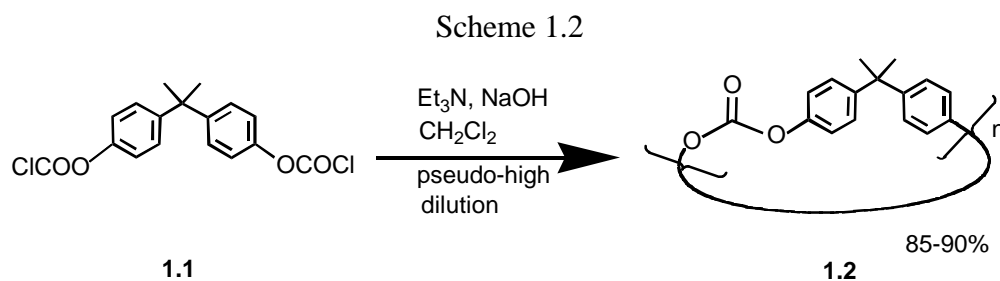
¹¹ Foti, S.; Giuffrida, M.; Maravigna, P.; Montaudo, G. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, 21, 1567.

¹² a) Knops, P.; Sendhoff, N.; Mekelburger, H. B.; Vogtle, F. in Weber, E.; Vogtle, F. ed. *Topics in Current Chemistry*, 1991, Vol 161, pp 1-36. b) Rossa, L.; Vogtle, F. *Top. Curr. Chem.* **1983**, 113, 1.

¹³ Galli, C. *Org. Prep. and Proced. Int.* **1992**, 24(3), 285-307.

¹⁴ (a) Brunelle, D. J.; Shannon, T. G. *Macromolecules*, **1991**, 24, 3035. (b) Brunelle, D. J.; Garbaskas, M. F. *Macromolecules*, **1993**, 26, 2724.

carbonates **1.2** were efficiently prepared in high yield via an amine catalyzed interfacial hydrolysis/condensation reaction of bisphenol-A bischloroformate **1.1** using a pseudo-high dilution procedure in which **1.1** was added slowly into a stirred mixture of triethylamine, aqueous sodium hydroxide and methylene chloride (Scheme 1.2). The reaction was completed in 30 minutes with a total feed up to 0.5 M. By HPLC analysis, the level of linear oligomers present in the reaction product was estimated to be 0.01-0.03%, which means that the selectivity for cyclics versus linears in this reaction was about 10,000 to 1. The low molecular weight cyclic mixture was isolated in 85-90% yield, with a ring size ranging from dimer to docosamer. This cyclic mixture melted at 200-220°C, while discrete cyclics had high melting points (cyclic dimer, 330-335°C; cyclic trimer, 345-350°C; and cyclic tetramer, 368-372°C).^{14b} The major macrocycles in the mixture were trimer, tetramer, and pentamer, each formed in 15-25% yield. The cyclic dimer (1-5%) had high ring strain according to single crystal X-ray analysis,^{14b} and thus its formation was restricted thermodynamically. Dynamic rheological spectroscopic methods showed that the viscosity of the cyclic oligomeric mixture was 10,000 times lower than commercial polycarbonate.¹⁵



A fundamental study on the polymerization of the BPA cyclic carbonates was reported by Evans et al.¹⁵ It was found that the melt polymerization of the cyclic carbonates can be initiated by a variety of anionic transesterification initiators, and can provide high molecular weight polycarbonates. Polymer molecular weights (M_w) as high as 700,000 were obtained and easily regulated by the amount of initiator and/or chain transfer agent. The polymerization was nearly thermo-neutral, but was driven by entropy to the ring-chain equilibrium point where only less than 0.1% cyclic oligomers remained. The chain-chain equilibration led to the polydispersity of about 2. It was also found that the ROP of cyclic carbonate **1.2** possessed some of the characteristics of a living polymerization. The living nature of the polymerization was seen from the fact that addition of more cyclics to a completed polymerization gave continued reaction and a higher molecular weight.

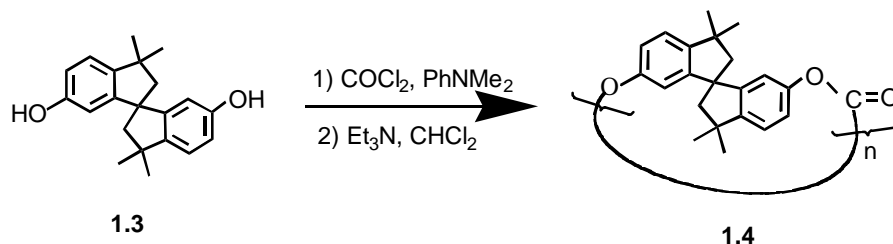
The cyclization and polymerization chemistry developed for the bisphenol-A system has been successfully applied to a variety of other bisphenols.¹⁶ One of most interesting bisphenols

¹⁵ (a) Evans, T. L.; Berman, C. B.; Carpenter, J. C.; Choi, D. Y.; Williams, D. A. *Am. Chem. Soc. Div. Polym. Chem. Polym. Preprints*, **1989**, 30(2), 573. (b) Stewart, K. R. *Am. Chem. Soc. Div. Polym. Chem. Polym. Preprints*, **1989**, 30(2), 575.

¹⁶ Brunelle, D. J.; Shannon, T. G. *Am. Chem. Soc. Div. Polym. Chem. Polym. Preprints*, **1992**, 33(1), 1198.

was spirobiindane bisphenol **1.3** (Scheme 1.3). Cyclization reactions using this bisphenol gave higher yields than using bisphenol-A due to the fact that the rigid spirobiindane structure provided a favorable conformation facilitating ring closure; a 95% yield of cyclic oligomeric carbonates **1.4** was isolated.¹⁷ And also due to the orthogonal orientation of the hydroxy functionalities, cyclic dimer **1.4** (n=2) has relatively low strain and was the major component in the cyclic mixture. One disadvantage of this system is that ring-chain equilibration becomes more favorable towards the ring side, which leads to significant amounts of cyclic oligomers being present at equilibrium in the polymerization.

Scheme 1.3



A variety of functional groups such as ester, amide, ketone, sulfone, and urethane groups have also been incorporated into polycarbonates using oligomeric bisphenols that contain the above functional groups.¹⁸ These aromatic cyclic carbonates were prepared in high yields ranging from 80% to 95% and were ring opening polymerized to high molecular weight polymers. In all of the reactions reported, the carbonate functionality acted as the key to high yield formation of cyclic oligomers and the site for ring opening polymerization.

1.2.2 Cyclic(arylene ether)s

Poly(arylene ether)s are an important class of engineering thermoplastics. The ether linkage provides additional hydrolytic stability compared to the carbonate, ester and amide bonds. Cyclic precursors of this class of materials have thus been extensively pursued. The aromatic nucleophilic substitution reaction between activated aromatic dihalides and bisphenols is one of the most common methods for preparation of poly(arylene ether)s.¹⁹ As we will see later, this method was conveniently adapted to prepare most of the cyclic(arylene ether)s under high dilution conditions. The ether linkage activated by electron withdrawing groups, such as ketone and

¹⁷ Brunelle, D. J.; Evans, T. L.; Shannon, T. G. U.S. Patent 4,736,016 (1988).

¹⁸ (a) Brunelle, D. J.; Shannon, T. G. *Am. Chem. Soc. Div. Polym. Chem. Polym. Preprints*, **1990**, 31(1), 14-15.

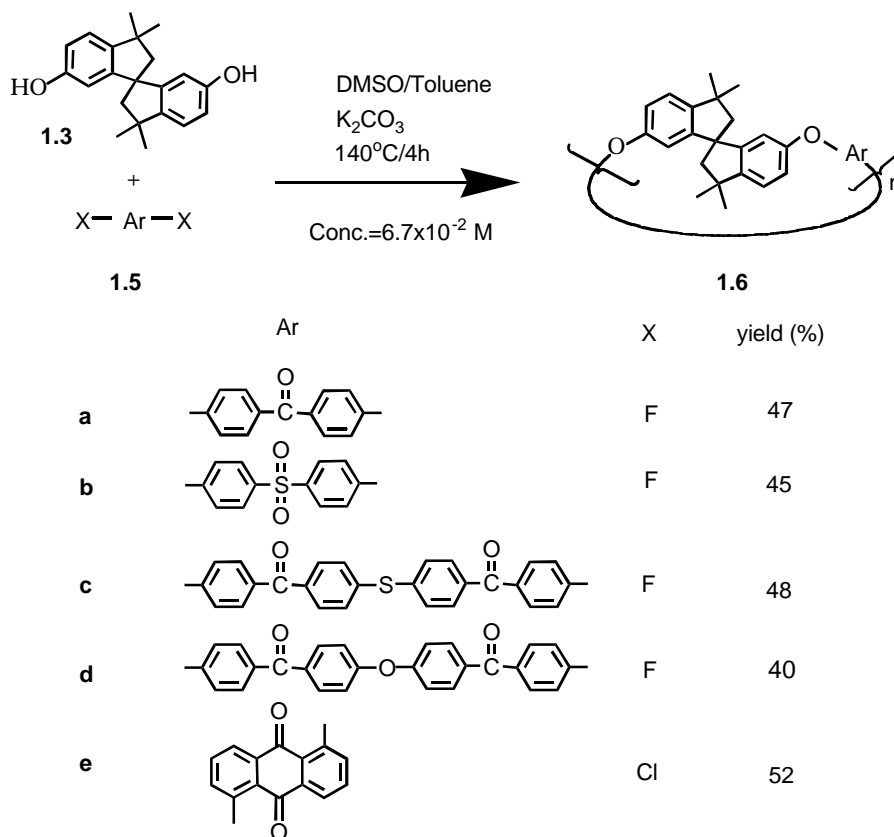
(b) Brunelle, D. J.; Shannon, T. G. *Makromol. Chem., Macromol. Symp.* **1991**, 42/43, 155.

¹⁹ (a) Johnson, R. N.; Farnham, A. G.; Clendinning, R. A.; Hale, W. F.; Merriam, C. L. *J. Poly. Sci., A-1*, **1967**, 5, 2375. (b) Attwood, T. E.; Newton, A. B.; Rose, J. B. *Br. Polym. J.* **1972**, 4, 391. (c) Rose, J. B. *Polymer* **1974**, 15, 456. (d) Farnham, A. G.; Robeson, L. M.; McGrath, J. E., *J. Appl. Poly. Sci., Symp.* **1975**, 26, 373. (e) Attwood, T. E.; Dawson, P. C.; Freeman, J. L.; Hoy, L. R. J.; Rose, J. B. *Polymer* **1981**, 22, 1096. (f) Viswanathan, R.; Johnson, B. C.; McGrath, J. E., *Polymer*, **1984**, 25, 1927. (g) Jurek, M. J.; McGrath, J. E., *Polymer (London)*, **1989**, 30, 1552.

sulfone, is the reactive site to induce the ring opening polymerization initiated by a nucleophile through an ether exchange reaction.

In 1989, Cella et al.²⁰, also from the GE Co., prepared aromatic cyclic(ether ketone) **1.6a**, **1.6d**, and **1.6e**, cyclic(ether thioether ketone) **1.6c**, and cyclic(ether sulfone) **1.6b** in moderate yields through aromatic nucleophilic substitution reactions of spirobiindane bisphenol **1.3** and various ketone or sulfone activated bishalides **1.5a-1.5e** under pseudo-high dilution conditions (Scheme 1.4). The reaction was stopped in 4 hours with a total feed of 6.7×10^{-2} M of the reactants, and the reaction temperature was controlled at 140°C. These cyclic mixtures were high melting crystalline solids, only sparingly soluble in common organic solvents. No melting points were specified in the report. Due to the high melting points, the ring opening polymerization of these cyclic ethers produced little success.²¹ Only the ether sulfone cyclics **1.6b** were reportedly polymerized at 380-400°C in the presence of 10 mol% of the disodium salt of bisphenol-A, providing a high molecular weight polymer (M_w 80,000).

Scheme 1.4

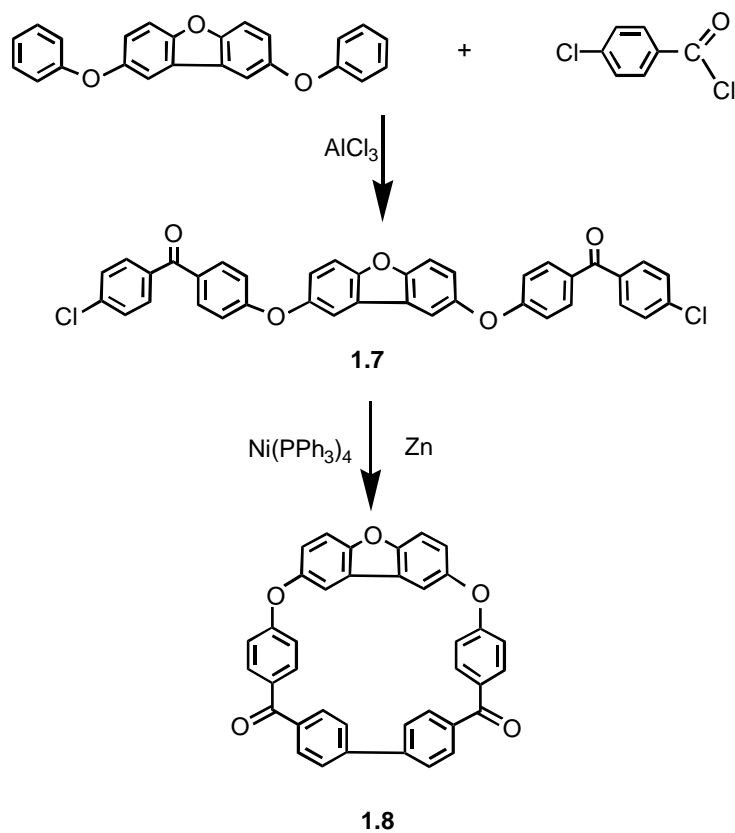


²⁰ Cella, J. A.; Talley, J. J.; Fukuyama, J. M. *Am. Chem. Soc. Div. Polym. Chem. Polym. Preprints*, **1989**, 30(2), 581.

²¹ Cella, J. A.; Fukuyama, J.; Guggenheim, T. L. *Am. Chem. Soc. Div. Polym. Chem. Polym. Preprints*, **1989**, 30(2), 142.

In 1990, Colquhoun et al. of ICI reported the synthesis of cyclic(aryl ether ketone)s by a nickel(0) catalyzed coupling reaction.⁶ Instead of obtaining a mixture of cyclic oligomers, they prepared a single sized cyclic monomer **1.8** through intramolecular coupling of bis(4-chlorobenzoyl)-terminated intermediate **1.7** to form a biaryl linkage under pseudo-high dilution conditions (Scheme 1.5). No details of the reaction conditions were given in the report. This macrocycle was obtained in 40% yield, despite high strain in the ring according to the single crystal X-ray structural analysis.

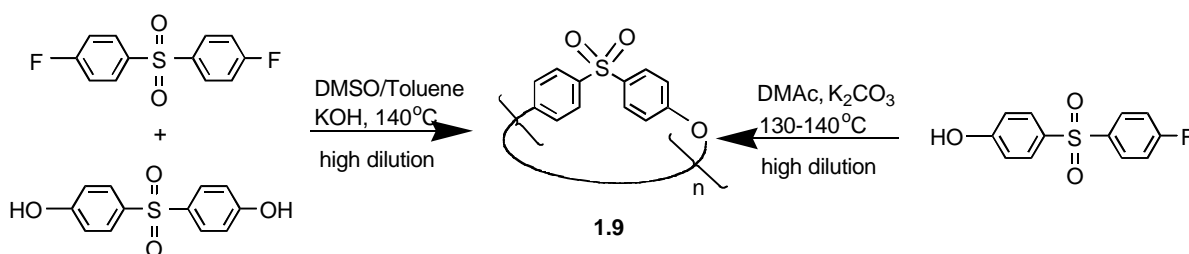
Scheme 1.5



Polymerization of the macrocycle by catalytic amounts (1-5 mol%) of cesium fluoride or the potassium salt of 4-hydroxybenzophenone at the melting point of the cyclic monomer (353°C) was found to be highly exothermic, consistent with the X-ray result, and was completed in 2-5 min. The resulting polymer was only partially soluble in sulfuric acid, which indicated a slight degree of crosslinking. Fully soluble polymer (inherent viscosity=0.4-0.7 dL/g) was obtained when 1-2 mol% of an end-capping reagent such as 4-(benzoyl)-4'-(4-fluorobenzoyl)biphenyl was used.

In 1991, Mullins et al. of the Dow Chemical Co. reported the synthesis of a cyclic(ether sulfone) **1.9** from 4,4'-difluorodiphenylsulfone and 4,4'-dihydroxydiphenylsulfone in 55% yield through an aromatic nucleophilic substitution reaction under pseudo-high dilution conditions (Scheme 1.6).²² They also reported an alternate method for the synthesis of the same cyclic mixture from 4-fluoro-4'-hydroxydiphenylsulfone.²³ The yield of **1.9** by the latter method was 40 to 75%. The reaction was typically carried out for 2 days with a total feed 6.0×10^{-2} M. The reaction temperature was controlled at 130-140°C. They found that at temperatures greater than 140°C, the cyclics underwent cleavage reactions through ether interchange, and the yield was reduced. Despite the fact that individual cyclics had extremely high melting points (trimer, 447°C, tetramer > 450°C) the mixture was amorphous and began to flow at ~250°C. Based on rheometry studies, the melt viscosity of the cyclic(ether sulfone) was found to be 1000 times lower than the linear poly(ether sulfone). Melt polymerization²³ of the cyclic(ether sulfone) at 300°C in the presence of cesium fluoride or cesium phenoxide yielded poly(ether sulfone) with M_w of 25,000 g/mol and M_n of 11,500 g/mol, comparable to those of ICI's Victrex 3600 poly(ether sulfone).

Scheme 1.6



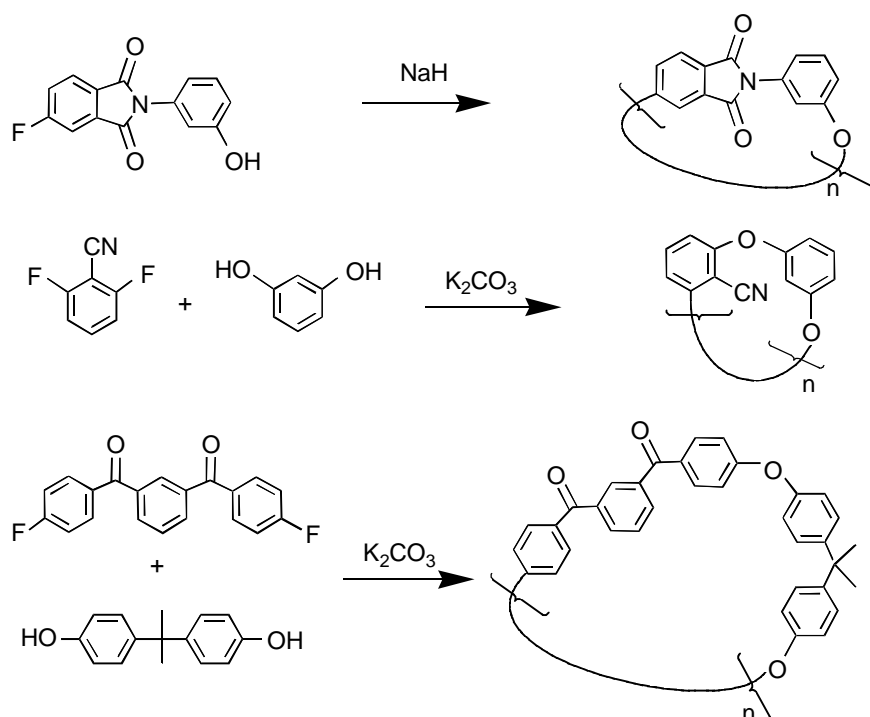
The techniques used to prepare ether sulfone cyclooligomers were applied to the syntheses of many other cyclooligomers by Mullins et al. (Scheme 1.7)^{5, 24}. These structures were chosen primarily for composite applications where high stiffness (modulus) and use temperatures are needed. In most cases the yields of cyclic oligomers were moderate, and purification such as by solvent extraction was required to obtain cyclic oligomers in high purity. Unfortunately, because of the stiff structures, the cyclic mixtures had poor solubility and extremely high melting temperatures, limiting either solution or melt ring opening polymerization.

²² Mullins, M. J.; Woo, E. P.; Chen, C. C.; Murray, D. J.; Bishop, M. T.; Balon, K. E. *Am. Chem. Soc. Div. Polym. Chem. Polym. Preprints*, **1991**, 32(2), 174.

²³ Mullins, M. J.; Galvan, R.; Bishop, M. T.; Woo, E. P.; Gorman, D. B.; Chamberlin, T. A. *Am. Chem. Soc. Div. Polym. Chem. Polym. Preprints*, **1992**, 33(1), 414.

²⁴ Mullins, M. J.; Woo, E. P., U.S. Patent 5,264,520 to Dow Chemical, 1993; Mullins, M. J.; Woo, E. P.; Balon, K. E.; Murray, D. J.; Chen, C. C., U.S. Patent 5,264, 538 to Dow Chemical, 1993.

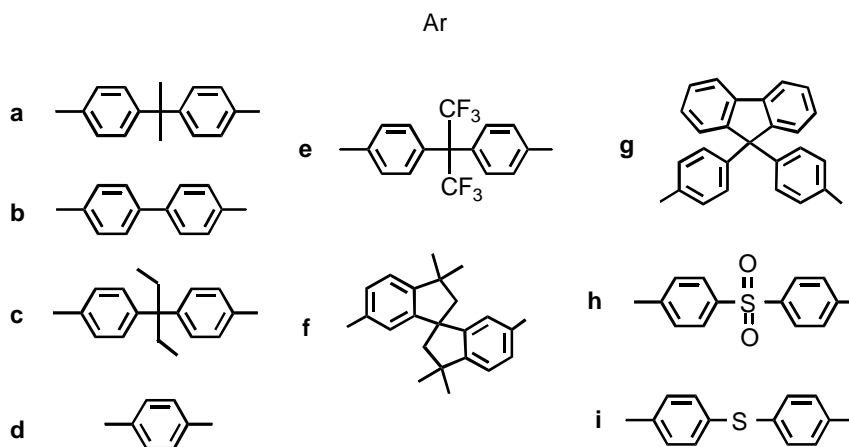
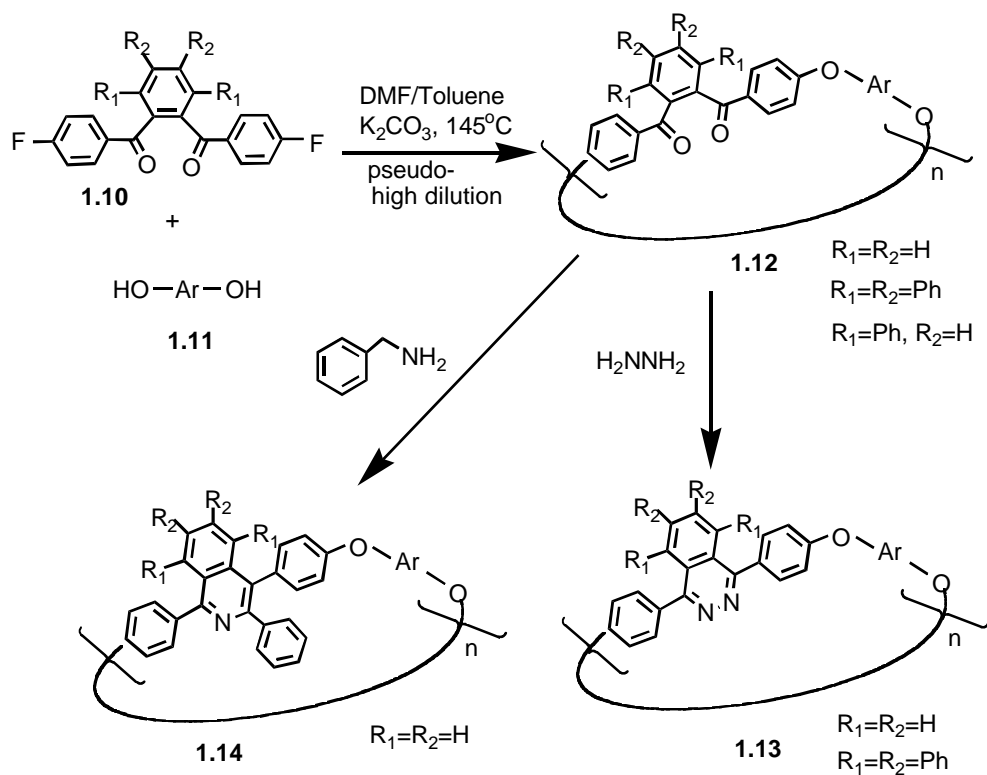
Scheme 1.7



The most recent work was seen in Hay et al.'s reports.²⁵ They prepared the cyclic(aryl ether)s **1.12a-1.12i**, all containing the 1,2-dibenzoylbenzene moiety, via aromatic nucleophilic substitution reactions (Scheme 1.8). Three high dilution techniques were used. A pseudo-high dilution condition was applied to most of these syntheses with a total feed 4.0×10^{-2} M. When spirobiindanediol **1.11f** was used, a batch-wise procedure was applied and a higher concentration was used (10×10^{-2} M),^{25b} since the spirobiindane-containing reactant is prone to cyclic formation, as has been shown before. The third high dilution technique was applied when the difluoride **1.10**, such as the tetraphenyl substituted difluoride with $R_1=R_2=Ph$, was poorly soluble in aprotic solvents such as DMF at room temperature so that slow addition through a syringe was not possible. In such a case, the high dilution was achieved by adding this reactant along with bisphenols (in solid form) in 10 small portions over 9 hours.^{25c} Typical reaction time was 16 hours, 8 hours for addition and 8 hours after addition. High yields (ranging from 55-95%, most above 80%) were obtained, which were attributed to the favorable conformation that the 1,2-dibenzoylbenzene moiety adopted to ring closures.

²⁵ (a) Chan, K. P.; Wang, Y.; Hay, A. S. *Macromolecules*, **1995**, *28*, 653. (b) Chan, K. P.; Wang, Y.; Hay, A. S.; Hronowski, X. L.; Cotter, R. J. *Macromolecules* **1995**, *28*, 6705-6717. (c) Ding, Y.; Hay, A. S. *Macromolecules* **1996**, *29*, 3090-3095.

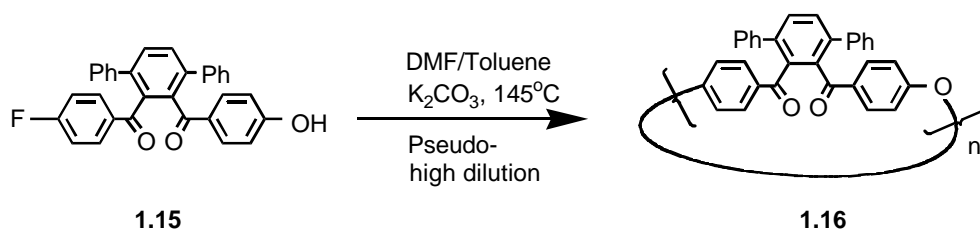
Scheme 1.8



Due to the “bent” structure of the 1,2-dibenzoylbenzene moiety, the cyclic mixtures **1.12** contained predominantly the dimers and trimers ($n=2$, $n=3$). As shown in Scheme 1.9, directly using AB-type monomer **1.15** provided 55% of cyclic dimer (**1.16**, $n=2$) out of total 80% isolated yield. Most mixtures were crystalline with high T_m , although the corresponding linear polymers are amorphous. Some melting points were close to the degradation temperatures of the cyclic

mixtures, thus limiting the application of ring opening polymerization. To overcome these problem they mixed two different bishalides **1.10** with $R_1=R_2=H$ and $R_1=H, R_2=Ph$ respectively to react with one bisphenol, forming random cocyclic mixtures.^{25b} These cocyclic mixtures were of amorphous nature and had relative low softening points. The compositions of the cyclic mixtures were characterized by GPC and HPLC, and MALDI-TOF mass spectrometry gave direct confirmation of the cyclic nature of the mixtures.

Scheme 1.9



Converting the ketone to the corresponding phthalazine **1.13** and isoquinolines **1.14** (Scheme 1.8) by treating them with hydrazine and benzylamine, respectively, yielded insoluble and infusible cyclics.

Rheological studies²⁶ showed that cyclic(aryl ether ketone)s were thermally stable in the melt, and their melt viscosities were several orders of magnitude lower than their high molecular weight linear counterparts. The molten cyclic oligomers behave like Newtonian fluids at shear rates above 10 s^{-1} . The cyclic(aryl ether thioether ketone)s, such as **1.12i**, were thermally unstable in the melt due to free radical ring opening polymerization initiated by thiyl radicals generated *in situ* in the melt. One evidence was that the rate of change in viscosity increased with temperatures and was promoted by the addition of a catalytic amount of elemental sulfur or a disulfide such as 2,2-dithiobis(benzothiazole) (DTB). The free radical nature of the polymerization was further confirmed by electron paramagnetic resonance spectroscopy (EPR).²⁷

Wang et al.²⁸ did fundamental studies of the ring opening polymerization of cyclic(aryl ether ketone) **1.12a** both in the melt and in the solution. They found that potassium carbonate was surprisingly an excellent initiator for the ROP through ether exchange reaction, but produced higher levels of crosslinked polymers, compared to other initiators, such as cesium fluoride, and alkali phenoxides. In the melt ROP, the polymerization reaction rate decreased in the order of $\text{K}^+ > \text{Na}^+ > \text{Cs}^+$, using alkali phenoxides as initiators, whereas in the solution polymerization in an aprotic solvent, Cs^+ was the most efficient counterion. Alkali salts of bisphenols were more efficient initiators than those of monophenols. High molecular weight polymers were obtained; however, a certain amount of cyclics remained in the polymer according to GPC traces. The

²⁶ Wang, Y.; Chan, K. P.; Hay, A. S. *J. Appl. Polym. Sci.* **1996**, *59*, 831-843.

²⁷ Wang, Y.; Chan, K. P.; Hay, A. S. *Macromolecules.* **1996**, *29*, 3717-3726.

²⁸ Wang, Y.; Chan, K. P.; Hay, A. S. *J. Polym. Sci.: Part A: Polym. Chem.* **1996**, *34*, 375-385.

unreacted cyclics mostly were low molecular weight cyclics, presumably resulting from crystallization upon heating due to their high melting points. Crosslinking was significant, increased with temperature, time and amount of initiator, though its mechanism was not indicated. The solution polymerization of the cyclic mixture using the dipotassium salt of 4,4'-biphenol indicated that the molecular weight (M_n) of the polymer was almost independent of the conversion and time, implying a chain type polymerization mechanism. It was also found that in the solution polymerization, a chain transfer agent, such as an linear oligomeric aryl ether sulfone, could regulate the molecular weight of polymer but led to lower conversions.

The free radical polymerization of cyclic(arylene ether thioether ketone)s, such as **1.12i**, was also investigated by Wang et al.²⁷ The polymerization can be effectively initiated by a catalytic amount of elemental sulfur or a disulfide such as 2,2-dithiobis(benzothiazole) (DTB) through the thioether linkage. It was found that in the free radical ROP, the molecular weight of the polymers obtained increased with conversion, different from the ether exchange mechanism.

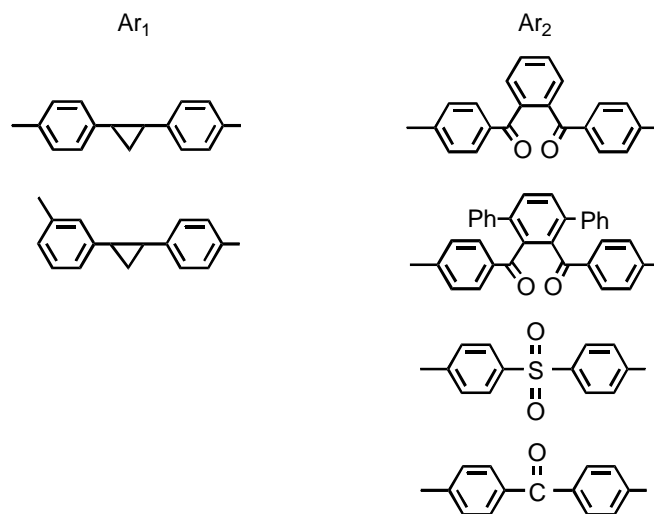
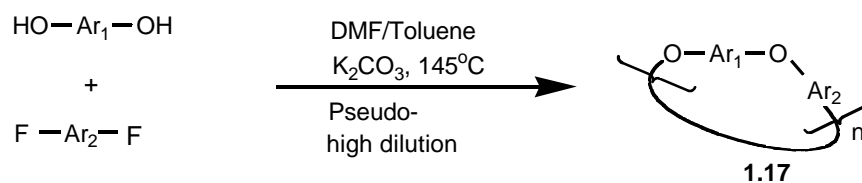
1.2.3 Crosslinkable cyclic(arylene ether)s

To produce crosslinked poly(arylene ether)s with increased solvent resistance and thermal stability by the ring opening polymerization technique, Hay et al. prepared cyclic(arylene ether)s containing crosslinkable *trans*-1,2-diphenylcyclopropane (Scheme 1.10)²⁹ or diphenylacetylene (Scheme 1.11)³⁰ via aromatic nucleophilic substitution reaction. These cyclic mixtures **1.17** and **1.18** were obtained in high yields using the procedure developed above. Most of the cyclic mixtures were crystalline and crosslinked through the cyclopropane and the acetylene moieties upon melting, with moderate increases in T_g . In the presence of an anionic initiator, the ring opening polymerization through ether exchange and the crosslinking occurred simultaneously to give tough crosslinked polymers which showed no observable swelling in chloroform.

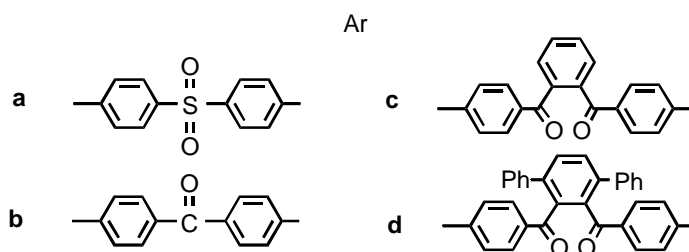
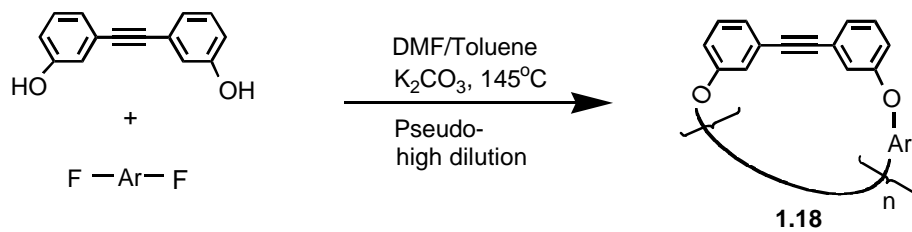
²⁹ Gao, C.; Hay, A. S. *Polymer*, **1995**, 36(21), 4141-6.

³⁰ Wang, Y.; Paventi, M.; Hay, A. S. *Am. Chem. Soc. Div. Polym. Chem. Polym. Preprints*, **1995**, 36(2), 128-9.

Scheme 1.10



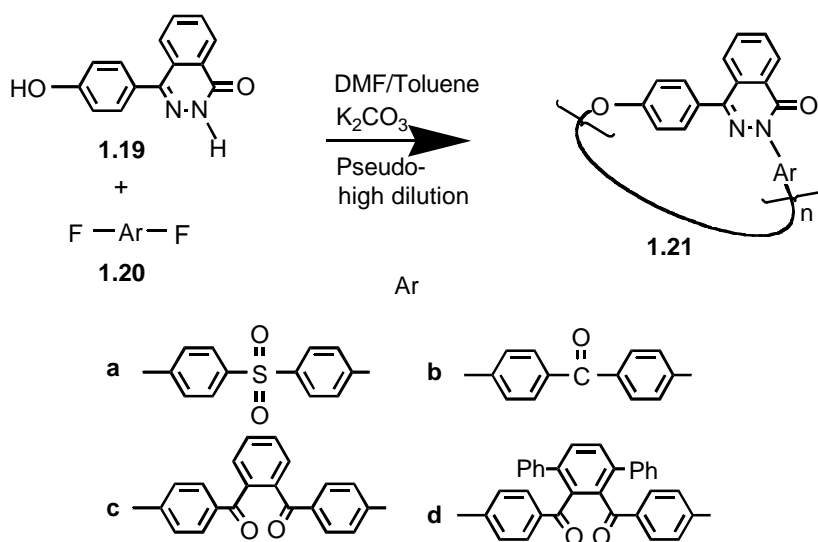
Scheme 1.11



1.2.4 Cyclic(arylene ether)s containing a heterocyclic ring group

The cyclic mixtures containing a phthalazinone heterocyclic moiety were synthesized through aromatic nucleophilic reactions of 1,2-dihydro-4-(4-hydroxyphenyl)(2H)phthalazin-1-one (**1.19**) and various difluorides **1.20a-1.20d** (Scheme 1.12) for production of heterocyclic polymers which have high glass transition temperatures.³¹ Since the structure of (**1.19**) can easily adapt to a conformation which favors the cyclization, yields above 94% were obtained even though the total feed was relatively high, about 10^{-1} M. This favorable conformation, however, led to high contents of cyclic dimers in the mixtures (>56%, for **1.21c** and **1.21d**), resulting in crystalline cyclic mixtures with melting points above 410°C. Thus, melt polymerization was not feasible. Accordingly, random cocyclic mixtures were prepared to produce amorphous cyclic oligomers which have relatively low softening points.

Scheme 1.12



1.2.5 Cyclic(sulfide)s

Hay et al. also reported cyclic oligomers for production of semicrystalline sulfide polymers.^{32,33,34} The first approach to the sulfide cyclic oligomers was accomplished in two steps (Scheme 1.13).³² First, cyclic sulfoxide oligomers **1.24** were prepared by an aromatic nucleophilic substitution reaction of the potassium salt of the bithiophenol N-propylcarbamates **1.22** and 4,4'-difluorodiphenyl sulfoxide **1.23** under high dilution conditions. The sulfoxide was then reduced quantitatively to the sulfide **1.25** with oxalyl chloride and tetrabutylammonium

³¹ Wang, Y.; Paventi, M.; Chan, K. P.; Hay, A. S. *J. Polym. Sci.: Part A: Polym. Chem.* **1996**, *34*, 2135-2148.

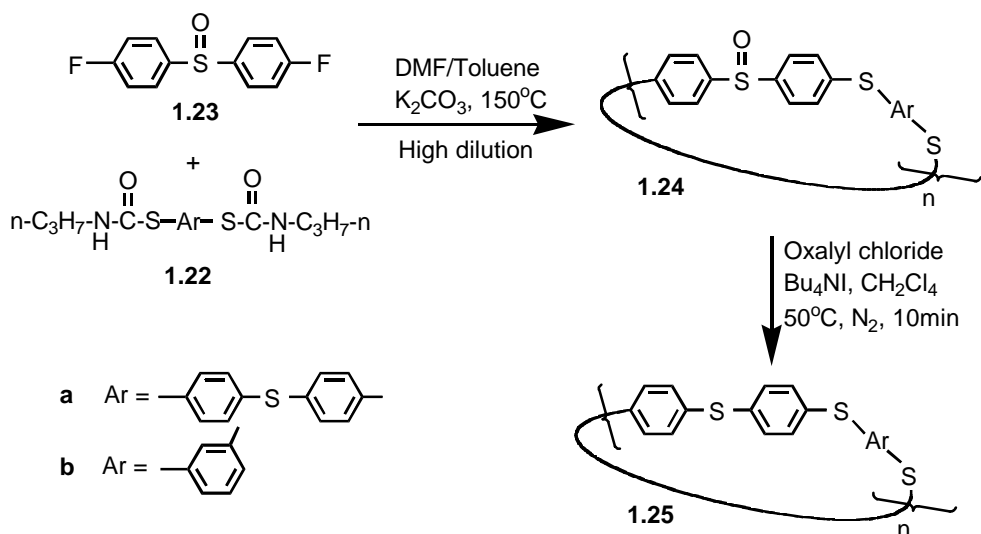
³² Wang, Y.; Hay, A. S. *Macromolecules*, **1996**, *29*, 5050-3.

³³ Wang, Y.-F.; Chan, K. P.; Hay, A. S. *Macromolecules*, **1995**, *28*, 6371.

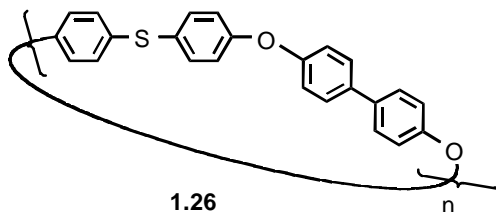
³⁴ Ding, Y.; Hay, A. S. *Macromolecules* **1996**, *29*, 4811-4812.

iodide. Both sulfoxide and sulfide cyclics were obtained in “quantitative” yields and were crystalline materials. **1.25a** was not soluble whereas **1.25b** was soluble due to its meta linkages. Both sulfide cyclics were polymerized through free radical polymerization in the presence of a catalytic amount of sulfur to form high molecular weight polymers.

Scheme 1.13

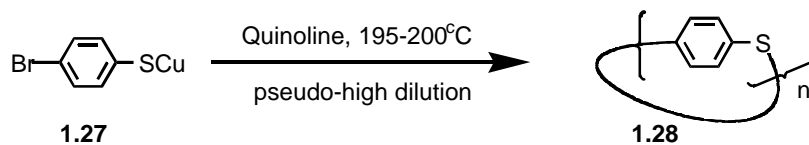


A similar reaction³³ led to cyclic(ether thioether) **1.26** starting from 4,4'-biphenol instead of bithiophenol N-propylcarbamates **1.22**. **1.26** was a crystalline material. The melt polymerization at 350°C in the presence of 1.0 mol% of 2,2'-dithiobis(benzothiazol) (DTB) in N₂ resulted in a tough and insoluble polymer with T_g of 150°C and a T_m of 313°C, which is comparable with those reported for the polymer.

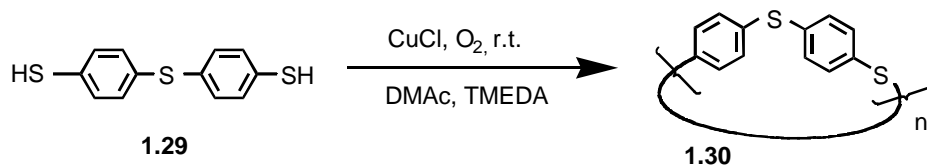


The second approach to sulfide cyclics was by coupling of copper(I) 4-bromobenzenethiolate (**1.27**) (Scheme 1.14)³³ and by reactive coupling of 4,4'-thiobisbenzenethiol (**1.29**) (Scheme 1.15)³⁴, respectively. Free radical polymerization of **1.28** in the presence of 1.0 mol% DTB at 340°C under N₂ led to the formation of poly(1,4-phenylene sulfide) (PPS) which had a T_m of 281°C. Thermal polymerization of **1.30** with p-dihalobenzene also gave linear PPS polymer of T_m 275°C.

Scheme 1.14



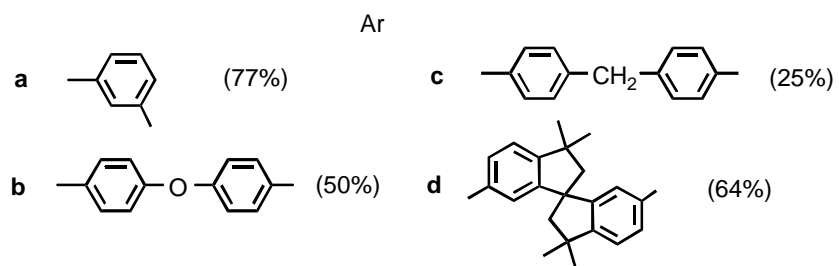
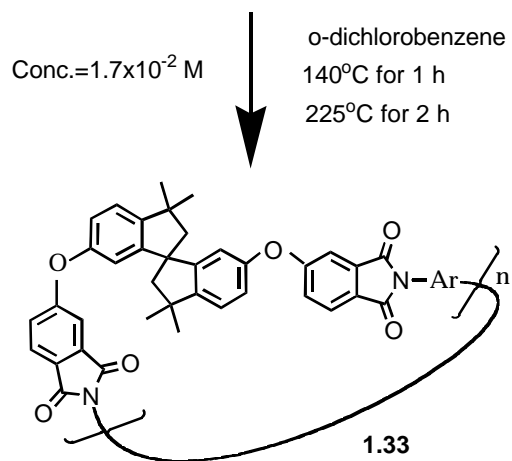
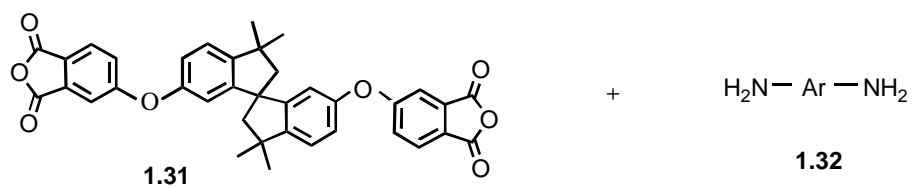
Scheme 1.15



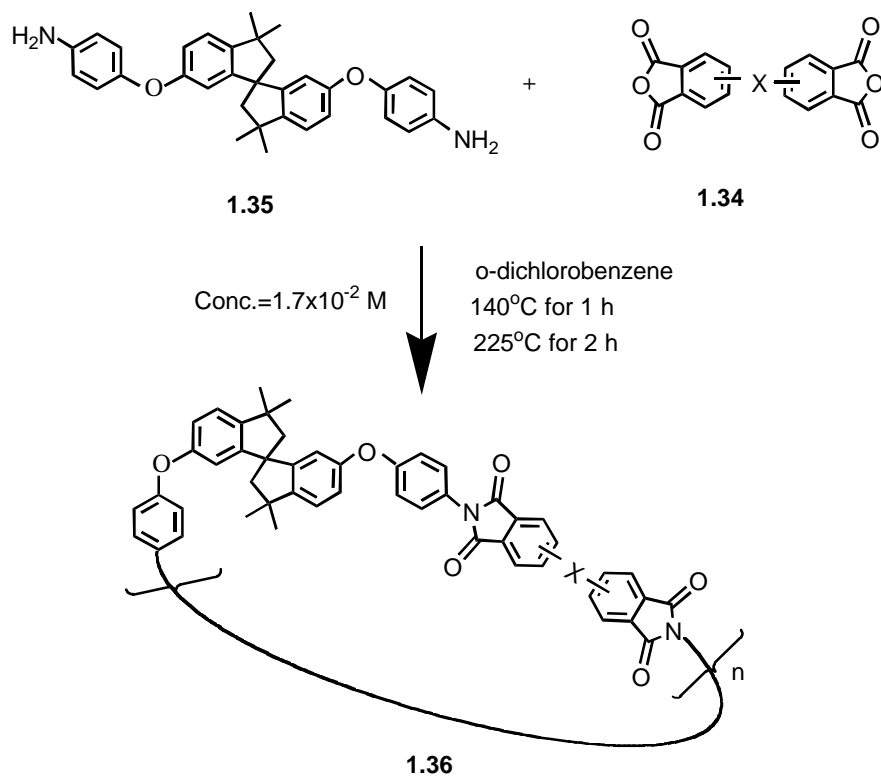
1.2.6 Cyclic(ether imide)s

Various cyclic(ether imide)s **1.33a-d** and **1.36a-f** were reported by Cella et al.²⁰ These cyclic mixtures were prepared by an imidization reaction between a spirobiindane-containing dianhydride **1.31** and various diamines **1.32a-d** (Scheme 1.16) or between various dianhydrides **1.34a-f** and a spirobiindane containing diamine **1.35** (Scheme 1.17). In these syntheses, reactants were slowly injected into a reaction vessel over a period of one hour at 140°C followed by an additional reaction time of two hours at 225°C, with a total feed 1.7×10^{-2} M. The yields were moderate. They were all crystalline solids with high melting points, only sparingly soluble in common organic solvents. No melting points was specified in this report; but in another paper²¹, it was reported that cyclic mixtures **1.36c** and **1.36d** had no melting points up to 450°C by DSC and were insoluble in all solvents. Due to the fact that they were infusible and insoluble, the study of polymerization was limited. However, model scrambling reactions of linear oligomeric(ether/thioether imide)s showed that cyclic(ether/thioether imide)s can be polymerized by ring opening through ether/thioether exchange initiated by various nucleophiles

Scheme 1.16



Scheme 1.17

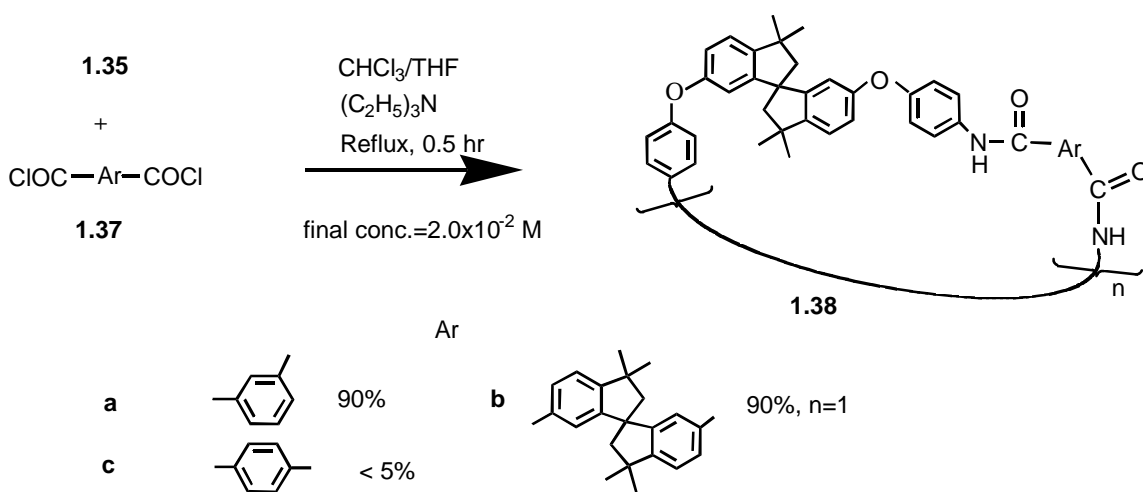


	X		yield (%)
a	—O—	(4,4)	40
b	—O—	(3,3)	30
c	—S—	(4,4)	40
d	—S—	(3,3)	75
e		(4,4)	45
f		(4,4)	40

1.2.7 Cyclic(aramide)s

The cyclic aramides **1.38a-c** were prepared via reaction of various diacid chlorides **1.37a-c** with spirobiindane-containing diamine **1.35** under pseudo-high dilution conditions with a total feed 2×10^{-2} M (Scheme 1.18).³⁵ The yield of **1.38a** was about 90%. The tendency for cyclization with spirobiindane containing diacid chloride **1.37c** was so great that 1+1 cyclic adduct ($n=1$) was isolated in 90% yield, whereas the reaction with terephthaloyl dichloride **1.37b** only gave less than 5% yield. No melting points were specified. The ring opening polymerization both in solution and in the melt in the presence of catalytic amounts of sodium hydride or tetrabutylammonium tetraphenylborate obtained little success due to significant decomposition. However, it was found that **1.38a** could be copolymerized with caprolactam using sodium hydride as catalyst, giving $M_n=20,000$

Scheme 1.18



1.2.8 Cyclic(ester)s

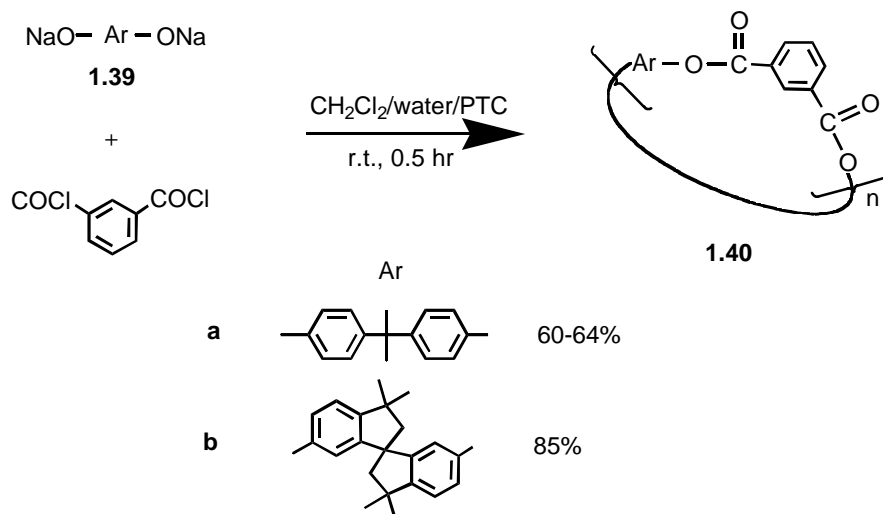
Guggenheim et al. reported cyclic(ester)s **1.40a-b**, prepared through interfacial reaction of bisphenol sodium salts **1.39a-b** and isophthaloyl dichloride (Scheme 1.19).³⁶ The reaction with spirobiindane bisphenol sodium salt **1.39b** provided the cyclic mixture in 85% yield, whereas with **1.39a**, only 65% was obtained. The reaction of **1.39a-b** and terephthaloyl dichloride under identical conditions gave much lower yields, 5% and 50% respectively. The higher yield of cyclics obtained using isophthaloyl dichloride and reactants containing the spirobiindane skeleton

³⁵ Guggenheim, T. L.; McCormick, S. J.; Guiles, J. W.; Colley, A. M. *Am. Chem. Soc. Div. Polym. Chem. Polym. Preprints*, **1989**, 30(2), 138.

³⁶ Guggenheim, T. L.; McCormick, S. J.; Kelly, J., J.; Brunelle, D. J.; Colley, A. M.; Boden, E. P.; Shannon, T. G. *Am. Chem. Soc. Div. Polym. Chem. Polym. Preprints*, **1989**, 30(2), 579.

is another manifestation of the geometry effect on cyclization. No ring opening polymerization of these cyclic mixture was reported.

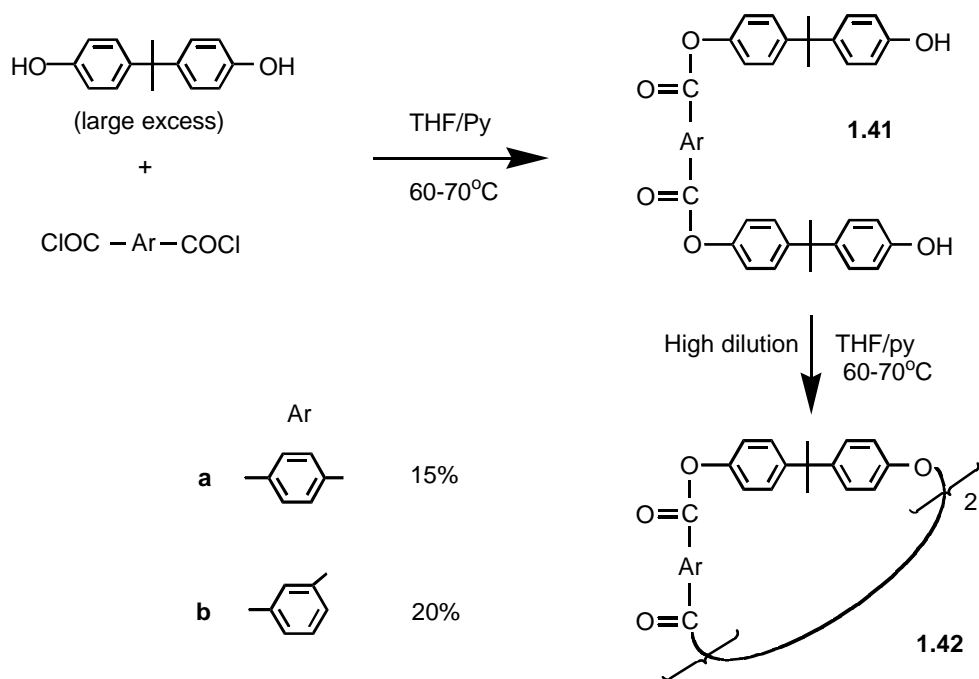
Scheme 1.19



Gibson et al. prepared biphenol-A based cyclic(ester)s through esterification of iso-, or tere-phthaloyl dichloride and bisphenol-A (BPA) in THF with pyridine as base.³⁷ A one step method was applied to synthesize cyclic mixtures directly from BPA and the diacid dichlorides, which gave 64% yield of tere-linked cyclic mixture, and 34% yield of iso-linked cyclic mixture. The two step method involved an oligomeric intermediate bisphenol **1.41a-b** (Scheme 1.20), aimed at obtaining single sized cyclic esters **1.42a-b** in high yields by condensation of **1.41a-b** with the acid chlorides. The yield of **1.42a** was 15%, whereas the yield of **1.42b** was 20%. No information about those cyclics, such as melting points, solubility, were specified. Also, no ring opening polymerization was reported.

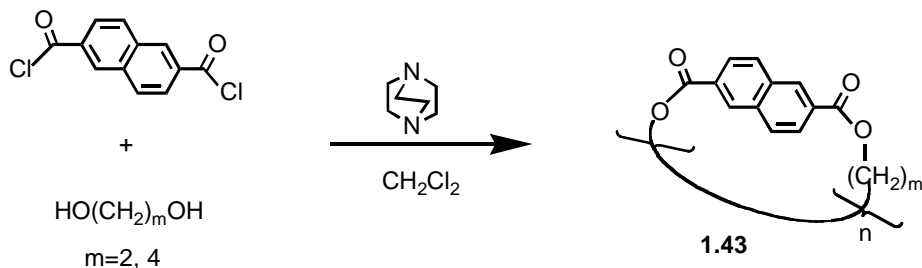
³⁷ Gibson, H. W.; Ganguly, S.; Yamaguchi, N.; Xie, D.; Chen, M.; Bheda, M.; Miller, P. *Am. Chem. Soc. Div. Polym. Chem. Polym. Preprints*, **1993**, 34(1), 576-7.

Scheme 1.20



Most recently, Brittain et al.³⁸ reported cyclic(ester)s as precursors of poly(ethylene naphthalate) (PEN) and poly(butylene naphthalate) (PBN). These cyclic(ester)s were prepared by reaction of 2,6-naphthalenedicarbonyl chloride with ethylene glycol or butanediol using diazabicyclo[2,2,2]octane catalyst under pseudo-high dilution conditions (Scheme 1.21). The reaction proceeded in 30 minutes with a total feed 2.5×10^{-2} M. The cyclic(ethylene naphthalate) mixture (1.43, $m=2$) was obtained in 57% yield, and the cyclic(butylene naphthalate) mixture (1.43, $m=4$) in 75%.

Scheme 1.21



³⁸ (a). Hubbard P.; Brittain, W. J. *Am. Chem. Soc. Div. Polym. Chem. Polym. Preprints*, **1995**, 36(2), 136-7; b) Hubbard P.; Brittain, W. J. *Am. Chem. Soc. Div. Polym. Chem. Polym. Preprints*, **1996**, 37(1), 238-9.

The ring opening polymerization was initiated by a transesterification initiator, such as dibutyl tin oxide. The resultant polymers had reduced solubilities in THF and increased viscosities. However, the inherent viscosity measured for the PEN polymer obtained from **1.43**, $m=2$ was 0.24 dL/g, and for the PBN polymer obtained from **1.43**, $m=4$ was 0.28 dL/g, significantly lower than those of commercial PEN and PBN polymers from AMOCO.

1.3 Summary and Conclusions

A wide variety of aromatic macrocycles, such as cyclic carbonates, aryl ethers, esters, aramides, ether imides and sulfides, have been successfully synthesized in good to excellent yields. These macrocycles can be used for production of various engineering thermoplastics. Some limited ROP studies have shown that high molecular weight polymers can be produced from the macrocycles by ROP in the presence of an initiating species, with ring-chain equilibrium much more favorable towards linear polymers. Because of the large ring size and lack of ring strain, the polymerization reactions are nearly thermoneutral, and are mainly driven by entropy.

Except in two cases^{6,37} the aromatic macrocycles prepared were all cyclic oligomeric mixtures of various ring sizes. The commercially attractive advantage of using cyclic mixtures is that they have relatively low melting points. One major disadvantage to the use of such complex mixtures, however, is the difficulty of removing low levels of linear oligomers or polymers. Control of the ROP is hard to achieve when linear molecules are present, because these linear species can function as initiators or chain transfer agents in the polymerization. Furthermore, individual small ring sized cyclics in the mixture are often highly crystalline with very high melting points despite the fact that the cyclic mixture is amorphous with relatively low softening points. The small cyclics tend to crystallize during the polymerization at reaction temperatures lower than their melting points, thus leading to a mixture of polymer and residual crystalline cyclics.

Chapter 2

Research Objectives and Scope

The objectives of this research are syntheses of engineering thermoplastics using single sized, pure aromatic macrocycles as monomers by the ring opening polymerization technique. Chapters 3-5 describe the synthesis of single sized cyclic monomers of ring sizes ranging from 30 to 55 atoms, in which unsymmetric macrocycles are the major focus (Chapter 4) due to their relatively low melting points. Chapter 6 describes the synthesis of oligomeric cyclic mixtures of average ring sizes ranging from 100 to 160 atoms. Chapter 7 describes the detailed studies of ROP of those cyclic monomers, in which the ROP of single sized macrocycles is the major focus. The synthesis and ROP of the cyclic oligomeric mixtures are the comparison studies.

Chapter 3

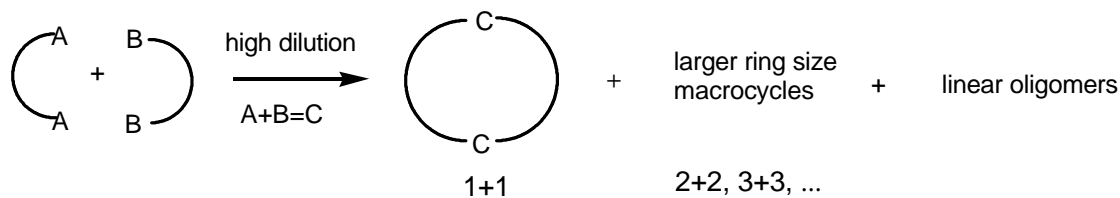
A Bisphenol-A Based 40-Membered Cyclic Arylene Ether Sulfone: Improved Synthesis and Properties¹

3.1 Introduction

The titled 40-membered cyclic arylene ether sulfone (**3.4**, $n=1$ Scheme 3.2) was the first single-sized aromatic macrocycle that we synthesized in an attempt to prepare a bisphenol-A based poly(arylene ether sulfone) by ring opening polymerization. High yield synthesis of the cyclic monomers is important in practical applications of the ring opening polymerization method. The previous preparation,² however, only provided the macrocycle in 11% yield. The purity and the amorphous nature of the reported macrocycle were also doubtful. These prompted us to re-examine the synthesis. This chapter describes the improved synthesis and properties of the macrocycle. Although the macrocycle is not suitable for the ring opening polymerization due to its high melting point ($\sim 500^\circ\text{C}$) near the degradation temperature, the detailed study of the effects of the degree of dilution, the reactivity of the dihalide, and the bisphenolate counterion on cyclization in the synthesis has served as a guide to syntheses of other macrocycles described in the following chapters.

3.2 Results and Discussion

As stated in Chapter 1, the basic principle in the synthesis of macrocycles is the use of high dilution conditions³ under which the first order intramolecular cyclization will be favored relative to the second order intermolecular polycondensation. Our general approach to the synthesis of single sized macrocycles was through joining two homofunctional pieces (A-A and B-B) together to form a 1+1 macrocycle under high dilution conditions. As depicted below, formation of 1+1 macrocycle is always in competition with formation of other larger ring sized macrocycles.



Although the probability of formation of the 1+1 macrocycle is the highest among all the macrocycles because of the favorable entropic effect for the ring closure, a high yield can only be obtained if the ring strain of this smallest macrocycle is low. Aromatic macrocycles are rigid, thus necessitating that long linear precursors, A-A and/or B-B, be used, so that the ring size will be large enough to avoid ring strain in the 1+1 macrocycle. Use of linear precursors with suitable lengths is our strategy to synthesize pure single sized, i.e., 1+1, macrocycles in good yields. In

¹ Xie, D.; Gibson, H. W. *Macromol. Chem. Phys.* **1996**, *197*, 2133-2148.

² Ganguly, S.; Gibson, H. W. *Macromolecules*, **1993**, *26*, 2408.

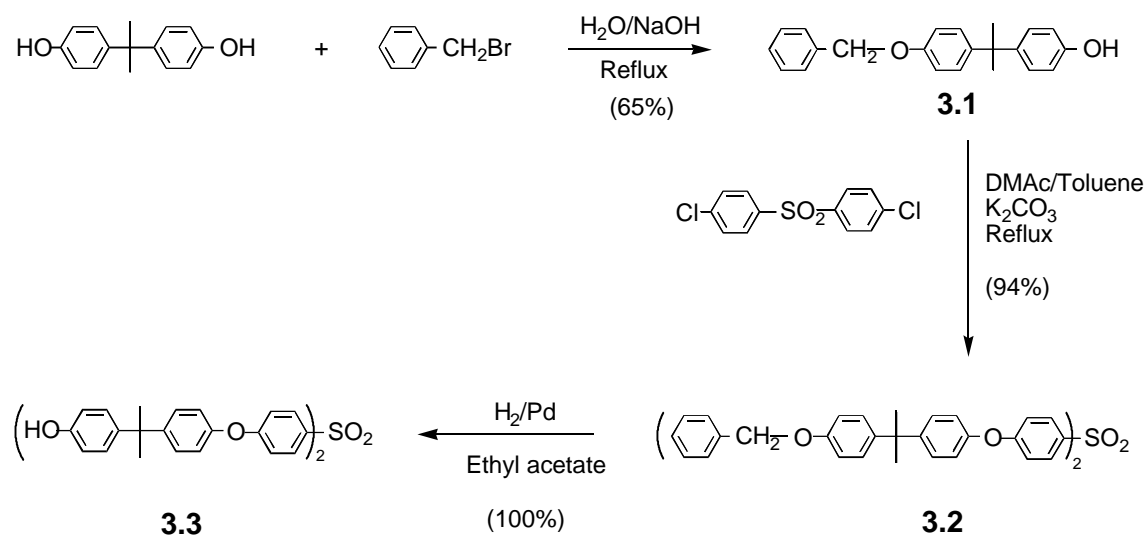
³ See refs. 12 and 13 in Chapter 1.

this study, the titled macrocycle (**3.4**, $n=1$, Scheme 3.2) was synthesized by condensation of a linear bisphenol **3.3** and a dihalodiphenyl sulfone through aromatic nucleophilic substitution reaction under high dilution conditions (Scheme 3.2). The long linear bisphenol containing the diphenyl sulfone moiety was prepared in three steps (Scheme 3.1).

3.2.1 Synthesis of linear bisphenol precursor **3.3**

One important factor for the high yield synthesis of macrocycles using A-A and B-B starting compounds is the maintenance of correct stoichiometries of the reactants⁴; this requires that they be highly pure. Following a reported one step procedure to prepare the linear precursor **3.3**,² reaction of a large excess (20 eq.) of bisphenol-A with 4,4'-dichlorodiphenyl sulfone produced a complex mixture that was difficult to purify. In order to obtain pure **3.3**, a three step synthetic scheme was designed, as shown in Scheme 3.1.

Scheme 3.1



In the first step, bisphenol-A was mono-protected by reaction with benzyl bromide in aqueous basic solution to form **3.1**. The only side reaction in this synthesis was the formation of the dibenzyl ether, which was easily removed by washing with hexanes. Further recrystallization provided pure compound **3.1** in 65% yield. This monophenol was then subjected to a normal aromatic nucleophilic substitution reaction with 4,4'-dichlorodiphenyl sulfone to afford pure **3.2** in 94% yield. Deprotection in the presence of a catalytic amount of palladium under a hydrogen pressure of 60 psi quantitatively converted **3.2** to the linear bisphenolic precursor **3.3**. The products in the first two steps were easily purified, which ensured the purity of **3.3**. This compound softened in a broad range from 94.5-108.4°C by capillary melting point measurements. Differential scanning calorimetry indicated that the compound exhibited a distinct glass transition

⁴ See ref. 5 in Chapter 1.

at 71°C, as well as crystallization at 141°C and melting at 183°C (peak maxima); the cooling after the melt, however, did not lead to recrystallization of the sample, as shown in Figure 3.1. The reluctance to crystallize was also observed in various solvent systems such as toluene/hexane, ethyl acetate/hexane, acetic acid/water, and methanol/water, in which **3.3** gave only a viscous oil.

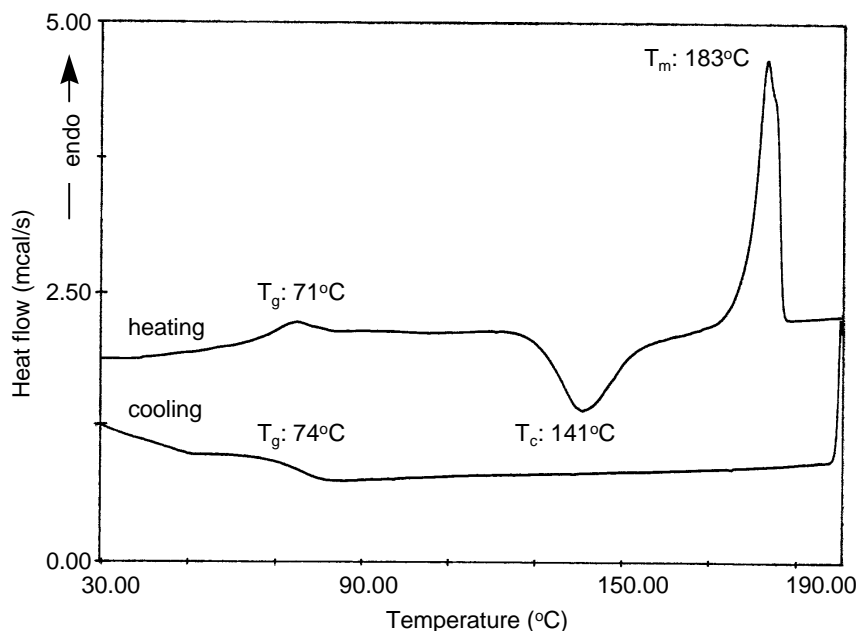


Figure 3.1 DSC (heating and cooling rates, 10°C/min) curves of linear precursor **3.3**

3.2.2 Cyclization

The synthesis of macrocycle **3.4**, $n=1$ was accomplished by condensation of **3.3** and a dihalodiphenyl sulfone via aromatic nucleophilic substitution reaction under pseudo-high dilution conditions (Scheme 3.2). Of the two high dilution techniques,³ batch-wise and pseudo-high dilution, discussed in Chapter 1, the pseudo-high dilution technique or the influxion procedure is practically more valuable in preparative syntheses, where the reactants are introduced slowly into the reaction medium at such a rate that low concentrations of reacting end groups are maintained. In this manner, the quantity of solvents used is minimized. The critical reaction parameter for the pseudo-high dilution procedure is the rate of feed v_f ,⁵ which is calculated as the molar amount of each reactant divided by the total addition time and the volume of solvent including one-half of the volume of solvent in which the reactants are dissolved.⁶ To keep steadily low concentrations of reactive end groups, v_f must be adjusted to make it comparable to or less than the rate of consumption of the reactive end groups to form unreactive macrocycles. However a theoretical

⁵ See ref. 12(b) in Chapter 1.

⁶ See ref. 15 in Chapter 1.

approach to find a mathematical description of the critical v_f where cyclization is dominant is not a trivial task. A general rule of thumb is that the smaller the v_f , the higher yield of the macrocycle will be.

Scheme 3.2

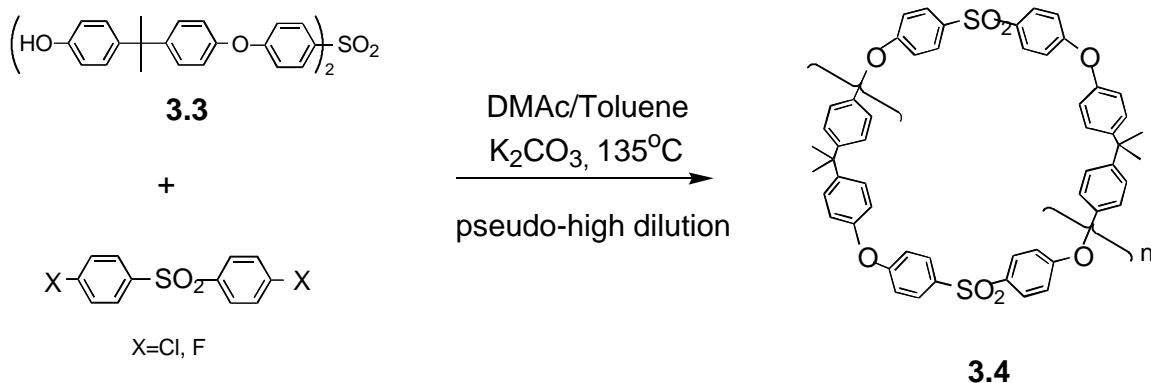


Table 3.1 Effects of feed rate (v_f), total feed (c_f), reactivity of monomers, and cesium ions on the yield of macrocycle **3.4**, $n=1$ according to Scheme 3.2.

exp	base	leaving group	$10^7 \cdot v_f^a$ (mol/L/sec)	$10^2 \cdot c_f^b$ (mol/L)	yield (%)
1	K_2CO_3	Cl	1.2	1.6	44
2	K_2CO_3	Cl	1.8	1.6	32
3	K_2CO_3	Cl	1.2	2.3	25
4	K_2CO_3	F	1.2	1.6	67
5	Cs_2CO_3	Cl	1.1	1.4	38

a) The rate of feed, calculated as the molar amount of each reactant divided by the total addition time and the volume of solvent including one-half of volume of solvent where the reactant are dissolved. b) The total feed, calculated as the result of v_f multiplied by the total addition time.

It can be seen from Table 3.1 that a lower yield, 32%, in Exp.2 was obtained at the higher v_f of 1.8×10^{-7} mol/L/sec (a lower dilution condition), and a higher yield, 44% in Exp. 1 at the lower v_f of 1.2×10^{-7} mol/L/sec (a higher dilution condition). Further increases in yield could be achieved if the v_f were decreased more at the expense of a longer addition time or a larger quantity of solvent. Use of more reactive substrates can produce macrocycles in higher yields at a given v_f due to the fact that a fast reaction system leads to lower concentrations of reactive end groups. For example, 4,4'-difluorodiphenyl sulfone is more reactive than 4,4'-dichlorodiphenyl sulfone in aromatic nucleophilic substitution with phenoxide, because of the greater electrophilicity of the aromatic carbon atom which is attached to the more highly electronegative

fluorine atom. Thus, a higher yield, 67%, was obtained using the fluorinated monomer (Exp.4), an increase of 23% compared to Exp.1 using the chlorinated monomer.

Another reaction parameter is the total feed c_f ($= v_f$ times the total addition time). When the rate of feed v_f is faster than the rate of consumption of reactants, the concentration of reacting groups will increase during the course of addition. In this case the yield of macrocycles will be lowered at a higher c_f (keeping the v_f at the same value), because more and more linear oligomers will be competitively produced under the less and less diluted conditions, especially in the later part of the addition. The effect of c_f on cyclization can be seen from Exps. 1 & 3 in Table 3.1. Thus, at a given v_f , the larger the c_f , the lower the yield. This may indicate that the experimental v_f is not optimal. However, a decrease in v_f will cost a longer reaction time and/or a larger volume of solvents.

The possibility of a favorable cesium effect on the formation of cyclics was also investigated. The utilization of cesium salts in macrocyclization reactions often has the advantage of high yields, or synthesis of compounds not otherwise available, as indicated in Vögtle et al.'s review.⁷ The true mechanism of the cesium effect is not clearly understood; there are many interpretations^{6, 7}. In dipolar aprotic solvents, such as DMSO and DMF, the cesium effect is explained by solubility and ion pair effects,⁸ which attribute the favored intramolecular course of cyclization reactions with cesium cations solely to the presence of solvent separated ion pairs, forming reactive anions, and to the high solubility of the organic cesium salts. In the cases that contact ion pairs with cesium as countercations favor an intramolecular cyclization reaction, the cesium effect is explained by preorganization of the reactants on the surface of the cesium cation.⁹ The cesium effect is also explained by the template effect through metal complexations with heteroatoms (O, N) which drive the folding of a suitable chain toward the ring-closure, such as the case in crown ether syntheses.⁶ In the synthesis of macrocycle **3.4**, $n=1$, since a dipolar aprotic solvent was used and the macrocycle is an aromatic ether sulfone containing eight oxygen atoms, the cesium effect through the ion-pair and the template effects was expected using cesium carbonate as base in the synthesis. However, such an effect was not observed, even though the dilution in this case (Exp. 5) was high compared to Exp. 1 with potassium carbonate as base. Probably, the presence of a large amount of the nonpolar solvent toluene reduces the polarity of the reaction medium, leading to the cesium cation being more associated with the phenolate anion and thus reducing the effectiveness of the counterion.

A common side reaction for aromatic nucleophilic etherification is ether exchange or transesterification caused by phenolate anion attack at the activated ether linkages.¹⁰ The ether exchange can result in ring cleavage to form chain extended linear molecules and also leads to the

⁷ Ostrowicki, A.; Koeppe, E.; Vögtle, F. *Topics in Current Chemistry*, **1991**, Vol. 161, pp 37-67 ; and references therein.

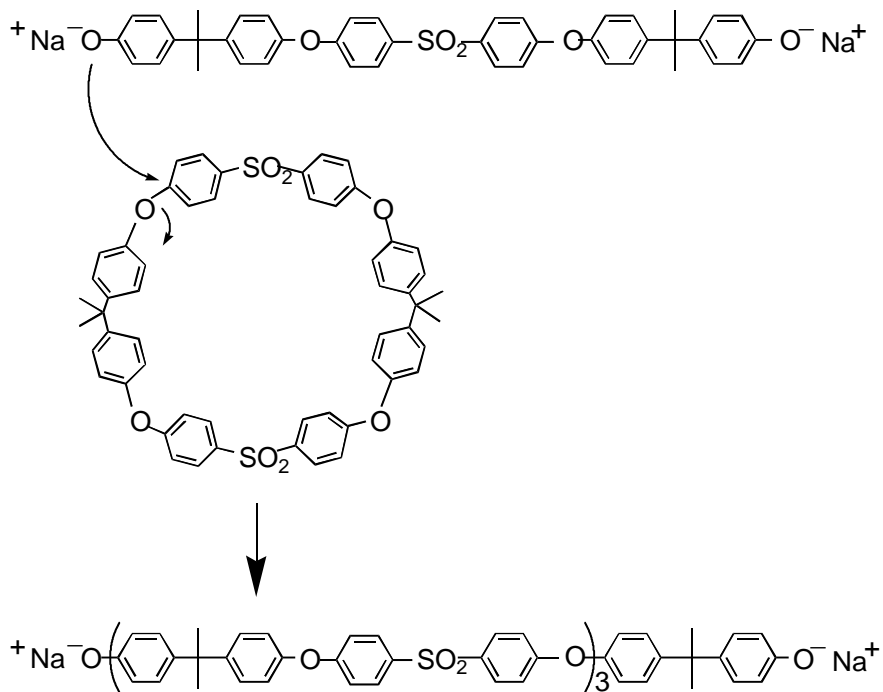
⁸ Dijkstra, G.; Kruizinga, W. H.; Kellogg, R. M. *J. Org. Chem.*, **1987**, 52, 4230.

⁹ a) Kruizinga, W. H.; Kellogg, R. M. *J. Am. Chem. Soc.*, **1981**, 103, 5184; b) Piepers, O.; Kellogg, R. M. *J. Chem. Soc., Chem. Commun.*, **1978**, 383.

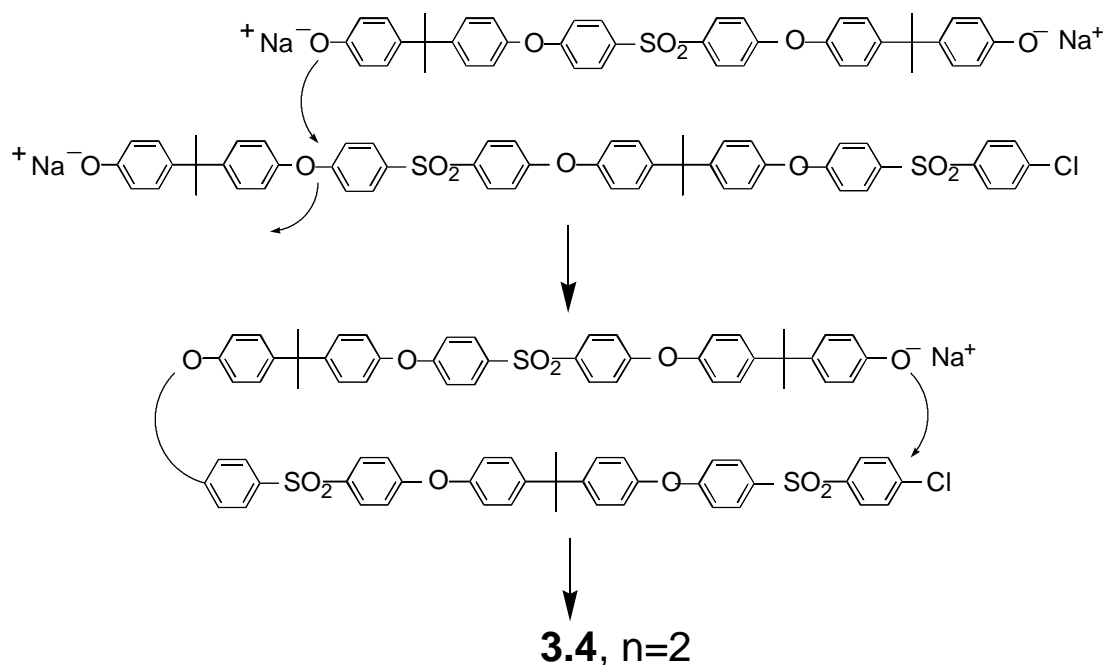
¹⁰ See ref. 19 in Chapter 1.

formation of macrocycles with odd ring sizes, such as trimer (n=2), pentamer (n=4) etc., which would not be produced by direct reaction of **3.3** with dihalodiphenyl sulfone by 1+1, 2+2, etc. processes. Scheme 3.3 illustrates the ring cleavage reactions, and Scheme 3.4 illustrates one possible route to the formation of trimer (**3.4**, n=2) by ether exchange followed by ring closure under high dilution conditions.

Scheme 3.3



Scheme 3.4



Indeed, It was found in the syntheses that the odd sized cyclics **3.4**, $n=2, 4$ were present. These cyclics together with the even sized large cyclics **3.4**, $n=3$ and 5 were isolated by column chromatography and characterized by reverse phase gradient HPLC and FAB-MS as shown in Figures 2 & 3. Two mixtures were obtained by column chromatography. One mixture contained macrocycles **3.4**, $n=1, 2$ and 3 , with the softening range (capillary) from $187-208^{\circ}\text{C}$ (Figure 3.2); the other mixture contained cyclics **3.4**, $n=2, 3, 4$, and 5 , with softening range (capillary) from $200-216^{\circ}\text{C}$ (Figure 3.3). Using 3-nitrobenzyl alcohol plus sodium iodide as matrix, FAB-MS clearly produced molecular ions complexed with sodium ion, giving signals at $907.3, 1349.6, 1792.5, 2234.9, 2677.4$ m/z corresponding to cyclics **3.4**, $n=1, 2, 3, 4$ and 5 , respectively.

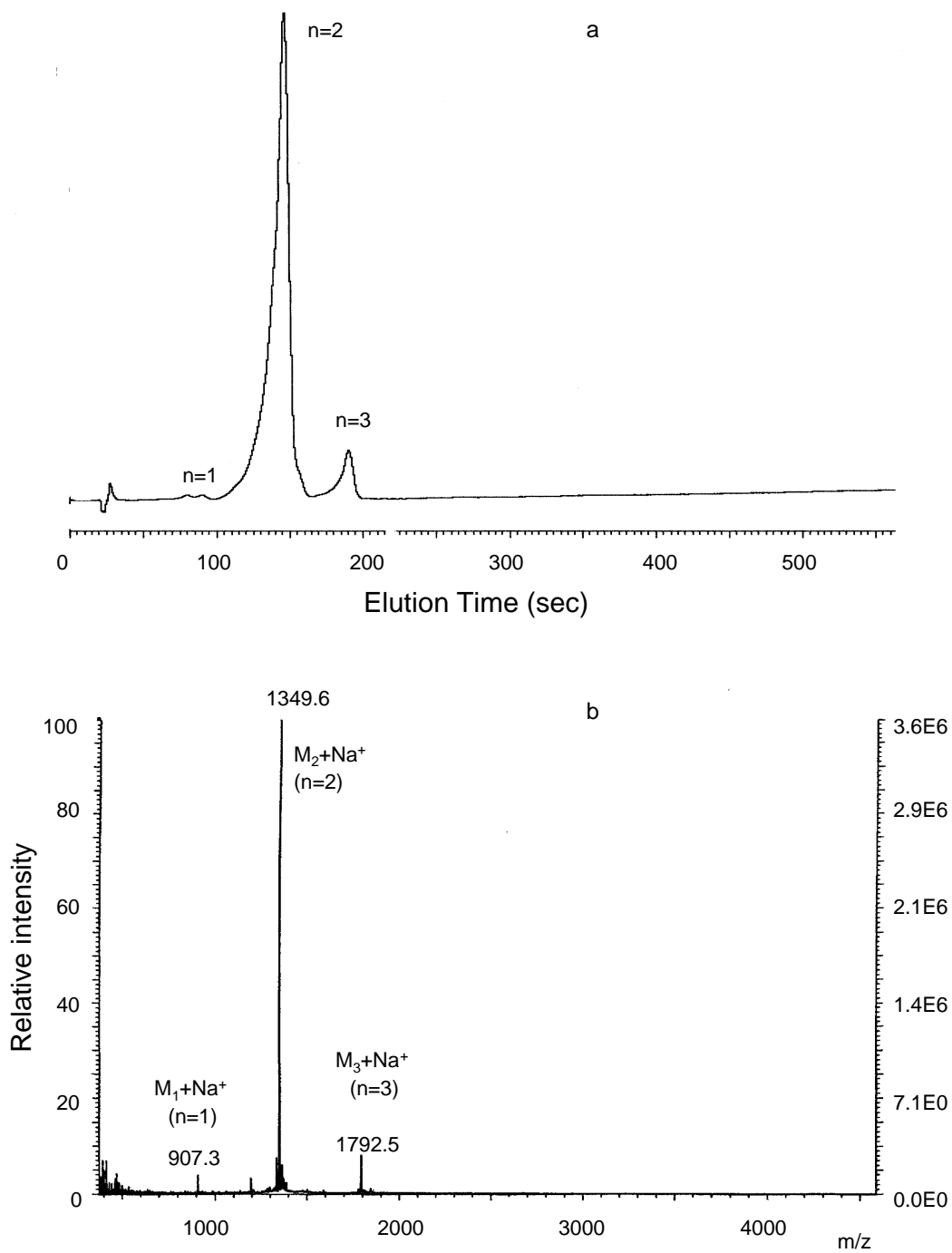


Figure 3.2 Cyclic mixture containing **3.4**, n=1, 2, 3: a) reverse-phase HPLC chromatogram (C18, THF/water, gradient); b) FAB mass spectrum in 3-nitrobenzyl alcohol plus sodium iodide matrix

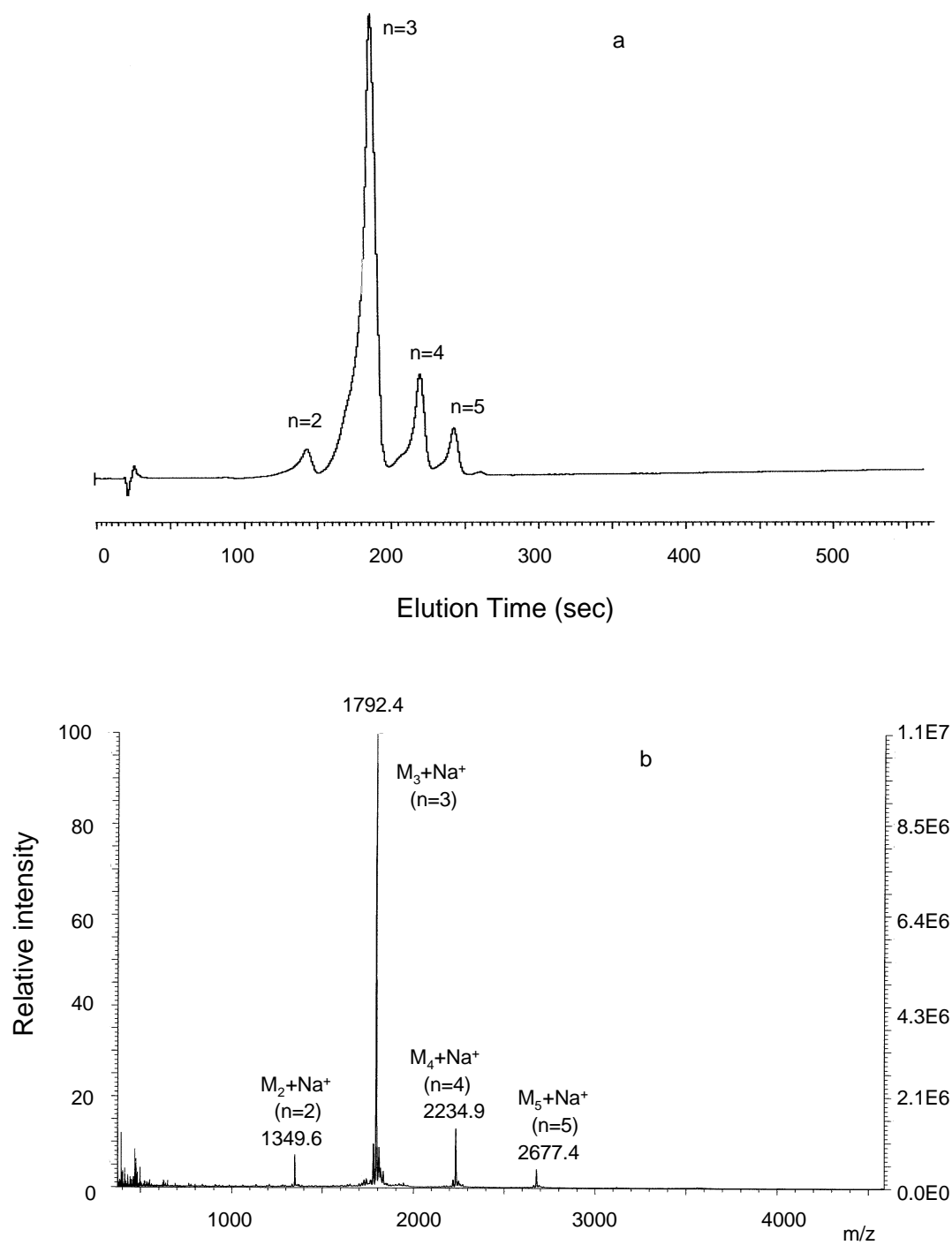


Figure 3.3 Cyclic mixture containing **3.4**, $n=1, 2, 3, 5$: a) reverse-phase HPLC chromatogram (C18, THF/water, gradient); b) FAB mass spectrum in 3-nitrobenzyl alcohol plus sodium iodide matrix

To reduce the chances of ether exchange, and to increase the yield of the desired macrocycle (**3.4**, $n=1$), low reaction temperatures are suggested, such as 135-140°C used in this synthesis. Although we don't have specific data on the synthesis at higher temperatures for comparison, Mullins et al.'s findings⁴ that the yield of cyclics is reduced at temperatures greater than 140°C indicate that use of low reaction temperatures is desirable.

3.2.3 Characterization and properties of macrocycle **4**, $n=1$

The 1+1 macrocycle **3.4**, $n=1$ was easy to free from linear macromolecules, since it was essentially insoluble in chloroform whereas the linears and large ring-sized cyclics were very soluble. It has been well characterized by NMR, FAB mass spectroscopies, HPLC, TGA and DSC.

Analysis by reverse-phase gradient HPLC indicated that **3.4**, $n=1$ was pure, as shown in Figure 3.4a. FAB-MS using 3-nitrobenzyl alcohol as matrix (Figure 3.4b) produced an intense protonated molecular ion peak at 885 m/z ; the peak at 869 m/z was the fragment after the macrocycle lost a methyl group; the peak at 795.6 m/z was the fragment after loss of sulfur monoxide and the isopropylidene group. Other intense peaks at 460.2, 613.2 and 766.4 m/z came from the matrix. Figure 3.5 shows the ¹H NMR spectrum of macrocycle **3.4**, $n=1$ as well as the spectrum of its linear precursor **3.3** for comparison. The simpler NMR signal pattern of the macrocycle indicates that a symmetric ring structure is formed. In the spectrum of the macrocycle, the singlet at 1.66 ppm is due to methyl protons of the isopropylidene group; doublets at 7.05 ppm and 7.06 ppm (partially overlapped) due to aromatic protons ortho to ether linkages; the doublet at 7.31 ppm due to aromatic protons ortho to the isopropylidene group; and the doublet at 7.89 ppm due to aromatic protons ortho to the sulfone group. Peak assignments in **3.3** and **3.4**, $n=1$ were confirmed by 2D-proton NMR spectroscopy.

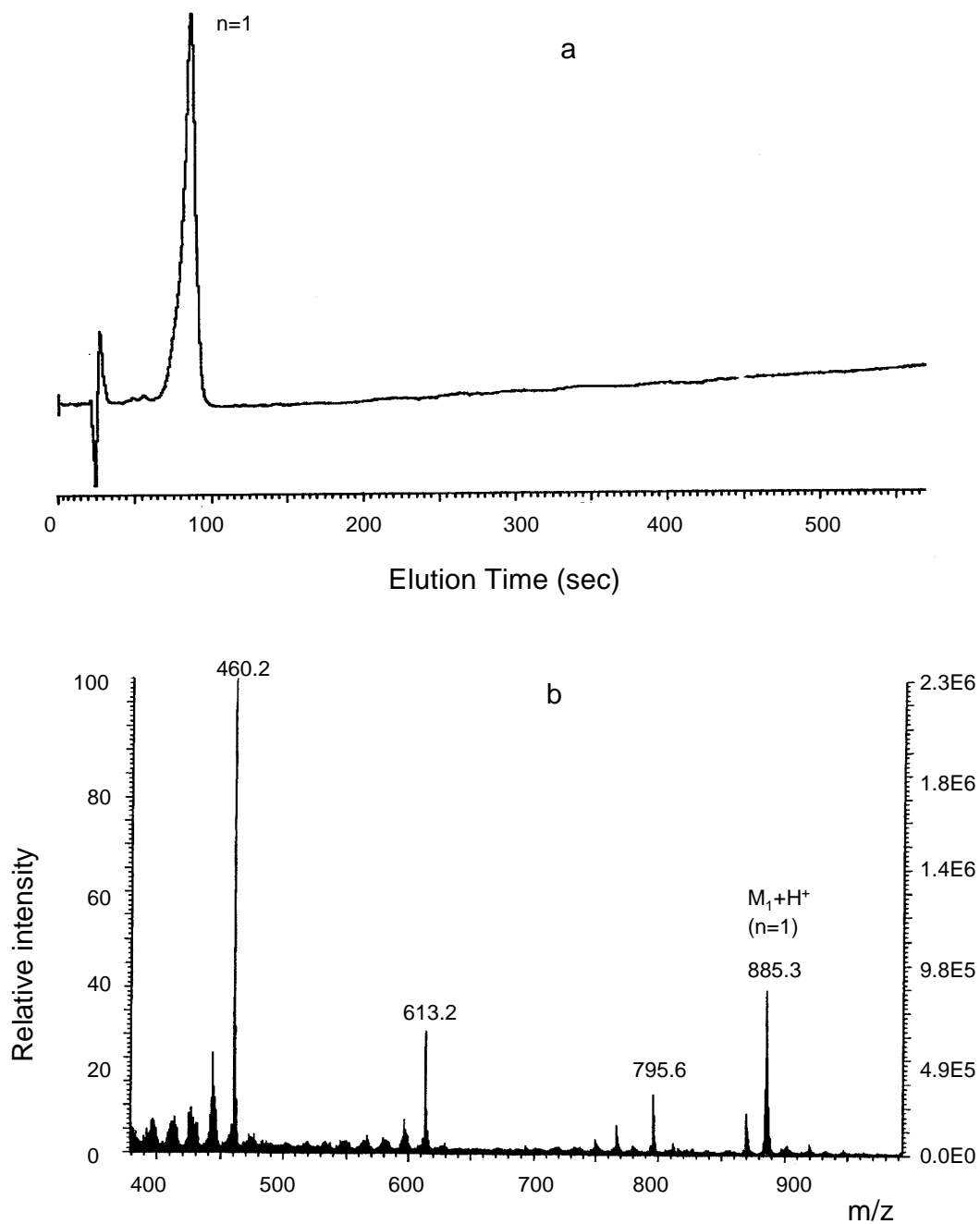


Figure 3.4 Pure macrocycle **3.4**, $n=1$: a) reverse-phase HPLC chromatogram (C18, THF/water, gradient); b) FAB mass spectrum in 3-nitrobenzyl alcohol plus sodium iodide matrix

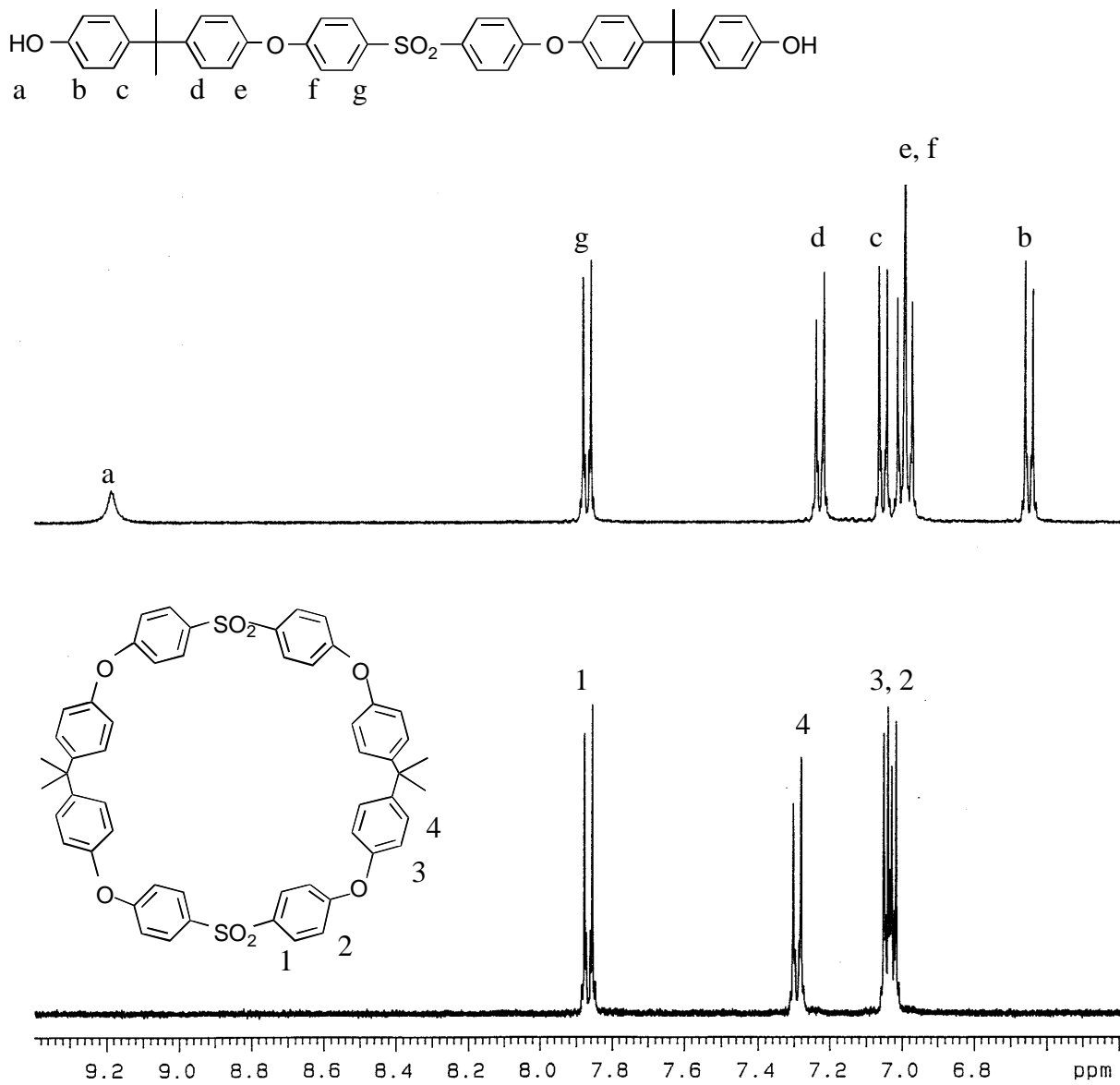


Figure 3.5 400 MHz ^1H NMR spectrum (aromatic regions) of linear precursor **3.3** and macrocycle **3.4**, $n=1$ in DMSO-d_6

Qualitative studies of **3.4**, $n=1$ indicated very poor solubility in generally good organic solvents such as chloroform, and in most of the high boiling dipolar aprotic solvents such as DMF, DMAc and DMSO. The solubility mentioned above is quite different from that of the same macrocycle reported in the literature² in which it was reported to be soluble in chloroform, methylene chloride and toluene. We believe that the macrocycle reported previously was not pure, possibly contaminated with rotaxane compounds.¹¹ It was observed by us in this study that a small amount of the macrocycle was precipitated by boiling the original clear chloroform filtrate after the insoluble macrocycle had been filtered (see experimental section). The precipitation is believed due to dethreading of the macrocycle from the rotaxanes derived from short oligomers. Formation of rotaxane structures increases the entropy of the system, thus enhancing the solubility.

Figures 3.6 and 3.7 show TGA and the DSC thermograms of macrocycle **3.4**, $n=1$. The TGA thermogram indicated that the macrocycle has high thermal stability with 5 % weight loss at 507°C in air and 542°C in nitrogen. The DSC analysis under nitrogen showed a crystallization transition at 268°C and no melting transition up to 480°C. Melting of the macrocycle was indeed observed at around 500°C using an aluminum block as a heat source under a nitrogen atmosphere. Since the melting temperature of this macrocycle is near the degradation temperature, ring opening polymerization of the macrocycle is precluded. Lowering the melting temperature is possible if the symmetry is decreased by incorporation of different structural units. In the following chapter, the synthesis of unsymmetric macrocycles with lower melting points is described.

¹¹ A rotaxane is a compound composed of macrocycle(s) threaded by a linear molecule with no covalent bonds between them. For reviews see refs, 1 and 3 in Chapter 1 of Part II

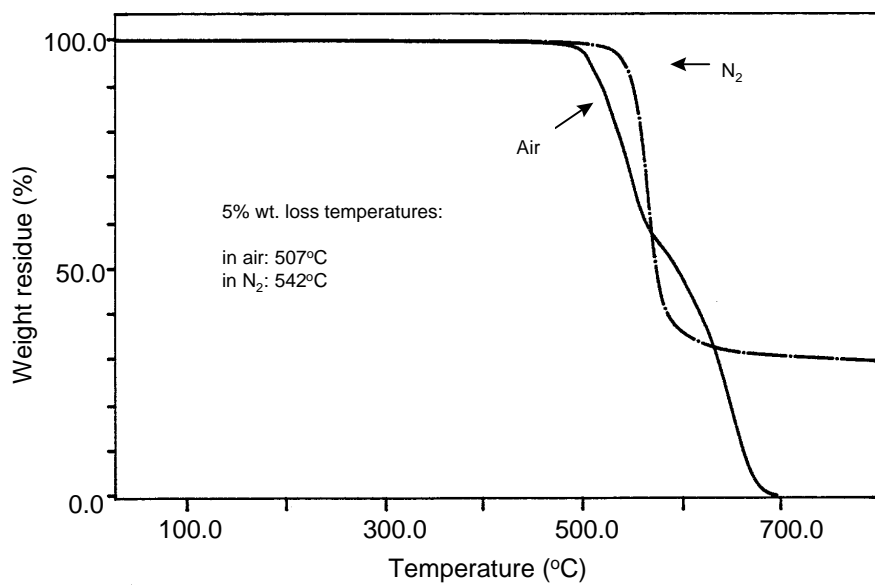


Figure 3.6 Thermal gravimetric curves of macrocycle **3.4**, n=1 in air and N₂ at a heating rate of 10°C/min

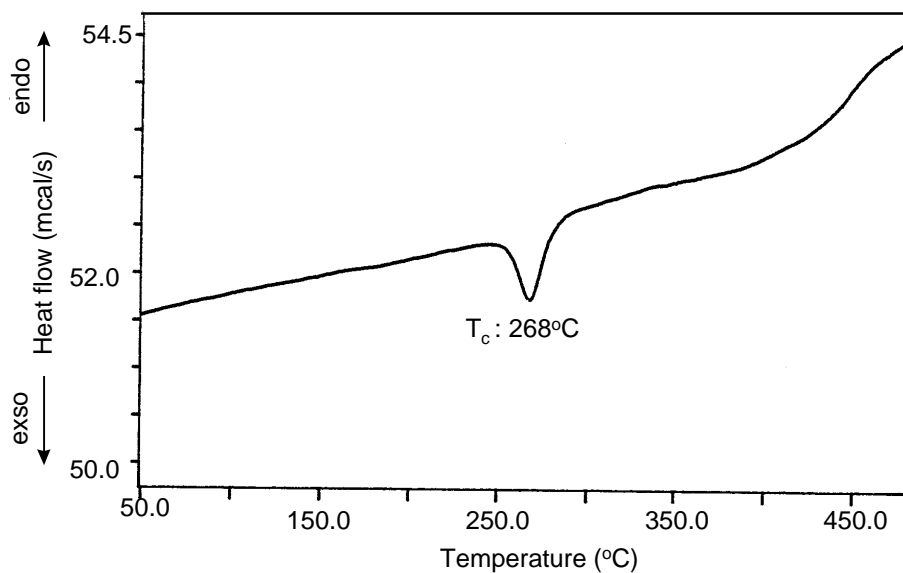


Figure 3.7 DSC curve of macrocycle **3.4**, n=1 at a heating rate of 10°C/min

3.3 Conclusions

The synthesis of macrocyclic arylene ether disulfone **3.4**, $n=1$ has been studied in detail in terms of the degree of dilution, the reactivity of monomers, and the counterion effect. Using the more reactive fluorinated precursor, purer bisphenol precursor **3.3** and higher dilution conditions, the yield of the macrocycle has been increased to 67% from the 11% reported previously.² With cesium cations as counterions of the phenolate anions, an expected increase in the yield of the cyclic was not observed. Macrocycle **3.4**, $n=1$ exhibits poor solubility, high thermal stability, and high melting point (ca. 500°C). Although the high melting point of the macrocycle precludes ring opening polymerization in the melt to form poly(ether sulfone), this study has provided a valuable guide to syntheses of other macrocycles in high yields.

3.4 Experimental

Materials and Instruments

Reagent grade reactants and solvents were used as received from chemical suppliers. Melting points were taken in capillary tubes with a Melt-Temp II melting point apparatus and have been corrected. ¹H NMR spectra were obtained in deuterated dimethyl sulfoxide with TMS as the internal standard at ambient temperature on a Varian 400 MHz spectrometer. Infrared spectra (KBr pellets) were recorded on a Nicolet MX-1 FTIR spectrometer. The mass spectrum was measured by the Mass Spectrometry Service Laboratory, University of Nebraska. The elemental analyses were performed by Atlantic Microlab of Norcross, GA. Thermogravimetric analyses were performed on a Perkin-Elmer TGA-7 at a scan rate of 10°C/min in air and N₂ atmospheres. Differential scanning calorimetry analyses were performed on a Perkin-Elmer DSC-7 at a scan rate of 10°C/min in a N₂ atmosphere. An Orion Sage model 355 syringe pump was used to control the addition of the reagents during macrocycle syntheses. Reverse-phase HPLC analyses were performed on an ISCO dual pump HPLC system comprising two Model 2350 pumps and the V⁴ Variable Wavelength UV/Vis Detector set at 274 nm. THF/water gradients were used for elution of products on a Novapak C-18 reverse-phase column at a flow rate of 2 mL/min. The gradient used for analysis was as follows: solvent A, THF; solvent B, 65% THF/water; the amount of B was changed from 100% to 0% over 10 min. The system was interfaced with the ISCO ChemResearch Chromatographic Data Management/System, used for data analyses.

2-(p-Benzyloxyphenyl)-2-(p-hydroxyphenyl)propane (3.1)

Bisphenol-A (45.66g, 200.0 mmol) was dissolved in a solution of NaOH (16.8 g, 420 mmol) in distilled water (1500 mL). The solution was heated to reflux and then to this solution was added benzyl bromide (34.20 g, 200.0 mmol) all at once. A milky emulsion immediately formed. The reaction was allowed to proceed for two hours under nitrogen atmosphere with mechanical stirring. Upon cooling, the white granular product was filtered, and then dissolved in 300 mL chloroform, neutralized with 10% aqueous HCl and washed with water three times (3 x100 mL). The organic phase was dried with sodium sulfate and evaporated, yielding a pale brown viscous oil which solidified upon boiling in hexane (300 mL). Recrystallization in ethyl acetate/hexane once provided pure compound (white). Yield: 41.27 g (65%); m.p.: 110.0-

111.6°C (reported:¹² 107-108°C). ¹H NMR (DMSO-d₆) δ 1.55 (s, 6 H, -CH₃), 5.05 (s, 2 H, -CH₂), 6.64 (d, *J*=8.7 Hz, 2 H), 6.89 (d, *J*=8.8 Hz, 2 H), 6.99 (d, *J*=8.7 Hz, 2 H), 7.10 (d, *J*=8.8 Hz, 2 H), 7.30-7.45 (m, 5 H, arom.), 9.14 (s, 1 H, -OH). FTIR (KBr) cm⁻¹: 3216 (-OH), 3037 (=CH), 2964 (-CH₃), 2864 (-CH₂), 1609, 1510 (C=C), 1231 (C-O-C), 826, 739, 670 (aromatic C-H, out of plane).

Bis[*p*-(benzyloxy)phenylisopropylidene-*p*-(phenoxy)phenyl] sulfone (3.2)

A mixture of **3.1** (35.03 g, 110.0 mmol) and K₂CO₃ (8.4 g, 61 mmol) in DMAc (260 mL) and toluene (150 mL) was heated at reflux for three hours under nitrogen with mechanical stirring. Water generated was removed by azeotropic distillation into a Dean-Stark trap with toluene. After that, toluene was distilled until the temperature was raised to about 160°C. 4,4'-Dichlorodiphenyl sulfone (15.79 g, 55.00 mmol) in DMAc (40 mL) was added all at once, and the reaction was allowed to proceed at ca. 160°C for 20 hours after the addition. Upon cooling, the reaction mixture was filtered to remove unreacted K₂CO₃ and KCl, and then the filtrate was rotary evaporated. The brown viscous oil obtained was dissolved in 300 mL chloroform and washed with distilled water (3 x 100 mL) to remove the DMAc and salt residues. The organic phase was dried with magnesium sulfate and evaporated, yielding a pale brown viscous oil. Recrystallization in ethyl acetate/methanol provided white, granular, loose crystals. Yield: 44.14 g (94%); m.p. 144.2-145.2°C; ¹H NMR (DMSO-d₆) δ 1.62 (s, 12 H, -CH₃), 5.06 (s, 4 H, -CH₂), 6.92 (d, *J*=8.9 Hz, 4 H), 7.02 (d, *J*=8.8 Hz, 4 H), 7.08 (d, *J*=8.8 Hz, 4 H), 7.14 (d, *J*=8.8 Hz, 4 H), 7.26 (d, *J*=8.8 Hz, 4 H), 7.30-7.45 (m, 10 H, arom.), 7.90 (d, *J*=8.9 Hz, 4 H); FTIR (KBr) 3070 (=CH), 2971 (-CH₃), 1609, 1589, 1503, 1490 (C=C), 1244 (C-O-C), 1164 (O=S=O), 852, 746, 686 (aromatic C-H, out of plane); Anal. calcd. for C₅₆H₅₀O₆S: C, 79.03; H, 5.92; S, 3.77; O, 11.28. Found: C, 79.03; H, 5.96; S, 3.85.

Bis[*p*-(hydroxy)phenylisopropylidene-*p*-(phenoxy)phenyl] sulfone (3.3)

Palladium on activated carbon (10%, 1.00 g) was added to a solution of **3.2** (22.36 g, 26.27 mmol) in ethyl acetate (300 mL) very slowly and partwise. The hydrogenation was carried out at room temperature for 12 hours with a starting pressure of 60 psi. After the reaction, the catalyst was filtered and the filtrate was rotary evaporated, yielding an off-white solid which was then dried under vacuum at 60°C overnight. Yield: 17.4 g (99%), m.p. (DSC) 182.5°C (reported capillary softening range²: 100-145°C); ¹H NMR (DMSO-d₆) δ 1.60 (s, 12 H, -CH₃), 6.65 (d, *J*=8.7 Hz, 4 H), 6.99 (d, *J*=8.8 Hz, 4 H), 7.00 (d, *J*=8.7 Hz, 4 H), 7.06 (d, *J*=8.7 Hz, 4 H), 7.23 (d, *J*=8.7 Hz, 4 H), 7.88 (d, *J*=8.8 Hz, 4 H), 9.20 (s, 2 H, -OH); FTIR (KBr) cm⁻¹: 3445 (-OH), 3064 (=CH), 2966 (-CH₃), 1588, 1504, 1490 (C=C, arom.), 1244 (C-O-C), 1145 (O=S=O), 829 (aromatic C-H, out of plane).

¹² Humphrey, J. S.; Shults, A. R.; Jaquiss, D. B. *Macromolecules* **1973**, *6*, 305.

Macrocyclic arylene ether sulfone (3.4, n=1)

The typical synthetic procedure is as follows. A solution (30 mL) of **3.3** (6.71 g, 10.0 mmol) and 4,4'-dichlorodiphenyl sulfone (2.87, 10.0 mmol) in DMAc was injected via a syringe at the rate of 0.8 mL/h into a refluxing (ca. 135°C) suspension of DMAc (400 mL), toluene (220 mL) and K₂CO₃ (2.1 g 15 mmol). The suspension was mechanically stirred and purged with nitrogen. Water generated was azeotroped by toluene into a Dean-Stark trap. The reaction was allowed to continue for an additional 18 hours at 135°C after injection. Upon cooling to room temperature, a small amount of the macrocycle precipitated as a white powder which was filtered together with salts. The macrocycle was isolated from salts by washing with water, followed by methanol and chloroform several times. The reaction mixture after filtration of salts and the precipitated macrocycle was evaporated; the resultant brown liquid (containing a small amount of DMAc) was then precipitated into water. The precipitate was filtered and washed with methanolic water and methanol, followed by chloroform several times. The second portion of the white powdered macrocycle was thus obtained in a larger quantity. The third and smallest portion of the macrocycle was extracted by boiling the residue in chloroform for half an hour, cooling down to room temperature and after a couple of hours, filtering. The extraction process was performed twice. All three portions of the macrocycle were combined and washed again with chloroform once. Yield: 5.92 g (67%); m.p. ~500°C; ¹H NMR (DMSO-d₆) δ 1.66 (d, 12 H, -CH₃), 7.03 (d, *J*=8.9 Hz, 8 H), 7.04 (d, *J*=8.8 Hz, 8 H), 7.29 (d, *J*=8.8 Hz, 8 H), 7.87 (d, *J*=8.9 Hz, 8 H); FTIR (KBr) 3070 (=CH), 2971 (-CH₃), 1589, 1503, 1490 (C=C, arom.), 1244 (C-O-C), 1151 (O=S=O), 872 (aromatic C-H, out of plane) cm⁻¹; MS (FAB): Calcd. for C₅₄H₄₅S₂O₈ [M+H]⁺: m/z 885.3 M⁺; found: m/z 885.3 [M+H]⁺. Elemental anal. calcd. for C₅₄H₄₄S₂O₈: C, 73.28; H, 5.01; S, 7.24; O, 14.47; found: C, 73.27; H, 5.07; S, 7.30.

Chapter 4

Synthesis and Characterization of Single Sized, Unsymmetric Aromatic Ether *co*-Macrocycles

4.1 Introduction

As indicated in Chapter 3, the symmetric homo-macrocyclic, bisphenol-A based 40-membered cyclic arylene ether sulfone **3.4** ($n=1$), is of high melting point (above 500°C), which precludes use of the macrocycle for ring opening polymerization application. In order to reduce melting points, unsymmetric *co*-macrocycles **4.11-4.23** were prepared; these contained sulfone/ketone or sulfone/phosphine oxide functional groups and/or different aromatic moieties. As will be shown, these *co*-macrocycles exhibit relatively low melting points, with which the ring opening polymerization has been readily investigated (see Chapter 7). By the same procedure developed for **3.4** ($n=1$), the single sized *co*-macrocycles were efficiently and conveniently synthesized in high yields through etherification of bisphenol and dihalide precursors of suitable length.

4.2 Results and Discussion

4.2.1 Synthesis of linear precursors

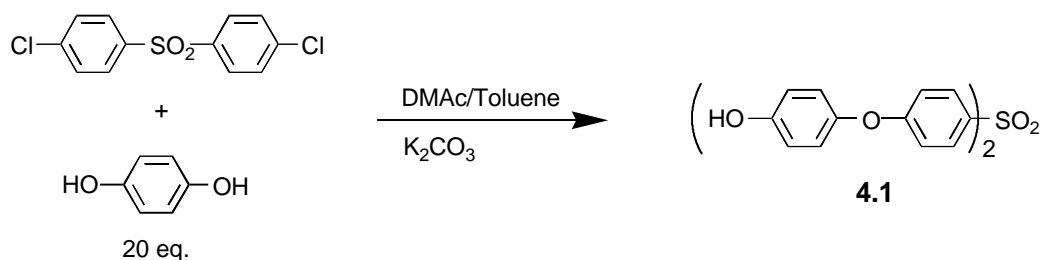
Table 4.1 lists all the bisphenol and dihalide precursors that were used for preparation of *co*-macrocycles with different structural units. Among them, 4,4'-bis(p-fluorobenzoyl)diphenyl sulfone (**4.6**) was supplied by this group; 1,4-bis(p-fluorobenzoyl)benzene (**4.5**), and 4,4'-difluorodiphenyl-phenyl phosphine oxide (**4.4**) were supplied by Prof. McGrath's group at Virginia Tech; difluorobenzophenone (**4.3**) and bisphenol-A (**4.2**) were commercial products. Bisphenol precursors **3.3** and **4.1**, and dihalide precursors **4.7-4.10** were prepared in this study.

Table 4.1 Bisphenol and dihalide precursors

Bisphenol precursors		Dihalide precursors	
3.3		4.3	
4.1		4.4	
4.2		4.5	
		4.6	
		4.7	
		4.8	
		4.9	
		4.10	

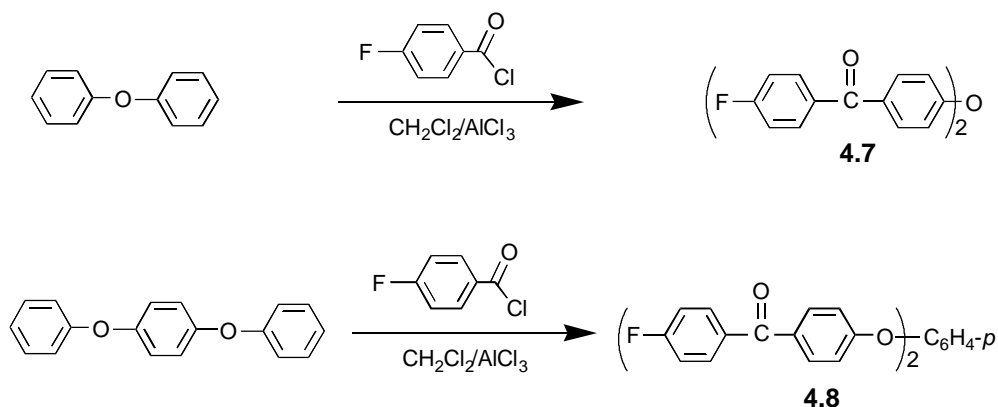
The synthesis of **3.3** has been discussed in Chapter 3. While to obtain bisphenol-A based precursor **3.3** of high purity required the three step method, the synthesis of hydroquinone-based precursor **4.1** was readily achieved by one step reaction of a large excess of hydroquinone (20 eq.) and 4,4'-dichlorodiphenyl sulfone via aromatic nucleophilic substitution (Scheme 4.1). Unlike the bisphenol-A system, the one step method provided a quantitative yield of **4.1**. Excess hydroquinone was easily removed by water, giving the product in high purity.

Scheme 4.1



Oligomeric dihalide precursors containing ketone or sulfone activating groups **4.7-4.10** were prepared via Friedel-Crafts reactions (Schemes 4.2 and 4.3). The difluoride precursors **4.7** and **4.8** were obtained by acylation (Scheme 4.2) of *p*-fluorobenzoyl chloride with diphenylether and 1,4-diphenoxybenzene, respectively, in methylene chloride in the presence of aluminum chloride. **4.7** was obtained in 92% yield and **4.8** in 98% yield. The reported yields¹ of these two compounds are 91% and 75%, respectively.

Scheme 4.2



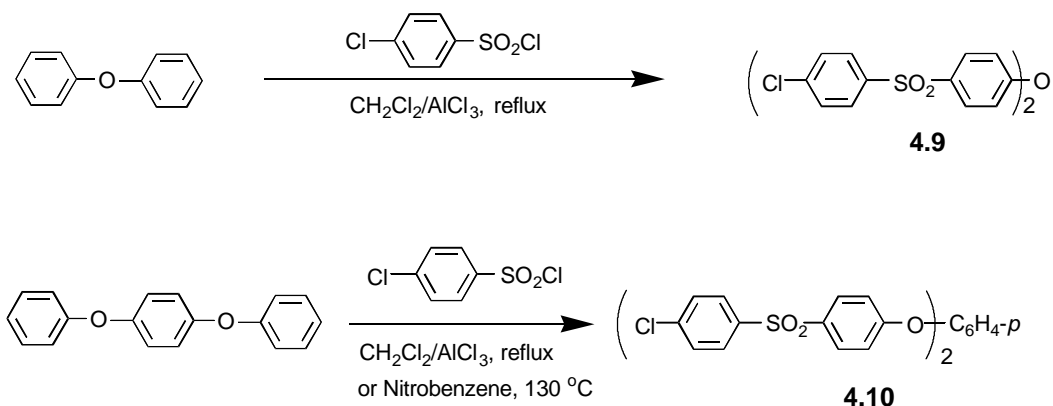
The sulfonylation reaction (Scheme 4.3) of diphenyl ether or 1,4-diphenoxybenzene with chlorobenzenesulfonyl chloride in refluxing methylene chloride and aluminum chloride for 24 hours only afforded 14% of **4.9** and 7% of **4.10**, respectively. When the reaction was carried out at a higher temperature (130°C) in nitrobenzene, the yield of **4.10** was improved to 66%. **4.9** was reported to be synthesized in refluxing nitrobenzene using 4,4'-oxydiphenyldisulfonyl chloride and chlorobenzene as starting materials with 38% yield.² The difficulty in getting high yields is due to the side reaction by ortho attack. The increased chance of ortho attack results from the sulfonylium cation intermediate not being well stabilized by charge delocalization because of poor

¹ Kricheldorf, H. R.; Delius, U.; Tonnes, K. U. *New Polymeric Mater.* **1988**, Vol 11, No. 2, 127-141.

² Ueda, M.; Ito, T. *Polym. J.* **1991**, Vol. 23, No. 4, 297-303.

size matching of oxygen and sulfur atoms.³ Besides, diphenyl ether, and 1,4-diphenoxybenzene, which are not deactivated by electron withdrawing groups, are labile to ortho attack in sulfonylation.³

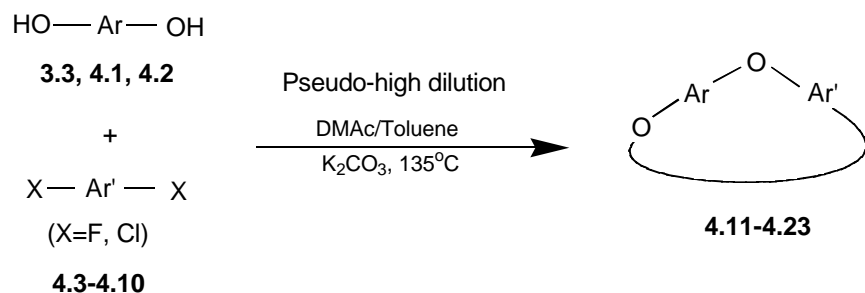
Scheme 4.3



4.2.2 Synthesis and Characterization of Macrocycles

Aromatic nucleophilic substitution reactions of bisphenols **3.3**, **4.1** and **4.2** and dihalides **4.3-4.10** in various combinations under pseudo-high dilution conditions provided the aromatic ether co-macrocycles **4.11-4.23** containing sulfone/ketone, or sulfone/phosphine oxide and/or different aromatic moieties (Scheme 4.4). Table 4.2 lists the combinations of precursors, corresponding cyclic structures, yields, melting points and TGA data of the macrocycles synthesized.

Scheme 4.4

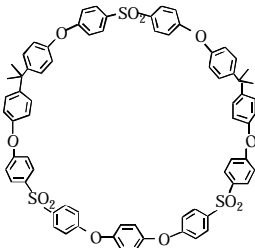
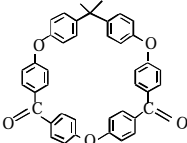
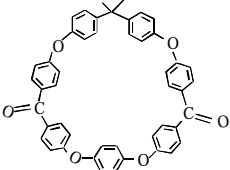
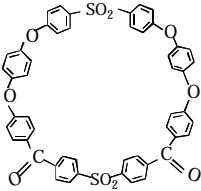
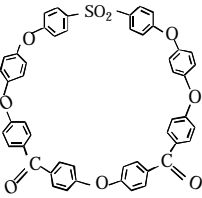
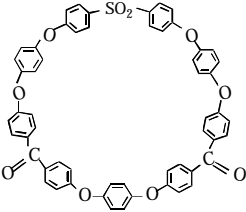
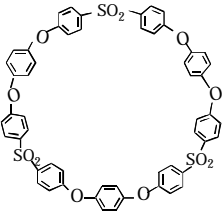


³ Cudby, M. E. A.; Feasey, R. G.; Jennings, B. E.; Hones, M. E. B.; Rose, J. B. *Polymer* **1965**, 6, 589-601.

Table 4.2 Precursors, structures, yields and physical properties of macrocycles

Macrocycle	Precursors	Structure	Yield/melting point/TGA(in N ₂)
4.11	3.3+4.3		68% 366.6-367.1°C 5%wt loss @ 465°C 30% char @ 800°C
4.12	3.3+4.4		44% 240 and 336°C (DSC) 5%wt loss @ 465°C 36% char @ 800°C
4.13	3.3+3.5		83% 365.9-366.7°C
4.14	3.3+3.6		44% 394.8-395.6°C
4.15	3.3+4.7		75% 196 and 323°C (DSC) 5%wt loss @ 483°C 17% char @ 800°C
4.16	3.3+4.8		63% 329.4-331.4°C 5%wt loss @ 483°C 48% char @ 800°C

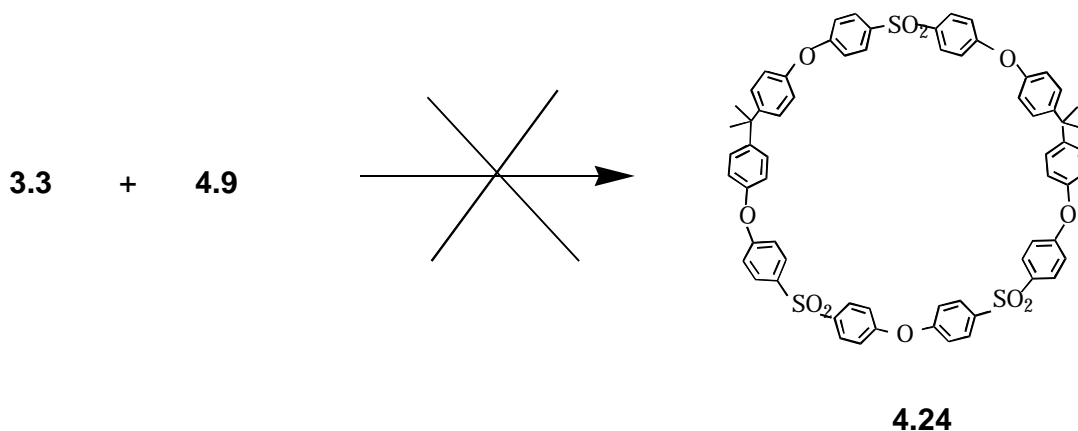
Table 4.2 (continued)

Macrocyclic	Precursors	Structure	Yield/melting point/TGA(in N ₂)
4.17	3.3+4.10		31% 185-215°C (containing ~10% 4.10)
4.18	4.2+4.7		66% > 400°C
4.19	4.2+4.8		80% 379.0-381.2°C 5%wt loss @ 472°C 52% char @ 800°C
4.20	4.1+4.6		21% 407-409°C
4.21	4.1+4.7		82% 404.2-406.2°C
4.22	4.1+4.8		76% 361.0-363.3°C 5%wt loss @ 531°C 54% char @ 800°C
4.23	4.1+4.10		39% > 425°C

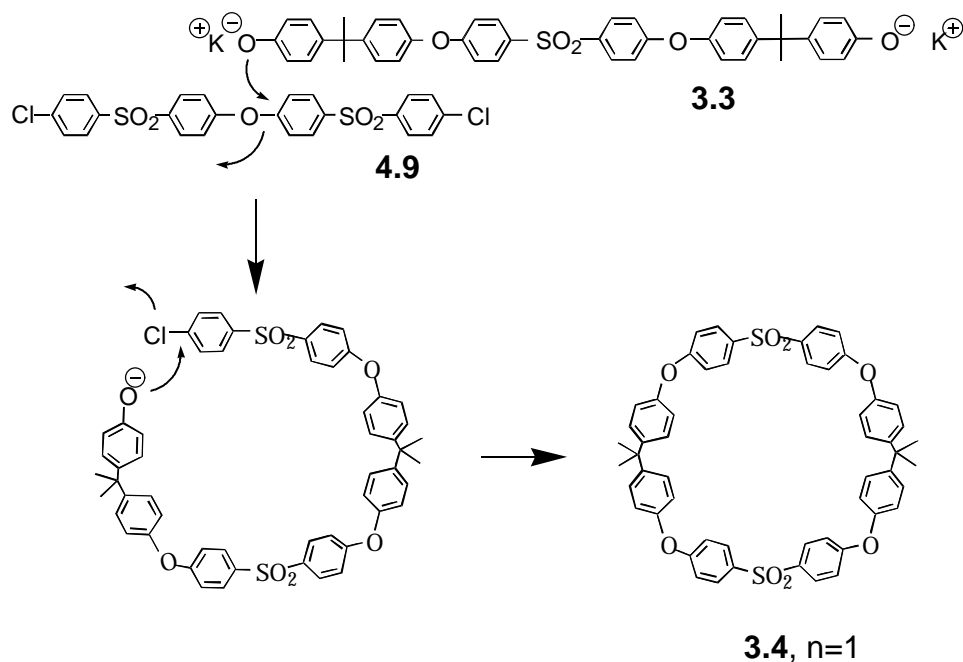
Two procedures were used in applying the pseudo-high dilution technique to the macrocycle syntheses. In most syntheses, both bisphenol and dihalide were dissolved in a small amount of solvent (DMAc) at room temperature, and the solution was then slowly injected via a syringe into the reaction flask containing DMAc/toluene and K_2CO_3 . The rate of feed v_f ranged from about 3.0×10^{-8} to 1.0×10^{-7} mol/L·sec, and the total feed c_f from about 3.0×10^{-3} to 1.6×10^{-2} mol/L. For the definitions and the effects on cyclization of these two parameters see Chapter 3. In the cases of difluoride precursors **4.5**, **4.7**, or **4.8** which are poorly soluble in DMAc at room temperature, the high dilution condition was achieved by addition of small aliquots of the difluoride together with a bisphenol (both dissolved in hot DMAc) in 12 hour time intervals. Each feed (the molar amount of each reactant added each time divided by the total amount of solvent used) was 7.7×10^{-4} to 1.3×10^{-3} mol/L and the total feed 3.0×10^{-3} to 5.0×10^{-3} mol/L. Both procedures effectively provided macrocycles in moderate to excellent yields, all purified yields, as shown in Table 4.2. In larger scale syntheses, using the first procedure at a rate of feed v_f 1.7×10^{-7} mol/L·sec and a total feed c_f 3.1×10^{-2} mol/L macrocycle **4.11** was obtained in 64% yield (24 g); using the second procedure at a feed 6.6×10^{-4} mol/L and a total feed 1.2×10^{-2} mol/L macrocycle **4.15** was obtained in 52% yield (11g).

As indicated in Chapter 3, ether exchange is a side reaction that reduces the yields of desired macrocycles. It was observed in this study that severe ether exchange occurred when sulfone dichloride precursor **4.9** was used. For example, the cyclization using **4.9** and **3.3** as precursors did not give the desired 50-membered macrocycle **4.24** (Scheme 4.5); instead, the 40-membered macrocycle **3.4** ($n=1$) was obtained in 22% yield. The formation of **3.4** ($n=1$) is believed due to the facile ether exchange of **4.9**. Scheme 4.6 shows one possible route proposed towards the formation of **3.4** ($n=1$).

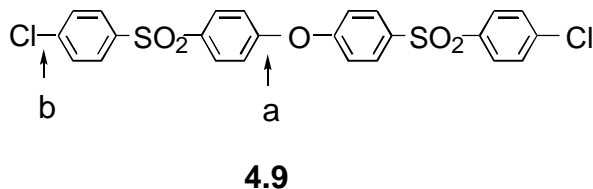
Scheme 4.5



Scheme 4.6

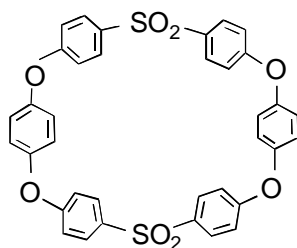


The labile ether linkage in **4.9** obviously results from the strong activating sulfone groups on both sides. As reported in the literature,⁴ the rate constant for bond fission of *a* is about 9 times larger than that of the *b* bond (Cl-C) in 80.5% DMSO/water at 120°C with hydroxide anions as nucleophiles.



The ether cleavage also occurred in the synthesis of macrocycle **4.17** where sulfone dichloride precursor **4.10** was used. In this case, **3.4** ($n=1$) was obtained in about 8% yield. Since the ether linkage in **4.10** is not activated as strongly as that in **4.9** due to the separation of two sulfone groups by a phenyl ring, desired macrocycle **4.17** was obtained in 31% yield. Similarly, the synthesis of macrocycle **4.23** using **4.1** and **4.10** yielded about 5% of macrocycle **4.25**, besides 39% of desired macrocycle **4.23**.

⁴ Newton, A. B.; Rose, J. B. *Polymer* **1972**, *13*, 465-474.



4.25

The above ether cleavage was little observed in the syntheses where ketone difluoride precursors **4.7** and **4.8** of similar structures were used, since the carbonyl group is a weaker electron withdrawing group than the sulfone group and the F-C bond is more reactive than the Cl-C bond. All macrocycles prepared from these two difluoride precursors were obtained in high yields, ranging from 63% to 82%.

Competing reactions in the syntheses were the formation of larger ring sized macrocycles and trace amounts of linear oligomers. While complete removal of linear oligomers to obtain a cyclic mixture is extremely difficult, isolation of a single sized macrocycle from the mixture can readily be done using conventional purification methods. Macrocycles **4.11-4.23** were purified by either column chromatography or recrystallization or simply washing with some solvent. Figure 4.1 shows the reverse phase HPLC chromatograms for both purified macrocycle **4.15** and the crude product (in the larger scale synthesis). The major signal, eluted at 2.4 min, corresponds to the desired macrocycle **4.15**, which accounts for about 70% of the crude product (curve a). Other signals, which are believed due to larger ring sized macrocycles and linear oligomers, were completely removed after purification by washing in chloroform (curve b). The yield after purification was 52% in this large scale synthesis. In the small scale synthesis, this macrocycle was purified by column chromatography, providing a 75% yield. The identity of the macrocycles was confirmed by ¹H NMR and FAB-MS. FAB mass spectrometry provided direct evidence that target macrocycles were obtained.

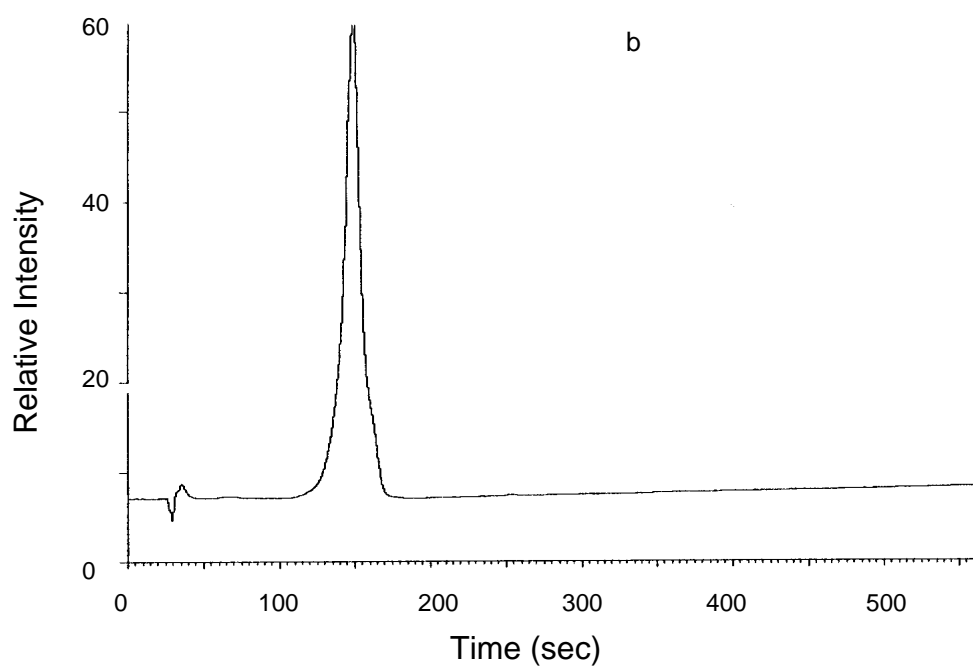
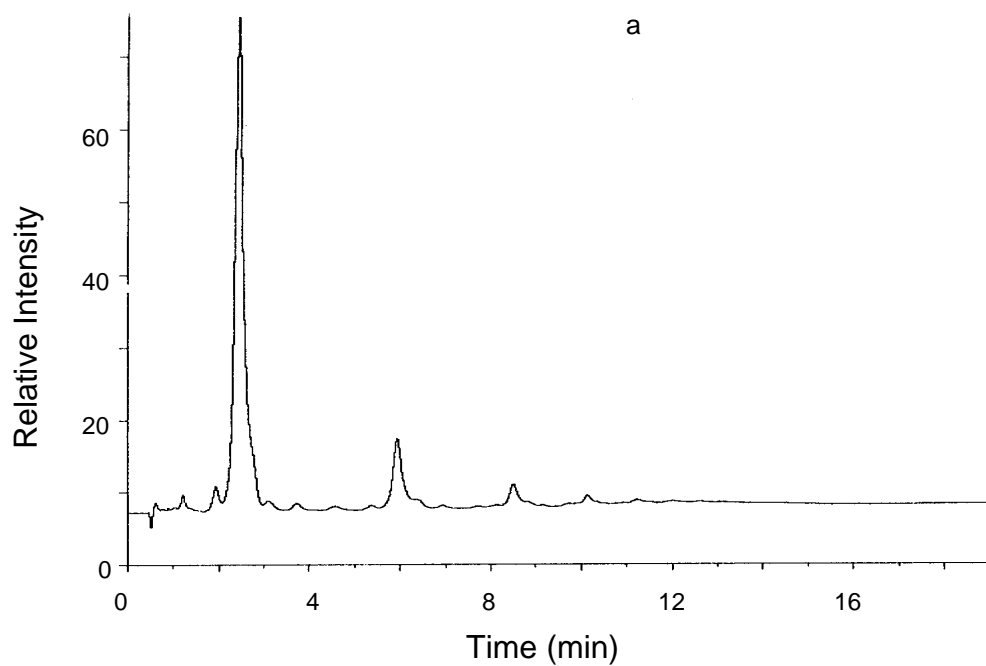


Figure 4.1 Reverse phase-HPLC chromatogram (C18, THF/water, gradient): a) crude product; b) purified macrocycle **4.15**.

As shown in Table 4.2, these co-macrocycles have relatively low melting points. Melting points of the ketosulfone macrocycle **4.11** (366-367°C) and the sulfone phosphine oxide macrocycle **4.12** are significantly lower than the corresponding disulfone macrocycle **3.4** ($n=1$) (above 500°C). Generally, the macrocycles containing bisphenol-A moieties (**4.11-4.19**) have lower melting points than the all-aromatic macrocycles (**4.20-4.23**). Macrocycles **4.12** and **4.15** exhibit two melting transitions by differential scanning calorimetry (DSC), indicating that two crystalline structures can be formed in these two macrocycles (polymorphism). DSC thermograms of these two macrocycles are given in Figures 4.2 and 4.3, respectively. The TGA data in Table 4.2 show that these macrocycles have high thermal stability, well above their melting points. Thus, melt ring opening polymerization at or somewhat above their melting points will not lead to decomposition.

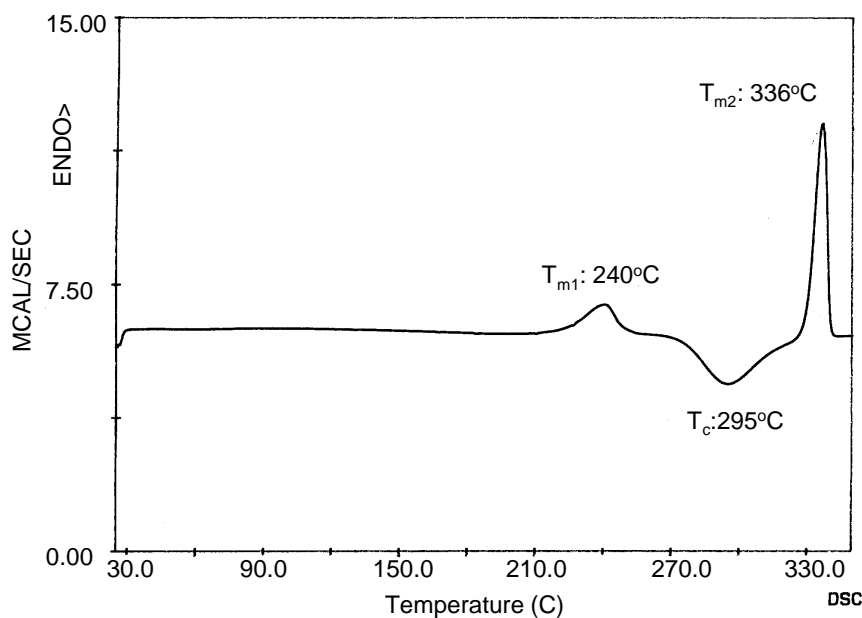


Figure 4.2 DSC curve of macrocycle **4.12** at a heating rate of 20°C/min

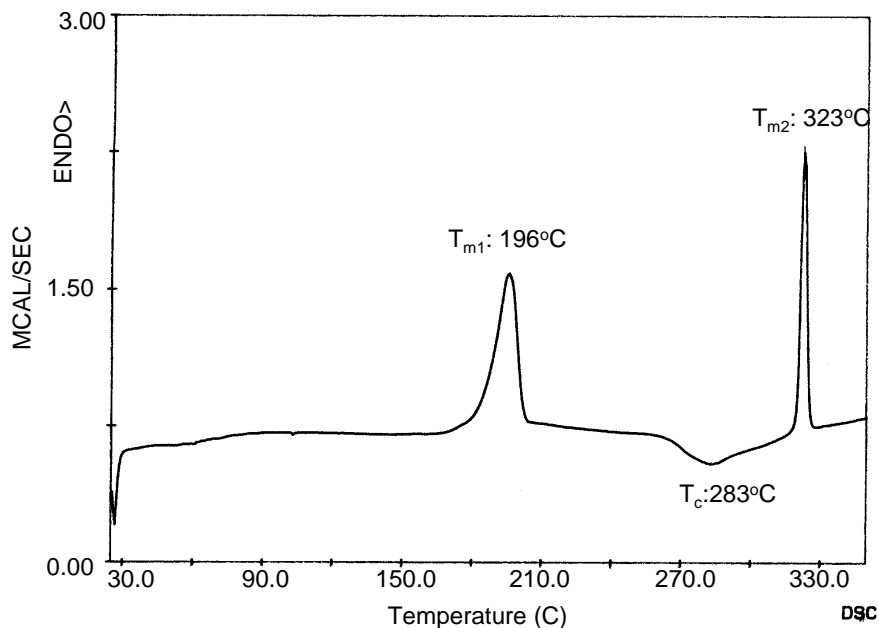


Figure 4.3 DSC curve of macrocycle **4.15** at a heating rate of 20°C/min

4.3 Conclusions

co-Macrocycles containing sulfone/ketone or sulfone/phosphine oxide groups and/or different aromatic moieties were successfully synthesized in moderate to excellent yields. These macrocycles exhibit high thermal stability and relatively low melting points, and thus are suitable for melt ring opening polymerization.

4.4 Experimental

Materials and Measurements

Reagent grade reactants and solvents were used as received from chemical suppliers. Monomer grade 4,4'-bis(p-fluorobenzoyl)diphenyl sulfone (**4.6**) was supplied by this group; monomer grade 1,4-bis(p-fluorobenzoyl)benzene (**4.5**), and 4,4'-difluorodiphenyl-phenyl phosphine oxide (**4.4**) were supplied by the Prof. McGrath group at Virginia Tech. For the Friedel-Crafts reactions, methylene chloride was dried over P₂O₅ and distilled prior to use; nitrobenzene was dried over CaH₂ and distilled under reduced pressure prior to use.

Melting points were taken in capillary tubes with a Melt-Temp II melting point apparatus and have been corrected. ¹H NMR spectra were obtained in deuterated dimethyl sulfoxide or chloroform with TMS as the internal standard at ambient temperature on a Varian 400 MHz

spectrometer. FAB mass spectra were recorded on a Fisons VG Quattro spectrometer using 3-nitrobenzyl alcohol as matrix. Thermogravimetric analyses were performed on a Perkin-Elmer TGA-7 at a scan rate of 10°C/min in air and N₂ atmospheres. Differential scanning calorimetric analyses were performed on a Perkin-Elmer DSC-7 at a scan rate of 20°C/min in a N₂ atmosphere. An Orion Sage model 355 syringe pump was used to control the addition of the reagents during macrocycle syntheses. Reverse-phase HPLC analyses were performed on an ISCO dual pump HPLC system comprising two Model 2350 pumps and the V⁴ Variable Wavelength UV/Vis Detector set at 274 nm. THF/water gradients were used for elution of macrocycle samples on a Novapak C-18 reverse-phase column at a flow rate of 1.5 mL/min. The system was interfaced with the ISCO ChemResearch Chromatographic Data Management/System, used for data analyses.

4,4'-Di(p-hydroxyphenoxy)diphenyl Sulfone (4.1)

A mixture of hydroquinone (66.0 g, 600 mmol) and K₂CO₃ (82.9 g, 600 mmol) in DMAc (400 mL) and toluene (250 mL) was refluxed at 133°C under nitrogen. Water generated from the deprotonation was removed by azeotropic distillation with toluene into a Dean-Stark trap. After five hours, toluene was distilled, and 4,4'-dichlorodiphenyl sulfone (8.62 g, 30.0 mmol) was added all at once. The reaction was allowed to proceed for 12 hours under the nitrogen atmosphere. Upon cooling after reaction, the mixture was neutralized by adding 10% HCl under N₂, then precipitated into 2500 mL water under stirring. The precipitated brown viscous oil was separated, dissolved into 300 mL chloroform and washed with distilled water (3 x 100 mL). The organic phase was dried with magnesium sulfate and decolorized with activated carbon. Evaporation of chloroform yielded a pink solid. The solid was dried under vacuum at 80°C overnight. Yield: 13.0 g (100%); m.p.:196.1-197.9°C (lit.⁵ 187-188°C); ¹H NMR (DMSO-d₆) δ 6.79(d, 4 H, J=8.8 Hz), 6.94 (d, 4 H, J=8.8 Hz), 6.98 (d, 4 H, J=8.8 Hz), 7.84 (d, 4 H, J=8.8 Hz), 9.52 (s, 2 H, -OH); FTIR (KBr) cm⁻¹:3382 (-OH), 3030 (=CH), 1589, 1510, 1490 (C=C), 1231 (C-O-C), 1145 (O=S=O), 832 (aromatic C-H, out of plane).

Bis[4-(4'-fluorobenzoyl)phenyl] ether (4.7)

4-Fluorobenzoyl chloride (6.66 g, 42.0 mmol) was added to a suspension of aluminum chloride (6.72 g, 50.4 mmol) in dry methylene chloride (40 mL). A solution of diphenyl ether (3.40 g, 20.0 mmol) in dry methylene chloride (20 mL) was then added dropwise at room temperature with stirring. After addition, the reaction was allowed to proceed at room temperature for one hour, and at reflux for another hour. Upon cooling, the reaction solution was poured into aq. HCl (5%, 100 mL). The precipitate was filtered, washed with water, methanol and methylene chloride, giving an off-white solid. Yield: 7.6 g (92%); mp: 215.0-217.5°C (lit¹.: 214-215°C); ¹H NMR (DMSO-d₆) δ 7.28 (d, 4 H, J=8.8 Hz), 7.41 (t, 4 H, J=5.6 Hz), 7.84 (d, 4 H, J=8.8 Hz), 7.85 (dd, 4 H, J₁=8.8 Hz, J₂=5.6 Hz).

⁵ Bayer, A. G. Patent: FR 1,514,802, 1966, *Chem. Abstr.* 70, 87309z, 1969.

***p*-Di[4-(4-fluorobenzoyl)phenoxy]benzene (4.8)**

By the use of the same reaction and purification procedure as above, the reaction of 4-fluorobenzoyl chloride (6.66 g, 42.0 mmol) and 1,4-diphenoxybenzene (5.25 g, 20.0 mmol) produced a white solid. Yield: 9.9 g (98%); mp: 230.4-231.9°C (lit¹: 223-225°C); ¹H NMR (DMSO-d₆) δ 7.15 (d, 4 H, J=8.8 Hz), 7.28 (s, 4 H), 7.40 (t, 4 H, J=5.6 Hz), 7.80 (d, 4 H, J=8.8 Hz), 7.82 (dd, 4 H, J₁=8.8 Hz, J₂=5.6 Hz).

Bis[4-(4'-chlorobenzenesulfonyl)phenyl] ether (4.9)

4-Chlorobenzenesulfonyl chloride (9.14 g, 42.0 mmol) was added to a suspension of aluminum chloride (6.72 g, 50.4 mmol) in dry methylene chloride (100 mL). A solution of diphenyl ether (3.40 g, 20.0 mmol) in dry methylene chloride (30 mL) was then added dropwise at room temperature with stirring. After addition, the reaction was heated at reflux for 24 hours. Upon cooling, the reaction solution was poured into aq. HCl (5%, 200 mL). The organic phase was then washed with water, dried with sodium sulfate and evaporated, yielding a brown liquid. Column chromatography using ethyl acetate and hexane (25/75) followed by recrystallization from toluene produced white crystals. Yield: 1.50 g (14.4%); mp: 212.3-213.3°C (lit²: 210-213°C); ¹H NMR (CDCl₃) δ 7.10 (d, 4 H, J=8.8 Hz), 7.49 (d, 4 H, J=8.8 Hz), 7.88 (d, 4 H, J=8.8 Hz), 7.93 (d, 4 H, J=8.8 Hz).

***p*-Di[4-(4'-chlorobenzenesulfonyl)phenoxy]benzene (4.10)**

Method 1: By the use of the same reaction and purification procedure as above, the reaction of 4-fluorobenzoyl chloride (6.66 g, 42.0 mmol) and 1,4-diphenoxybenzene (5.25 g, 20.0 mmol) provided white crystals. Yield: 0.8 g (7.0%); mp: 260.3-261.9 °C; ¹H NMR (CDCl₃) δ 7.04 (d, 4 H, J=8.8 Hz), 7.07 (s, 4 H), 7.48 (d, 4 H, J=8.8 Hz), 7.87 (d, 4 H, J=8.8 Hz), 7.89 (d, 4 H, J=8.8 Hz).

Method 2: 4-Chlorobenzenesulfonyl chloride (4.57 g, 21.0 mmol) was added to a suspension of aluminum chloride (3.36 g, 25.2 mmol) in dry nitrobenzene (40 mL). The solution was heated with stirring under nitrogen to around 130°C, and then a solution of 1,4-diphenoxybenzene (2.68 g, 10.0 mmol) in dry nitrobenzene (30 mL) was added dropwise. After addition, the reaction was allowed to proceed for 24 hours at 130°C under nitrogen. Nitrobenzene was distilled under reduced pressure, yielding a tar-like viscous oil. The crude product was extracted with chloroform and subjected to column chromatography using chloroform as eluent to isolate the compound. Yield: 4.04 g (66%); ¹H NMR (CDCl₃): the same as above.

Cyclo(oxy-1,4-benzoyl-1,4-phenyleneoxy-1,4-phenyleneisopropylidene-1,4-phenyleneoxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenylene-isopropylidene-1,4-phenylene) (4.11)

A solution (50 mL) of **3.3** (10.06 g, 15.00 mmol) and **7** (3.27 g, 15.0 mmol) in DMAc was injected into a refluxing suspension of DMAc (600 mL), toluene (300 mL) and K₂CO₃ (3 g, 22 mmol) at a rate of 0.8 mL/hr. The suspension was mechanically stirred and purged with nitrogen. Water generated was azeotroped by toluene into a Dean-Stark trap. After injection, the reaction was allowed to continue for 24 hours. Upon cooling, KF and K₂CO₃ salts were filtered and

solvents evaporated; the resultant brown liquid (containing a small amount of DMAc) was then precipitated into water to give an off-white solid. The macrocycle (white solid) was isolated from linear oligomers by chromatography using a silica gel column and chloroform/ethyl acetate (50/1) as eluent. Yield: 8.6 g (68%); mp: 366.6-367.1°C; ¹H NMR (CDCl₃) δ 1.69 (s, 12 H, -CH₃), 6.94 (d, 4 H, *J*=8.8 Hz), 6.97 (d, 4 H, *J*=8.8 Hz), 6.98 (d, 4 H, *J*=8.8 Hz), 7.00 (d, 4 H, *J*=8.8 Hz), 7.23 (d, 4 H, *J*=8.8 Hz), 7.26 (d, 4 H, *J*=8.8 Hz), 7.78 (d, 4 H, *J*=8.8 Hz), 7.81 (d, 4 H, *J*=8.8 Hz); FABMS: calcd for C₅₅H₄₅O₇S: 849.3 [M+H]⁺ m/z, found: 849.4 [M+H]⁺ m/z.; elemental anal.: calcd for C₅₅H₄₄O₇S: C, 77.81; H, 5.22; S, 3.78; found: C: 77.86; H, 5.26; S, 3.85.

Cyclo(oxy-1,4-phenylene-phenylphosphonyl-1,4-phenyleneoxy-1,4-phenyleneisopropylidene-1,4-phenyleneoxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenyleneisopropylidene-1,4-phenylene) (4.12)

The same procedure as above was used. Thus, a solution (100 mL) of **3.3** (13.41 g, 20.00 mmol) and **4.4** (6.285 g, 20.00 mmol) in DMAc was injected at the rate of 1.5 mL/h into a suspension of DMAc (1000 mL), toluene (550 mL) and potassium carbonate (4.0 g, 28.9 mmol). Pure macrocycle **4.12** was isolated as a white powder from the crude mixture by silica gel column chromatography using chloroform/ethyl acetate (6.5/3.5) as eluent. Yield: 8.2 g (44%); mp (DSC): 240.3°C and 336.2°C (both are peak maxima); ¹H NMR (CDCl₃) δ 1.69 (s, 12 H), 6.95 (d, *J*=8.8 Hz, 4 H), 6.96 (d, *J*=8.8 Hz, 4 H), 6.97 (d, *J*=8.8 Hz, 4 H), 7.00 (d, *J*=8.8 Hz, 2 H), 7.01 (d, *J*=8.8 Hz, 2 H), 7.21 (d, *J*=8.8 Hz, 4 H), 7.25 (d, *J*=8.8 Hz, 4 H), 7.38-7.45 (m, 2 H), 7.55-7.53 (m, 1 H), 7.56 (d, *J*=8.8 Hz, 2 H), 7.59 (d, *J*=8.8 Hz, 2 H), 7.80 (d, *J*=8.8 Hz, 4 H); FABMS (in 3-NBA matrix): calc for C₆₀H₅₀O₇PS: 945.3 [M+H]⁺ m/z, found: 945.3 [M+H]⁺ m/z; elemental anal.: calcd for C₆₀H₄₉O₇PS: C, 76.25; H, 5.23; S, 3.39; found: C: 76.15; H, 5.27; S, 3.31.

Cyclo(oxy-1,4-benzoyl-1,4-benzoyl-1,4-phenyleneoxy-1,4-phenylene-isopropylidene-1,4-phenyleneoxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenyleneisopropylidene-1,4-phenylene) (4.13)

To a refluxing suspension of DMAc (400 mL), toluene (220 mL) and K₂CO₃ (0.4 g, 3 mmol), four aliquots of **3.3** (0.3354 g, 0.5000 mmol) and **4.5** (0.1612 g, 0.5000 mmol) dissolved in hot DMAc (15 mL) were added at 0, 12, 24, 36 hours, respectively. The suspension was mechanically stirred and purged with nitrogen. Water generated was azeotroped by toluene into a Dean-Stark trap. After the fourth addition, the reaction was allowed to continue for 12 more hours. Upon cooling, salts were filtered and solvents evaporated; the resultant brown liquid (containing a small amount of DMAc) was then precipitated into water, and filtered to give the crude product. Column chromatography (silica gel, 20/1 chloroform/ethyl acetate) was applied to isolate the macrocycle as a white solid. Yield: 1.58 g (83%); mp: 365.9-366.7°C. ¹H NMR (CDCl₃) δ 1.70 (s, 12 H, -CH₃), 6.93 (d, *J*=8.8 Hz, 4 H), 6.97 (d, *J*=8.8 Hz, 4 H), 6.99 (d, *J*=8.8 Hz, 4 H), 7.03 (d, *J*=8.8 Hz, 4 H), 7.24 (d, *J*=8.8 Hz, 4 H), 7.24 (d, *J*=8.8 Hz, 4 H), 7.81 (s, 4 H), 7.81 (d, *J*=8.8 Hz, 4 H), 7.83 (d, *J*=8.8 Hz, 4 H); FABMS (in 3-NBA matrix): calc for

C₆₂H₄₉O₈S: 953.3 [M+H]⁺ m/z, found: 953.2 [M+H]⁺ m/z; elemental anal.: calcd for C₆₂H₄₈O₈S: C, 78.13; H, 5.08; S, 3.36; found: C: 78.19; H, 5.13; S, 3.27.

Cyclo(oxy-1,4-benzoyl-1,4-phenylenesulfonyl-1,4-benzoyl-1,4-phenyleneoxy-1,4-phenyleneisopropylidene-1,4-phenyleneoxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenyleneisopropylidene-1,4-phenylene) (4.14)

The same procedure as in the synthesis of **4.11** was used. Thus, a solution (30 mL) of **3.3** (3.354 g, 5.000 mmol) and **4.6** (2.312 g, 5.000 mmol) in DMAc was injected into a refluxing suspension of DMAc (550 mL), toluene (250 mL) and K₂CO₃ (1.0 g, 7 mmol) at the rate of 1.9 mL/hr. The pure macrocycle (white powder) was isolated by chromatography using silica gel column and chloroform/ethyl acetate (40/1) eluent. Yield: 2.3 g (44%); mp: 394.8-395.6°C; ¹H NMR (CDCl₃) δ 1.70 (s, 12 H, -CH₃), 6.93 (d, 4 H, *J*=8.8 Hz), 6.98 (d, 4 H, *J*=8.8 Hz), 6.99 (d, 4 H, *J*=8.8 Hz), 7.01 (d, 4 H, *J*=8.8 Hz), 7.23 (d, 4 H, *J*=8.8 Hz), 7.24 (d, 4 H, *J*=8.8 Hz), 7.74 (d, 4 H, *J*=8.8 Hz), 7.83 (d, 4 H, *J*=8.8 Hz), 7.84 (d, 4 H, *J*=8.8 Hz), 8.07 (d, 4 H, *J*=8.8 Hz); FABMS (in 3-NBA matrix): calc for C₆₈H₅₃O₁₀S₂: 1093 [M+H]⁺ m/z, found: 1093 [M+H]⁺ m/z; elemental anal.: calcd for C₆₈H₅₂O₁₀S₂: C, 74.71; H, 4.79; S, 5.86; found: C: 74.81; H, 4.83; S, 5.75.

Cyclo(oxy-1,4-benzoyl-1,4-phenyleneoxy-1,4-benzoyl-1,4-phenyleneoxy-1,4-phenyleneisopropylidene-1,4-phenyleneoxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenyleneisopropylidene-1,4-phenylene) (4.15)

The same procedure as in the synthesis of **4.13** was used. *Small scale*: To a refluxing suspension of DMAc (500 mL), toluene (275 mL) and K₂CO₃ (0.8 g, 6 mmol), four aliquots of **3.3** (0.671 g, 1.00 mmol) and **4.7** (0.414 g, 1.00 mmol) dissolved in hot DMAc (10 mL) were added at 0, 12, 24, 36 hours, respectively. Purification by column chromatography using a silica gel column and chloroform/ethyl acetate (20/1) eluent provided a white solid. Yield: 3.1 g (75%); mp: 196°C and 323°C (DSC); ¹H NMR (CDCl₃) δ 1.70 (s, 12 H, -CH₃), 6.93 (d, 4 H, *J*=8.8 Hz), 6.99 (d, 4 H, *J*=8.8 Hz), 7.00 (d, 4 H, *J*=8.8 Hz), 7.03 (d, 4 H, *J*=8.8 Hz), 7.11 (d, 4 H, *J*=8.8 Hz), 7.23 (d, 4 H, *J*=8.8 Hz), 7.25 (d, 4 H, *J*=8.8 Hz), 7.79 (d, 4 H, *J*=8.8 Hz), 7.82 (d, 4 H, *J*=8.8 Hz), 7.83 (d, 4 H, *J*=8.8 Hz); FABMS (in 3-NBA matrix): calc for C₆₈H₅₃O₉S: 1045.3 [M+H]⁺ m/z, found: 1045 [M+H]⁺ m/z; elemental anal.: calcd for C₆₈H₅₂O₉S: C, 78.14; H, 5.01; S, 3.07; found: C: 78.25; H, 5.07; S, 2.96.

Large scale: To a refluxing mixture of DMAc (1000 mL), toluene (550 mL) and potassium carbonate (4.0 g, 28.9 mmol), twenty aliquots of **3.3** (0.670 g, 1.00 mmol) and **4.7** (0.414 g, 1.00 mmol) in hot DMAc (10 mL) were added in four hour time intervals during days and in twelve hour time intervals during nights. Pure macrocycle was obtained by washing the crude product with chloroform, providing a white solid. Yield: 10.9 g (52%); mp and ¹H NMR: the same as above.

Cyclo(oxy-1,4-benzoyl-1,4-phenyleneoxy-1,4-phenyleneoxy-1,4-benzoyl-1,4-phenyleneoxy-1,4-phenyleneisopropylidene-1,4-phenyleneoxy-1,4-phenylene-sulfonyl-1,4-phenyleneoxy-1,4-phenyleneisopropylidene-1,4-phenylene) (4.16)

The same procedure as above was used. Thus, to a refluxing suspension of DMAc (500 mL), toluene (275 mL) and K₂CO₃ (0.8 g, 6 mmol), four aliquots of **3.3** (0.671 g, 1.000 mmol) and **4.8** (0.507 g, 1.000 mmol) dissolved in hot DMAc (10 mL) were added at 0, 12, 24, 36 hours, respectively. The pure macrocycle was isolated as a white solid by chromatography using a silica gel column and chloroform/ethyl acetate (20/1) eluent. Yield: 2.9 g (63%); mp: 329.4-331.4°C; ¹H NMR (CDCl₃) δ 1.71 (s, 12 H, -CH₃), 6.94 (d, 4 H, *J*=8.8 Hz), 6.99-7.03 (m, 16 H), 7.13 (s, 4 H), 7.25 (d, 8 H, *J*=8.8 Hz), 7.78 (d, 4 H, *J*=8.8 Hz), 7.79 (d, 4 H, *J*=8.8 Hz), 7.84 (d, 4 H, *J*=8.8 Hz); FABMS (in 3-NBA matrix): calc for C₇₄H₅₇O₁₀S: 1137.4 [M+H]⁺ m/z, found: 1137 [M+H]⁺ m/z; elemental anal.: calcd for C₇₄H₅₆O₁₀S: C, 78.15; H, 4.96; S, 2.82; found: C: 78.21; H, 5.02; S, 2.74.

Cyclo(oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenyleneoxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenyleneisopropylidene-1,4-phenyleneoxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenylene-isopropylidene-1,4-phenylene) (4.17)

The same procedure as in the synthesis of **4.11** was used. Thus, a solution (30 mL) of **3.3** (0.939 g, 1.40 mmol) and **4.10** (0.856 g, 1.40 mmol) in DMAc was injected into a refluxing suspension of DMAc (300 mL), toluene (160 mL) and K₂CO₃ (0.28 g, 2 mmol) at the rate of 1 mL/hr. The macrocycle **3.4** (n=1) was isolated by washing the crude product with chloroform. Yield: 0.14 g (8%). The chloroform filtrate was directly loaded into a column (silica gel) for chromatographing using chloroform/ethyl acetate (20/1) as eluent. This isolated the desired macrocycle **4.17** plus about 10 wt% (18 mol%) **4.10**. These two compounds overlap with each other, observed by TLC in other eluting solvent systems (such as chloroform/hexanes and ethyl acetate/hexanes) besides the above one, and thus separation was unsuccessful. Yield (the mixture of **4.17** and **4.10**): 0.53 g (31%); mp: 185-215°C; ¹H NMR (CDCl₃) δ 1.69 (s, 12 H, -CH₃), 6.93 (d, *J*=8.8 Hz, 4 H), 6.94 (d, *J*=8.8 Hz, 4 H), 6.99 (d, *J*=8.8 Hz, 4 H), 7.00 (d, *J*=8.8 Hz, 4 H), 7.01 (d, *J*=8.8 Hz, 4 H), 7.06 (s, 4 H), 7.07 (s, impurity **4.10**), 7.23 (d, *J*=8.8 Hz, 4 H), 7.24 (d, *J*=8.8 Hz, 4 H), 7.48 (d, impurity **4.10**), 7.84 (d, *J*=8.8 Hz, 4 H), 7.86 (d, *J*=8.8 Hz, 4 H), 7.87 (d, *J*=8.8 Hz, 4 H) 7.87 (d, impurity **4.10**, partially overlapped), 7.89 (d, impurity **4.10**, partially overlapped), other peaks of **4.10** completely overlap with those of **4.17**; FABMS (3-NBA): calc for C₇₂H₅₇O₁₂S₃ (**4.17**): 1209.3 [M+H]⁺ m/z, found: 1209 [M+H]⁺ m/z, the molecular ion peak for **4.10** was not observed; elemental anal.: calcd for C_{64.44}H_{49.50}O_{10.92}S_{2.82}Cl_{0.36} (82 mol% **4.17** plus 18 mol% **4.10**): C, 70.24; H, 4.54; S, 8.21; found: C: 70.82; H, 4.70; S, 7.88.

Cyclo(oxy-1,4-benzoyl-1,4-phenyleneoxy-1,4-benzoyl-1,4-phenyleneoxy-1,4-phenyleneisopropylidene-1,4-phenylene) (4.18)

The same procedure as in the synthesis of **4.13** was used. Thus, to a refluxing suspension of DMAc (400 mL), toluene (220 mL) and K₂CO₃ (0.4 g, 3 mmol), four aliquots of bisphenol-A **4.2** (0.114 g, 0.500 mmol) and **4.7** (0.207 g, 0.500 mmol). Column chromatography (silica gel, 50/1 chloroform/ethyl acetate) isolated the macrocycle as a white solid. Yield: 0.80 g (66%), mp

>400°C. ¹H NMR (CDCl₃) δ 1.73 (s, 6 H, -CH₃), 6.97 (d, *J*=8.8 Hz, 4 H), 7.01 (d, *J*=8.8 Hz, 4 H), 7.02 (d, *J*=8.8 Hz, 4 H), 7.32 (d, *J*=8.8 Hz, 4 H), 7.66 (d, *J*=8.8 Hz, 4 H), 7.67 (d, *J*=8.8 Hz, 4 H); FABMS (in 3-NBA matrix): calc for C₄₁H₃₁O₅: 603.2 [M+H]⁺ m/z, found: 603 [M+H]⁺ m/z; elemental anal.: calcd for C₄₁H₃₀O₅: C, 78.70; H, 4.83; found: C: 78.63; H, 5.00.

Cyclo(oxy-1,4-benzoyl-1,4-phenyleneoxy-1,4-phenyleneoxy-1,4-benzoyl-1,4-phenyleneoxy-1,4-phenyleneisopropylidene-1,4-phenylene) (4.19)

The same procedure as above was used. Thus, to a refluxing suspension of DMAc (400 mL), toluene (220 mL) and K₂CO₃ (0.4 g, 3 mmol), four aliquots of bisphenol-A (**4.2**) (0.114 g, 0.500 mmol) and **4.8** (0.253 g, 0.500 mmol) dissolved in DMAc (15 mL) were added at 0, 12, 24, 36 hours, respectively. The pure macrocycle was isolated as a white powder by chromatography using a silica gel column and chloroform/ethyl acetate (50/1) eluent. Yield: 1.1 g (80%); mp: 379.0-381.2°C; ¹H NMR (CDCl₃) δ 1.68 (s, 6 H, -CH₃), 6.99 (d, *J*=8.8 Hz, 4 H), 6.99 (d, *J*=8.8 Hz, 4 H), 7.09 (d, *J*=8.8 Hz, 4 H), 7.14 (s, 4 H), 7.28 (d, *J*=8.8 Hz, 4 H), 7.80 (d, *J*=8.8 Hz, 4 H), 7.86 (d, *J*=8.8 Hz, 4 H); FABMS (in 3-NBA matrix): calc for C₄₇H₃₅O₆: 695.2 [M+H]⁺ m/z, found: 695 [M+H]⁺ m/z; elemental anal.: calcd for C₄₇H₃₄O₆: C, 81.25; H, 4.93; found: C: 81.35; H, 4.96.

Cyclo(oxy-1,4-benzoyl-1,4-phenylenesulfonyl-1,4-benzoyl-1,4-phenyleneoxy-1,4-phenyleneoxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenylene) (4.20)

The same procedure as in the synthesis of **4.11** was used. Thus, a solution (30 mL) of **4.1** (2.174 g, 5.000 mmol) and **4.6** (2.312 g, 5.000 mmol) in DMAc was injected into a refluxing suspension of DMAc (550 mL), toluene (250 mL) and K₂CO₃ (1.0 g, 7 mmol) at the rate of 1.9 mL/hr. Recrystallization in chloroform provided white crystals. Yield: 0.9 g (21%); mp: 407-409°C; ¹H NMR (CDCl₃) δ 7.01 (d, 4 H, *J*=8.8 Hz), 7.04-7.12 (m, 12 H), 7.80 (d, 4 H, *J*=8.8 Hz), 7.87 (d, 4 H, *J*=8.8 Hz), 7.95 (d, 4 H, *J*=8.8 Hz), 8.08 (d, 4 H, *J*=8.8 Hz); FABMS (in 3-NBA matrix): calc for C₅₀H₃₃O₁₀S₂: 857.1 [M+H]⁺ m/z, found: 857 [M+H]⁺ m/z; elemental anal.: calcd for C₅₀H₃₂O₁₀S₂: C, 70.08; H, 3.76; S, 7.48; found: C: 70.04; H, 3.76; S, 7.38.

Cyclo(oxy-1,4-benzoyl-1,4-phenyleneoxy-1,4-benzoyl-1,4-phenyleneoxy-1,4-phenyleneoxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenylene) (4.21)

The same procedure as in the synthesis of **4.13** was used. Thus, to a refluxing suspension of DMAc (400 mL), toluene (220 mL) and K₂CO₃ (0.4 g, 3 mmol), four aliquots of **4.1** (0.217 g, 0.500 mmol) and **4.7** (0.207g, 0.500 mmol) dissolved in hot DMAc (10 mL) were added at 0, 12, 24, 36 hours, respectively. The macrocycle was isolated as a white solid by chromatography using a silica gel column and chloroform/ethyl acetate (20/1) eluent. Yield: 1.3 g (82%); mp: 404.2-406.2°C; ¹H NMR (CDCl₃) δ 6.97 (d, 4 H, *J*=8.8 Hz), 7.02 (d, 4 H, *J*=8.8 Hz), 7.08-7.15 (m, 12 H), 7.82 (d, 4 H, *J*=8.8 Hz), 7.84 (d, 4 H, *J*=8.8 Hz), 7.86 (d, 4 H, *J*=8.8 Hz); FABMS (in 3-NBA matrix): calc for C₅₀H₃₃O₉S: 809.1 [M+H]⁺ m/z, found: 809 [M+H]⁺ m/z; elemental anal.: calcd for C₅₀H₃₂O₉S: C, 74.25; H, 3.99; S, 3.96; found: C: 74.35; H, 4.05; S, 3.84.

Cyclo(oxy-1,4-benzoyl-1,4-phenyleneoxy-1,4-phenyleneoxy-1,4-benzoyl-1,4-phenyleneoxy-1,4-phenyleneoxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenylene) (4.22)

The same procedure as above was used. Thus, to a refluxing suspension of DMAc (400 mL), toluene (220 mL) and K_2CO_3 (0.4 g, 3 mmol), four aliquots of **4.1** (0.217 g, 0.500 mmol) and **4.8** (0.253g, 0.500 mmol) dissolved in hot DMAc (10 mL) were added at 0, 12, 24, 36 hours, respectively. The pure macrocycle was isolated as a white solid by chromatography using a silica gel column and chloroform/ethyl acetate (20/1) eluent. Yield: 1.4 g (76%); mp: 361.0-363.3°C. 1H NMR ($CDCl_3$) δ 6.99-7.08 (m, 16 H), 7.11 (s, 4 H), 7.78 (d, 4 H, $J=8.4$ Hz), 7.80 (d, 4 H, $J=8.4$ Hz), 7.88 (d, 4 H, $J=8.4$ Hz); FABMS (in 3-NBA matrix): calc for $C_{56}H_{37}O_{10}S$: 901.2 $[M+H]^+$ m/z, found: 901 $[M+H]^+$ m/z; elemental anal.: calcd for $C_{56}H_{36}O_{10}S$: C, 74.66; H, 4.03; S, 3.56; found: C: 74.61; H, 4.06; S, 3.49.

Cyclo(oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenyleneoxy-1,4-phenylenesulfonyl-1,4-benzoyl-1,4-phenyleneoxy-1,4-phenyleneoxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenylene) (4.23)

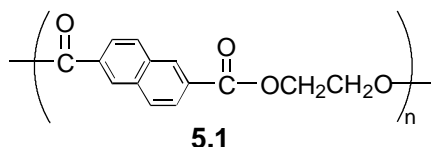
The same procedure as in the synthesis of **4.11** was used. Thus, a solution (30 mL) of **4.1** (0.869 g, 2.000 mmol) and **4.10** (1.223 g, 2.000 mmol) in DMAc was slowly injected into a refluxing suspension of DMAc (400 mL), toluene (220 mL) and K_2CO_3 (0.4 g, 3 mmol) at the rate of 1.0 mL/hr. The macrocycle was isolated as a white solid by column chromatography using chloroform/ethyl acetate (20/1) as eluent. Yield: 0.76 g (39 %); mp: > 425° C (not melted); 1H NMR ($DMSO-d_6$) δ 7.13 (d, 12 H, $J=8.8$ Hz), 7.22 (s, 12 H), 7.93 (d, 12 H, $J=8.8$ Hz); FABMS (in 3-NBA matrix): calc for $C_{54}H_{37}O_{12}S_3$: 973.1 $[M+H]^+$ m/z, found: 973 $[M+H]^+$ m/z; elemental anal.: calcd for $C_{54}H_{36}O_{12}S_3$: C, 66.66; H, 3.73; S, 9.88; found: C: 66.08; H, 3.85; S, 9.68.

Chapter 5

Synthesis and Characterization of 24-Membered Cyclo(ethylene 2,6-naphthalate)

5.1 Introduction

Poly(ethylene 2,6-naphthalate) (PEN) **5.1** has gained commercial interest for its good thermal, mechanical, chemical and dielectric properties which are generally superior to those of poly(ethylene terephthalate) (PET).^{1,2} For example, PEN has a glass transition temperature of 113°C, an increase by about 43°C compared to PET; its modulus and tensile strength are 50% and 35%, respectively, higher than those of PET. The electrical insulation, radiation resistance and gas barrier properties of PEN are also superior to PET. Because of these good properties, PEN has many potential advanced applications,² such as industrial fiber cords for rubber reinforcement, film substrates for abrasive, long-lasting magnetic recording tapes, flexible printed circuit boards, electronic insulators and packaging.



PEN is typically prepared by a transesterification process, wherein dimethyl 2,6-naphthalate is reacted with ethylene glycol in the presence of a suitable catalyst at high temperatures and reduced pressures.³ The process is analogous to producing PET from dimethyl terephthalate; thus existing PET production lines can be modified to manufacture PEN². Recently in an effort to avoid high melt viscosity in processing, ring opening polymerization (ROP) was attempted for preparation of this polyester.⁴ The reported ROP method, however, only provided PEN with low intrinsic viscosity compared to the commercial material. This low molecular weight presumably resulted from linear impurities which would participate in the reaction and reduce the molecular weight of polymer.

As a part of our research in pursuit of single-sized pure macrocycles for preparation of engineering thermoplastics, the titled 24-membered cyclo(ethylene 2,6-naphthalate) (**5.7**) was synthesized as a cyclic precursor to PEN. ROP of the single-sized, pure macrocycle should be well controlled under appropriate reaction conditions. This chapter describes the synthesis and characterization of this macrocycle.

¹ a) Ouchi, I.; Aoki, H.; Shimotsuma, S.; Asai, t.; Hosoi, M. *Proc. 17th Japan. Congr. Materials Research*, **1974**, 217-223. b) Furukawa, T.; Sakai, K. *Japan Plastics Age*, **June, 1974**, 20-25.

² Michaels, F. *High-Performance Resin Competes for Tough Job Despite Cost* in Toensmeier, P. A. ed. *Modern Plastics Encyclopedia*, McGraw-Hill, Inc., New York, 1996, pp B-51 to B-53.

³ Wiener, M. V. U. S. Patent 3,377,319, 1968.

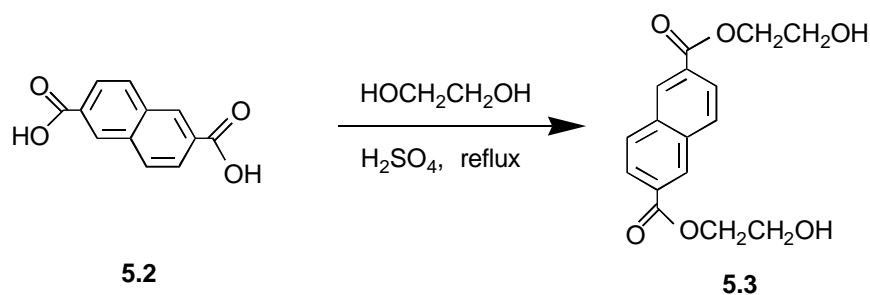
⁴ See ref. 38 in Chapter 1

5.2 Results and Discussion

5.2.1 Synthesis of linear precursors to the macrocycle

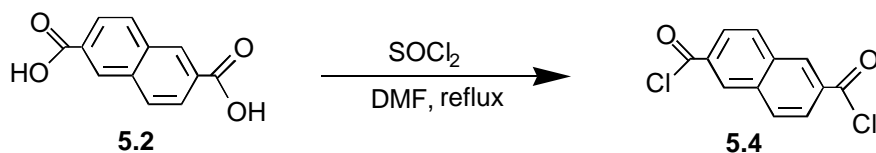
One approach to the titled macrocycle (**5.7**) was designed through bimolecular cyclization between diol **5.3** and diacid chloride **5.4** (Scheme 5.4, see section 5.2.2). This approach is similar to that used in the syntheses of single sized aromatic ether macrocycles, as described in preceding chapters. Thus both **5.3** and **5.4** were prepared, starting from naphthalene-2,6-dicarboxylic acid (**5.2**). The diol **5.3** was synthesized by refluxing the diacid **5.2** in a large excess ethylene glycol in the presence of catalytic amount of mineral acid (Scheme 5.1). The product was isolated from the excess ethylene glycol by extraction with ethyl acetate. Recrystallization in toluene once provided white crystals in 38% yield. The melting point, 146.0-148.6°C, is about 17°C higher than the reported value.⁵

Scheme 5.1



Synthesis of diacid chloride **5.4** was achieved by refluxing diacid **5.2** in a large excess of thionyl chloride which was also used as solvent (Scheme 5.2). Since the reaction occurred in two phases, it took more than four days to complete. Addition of several drops of DMF as a phase transfer agent greatly decreased the reaction time to a few hours. The reaction yielded 90% of **5.4** with mp of 189.2-191.0°C after recrystallization in THF / hexane. The reported yield is 94% and mp 188.5-189.5°C.⁶

Scheme 5.2



Another approach to macrocycle **5.7** was designed through unimolecular cyclization of hydroxy acid **5.6** in the presence of DCC (dicyclohexylcarbodiimide). Use of the DCC method

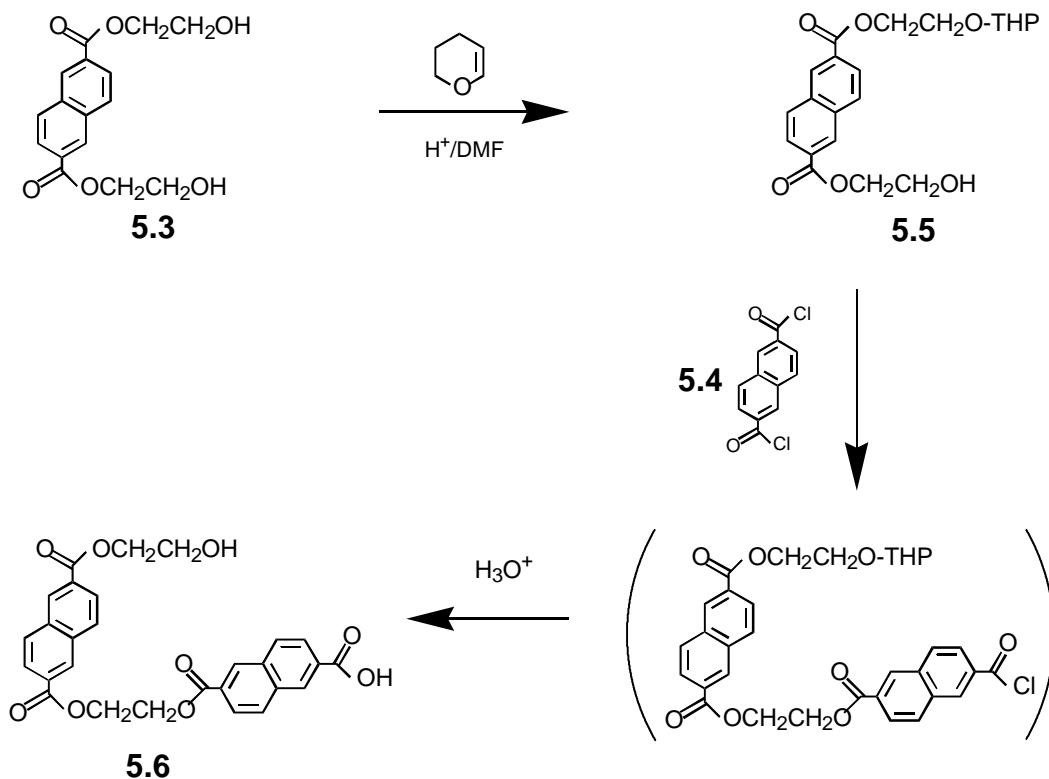
⁵ Wang, C. S.; Sun, Y. M. *J. Polym. Sci.: Part A: Polym. Chem.* **1994**, *32*, 1305-1315.

⁶ Burdett, K. A. *Synthesis* **1991**, *6*, 441-442.

for preparation of cyclic esters (lactones) has been seen in the literature,⁷ in which lactones with ring sizes up to 17 were shown to be readily obtained in high yield by intramolecular macrolactonization of various hydroxy acids under high dilution conditions. The intramolecular cyclization avoids the problem of stoichiometric imbalance.

Thus, preparation of the hydroxy acid **5.6** was attempted, as shown in Scheme 5.3. First, the diol **5.3** was mono-protected by THP (tetrahydropyran) at the one end to form mono THP-ether **5.5** using pyridinium p-toluenesulfonate as catalyst. To have only one end protected, **5.3** was used in excess relative to dihydropyran. The reaction yielded 62% of **5.5** after purification by column chromatography. The structure of the mono THP-ether was confirmed by ¹H NMR spectroscopy, as shown in Figure 5.1. Due to formation of THP-ether, a chiral center (asterisk labeled carbon) is generated in the molecule, which results in nonequivalence of the vicinal methylene protons and the C-6 methylene protons, *H_a*, *H_e*, and protons *b*. The nonequivalence results in multiplicities of these protons and protons *c* adjacent to protons *b*. The equatorial proton (*H_e*) and the axial proton (*H_a*) are nonequivalent; they occur at about 3.96 and 3.46 ppm, respectively.

Scheme 5.3



⁷ Boden, E. P.; Keck, G. E. *J. Org. Chem.* **1985**, *50*, 2394-2395.

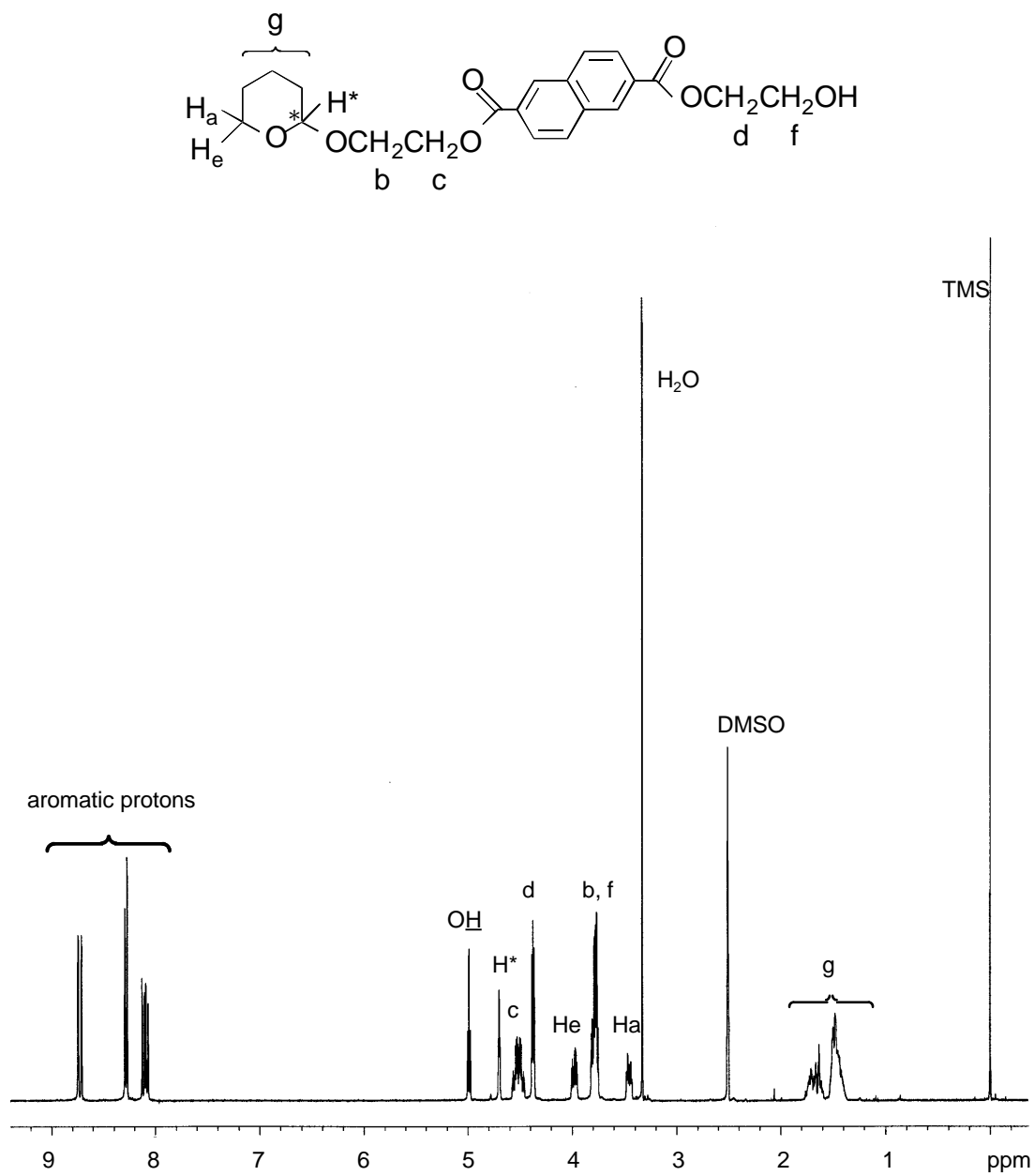


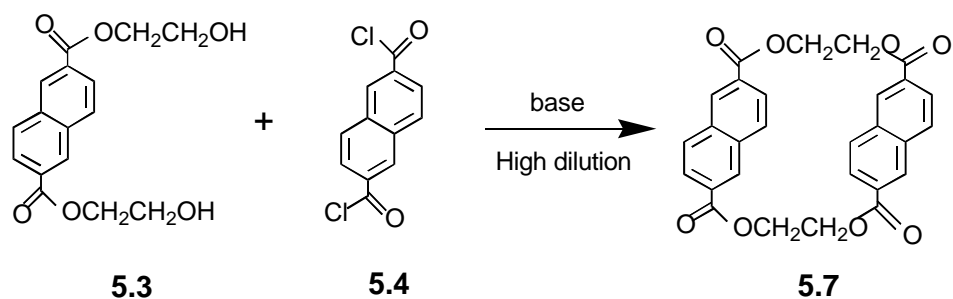
Figure 5.1 400 MHz ^1H NMR spectrum of **5.5** in DMSO-d_6 .

Preparation of **5.6** was carried out by reaction of **5.5** and excess **5.4** in THF/pyridine at the room temperature, followed by hydrolysis of the acid chloride moiety in dilute aqueous sodium hydroxide. Unfortunately, since the product before and after hydrolysis was insoluble in common organic solvents, it is extremely difficult to purify. Thus, the hydroxy acid **5.6** was not obtained and the synthesis of macrocycle **5.7** by unimolecular cyclization of **5.6** was not able to be carried out.

5.2.2 Cyclization

The 24-membered macrocycle **5.7** was prepared by bimolecular cyclization between elongated diol **5.3** and diacid chloride **5.4** under high dilution conditions (Scheme 5.4). Instead of using the influx procedure to achieve high dilution, as described in Chapter 1, high dilution was controlled by adding small aliquots of equal molar amounts of **5.3** and **5.4** in 4 hour time intervals. The total feed was about 5.3×10^{-3} mol/L.

Scheme 5.4



The macrocycle **5.7** has different chemical shifts from other components in the product mixture; thus the reaction can essentially be monitored by ^1H NMR spectroscopy. It was found that using triethylamine as catalyst in either refluxing THF or methylene chloride, no target macrocycle was observed in ^1H NMR spectra, whereas using pyridine as catalyst, about 10% macrocycle **5.7** was detected (column chromatography isolated 9% of the macrocycle). While pyridine is more efficient towards the cyclization, the yield is low. One reason for the low yield may be due to the hydrolysis of **5.4**, since a small amount of naphthalene 2,6-dicarboxylic acid (hydrolysis product of **5.4**) was found after reaction. The hydrolysis would lead to the imbalance of two compounds during reaction and therefore the low yield of the macrocycle. Another reason, probably most important, may be due to reluctance of ring closure because of ring strain in the macrocycle. In the literature⁴ where the synthesis of a cyclic mixture (**1.43**, $m=2$) from ethylene glycol and **5.4** is described, it is found that the dimer (**1.43**, $m=2$, $n=2$) of the same structure as **5.7** is difficult to observe in the mass spectrum although the authors anticipated that the dimer is the major component in the mixture. The “absence” of this macrocycle in the mixture is supporting evidence for the low yield in our intended synthesis of this macrocycle. In another cyclic mixture (**1.43**, $m=4$), cyclo(butylene 2,6-naphthalate) synthesized from butanediol and **5.4**,

the dimer (**1.43**, $m=4$, $n=2$), which is four atoms larger than **5.7**, is the most abundant component by mass spectrometry.⁴

The identity of macrocycle **5.7** is confirmed by proton NMR and FABMS. Due to formation of a symmetric cyclic structure, the ^1H NMR spectrum (Figure 5.2) is simple with no terminal groups observed. The singlet at 4.83 ppm is due to the methylene proton, the doublet at 7.31 ppm due to the protons at the 4 position (c), the doublet of doublets at 7.65 ppm due to the protons at the 3 position (b) and the doublet at 8.04 ppm due to the protons at the 1 position (a). FAB mass spectrometry (in 3-NBA) (Figure 5.3) provides direct evidence that the target macrocycle was obtained. The macrocycle melts at 245.5-246.3°C, and is soluble in chloroform, while PEN polymer is not.

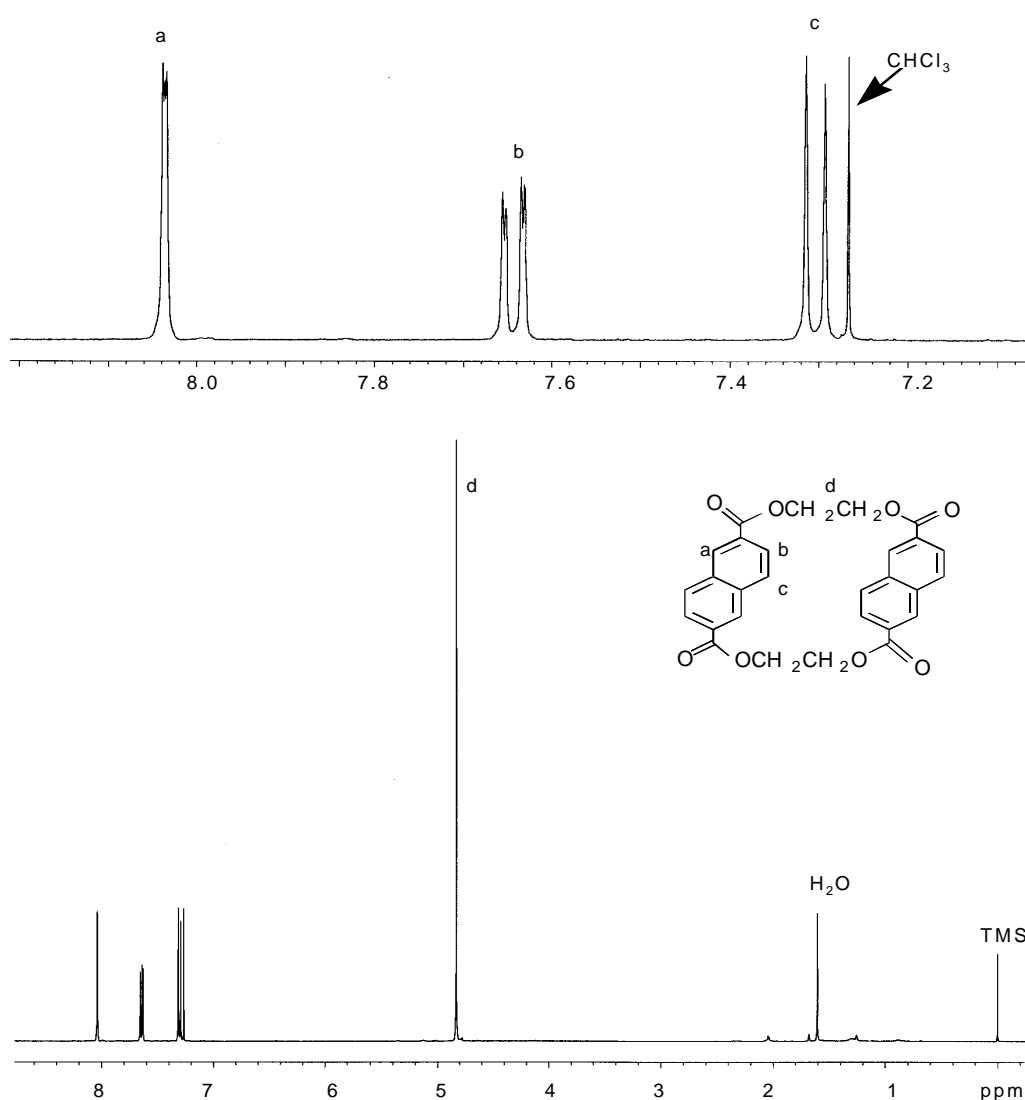


Figure 5.2 400 MHz ^1H NMR spectrum of macrocycle **5.7** in CDCl_3

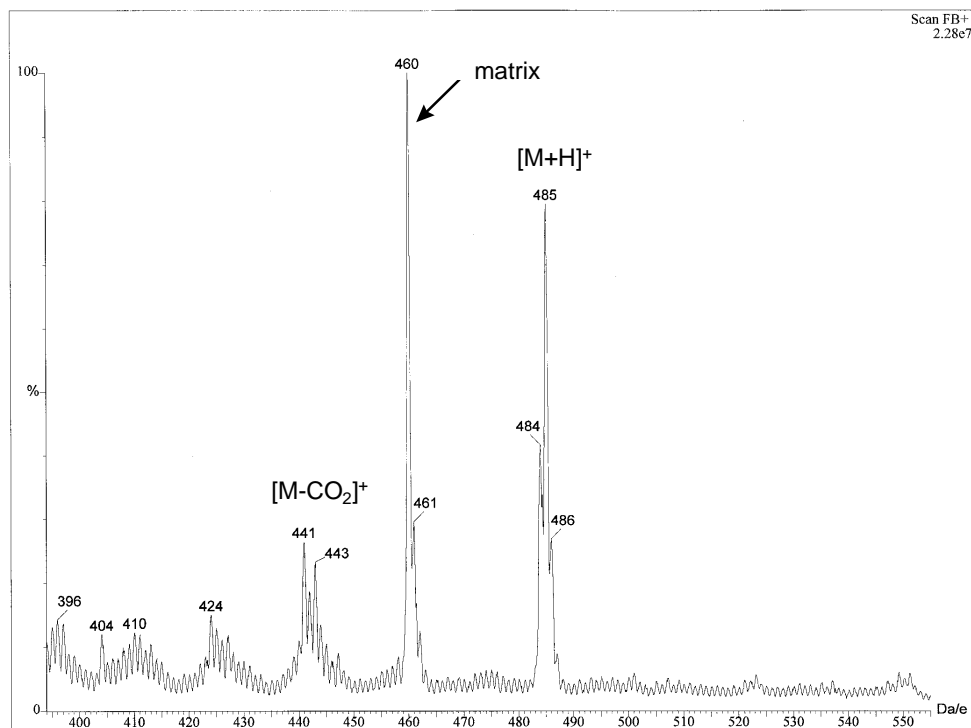


Figure 5.3 FAB-MS (in 3-nitrobenzyl alcohol matrix) of macrocycle **5.7**

5.3 Conclusions

The synthesis of 24-membered cyclo(ethylene 2,6-naphthalate) **5.7** met little success. Although the hydrolysis of the diacid chloride **5.4** during reaction is one reason, the main reason is presumably due to high ring strain in the macrocycle, which retards ring closure. Increasing ring size to release ring strain may increase the yield of a larger macrocycle, but the synthesis of corresponding longer linear precursors will be very tedious and costly, and also the longer precursor will possibly be of low solubility, not easily prepared.

5.4 Experimental

Materials and Measurements

Tetrahydrofuran was distilled from the purple solution of benzophenone/Na, and methylene chloride was distilled from calcium hydride prior to use. Other reactants and solvents were used as received from chemical suppliers.

Melting points were taken in capillary tubes with a Melt-Temp II melting point apparatus and have been corrected. ^1H NMR spectra were obtained at ambient temperature on Bruker WP 270-MHz and Varian 400 MHz spectrometers in deuterated dimethyl sulfoxide or chloroform

with TMS as the internal standard. FTIR (KBr pellet) spectra were recorded on a Perkin Elemer 1720-X spectrometer at the resolution of 4 cm^{-1} . FAB mass spectra were recorded on a Fisons VG Quattro spectrometer using 3-nitrobenzyl alcohol (3-NBA) as matrix.

2-Hydroxyethyl 2,6-naphthalate (5.3)

Sulfuric acid (conc., 2.5 mL) was added to a slurry of naphthalene-2,6-dicarboxylic acid (6.00g, 27.75 mmol) in ethylene glycol (90 mL), and the mixture was brought to reflux under nitrogen. After half an hour, the original slurry became clear. The reaction was allowed to proceed for a total of four hours. Upon cooling, the clear solution was precipitated into ice-cooled water (200 mL) under stirring. A saturated aqueous NaHCO_3 solution was added to neutralize the liquid phase; however, this led to formation of an emulsion. The product was thus extracted with ethyl acetate (3 x 200 mL). The combined ethyl acetate phase was dried with Na_2SO_4 and evaporated to give a brownish oil. Recrystallization from toluene once isolated the desired compound as white crystals. Yield: 3.24g (38.4%); mp: 146.0-148.6°C (lit.⁵ 129-131°C); $^1\text{H NMR}$ (DMSO-d_6) δ 3.74 (m, 4 H), 4.35 (t, $J=4.7$ Hz, 4 H), 4.97 (t, $J=4.7$ Hz, 2 H), 8.09 (d, $J=8.4$ Hz, 2 H), 8.26 (d, $J=8.4$ Hz, 2 H), 8.73 (s, 2 H). FTIR (KBr) cm^{-1} 3465, 3400, 3068, 2966, 2937, 2881, 1724, 1701, 1603, 1457, 1368, 1277, 1267, 1191, 1071, 771.

2,6-Naphthoyl chloride (5.4)

Five drops of DMF was added to a slurry of naphthalene-2,6-dicarboxylic acid (**5.2**) (21.6 g, 0.1 mol) and thionyl chloride (300 mL, 4 mol). The mixture was then brought to reflux with stirring under a nitrogen atmosphere. The reaction took about five hours to complete and the original slurry became a clear solution. The solution was filtered hot to remove a trace amount of intractable solid, then evaporated with a rotary evaporator. Recrystallization in THF/hexane provided yellow needle-like crystals. Yield: 8.4 g (90%), mp 189.2-191.0°C (lit.⁶ 188.5-189.5°C); $^1\text{H NMR}$ (CDCl_3) δ 8.13 (d, $J=8.4$ Hz, 2 H), 8.19 (d, $J=8.4$ Hz, 2 H), 8.80 (s, 2 H); FTIR (KBr) cm^{-1} 3089, 1751, 1597, 1384, 1338, 1278, 1218, 1164, 1124, 941, 916, 813, 704.

2-(2-Hydroxyethyl), 6-[2-(tetrahydropyran-1-oxy)ethyl] naphthalate (5.5)

Pyridium *p*-toluenesulfonate (0.25 g, 1.0 mmol) was added to a solution of **5.3** (6 g, 20 mmol), dihydropyran (2.52 g, 10.0 mmol) at 55°C in anhydrous DMF (50 mL). The solution was stirred at 55°C under nitrogen for 5 hours, and then cooled to room temperature. The cooled solution was precipitated into ice-cooled water with stirring, filtered, rinsed with fresh water and dried under vacuum. Excess, unreacted **5.3** was removed by boiling the product in toluene (150 mL) twice and filtering upon cooling. The filtrate contained the desired product **5.5** which was purified by flash silica gel column chromatography using ethyl acetate/hexane (6/4) as eluent. This provided a colorless oil. Yield: 2.4 g (62%). Recrystallization in ethyl acetate/hexane provided white crystals; mp: 62.1-64.3°C ; $^1\text{H NMR}$ (DMSO-d_6) δ 1.39-1.79 (m, 6 H), 3.44-3.48 (m, 1 H), 3.75-3.82 (m, 4 H), 3.95-4.00 (m, 1 H), 4.37 (t, $J=5.0$ Hz, 2 H), 4.46-4.57 (m, 2 H), 4.70 (t, $J=3.2$ Hz 1 H), 4.99 (t, $J=5.0$ Hz 1 H), 8.08 (d, $J=8.4$ Hz, 1 H), 8.11 (d, $J=8.4$ Hz, 1 H), 8.28 (d, $J=8.4$ Hz, 2 H), 8.71 (s, broad, 1 H), 8.74 (s, broad, 1 H); elemental anal.: calcd for $\text{C}_{21}\text{H}_{24}\text{O}_7$: C, 64.94; H, 6.23; found: C, 64.83; H, 6.27.

Ethylene Naphthalate Macrocycle **5.7**

A typical procedure is as follows: To a refluxing solution of dry THF (600 mL) and pyridine (0.4 mL, 5 mmol), four aliquots of **5.3** (0.3043 g, 1.000 mmol) in dry THF (10 mL) and **5.4** (0.2531 g, 1.000 mmol) in dry THF (10 mL) were transferred using a cannula at 0, 4, 8, 12 hours, respectively. In each transfer, both flasks containing **5.3** and **5.4** were washed with dry THF (2 x 5 mL) and the washings were then transferred into the reaction solution. The solution was magnetically stirred and purged with nitrogen. After the fourth addition, the reaction was continued for an additional 12 hours. Upon cooling, the pyridinium chloride salt was filtered and the solvent evaporated, yielding a brownish solid. The solid was washed with water to remove a small amount of salt and pyridine, filtered and dried under vacuum at 80°C overnight. The crude product was washed with chloroform (2 x 50 mL), and the combined chloroform washings were directly loaded into a column (silica gel, 20/1 chloroform/ethyl acetate as eluent) for separation, which isolated the pure macrocycle. Yield: 0.17 g (9%); mp 245.5-246.3.°C; ¹H NMR (CDCl₃) δ 4.83 (s, 8 H, -CH₂), 7.30 (d, J=8.4 Hz, 4 H), 7.64 (d, J=8.4 Hz, 4 H), 8.04 (s, 4 H); FTIR (KBr) cm⁻¹ 3070, 2956, 1717, 1598, 1455, 1380, 1338, 1287, 1271, 1211, 1187, 1143, 1095, 797, 771, 760, 734; FABMS (3-NBA): calc. for C₂₈H₂₁O₈ 485.5 [M+H]⁺, m/z, found: 485 [M+H]⁺, m/z; elemental anal.: calcd for C₂₈H₂₀O₈: C, 69.42; H, 4.16; found: C, 69.13; H, 4.27.

Chapter 6

Synthesis and Characterization of Bisphenol-A Based Arylene Ether Sulfone Cyclo-oligomeric Mixtures

6.1 Introduction

The commercial attractiveness of using cyclo-oligomeric mixtures as precursors for preparation of polymers is that cyclic mixtures have significantly lower melting points than discrete macrocycles.¹ A problem, however, is that preparation of cyclic mixtures inevitably brings in certain amounts of linear oligomers or polymers which are extremely difficult to remove. The presence of linears would lead to difficulties in the control and in the fundamental study of the ring opening polymerization process.² Furthermore, since discrete macrocycles of small ring sizes in a cyclic mixture normally have very high melting points, despite the fact that the melting point of the cyclic mixture is low, they tend to crystallize during melt polymerization of the cyclic mixture, thus leading to a product of polymer and residual crystalline cyclics.³ To further address the above problems and to compare the ring opening polymerization of cyclic mixtures with that of pure single-sized macrocycles, the syntheses and ring opening polymerizations of the titled cyclic mixtures were carried out. This chapter describes the synthesis and characterization; the ring opening polymerization is discussed in Chapter 7 in comparison to that of single ring sized macrocycles.

6.2 Results and Discussion

6.2.1 Synthesis

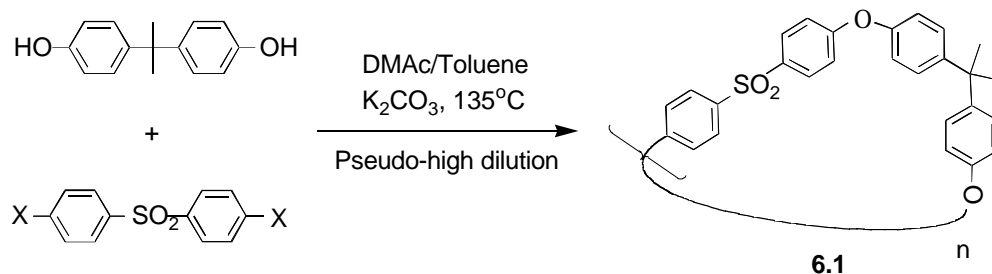
Bisphenol-A based arylene ether sulfone cyclooligomeric mixtures **6.1** were prepared directly from bisphenol-A (BPA) and 4,4'-difluorodiphenyl sulfone (DFDPS) or 4,4'-dichlorodiphenyl sulfone (DCDPS) via aromatic nucleophilic substitution reactions under pseudo-high dilution conditions (Scheme 6.1). As usual, pseudo-high dilution was achieved by slow injection of bisphenol-A and the dihalide, both dissolved in a small amount of DMAc, into a reaction flask containing a refluxing suspension (~135°C) of DMAc, toluene and potassium carbonate. In the synthesis of **6.1a** where difluorodiphenyl sulfone was used, the rate of feed v_f was 1.7×10^{-7} mol/L•sec and the total feed c_f 3.1×10^{-2} mol/L. Total reaction time was 42 hours, 30 hours for injection of the reactants and 12 hours after injection. The product was collected in 99% yield. It was found that cyclic dimer **6.1a**(n=2) was formed in 35% yield in this reaction. This macrocycle was isolated by washing the product with chloroform. Recall that in Chapter 3, the cyclic dimer, the 40-membered disulfone macrocycle **3.4**(n=1), was deliberately prepared from elongated bisphenol precursor **3.3** and difluorodiphenyl sulfone in 67% yield, and has been shown to have a very high melting point (above 500°C) and poor solubility. Removal of the cyclic dimer is necessary, since it quickly crystallizes out of the product mixture upon heating above 300°C to form a separate crystalline phase inert to melt ring opening polymerization, while the rest of product is amorphous and completely melts at 300°C.

¹ See ref. 4 in Chapter 1

² See ref. 15(a) and 23 in Chapter 1

³ See ref.5 in Chapter 1

Scheme 6.1



	%yield of 6.1	% dimer 6.1 (n=2)
a: X=F, 12 hrs, after injection,	99	35
b: X=Cl, 24 hrs, after injection,	96	22
c: X=Cl, 36 hrs, after injection,	97	24

When dichlorodiphenyl sulfone, a much cheaper dihalide, was used, the cyclic dimer was found to contribute 22% and 24% in the product mixtures **6.1b** and **6.1c**, respectively (Scheme 6.1). The low yields were presumably due to low reactivity of the chloride which increased the chance of chain elongation to form larger ring sized macrocycles. Although the content of the cyclic dimer is reduced, it still causes the same problem as above upon heating. Thus, it was removed from both product mixtures. The residual products completely melt at about 300°C as above. Considering the low reactivity of the chloride, higher dilution conditions and longer reaction times were applied in both syntheses. The rate of feed v_f was 1.2 mol/L•sec and the total feed c_f 2.83 mol/L. The reaction time after injection was increased to 24 hours and 36 hours, respectively. As will be shown later, the 24 hour reaction time was not enough; higher levels of linear oligomers were formed in **6.1b**.

The molecular weight of the residual products after removal of the dimer was determined by gel permeation chromatography (GPC), as shown in Table 6.1. Assuming that these products consist entirely of macrocycles, the average ring size of **6.1a** is then 5, whereas it is 8 for **6.1c**. From GPC curves (Figure 6.1) it can be seen that **6.1a** (curve 1) contains higher levels of small macrocycles than **6.1c** (curve 3). The abnormal GPC curve (curve 2) of **6.1b** is due to the presence of a large amount of linear oligomers whose hydrodynamic volumes are different from cyclics.

Table 6.1. GPC^a results of the residual products without cyclic dimer **6.1**(n=2).

mixture	M_n	PDI	average no. of repeating units
6.1a	2300	1.8	5.2
6.1b	2000	1.5	4.5
6.1c	3600	1.5	8.1

a) In NMP, 60°C, universal calibration.

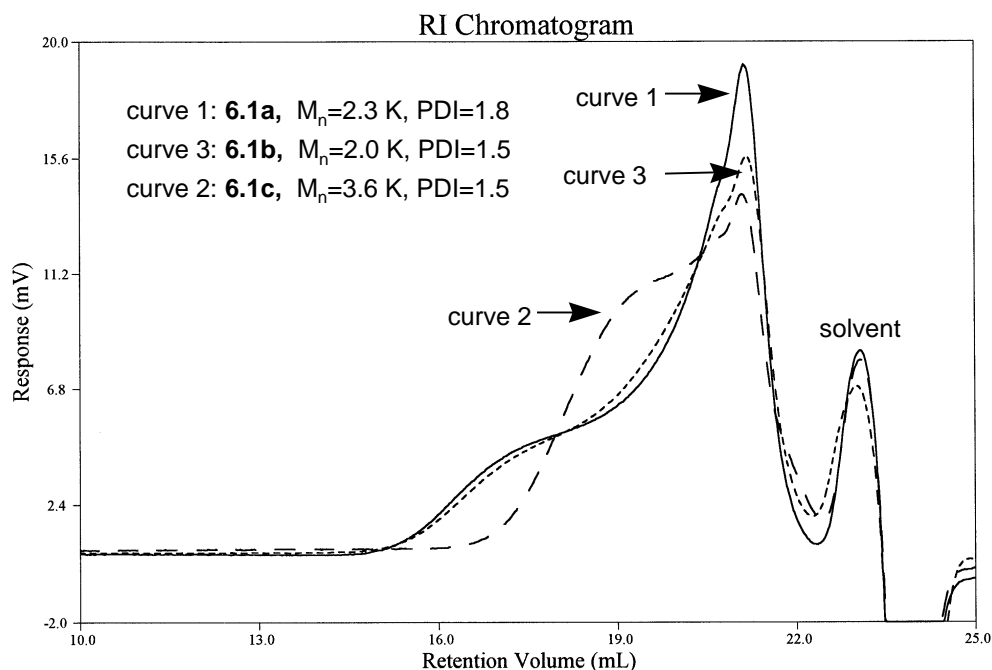


Figure 6.1 GPC traces (RI response) of cyclic mixtures **6.1a**, **6.1b** and **6.1c**. Solvent: NMP+P₂O₅; flow rate: 1.0 mL/min; temp: 60°C.

6.2.2 Characterization

The residual products **6.1a-6.1c** after removal of the cyclic dimer were analyzed by ¹H NMR spectroscopy. The presence of terminal groups was detected. As shown in the ¹H NMR spectra (Figures 6.2-6.4), the singlet around 9.2 ppm comes from the terminal phenolic protons, the broad peak around 6.6 ppm from the protons ortho to OH of the terminal phenol, and the broad peak around 7.7 ppm from the protons ortho to F or Cl in the terminal halophenyl moieties. Based on the integral ratios of these small terminal peaks relative to the main peaks and assuming all the molecules are linear, molecular weights about 10 times higher than those determined by GPC would be predicted. The large discrepancy between the calculated molecular weight and the experimental molecular weight indicates that the samples contain large amounts of macrocycles which have no terminal groups. This is indirect evidence of the cyclic nature of the products although they are contaminated with linears as indicated by the presence of terminal groups. Quantitative estimation of the amount of cyclics present in these products can be made by combining ¹H NMR and GPC data, assuming that the linears are terminated by a phenol at the one end and a phenyl chloride at the other end. If we denote L as the integral of the protons ortho to OH of the terminal phenol at 6.6 ppm, and M as the integral of the protons ortho to sulfone at 7.8-8.0 ppm, then the molar percentage of cyclics in the mixtures is

$$\frac{M/4n - L/2}{M/4n} \times 100$$

where $L/2$ is proportional to the number of linear molecules present, and $M/4n$ (n is the average number of the repeating units determined by GPC) is proportional to the total number of molecules including cyclics and linears. Assuming that the linears have the same molecular weights as the cyclics, then the molar percentage is equal to the weight percentage. The cyclics in the residual products **6.1a-6.1c** are thus calculated as follows:

6.1a	79%
6.1b	46%
6.1c	84%

If the cyclic dimer is counted, the cyclics in the crude products are 87%, 60% and 88%, respectively. Accordingly, the linears are 13%, 40% and 12%. Attempts to remove the linears by solvent extraction were not successful, due to the solubility characteristics similar to the cyclics (especially the large macrocycles).

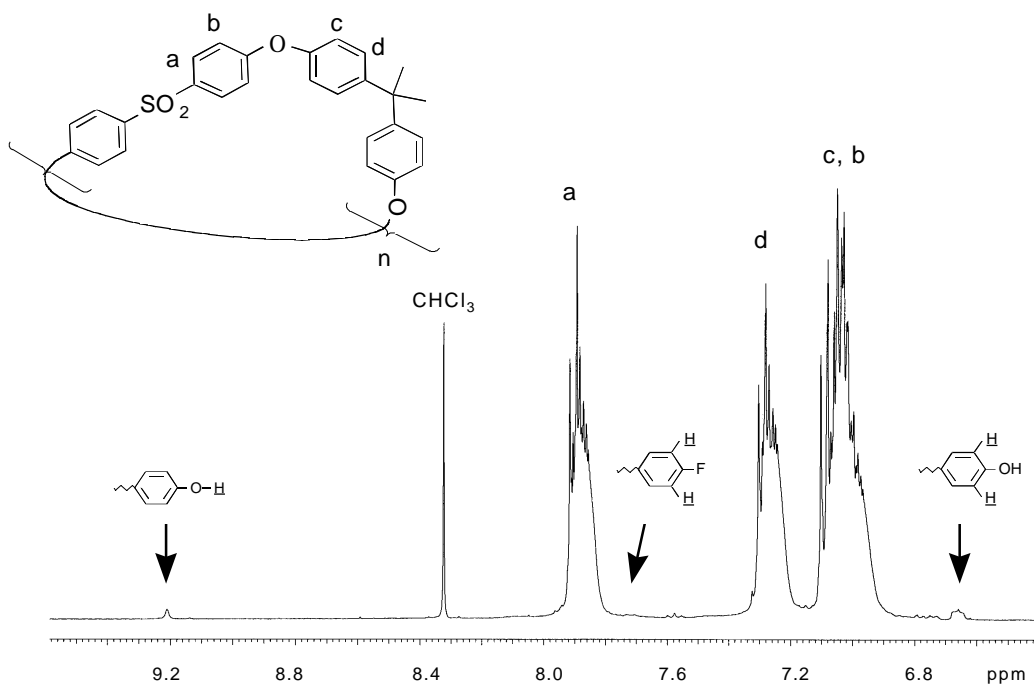


Figure 6.2 400 MHz ^1H NMR spectrum (aromatic region, in DMSO-d_6) of cyclic mixture **6.1a**. The arrow marked peaks come from the terminal groups of linear oligomers present in the cyclic mixture

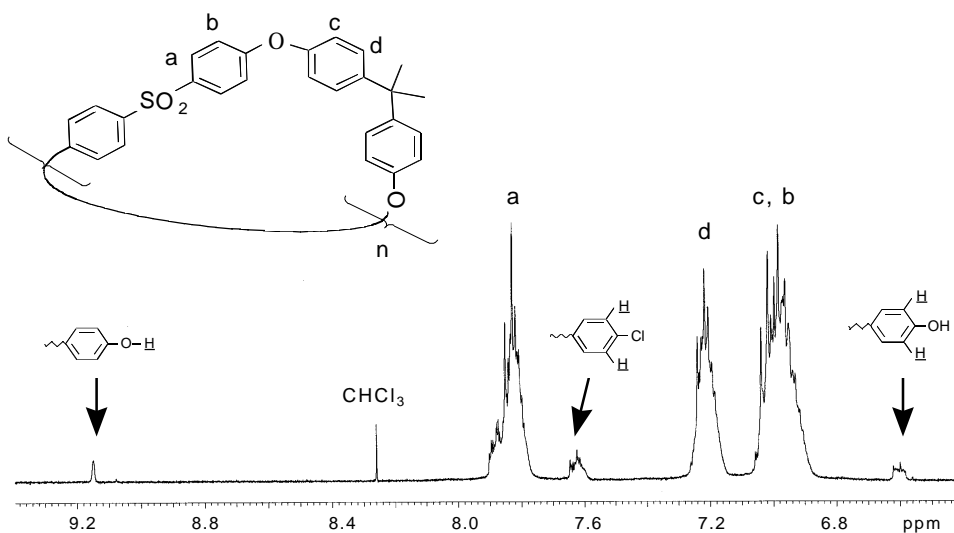


Figure 6.3 400 MHz ^1H NMR spectrum (aromatic region, in DMSO-d_6) of cyclic mixture **6.1b**. The arrow marked peaks come from the terminal groups of linear oligomers present in the cyclic mixture

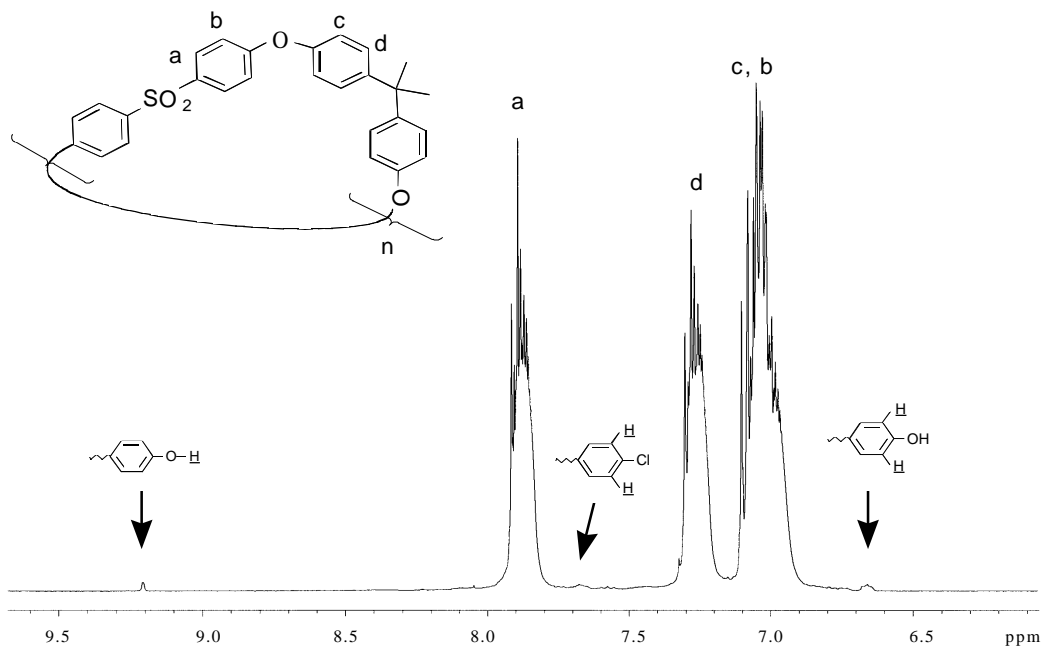


Figure 6.4 400 MHz ^1H NMR spectrum (aromatic region, in DMSO-d_6) of cyclic mixture **6.1c**. The arrow marked peaks come from the terminal groups of linear oligomers present in the cyclic mixture

Direct confirmation of the cyclic structures is provided by employing matrix assisted laser desorption/ionization-time of flight-mass spectrometry (MALDI-TOF-MS). By this technique, individual macrocycles in mixtures **6.1a** and **6.1c** after removal of the cyclic dimer are detected up to $n=11$ using 1,8,9-anthracenetriol (dithranol) as matrix, as shown in Figures 6.5 and 6.6. Tables 6.2 and 6.3 list the assignment of each signal and the calculated molecular weight corresponding to the assignment. Molecular ions of individual cyclics as well as pseudomolecular ions of the sodium adducts and/or the potassium adducts, where sodium and potassium apparently come from the glass container, are observed. Fragmentation of macrocycles is observed through methyl and ether bond cleavages. No linear oligomers are visible in the spectra. A trace amount of the dimer which remains in the product after purification is found in one of the spectra (Figure 6.6). From Tables 6.2 and 6.3, it can be noticed that between the experimental data and the calculated ones there exist some deviations ranging from 1 to 8 mass units. These deviations likely result from low signal to noise ratios of the spectra and calibration error. Addition of AgCF_3CO_2 as a cationization agent in the dithranol matrix reportedly could yield MS spectra of higher quality with better signal to noise ratios.⁴

⁴ See ref.31 in Chapter 1

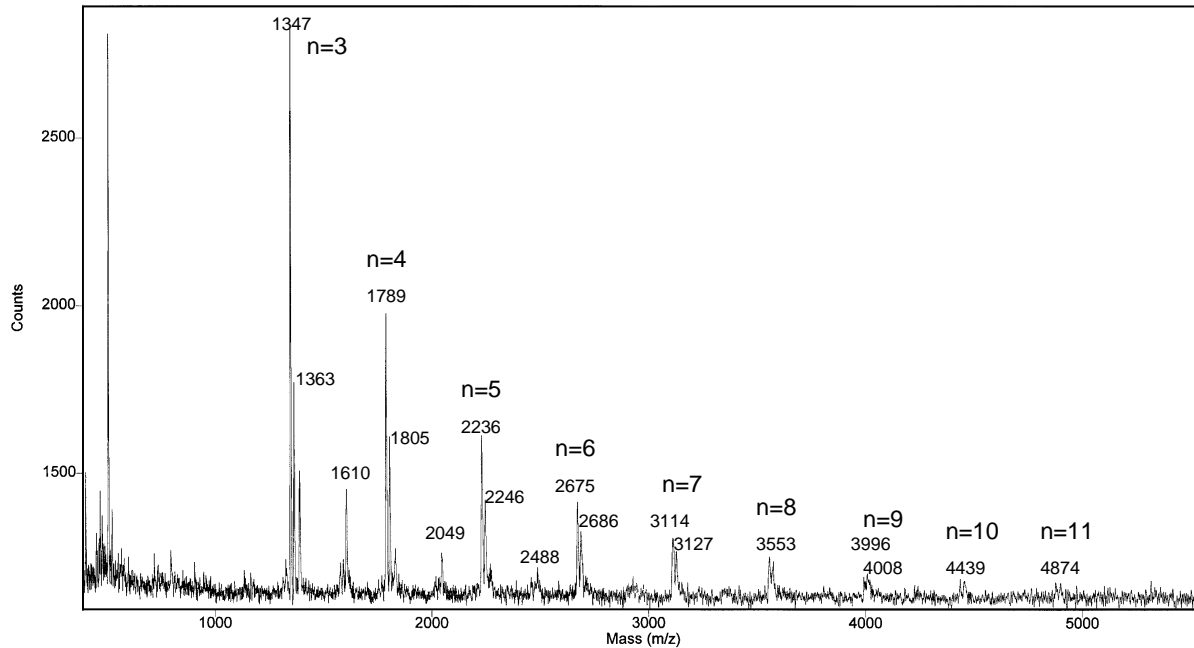


Figure 6.5 Positive ion MALDI-TOF mass spectrum (in dithranol) of cyclic mixture **6.1a**

Table 6.2 Positive ion MALDI-TOF-MS (in dithranol matrix) data of cyclic mixture **6.1a**

signal (m/z)	assignment ^a	calculated m/z	deviation ^d
1347, 1363	M_3+Na , M_3+K	1349, 1365	+2, +2
1610	$M_4-R_1^b+K$	1614	+4
1789, 1805	M_4+Na , M_4+K	1791, 1807	+2, +2
2049	$M_5-R_2^c+Na+K$	2047	-2
2236, 2246	M_5+Na , M_5+K	2234, 2250	-2, +4
2488	$M_6-R_2^c+Na+K$	2489	+1
2675, 2686	M_6+Na , M_6+K	2676, 2692	+1, +6
3114, 3127	M_7+Na , M_7+K	3118, 3134	+4, +7
3553	M_8+Na	3560	+7
3996, 4008	M_9+Na , M_9-CH_3+K	4002, 4003	+6, -5
4439	$M_{10}+Na$	4444	+5
4874	$M_{11}-CH_3+Na$	4871	-3

a) M_n represents molecular ion with n repeating units of structure **6.1**. b) $R_1=C_6H_4C(CH_3)_2C_6H_4$.
c) $R_2=OC_6H_4C(CH_3)_2C_6H_4O$. d) deviation=calculated value-experimental value

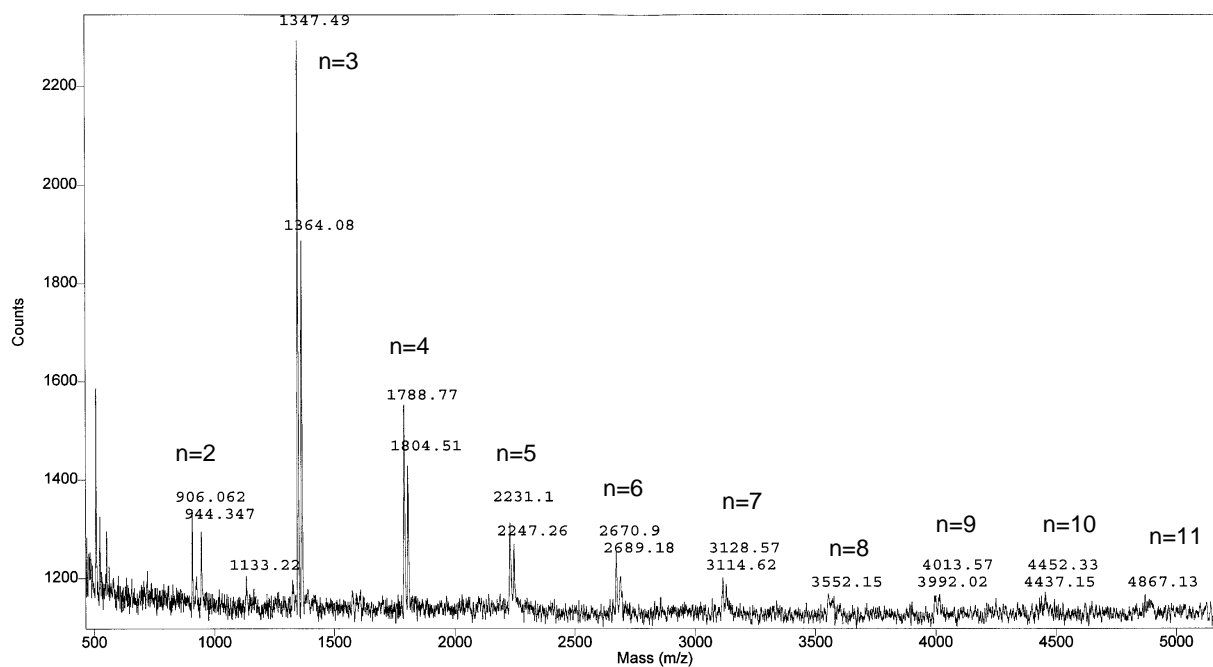


Figure 6.6 Positive ion MALDI-TOF mass spectrum (in dithranol) of cyclic mixture **6.1c**

Table 6.3 Positive ion MALDI-TOF-MS (in dithranol matrix) data of cyclic mixture **6.1c**

signal (m/e)	assignment ^a	calculated m/e	deviation ^c
906, 944	M_2+Na, M_2+Na+K	907, 946	+1, +2
1133	M_3-R^b+Na	1133	0
1347, 1364	M_3+Na, M_3+K	1349, 1365	+2, +1
1789, 1805	M_4+Na, M_4+K	1791, 1807	+2, +2
2231, 2247	M_5+Na, M_5+K	2234, 2250	+3, +3
2671, 2689	M_6+Na, M_6+K	2676, 2692	+5, +3
3115, 3129	M_7+Na, M_7+K	3118, 3134	+3, +5
3552	M_8+Na	3560	+8
3992, 4013	M_9-CH_3+Na, M_9+K	3987, 4018	-5, +5
4437, 4452	$M_{10}+Na, M_{10}+K$	4444, 4460	+7, +8
4867	M_{11}	4863	-4

a) M_n represents molecular ion with n repeating unit of structure **6.1**. b) $R=C_6H_4SO_2C_6H_4$.

c) deviation=calculated value-experimental value

Reverse phase HPLC with an appropriate choice of solvent combination (THF/water), and gradient program (curved gradient) was found to be a very useful method to achieve a good separation of the individual cyclics of a cyclic mixture. It can be seen from the HPLC curves (Figures 6.7 & 6.8) that the individual cyclics from $n=2$ to $n=15$ in cyclic mixtures **6.1a** and **6.1c** are well separated from each other. Cyclics **6.1** of ring sizes $n=2$ to 6 have the same retention times as those of the corresponding macrocycles **3.4** of ring sizes $n=1$ to 5 described in Chapter 3 where **3.4**($n=1$) to **3.4**($n=5$) have been proved by FAB-MS. Linear oligomers are observed in the HPLC curves (more obviously in **6.1a**, Figure 6.7) as small shoulders on the cyclic signals.

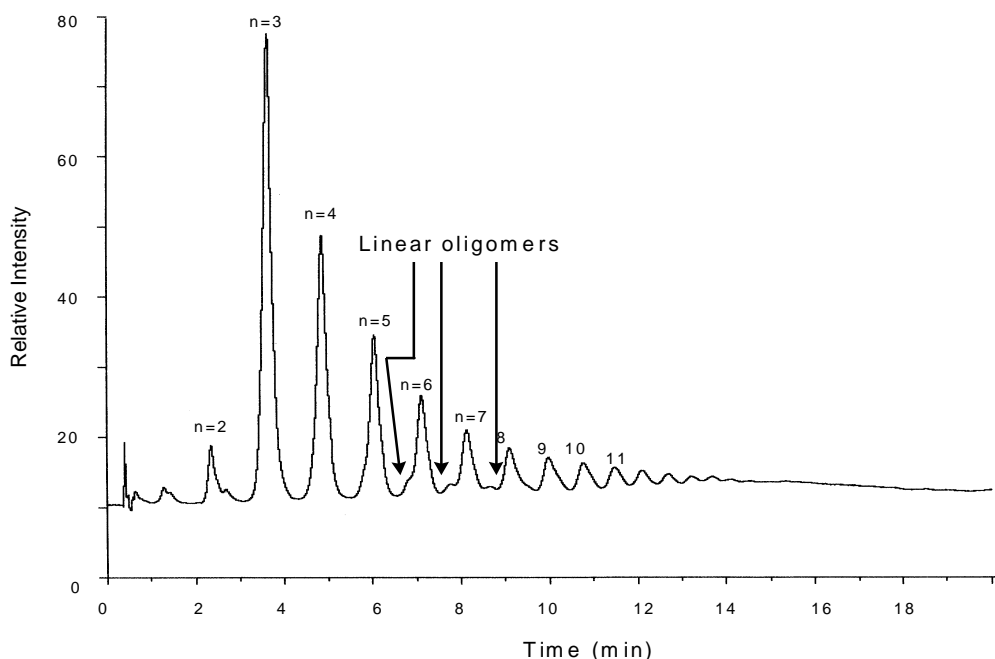


Figure 6.7 Reverse phase-HPLC chromatogram of cyclic mixture **6.1a**. (C18, THF/water, UV detector)

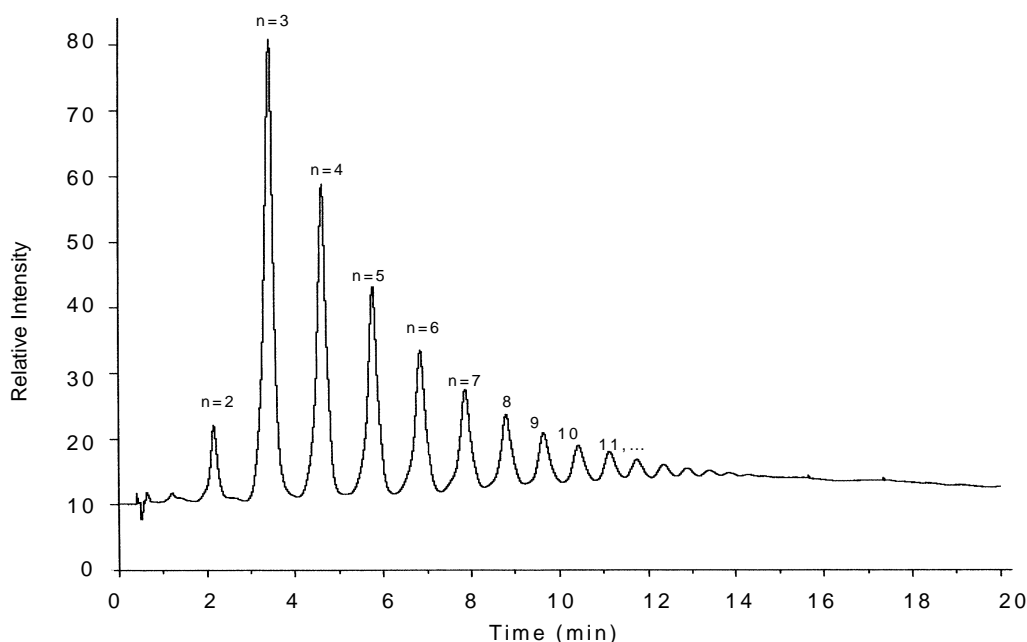


Figure 6.8 Reverse phase-HPLC chromatogram of cyclic mixture **6.1c**. (C18, THF/water, UV detector)

6.3 Conclusions

Bisphenol-A based arylene ether sulfone cyclooligomeric mixtures **6.1a-6.1c** were synthesized. According to ^1H NMR analysis, the mixtures were contaminated with 12-40% linear oligomers. Removal of these linears from the mixtures by solvent extraction is extremely difficult due to similarity in solubility to the cyclics. Cyclic dimer **6.1**($n=2$) was found in the mixtures in 22-35% yields. This small macrocycle has a very high melting point (above 500°C) and quickly crystallizes upon heating above 300°C , thus necessitating that it be removed to prevent its crystallization during ring opening polymerization. The mixtures after removal of the cyclic dimer are amorphous and completely melt at about 300°C . The cyclic nature of the mixtures was confirmed by ^1H NMR and MALDI-TOF-MS.

6.4 Experimental

Materials and measurements

Bisphenol-A, 4,4'-dichloro- and 4,4'-difluorodiphenyl sulfone were recrystallized in toluene twice prior to use. Reagents and solvents were used as received from chemical suppliers.

Melting points were taken in capillary tubes with a Melt-Temp II melting point apparatus and have been corrected. ^1H NMR spectra were obtained on a Varian 400 MHz in deuterated dimethyl sulfoxide with TMS as the internal standard at ambient temperature. Matrix-assisted

laser desorption/ionization time of flight (MALDI-TOF) mass spectra were measured by the Washington University Mass Spectrometry Resource. Reverse-phase HPLC analyses were performed on an ISCO dual pump HPLC system comprising two Model 2350 pumps and the V⁴ variable wavelength UV/Vis detector set at 274 nm. THF/water curved gradient (curve 6) was used for elution of the products on a reverse-phase column (Novapak 100 Å, 4 µm C18, 150 x 3.9 mm i.d.) at a flow rate of 1.5 mL/min. The gradient program was as follows: solvent A, THF/water (65/35) reduced from 100% to 50% over 20 min; at the same time, solvent B, THF increased from 0% to 50% over 20 min. The system was interfaced with the ISCO ChemResearch Chromatographic Data Management/System, used for data analyses. Gel permeation chromatography (GPC) was carried out in a Waters GPC/ALC 150-C chromatograph equipped with a differential refractometer detector and an on-line differential viscometric detector (Viscotek 150R) coupled in parallel. Two columns which were packed with 10³ and 10⁴ Å uStyragel HT were used. The mobile phase was NMP containing 0.02 M P₂O₅ and data was recorded at 60°C at a flow rate of 1.0 ml/min.

Cyclic Mixture 6.1a

To a refluxing mixture of DMAc (400 mL), toluene (220 mL) and potassium carbonate (2.76 g, 40.0 mmol) a solution (30 mL) of bisphenol-A (4.566 g, 20.00 mmol) and 4,4'-difluorodiphenyl sulfone (5.085 g, 20.00 mmol) in DMAc was injected at the rate of 1.0 mL/hr. The reaction mixture was mechanically stirred and protected by nitrogen. Water generated during deprotonation of the bisphenol was azeotroped into a Dean-Stark trap by toluene. After the injection, the reaction was allowed to continue for an additional 12 hours. The reaction mixture was cooled to room temperature, filtered and rotary evaporated to remove most of the solvent, and then precipitated into water (800 mL, 10 ml 5% HCl added). The precipitate was filtered and dried, providing a pale brown solid. Upon boiling the solid in chloroform, an insoluble white powder precipitated. Filtration yielded 3.1 g (35%) of the white powder which was the cyclic dimer (**6.1**, n=2). The chloroform filtrate was evaporated to 50 mL and then precipitated into methanol (800 mL). This provided an off-white solid. Yield: 5.7 g (64%); completely melting at about 300°C; ¹H NMR (DMSO-d₆) δ 1.5-1.8 (m, 6n H, -CH₃), 6.9-7.15 (m, 8n H), 7.2-7.35 (m, 4n H), 7.8-8.0 (m, 4n H).

Cyclic mixtures 6.1b and 6.1c

The same procedure as above was used but on a different scale. Thus, to a refluxing mixture of DMAc (1100 mL), toluene (600 mL) and potassium carbonate (10.0 g, 72.4 mmol) a solution of bisphenol-A (11.41 g, 50.00 mmol) and dichlorodiphenyl sulfone (14.36 g, 50.00 mmol) in DMAc (130 mL) was injected at the rate of 2.0 mL/hr. For **6.1a**, the reaction was allowed to continue for an additional 24 hours after injection. Yield of the cyclic dimer (**6.1**, n=2): 4.9 g (22%); yield of the rest: 16.4 g (74%). For **6.1c**, the reaction was allowed to continue for an additional 36 hours after injection. Yield of the cyclic dimer (**6.1**, n=2): 5.3 g (24%); Yield the rest: 16.2 g (73%). Both products after removal of the cyclic dimer completely melted at about 300°C; ¹H NMR (DMSO-d₆): the same as above.

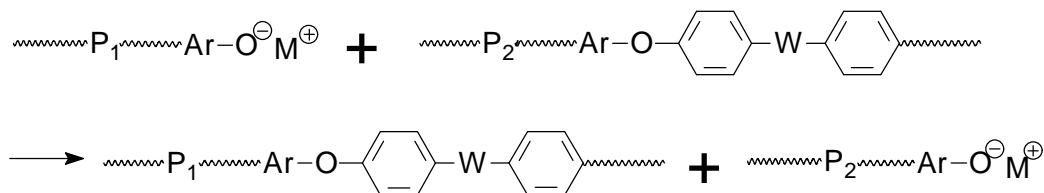
Chapter 7

Ring Opening Polymerization of Arylene Ether Macrocycles

7.1 Introduction

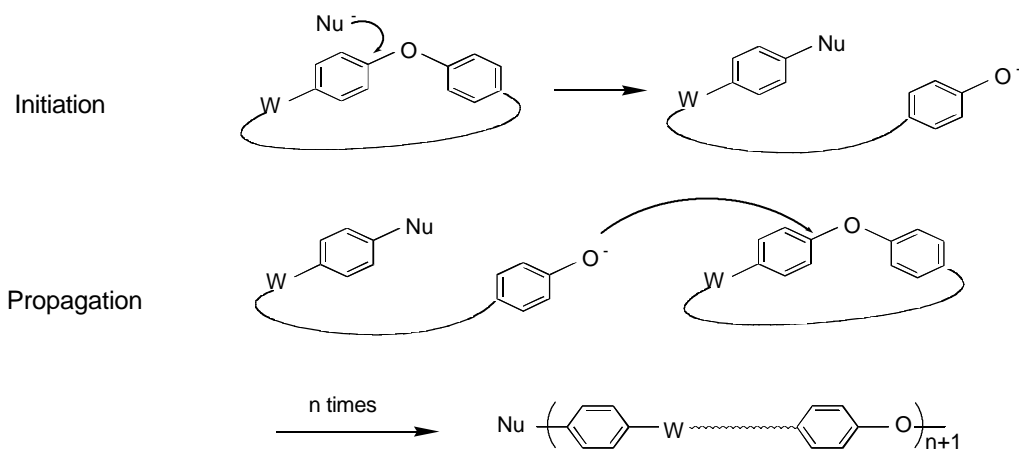
Ether linkages between phenyl nuclei, activated by electron-withdrawing groups, are labile to attack by nucleophiles; this is responsible for ether exchange¹ (Scheme 7.1) in poly(aryl ether) syntheses via aromatic nucleophilic substitution reactions. Arylene ether macrocycles containing activated ether linkages can be ring-opened through such ether exchange reactions induced by a nucleophile (Scheme 7.2). It has been shown that such macrocycles are readily converted to high molecular weight polymers in the presence of various nucleophilic initiators, with the ring-chain equilibrium much more favorable towards linear polymers.² Because of the lack of ring strain in the large ring sized oligomeric cyclics, the polymerization apparently is driven by entropy.

Scheme 7.1



W=electron-withdrawing group, Ar=aromatic group, P₁, P₂=polymer chains

Scheme 7.2



Nu =Nucleophile, W =Electron withdrawing group

¹ See ref. 19 in Chapter 1

² See refs. 5, 6, 20-31 in Chapter 1

Detailed studies of ROP of arylene ether macrocycles, both in solution and in the melt, have been reported for a cyclic oligomeric ether ketone mixture.³ Cyclic mixtures generally have the advantage of low melting points, favored commercially. The major disadvantage to the use of such a complex mixture is the difficulty of removing low levels of linear impurities which affect the rigorousness of the ROP studies. On the other hand, although single sized macrocycles can easily be freed of linear contaminants which would interfere the ROP, their ROP studies have in the past been limited not only by low-yielding procedures for their preparation but also by the high melting points of the macrocycles. In Chapter 4 we have described high yield syntheses of unsymmetric single sized macrocycles. These macrocycles are free of linear impurities and have relatively low melting points, which enables us to investigate ROP readily. The present chapter describes a fundamental study of ROP of bisphenol-A based single sized pure macrocycles (**4.11**, **4.12**, and **4.15**). ROP of cyclic mixtures **6.1a-6.1c** is also described for comparison to that of the pure macrocycles.

7.2 Results and Discussion

7.2.1 Melt ROP of Single-Sized Pure Macrocycles

A Characteristics of the polymerization

ROP of single-sized pure macrocycles was most systematically investigated for 40-membered phosphine oxide sulfone macrocycle **4.12**. The polymerization of this macrocycle was carried out at 340°C under argon. Figure 7.1 shows the conversion versus time relationship for the polymerization of this macrocycle with 1 mol% of potassium *p*-phenylphenoxide as initiator. Each data point in the figure (as well as in the following figures) corresponds to an individual reaction because it was difficult to pull out portions of samples from the reaction mixture during the progress of the reaction for analysis. The conversion was determined by proton NMR spectroscopy based on integrals of the peaks corresponding to protons ortho to the sulfone moiety in the macrocycle and in the resultant polymer owing to their different chemical shifts.

From Figure 7.1, it is clearly seen that there are two distinct stages in the polymerization. In the first stage (0-3 min), the rate of monomer consumption was very fast, 63% of the macrocycle being consumed within 3 minutes. The reaction in the second stage (after 3 min) was slow, and only 2% of monomer was consumed during the last 30 minutes of reaction. According to gel permeation chromatography (GPC) analyses, the molecular weight of the polymer was built up instantaneously and almost independent of time (Figure 7.2). The fast built-up of molecular weight suggests that the later stage of the polymerization experiences a highly viscous condition under which diffusion of unreacted macrocycles towards reaction centers was retarded. In fact, during the polymerization, the molten macrocycle thickened rapidly to an unstirrable mass of polymer and unreacted macrocycle. Therefore, the second stage of the polymerization is likely diffusion controlled (the kinetic effect). The fast reaction in the first stage apparently is driven by a large entropy difference between the macrocycle and the linear polymer. The heat of polymerization may be neglected because the ring size of the macrocycle is large enough to release ring strain although there is no direct experimental evidence to prove that.

³ See ref. 28 in Chapter 1

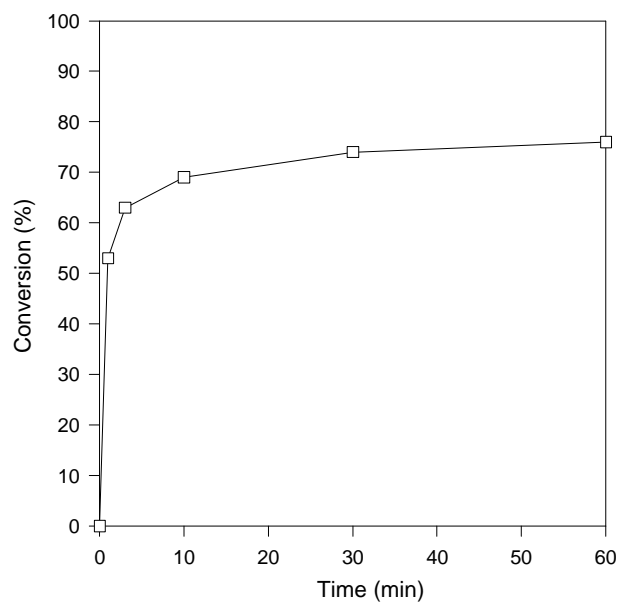


Figure 7.1 Conversion as function of reaction time in the ROP of macrocycle **4.12** (1 mol% potassium *p*-phenylphenoxide, at 340°C under argon)

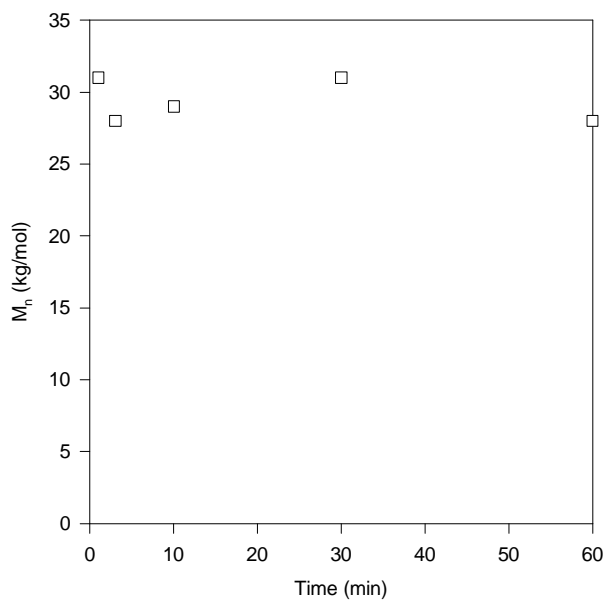
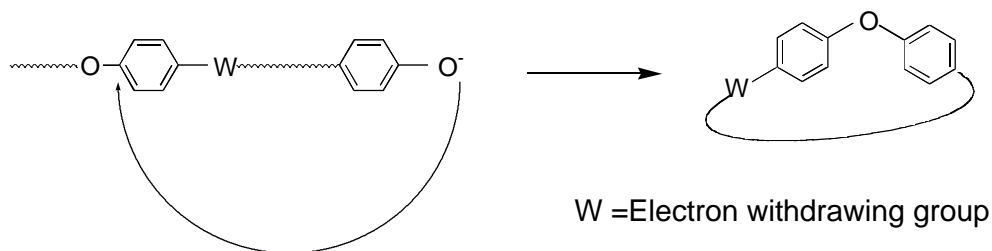


Figure 7.2 Molecular weight (M_n) as function of reaction time in the ROP of macrocycle **4.12** (1 mol% potassium *p*-phenylphenoxide, at 340°C under argon)

Small amounts of gel were formed in the polymerization, as was observed in reported melt ring opening polymerizations of other aromatic ether macrocycles.² The amount of gel ranged from 0 (1 min) to 3% (60 min) and increased with time (Table 7.1). The sol fraction of the polymer, extracted by chloroform, was subjected to GPC analyses, which gave tri-modal traces (Figure 7.3). It is shown that the tri-modality is more apparent in the DV chromatogram (b, recorded by differential viscosity detector) than in the RI chromatogram (a, recorded by refractive index detector). Peaks at the low retention end of the chromatograms correspond to molecular weights in the millions. These high molecular weight polymers in the sol are likely due to light crosslinking or branching. The intensities of these peaks increased significantly with time, correlated to higher levels of gel fraction as time increases. Due to branching, molecular weight distributions are anomalously broad. For this particular macrocycle, **4.12**, as high as 52 polydispersity index (M_w/M_n) was reached using potassium p-phenylphenoxide as initiator. Other macrocycles, **4.11** and **4.15**, have narrower molecular weight distributions with M_w/M_n below 10. The difference probably relates to the structure of the macrocycles and the mechanism of branching. Further discussion of branching mechanisms is given in Section **D**.

In the GPC traces (Figure 7.3), unreacted starting macrocycle appeared as a sharp peak, well separated from the polymer peak. This suggests that during the polymerization there are no large ring sized macrocycles, which could be formed if the intra-molecular ether exchange took place, as illustrated in Scheme 7.3. Analyses of the sol fractions by high performance liquid chromatography (HPLC) provided more convincing evidence for that. As shown in HPLC chromatograms (Figure 7.4), except for starting macrocycle **4.12** there are no other macrocycles observed even after longer reaction time (60 min). These data indicate that ring-chain equilibration does not exist in the polymerization, perhaps due to the fact that fast reaction creates highly viscous conditions so that it is difficult for polymer chains to fold over.

Scheme 7.3



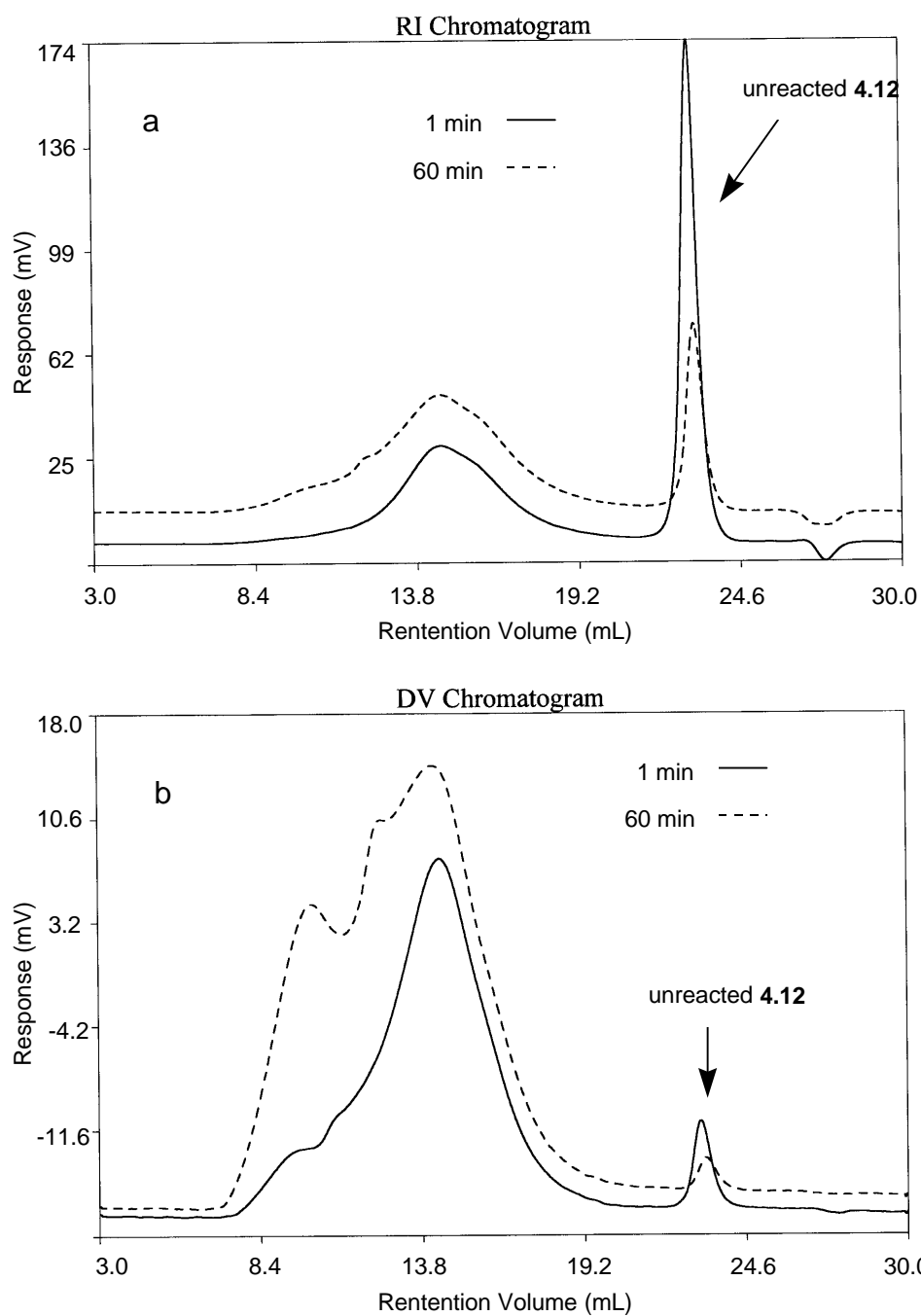


Figure 7.3 GPC traces (CHCl_3 , 35°C , 1 mL/min) of the sol fractions of the products of the ROP of macrocycle **4.12** (1 mol% potassium p-phenylphenoxide, 340°C under argon, for 1 min and 60 min): a) refractive index chromatogram; b) differential viscosity chromatogram

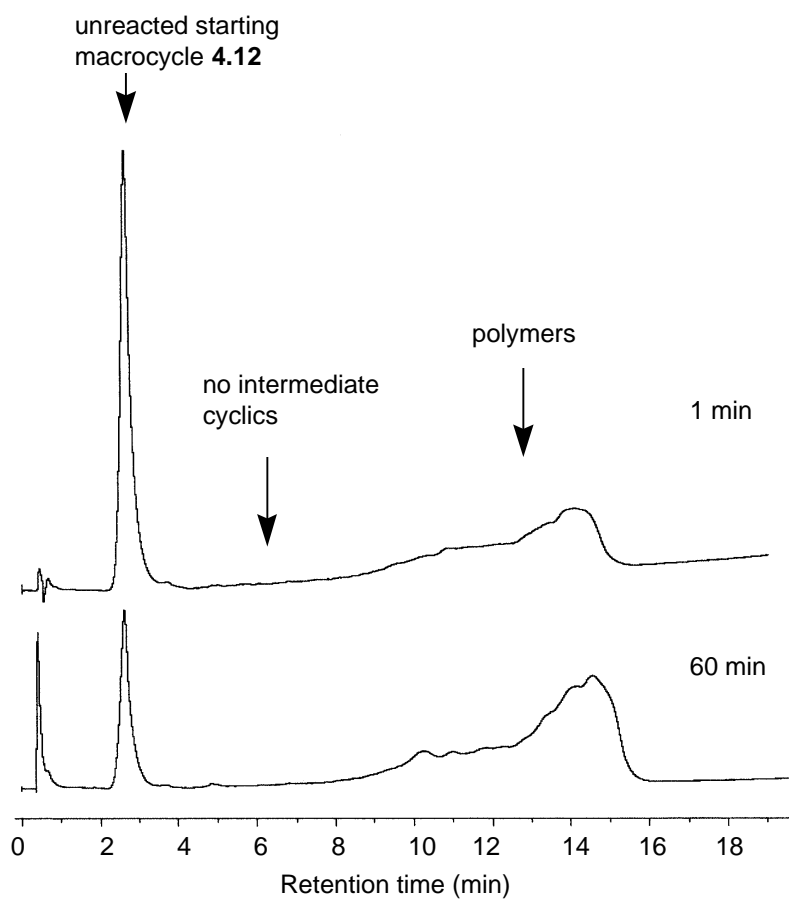


Figure 7.4 RP-HPLC chromatograms (C18, THF/water, gradient, UV detector) of the sol fractions of the products of the ROP of macrocycle **4.12** (1 mol% potassium p-phenylphenoxide, 340°C under argon, 1 min and 60 min.)

B Effect of the alkali counterion of nucleophilic initiators

The ROP of 40-membered phosphine oxide sulfone macrocycle **4.12** was also examined using 1 mol% sodium or cesium salt of *p*-phenylphenoxide as initiator. The effect of changing alkali counter-ion (Na, K, and Cs) of the phenoxide on conversion is shown in Figure 7.5.

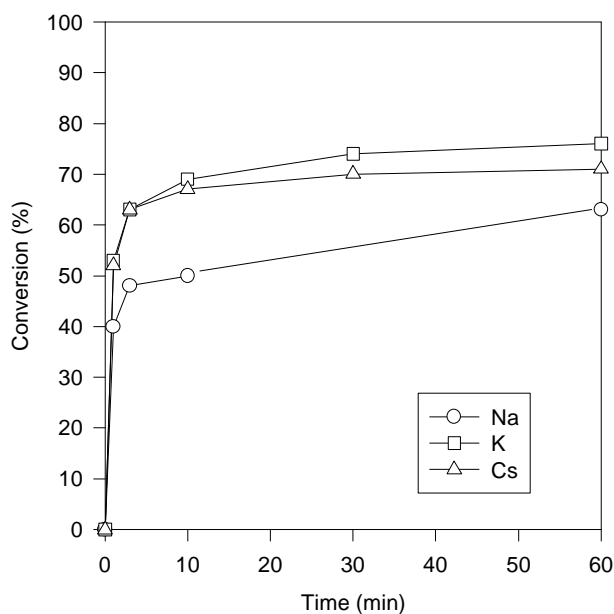


Figure 7.5 The effect of alkali counterion (Na, K, and Cs) on the ROP of macrocycle **4.12** (1 mol% alkali *p*-phenyl phenoxide, at 340°C under argon)

It can be seen that the two stage characteristic of the polymerization is observed with each of these three initiators. As discussed above, the second stage of the polymerization is diffusion controlled; thus, the reactivity of the initiators are reflected in the first stage of polymerization (0-3 min). By this consideration, the effect of alkali counterion on the reactivity of phenoxide initiator is in the order of Cs = K > Na. Although cesium phenoxide is as reactive as potassium phenoxide, it gives lower conversion overall. In other words, it is less efficient than potassium phenoxide for the ROP of **4.12**. The difference in final conversion for these two initiators obviously comes from the diffusion-controlled second stage of polymerization. Comparing with each other the GPC traces (Figure 7.6) of the sol polymers from the polymerizations of **4.12** using these two initiators, it is observed that the sol fraction from cesium phenoxide contains a significantly higher ratio of polymer with molecular weight above 10^6 , indicated by a larger intensity of the peak at about 10 mL retention volume. The higher tendency of branching or crosslinking using cesium phenoxide may have resulted in higher viscosity condition under which

the polymerization was more heavily prevented in the second stage; thus lower conversion was obtained at the end. It may also suggest that cesium phenoxide is actually a more reactive initiator than potassium phenoxide. In fact, in the polymerization of macrocycles **4.11** (40-membered ketosulfone) and **4.15** (50-membered ketosulfone), cesium *p*-phenylphenoxide was found to be more efficient than potassium *p*-phenylphenoxide (see Tables 7.4 and 7.5). In these latter two macrocyclic systems, although the cesium counterion also led to a higher degree of branching and crosslinking, the situation might not effectively increase viscosity enough to slow down the polymerization, because these two macrocycles themselves have less tendency for branching (see discussion in Section D) than **4.12**, as indicated by their narrower molecular weight distributions. Sodium phenoxide is the least reactive initiator, which led to the lowest conversion in the polymerization of all three macrocycles. It should be pointed out, however, that the rate of molecular weight built-up is nearly independent of whether the polymerization is initiated by sodium, potassium or cesium phenoxide. This can be found in Tables 7.1-7.3. In all three initiator systems, the molecular weight is built up immediately and is relatively unchanged during the polymerization.

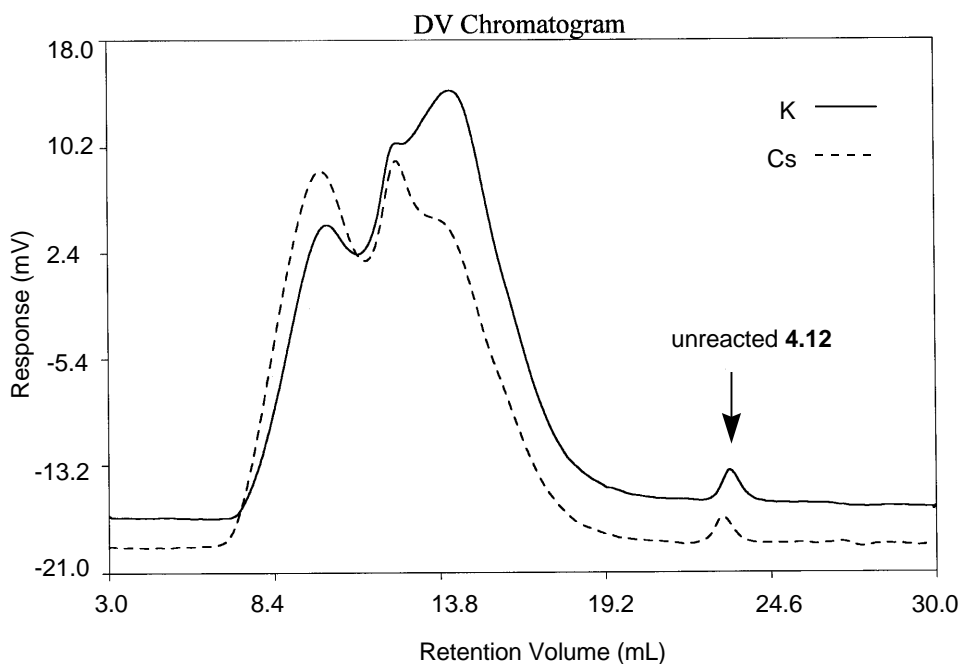


Figure 7.6 GPC traces (differential viscosity chromatograms, CHCl_3 , 35°C , 1 mL/min): the effect of alkali counterion on branching in the ROP of macrocycle **4.12** (1 mol% alkali *p*-phenylphenoxide, 340°C under argon, for 60 min)

Table 7.1 Results of the melt ROP of macrocycle **4.12** in the presence of 1 mol% **potassium** *p*-phenylphenoxide at 340°C under argon for various reaction times

time (min)	M_n (kg/mol)	M_w (kg/mol)	M_w/M_n	gel fraction (%)	conversion (%)	
					by NMR	by GPC
1.0	31	340	11	0	53	50
3.0	28	655	24	2	63	63
10	29	1054	36	2	69	71
30	31	1160	43	3	74	72
60	28	1456	52	3	76	73

Table 7.2 Results of the melt ROP of macrocycle **4.12** in the presence of 1 mol% **cesium** *p*-phenylphenoxide at 340°C under argon for various reaction times

time (min)	M_n (kg/mol)	M_w (kg/mol)	M_w/M_n	gel fraction (%)	conversion (%)	
					by NMR	by GPC
1.0	21	914	43	0	52	43
3.0	28	1253	45	3	63	67
10	26	2029	79	3	67	65
30	22	2773	128	4	70	72
60	16	4200	262	8	71	75

Table 7.3 Results of the melt ROP of macrocycle **4.12** in the presence of 1 mol% **sodium** *p*-phenylphenoxide at 340°C under argon for various reaction times

time (min)	M_n (kg/mol)	M_w (kg/mol)	M_w/M_n	gel fraction (%)	conversion (%)	
					by NMR	by GPC
1.0	26	537	21	0	40	48
3.0	29	962	34	2	48	50
10	28	1158	42	8	50	49
60	23	2679	118	6	63	68

Table 7.4 Results of the melt ROP of macrocycle **4.15** in the presence of 3 mol% alkali p-phenylphenoxide at 325°C under argon for 30 min

alkali counterion	M_n (kg/mol)	M_w (kg/mol)	M_w/M_n	gel fraction (%)	conversion (%) by GPC
Na	35	82	2.3	1	43
K	32	102	3.2	3	75
Cs	25	155	6.2	12	97

Table 7.5 Results of the melt ROP of macrocycle **4.11** in the presence of 5 mol% alkali p-phenylphenoxide at 370°C under argon for 30 min

alkali counterion	M_n (kg/mol)	M_w (kg/mol)	M_w/M_n	gel fraction (%)	conversion (%) by GPC
Na	12	42	3.5	10	27
K	13	80	6.4	16	73
Cs	11	95	8.6	22	89

The efficiency of potassium and cesium fluorides as initiators was also examined. Similarly, cesium fluoride is a better initiator than potassium fluoride, though it causes a higher degree of crosslinking, in the polymerization of macrocycles **4.11** and **4.15** (Tables 7.6 and 7.7). Both fluorides have been compared to corresponding phenoxide initiators. The conversion was relatively lower when the fluorides were used as initiators. For example, cesium fluoride led to 72% conversion (Table 7.6) in the polymerization of **4.15**, while cesium p-phenylphenoxide led to 97% conversion (Table 7.4) under the same conditions. On the other hand, the molecular weight with cesium fluoride, however, was significantly higher, 49 kg/mol, compared to 25 kg/mol with the cesium phenoxide. The same thing can be found when potassium fluoride and potassium p-phenylphenoxide are compared under the same conditions (Tables 7.4 and 7.6). Perhaps, the lower conversion using the fluorides as initiator resulted from the higher molecular weight which led to higher viscosity and thus more restricted the motion of polymer chains and unreacted macrocycles during the diffusion-controlled stage of polymerization. The different outcomes of the polymerizations using these two types of initiators apparently came from the initiation step in which different nucleophiles were involved in the reaction. After initiation, growing chains in both cases bore phenoxide anion ends which attacked other macrocyclic monomers for chain extension (propagation).

Table 7.6 Results of the melt ROP of macrocycle **4.15** in the presence of 3 mol% alkali fluoride at 325°C under argon for 30 min

initiator	M_n (kg/mol)	M_w (kg/mol)	M_w/M_n	gel fraction (%)	conversion (%) by GPC
KF	52	174	3.4	2	16
CsF	49	224	4.6	19	72

Table 7.7 Results of the melt ROP of macrocycle **4.11** in the presence of 5 mol% alkali p-phenylphenoxide at 370°C under argon for 30 min

initiator	M_n (kg/mol)	M_w (kg/mol)	M_w/M_n	gel fraction (%)	conversion (%) by ^1H NMR
KF	23	55	2.4	0	18
CsF	22	99	4.4	7	69

C Efforts to increase conversion

As we have seen above, the conversion of the polymerization is essentially determined in the first stage of the reaction and further reaction is greatly restricted by the highly viscous condition created by the initially formed high molecular weight polymer. Several experiments were thus carried out to reduce the viscosity of the reaction system, trying to facilitate the second stage of reaction and thereby to increase polymer yields.

1) Increases of the reaction temperature. The effect of reaction temperature on conversion was examined for the polymerization of macrocycles **4.12** and **4.15** in the presence of 1 mol% potassium p-phenylphenoxide under argon for 30 min. It was expected that at higher temperatures polymerization would be more complete, since viscosity should be lower at a higher temperature. However, the polymerization of 40-membered phosphine oxide sulfone macrocycle **4.12** (Table 7.8) indicates that the conversion was essentially not changed but more polymer was crosslinked when the reaction temperature was increased from 340°C to 370°C. The conversion in the polymerization of **4.15** increased by about 15% when the reaction temperature was increased from 325°C to 355°C (Table 7.9). Perhaps, the effect of reducing viscosity at higher temperatures was offset by an increased viscosity resulting from higher degrees of crosslinking. This is particularly a case in the polymerization of macrocycle **4.12** since this macrocycle has a higher tendency for crosslinking as reflected by its broader molecular weight distribution and

larger gel fractions in its polymerization product. In both cases, molecular weights (M_n) of the sol fractions were relatively unchanged with increases in temperature.

Table 7.8 Result of the melt ROP of macrocycle **4.12** in the presence of 1 mol% potassium p-phenylphenoxide under argon for 30 min at different temperatures

temperature (°C)	M_n (kg/mol)	M_w (kg/mol)	M_w/M_n	gel fraction (%)	conversion (%)	
					by NMR	by GPC
340	31	1160	43	3	74	72
355	21	1484	71	6	71	73
370	21	1528	72	14	72	75

Table 7.9 Result of the melt ROP of macrocycle **4.15** in the presence of 1 mol% potassium p-phenylphenoxide under argon for 30 min at different temperatures

temperature (°C)	M_n (kg/mol)	M_w (kg/mol)	M_w/M_n	gel fraction (%)	conversion (%)
					by GPC
325	39	144	3.7	2	41
340	39	159	4.1	6	56
355	44	203	4.6	5	55

2) Increases of the molar ratio of initiator. It is shown in Table 7.10 that when the molar ratio of initiator, potassium p-phenylphenoxide, was increased from 1% to 5% in the polymerization of **4.12**, the conversion increased from 74% to 100%. The conversions determined by GPC are in good agreement with those determined by NMR. The same general effect was seen in the polymerizations of macrocycles **4.11** and **4.15** (Table 7.11 and 7.12). For macrocycle **4.15** the conversion increased from 41% to 95%, while for macrocycle **4.11** the conversion increased from 21% to 73%, as the amount of initiator was increased from 1 mol% to 7 mol%. The increases of conversion with increases of initiator concentration may have resulted from increased distribution of the initiator in macrocycles. For bulk polymerizations, especially the ROP of aromatic macrocycles where the reaction is so fast that molten macrocycles quickly thicken to an unstirrable mass and further reaction is diffusion controlled, distribution of the initiator obviously is a critical factor for complete polymerization. Higher concentrations of initiator increased its distribution in macrocycles and thus gave higher conversions. Another

reason for higher conversions when more initiator was used may be due to reduced viscosity as the result of the decrease of molecular weight which is inversely changed with the initiator concentration. Lower viscosity could facilitate the diffusion-controlled second stage of the polymerization and thus allow the polymerization to be more complete. Particularly in the polymerizations of macrocycles **4.12** (Table 10) and **4.15** (Table 11), the decrease of molecular weight was relatively fast and thus the polymerizations nearly reached completion when potassium p-phenylphenoxide was increased to 5 mol%. For the macrocycle **4.11** (Table 12), since molecular weight decreased slowly, the polymerization was not complete even when the initiator was increased to 7 mol%.

Table 7.10 Result of the melt ROP of macrocycle **4.12** in the presence of various amounts of potassium p-phenylphenoxide at 340°C for 30 min under argon.

mole% of initiator	M _n (kg/mol)	M _w (kg/mol)	M _w /M _n	gel fraction (%)	conversion (%)	
					by NMR	by GPC
1.0	31	1160	43	3	74	72
1.5	25	612	24	3	83	82
3.0	15	303	19	4	92	94
5.0	11	242	21	5	100	98

Table 7.11 Result of the melt ROP of macrocycle **4.15** in the presence of various amounts of potassium p-phenylphenoxide at 325°C for 30 min under argon

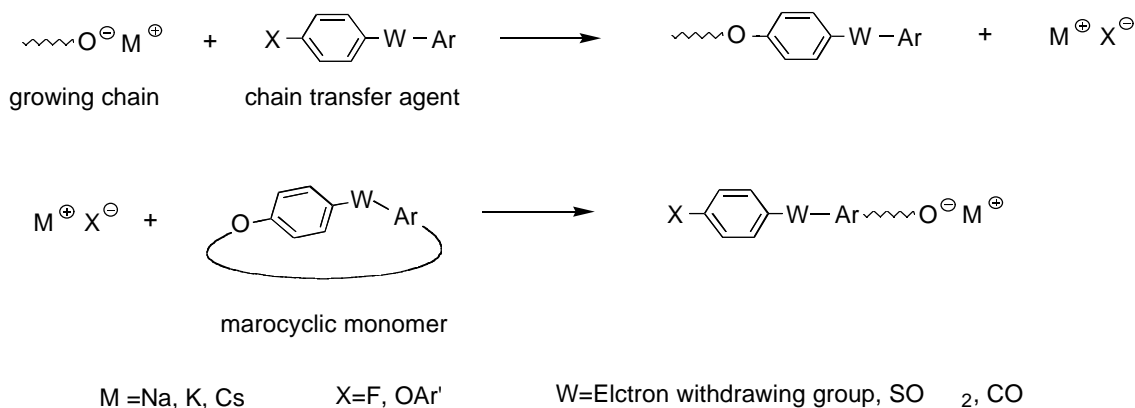
mole% of initiator	M _n (kg/mol)	M _w (kg/mol)	M _w /M _n	gel fraction (%)	conversion (%)
					by GPC
1.0	39	144	3.7	2	41
3.0	32	102	3.2	3	75
5.0	24	81	3.4	7	94
7.0	17	58	3.4	5	95

Table 7.12 Result of the melt ROP of macrocycle **4.11** in the presence of various amounts of potassium p-phenylphenoxide at 370°C for 30 min under argon

mole% of initiator	M_n (kg/mol)	M_w (kg/mol)	M_w/M_n	gel fraction (%)	conversion (%)	
					by NMR	by GPC
1.0	20	56	3.0	5	21	19
1.5	15	66	4.4	6	37	35
3.0	13	68	5.3	8	59	55
5.0	13	80	6.4	16	73	70
7.0	12	77	6.5	25	81	78

3) Addition of chain transfer agents. Chain transfer is a chain-breaking reaction; it results in a decrease in size of the propagating polymer chain. As shown above, when the molecular weight was reduced, higher conversions were obtained. The effect of chain transfer on the polymerization is dependent on whether the reinitiation is comparable to that of original propagating species. This means that for our studies the chain transfer reaction must generate a new initiator (M^+X^-), effectively re-initiating the ROP (Scheme 7.4).

Scheme 7.4



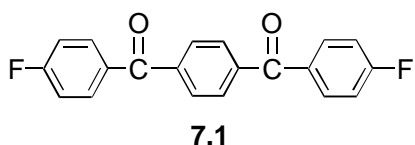
In this work, the fluoroketone, bis(*p*-fluorobenzoyl)benzene (**7.1**), was used as a chain transfer agent, and cesium fluoride and cesium p-phenylphenoxide as initiators. Thus the new *in situ* generated initiator (M^+X^-) was CsF which is a relatively good initiator for the ROP. Unfortunately, addition of the chain transfer agent reduced the conversion instead and 95%-98% of macrocyclic monomers were eventually recovered after reaction when the fluoroketone was increased to 2.5 mol%, as indicated in Table 7.13. The decrease in conversion perhaps resulted

from some side reactions between the initiator and the fluoroketone which preferentially took place and thus led to destruction of the initiator.

Table 7.13 The effect of chain transfer agents on the ROP of macrocycle **4.12** at 340°C under argon for 30 min

mole% of initiator	M _n (kg/mol)	M _w (kg/mol)	M _w /M _n	gel fraction (%)	conversion (%)	
					by NMR	by GPC
1.0	20	56	3.0	5	21	19
1.5	15	66	4.4	6	37	35
3.0	13	68	5.3	8	59	55
5.0	13	80	6.4	16	73	70
7.0	12	77	6.5	25	81	78

To find out what kind of reactions destroyed the initiators, model studies were carried out using the above two initiators and **7.1**. It was found that some reaction took place between CsF and **7.1** when they were heated at 340°C for 30 min under argon in the absence of macrocycles. There were about 5% intractable materials in the product, insoluble even in conc. sulfuric acid and the soluble part of the product also contained trace amounts of other components besides **7.1** according to RP-HPLC. Due to difficulties in characterization of the intractable material and the trace components in the sol fraction, mechanisms for the reactions could hardly be elucidated.



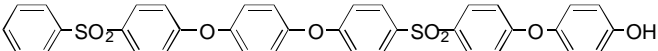
When cesium *p*-phenylphenoxide and **7.1** were heated under the same conditions, a complex mixture was produced. This was probably due to the facts that the phenoxide could also serve as an electron donor and single electron transfer might be one of reaction mechanisms that led to the byproducts. In this case, all the products were soluble in a solvent mixture of chloroform and ethanol. Also, no reaction mechanism was recognized.

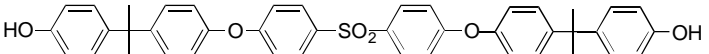
4) Use of difunctional initiator It is shown in Table 14 that a difunctional initiator, the bispotassium salt of bisphenol **3.3**, provided a higher conversion (83%) than a monofunctional initiator, the potassium salt of monophenol **7.2** which provided 64% conversion in the polymerization of macrocycle **4.12** under the same reaction condition. The molecular weights of the polymers in both cases were about the same. The higher conversion from the difunctional initiator is probably due to the fact that at the same molar amount it has twice as many as reactive

centers as the monofunctional initiator. However, because the concentration of phenoxide anions doubled with the difunctional initiator, crosslinking significantly increased.

Table 7.14 The effect of functionality on the ROP of macrocycle **4.12** in the presence of 1.0 mol% initiator at 340°C under argon for 30 min

initiator	M_n (kg/mol)	M_w (kg/mol)	M_w/M_n	gel fraction (%)	conversion (%) by GPC
a	30	98	3.3	2	64
b	31	118	3.8	15	83

a: potassium salt of  (7.2)

b: dipotassium salt of  (3.3)

D Model Studies of Crosslinking

Crosslinking is the common side reaction which takes place in the ring opening polymerization of aromatic ether macrocycles. Due to the crosslinking, polymerization is not well controlled. Crosslinking also increases viscosity and is one of the factors limiting conversion of the ROP. Thus, it is important to know what reaction(s) caused crosslinking, in order to be able to better control the ROP. Several model reactions were thus carried out trying to find out the crosslinking mechanism. Although there is no clear answer yet, some clues were obtained.

The reactants used for the model studies were cesium phenoxide and 4,4'-diphenoxydiphenyl sulfone **7.3**. The reaction between these two compounds should yield no new compounds even though ether exchange reactions could take place. However, this reaction produced something else. Figure 7.7 is the ^1H NMR spectrum of the product after heating cesium phenoxide and **7.3** at 340°C for 30 min under argon. Notice in this NMR spectrum that some small peaks appear within the range of 7.80-7.85 ppm beside the main doublet at 7.86 ppm which corresponds to the proton ortho to the sulfone group in **7.3**. These small peaks should come from the protons near the sulfone group in the newly generated compounds. In other words, there was some reactions that occurred on the phenyl ring attached to the sulfone group. Presumably, such reaction might have led to branched and a finally crosslinked polymer in the ROP of aromatic macrocycles containing sulfone (SO_2), ketone ($\text{C}=\text{O}$), or phosphine oxide ($\text{P}=\text{O}$) functional groups.

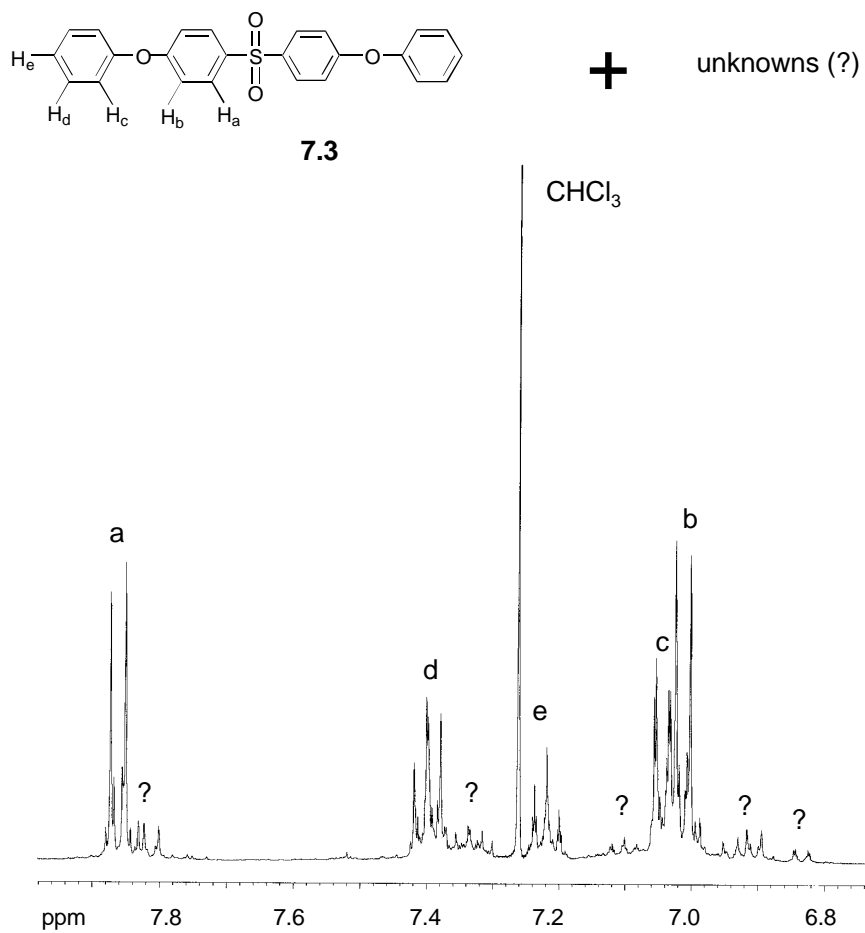


Figure 7.7 400 MHz ¹H NMR spectrum (in CDCl₃) of the crude product from heating a mixture of cesium phenoxide and 4,4'-diphenoxydiphenyl sulfone (7.3) at 340°C for 30 min under argon.

Some polymerization data may support the above speculation. As pointed out earlier, the polymer from 40-membered phosphine oxide sulfone macrocycle **4.12** has a much broader molecular weight distribution than the polymers from 40- and 50-membered ketosulfone macrocycles **4.11** and **4.15**. In GPC traces (differential viscosity chromatograms, Figure 7.8), the polymer from **4.12** yields a more irregular shaped curve with a large peak at the high molecular weight end of the chromatogram. The reason for this is probably due to the fact that the phosphine oxide functional group in macrocycle **4.12** has three phenyl rings, providing more reactive sides for branching through the mechanism illustrated in Scheme 7.5.

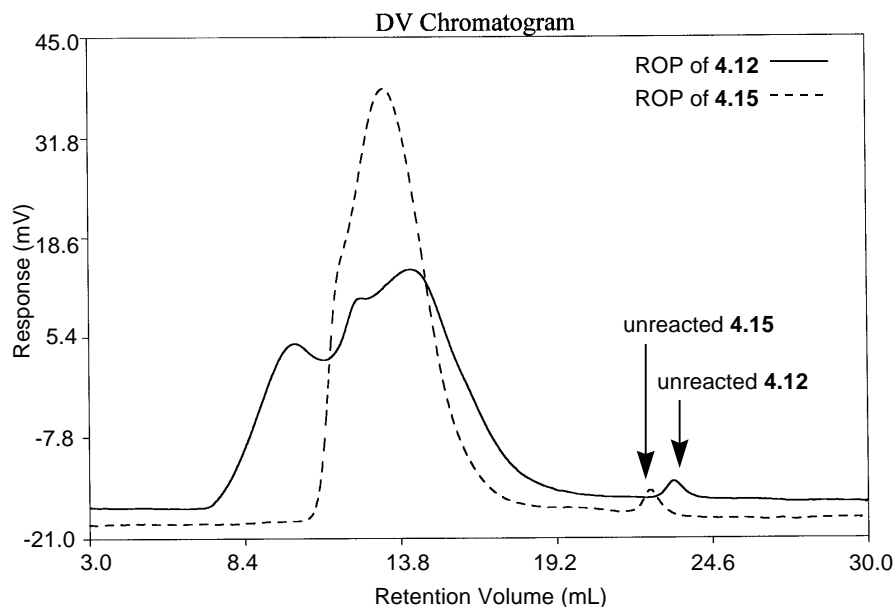


Figure 7.8 GPC traces (differential viscosity chromatograms, CHCl_3 , 35°C , 1 mL/min): the structural effect of macrocycle on molecular weight distribution. ROP of **4.12**: 1 mol% potassium p-phenylphenoxide, 340°C under argon, for 60 min; ROP of **4.15**: 1 mol% potassium p-phenylphenoxide, 325°C under argon, for 60 min

7.2.2 Melt ROP of Cyclic Mixtures

Similar studies of ring opening polymerization were carried out with cyclic oligomeric mixtures **6.1a-6.1c** using potassium p-phenylphenoxide as initiator. Since the cyclic dimer ($n=2$), 24-35% in the mixtures, crystallized out during heating and does not melt below 500°C , it was removed from the mixtures. The residual cyclic mixture completely melts at about 300°C , giving transparent viscous liquids. The polymerization was conducted at 330°C to make sure that the starting viscosity of the molten cyclic mixture was low.

Figure 7.9 shows the conversion vs time relationship for the polymerization of **6.1a** at 330°C under vacuum in the presence of 0.5 wt% potassium p-phenylphenoxide. Similar to the ROP of single sized macrocycles, the polymerization shows the same two stage characteristics, fast in the first stage but slow in the second stage. It should be pointed out that the conversion determined by GPC may be over-estimated, because the polymer and unreacted cyclic mixture are not well separated and distinguished from each other, especially in the early stage (1 min) of the polymerization (see GPC traces in Figure 7.12).

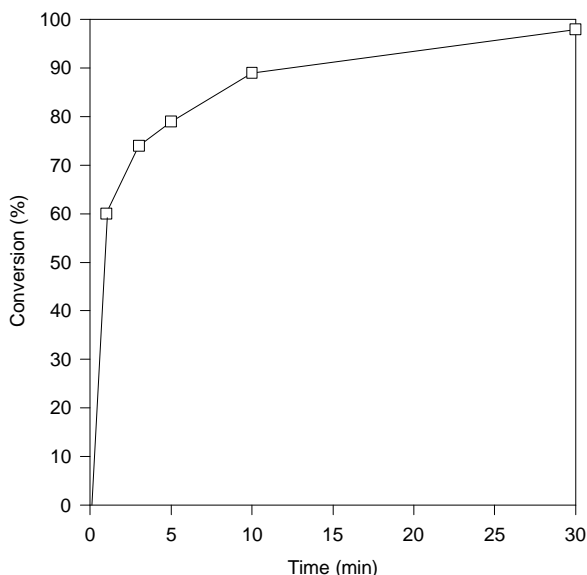


Figure 7.9 Conversion as function of reaction time in the ROP of cyclic mixture **6.1a**: 0.5 wt% potassium p-phenylphenoxide, at 330°C under vacuum.

Unlike the polymerization of single sized pure macrocycles in which high molecular weights were built up instantaneously and independent of reaction time, only medium molecular weight (13 K) was obtained initially and then it increased with reaction time (Figure 7.10). When the molecular weight is plotted vs conversion, a nearly linear relationship is observed starting from 60% conversion (Figure 11); while starting from 0% conversion there is no linear relationship. Keeping it in mind that the polymer and the unreacted cyclic mixture are not distinguishable, as mentioned above, and the molecular weight data between from the 0% (0 min) to the 60% conversion (1 min) are not available, the exact relationship between the molecular weight and the conversion is difficult to know. Whatever it is, the fact is that the molecular weight increases with conversion, which is not the case in the ROP of single sized macrocycles.

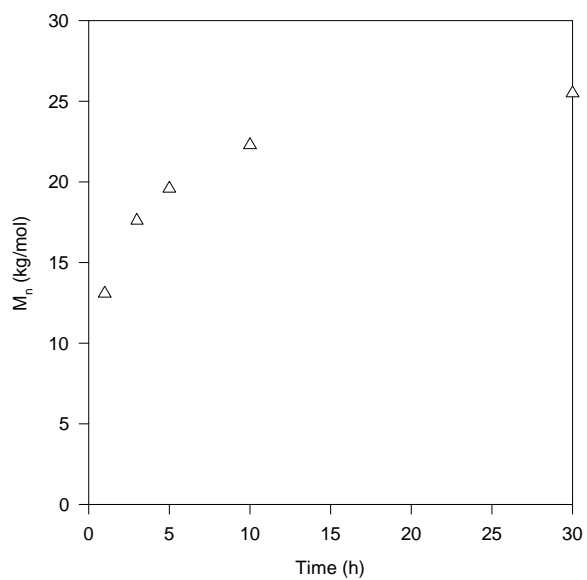


Figure 7.10 Molecular weight (M_n) as function of reaction time in the ROP of cyclic oligomeric mixture **6.1a** (0.5 wt% potassium p-phenylphenoxide, at 330°C under vacuum)

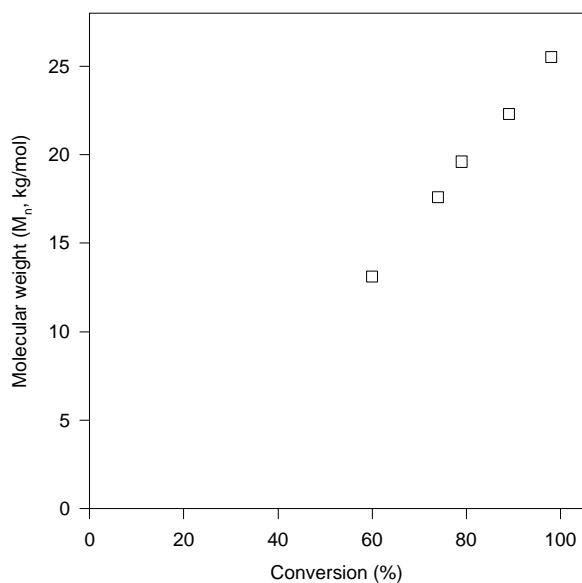


Figure 7.11 Molecular weight (M_n) as function of conversion in the ROP of cyclic oligomeric mixture **6.1a** (0.5 wt% potassium p-phenylphenoxide, at 330°C under vacuum)

Figure 7.12 shows the growing of the polymer peak which increases in intensity and moves towards the high molecular weight end of the chromatogram. Relatively slow polymerization of the cyclic mixture is probably due to the low reactivity, since average ring size is much larger than single ring sized macrocycles, which, more or less, lowers the viscosity of the reaction system and thus high conversion is more readily achieved. As normal, gels were also formed and gel content increased with reaction time. The molecular weight distribution of sol polymers increased with time too, as more branching took place over the period of the polymerization (Table 7.15).

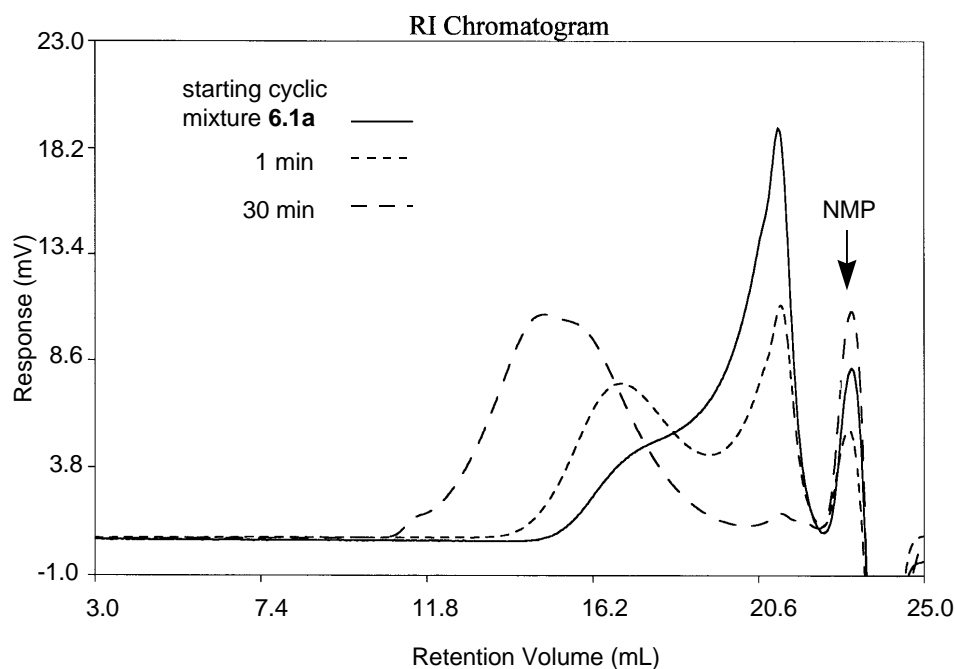


Figure 7.12 GPC traces (NMP+P₂O₅, 60°C, 1 mL/min). The ROP of cyclic mixture **6.1a** in the melt: 0.5 wt% potassium p-phenylphenoxide, at 330°C under vacuum.

Table 7.15 Results of the melt ROP of cyclic mixture **6.1a** in the presence of 0.5 wt% potassium p-phenylphenoxide at 330°C under vacuum for various reaction times

time (min)	M _n (kg/mol)	M _w (kg/mol)	M _w /M _n	gel fraction (%)	conversion (%)
1.0	13	19	1.4	0	60
3.0	18	30	1.7	0	74
5.0	20	34	1.8	1	79
10	22	55	2.5	2	89
30	26	100	3.9	4	98

Similar to the ROP of single sized macrocycles, the conversion for the ROP of cyclic mixture **6.1a** increased with the concentration of initiator. As shown in Table 7.16, a 100% conversion was achieved in 30 minutes when the concentration of initiator was increased to 1 wt%. Increasing the concentration of initiator, however, did not sacrifice molecular weights of the polymers from the cyclic mixture, at least in the range of concentration 0.1-0.3 wt% (Table 7.16). The molecular weight slightly decreased with the concentration of initiator starting from 0.3 wt%.

Table 7.16 Results of the melt ROP of cyclic mixture **6.1a** in the presence of various amount of potassium p-phenylphenoxide at 330°C under vacuum for 30 min

wt% of initiator	M_n (kg/mol)	M_w (kg/mol)	M_w/M_n	gel fraction (%)	conversion (%)
0.1	20	43	2.2	1	80
0.2	26	69	2.7	1	93
0.3	28	90	3.3	2	97
0.5	26	100	3.9	4	98
1.0	23	104	4.5	14	100

The conversion also increased with temperature (Table 1.17). At 330°C, only 80% conversion was achieved, whereas increasing the temperature to 365°C increased the conversion to 97%. The molecular weight (M_n) increased by 11 kg/mol as temperature was raised from 330°C to 350°C, and then reduced by 6 kg/mol as temperature was further raised to 365°C. Although the polymerization was favorable at 365°C, crosslinking was more severe. A 13% gel fraction was observed at this temperature, compared to 1% at 330°C and 3% at 350°C.

Table 7.17 The effect of temperature on the melt ROP of cyclic mixture **6.1a** in the presence of 0.1 wt% potassium p-phenylphenoxide under vacuum for 30 min at various reaction temperatures

temperature (°C)	M_n (kg/mol)	M_w (kg/mol)	M_w/M_n	gel fraction (%)	conversion (%) by GPC
330	20	43	2.2	1	80
350	31	98	3.1	3	90
365	25	99	4.0	13	97

The ROP of the cyclic mixtures **6.1b** and **6.1c** prepared using 4,4'-dichlorodiphenyl sulfone (DCDPS), instead of the difluoro compound, were not successful. **6.1b**, which contained a high level of linear oligomers (40%, see Chapter 6), essentially did not undergo polymerization even using high loadings of initiator (potassium p-phenylphenoxide). The product was very brittle without any mechanical strength at all. This may have resulted from the reaction of the initiator with the chloro-terminated linear oligomers, generating unreactive KCl. **6.1c**, also prepared using DCDPS, contains 12% linear oligomers, less than those contained in **6.1a** prepared using 4,4'-difluorodiphenyl sulfone (DFDPS). This cyclic mixture was only partially polymerized (79% conversion) in the presence of 1.0 wt% potassium p-phenylphenoxide, compared to 100% conversion in the polymerization of **6.1a** under the same reaction conditions. One reason for this could be formation of unreactive KCl as pointed above. Another reason could be that **6.1c** contains more macrocycles of larger ring sizes due to its higher molecular weight, 3.6 kg/mol compared to 2.3 kg/mol of **6.1a**. This might result in slower reaction in the polymerization of **6.1c** because of a smaller entropy force for the ROP of larger macrocycles. The polymerization of **6.1c** probably needs longer reaction times for completion.

7.2.3 Preliminary Studies of Solution ROP

To better understand the nature of ring opening polymerization of aromatic ether macrocycles, the polymerization of a single sized macrocycle was conducted in solution in the presence of potassium or cesium p-phenylphenoxide as initiator. Initially, N,N'-dimethylacetamide (DMAc) was used as solvent, but the polymerization of 40-membered phosphine oxide sulfone macrocycle **4.12** did not take place using the above initiators up to 5 mol%, even after 24 hour's reflux at 165°C. This may indicate that the macrocycle requires high activation energy for ring cleavage. Thus, diphenyl sulfone was used as solvent, with which the reaction temperature was increased to 250°C. The ring opening polymerization of **4.12** proceeded at this temperature. The above two initiators were used and the cation effects for the polymerization were compared.

Figure 7.13 shows the conversion-time relationship for the solution polymerization of **4.12** at 250°C in the presence of 5 mol% initiator. It is shown that the cesium phenoxide is much more reactive than potassium phenoxide. The higher reactivity with cesium counterion can be ascribed to the presence of solvent separated ion pairs, which form more reactive anions, and to the high solubility of the organic cesium salts in the dipolar aprotic solvent, diphenylsulfone. In both cases, the polymerization proceeded fast initially and then slowed down significantly later, especially with cesium phenoxide as initiator. As a result, complete polymerization was not obtained, even after 24 hours. Ring-chain equilibration is not the reason for the incomplete polymerization, because intermediate macrocycles were not observed in the HPLC chromatogram as shown in Figure 7.14. The polymerization was not retarded by viscosity either, as it was in the melt (bulk) ring opening polymerization, for the reaction mixture was diluted with solvent (diphenyl sulfone) and was stirrable over the entire period of the polymerization even though the solvent sublimed a little bit. The most probable reason may be that the reactivity of phenoxide anions decrease as polymer chain grows. This is supported by slow growth of the molecular weight of polymer in

the later period of polymerization as shown in Figure 7.15. It is also shown that with the less reactive potassium phenoxide, growing of polymer chains was even slower. We have already seen that in the melt polymerization, the molecular weight of polymers was built up immediately, independent of time and type of initiators. In that case, since the reaction temperature was higher, 340°C, the reactivity might not have been affected much by the growing of the chains.

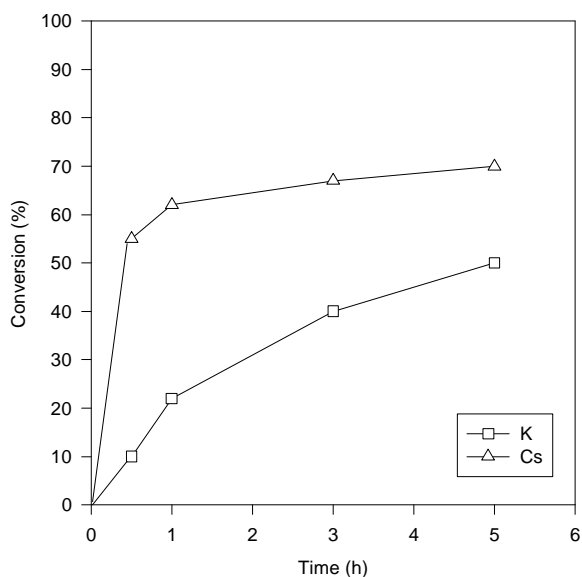


Figure 7.13 Conversion as function of reaction time in the solution ROP of macrocycle **4.12** (5.0 mol% alkali p-phenylphenoxide, at 250°C under nitrogen, diphenyl sulfone as solvent)

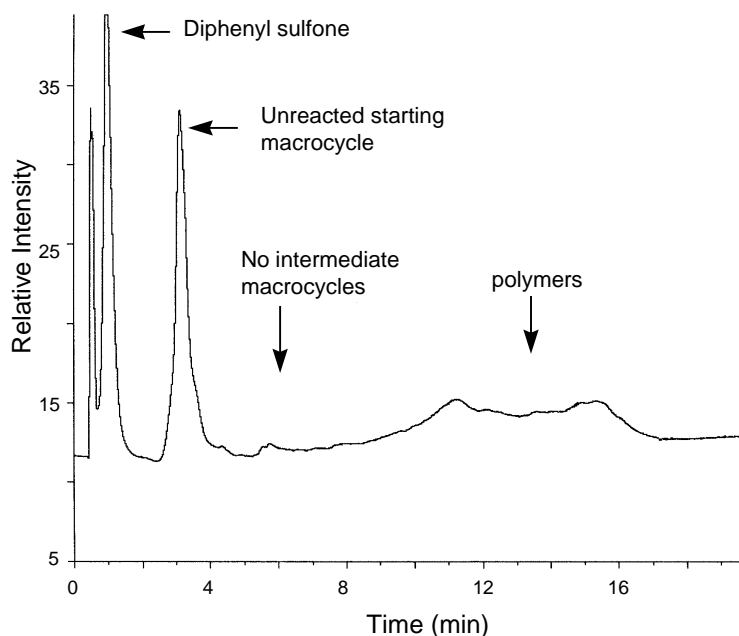


Figure 7.14 RP-HPLC chromatograms (C18, THF/water, gradient, UV detector) of the product of the solution ROP of macrocycle **4.12** in diphenyl sulfone (5.0 mol% potassium p-phenylphenoxide, at 250°C under nitrogen, for 24 hours).

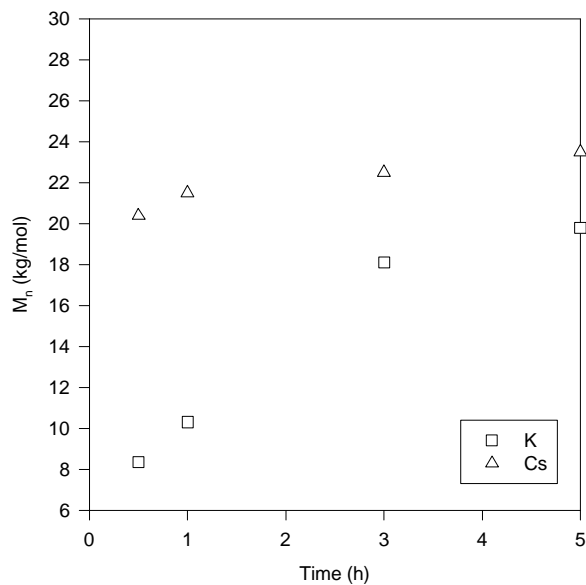


Figure 7.15 Molecular weight (M_n) as function of reaction time in the solution ROP of macrocycle **4.12** (5.0 mol% alkali p-phenylphenoxide, at 250°C under nitrogen, diphenyl sulfone as solvent)

No gel was formed in the solution ring opening polymerization. However, GPC traces of the products were bi-modal. Besides the unreacted macrocycles and diphenyl sulfone solvent, there were two polymer peaks as seen in Figure 7.16. The lower molecular weight peak gives about $M_n=18$ kg/mol, while the higher molecular weight peak gives $M_n=46$ kg/mol. It is not clear whether or not the higher molecular peak is due to branched polymer.

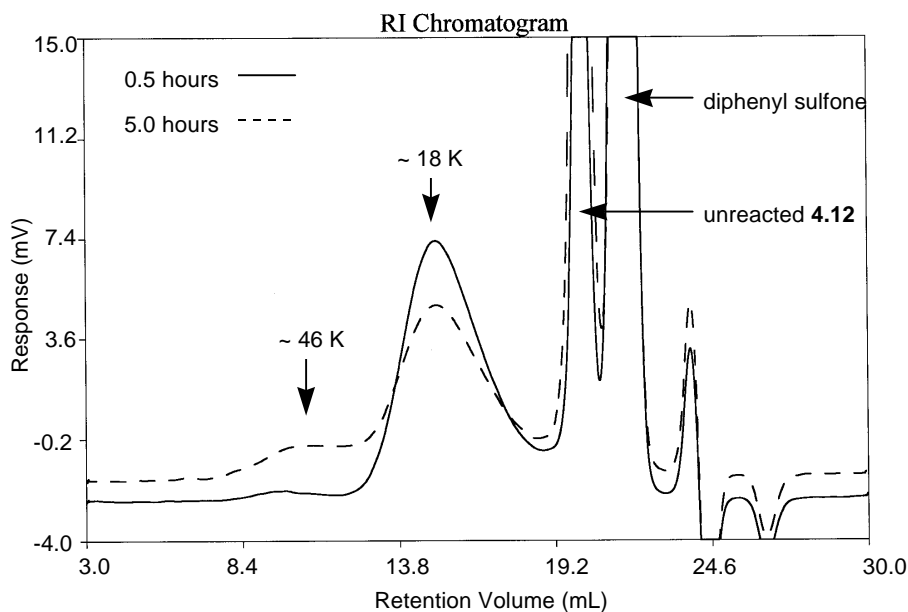


Figure 7.16 GPC traces (differential viscosity chromatogram, CHCl_3 , 35°C , 1 mL/min). The solution ROP of **4.12** in diphenyl sulfone: 5.0 mol% cesium p-phenylphenoxide, 250°C under nitrogen, for 0.5 h and 5.0 h.

7.3 Conclusions

The ring opening polymerization of single sized aryl ether macrocycles in the melt exhibits two stage characteristics. The fast reaction in the first stage is largely driven by the entropy difference between the macrocycle and the linear polymer, while the slow reaction in the second stage is diffusion controlled, which retards the polymerization towards completion. Complete polymerization can be achieved at the expense of losing molecular weight at high initiator concentrations. The molecular weights of the polymers were built up instantaneously, independent of conversion, reaction time and type of initiator. This behavior resembles that of chain growth polymerization. The polymerization can be initiated by CsF and alkali phenoxides. In general, an initiator with cesium counterion is more efficient for the ROP than an initiator with

potassium or sodium counterion, while a phenoxide initiator is more efficient than a fluoride initiator. Furthermore, a difunctional initiator is more efficient than a monofunctional initiator. Crosslinking was a common side reaction encountered in the ROP of aromatic ether macrocycles, which most likely involves the formation of biphenyl linkages.

By comparison, the ROP of cyclic mixtures was relative slow because of less entropy force due to macrocycles of larger ring sizes. The molecular weight of resultant polymers increased with time and conversion. Higher temperatures provided higher conversions and more crosslinked polymers. The polymerization is sensitive to the amount of linear contaminants and the average ring size of macrocycles present in the mixture.

7.4 EXPERIMENTAL

Measurements

^1H NMR spectra were obtained on a Varian 400 MHz instrument in deuterated dimethyl sulfoxide or chloroform with TMS as the internal standard at ambient temperature. Reverse-phase HPLC analyses were performed on an ISCO dual pump HPLC system comprising two Model 2350 pumps and the V⁴ Variable Wavelength UV/Vis Detector set at 274 nm. THF/water gradients were used for elution of products on a reverse-phase column (Novapak 100 Å, 4 mm C18, 150 x 3.9 mm i.d.) at a flow rate of 1.5 mL/min. The gradient program was as follows: solvent A, THF/water (60/40) reduced from 100% to 0% over 20 min; at the same time, solvent B, THF increased from 0% to 100% over 20 min. The system was interfaced with the ISCO ChemResearch Chromatographic Data Management/System, used for data analyses. Two sets of gel permeation chromatography (GPC) instruments were used for molecular weight characterization. For polymers obtained from cyclic mixtures **6.1a-6.2c**, GPC was carried out in a Waters GPC/ALC 150-C chromatograph equipped with a differential refractometer detector and an on-line differential viscometric detector (Viscotek 150R) coupled in parallel. Two columns which were packed with 10^3 and 10^4 Å uStyragel HT were used. The mobile phase was NMP containing 0.02 M P_2O_5 and data was recorded at 60°C at a flow rate of 1.0 ml/min. For polymers obtained from pure macrocycles (**4.11**, **4.12** and **4.15**), GPC was carried out in a Waters 590 chromatograph equipped with a differential refractometer detector (Viscotek Laser Refractometer) and an on-line differential viscometric detector (Viscotek 100) coupled in parallel. Two columns which were packed with 10^3 and 10^4 Å uStyragel HT were used. The mobile phase was chloroform and data was recorded at 35°C at a flow rate of 1.0 ml/min.

Preparation of initiator solutions in ethanol

For preparing CsF and KF ethanol solutions, the two fluorides were directly dissolved in absolute ethanol or ethanol/water. Thus, oven dried CsF was weighed and dissolved in ethanol to make a 13.13 mM solution in a 1 L volumetric flask. Similarly, oven dried KF was weighed and dissolved in ethanol with addition of a minimum amount of distilled water to make a 18.30 mM solution in a 250 mL volumetric flask.

For preparing alkali (Na, K, or Cs) phenoxide initiators in ethanol, a standardized *aq.* alkali hydroxide (NaOH 99.91 mM, KOH 99.41 mM, or CsOH 103.4 mM) was placed in a 100

mL flask using a volumetric pipette (4, 10 or 20 mL) and rotary evaporated. The solid hydroxide was then dissolved in ethanol (20 ml). To help dissolve the hydroxide completely, 1-2 mL distilled water was added. The ethanol solution of the hydroxide was completely transferred into a 200 mL volumetric flask containing an ethanol solution of a phenol which was weighed exactly according to the molar amount of the hydroxide used, and the mixed solution was shaken and diluted to the mark with ethanol. Since phenol **7.2** has low solubility in ethanol, 5-10 ml chloroform was added to help dissolve it and 4 mL standardized aq. KOH were directly transferred to the phenol solution using a 4 mL volumetric pipette.

The specific concentrations of initiator solutions in ethanol are as follows: potassium *p*-phenylphenoxide, 7.993 mM; sodium *p*-phenylphenoxide, 3.976 mM; cesium *p*-phenylphenoxide, 10.34 mM; potassium salt of **3.3**, 3.996 M; potassium salt of **7.2**, 1.998 M.

Melt ring opening polymerization

A dried mixture of a macrocycle and an initiator was first prepared prior to polymerization. For an already finely powdered macrocycle, such as **4.12** and **4.15**, a minimum amount of absolute ethanol was added to cyclic monomer (200.0 mg) placed in a 25 mL round bottom flask to make a slurry. For macrocycles not finely powdered, such as **4.11** and **6.1a-6.1c**, the cyclic monomer (200.0 mg) was dissolved in a minimum amount of chloroform in a 25 mL round bottom flask, into which a minimum amount of absolute ethanol was then added to precipitate the macrocycle, forming a milky suspension. An ethanol solution of initiator was transferred to the slurry or the suspension using a 1 mL graduated pipette (1/100 scale). To give 5% molar ratio of potassium *p*-phenylphenoxide to macrocycle **4.12**, for example, 1.32 mL of the salt solution (7.993 mM) was added. Solvents were then carefully rotary evaporated, and the flask was connected to a vacuum line to dry the sample under high vacuum at 110°C. Once the vacuum reached about 2×10^{-5} Torr in several hours, the sample was purged with argon and re-evacuated three times. For polymerization of single sized macrocycles, the flask was filled with argon and inserted into a preheated salt bath (KNO₃/NaNO₂, 10.0/8.5 by weight). For the polymerization of cyclic mixtures, the evacuated flask was inserted into the preheated salt bath. Time zero was recorded once all the sample melted. After it had cooled to room temperature, the product was immersed in chloroform for two hours, then removed to a 100 mL beaker, stirred in 50 mL chloroform overnight and filtered. The filtrate was placed in a pre-weighed flask and rotary evaporated, then dried under vacuum at 100°C overnight.

Solution ROP of macrocycle 4.12

A mixture of potassium *p*-phenylphenoxide (5.52 mg, 0.0265 mmol, 5.0 mol% of the macrocycle) and macrocycle **4.12** (500 mg, 0.529 mmol) was prepared and dried as above. Diphenyl sulfone (1.5 g) was then added to the mixture. The mixture was magnetically stirred in a salt bath (KNO₃/NaNO₂, 10.0/8.5 by weight) at 250°C under nitrogen. A small amount of sample was periodically pulled out and directly subjected to GPC analysis without any purification.

4-{p-[p-(Phenylsulfonyl)phenoxy]phenoxy}-4'-(p-hydroxyphenoxy)phenyl sulfone (7.2)

A mixture of **4.1** (5.2 g, 12 mmol) and K₂CO₃ (2.0 g, 14 mmol) in DMAc (30 mL) and toluene (15 mL) was refluxed with magnetic stirring for 5 hours under nitrogen. Water generated during deprotonation was azeotroped into a Dean-Stark trap by toluene. Toluene was then distilled and 4-chlorodiphenyl phenyl sulfone (2.53 g, 10.0 mmol) was added all at once. The reaction was allowed to proceed under nitrogen for 12 hours at reflux. After it had cooled to room temperature, the reaction mixture was precipitated into dilute HCl (600 mL). The precipitate was filtered, rinsed with water several times and dried under vacuum. The crude product was then subjected to silica gel column chromatography with chloroform/ethyl acetate (85/15) as eluent, which isolated **7.2** as a white solid. Yield: 3.56 g (55%); mp: 215.5-217.0°C; ¹H NMR (DMSO-d₆) δ 6.82 (d, 2 H, J=8.8 Hz), 6.96 (d, 2 H, J=8.8 Hz), 7.02 (d, 2 H, J=8.8 Hz), 7.14 (d, 2 H, J=9.2 Hz), 7.15 (d, 2 H, J=9.2 Hz), 7.61-7.71 (m, 3 H), 7.89 (d, 2 H, J=8.8 Hz), 7.91 (d, 2 H, J=9.2 Hz), 7.94-7.96 (m, 2 H), 7.96 (d, 2 H, J=9.2 Hz), 9.53 (s, 1 H); elemental anal.: calcd for C₃₆H₂₆S₂O₈: C, 66.45; H, 4.03; S, 9.85; found: C, 66.47; H, 4.02; S, 9.91.

Synthesis of 4,4'-diphenoxydiphenyl sulfone (7.3)

A mixture of phenol (6.0 g, 63 mmol) and potassium carbonate (5 g, 36 mmol) in N, N'-dimethylacetamide (40 mL) and toluene (40 mL) was refluxed for three hours to deprotonate phenol. Water generated was removed in a Dean-Stark trap. Toluene was then distilled and 4,4'-dichlorodiphenyl sulfone (7.18 g, 25.0 mmol) was added. The reaction was allowed to proceed for 12 hours. The reaction mixture was poured into water (500 mL) after cooling, and the product was extracted with methylene chloride (3x100 mL). The combined organic phase was washed with water, dried with sodium sulfate and evaporated. Recrystallization in ethanol/chloroform once provided a white solid. Yield: 9.7 g (97%), mp: 191-193°C (lit.⁴ 141-143°C); ¹H NMR (CDCl₃) δ 7.01 (d, 4 H, J=9.2 Hz), 7.04 (complex d, 4 H, J=8.8 Hz), 7.22 (complex t, 2 H, J=8.8 Hz), 7.40 (complex t, 4 H, J=8.8 Hz), 7.86 (d, 4 H, J=9.2 Hz).

Model studies

a) CsF with p-bis(p'-fluorobenzoyl)benzene (7.1). An ethanol solution (20 mL, 13.13 mM) of CsF was added to a solution of **7.1** (42.3 mg, 0.12 mmol) in chloroform, and the solvents were then evaporated. The mixture was dried under vacuum and inserted into a pre-heated salt bath (KNO₃/NaNO₂, 10.0/8.5 by weight). The reaction was carried out at 340°C under argon for 30 min. After reaction, the mixture was stirred in water for several hours to remove CsF. The product was filtered, dried, and dissolved in chloroform. About 5% of the product was isolated which was not soluble in chloroform and conc. sulfuric acid.

b) Cesium p-phenylphenoxide with 7.1 The preparation was the same as in a). The phenoxide: 20 mL, 10.34 mM ethanol solution; compound **7.1**: 33.3 mg, 0.103 mmol. After reaction, the product was completely soluble in the chloroform/ethanol solvent mixture.

⁴ Amiri, M. J. *Chem. Soc., Perkin Trans. 2*, **1979**, 8, 7.

c) *Cesium phenoxide with 7.3*. The sample preparation was similar to a). The phenoxide: 20 mL, 10.34 mM ethanol solution; compound **7.3**: 41.6 mg, 0.103 mmol. After reaction, the product was completely soluble in the chloroform/ethanol solvent mixture.

Chapter 8

Suggestions and Future Work

A. To make parallel comparisons between single sized macrocycles and cyclic mixtures in preparation of engineering thermoplastics by ring opening polymerization, it is suggested that the following experiments be carried out in the future.

1) ROP of single sized macrocycles under vacuum condition to compare that of cyclic mixtures which has already been done under this condition.

2) ROP of cyclic mixtures under argon condition to compare that of single sized macrocycles which has already been done under this condition. From preliminary studies, under argon atmosphere, only very poor conversions were obtained.

3) It was found that there were some volatile materials released upon heating the cyclic mixtures in the presence of an initiator. These volatile materials were removed under vacuum, but suppressed under argon pressure. Presumably, the suppressed volatile stuff may be the major reason that led to poor conversions under the argon condition. Thus, it would be helpful to identify these material in order to increase conversion. TGA-MS may be a useful technique to track these materials during heating.

B. One of important applications of ROP is to make engineering thermoplastic composite materials, taking advantages of fast polymerization, no formation of volatile byproducts and better wetting ability of low molecular weight cyclic monomers. Preparation of carbon fiber composite has already been in consideration with collaboration from the Department of Chemical Engineering. With the all the information we have about the melt ROP of arylene ether macrocycles, the studies of composite materials by ROP should be carried out appropriately.

Part Two

Synthesis of Polyrotaxanes

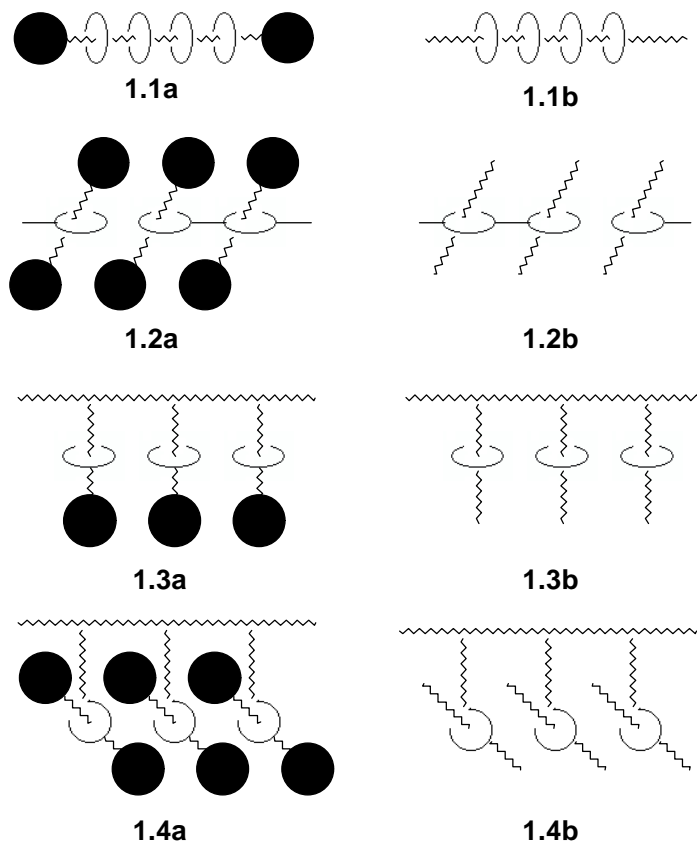
Chapter 1

Literature Review

1.1 Introduction

Polyrotaxanes are novel polymers composed of linear polymer molecules threaded by cyclic molecules with no covalent bond between the two components.¹ Scheme 1.1 illustrates various types of polyrotaxanes. **1.1** and **1.2** represent two types of main chain polyrotaxanes, while **1.3** and **1.4** represent two types of side chain polyrotaxanes. The black solid circles in **1.1a**, **1.2a**, **1.3a** and **1.4a** represent bulky blocking groups which are used to prevent diffusional dethreading of the cyclic species (the open circles). Polypseudo-rotaxanes **1.1b**, **1.2b**, **1.3b** and **1.4b** do not contain the blocking groups; their stabilities rely on kinetic retardation of dethreading by random coiling or on strong attractions between the cyclic and the linear components. Since the cyclic component can potentially move along the linear component, these systems are expected to possess unique properties.

Scheme 1.1 Schematic representations of various types of polyrotaxanes.

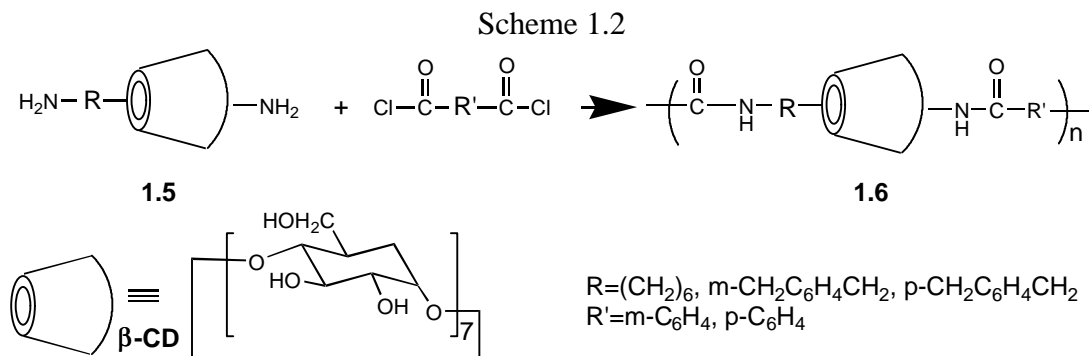


¹ a) Gibson, H. W.; Bheda, M. C.; Engen, P. T. *Prog. Polym. Sci.*, **1994**, *19*, 843-94. b) Gibson, H. W., chapter in "Large Ring Molecules", edited by Semlyen, J. A., John Wiley & Sons, New York, **1996**, Ch. 6, pp 191-262.

The first experimental demonstration of the existence of rotaxanes (monomeric analogs of polyrotaxanes) was in 1967.² Since then, much progress has been made in development of these novel physically linked structures, including both rotaxanes and polyrotaxanes. The present chapter is designed to afford an overview of polyrotaxanes. For monomeric rotaxanes, interested readers are referred to the reviews cited in Refs.1 and 3. As will be shown in the following sections, a variety of polyrotaxanes have been successfully synthesized by threading macrocycles onto a wide range of polymeric materials. These polyrotaxanes show interesting changes of physical properties, such as morphology, crystallinity, solubility, viscosity, etc.

1.2 Main Chain Polyrotaxanes

The first polyrotaxanes synthesized were main chain polyrotaxanes **1.6** consisting of polyamides and β -cyclodextrin (β -CD) units. They were obtained by conducting interfacial or low temperature solution polycondensations between isolated 1:1 inclusion compounds **1.5** of β -CD with various diamines and diacid chlorides,⁴ as shown in Scheme 1.2. No indication of the extent of threading was given and molecular weights were apparently low. Due to threading of β -CD, solubility and water sorption of the polyrotaxanes were greatly altered relative to the standard polyamides.



The above synthesis features the template approach to polyrotaxanes.¹ Cyclodextrins are water soluble macrocyclic oligosaccharides which have hydrophobic cavities. They can include a variety of organic/inorganic compounds and organic salts in their cavities by complexation via hydrophilic-hydrophobic, van der Waals interactions and possibly hydrogen bonding.⁵ The strong complexation provides monomeric rotaxanes (such as **1.5**) which can be isolated and polymerized with other reactants to form polyrotaxanes of high cyclodextrin contents. This template approach

² a) Harrison, I. T.; Harrison, S. *J. Am. Chem. Soc.*, **1967**, 89, 5723. b) Schill, G.; Zollenkopf, H. *Nachr. Chem. Techn.*, **1967**, 79, 149.

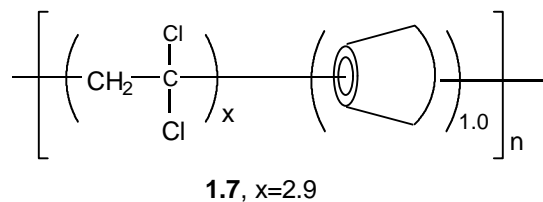
³ Amabilino, D. B.; Stoddart, J. F. *Chem. Rev.*, **1995**, 95, 2725-2828. b) Philp, D.; Stoddart, J. F. *Angew. Chem. Int. Ed. Engl.* **1996**, 35, 1154-1196.

⁴ Ogata, N.; Sanui, K.; Wada, J. *J. Polym. Sci., Polym. Lett. Ed.* **1975**, 14, 459.

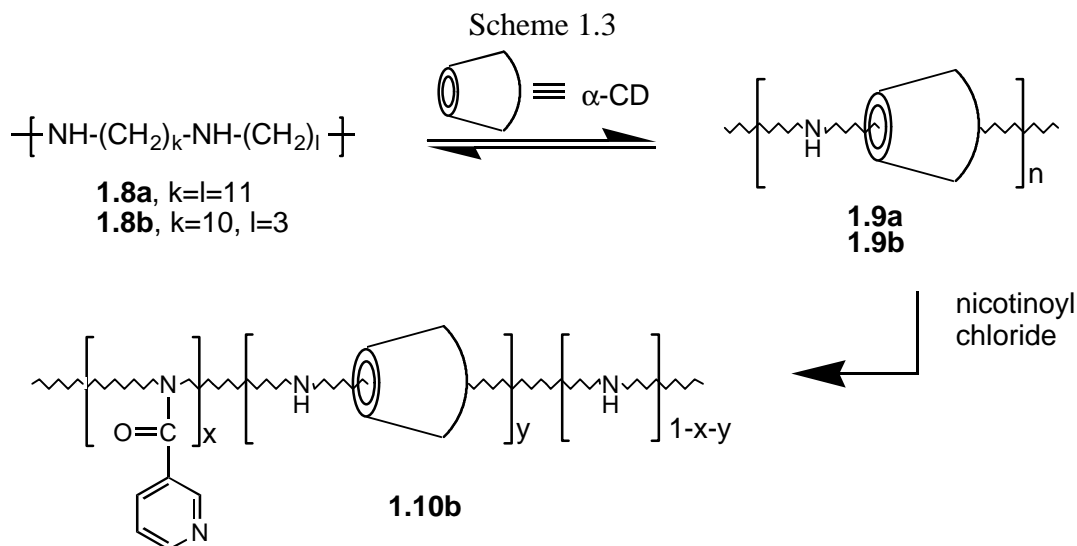
⁵ a) Frank, S. G. *J. Pharm. Sci.* **1975**, 64, 1585. b) Bergeron, R. J. *J. Chem. Edu.* **1977**, 54, 204. c) Saenger, W. *Angew. Chem. Int. Ed. Engl.* **1980**, 19, 344. d) Wenz, G. *Angew. Chem. Int. Ed. Engl.* **1994**, 33, 803

to the synthesis of polyrotaxanes containing cyclodextrins was successfully applied by many researchers.

Maciejewski prepared polyrotaxane **1.7** by the radiation polymerization of the crystalline adduct of vinylidene chloride and β -CD units.⁶ The polyrotaxane contains 80% cyclodextrin and had a molecular weight of ca. 20,000, which corresponds to one macrocycle for every 2.9 repeat units of vinylidene chloride.



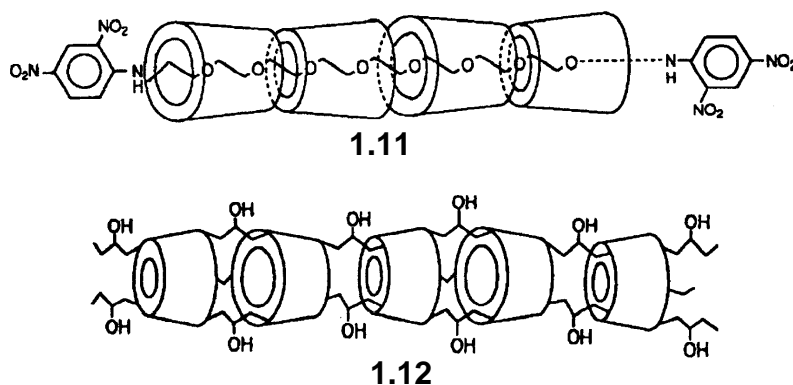
Wenz and Keller used preformed polymers **1.8a** and **1.8b** to prepare polyrotaxanes **1.9a** and **1.9b** in the presence of α -cyclodextrin (α -CD). When **1.9b** was treated with nicotinoyl chloride to introduce blocking group along the polymer chain, polyrotaxane **1.10b** of molecular weight M_w 55 K (determined by light scattering) was obtained with an average of 37 α -CD rings permanently threaded onto the chain (Scheme 1.3).⁷ This work demonstrated the efficiency of this template approach even when preformed high molecular weight polymers were used.



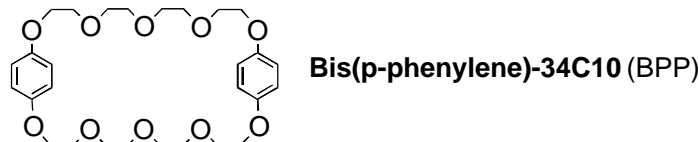
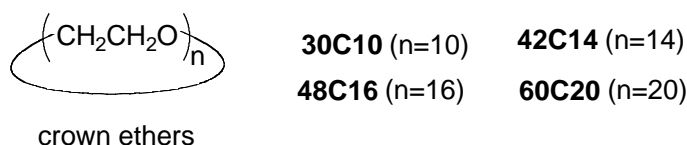
⁶ a) Maciejewski, M. J. *Macromol. Sci. Chem.* **1979**, A18 (1), 77. b) Maciejewski, M. J.; Gwizdowski, A.; Peczak and, P.; Pietrak, A. *J. Macromol. Sci. Chem.* **1979**, A13(1), 87.

⁷ Wenz, G.; Keller, B. *Angew. Chem. Int. Ed. Engl.* **1992**, 31, 197.

More exciting work was reported by Harada and coworkers.⁸ They threaded preformed diamine-terminated oligomeric ethylene glycol through α -cyclodextrin and the resultant polypseudo-rotaxane was then end capped by dinitrophenyl end blockers attached at both ends to form stable polyrotaxane **1.11**. Reaction of the polyrotaxane with epichlorohydrin linked the α -CD rings together and then cleavage of the end blockers and extrusion of the poly(ethylene glycol) produced a molecular tube **1.12** which consisted of about 15 bridged α -CD units. This work indicates that the formation of polyrotaxanes can be a way to organize and connect segments into “nanotubules”.



Crown ether macrocycles, 30C10, 42C14, 48C16, 60C20 and BPP, were employed by Gibson and coworkers in syntheses of a series of main chain polyrotaxanes based on various types of polymeric backbones and polymerization techniques.

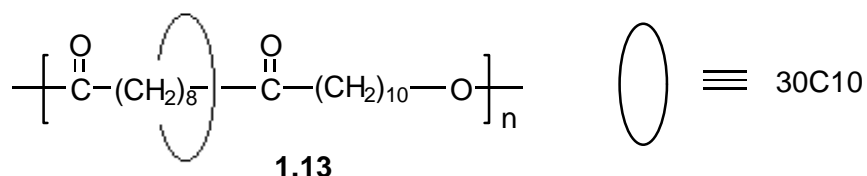


The first main chain polyrotaxane of type **1.1** synthesized by Gibson and coworkers was polyester rotaxane **1.13** by polycondensation from sebacoyl chloride and 1,10-decanediol using 30C10 as solvent.⁹ With 3.42 moles of the crown ether per mole of diol, a value of $m/n=0.15$ (the

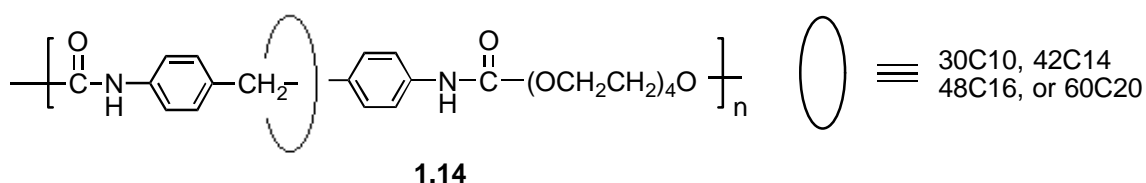
⁸ a) Harada, A; Kamachi, M. *Macromolecules* **1990**, 23, 2821. b) Harada, A.; Li, J.; Kamachi, M. *Nature* **1992**, 356, 325. c) Harada, A. Li, J.; Kamachi, M. *Macromolecules*, **1993**, 26, 5698.

⁹ Gibson, H. W.; Engen, P.; Lecavalier, P. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1988**, 29(1), 248.

number of crown ethers per repeat unit) was achieved; this corresponds to 16 wt% of crown ether. A variety of other aliphatic polyester-crown ether rotaxanes were synthesized later on either by acid chloride esterification or transesterification techniques.¹⁰ The content of crown ethers in the polyrotaxanes ranges from 6-63 wt%, depending on the feed ratio of crown to monomer, reaction temperature, and the ring size of crown ethers. Attachment of blocking groups at the both ends of polymeric backbones or inclusion of stoppers along the backbone to prevent threaded crown ethers slipping off the backbone significantly increase the crown content in the final purified polyrotaxanes. In all the syntheses, hydrogen bonding of the monomeric diols with the crown ethers was considered to provide the driving force for these threading process, and formation of the ester linkage captures the rings hydrogen-bonded to the OH groups of the diol monomers.



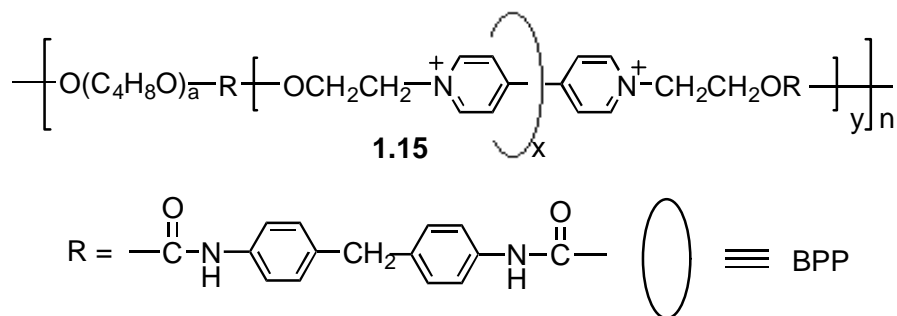
A family of polyurethane rotaxanes **1.14** was synthesized by Shen, Xie and Gibson from tetraethylene glycol and bis(p-isocyanatophenyl)methane (MDI) using various crown ethers.¹¹ The polyrotaxanes were prepared by carrying out the polycondensation using melted crown ethers as solvents at 90°C. Crown ether incorporated ranged from 16-63% of the total mass of the polyrotaxane, increasing with the ring size of crown ethers. Again, hydrogen bonding of the diol with the crown ethers may have played an important role in driving the threading, and hydrogen bonding of the resultant urethane linkage (-NHCO-) served as an anchor to prevent dethreading. No blocking group was used in this synthesis.



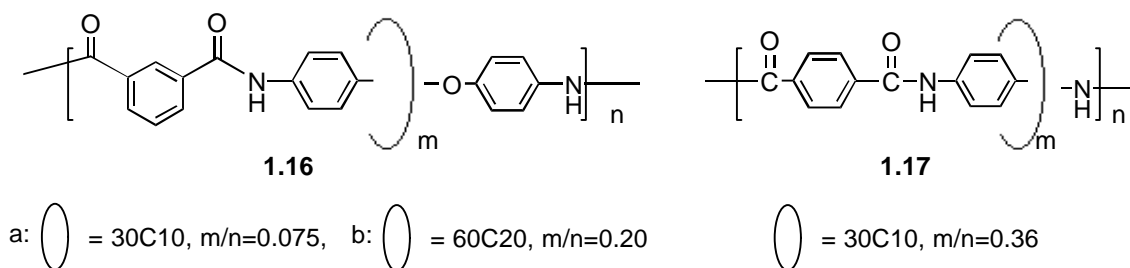
¹⁰ a) Wu, C.; Bheda, M. C.; Lim, C.; Shen, Y. X.; Sze, J.; Gibson, H. W. *Polym. Commun.* **1991**, 32, 204. b) Gibson, H. W.; Liu, S.; Lecavalier, P.; Wu, C.; Shen, Y. X. *J. Am. Chem. Soc.*, **1995**, 117, 852. c) Liu, S. *Ph.D. Dissertation*, Virginia Polytechnic and State University, 1995. d) Gong, C.; Gibson, H. W. *Macromolecules* **1996**, 29, 7029-7033.

¹¹ a) Shen, Y.; Xie, D.; Gibson, H. W. *J. Am. Chem. Soc.*, **1993**, 116, 537. b) Shen, Y. *Ph.D. Dissertation*, Virginia Polytechnic Institute and State University, 1992

Inspired by the work of Stoddart et al.,¹² Shen, Bheda and Gibson synthesized a series of segmented, elastomeric polyurethane rotaxanes **1.15** based upon poly(tetramethylene oxide) of three different molecular weights, MDI, N,N'-bis(2-hydroxyethyl)-4,4'-bipyridinium hexafluorophosphate and BPP.^{13,11b} Since the latter two components have been demonstrated to form the threaded host-guest complex quantitatively, the *in situ* polymerization of the monomeric rotaxane provided the polyrotaxane (**1.15**) containing threaded BPP up to x/y=1. This work demonstrates again that the template approach is a very efficient way to synthesize polyrotaxanes, especially when there is strong interaction between macrocycles and monomers.



Polyamide rotaxanes **1.16** were prepared by Bheda and Gibson from isophthalic acid and bis(p-aminophenyl)ether using 30C10 and 60C20.^{14,15} **1.16a** contains 9.1% crown by mass, and **1.16b**, 35%. They also synthesized a Kevlar based polyrotaxane **1.17** by reaction of terephthalic acid and p-phenylenediamine in the presence of 30C10.^{14,15} According to solid state ¹³C NMR spectroscopy, **1.17** contained 57% macrocycle by mass. In both syntheses, hydrogen bonding apparently is a driving force for threading.



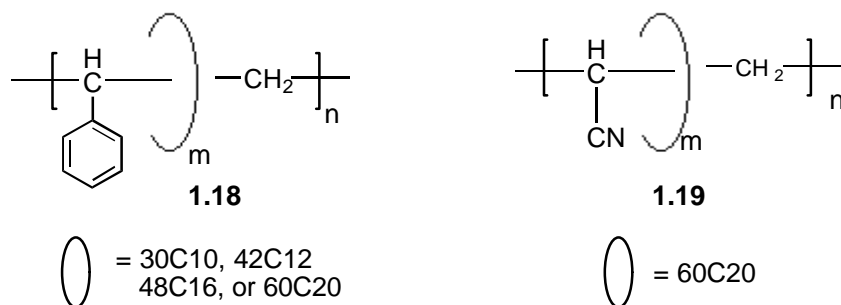
¹² a) Allwood, B. L.; Spencer, N.; Shahriari-Zavareh, H.; Stoddart, J. F.; Williams, D. J. *J. Chem. Soc. Chem. Commun.* **1987**, 1061, 1064. b) Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Williams, D. J. *J. Chem. Soc. Chem. Commun.* **1987**, 1070. c) Ashton, P. R.; Philp, D.; Reddington, M. V.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Williams, D. J. *J. Chem. Soc. Chem. Commun.* **1991**, 1680.

¹³ Shen, Y. X.; Engen, P. T.; Berg, M. A. G.; Merola, J. S.; Gibson, H. W. *Macromolecules*, **1992**, *25*, 2786.

¹⁴ Bheda, M. C. *Ph.D. Dissertation*, Virginia Polytechnic Institute and State University, 1992.

¹⁵ Gibson, H. W.; Marand, H. *Adv. Mater.*, **1993**, *5*, 11-21.

By free-radical polymerization techniques, Gibson and coworkers synthesized a family of polystyrene-based rotaxanes **1.18**^{15,16,17} and polyacrylonitrile-based rotaxanes **1.19**^{15,16,18} using various crown ethers. In some cases an azo initiator containing triaryl alkyl groups was used to provide end blocks in order to obtain stable polyrotaxanes. Since there was no strong attractive interaction, or perhaps even repulsion, between the crown ether macrocycles and the monomers or the polymer backbones in these systems, the threading was apparently driven entropically. This process is called statistical threading.¹ The main advantage of the statistical approach is that the macrocycle and linear monomer need not complement each other for complexation as indicated in the above cases; thus the two components are independently variable and the approach can be applied to any types of polymer backbones. A disadvantage is that significant quantities of macrocycle are required to achieve a high proportion of macrocycle incorporation, based on Le Chatelier's principle.



1.3 Side Chain Polyrotaxanes

Compared to main chain polyrotaxanes, side chain polyrotaxanes are rarely seen in the literature. A few examples of this system were reported by Ritter and coworkers.¹⁹ They used cyclodextrins, which have good complexation ability as mentioned earlier, as the cyclic component in polyrotaxane structures. A general approach in their syntheses is attachment of a low molar mass rotaxane with one reactive end and one stopper at the other end to a reactive polymer. For example, in the synthesis of side chain polyrotaxane **1.23**,^{19a} an amino amide **1.20** was complexed with 2,6-dimethyl- β -cyclodextrin to make rotaxane **1.21**. This rotaxane was isolated and allowed to react with a poly(methyl methacrylate) copolymer **1.22** bearing anhydride terminated pendant groups to produce side chain polyrotaxane **1.23**.

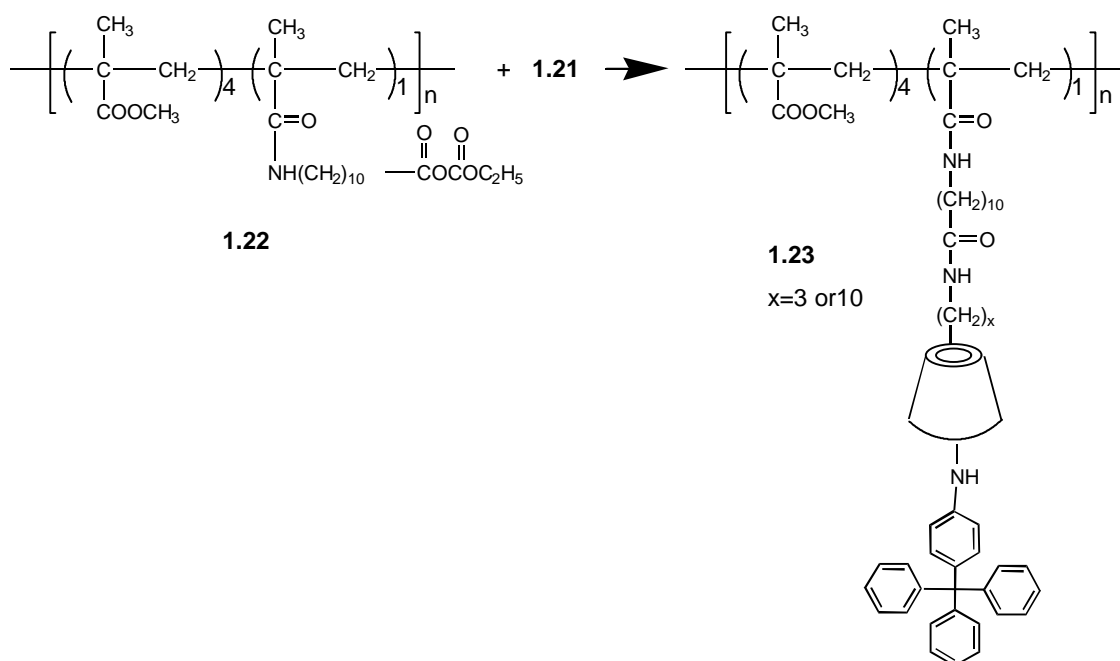
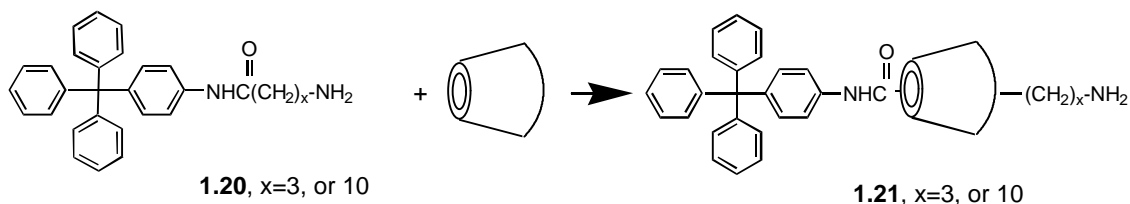
¹⁶ Engen, P. T. *Ph.D. Dissertation*, Virginia Polytechnic Institute and State University, 1991.

¹⁷ Lee, S. H. *Ph.D. Dissertation*, Virginia Polytechnic Institute and State University, 1996.

¹⁸ a) Gibson, H. W.; Engen, P. T.; Lee, S. H.; Liu, S.; Marand, H.; Bheda, M. C. *Polym Prepr. Am. Chem. Soc. Div. Polym Chem.* **1993**, 34(1), 64. b) Gibson, H. W.; Engen, P. T. *New J. Chem.* **1993**, 17, 723.

¹⁹ a) Born, M.; Ritter, H. *Makromol. Chem., Rapid Commun.*, **1991**, 12, 471. b) Born, M.; Ritter, H. *Angew. Chem. Int. Ed. Engl.*, **1995**, 34, 309. c) Born, M.; Koch, T.; Ritter, H. *Acta Polym.*, **1994**, 45, 68. d) Born, M.; Koch, T.; Ritter, H., *Macromol. Chem. Phys.*, **1995**, 196, 1761.

Scheme 1.4



1.4 Some Physical Properties of Polyrotaxanes

1.4.1 Solution behavior

The incorporation of macrocycles into polymeric materials by threading induces solubility changes, which is the most manifest result of formation of polyrotaxanes. The solubility change relies on intrinsic properties of the threaded macrocycles as well as on how the threaded macrocycles interfere with the intermolecular interactions of the backbone molecules. For example, cyclodextrins are water soluble oligosaccharides. Polyamide rotaxanes **1.6** that contain β -cyclodextrin exhibit water sorption as well as enhanced solubility in a variety of organic solvents, compared to their parent polyamides.⁴ Cyclodextrin containing poly(methyl methacrylate)-based side chain rotaxane **1.23** becomes soluble in ether, whereas the parent polymer is not, apparently due to shielding of the amide moieties by the cyclodextrin macrocycle, which prevents intermolecular hydrogen bonding of the amide moieties.^{19a}

In the crown ether containing polyrotaxanes, since the crown ethers are quite soluble in a wide range of aromatic and polar solvents as well as in water, their presence enhances the solubilities of polyrotaxanes relative to the parent polymers. Poly(alkylene sebacate)s-crown ether rotaxanes show solubilities in methanol and water.¹⁰ Likewise polyurethane rotaxanes containing crown ethers show similar changes in solubility; in fact they become soluble in water through the formation of micelles.¹¹ A well-known intractable polymer, polyacrylonitrile, can be made methanol soluble through the formation of rotaxane structure with 60C20.^{16,18}

Threading of macrocycles onto polymeric materials also induces changes of solution viscosity. For example, Liu, and Gibson found that poly(butylene sebacate) rotaxane containing one 42C14 per molecule exhibited a doubling of the intrinsic viscosity in chloroform.^{10c,20} This may suggest that threaded macrocycles restrict the conformational mobility of the backbone, thus increasing the chain stiffness which would lead to increased hydrodynamic volume.

1.4.2 Glass transitions

The formation of polyrotaxanes leads to changes in the glass transition temperature T_g , depending on the phase miscibility of the cyclic and backbone components. For example, polystyrene rotaxanes containing immiscible crown ethers exhibit two glass transition temperatures, one for the polystyrene backbone and one at lower temperature near that of the pure crown ether,¹⁶ though some phase mixing does occur.¹⁷ Polyurethane-crown ether rotaxanes in which both components are miscible possess a depressed single T_g which is the weight average of the two components.¹¹ This suggests that by judicious choice of a macrocycle, it should be possible to control the glass transition temperature of a polymer by threading the macrocycle onto it.

1.4.3 Phase transitions

When the content of macrocycle in the polyrotaxane is sufficient, the cyclic component can crystallize independently. This results from the aggregation of the threaded macrocycles which are not covalently bonded to the backbone and can potentially move along the chain. For example, poly(alkylene sebacate)-crown ether rotaxanes exhibit two crystalline melting points: one associated with the polyester backbone and the other with the crown ether component.¹⁰

In polyamide-crown ether rotaxanes **1.16**, upon heating the solid samples an irreversible exothermic transition is observed by DSC. This transition is attributed to a solid state rearrangement which destroys intraannular hydrogen bonds between the crown ethers and the amide NH and creates the stronger, more stable, intermolecular amide-amide hydrogen bonds.^{14,15}

²⁰ Gibson, H. W.; Liu, S.; Shen, Y. X.; Bheda, M. C.; Lee, S. H.; Wang, F. in *Molecular Engineering for Advanced Materials*, Becher, J.; Schaumburg, R. eds., Kluwer Academic Publishers, Dordrecht, The Netherlands, 1995, pp. 41-58.

Chapter 2

Research Objectives and Scope

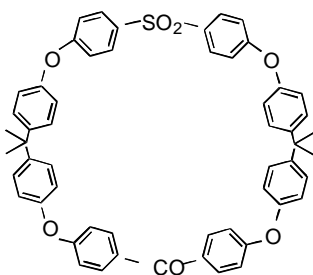
The objectives of this research are syntheses of novel polyrotaxanes based on high performance polymers. Chapter 3 describes attempted syntheses of main chain polyrotaxanes with aromatic macrocycles as cyclic components. This chapter also includes syntheses of blocking groups which were used to prevent dethreading of the rigid aromatic macrocycle. Chapter 4 describes syntheses of polyrotaxanes with crown ethers as cyclic components. These include main chain poly(arylene ether) rotaxanes and hyperbranched poly(ether ether ketone) rotaxanes. HPLC analyses of various crown ethers are also described therein.

Chapter 3

Attempted Synthesis of Polyrotaxanes: Aromatic Macrocycles as Cyclic Components

3.1 Introduction

As seen in Chapter 1, crown ethers and cyclodextrins were two major cyclics used in polyrotaxane studies. Gibson's group has made significant contributions to the development of polyrotaxanes based on crown ethers.¹ It has been shown that threading of crown ethers onto a polymer backbone leads to changes in physical properties of the polymer, such as increasing the solubility and lowering the glass transition temperature. So far, aromatic macrocycles, such as those indicated in Part I, have not been used in polyrotaxane syntheses. These rigid aromatic macrocycles are highly thermally stable and have relatively open cavities, compared to aliphatic crown ether macrocycles. Polyrotaxanes with these aromatic macrocycles as cyclic components would surely increase the thermal stability of the polymer backbone and probably in many cases T_g . More interestingly, ring opening polymerization of the cyclic components in the polyrotaxane would possibly yield a composite material with desirable properties. In this chapter, syntheses of polyrotaxanes in the presence of arylene ether ketosulfone macrocycle **3.1** were attempted. Since the macrocycle is rigid, a blocking group may be necessary to prevent its dethreading from a polymer backbone. In section **3.2.1**, the synthesis of blocking groups is described. Section **3.2.2** describes the synthesis of a low molar mass arylene ether sulfone rotaxane, while section **3.2.3** describes the synthesis of a high molar mass polyurethane rotaxane.



3.1 (or **4.11** in Part I)

3.2 Results and Discussion

3.2.1 Synthesis of Blocking Groups

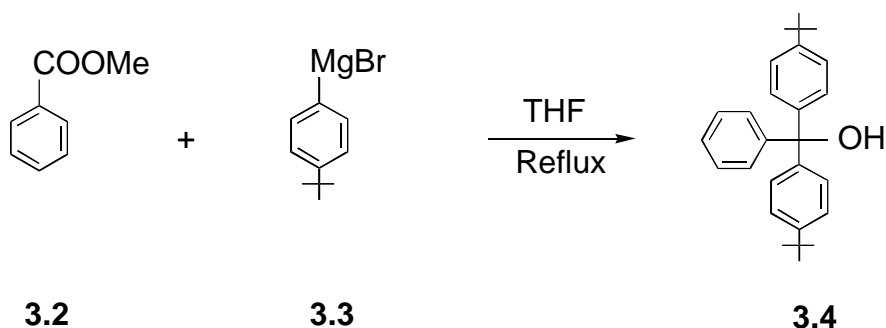
The function of blocking groups in the molecular structure of rotaxanes is to prevent cyclic components from dethreading from the linear components. In some cases where there are strong attractive interactions, such as hydrogen bonding or complexation between cyclic and linear components, the blocking group is not necessary to obtain stable rotaxanes. In other cases

¹ See refs. 1, 9-11, 13-18, and 20 in Chapter 1.

where there is no strong attractive interactions which can bind the cyclic and linear components, the blocking group might be necessary, especially when the cyclic and/or linear components are rigid. Our proposed polyrotaxanes belong to the latter case, where the cyclic component is a rigid arylene ether ketosulfone macrocycle **3.1** and the linear backbone is poly(arylene ether).

The most important thing to be considered in the design of blocking groups is their sizes, which have to be bigger than the cavities of the macrocycles to be blocked. The size of a blocking group required to block a specific macrocycle can be simply examined with a CPK molecular model. Based on CPK molecular modeling, the bis(*p*-tertbutylphenyl)phenylmethyl group is large enough to completely block macrocycle **3.1**.

Scheme 3.1



Synthesis of the bis(*p*-tertbutylphenyl)phenylmethyl blocking group started with the Grignard reaction between methyl benzoate **3.2** and the Grignard reagent **3.3** derived from *p*-tertbutylbromobenzene in refluxing THF (Scheme 3.1). Bis(*p*-tert-butylphenyl)phenylmethanol **3.4** was thus obtained in 56% yield after purification. This compound softens at about 50°C and viscously melts at about 64°C. The melting point is significantly lower than the reported melting point 111-112°C.² In the ¹H NMR spectrum (Figure 3.1) it is found that the chemical shifts at 2.75 ppm corresponding to the hydroxy proton and at 1.31 ppm corresponding to the methyl proton also disagree with the reported ones which are 2.98 and 1.27 ppm, respectively.² The reported ¹H NMR data, however, are found to be similar to those of pinacol, 1,2-dihydroxy-1,2-diphenyl-1,2-di(*p*-*t*-butylphenyl)ethane **3.5**, a side product obtained in our synthesis. This side product was presumably formed by radical coupling via the Gomberg-Bachmann mechanism.³ Since it has three stereoisomers, the methyl protons appear as two singlets in the ¹H NMR spectrum (Figure 3.2), due to different chemical and physical properties of diastereomers. Such an ¹H NMR pattern was reported in an intended synthesis of **3.5** by photoreduction of 4-tert-butylbenzophenone in the presence of 2-propanol.⁴ No melting point was indicated by this report.

² Gibson, H. W.; Lee, S.-H.; Engen, P. T.; Lecavalier, P.; Sze, J.; Shen, Y. X.; Bheda, M. *J. Org. Chem.* **1993**, *58*, 3748.

³ Bachmann, W.E.; Shankland, R. V. *J. Am. Chem. Soc.* **1929**, *51*, 306. Gomberg, M.; Van Natta, F. J. *J. Am. Chem. Soc.* **1929**, *51*, 2238.

⁴ Naguib, Y. M. A.; Steel, C.; Cohen, S. C. *J. Phys. Chem.* **1988**, *92*, 6574-6579.

By repetitive recrystallization in petroleum ethers, one of the diastereomers, maybe the *meso* compound, or the D,L pair of enantiomers, was isolated, and its ^1H NMR shows a single peak at 1.27 ppm (Figure 3.3), similar to that claimed in the literature.² However, neither the melting point of the diastereomeric mixture of the pinacol, 182.9-184.2°C, nor the melting point of the *meso* compound or the D,L pair of enantiomers, 173.2-174.7°C, is close to 111-112°C, reported in the literature for **3.4**.²

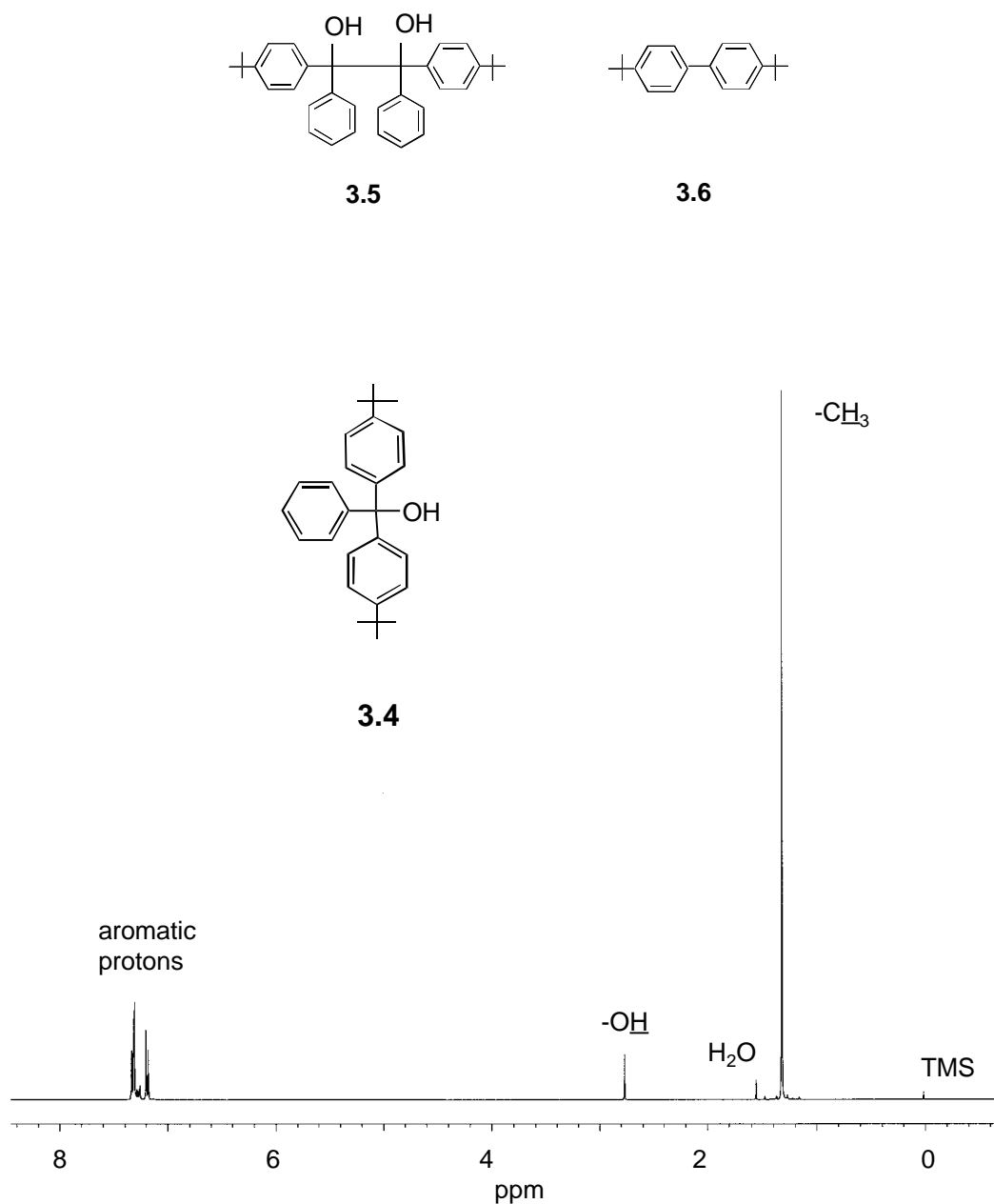


Figure 3.1 400 MHz ^1H NMR spectrum of compound **3.4** in CDCl_3

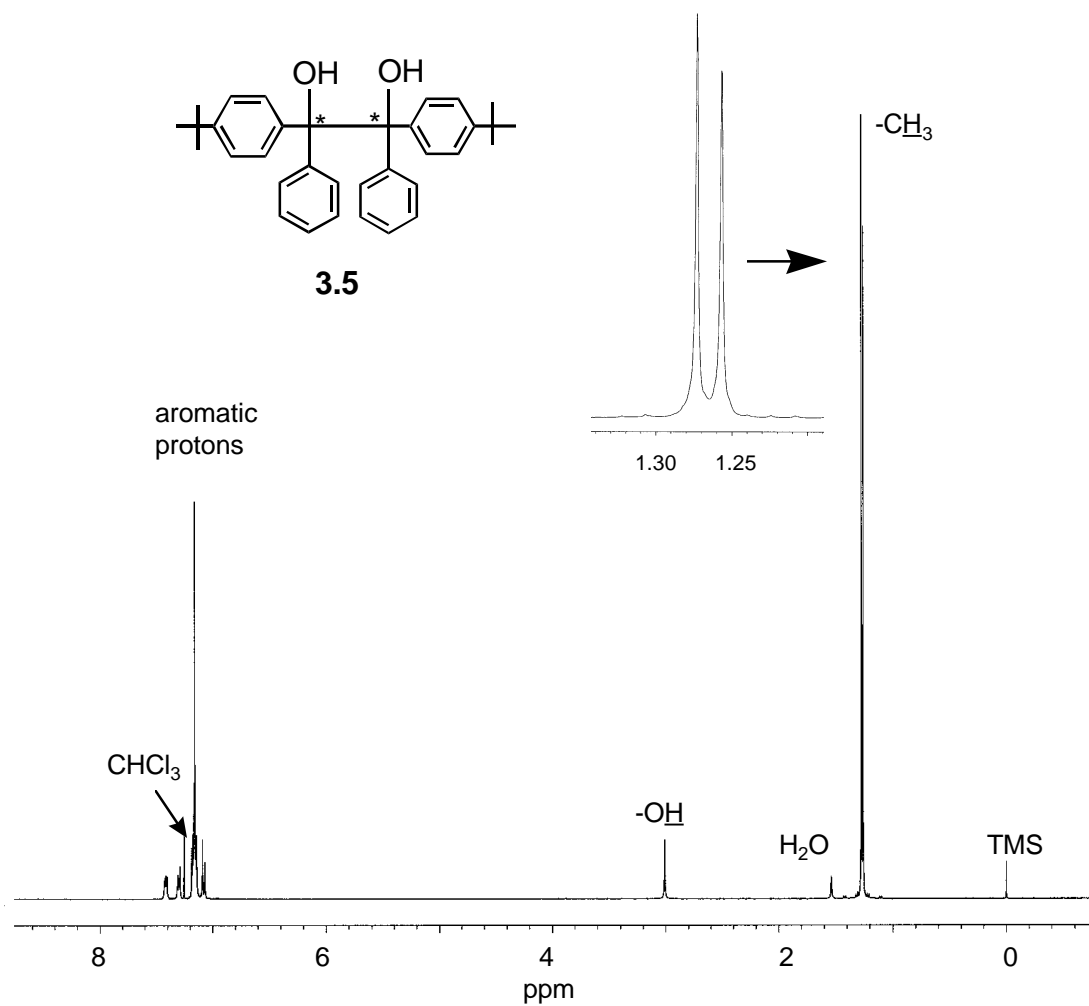


Figure 3.2 400 MHz ¹H NMR spectrum of diastereomers **3.5** in CDCl₃

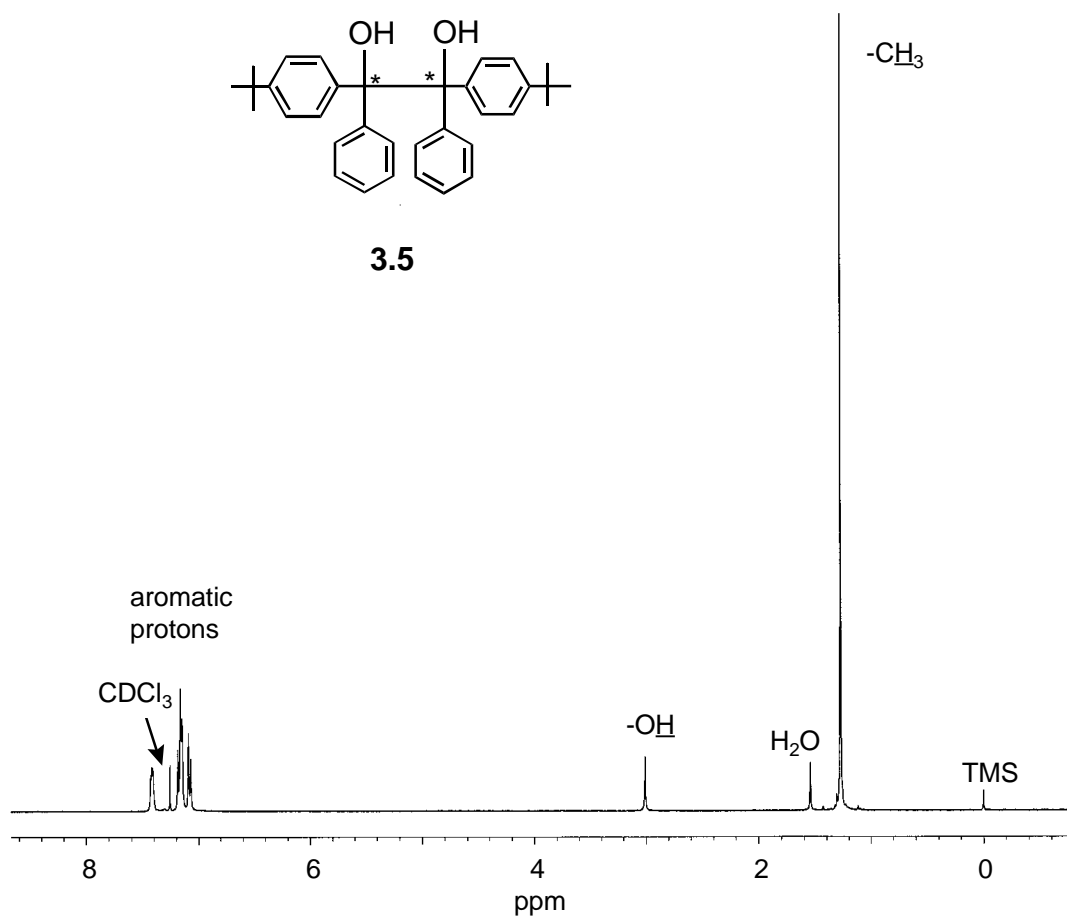


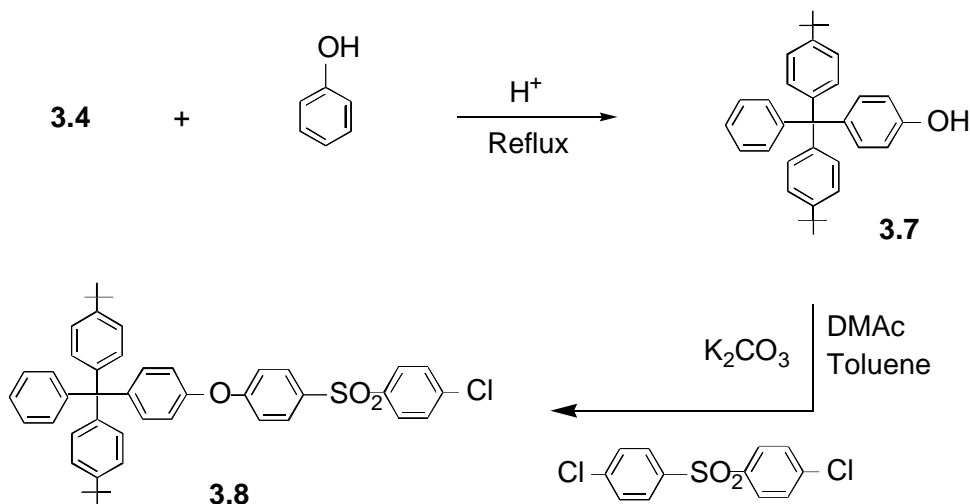
Figure 3.3 400 MHz ¹H NMR spectrum of a meso compound **3.5** or the D,L pair of enantiomers **3.5** in CDCl₃

It should be pointed out that the addition of iodine to induce the Grignard reaction in the synthesis of **3.4** gave much lower yield (37%). This is because iodine can accelerate the formation of radicals which couple to form the pinacol byproduct.³ Another major byproduct is 4,4'-di-*t*-butylbiphenyl **3.6** which is also a coupling product.

The triarylmethanol **3.4** cannot be directly used to end-cap the oligomeric bisphenol **3.13** in the synthesis of low molar mass rotaxanes (see Section **3.2.2**) because it is an alcohol, obviously unreactive towards the bisphenol. Therefore, it is necessary to attach a reactive functional group to it. To avoid the triaryl ether linkages which are hydrolytically unstable, instead of converting **3.4** to the triarylmethyl chloride, the hydroxyl component was reacted with

phenol to form **3.7** which was then reacted with 4,4'-dichlorodiphenyl sulfone to form a monochlorosulfone functionalized compound **3.8** (Scheme 3.2).

Scheme 3.2

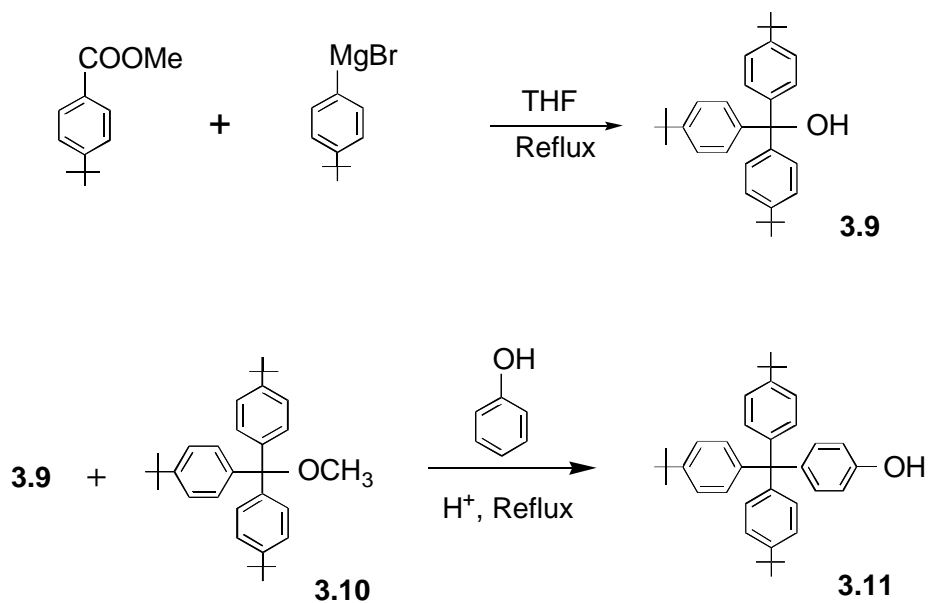


The formation of bis (*p*-*tert*-butylphenyl)phenyl(4-hydroxyphenyl)methane **3.7** was accomplished in 70% yield by direct reaction of **3.4** with phenol under acidic conditions. Phenol was also used as solvent in the reaction. This aromatic electrophilic substitution reaction is a Friedel-Crafts type reaction with the use of a catalyst (HCl). The carbocation formed by the acid catalyzed ionization of **3.4** attacks the para-position of phenol to form the desired compound (**3.7**). The product was purified by multiple washings with aqueous sodium hydroxide (5%) in toluene to remove phenol and then boiling in hexanes twice. The melting point of the purified product was 211.1-212.2°C, close to the reported 210.0-210.9°C.²

The chlorophenyl sulfone functionalized blocking group **3.8** was formed by the reaction of **3.7** with excess 4,4'-dichlorodiphenyl sulfone (DCDPS) in the presence of K_2CO_3 (Scheme 3.2). This is an aromatic nucleophilic substitution reaction. Toluene was used to azeotrope water generated in the formation of the reactive nucleophile, the phenolate anion. The yield of compound **3.8** was 64% after purification.

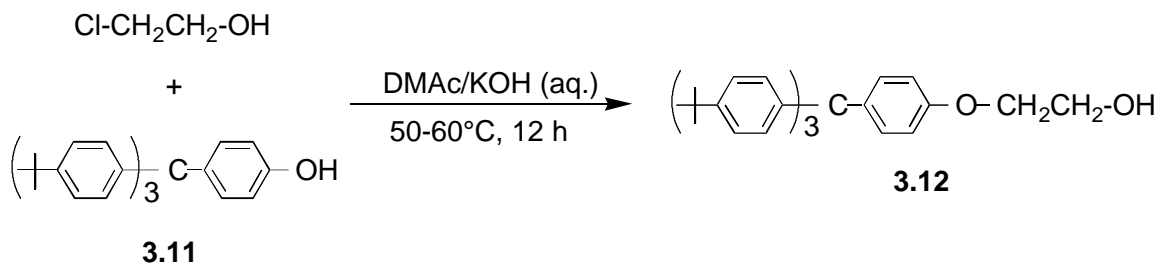
Similarly, phenol-functionalized tris(*p*-*t*-butylphenyl)methyl blocking group **3.11** was synthesized (Scheme 3.3) in 85% yield, according to the reported procedure.² This compound has an additional *t*-butyl group, and was relatively easy to prepare. Compound **3.10** was accidentally obtained during purification by boiling in methanol, but that had no influence on the next electrophilic substitution reaction to form **3.11**.

Scheme 3.3



An alcohol functionalized blocking group **3.12** was synthesized by reaction between **3.11** and 2-chloroethanol in DMAc using KOH (aq.) as base (Scheme 3.4). The yield was 40%. This blocking group was used in the polyurethane rotaxane synthesis (See section 3.2.3).

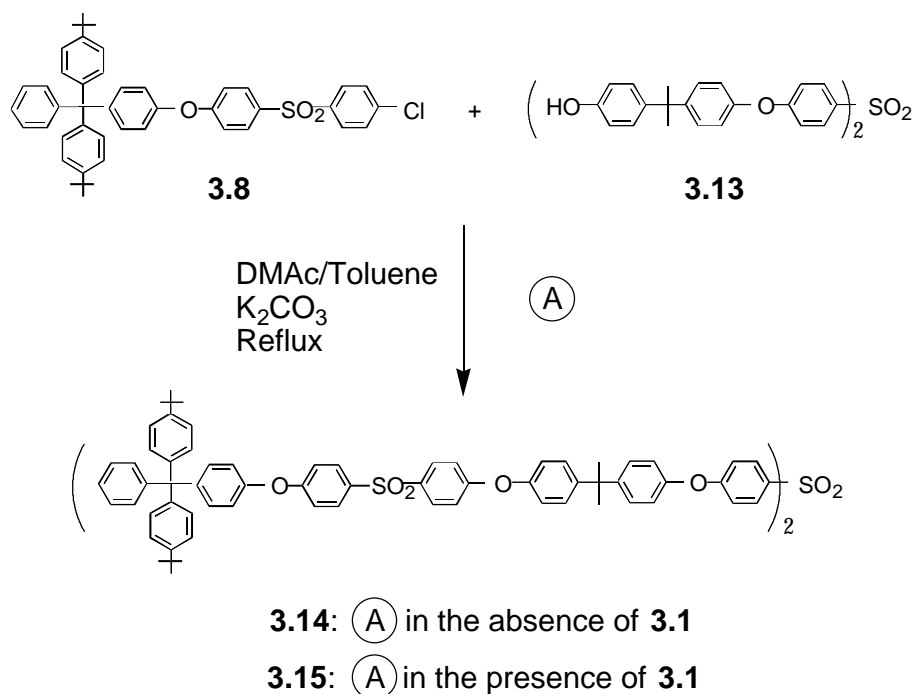
Scheme 3.4



3.2.2 Attempted Synthesis of Low Molar Mass Arylene Ether Rotaxane

In this study, bisphenol-A based oligomeric arylene ether sulfone bisphenol **3.13** was used as the linear component for the rotaxane, whereas 40-membered ketosulfone macrocycle **3.1** was used as the cyclic component (Scheme 3.5). Chlorophenyl sulfone functionalized triaryl blocking group **3.8**, which is big enough to prevent dethreading of the macrocycle according to a CPK model, was used to end-cap the bisphenol

Scheme 3.5



The synthesis was first conducted without addition of the macrocycle. This was to obtain the triaryl end-capped compound for comparison with the corresponding rotaxane later on. In this synthesis, the blocking group **3.8** was used in 50% excess to ensure complete end capping. Compound **3.14** was produced in 57% yield through the aromatic nucleophilic substitution reaction. The low yield is due to the loss of the compound during purification. The ^1H NMR spectrum of the product is given in Figure 3.4 where integral ratios match the chemical structure of **3.14**.

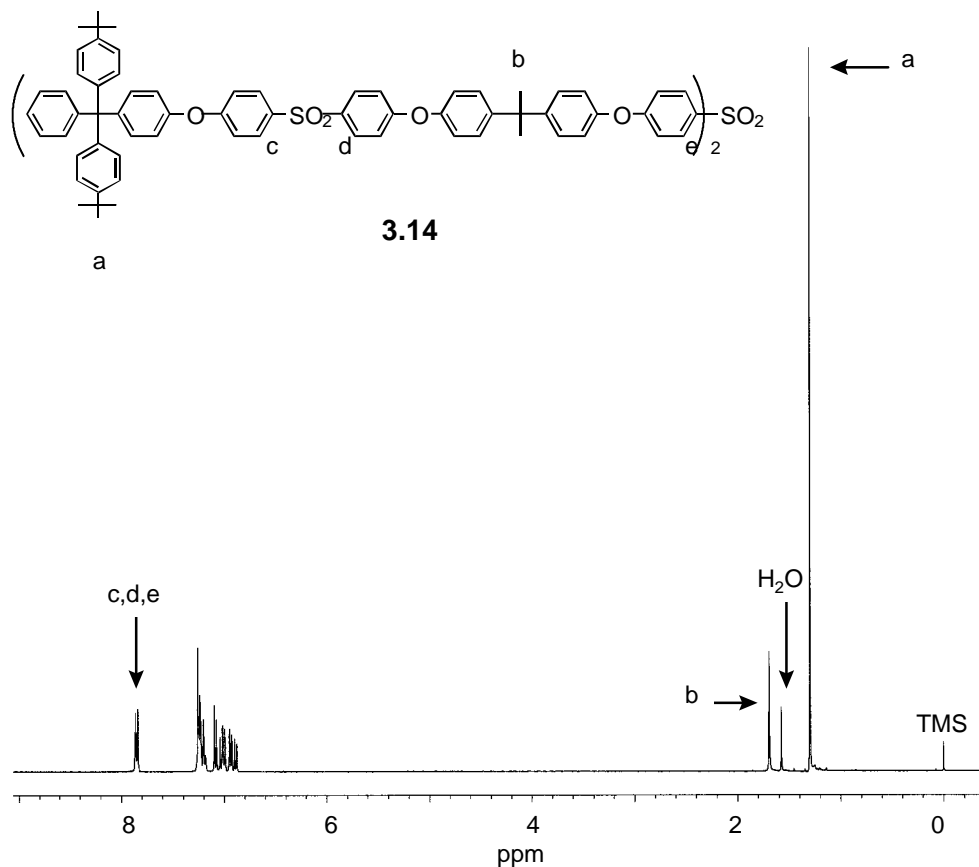


Figure 3.4 400 MHz ^1H NMR spectrum of end-capped oligomeric arylene ether sulfone **3.14** in CDCl_3

The rotaxane synthesis (**3.15**) was attempted in the presence of macrocycle **3.1** (Scheme 3.5). First of all, the macrocycle (**3.1**, 5 mmol) and the linear molecule (**3.13**, 1 mmol) were mixed in DMAc (15 mL); the solution was refluxed under stirring for 14 hours for pre-threading. It was observed that the solution became a little more viscous than at the beginning. No ring-opening of the macrocycle was observed after 14 hours' stirring at the reflux temperature according to TLC. Enough toluene and excess K_2CO_3 were subsequently added to deprotonate the bisphenol. After addition of the chlorosulfone blocking group **3.8** (50% excess), the reaction was carried out for 15 hours at 165°C under nitrogen. According to TLC, the crude product contained four major components: the blocking group (**3.8**), the linear end capped compound (**3.14**), the macrocycle (**3.1**) and unknown products which did not move on the TLC plate. The unknowns may be a mixture of oligomeric rotaxanes. Column chromatography, using chloroform

as eluent, isolated one of the unknowns in 69% yield. As indicated in the ^1H NMR spectrum (Figure 3.5), the pure unknown gives a doublet at 7.78 ppm corresponding to the aromatic protons ortho to the ketone group which does not appear in the spectrum of **3.14** (Figure 3.4). In the ^{13}C NMR spectrum (Figure 3.6) a carbonyl carbon is also observed at 194 ppm. This is kind of encouraging because only the macrocycle contains the ketone group. The more impressive thing is that when compared to the ^1H NMR spectrum of a physical mixture of macrocycle **3.1** and end-capped linear backbone **3.14** (Figure 3.7), it was found that the ortho-to-carbonyl proton in the unknown is shifted downfield by 0.01 ppm from 7.77 ppm in the physical mixture and that the original single isopropylidene proton peak at 1.69 ppm in the physical mixture splits into two singlets in the unknown, appearing at 1.69 and 1.70 ppm respectively. The downfield shift and the splitting might have resulted from the interactions between the threaded macrocycle and the linear component.

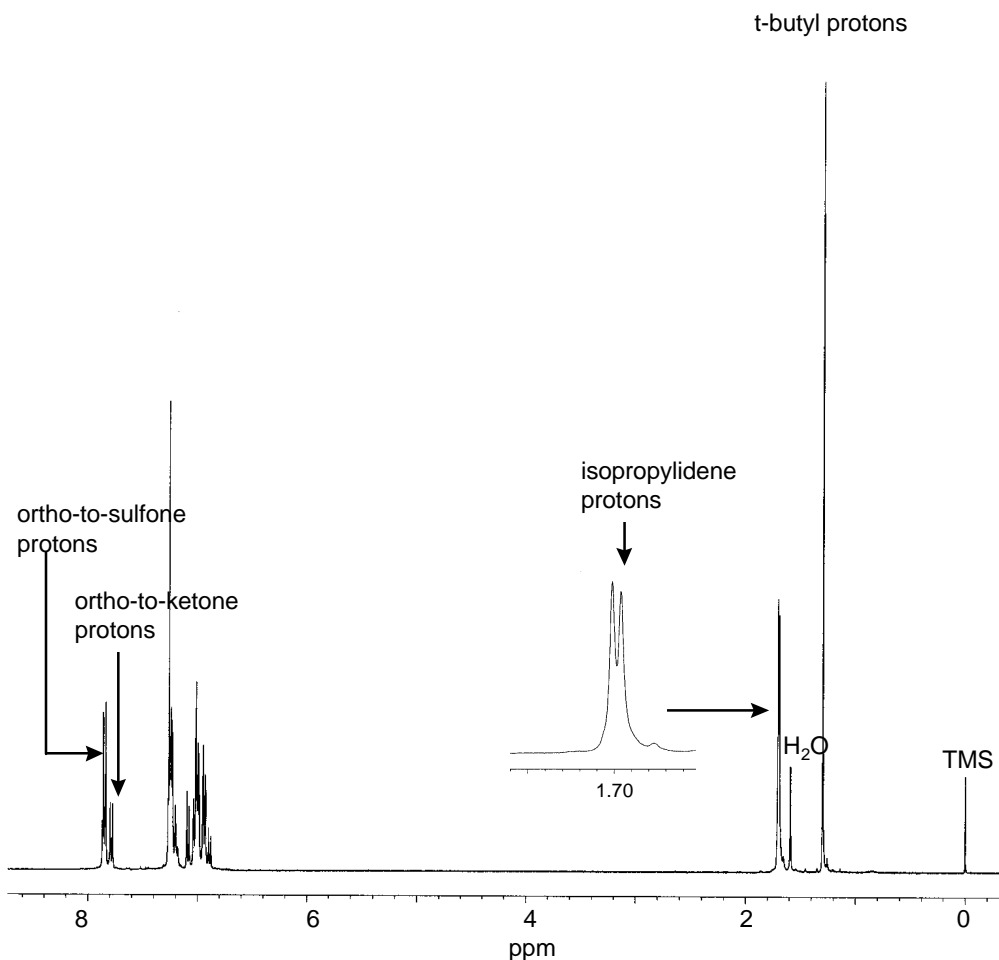


Figure 3.5 400 MHz ^1H NMR spectrum of low molar mass “rotaxane” **3.15** in CDCl_3 . The ortho-to-ketone proton comes from the ketone macrocycle (**3.1**)

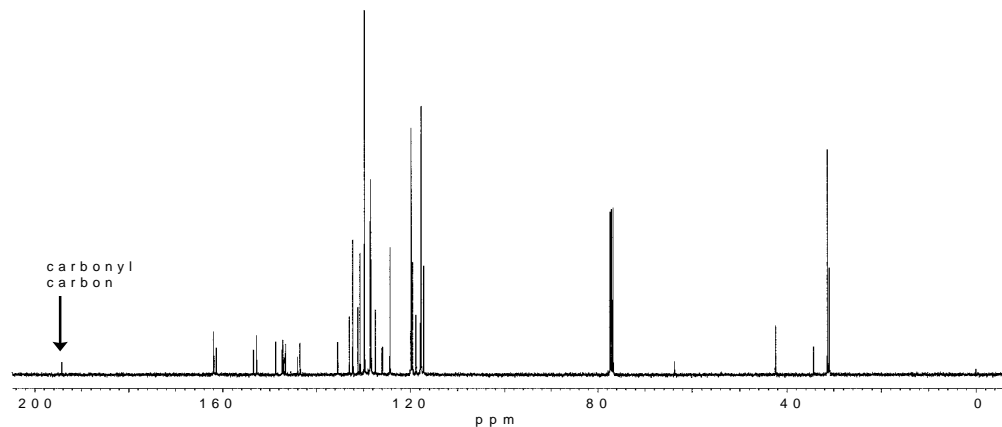


Figure 3.6 100 MHz ^{13}C NMR spectrum of low molar mass “rotaxane” **3.15** in CDCl_3 . The carbonyl carbon comes from the ketone macrocycle (**3.1**).

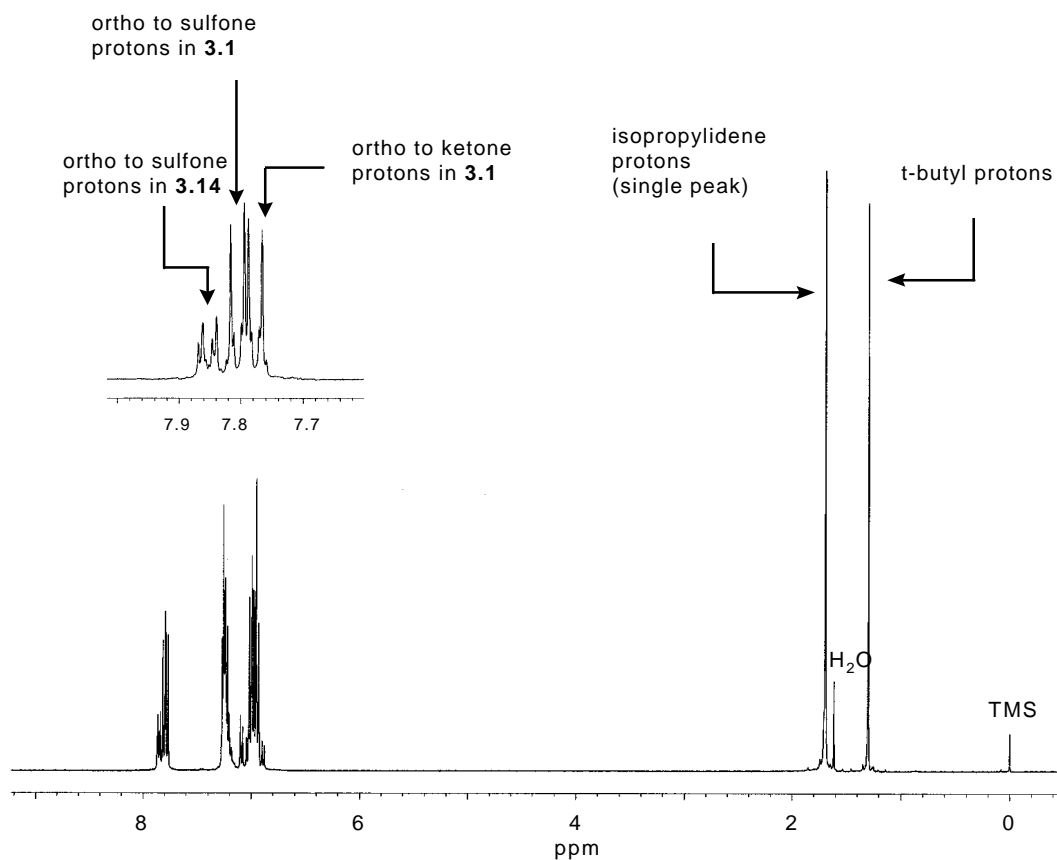


Figure 3.7 400 MHz ^1H NMR spectrum of the physical mixture of macrocycle **3.1** and the end-capped oligomer **3.14** in CDCl_3 .

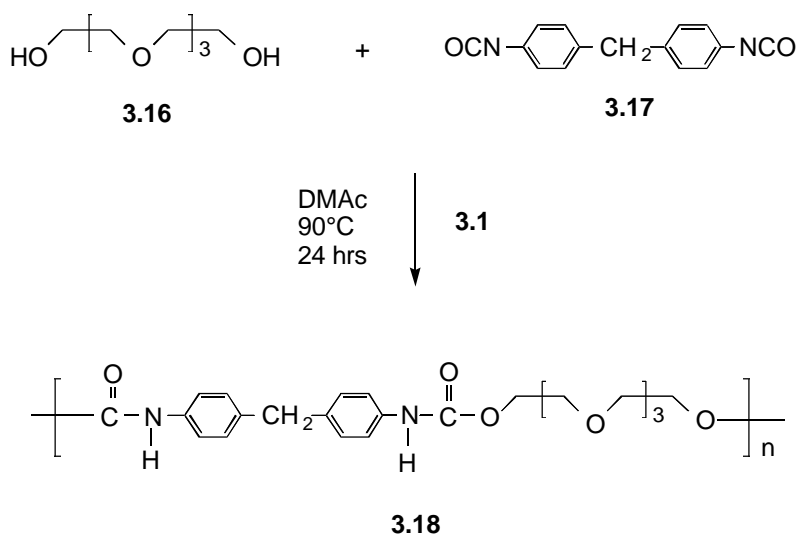
Assuming that the unknown molecule is completely capped at both ends by the blocking group, the number of the macrocycles per unknown molecule was estimated to be 3, based on either the integral ratio of the total isopropylidene protons at 1.70 ppm to the total *t*-butyl protons at 1.30 ppm, or the integral ratio of the total aromatic protons ortho to sulfone and ketone groups at 7.77-7.87 ppm to the *t*-butyl protons. Considering the fact that there is no strong attractive interaction between the linear component and the cyclic component, it is quite unlikely that three macrocycles could be threaded onto the linear molecule (**3.13**) and then blocked by the end capper. In a model study where **3.1** and **3.13** were refluxed at 165°C in DMAc/toluene in the presence of K₂CO₃, the macrocycle was found to decompose according to TLC since there were lots of new spots observed. Thus it is probable that some macrocycle was ring opened and incorporated into the linear backbone, giving a high threading number. The changes of chemical shifts most likely resulted from the ring opening; in the polymer obtained from the ring opening polymerization of the macrocycle, the proton ortho to the ketone group gives a doublet at 7.78 ppm, similar to that of the above unknown. Therefore, it can not be concluded that a rotaxane was obtained from this synthesis.

The ring cleavage problem under the above reaction conditions prompted us to look for other reaction systems under which the macrocycle will not undergo such reaction. The polyurethane system was thus selected. The following section describes the attempted synthesis of a polyurethane based rotaxane in the presence of macrocycle **3.1**.

3.2.3 Attempted Synthesis of Polyurethane Rotaxane

The polyurethane backbone selected is the one derived from tetra(ethylene glycol) (**3.16**) and bis(*p*-isocyanatophenyl) methane (MDI) (**3.17**) structural units. The polyrotaxane synthesis was conducted by reacting **3.16** with **3.17** in the presence of macrocycle **3.1** (Scheme 3.6).

Scheme 3.6



In this synthesis, the feed ratio of the macrocycle to the monomer was 2 (molar ratio). A minimum amount of N,N-dimethylacetamide (DMAc) (25 mL) was added to dissolve the macrocycle (6 mmol). Initially, no blocking group was added, since we believed that the hydrogen bonding between the polyurethane backbone and the macrocycle would serve as an anchor to prevent the macrocycle from dethreading from the linear backbone, just as in the synthesis of polyurethane rotaxanes using crown ethers as the cyclic component.⁵ After reaction, the product was purified by reprecipitation into toluene from THF solution by which the free macrocycle was removed. According to the ¹H NMR spectrum (Figure 3.8), however, no rotaxane was obtained. Probably, the anchor effect of the hydrogen bonding between the macrocycle and the linear backbone was not effective owing to the weak electron-donating character of the aromatic ether oxygen in the macrocycle so that the dethreading of macrocycle could take place during the reaction and/or purification stages. Besides, compared to the crown ether-polyurethane rotaxane synthesis in which no solvent was added except crown ethers, the concentration of macrocycle **3.1** in this synthesis was much lower because a solvent was used to dissolve the macrocycle. The low cyclic concentration will decrease the threading efficiency.

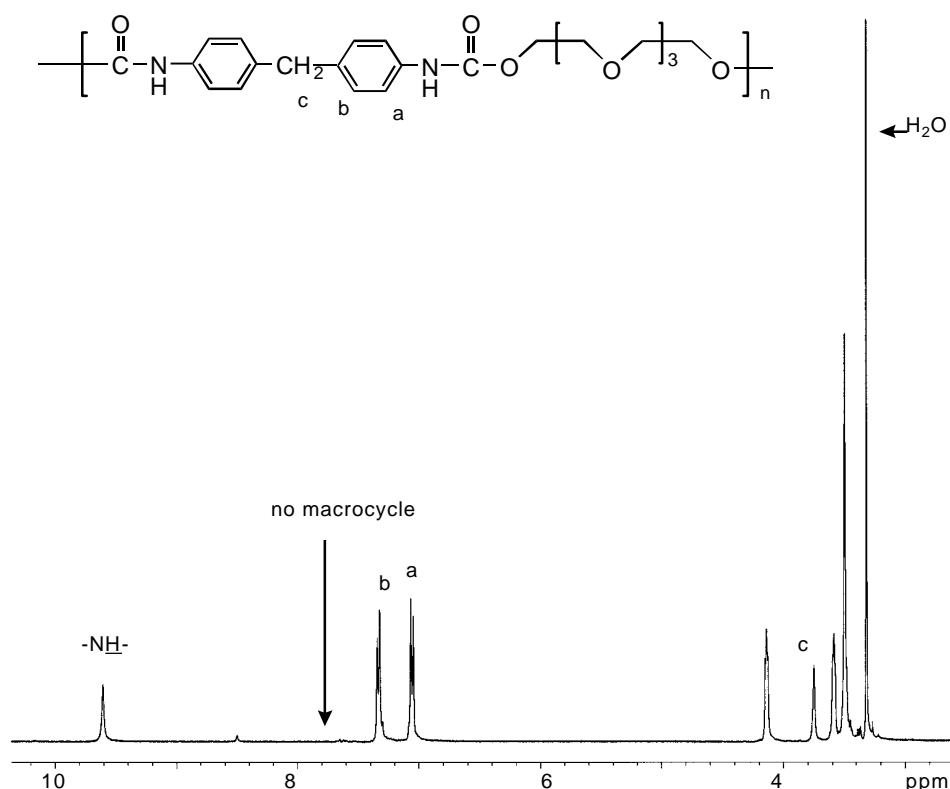


Figure 3.8 400 MHz ¹H NMR spectrum (in DMSO-d₆) of polyurethane **3.18** synthesized in the presence of macrocycle **3.1**.

⁵ See ref. 11 in Chapter 1.

To prevent dethreading of the macrocycle, the synthesis was then carried out with the addition of a blocking group reagent. In this synthesis, mono-alcoholic triaryl compound **3.12** was used as the blocking group. The amount of this compound was adjusted so that the molecular weight of polyurethane backbone would be 10 K. The reaction conditions were the same as that in the above synthesis. However, no rotaxanes were obtained either, although the blocking group had been attached to the polymer backbone, according to the proton NMR spectrum (Figure 3.9). From the NMR spectrum the molecular weight (M_n) of the polymer was estimated to be 8 K. Perhaps, low cyclic concentration is the major factor for the zero threading.

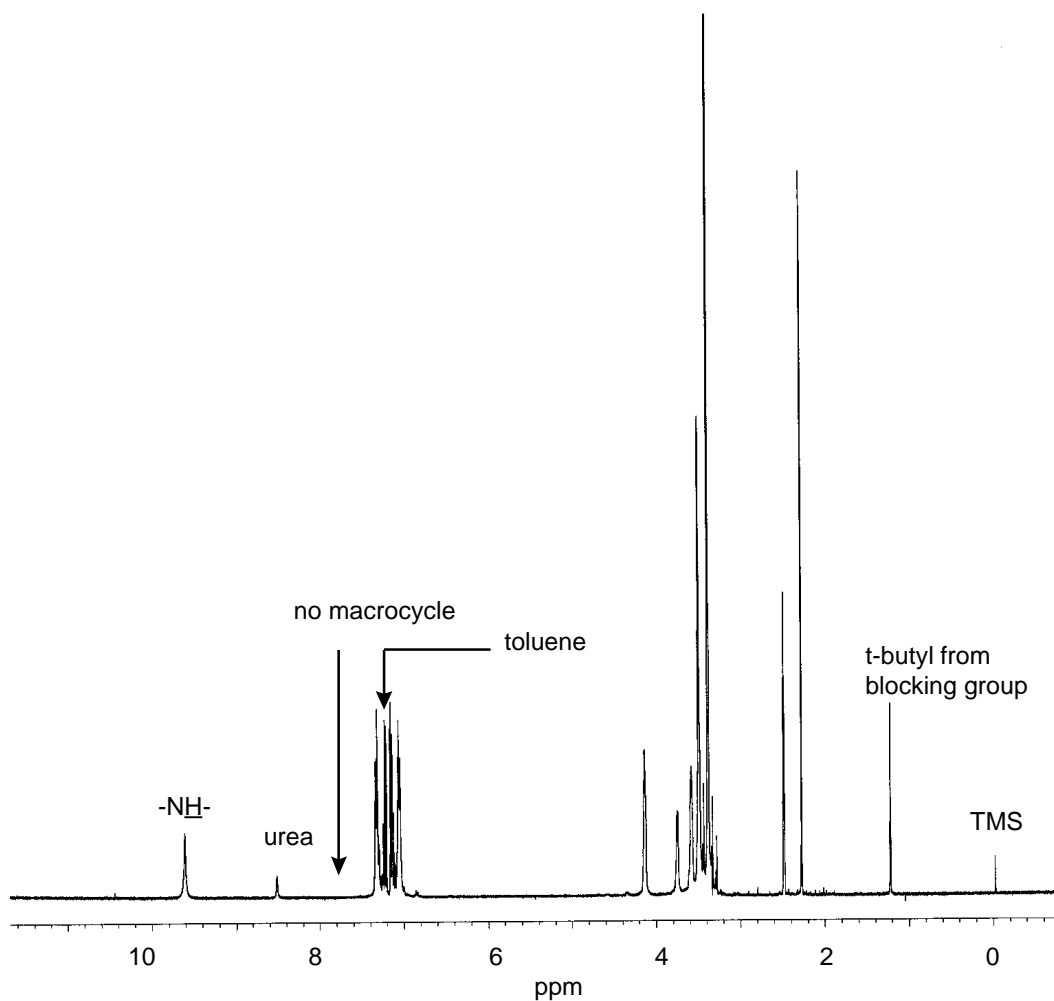


Figure 3.9 400 MHz ^1H NMR spectrum (in DMSO-d_6) of end-blocked polyurethane **3.18** synthesized in the presence of macrocycle **3.1** and blocking group **3.12**.

3.3 Conclusions and Suggestions

The syntheses of polyrotaxanes in the presence of an arylene ether macrocycle (**3.1**) were not successful. In the low molar mass arylene ether sulfone rotaxane synthesis, it was difficult to determine whether or not the macrocycle was threaded onto the linear backbone, since the macrocycle underwent the ring cleavage reaction under the reaction conditions and it is probable that the ring opened macrocycle was incorporated into the backbone.

In the polyurethane rotaxane synthesis under whose conditions the macrocycle is stable, no threading was found even though blocking groups were attached to the polymer backbone. The reasons for this are probably low concentrations of macrocycle in the synthesis and lack of strong interactions between the linear component and the cyclic component.

From both polyrotaxane syntheses, especially the polyurethane rotaxane syntheses, it would be suggested that in the future an aromatic macrocycle having good solubility and/or special moieties which can have some specific interactions with a chosen linear backbone should be used to drive threading.

3.4 Experimental

Materials and Measurements

THF was distilled from the purple solution of benzophenone/Na. MDI and tetra(ethylene glycol) were purified by vacuum distillation twice. Other reactants and solvents were used as received from chemical suppliers. Melting points were taken in capillary tubes with a Melt-Temp II melting point apparatus and have been corrected. ¹H NMR spectra were obtained at ambient temperature on a Bruker WP 270-MHz and a Varian 400 MHz spectrometer in deuterated dimethyl sulfoxide and chloroform with TMS as the internal standard. ¹³C NMR spectra were obtained at ambient temperature on a Varian 100 MHz spectrometer in deuterated chloroform with TMS as the internal standard.

Bis(*p*-*t*-butylphenyl)phenylmethanol (**3.4**)

Into an oven-dried 1 L three-necked round bottom flask equipped with a condenser, dropping funnels, a mechanical stirrer and a nitrogen bubbler were placed magnesium turnings (6.1 g, 0.25 mol) with dry THF (400 mL). *p*-*t*-Butylbromobenzene (**3.3**) (50 g, 0.24 mol) in dry THF (100 mL) was added dropwise over about one hour with heating; when the reaction started the heat was removed. The reaction was allowed to go for two hours and a black-gray color was observed. Methyl benzoate (**3.2**) (15 g, 0.11 mol) in dry THF (50 mL) was added dropwise over one hour without heating. The mixture was then stirred for 12 hours at reflux under nitrogen, with the appearance of a brown color. The mixture was cooled to room temperature and neutralized by pouring into 1 L cool aqueous HCl solution (5%). Product was extracted with hexanes (2 x 500 mL). The combined organic phase was washed with water (3 x 300 mL), followed by drying (Na₂SO₄). Evaporation of solvent gave an amber-colored semi-solid. Most of pure byproduct **3.5** was removed by recrystallization of the crude product in petroleum ethers. A mixture (29 g, 70%) of the desired compound (**3.4**) and another byproduct (**3.6**) was obtained

by 3-4 recrystallizations in MeOH, each time reducing the amount of MeOH. Freezing and seeding (or agitating) the solution during recrystallizations were necessary to obtain as much product as possible. The mixture was then subjected to flash column chromatography using hexanes as eluent to isolate the desired compound **3.4**. Recrystallization again in MeOH provided white crystals. Yield: 23.2 g (56%); mp: 50°C (soften), 64°C (viscous melt) (lit² mp 111-112°C). ¹H NMR (CDCl₃) δ 1.31 (s, 18 H, -CH₃), 2.75 (s, 1 H, -OH), 7.16-7.32 (m, 13 H, arom.); ¹³C NMR (CDCl₃) δ 31.34, 34.44, 81.67, 124.76, 126.99, 127.58, 127.77, 127.85, 144.01, 147.14, 149.95.

Yield of **3.5**: 25 mol% in the crude product by ¹H NMR; the mixture of diastereomers: mp 182.9-184.2°C, ¹H NMR (CDCl₃) δ 1.27 (d, 18 H), 2.98 (s, 2 H), 7.08 (d, J=8.8 Hz, 2 H), 7.14-7.18 (m, 12 H), 7.29-7.31 (m, 2 H), 7.40-7.42 (m, 2 H); the meso or D,L pair of enantiomers: 173.2-174.7°C, ¹H NMR (CDCl₃) δ 1.27 (s, 18 H), 2.98 (s, 2 H), 7.08 (d, J=8.8 Hz, 4 H), 7.14-7.18 (m, 10 H), 7.40-7.43 (m, 4 H).

Bis(*p*-*tert*-butylphenyl)phenyl(4-hydroxyphenyl)methane (3.7)

Into a 250 mL one-necked round bottom flask equipped with a magnetic stirrer and condenser were placed **3.4** (15.0 g, 39.8 mmol) and phenol (50.0 g, 13.3 eq.). The flask was warmed in an oil bath to dissolve the starting materials, yielding a brown solution. HCl (37%, 1 mL) was added to initiate the Friedel-Crafts reaction. A deep reddish brown color was observed immediately. The mixture was heated at reflux for 24 hours under nitrogen. Before it could solidify, the liquid mixture was poured into aqueous NaOH (5%, 500 mL), and the product was extracted with toluene (3 x 200 mL). The combined organic phase was washed with 5% aqueous NaOH (6 x 200 mL) followed by water (6 x 200 mL) and dried (Na₂SO₄) after decolorization with activated carbon. Evaporation of solvent yielded a light brown oil. Pale yellow solid product was obtained after the oil was boiled in hexanes twice. Yield: 12.5 g (70%); mp: 211.1-212.2°C (lit.² mp 210.0-210.9°C): ¹H NMR (DMSO-d₆) δ 1.25 (s, 18 H, -CH₃), 6.66 (d, J=8.8 Hz, 2 H), 6.91 (d, J=8.8 Hz, 2 H), 7.06 (d, J=8.8 Hz, 4 H), 7.12-7.26 (m, 5 H), 7.29 (d, J=8.8 Hz, 4 H), 9.38 (s, 1 H, -OH).

4-Chlorophenyl-4'-{*p*-[bis(*p*'-*t*-butylphenyl)phenyl]methyl}phenoxyphenyl sulfone (3.8)

Into a 1 L three-necked round bottom flask equipped with a mechanical stirrer, a Dean-Stark trap along with a condenser and a nitrogen bubbler were placed **3.7** (11.0 g, 24.5 mmol), DMAc (400 mL), toluene (220 mL), and K₂CO₃ (5.0 g, 36.8 mmol). The mixture was then heated at reflux (about 130°C) for 5 hours. Water generated in the abstraction of the acidic proton by the base was removed by azeotropic distillation with toluene. 4,4'-Dichlorodiphenyl sulfone (DCDPS) (28.1 g, 98 mmol) was added after toluene was distilled. The substitution reaction was allowed to proceed for 20 hours at reflux (about 166°C) under the nitrogen atmosphere. Upon cooling, salts (KCl, K₂CO₃) were filtered and solvent was rotary evaporated, yielding a brown oil. The product was purified by fractional reprecipitation in MeOH from chloroform (20 mL). After removal of MeOH, a white solid was obtained. Yield: 11.0 g (64%); mp: 185-187°C; ¹H NMR (DMSO-d₆) δ 1.25 (s, 18 H, -CH₃), 7.03-7.32 (m, 19 H), 7.69 (d, 2 H,

$J=8.8$ Hz, ortho to Cl), 7.95 (d, 2 H, $J=8.8$ Hz, ortho to SO₂ and meta to Cl), 7.96 (d, 2 H, $J=9.2$ Hz, ortho to SO₂ and meta to O); elemental anal.: calcd for C₄₅H₄₃O₃Cl: C, 77.29; H, 6.20; S, 4.58; Cl, 5.07; found: C, 77.32; H, 6.20, S, 4.53; Cl, 5.12.

Tris(*p*-*t*-butylphenyl)Methanol (3.9)

Into an oven-dried 1 L three-necked round bottom flask equipped with a condenser, dropping funnels, a mechanical stirrer and a nitrogen bubbler were placed magnesium turnings (12.2 g, 500 mmol) with dry THF (400 mL). *p*-*t*-Butylbromobenzene (**3.3**, 100 g, 469 mmol) in dry THF (150 mL) was added dropwise over about two hours with heating; when the reaction started the heat was removed. The reaction was allowed to go for two hours and a black-gray color was observed. Ethyl (*p*-*t*-butyl)benzoate (45.4 g, 220 mmol) in dry THF (100 mL) was added dropwise over one hour without heating. The mixture was then stirred for 12 hours at reflux under nitrogen, with the appearance of a brown color. The mixture was cooled to room temperature and neutralized by pouring into 1 L cool aqueous HCl solution (5%). The obtained greenish solid was then boiled in hexanes (300 mL), yielding an off-white solid. When boiled further in methanol, some product was converted to methyl ether **3.10**. This mixture was used directly in the next reaction without further purification.

Tris(*p*-*t*-butylphenyl)(4-hydroxyphenyl)methane (3.11)

Into a 500 mL one-necked round bottom flask equipped with a magnetic stirrer and condenser were placed the above mixture (20g) and phenol (70 g). Then the same procedure as that in the synthesis of **3.7** was followed. Yield: 13.6 g (85%); mp: 302.7-304.9°C. Recrystallization from a toluene/hexane mixture twice provided white crystals, mp: 311.8-312.4°C (lit.²: 304.0-305.8°C); ¹H NMR (DMSO-*d*₆) δ 1.24 (s, 27 H, -CH₃), 6.64 (d, $J=8.4$ Hz, 2 H), 6.91 (d, $J=8.4$ Hz, 2 H), 7.05 (d, $J=8.4$ Hz, 6 H), 7.26 (d, $J=8.4$ Hz, 6 H), 9.38 (s, 1 H, -OH).

2-[*p*-tris(*p*-*t*-butylphenyl)methylphenoxy]ethanol (3.12)

Tris(*p*-*tert*-butylphenyl)(4-hydroxyphenyl)methane (**3.11**, 5.04 g, 10.0 mmol) was dissolved in DMAc (100 mL). The solution was then heated under nitrogen at 50-60°C. Aqueous KOH (3.6 mL, 3.0 mM) was added and the mixture was magnetically stirred for one hour. After 2-chloroethanol (0.322 g, 40.0 mmol) was added, the substitution reaction was allowed to proceed for 12 hours. Upon cooling, the reaction mixture was precipitated into water (600 mL), yielding a white solid which showed two spots in the TLC plate. The pure compound **3.12** was separated by column chromatography (silica gel, ethyl acetate/hexane, 3/7). Yield: 2.2 g, (40%); mp: 329.2-330.5 °C; ¹H NMR (CDCl₃) δ 1.30 (s, 9 H), 2.00 (t, 1 H), 3.96 (q, 2 H), 4.05 (t, 2 H), 6.78 (d, 2 H, arom.), 7.09 (m, 8 H, arom.), 7.23 (d, 6 H, arom.).

Triaryl end-capped oligomeric arylene ether sulfone (3.14)

Into a 50 mL two-necked round bottom flask equipped with a magnetic stirrer, a Dean-Stark trap along with a condenser and a nitrogen bubbler were placed **3.13** (0.335 g, 0.500 mmol), DMAc (10 mL), toluene (10 mL), and K₂CO₃ (0.14 g, 1.0 mmol). The mixture was then heated at reflux (about 130°C) for 5 hours. Water generated in the abstraction of the acidic proton by

the base was removed by azeotropic distillation with toluene. **3.8** (1.05 g, 1.50 mmol) was added after toluene was distilled. The substitution reaction was allowed to proceed for 20 hours at reflux (about 166°C) under the nitrogen atmosphere. Upon cooling, the mixture was poured into water (300 mL) under stirring to remove DMAc and salts. The filtered product was washed with water/MeOH (50/50) and dried. After column chromatographic separation using chloroform as eluent, a pale yellow solid product was obtained. Yield: 0.57 g (57%); mp: 212-216°C; ¹H NMR (CDCl₃) δ 1.30 (s, 36 H, *t*-butyl), 1.69 (s, 12 H, -CH₃), 6.88-7.10 (m, 34 H), 7.18-7.26 (m, CHCl₃ included), 7.84-7.87 (m, 12 H, ortho to SO₂); elemental anal.: calcd for C₁₃₂H₁₂₂O₁₂S₃: C, 79.41; H, 6.16; S, 4.82; found: C, 79.39, H, 6.13; S, 4.74.

Attempted synthesis of low molar mass arylene ether rotaxane

Into a 50 mL two-necked round bottom flask equipped with a magnetic stirrer, a Dean-Stark trap along with a condenser and a nitrogen bubbler were placed **3.13** (0.671 g, 1 mmol), **3.1** (4.250 g, 5 mmol) and DMAc (15 mL). The mixture was then refluxed for 14 hours. After toluene (12 mL, of which 6.5 mL was in the Dean-Stark trap) and K₂CO₃ (0.28 g, 2.0 mmol) were added, the mixture was refluxed for 8 h. Water generated by the abstraction of the acidic proton by the base was removed by azeotropic distillation with toluene. The blocking group **3.8** (2.10 g, 3.00 mmol) was added after toluene was distilled. The substitution reaction was allowed to proceed for 20 hours at reflux under the nitrogen atmosphere. Upon cooling, the mixture was poured into water (500 mL) under stirring to remove DMAc and salts. The filtered product was washed with water/MeOH (50/50) and dried. Column chromatography, using chloroform as eluent, isolated an unknown compound (a pale yellow solid). Yield: 0.69 g (69%); mp: 185-240°C; ¹H NMR (CDCl₃) δ 1.30 (s, 36 H, *t*-butyl), 1.70 (two s, 42 H, -CH₃), 6.88-7.10 (m, 74 H), 7.78 (d, J=8.4 Hz, 10 H, ortho to CO), 7.84-7.87 (m, 24 H, ortho to SO₂).

Attempted synthesis of polyurethane rotaxane without addition of a blocking group

A mixture of tetra(ethylene glycol) (**3.16**, 0.571 g, 2.94 mmol), macrocycle **3.1** (5.1 g, 6.0 mmol) and DMAc (25 mL) was warmed up with stirring in an oil bath (90°C) under nitrogen to yield a homogeneous solution. The solution was then stirred for one hour for prethreading. Methylene-di-*p*-phenyl diisocyanate (MDI) **3.17** (0.795 g, 3.18 mmol) was then added. A light brown color and an increase in viscosity were observed in a few minutes. The polymerization reaction was allowed to proceed for 24 hours. Upon cooling, the polymer solution was diluted with DMAc to 80 mL and the clear solution was then precipitated into water in a blender. The product was filtered and re-dissolved in THF to make an 80 mL solution which was re-precipitated into toluene to remove free macrocycle. Yield, 1.1 g (80%); ¹H NMR (DMSO-*d*₆) δ 3.50 (s, 8n H), 3.58 (m, 4n H), 3.75 (s, 2n H), 4.14 (m, 4n H), 7.05 (d, J=8.4 Hz, 4n H, arom.), 7.33 (d, J=8.4 Hz, 4n H, arom.), 9.60 (s, 2n H, -NH).

Attempted synthesis of polyurethane rotaxane with addition of a blocking group

The same procedure as above was used. The blocking group, 2-[*p*-tris(*p*-*tp*butylphenyl)methylphenoxy]ethanol (**3.12**, 0.154 g, 0.280 mmol) was added at the beginning

with the macrocycle and tetra(ethylene glycol). Yield: 1.4 g (75%). No threading was observed.
 ^1H NMR: the same as above.

Chapter 4

Synthesis of Poly(arylene ether) Based Polyrotaxanes: Crown Ethers as Cyclic Components

4.1 Introduction

Varieties of polymers, such as polyesters, polyamides, vinyl polymers, polyurethanes and poly(phenylenevinylene) have been used as linear backbones in polyrotaxane studies.¹ Threading of crown ether cyclics, such as 30C10, 42C14 and 60C20, onto these polymeric backbones has led to changes in physical properties of the polymers, as pointed out before. In this chapter, new polyrotaxanes with linear and hyperbranched poly(arylene ether)s as backbones and crown ethers as cyclic components are described. The synthesis of this type of polyrotaxane involves an aromatic nucleophilic substitution reaction between bisphenolates and dihalides. The interest in this synthesis is stimulated by the expectation that the template effect of the metal counterion of phenolate might effectively increase the threading efficiency of electronically rich crown ethers, in view of the fact that relative high threading yields have been achieved even under dilute conditions (low concentrations of crown ethers) in the anionic preparation of polystyrene rotaxanes² and in the interfacial polymerization of polyester rotaxanes.³ Since formation of polyrotaxanes with crown ethers as the cyclic components leads to an increase in solubility of the polymer backbone, it was also of interest to see if that could significantly lower the reaction temperature in the synthesis of poly(ether ether ketone) (PEEK) which is normally prepared in diphenyl sulfone at high temperatures (~300°C) due to the low solubility of this highly crystalline polymer. In the following, section 4.2.1 describes the first successful HPLC characterization of large ring sized crown ethers, such as 42C14, 48C16 and 60C20. Section 4.2.2 describes the synthesis of linear poly(arylene ether) rotaxanes, followed by the synthesis of hyperbranched poly(ether ether ketone) rotaxanes in section 4.2.3. In all polyrotaxane syntheses, 42C14 was used as the cyclic component.

4.2 Results and Discussion

4.2.1 HPLC analysis of crown ethers

The purity of large ring size crown ethers, such as 42C14, 48C16 and 60C20, is an important factor in fundamental studies of polyrotaxanes. Normally, there are two major impurities in the crown ethers: linear poly(ethylene oxide) and other ring size crown ethers; both are byproducts produced in the synthesis. The NMR spectroscopy technique can detect end groups of the linear PEO which have different chemical shifts from those of the cyclic crown ethers. After recrystallization and treatment with poly(methacryl chloride), the linear PEO can properly be removed, showing no end group signals in the NMR spectrum. However, NMR spectroscopy can not detect whether or not other ring size crown ethers exist besides the desired

¹ Polyester rotaxanes: see ref.10 in Chapter 1; polyamide and vinyl polymer rotaxanes: see refs. 14-18 in Chapter 1; polyurethane rotaxanes: see ref. 11 in Chapter 1; poly(phenylvinylene) rotaxanes: see Wang, F., Masters Thesis, Virginia Tech, 1995.

² See ref. 14 in Chapter 1.

³ See ref. 10c in Chapter 1

ones, due to the fact that they (above 36 atoms) all have the same chemical shifts. High performance liquid chromatography (HPLC) is a powerful analytical tool to analyze the purity of compounds. This analytical technique was applied to characterize the above crown ethers before, but met no success.⁴ In the present study, by an appropriate choice of eluting solvent and use of a reverse phase column, the multiplicity of large ring sized crown ethers, 42C14, 48C16 and 60C20, was determined.

In order to properly analyze the above crown ethers, small ring sized crown ethers, 15C5, 18C6, 27C9, and 30C10, whose purity was already known, were firstly analyzed to search for an eluting solvent system (the solvent combination and its ratio). A mixture of water and acetonitrile in a ratio of 80/20 (v/v) was found to be the best eluting solvent system. In Figure 4.1, it is shown that in a physical mixture the above five crown ethers are well separated from each other with increasing retention time as the ring size increases. The peak eluting at 35 sec might result from hydration of crown ethers with water. This peak appears in chromatograms of each individual crown ether. Pure water eluted at the same retention time but in opposite polarity.

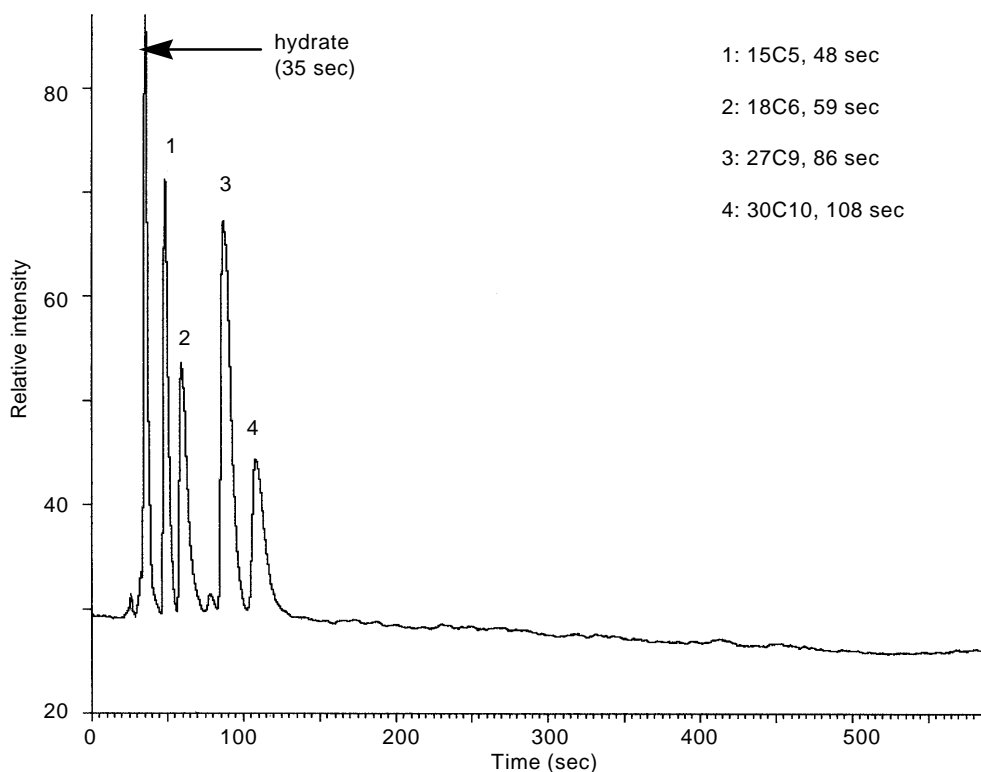


Figure 4.1 RP-HPLC chromatogram of a physical mixture of 15C5, 18C6, 27C9 and 30C10. (C18, 80/20 water/acetonitrile, 2 mL/min, RI detector)

⁴ Gibson, H. W.; Bheda, M. C.; Engen, P.; Shen, Y. X.; Sze, J.; Zhang, H.; Gibson, M. D.; Delaviz, Y.; Lee, S. H.; Wang, L.; Nagvekar, D.; Rancourt, J.; Taylor, L. *J. Org. Chem.* **1994**, *59*, 2186-2196.

The above analyses serve as bases for identification of large crown ethers. Since the retention time increases with ring size as indicated in Figure 4.1, 42C14, 48C16 and 60C20 crown ethers should elute at times larger than that for 30C10 with the same solvent system. However, no peaks at high retention times were observed in the HPLC chromatograms of these large crowns eluted with 80/20 water/acetonitrile, as indicated in Figure 4.2. Notice that all the samples produced a major peak at 35 sec, which is believed to be the hydrate of the crown ethers as mentioned above.

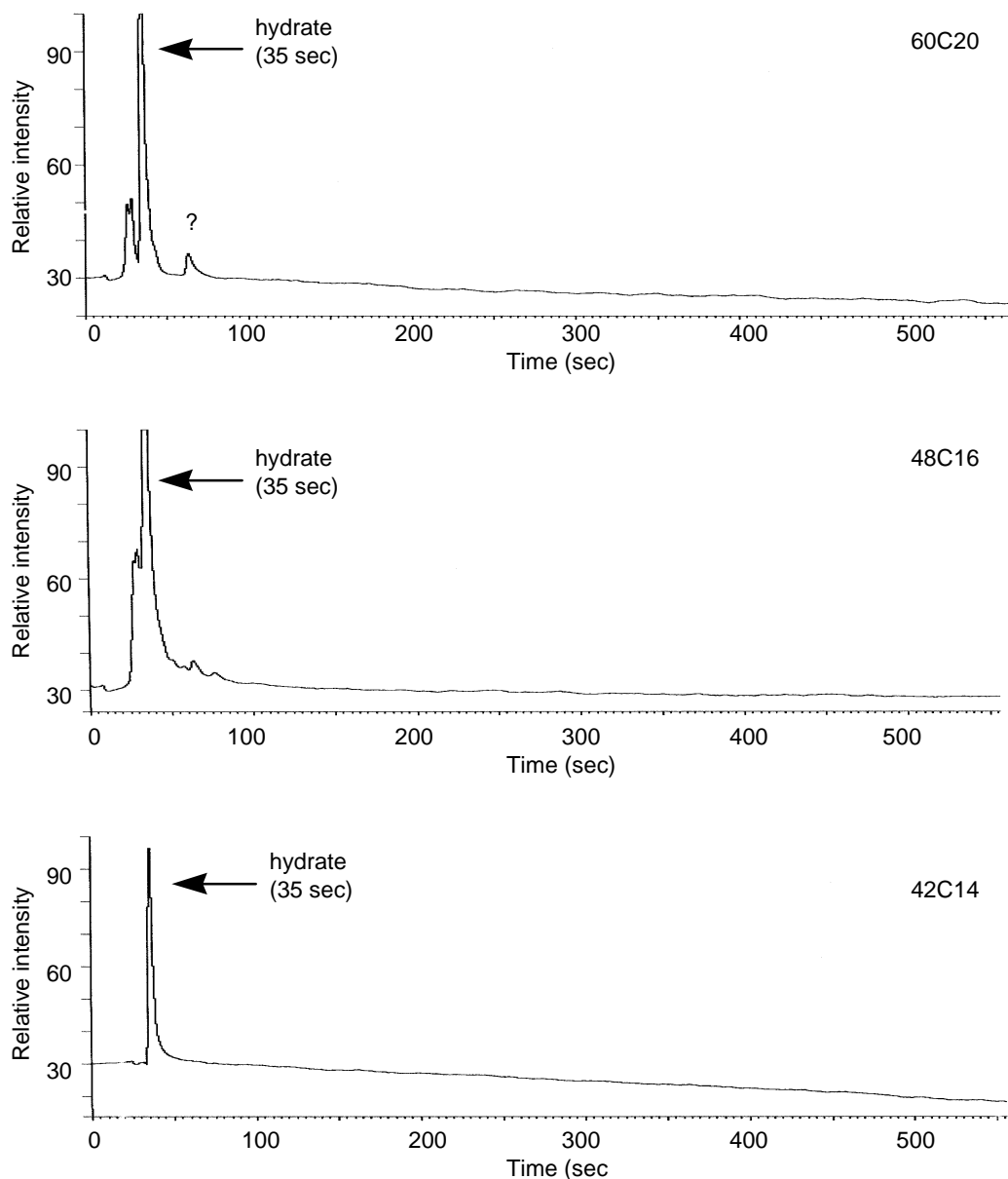


Figure 4.2 RP-HPLC chromatograms of 42C14, 48C16 and 60C20 prepared according to the reported procedures. (C18, 80/20 water/acetonitrile, 2 mL/min, RI detector)

Peaks at high retention times are usually broad and eventually will merge into the bumpy baseline with increasing retention times. Therefore, the polarity of the solvent was reduced from 80/20 to 70/30 (water/acetonitrile). For the reverse phase HPLC, the less polar the solvent (less water), the faster eluting, so that peaks will be sharpened with higher responses. For example, at the 70/30 ratio, 30C10 is eluted at 43 sec (Figure 4.3), compared to 108 sec eluted using the 80/20 ratio. The so-called hydration peak now appears at 32 sec. As the ratio of water to acetonitrile is reduced from 80/20 to 70/30, the large ring sized crown ethers, 42C14, 48C16 and 60C20, produce multiple peaks as shown in Figure 4.4. These multiple peaks are not well separated from each other and each peak may not correspond to an individual crown ether. The above results suggest that the all the large crown ethers synthesized previously according to the reported procedures⁴ are the cyclic oligomeric ethylene oxides of various ring sizes.

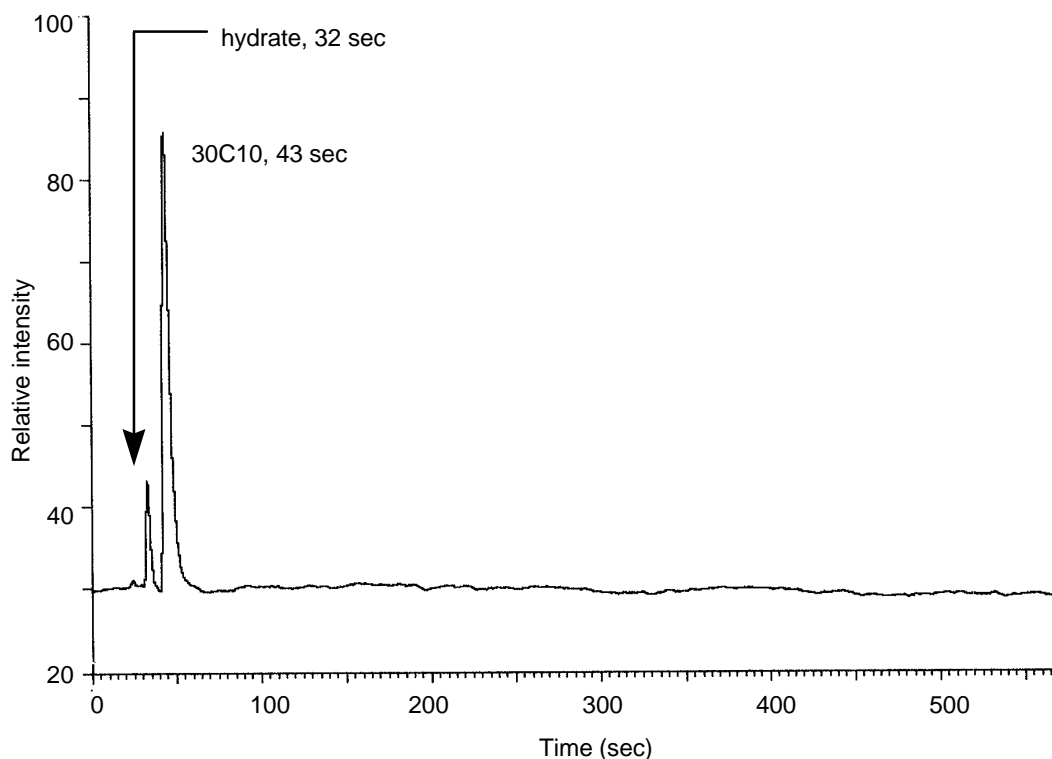


Figure 4.3 RP-HPLC chromatogram of 30C10. (C18, 70/30 water/acetonitrile, 2 mL/min, RI detector)

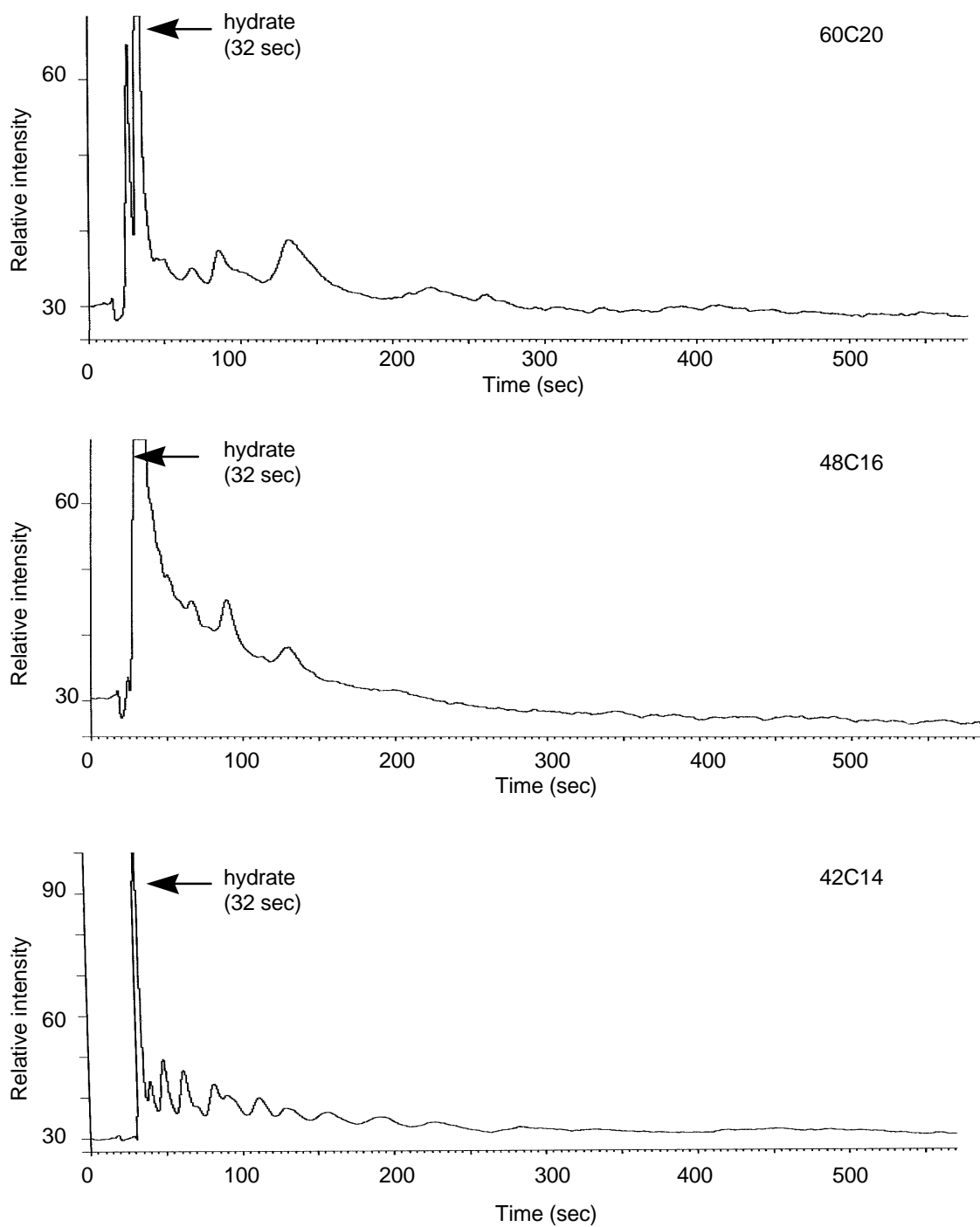


Figure 4.4 RP-HPLC chromatograms of 42C14, 48C16 and 60C20 prepared according to the reported procedures. (C18, 70/30 water/acetonitrile, 2 mL/min, RI detector)

Most recently, 42C14 was synthesized by the two piece combination procedure in which two pieces were added into a reaction flask simultaneously using a syringe pump.⁵ Reverse-phase HPLC analyses of the crude product found that there is a major peak appearing at a retention time of 252 sec using the 80/20 ratio of the eluting solvent (water/acetonitrile) (Figure 4.5), and at 106 sec using the 70/30 ratio of the eluting solvent (Figure 4.5). By HPLC-MS analyses,⁵ this major peak corresponds to 42C14. This result supports the above conclusion that previously synthesized large ring sized crown ethers are mixtures.

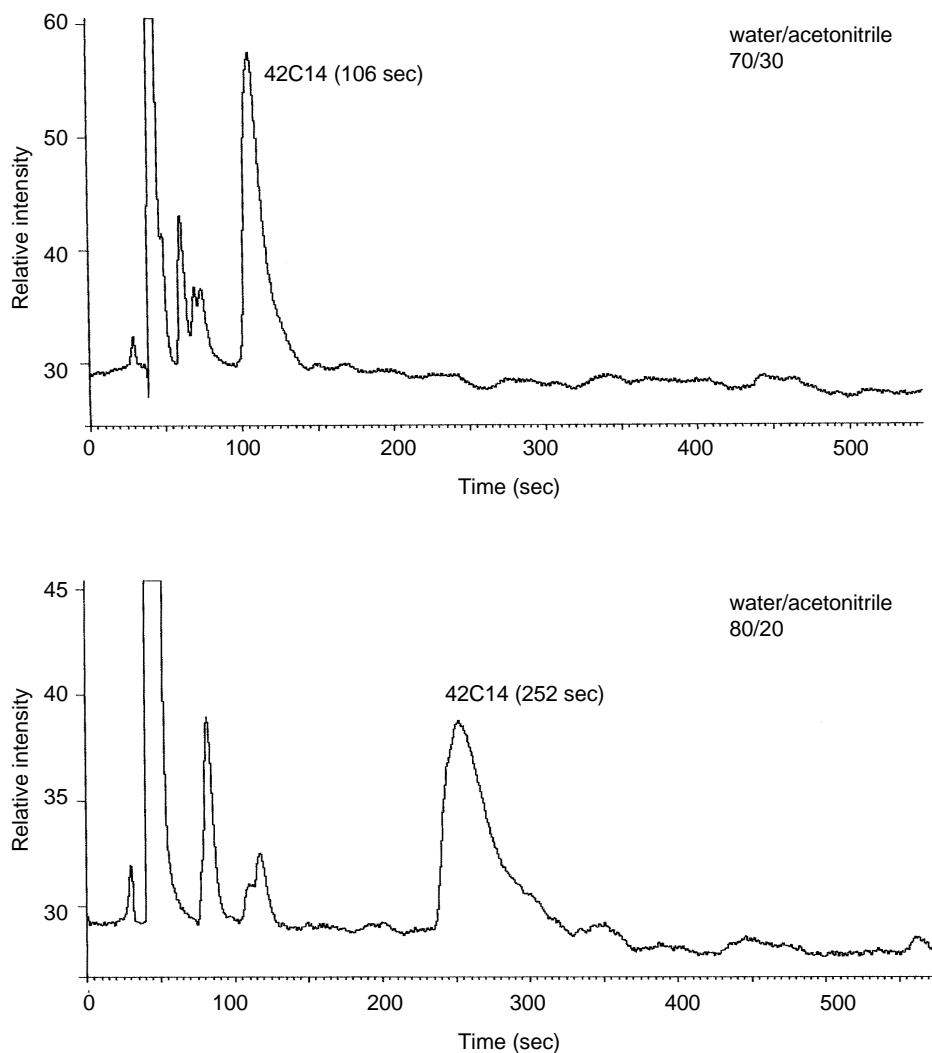


Figure 4.5 RP-HPLC chromatograms of the crude 42C14 by a two piece combination procedure under high dilution conditions. (C18, water/acetonitrile, 2 mL/min, RI detector)

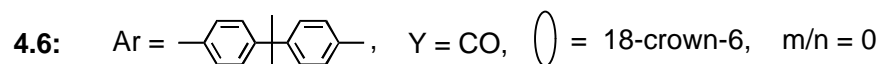
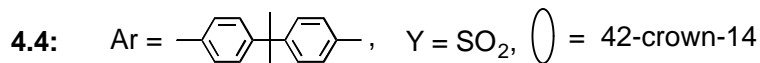
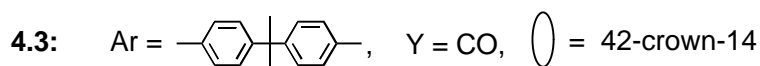
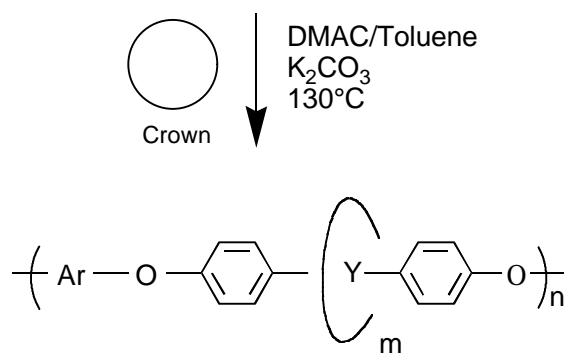
⁵ This was done by Mr. Caiguo Gong in this group, unpublished yet. Previously, 42C14 was prepared by a four piece combination procedure and the four pieces were not added simultaneously. See ref.4 for details.

4.2.2 Linear Poly(arylene ether) Rotaxanes

A Synthesis

The syntheses of poly(arylene ether) rotaxanes were conducted through aromatic nucleophilic substitution reactions between bisphenols **4.1** and difluorides **4.2** in the presence of 42C14 (Scheme 4.1).

Scheme 4.1



Unlike other systems¹ in which crown ethers were also used as solvent, an aprotic polar solvent, N,N-dimethylacetamide (DMAc), was necessary in this case to help dissolve the reactants and the resultant polymers. Toluene was added to azeotrope water generated in deprotonation of bisphenols. The monomer concentration in the combined solvents was about 0.3 M, while the feed ratio of the crown ether (assuming it to be pure 42C14) to each of the monomers was one to one. Polyrotaxanes **4.3**, **4.4** and **4.5** were obtained by refluxing corresponding bisphenol **4.1** and dihalide **4.2** in the presence of 42C14 at 130±5°C for about 18 hours in a mixture of DMAc/toluene and K₂CO₃. In the case of preparation of the poly(ether ether ketone) rotaxane **4.5**, it was observed that the polymer precipitated out of the solution after 4 hour's reaction,

indicating the poor solubility of the polymer even though crown ether macrocycles were threaded onto the backbone.

The reaction where 18C6 was used instead of 42C14 was an important model study (4.6). Since the cavity of 18C6 is too small to be threaded by polymer chains, the reaction demonstrated that unthreaded crown ethers can be removed completely by precipitation into a solvent which is a good solvent for crown ethers but a poor solvent for polymers and polyrotaxanes. This model reaction also demonstrated that under the reaction conditions crown ethers were stable, for recovered 18C6 after reaction showed only one single peak according to ^1H NMR spectroscopy and the polyether contained no ethyleneoxy moieties.

B Purification

Poly(ether ketone) rotaxane 4.3 was purified by three precipitations. The first precipitation in water from the DMAc solution was relatively good, and the precipitate was easily isolated by centrifugation. The second and third precipitations were carried out in methanol from the THF solution, which resulted in fractionation of the polyrotaxane: one fraction was the precipitate which was isolated by centrifugation; the other was an emulsion in methanol. After the third precipitation, the crown content in the precipitated fraction (4.3a) became constant, according to ^1H NMR spectroscopy. The combined emulsions were evaporated to complete dryness, and the resultant solid was further washed by stirring in methanol for 24 hours. This fraction (4.3b) accounts for about one third of the product, and the crown ether content is higher than that in the precipitated one, as shown in Table 4.1. This result indicates that the solubility of the polyrotaxane increases with the amount of crown ether threaded onto the backbone.

For poly(ether sulfone) rotaxane 4.4, a severe emulsion was formed when the polymer solution was precipitated in water. This is believed due to the low molecular weight of the polyrotaxane and high threading of the crown ether macrocycle. After all, the polyrotaxane was purified by multiple washings in water. Prior to washing, the polar solvent (DMAc) was removed by rotary evaporation to reduce the possibility to form an emulsion. The polyrotaxane was then washed by stirring in water, which removed free, unthreaded crown ethers as well as salts generated in the reaction. After 24 hour's stirring, the polymer was filtered and fresh water was added. This process was continued till the crown ether content in the polyrotaxane became constant as monitored by ^1H NMR spectroscopy.

The purification of the poly(ether ether ketone) rotaxane 4.5 was much easier due to its poor solubility. The polyrotaxane was first washed with water to remove free, unthreaded crown ether as well as salts and DMAc, then stirred in methanol for 24 hours.

C ^1H NMR Analyses

Figures 4.6 show the ^1H NMR spectra of the poly(ether ketone) rotaxane (4.3) in deuterated chloroform. The crown ether signal appears at 3.65 ppm as a singlet. The chemical shifts for the poly(ether ketone) backbone were not affected by the threaded macrocycle; neither

was the chemical shift of the crown ether. The same thing can be found for the poly(ether sulfone) rotaxane (**4.4**) (Figure 4.7). For the poly(ether ether ketone) rotaxane (**4.5**), the ^1H NMR spectrum was obtained in deuterated sulfuric acid (Figure 4.8). The 56 methylene protons of the crown ether appear at 4.01-4.06 ppm. Two peaks in this region are probably due to hydrogen bonding with protonated carbonyl groups. The aromatic protons of the PEEK backbone appear in the region of 7.15 to 8.00 ppm.

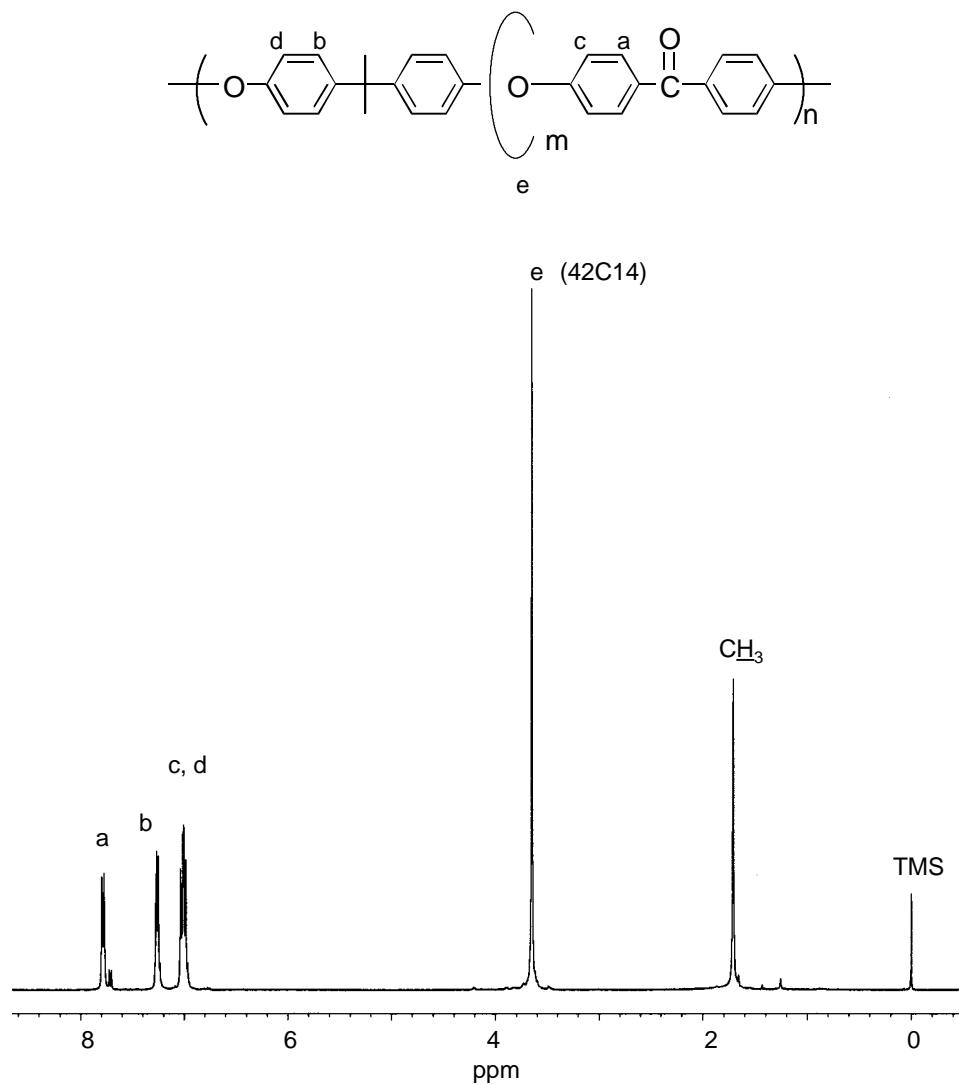


Figure 4.6 400 MHz ^1H NMR spectrum of poly(arylene ether ketone) rotaxane **4.3b** in CDCl_3

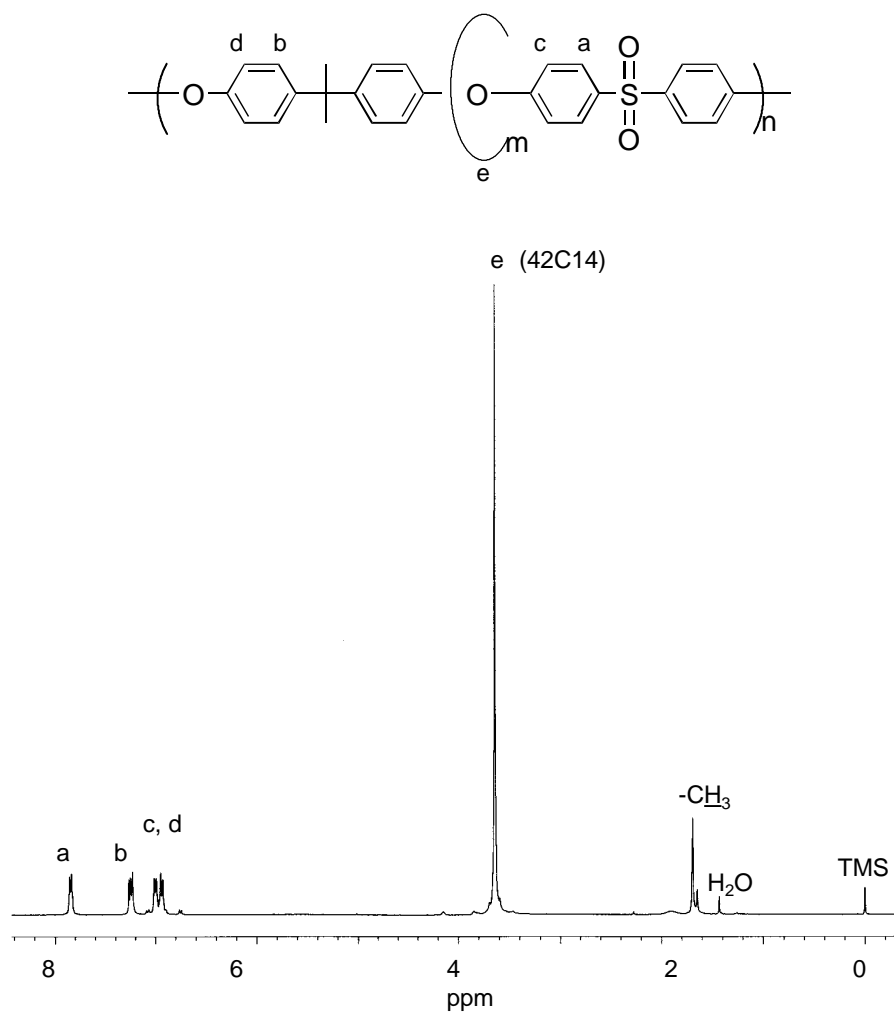


Figure 4.7 400 MHz ¹H NMR spectrum of poly(arylene ether sulfone) rotaxane **4.4a** in CDCl₃

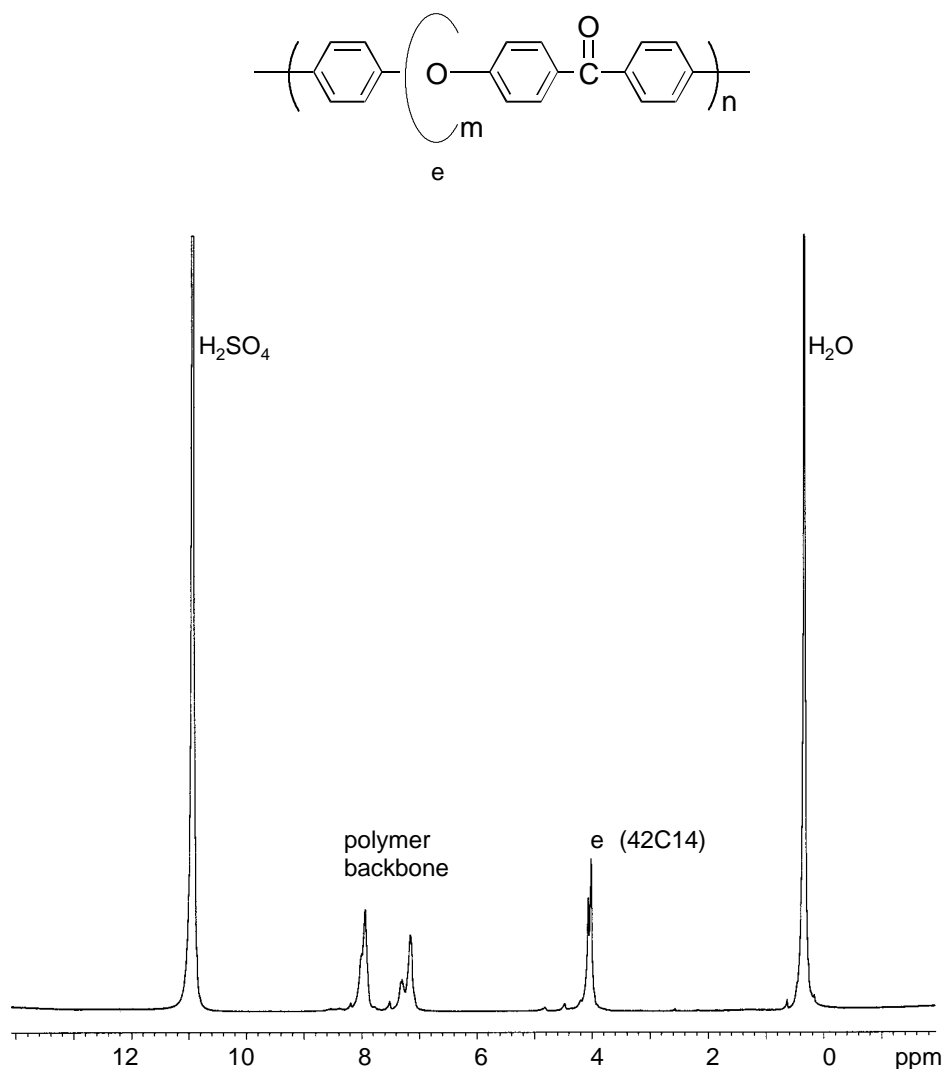


Figure 4.8 400 MHz ¹H NMR spectrum of poly(ether ether ketone) rotaxane **4.5** in D₂SO₄

The crown contents in the polyrotaxanes were determined from the integration ratios, and are evaluated by the m/n value, that is, the number of moles of cyclic per repeat unit. For polyrotaxanes **4.3** and **4.4**, the m/n was estimated by comparison of the integrals for 42C14 protons (at 3.65 ppm) and four protons ortho to sulfone (at 7.85 ppm in **4.4**) or ortho to ketone (at 7.78 ppm, in **4.3**) per repeat unit. For polyrotaxane **4.5**, the crown ether integral was compared with integrals of all aromatic signals for 12 protons per repeat unit to estimate m/n. These m/n values as well as corresponding weight percentages of crown in the polyrotaxanes are listed in Table 4.1. The poly(ether sulfone) rotaxane has high m/n values, 0.48 for **4.4a** prepared

via a two stage procedure (see Experimental) and 0.31 for **4.4b** prepared by a one stage procedure (see Experimental). For the poly(ether ketone) rotaxanes, the precipitated fraction (**4.3a**) has $m/n=0.11$, while the fraction (**4.3b**) forming emulsion in methanol has 0.20. PEEK rotaxane **4.5** has $m/n=0.20$. Considering that all these polyrotaxanes were synthesized under the conditions of low cyclic concentrations, these values are high. The complexation of the crown macrocycle with potassium counterions of the phenolates must play an important role in the threading process.

Table 4.1 Crown contents in the polyrotaxanes

polymer	m/n ratio in polymer			final wt % 42C14	% polymer recovered ^e
	1st ppt	2nd ppt	3rd ppt		
4.6	0.00	0.00	–	0.00	96
4.3a ^a	0.13 ^f	0.09 ^g	0.08 ^g	11	55
4.3b ^b	0.20 ^h	–	–	24	22
4.4a ^c	0.50/0.70 ⁱ	0.46 ^j	0.48 ^k	41	83
4.4b ^d	0.34 ^l	0.31 ^k	0.31 ^k	30	95
4.5	0.12 ^m	–	–	20	96

^aThe precipitated fraction of **4.3**. ^bThe fraction which forms an emulsion when THF solution of **4.3** was precipitated into methanol. ^cObtained by the two stage procedure. ^dObtained by the one stage procedure. ^eThe weight of crown is not included. ^fMeasured after precipitation in water. ^gMeasured after precipitation in methanol. ^hMeasured after stirring in methanol for 24 hours. ⁱMeasured for two portions after washing in water (see Experimental), ^jMeasured after immersing in water for one week. ^kMeasured after stirring in water for 24 hours. ^lMeasured for two combined portions after washing in water (see Experimental). ^mMeasured after washing in water and stirring in methanol for 24 hours.

As shown in the above table, the crown ether content in poly(aryl ether sulfone) rotaxane **4.4** is higher than that in poly(ether ketone) rotaxane **4.3**. The higher threading efficiency of poly(ether sulfone) rotaxanes may be due to two major reasons. First of all, the poly(ether sulfone) backbone is more randomly coiled because of the structural nature of the sulfone group. Random coiling of the backbone apparently traps the macrocycle in chain folds, preventing dethreading of the macrocycles in the polyrotaxane without bulky blocking groups at both chain ends. Of course, the more coiled the backbone, the larger the number of macrocycles that could be trapped. Secondly, the sulfur in the sulfone group is more positively charged than the carbonyl carbon, which could lead to stronger Lewis acid-base interactions with the oxygen atoms in the crown ether macrocycles. The stronger interaction supplies an enthalpic driving force for threading of the macrocycles.

The PEEK rotaxane (**4.5**) has an m/n value of 0.20. However, the solubility of the rotaxane is not improved as expected. The polymer actually precipitated out of the solution in the polymerization. The same kind of situation also occurs in the polyrotaxanes based on Kevlar¹ and on PPV¹. Probably, rigid macrocycles instead of the flexible crown need to be used to effectively break down strong intermolecular interactions for those polymers, thereby improving solubility.

D GPC Analyses

Gel permeation chromatography (GPC) was used to determine whether or not the free crown ether “42C14” was present in the purified polyrotaxanes. Comparing the GPC curve (curve **b**) of the physical mixture of **4.4b** plus “42C14” (33%) and that (curve **c**) of **4.4b** (Figure 4.9), it can be seen that **b** is broader than **c**. The broadening is due to the addition of “42C14” which is not threaded onto the polymer backbone. The purified polyrotaxane **4.4b** produced a narrower and more symmetric GPC trace (curve **c**), indicating that the crown ethers detected in **4.4b** are threaded ones. However, it should be pointed out that due to partial overlapping of polyrotaxane (**b**) and the “42C14” curves (**a**) it is difficult to know that all the free crown ether was removed. The small peaks at high elution volumes (26-28 mL) are probably due to cyclic(arylene ether)s formed in the polymerization.

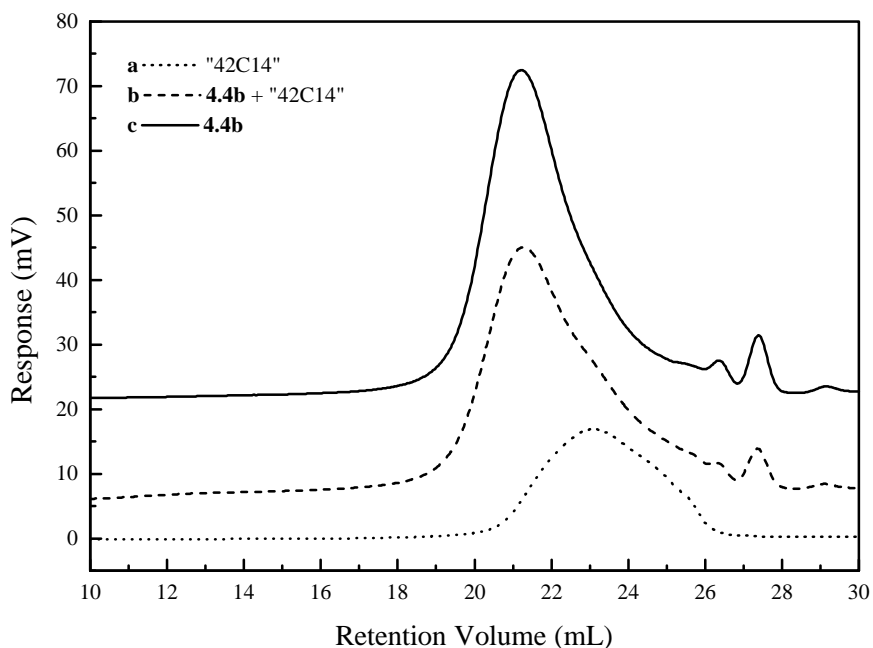


Figure 4.9 Determination of the absence of the free crown ether “42C14” in purified polyrotaxane **4.4b** by GPC (chloroform, 35°C, 1 mL/min, RI detector)

Molecular weights of the polymers, determined by GPC, are listed in Table 4.2. It is shown that the molecular weights for polyrotaxanes are much lower than that of the model polymer, even though the reaction times are longer. There are several reasons for these low molecular weights. One of the reasons might be that the 42C14 brought in some reactive impurities which upset the stoichiometry. Another reason is probably due to reduced reactivity of the nucleophile (phenolate anion), resulting from the complexation of the crown with the counterion (K^+) of the nucleophile; the complexed crown ether would sterically block reaction pathways in the polymerization. It is also shown in the table that for the poly(ether ketone) rotaxane, the fraction (**4.3b**) forming the emulsion in methanol has a higher molecular weight than that of the precipitated fraction (**4.3a**). This is due to the higher threading content of the crown ether for this fraction, which increases both the molecular weight and the solubility. Poly(ether sulfone) rotaxane **4.4a**, prepared by the two stage procedure, has a lower molecular weight than **4.4b**, prepared by the one stage procedure.

Table 4.2. GPC results (PS standards, chloroform, 25°C, 1 mL/min)

polymer	M_n (kg/mol)	M_w (kg/mol)	M_w/M_n
4.6	34.2	88.8	2.59
4.3a ^a	8.1	22.1	2.72
4.3b ^b	10.6	27.7	2.60
4.4a ^c	2.8	12.9	4.54
4.4b ^d	8.2	18.6	2.26

^{a,b,c,d} are the same as in Table 4.1.

4.2.3 Hyperbranched Poly(ether ether ketone) Rotaxanes

Hyperbranched polymers are highly branched polymers prepared using an AB_x ($x \geq 2$) type monomer having one functional group (A) of one kind and two or more of another (B) capable of reacting with the former. Due to the branches, these materials adopt globular, three dimensional structures with numerous functional groups at the branch ends. They possess unusual characteristics such as the absence of the classical chain entanglements found in linear polymers and low viscosity as well as high solubility. Although Flory theoretically described such polymer systems in 1952,⁶ it was not until recently that they received much attention.⁷ The recent interest

⁶ Flory, P. J. *J. Am. Chem. Soc.* **1954**, *74*, 2718.

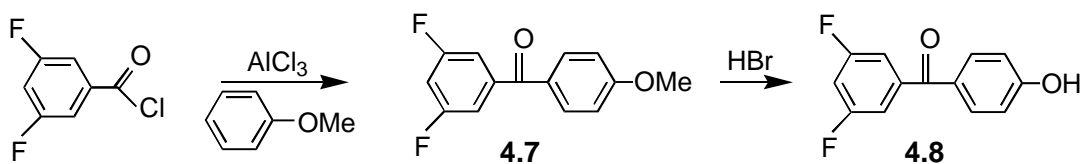
⁷ a) Kim, Y. H.; Webster, W. *J. Am. Chem. Soc.* **1990**, *112*, 4592; b) Hawker, C. J.; Lee, R.; Frechet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4583; c) Uhrich, K. E.; Hawker, C. J.; Frechet, J. M. J. *Macromolecules* **1992**, *25*, 4583; d) Kim, Y. H.; Webster, O. W. *Macromolecules* **1992**, *25*, 5561; e) Miller, T. M.; Neenan, T. X.; Kwock, E. W.; Stein, S. S. *J. Am. Chem. Soc.* **1993**, *115*, 356.

in hyperbranched polymers is stimulated by the rapidly growing synthesis of dendrimers.⁸ Dendrimers also have highly branched structures, but unlike hyperbranched polymers, their branches are well defined, radiating from a central core, and their sizes and architectures can be specifically controlled by precise stepwise synthesis. Well designed dendrimers have demonstrated a number of potential applications, such as host-guest molecules,⁹ unimolecular micelles,¹⁰ sensor materials,¹¹ etc. Due to the nature of stepwise synthesis, dendrimers are difficult to obtain in large quantity. In comparison, hyperbranched polymers can be obtained just in one step synthesis, whereas their properties mimic those of dendrimers. This section provides preliminary results on the synthesis and characterization of polyrotaxanes based on hyperbranched poly(ether ether ketone)s.

A Synthesis of AB₂ monomers

To prepare hyperbranched poly(ether ether ketone)s by aromatic nucleophilic substitution, 3,5-difluoro-4'-hydroxybenzophenone (**4.8**) and 3,5-dihydroxy-4'-fluorobenzophenone (**4.11**) were chosen and prepared according to the reported procedures (Schemes 4.2 and 4.3).¹² Monomer **4.8** was obtained in 81% overall yield. The melting point of this compound was 143.8-144.4°C, about 9°C higher than reported, while its ¹H NMR spectrum matched the structure. Monomer **4.11** was obtained in 71% overall yield; its melting point and ¹H NMR spectrum matched those reported.

Scheme 4.2



⁸ Tomalia, D. A.; Naylor, A. M.; Goddard, W. A., III *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 138; Tomalia, D. A.; Baker, H.; Dewald, J.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. *Polym. J. (Tokyo)*, **1985**, *17*, 117; Newkome, G. R.; Moorefield, C. N.; Baker, G. R.; Johnson, A. L.; Behera, R. K. *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1176; Hawker, C. J.; Frechet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638; Wooley, K. L.; Hawker, C. J.; Frechet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4252; Moor, J. S.; Xu, Z. *Macromolecules* **1991**, *24*, 5893; Kwock, E. W.; Neenan, T. X.; Miller, T. M. *Chem. Mater.* **1991**, *3*, 775-777

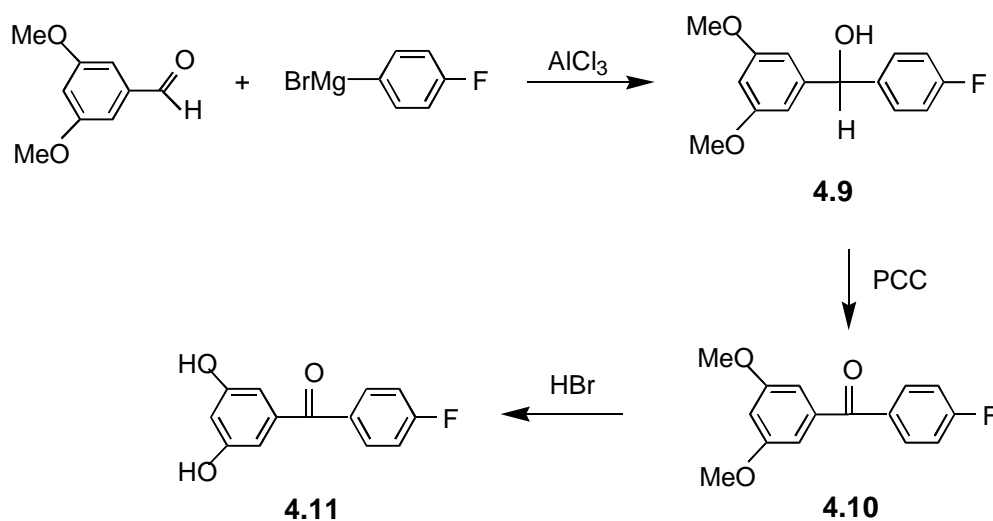
⁹ Jansen, J. F. G. A.; de Brabnder, E. M. M.; Meijer, E. W. *Science*, **1994**, *266*, 1226; Meijer, E. W.; Jansen, J. F. G. A.; de brabnder, E. M. M. *J. Am. Chem. Soc.* **1995**, *117*, 4417.

¹⁰ Hawker, C. J.; Wooley, K. L.; Frechet, J. M. J. *J. Chem. Soc. Perkin Trans. Part I* **1993**, 1287.

¹¹ Well, M.; Crooks, R. M. *J. Am. Chem. Soc.* **1996**, *118*, 3988.

¹² Chu, F.; Hawker, C. J. *Polymer Bulletin* **1993**, 262

Scheme 4.3

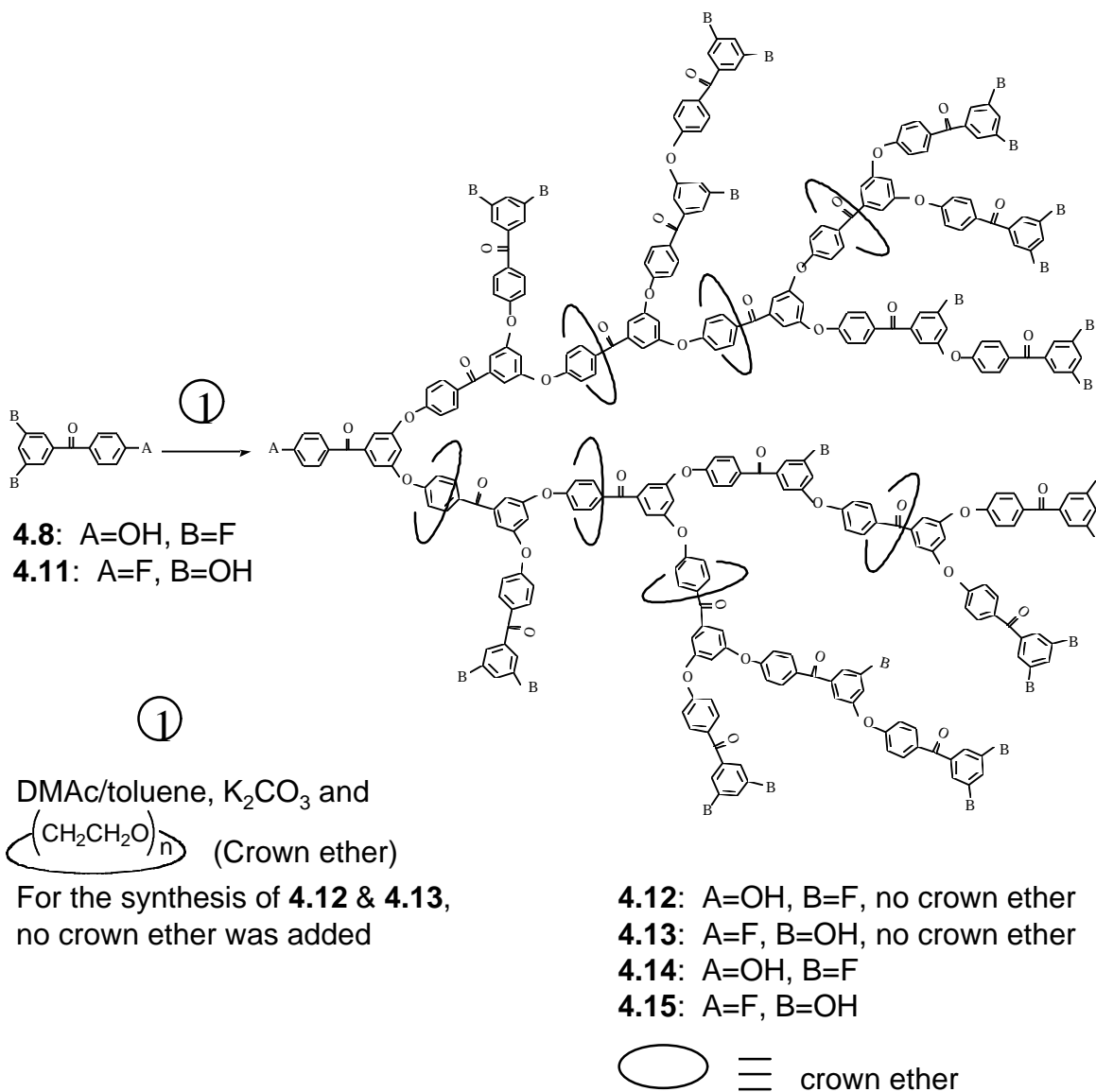


B Synthesis of hyperbranched polyrotaxanes

The synthesis of hyperbranched poly(ether ether ketone)s using monomers **4.8** and **4.11** was also reported.¹² This was done at 200°C in an N-methylpyrrolidone/toluene solvent mixture using potassium carbonate as base. Under such conditions, high molecular weight hyperbranched polymers were obtained, 20 kg/mol from **4.8** and 95 kg/mol from **4.11**. In our studies, considering the limited thermal stability of crown ethers that were used as cyclic components for the polyrotaxanes, we carried out the polymerization at about 160°C in a lower boiling N,N-dimethylacetamide/toluene solvent mixture. Both monomers were polymerized under these conditions with and without the presence of crown ethers (Scheme 4.4).

The polymerization in the absence of crown ether served as a model study to see how the reaction proceeds under the above conditions and to obtain polymers for comparison with their polyrotaxane analogs. The fluoro-terminated hyperbranched poly(ether ether ketone) **4.12** was thus obtained in 37% yield by reaction of **4.8**, with M_n of 4.14 kg/mol and polydispersity of 73.6, whereas the reaction of **4.11** gave the hydroxy-terminated poly(ether ether ketone) **4.13** in 82% yield with M_n of 8.56 kg/mol and polydispersity of 4.29. Both molecular weights were determined by GPC using NMP as solvent and universal calibration. Compared to the reported¹² hyperbranched poly(ether ether ketone)s, these are much lower molecular weights, and yields are low. The low molecular weights were believed to result from poor reactivity of the monomers at the relatively low reaction temperature used. The reason for the difference in molecular weights of polymers **4.12** and **4.13** may be due to the relative reactivity of monomers **4.8** and **4.11**. Monomer **4.11** is more reactive because the hydroxyl groups are at meta positions and the fluoro group at the para position to the ketone group.

Scheme 4.4



Although relatively low molecular weight hyperbranched polymers were obtained at the relatively low reaction temperature, 160°C, the synthesis of hyperbranched polyrotaxanes was still conducted at this temperature considering the limited thermal stability of crown ethers. Thus, monomer **4.8** or **4.11** was polymerized under the same reaction conditions as above in the presence of crown ethers to obtain the corresponding polyrotaxanes. The crown ethers, originally thought of as 42C14, were a mixture composed of various ring sized individual crown ethers. The ratio of number of C₂H₄O units to monomer was 14, i.e., 1 equivalent assuming it was pure 42C14. The crown ethers also served as cosolvent along with DMAc and toluene. The threaded

cyclics were expected to be retained within branched structures once the hyperbranched polymer was formed. Unthreaded crown ethers were removed after the synthesis. For hydroxyl-terminated hyperbranched polyrotaxane **4.15**, this was done by multiple precipitations and washings in water until the crown content in the polymer was constant according to ^1H NMR measurements. For fluoro-terminated hyperbranched polyrotaxane **4.14**, due to its solubility in water, it was purified by continuous liquid-liquid-extraction using toluene/water to remove free crown ethers, followed by dialysis in water using a cellulose membrane (Molecular weight cut off: 1000) to remove inorganic salts. The efficiency of the purification methods was demonstrated by gel permeation chromatography (GPC). As shown in Figure 4.10, the purified **4.14** produced a GPC trace (curve **c**) without observation of the free crown ether “42C14” (curve **a**) which would increase the low molecular weight side of the curve for **4.14**, as is the case (curve **b**) for the physical mixture of **4.14** and “42C14”.

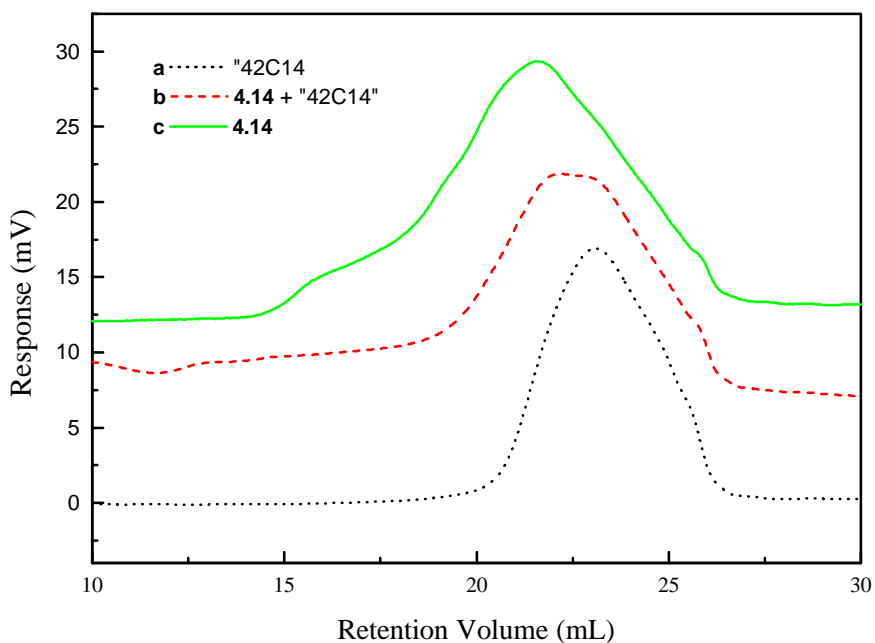


Figure 4.10 Determination of the absence of the free crown ether “42C14” in purified polyrotaxane **4.14** by GPC (chloroform, 35°C, 1 mL/mol, RI detector).

The molecular weights of both polymers were determined by GPC using NMP as solvent and universal calibration. Again, relatively low molecular weights were observed, around 5 kg/mol for both polyrotaxanes (see Table 4.3).

Table 4.3 Yields, molecular weights and crown contents of hyperbranched polyrotaxanes

	yield (%)	M_n^b (kg/mol)	M_w/M_n	m/n ^c	mass% cyclic
4.12	37	4.14	73.6	0	0
4.13	82	8.56	4.29	0	0
4.14	228 ^a	5.73	12.5	21	82
4.15	98 ^a	5.14	5.64	1.5	24

a) Based on theoretical yield of the polymer backbone. b) Absolute molecular weight by GPC (NMP, 60°C universal calibration). c) m is the average number of C₂H₄O units per repeat unit in the polymer.

The solubility of hyperbranched poly(ether ether ketone)s was greatly enhanced compared to their linear analogs. Both **4.12** and **4.13** had high solubilities in common organic solvents, such as THF and acetone. The enhanced solubility is undoubtedly due to the branched structure which prevents close packing and crystallization of the polymer segments and chains. The solubility was also influenced by the presence of numerous terminal groups of the branches. For example, the hydroxyl-terminated hyperbranched poly(ether ether ketone) **4.13** was very soluble in DMSO and in aqueous NaOH solution, whereas the fluoro-terminated hyperbranched poly(ether ether ketone) **4.12** was only sparingly soluble in DMSO and totally insoluble in water. When the hyperbranched poly(ether ether ketone) were made in the presence of crown ethers, the obtained polyrotaxanes had even better solubilities. The fluoro-terminated polyrotaxane **4.14**, compared to **4.12**, was now soluble freely in DMSO and even in water, whereas the hydroxy-terminated polyrotaxane **4.15**, compared to **4.13**, was now freely soluble in chloroform.

C ¹H NMR analysis of hyperbranched PEEK rotaxanes

Proton NMR spectroscopy is a useful tool to determine the amount of crown ether in the product. If the crown content becomes constant after a number of purification processes, the unthreaded free crown ethers are said to be removed and the remaining crown ethers are threaded ones. The amount of threaded crown ethers can be characterized by the m/n value, the average number of C₂H₄O units per repeat unit in the polymer.

According to the ¹H NMR spectrum (Figure 4.11), the m/n value of hydroxyl-terminated polyrotaxane **4.15** is 1.5, calculated from the integration values of the crown peak at 3.51 ppm (in

DMSO- d_6) and the broad peak “a” at 7.55-7.97 ppm which corresponds to the aromatic protons ortho to the ketone group of para-substituted phenyl rings in the polymer. This number means that there are on average 1.5 C_2H_4O units of crown ether around one repeat unit of a polymer backbone molecule, or assuming the crown was pure 42C14 one macrocycle per 9.3 repeat units. This corresponds to 24 wt% crown ether in the polyrotaxane.

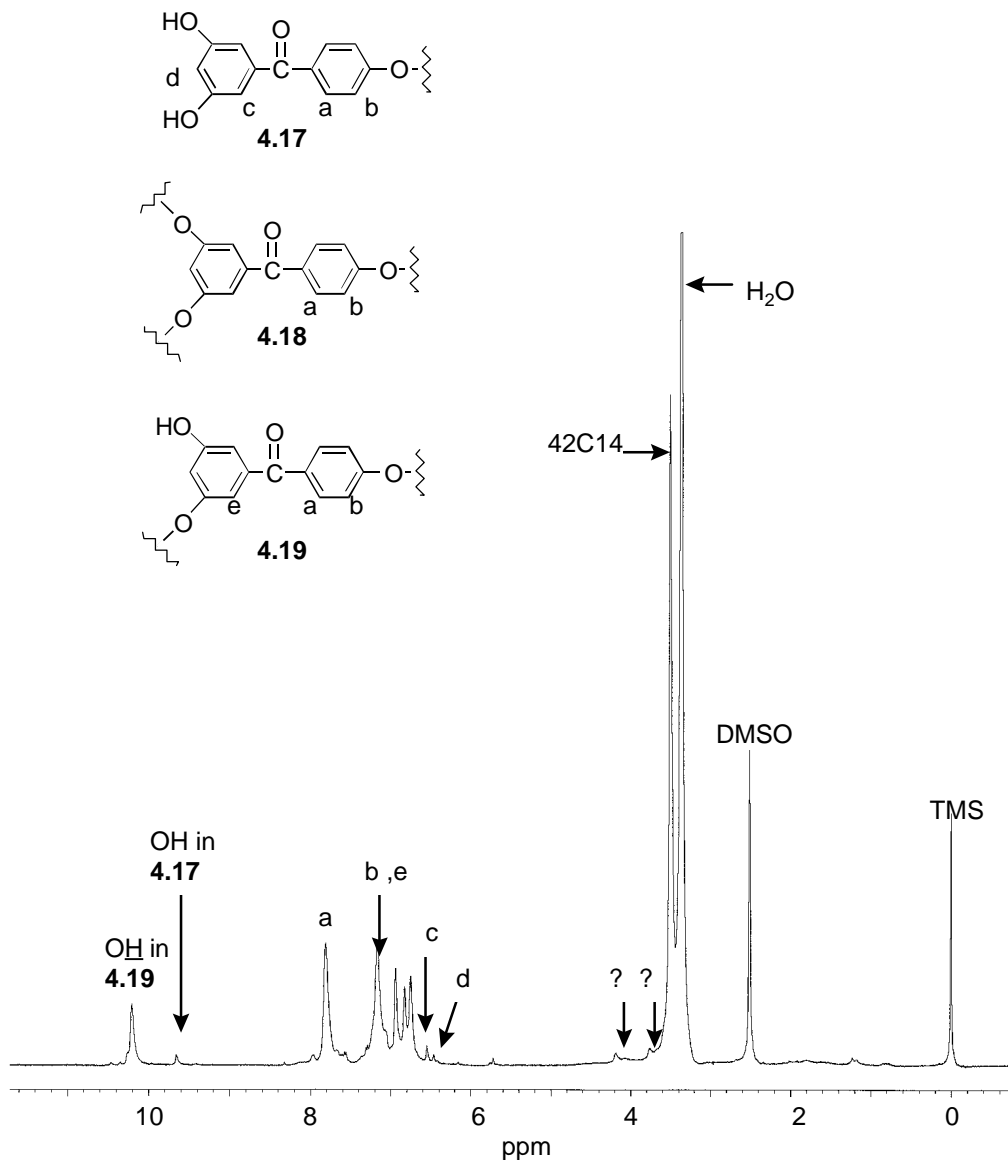


Figure 4.11 400 MHz 1H NMR spectrum of hydroxyl-terminated polyrotaxane **4.15** in DMSO- d_6

Similarly, the m/n of fluoro-terminated polyrotaxane **4.14** was calculated to be 21 from the crown peak at 3.64 ppm (in CDCl₃) and the broad peaks (“a”) between 7.55-7.86 ppm of the polymer backbone (Figure 4.12). Both m/n values for polyrotaxanes **4.14** and **4.15** are summarized in Table 4.3. It should be pointed out that the crown content in **4.14**, 21 (m/n) is much larger than the feed ratio of crown to monomer, 14 (average no. of C₂H₄O units of crown ethers per monomer molecule). This probably suggests that there are some free crown ethers not being removed in the purification. It is also possible that some crown ethers were ring opened and incorporated into the polymers. By carefully examining the NMR spectrum (Figure 4.12), it is found that there are two small peaks at 3.86 ppm and 4.15 ppm near the crown peak (3.64 ppm). These two peaks are coupled to each other according to the 2D COSY proton spectrum (Figure 4.13). The coupled peaks could be from the methylene protons on two adjacent terminal carbons of the ring-opened crown ethers, because in the ¹³C NMR spectrum (Figure 4.14) two extra peaks at 58.97 and 61.51 ppm were observed besides the main peak at 70.48 ppm. In other words, the crown ether may have been subjected to ring cleavage in the polymerization and the ring-opened crown ethers were incorporated into the polymer backbone. Further evidence of the ring opening and the incorporation of “42C14” were provided by a model reaction. In this reaction, difluoro-hydroxy monomer **4.8** was polymerized in the presence of 18C6 instead of “42C14”; other reaction conditions were the same. Most of the product was abnormally intractable, even in conc. sulfuric acid. After the product was washed with water, the soluble part of the product was extracted by chloroform, which gave a peak (broad at the bottom) at 3.65 ppm in the aliphatic region of its ¹H NMR spectrum (Figure 4.15, top). Since 18C6 is too small to be threaded by the polymer backbone and the chemical shift (proton) of free 18C6 is 3.69 ppm, the peak at 3.65 probably comes from the ring opened 18C6 which is incorporated into the polymer backbone. The small peak at 68.10 ppm besides the main peak at 70.37 ppm in the aliphatic region of the ¹³C NMR spectrum (Figure 4.15, bottom) probably came from the terminal carbons of the linear poly(ethylene oxide)s (PEO) resulted from the ring opened 18C6. The residue in the water washing was found to be pure 18C6, which suggests that only part of 18C6 was subjected to ring opening.

The ring opening of “42C14” and subsequent incorporation into polymer backbones is also observed in the hydroxy-terminated polyrotaxane **4.15**, as indicated by two small peaks at 3.75 ppm and 4.18 ppm in Figure 4.11. It is, however, difficult to determine how much crown ether was cleaved and incorporated into the polymer backbone because the crown ethers give the same chemical shift in ¹H NMR as linear poly(ethylene oxide)s except the terminal groups.

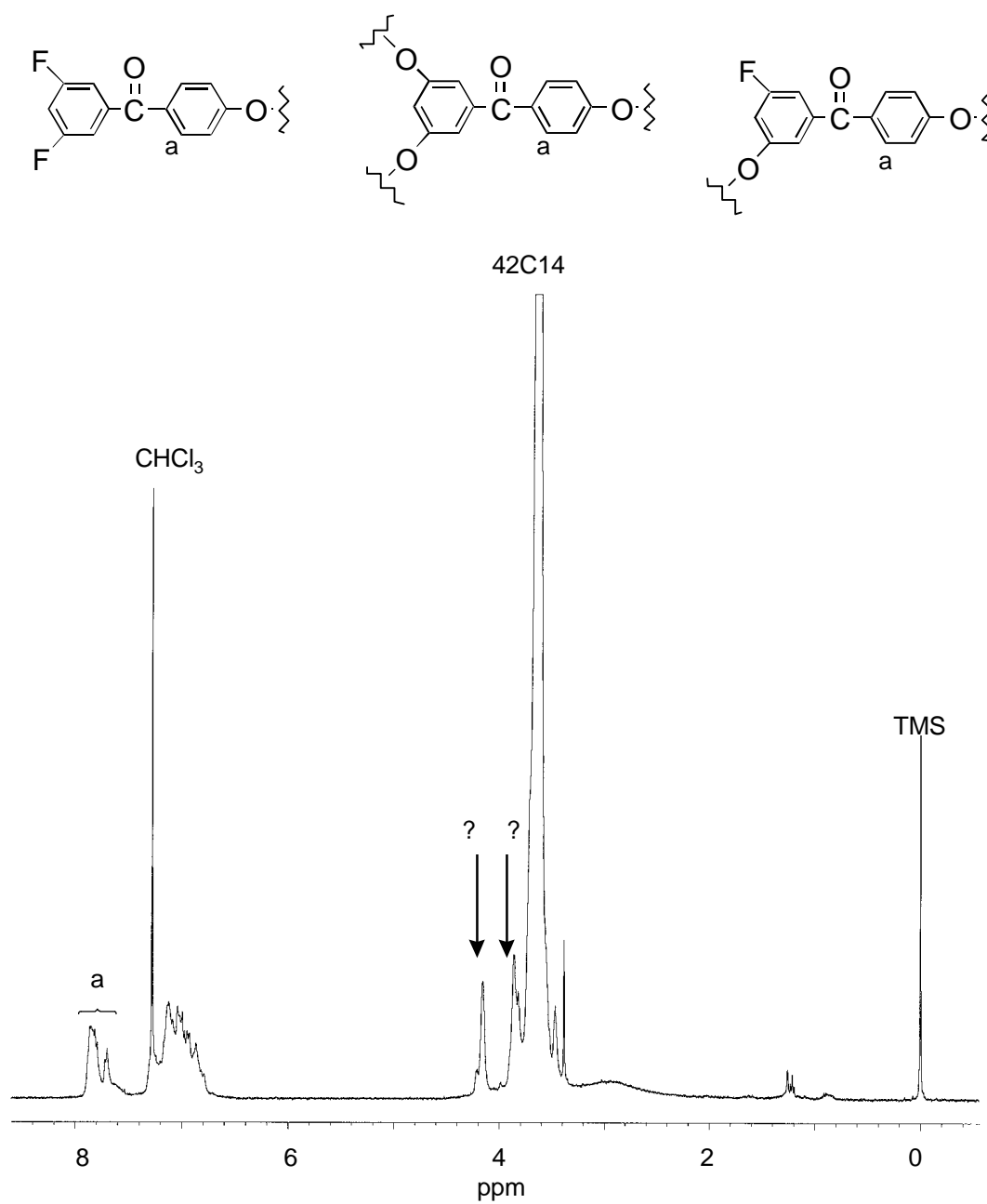


Figure 4.12 400 MHz ¹H NMR spectrum of fluoro-terminated polyrotaxane **4.14** in CDCl₃

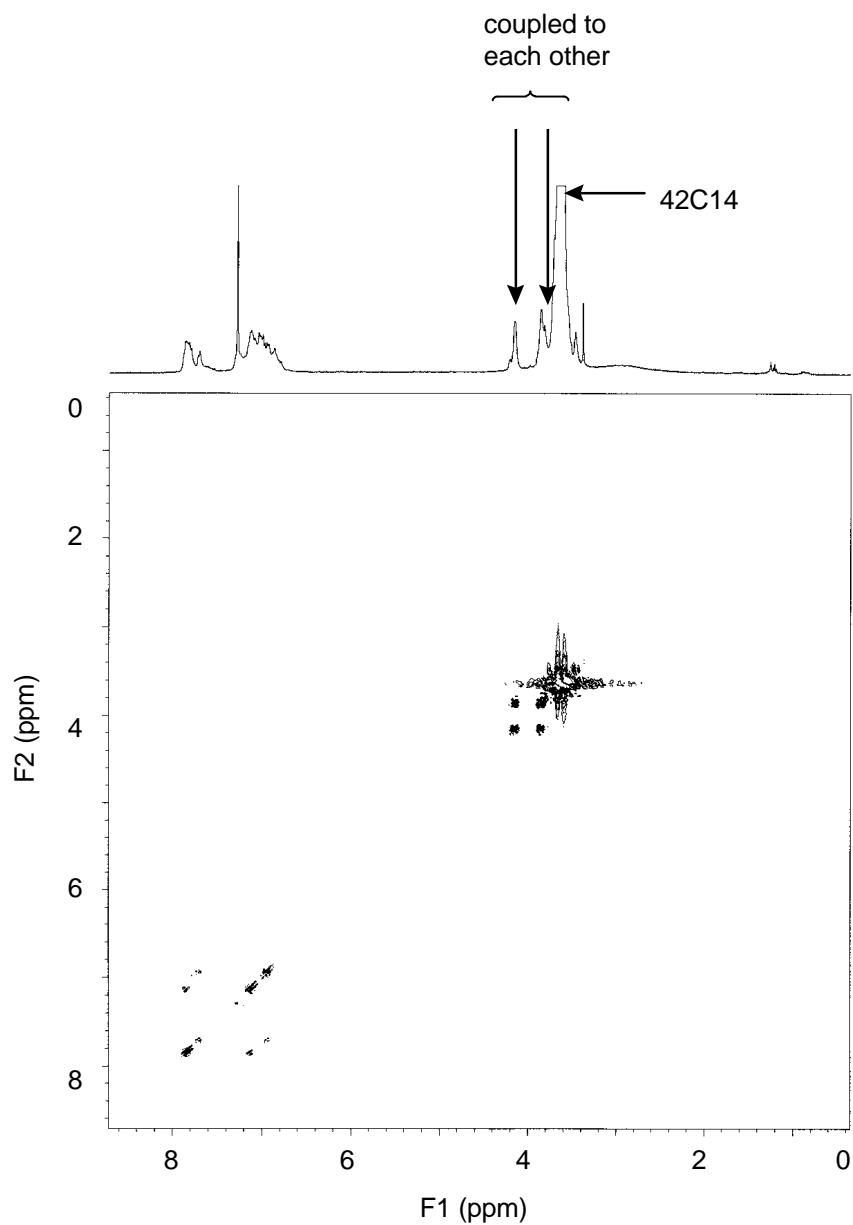


Figure 4.13 400 MHz 2D-DQCOSY ^1H NMR spectrum of fluoro-terminated polyrotaxane **4.14** in CDCl_3

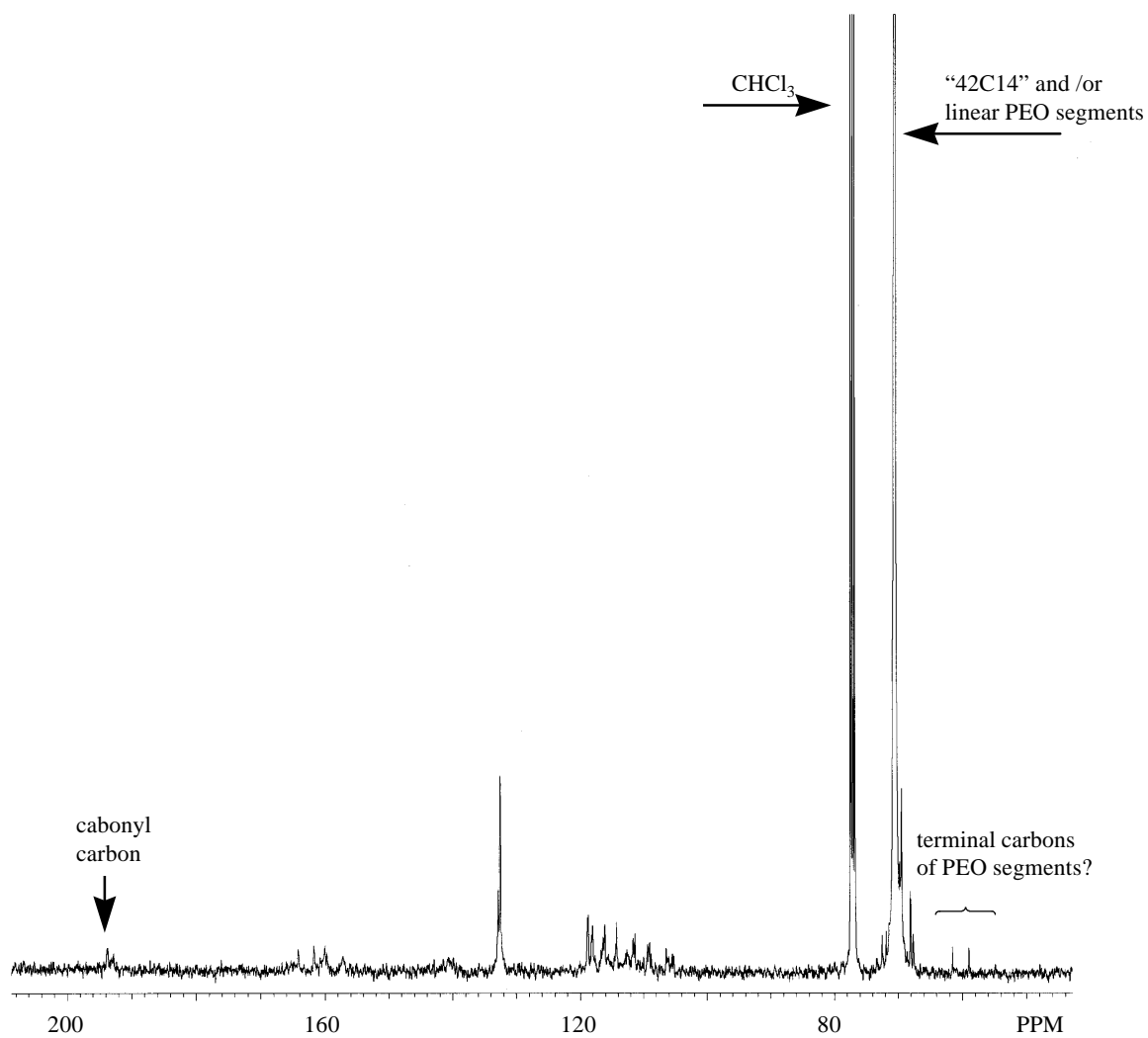


Figure 4.14 100 MHz ^{13}C NMR spectrum of fluoro-terminated polyrotaxane **4.14** in CDCl_3

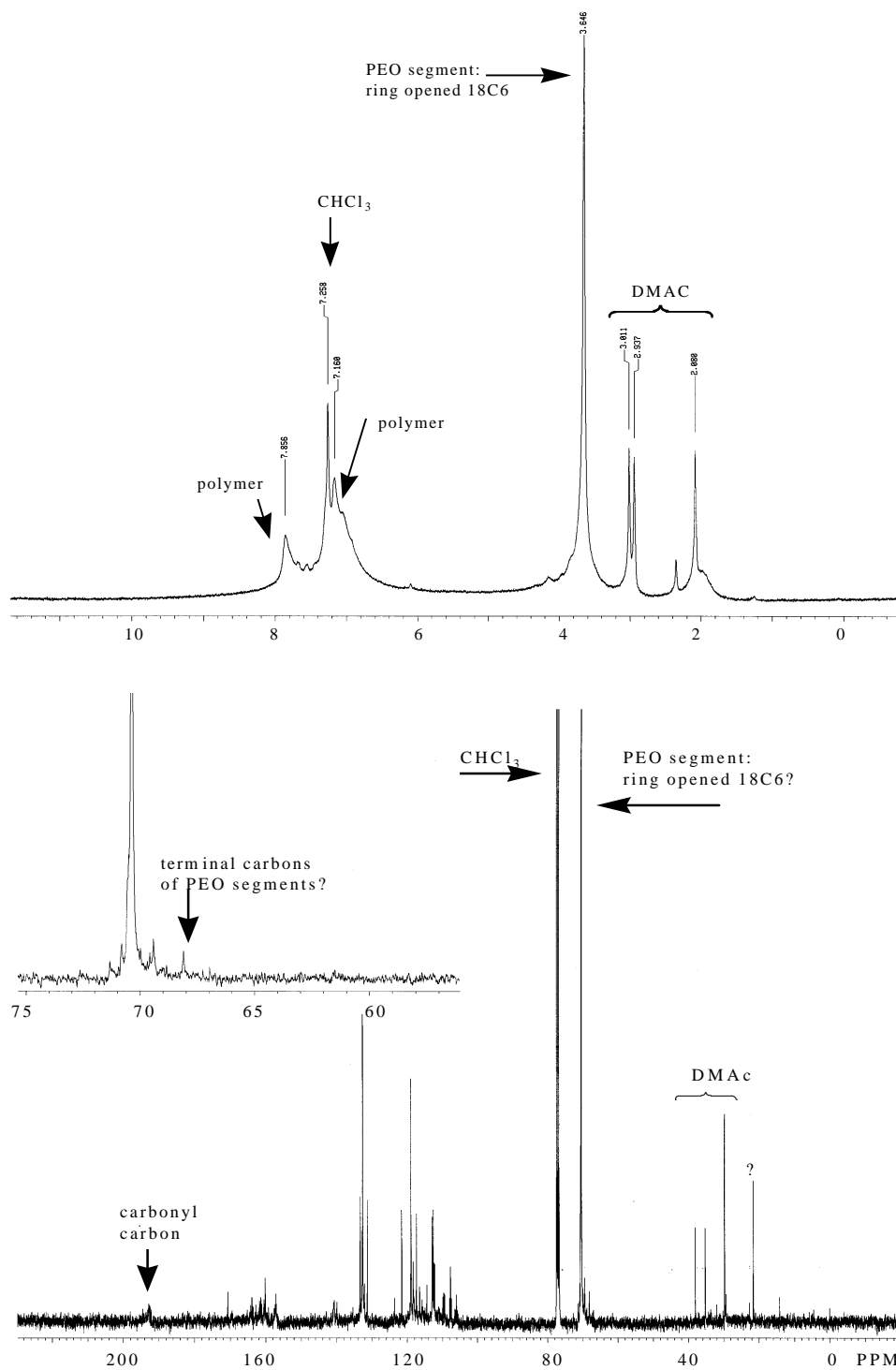


Figure 4.15 The sol fraction of the product from the model reaction in the presence of 18C6: top, 400 MHz ^1H NMR spectrum (in CDCl_3); bottom, 100 MHz ^{13}C NMR spectrum (in CDCl_3)

D Determination of degree of branching

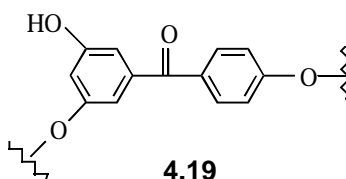
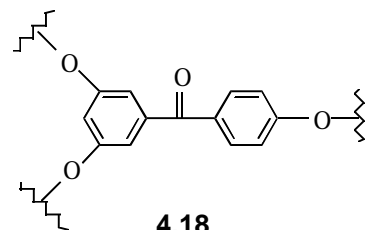
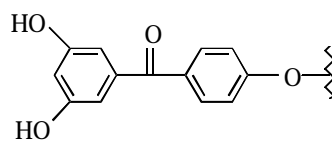
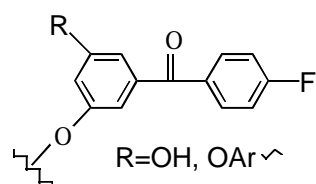
There are four different types of subunits possibly present in the irregular hyperbranched polymer structure. Taking the polymer **4.13** as an example, these subunits include, as shown below, the core unit **4.16**, the terminal units **4.17** which have two phenolic groups, the dendritic units **4.18**, and the linear units **4.19** which have one phenolic group. The degree of branching (DB) is defined as¹³

$$\text{DB (\%)} = \frac{(\text{no. of dendritic units}) + (\text{no. of terminal units})}{\text{total no. of units}} \times 100$$

If the core units **4.16** are neglected, the degree of branching would be

$$\text{DB (\%)} = 1 - \frac{\text{no. of linear units}}{\text{total no. of units}} \times 100$$

For a linear polymer, DB would be 0; and for a perfect dendritic macromolecule DB would be 100%.



In the ¹H NMR spectrum of hyperbranched polymer **4.13** (Figure 4.16), the broad singlet at 10.19 ppm comes from the phenolic proton of the linear units **4.19**. The integration of this singlet gives the average number of linear units per molecule. The total number of units per molecule can be measured by the integration of the broad singlet at 7.78 ppm which corresponds to the aromatic protons ortho to the ketone group of para-substituted phenyl groups in all the subunits (“a”). The DB of polymer **4.13** was thus determined to be 42% from the second equation. It was also calculated as 44% according to the first equation. In this case, the number

¹³ See ref. 7b.

of terminal units was measured by the integration of the singlet at 9.64 ppm which corresponds to the terminal phenolic protons; the number of dendritic units was measured by subtraction from the integration of the singlet at 7.78 ppm that of the singlet at 7.15 ppm, which corresponds to the protons ortho to the ketone group of tri-substituted phenyl rings (“e”) in the dendritic units and the protons ortho to ether linkages of para-substituted phenyl rings in all the subunits (“b”). The DB of the hydroxyl-terminated hyperbranched polyrotaxane **4.15** was similarly calculated as 32%. The DB of the fluoro-terminated hyperbranched polymers **4.12** and **4.14** could not be calculated because their ^1H NMR spectra (Figures 4.17 and 4.12, respectively) are not well resolved.

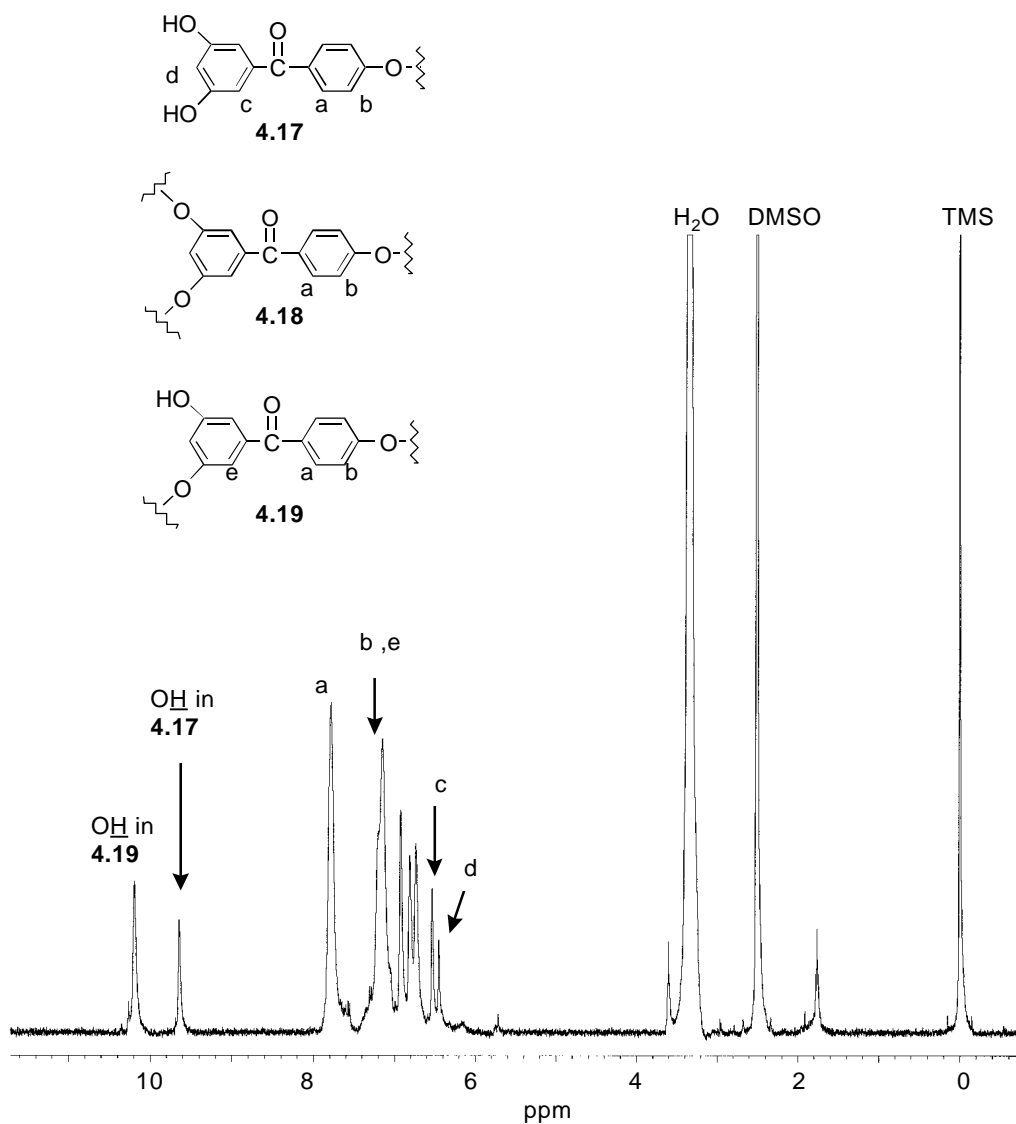


Figure 4.16 400 MHz ^1H NMR spectrum of hydroxyl-terminated hyperbranched poly(ether ether ketone) **4.13** in DMSO-d_6

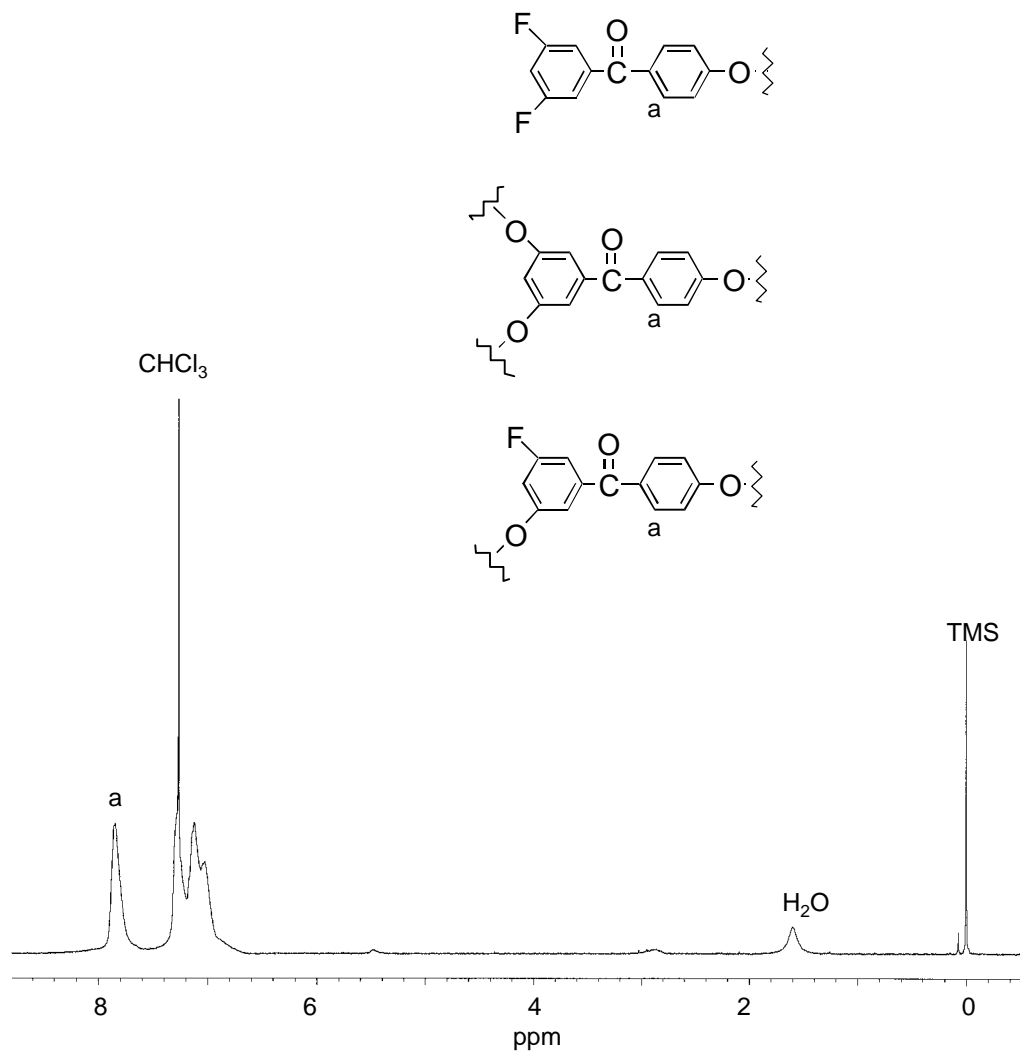


Figure 4.17 400 MHz ^1H NMR spectrum of fluoro-terminated hyperbranched poly(ether ether ketone) **4.12** in CDCl_3

4.3 Conclusions

A new family of main chain polyether rotaxane systems, including poly(ether ketone), poly(ether sulfone) and poly(ether ether ketone) rotaxanes, has been synthesized using 42-crown-14 as cyclic component. High crown ether macrocycle contents in these polyrotaxanes indicate that the template effect of the potassium counterions of phenolates must play an important role in the threading process. Higher macrocycle contents in the poly(ether sulfone) rotaxane, compared to the poly(ether ketone) rotaxane, are believed to be due to the more coiled nature of the polymer backbone in the solution and the stronger acid-base interaction between sulfur atoms in the backbone and oxygen atoms in the crown ether macrocycle. The solubility of poly(ether ether ketone) rotaxane is not improved as expected, which is probably due to the low threading yield of the macrocycles and strong intermolecular interactions of the polymer backbone.

Syntheses of polyrotaxanes based on hyperbranched poly(ether ether ketone)s were attempted, using a crown ether mixture as the cyclic component. Under the reaction conditions used, the crown ethers may undergo ring cleavage and incorporate into the polymer backbones, according to ^1H NMR spectroscopy. The molecular weights for both model polymers (**4.12** & **4.13**) and polyrotaxanes (**4.14** & **4.15**) were relatively low due to the poor reactivities of AB_2 monomers (**4.8** & **4.11**) at the low reaction temperature used (160°C). Increasing reaction temperature is not be feasible because of limited thermal stability of crown ethers. The solubility of the “polyrotaxanes” is greatly enhanced compared to the model polymers.

4.4 Experimental

Materials

Bisphenol-A was recrystallized in toluene three times and dried under vacuum prior to use. Difluorobenzophenone was recrystallized in ethanol three times and dried under vacuum prior to use. Hydroquinone was purified by sublimation. 15C5 and 18C6 were purchased from Aldrich; other crown ethers, 27C9, 30C10, 42C14, 48C16 and 60C20, were supplied by this group.

Measurements

Melting points were taken in capillary tubes with a Melt-Temp II melting point apparatus and have been corrected. ^1H NMR spectra were obtained on a Varian 400 MHz spectrometer in deuterated dimethyl sulfoxide or chloroform with TMS as the internal standard at ambient temperature. For linear poly(arylene ether) rotaxanes, molecular weights were determined by gel permeation chromatography (GPC) at room temperature in chloroform using a Waters 490 equipped with a refractive index detector which was calibrated with polystyrene standards. For hyperbranched poly(ether ether ketone) rotaxanes, GPC was carried out in a Waters GPC/ALC 150-C chromatograph equipped with a differential refractometer detector and an on-line differential viscometric detector (Viscotek 150R) coupled in parallel. The mobile phase was NMP containing 0.02 M P_2O_5 and data was recorded at 60°C at the flow rate of 1.0 ml/min. The molecular weights were calculated according to universal calibration. HPLC analyses were performed on an ISCO dual pump HPLC system comprising two Model 2350 pumps. A Waters' differential refractometer R401 was connected for analyses of crown ethers. The system was interfaced with the ISCO ChemResearch Chromatographic Data Management/System, used for

data analyses. Column: Novapak C18; L, 15 cm; ID, 3.9 μ m; pore size, 100 Å; particle size, 4 μ m. Flow rate: 2 mL/min. Sample solutions: 0.1%-10% prepared using eluting solvent. Sample volume injected: 20 mL. Eluting solvent: water/acetonitrile (80/20 and 70/30 v/v).

Model poly(ether ketone) (4.6)

A mixture of bisphenol-A (0.6849 g, 3.000 mmol), 18C6 (0.8 g, 3 mmol), DMAc (5 mL), toluene (10 mL, 5 mL of which went into the Dean Stark trap), difluorobenzophenone (0.6546 g, 3.000 mmol) and potassium carbonate (0.62 g, 4.5 mmol) was heated to reflux under nitrogen with magnetic stirring. Water generated was azeotroped by toluene into the Dean-Stark trap. The temperature of the mixture was around 130 \pm 5 $^{\circ}$ C. High viscosity was observed after two and half hours. The polymerization was allowed to proceed for a total of 4 hours. After cooling, the reaction mixture was diluted with DMAc (5 mL), then precipitated in water (500 mL), filtered and dried. The 2nd precipitation was carried out in methanol (500 mL) from THF solution (25 mL). Yield: 1.18 g (96%), $^1\text{H NMR}$ (CDCl_3) δ 1.71 (s, -CH₃, 6n H), 6.99 (d, J=8.8 Hz, 4n H), 7.02 (d, J=8.8 Hz, 4n H), 7.26 (d, J=8.8 Hz, 4n H), 7.78 (d, J=8.8 Hz, 4n H). 18-Crown-6 was recovered from the filtrates of the reprecipitations, and gave a single sharp peak at δ 3.69 in its $^1\text{H NMR}$ spectrum in CDCl_3 .

Poly(ether ketone)-rotaxa-(“42-crown-14”) (4.3)

Exactly the same procedure was used as described above for the model polymer (4.6), except that “42C14” (1.85, 3 mmol) was used instead of 18C6. The viscosity increased slowly in this case. Thus, the polymerization was allowed to proceed for 18 hours. After reaction, the polymer was first precipitated into water (500 mL) from the reaction solution. Most of the polymer precipitated as solid, while the rest formed an emulsion in water. By centrifugation, the precipitated polymer was separated, and the dilute emulsion was discarded. The 2nd and 3rd reprecipitations were carried out in methanol (500 mL) from THF solution (25 mL). In the latter two precipitations, more severe emulsions were formed. The precipitated polymer (4.3a) was isolated by centrifugation. Yield (4.3a): 0.75 g (55%). The combined emulsions in methanol were evaporated to complete dryness and the resultant solid product was stirred in methanol for 24 hours, filtered and dried. This portion (4.3b) weighed 0.35 g (22%). The $^1\text{H NMR}$ spectra of both portions were exactly the same as that for 4.6, except that an extra sharp singlet at 3.65 ppm, which comes from the crown ether, was present.

Poly(ether sulfone)-rotaxa-(“42-crown-14”) (4.4a) (two stage synthesis)

In the first stage, a mixture of bisphenol-A (0.6849 g, 3.000 mmol), “42C14” (1.85 g, 3 mmol), DMAc (5 mL), toluene (10 mL, 5 mL of which went into the Dean Stark trap), and potassium carbonate (0.62 g, 4.5 mmol) was heated to reflux for 4 hours under nitrogen with magnetic stirring. Water generated was azeotroped by toluene into the Dean-Stark trap. The temperature of the mixture was 130 $^{\circ}$ C. After stirring for 4 hours, difluorodiphenyl sulfone (0.7628 g, 3.000 mmol) was added, and the reaction was allowed to proceed for 18 hours. When the reaction mixture was poured into water/methanol (500 mL, 50/50), an emulsion was formed without any precipitate. Thus the emulsion was evaporated, to give a waxy product. The waxy

product was then washed in a small amount of water (100 mL) in which only a certain amount of polymer formed an emulsion. The polymer was isolated by centrifugation, washed with water another two times, and isolated again by centrifugation. Yield: 1.2 g, m/n: ~0.50. The emulsions formed in the three washings were combined and evaporated to complete dryness, then washed in water (50 mL) and centrifuged again. This recovered 0.67 g of polymer; m/n: 0.72. Both portions were combined together and immersed in water (200 mL) for one week without stirring (stirring caused the formation of emulsion at this time when the crown content was high). The polymer was filtered, and then stirred in water (200 mL) for a 24 hour time period. After the 2nd 24 hour time period, the m/n reached a constant value. Weight: 1.87 g (83%). ^1H NMR (CDCl_3) δ 1.69 (s, $-\text{CH}_3$, 6n H), 3.64 (s, crown, 56m H), 6.94 (d, $J=8.4$ Hz, 4n H), 7.00 (d, $J=8.4$ Hz, 4n H), 7.24 (d, $J=8.4$ Hz, 4n H), 7.84 (d, $J=8.4$ Hz, 4n H).

Poly(ether sulfone)-rotaxa-("42-crown-14") (4.4b) (one stage synthesis)

The reaction scale for this synthesis was reduced to the half of the above two stage synthesis. Toluene was only reduced by 2.5 mL. In this synthesis, everything was added together before heating, as in the synthesis of the model polymer. The polymerization was allowed to proceed for 18 hours. The polymer was first precipitated into water (250 mL). An emulsion was formed, but some polymer precipitated as a solid. The precipitate was isolated by centrifugation. The emulsion was evaporated to complete dryness, and the resultant solid product was washed with water and then filtered. The two portions were combined in THF. THF was evaporated and the m/n value determined by ^1H NMR spectroscopy. The polymer was then stirred in water (200 mL) for a 24 hour period to further remove free crown ether. After the 2nd time period, the m/n reached a constant value. Weight: 0.9 g (95%). The ^1H NMR spectrum is exactly the same as that of **4.4a**.

Poly(ether ether ketone)-rotaxa-("42-crown-14") (4.5)

A mixture of hydroquinone (0.1652 g, 1.500 mmol), "42C14" (0.93 g, 1.5 mmol), DMAc (2.5 mL), toluene (7.5 mL, 5 mL of which went into the Dean Stark trap), difluorobenzophenone (0.3273 g, 1.500 mmol) and potassium carbonate (0.35 g, 2.3 mmol) was heated to reflux under nitrogen with magnetic stirring. Water generated was azeotroped by toluene into the Dean-Stark trap. Four hours later, the polymer precipitated out of solution. The polymerization was allowed to continue for additional 14 hours. The polymer was first washed with water to remove free crown ether as well as salts and solvents. It was then stirred in methanol for 24 hours to further remove free, unthreaded crown ether. The polymer obtained was a fine brown powder. Yield: 0.52g (96%). ^1H NMR (D_2SO_4) δ 4.01-4.06 (m, crown, 56m H), 7.15-8.00 (m, 12n H).

3,5-Difluoro-4'-methoxybenzophenone (4.7)¹²

To a mixture of anisole (3.8 g, 35 mmol) and aluminum chloride (4.9 g, 37 mmol) in dry methylene chloride (20 mL) was added dropwise 3,5-difluorobenzoyl chloride (5.00 g, 28.23 mmol) in dry methylene chloride (10 mL). The mixture was stirred at room temperature under nitrogen for 5 hours. Then it was poured slowly into water (400 mL) and the product was

extracted with methylene chloride (300 mL). The organic phase was washed with water (2 x 100 mL), dried with sodium sulfate and evaporated, giving an off-white solid, 8.24 g. The product was directly used in the next step without purification.

3,5-Difluoro-4'-hydroxybenzophenone (4.8)¹²

The product prepared in the last step was dissolved in glacial acetic acid (50 mL). To this solution HBr (48%, 35 mL) was added, and the mixture was refluxed for 8 hours. The mixture was cooled and evaporated to dryness, giving a brown oil. Water (200 mL) was added, and the product was extracted with ether (5 x 100 mL). The combined organic phase was evaporated to dryness. Then the residue was subjected to flash column (silica gel) chromatography, eluting with methylene chloride followed by ethyl acetate/methylene chloride (1/20). A white solid was obtained. Overall yield (through two steps): 5.32 (81%), mp: 143.8-144.4°C (lit¹²: 134-135°C). ¹H NMR (DMSO-d₆) δ 6.92 (d, J=8.8 Hz, 2 H), 7.34 (d, J=9.6 Hz, 2 H), 7.54 (t, J=9.6 Hz, 1 H), 7.70 (d, J=8.8 Hz, 2 H), 10.60 (s, 1H)

3,5-Dimethoxy-4'-fluorobenzhydrol (4.9)¹²

A solution of 3,5-dimethoxybenzaldehyde (5.00 g, 30.0 mmol) in dry THF (10 mL) was added dropwise to a 2.0 M ether solution of 4-fluorophenylmagnesium bromide (18 mL). The mixture was then heated at reflux under nitrogen for two hours. Upon cooling to room temperature, the mixture was hydrolyzed with water (5 mL), filtered and the filtrate was evaporated to dryness. The product was purified by silica gel column chromatography, eluting with methylene chloride. The benzhydrol **4.9** was obtained as a colorless oil (lit¹²: oil). Yield: 84%; ¹H NMR (CDCl₃) δ 2.24 (d, J=3.4 Hz, 1 H), 3.77 (s, 6 H), 5.75 (d, J=3.4 Hz, 1 H), 6.37 (t, J=2.3 Hz, 1 H), 6.52 (d, J=2.3 Hz, 2 H), 7.01 (t, J=8.6 Hz, 2 H), 7.35 (q, J=8.6 Hz, 2 H)

3,5-Dimethoxy-4'-fluorobenzophenone (4.10)¹²

To a mixture of pyridinium chlorochromate (6.5 g, 30 mmol) and sodium acetate (0.80 g, 5.9 mmol) in methylene chloride (30 mL) was added a solution of the benzhydrol **4.9** (6.64 g, 25.3 mmol) in methylene chloride (15 mL). The mixture was stirred under nitrogen at room temperature for one hour. After standing for a while, the upper solution layer was decanted, and the bottom thick black oil was washed with methylene chloride several times. The combined organic solutions were evaporated to dryness. The product was purified by silica gel column chromatography, eluting with methylene chloride. The fluorobenzophenone **4.10** was obtained as a colorless oil (lit¹²: oil); yield: 6.3 g (96%); ¹H NMR (CDCl₃) δ 3.83 (s, 6 H), 6.67 (t, J=2.3 Hz, 1 H), 6.88 (d, J=2.3 Hz, 2 H), 7.15 (t, J=8.6 Hz, 2 H), 7.86 (q, J=8.6 Hz, 2 H)

3,5-Dihydroxy-4'-fluorobenzophenone (4.11)¹²

The dimethoxy ether **4.10** (6.30 g, 24.2 mmol) was dissolved in glacial acetic acid (80 mL). To this solution, HBr (48% 30 mL, 45 w/v%, 20 mL) was added, and the mixture was heated at reflux under nitrogen for 14 hours. Upon heating, the mixture became deep reddish-brown. After cooling, the mixture was poured into water (500 mL) and the product extracted with diethyl ether (5 x 150 mL). The combined ether phase was evaporated to dryness. Then the

residue was subjected to flash column chromatography eluting with ethyl acetate/hexane (7/3). The dihydroxy compound **4.11** was obtained as a yellowish solid; yield: 4.95 g (88%); mp: 142.3-143.4°C (lit¹²: 142-143°C); ¹H NMR (DMSO-d₆) δ 6.46 (t, J=2.4 Hz, 1 H), 6.52 (d, J=2.4 Hz, 2 H), 7.36 (t, J=8.8 Hz, 2 H), 7.78 (q, J=8.8 Hz, 2 H), 9.67 (s, 2 H).

Fluoro-terminated hyperbranched poly(ether ketone) (4.12)

A mixture of **4.8** (1.00 g, 4.27 mmol), N,N-dimethylacetamide (3 mL), toluene (8 mL, 5 mL of which went into the Dean-Stark trap) and potassium carbonate (0.44 g, 3.2 mmol) was heated at reflux under nitrogen. Water generated in deprotonation was azeotroped by refluxing toluene and collected in a Dean Stark trap. After 6 hours, toluene was distilled until the temperature reached ca. 160°C. The reaction was continued at this temperature for 12 hours. After cooling to room temperature, the reaction mixture was diluted with DMAc (5 mL) and then precipitated into water (250 mL). The precipitated polymer was filtered, redissolved in THF (10 mL) and reprecipitated into methanol (250 mL). This provided an off-white solid polymer: yield 0.34 g (37%). ¹H NMR (CDCl₃) δ 6.8-7.4 (m), 7.84 (br. s).

Hydroxy-terminated hyperbranched poly(ether ketone) (4.13)

This polymer was prepared from **4.11** using the same scale and similar procedure as above. The reaction discontinued after 8 hours due to difficulty in stirring because of then high viscosity produced. After cooling to room temperature, the reaction mixture was diluted with DMAc (5 mL) and then precipitated into water (pH~1, 250 mL). The precipitated polymer was filtered, redissolved in THF (10 mL) and reprecipitated into water (250 mL). This provided an off-white solid polymer: yield 0.75 g (82%). ¹H NMR (DMSO-d₆) δ 6.45 (br s), 6.54 (br s), 6.74 (br s), 6.81 (br s), 6.93 (br s), 7.18 (br d), 7.79 (br s), 9.64 (br s), 10.19 (br s)

Fluoro-terminated hyperbranched poly(ether ketone) rotaxane (4.14)

A mixture of **4.8** (1.00 g, 4.27 mmol), N,N-dimethylacetamide (3 mL), toluene (8 mL, 5 mL of which went into the Dean-Stark trap), "42C14" (2.63 g) and potassium carbonate (0.44 g, 3.2 mmol) was heated at reflux (ca. 130°C) under nitrogen for 6 hours. Water generated in deprotonation was azeotroped by refluxing toluene, and collected in a Dean Stark trap. After 6 hours, toluene was removed by distillation until the temperature of the reaction mixture reached ca. 160°C. At this temperature the reaction was allowed to continue for 12 hours. After it had been cooled down, the mixture was dissolved in water and subjected to continuous liquid-liquid extraction with toluene for three and a half days to remove unthreaded crown ether. The water solution of the product after extraction was filled in a cellular membrane (MWCO: 1000) bag, and then immersed in water for dialysis to move inorganic salts. The dialysis proceeded for three days during which fresh water was replaced at the end of each day. After dialysis, the product was recovered by rotary evaporation and dried under vacuum overnight at 100°C. This provided a brown solid. Yield: 2.1 g (228%, based on the theoretical yield of the polymer backbone); ¹H NMR (CDCl₃) d 3.64 (s, crown ethers), 6.8-7.3 (m), 7.6-7.9 (m).

OH-terminated hyperbranched poly(ether ether ketone) rotaxane (4.15)

This polyrotaxane was prepared from **4.11** using the same scale and similar procedure as above. After cooling to room temperature, the reaction mixture was diluted with DMAc (5 mL) and then precipitated into water (pH~1, 250 mL). The precipitated polymer was filtered, dissolved in THF (10 mL) and precipitated again into water (250 mL). The filtered polymer was then stirred in water for two days; at the end of each day fresh water was replaced. The polymer was filtered and dried under vacuum overnight at 100°C. This provided a yellow solid. Yield: 0.9 g (98%, based on the theoretical yield of the polymer backbone); ¹H NMR (DMSO-d₆) δ 3.50 (s, crown ether), 6.45 (br. s), 6.55 (br. s), 6.75 (br. s), 6.83 (br. s), 6.94 (br. s), 7.17 (br. s), 7.80 (br. s), 9.65 (br. s), 10.21 (br. s).

Model reaction in the presence of 18C6

This reaction was carried out using the same procedure as in the synthesis of **4.14**. 18C6 (1.13 g, 4.27 mmol) was used instead of “42C14”. Gelation occurred after about 12 hours. Thus, the product was purified by washing with water. The residue in the water washing contained pure 18C6 (3.69 ppm according to ¹H NMR spectroscopy in CDCl₃). The sol fraction of the product was extracted by chloroform; its ¹H NMR spectrum is given in Figure 4.15 in which a peak at 3.65 ppm in the aliphatic region is observed.

Chapter 5

Suggestions and Future Work

The preparation of poly(ether ether ketone) (PEEK) rotaxane containing crown ether macrocycles should continue to be explored in the future. PEEK is a very important engineering thermoplastic. This polymer is highly crystalline and is normally prepared at high temperatures (320°C) due to its very poor solubility. As we have discussed before, one of the major property changes by formation of polyrotaxane is significant improvement of solubility. Thus, it is of great interest to see if that can help facilitate the production of PEEK, such as allowing the synthesis at lower temperatures in low boiling solvents as the result of improved solubility. From the preliminary results (see section 4.2.2 in Chapter 4 of Part II) it looks like aliphatic crown ethers are too flexible to break down the strong intermolecular interactions of the PEEK macromolecules even at 20% (by mass) crown ether (“42C14”); the polyrotaxane precipitated out during the reaction at 160°C. Thus, it is suggested that further studies should use semi-rigid crown ethers. Oligomeric cyclic mixtures may be used because they can be prepared at low cost, and also because of large threading-dethreading equilibrium constants for the large ring size macrocycles. There is no concern of dethreading during the purification period after reaction; after all, the unthreaded crown ethers need to be removed. If the synthesis is successful, the method may be extended to other high performance polymers which are difficult to prepare due to their poor solubilities.

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