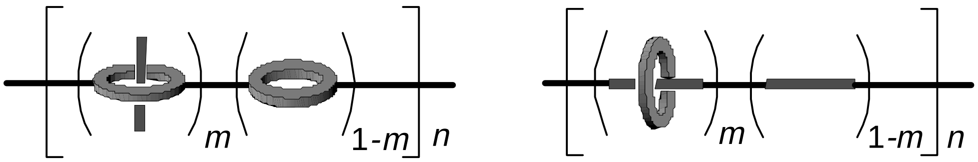
Chapter 13

Synthesis of Main-Chain Polymacrocycles as Precursors to Novel Polypseudorotaxanes

13.1. Introduction

A polypseudorotaxane is a supramolecular structure in which macrocycles are threaded by linear segments and one of the components is part of a macromolecule. There are two types of main-chain polypseudorotaxanes to be realized as illustrated in Figure 13.1. Because of their unique architectures these supramolecular structures possess intriguing properties.[1] To date we and others using noncovalent forces of hydrogen bonding, charge transfer interaction, metal coordination, etc have successfully constructed main-chain polypseudorotaxanes of both types **1** and **2**.[1-6] Recently, Gong and Gibson prepared a main-chain polypseudorotaxane of type **1** in solution from poly(ester crown ether) **3** and *N*,*N*'-bis(β-hydroxyethyl)-4,4'-bipyridinium bis(hexafluorophosphate) (**4**) and its formation was evidenced by the color change due to charge transfer interaction and by ^{1}H NMR spectroscopy.[1] The formation of this new class of main-chain polypseudorotaxane **5** is driven by hydrogen bonding and electrostatic interactions between the π-electron rich aromatic rings of the crown ether units incorporated in **5** and the π-electron deficient bispyridinium salt unit in **4**. It was shown that solution viscosity, thermal properties, and solubility of **5** are tunable by altering the fractions of the complexation sites along the polymer backbone, *i.e.*, *m*/*n* values. For larger *m*/*n* values, higher solution viscosity and glass transition temperatures (T_g) and better solubility of **5** were observed. Inspired by these preliminary results, new main-chain polymacrocycles, poly(ester crown ether) and poly(urethane crown ether), were synthesized as precursors to the corresponding main-chain polypseudorotaxanes of type **1**.



1 **2**

Figure 13.1. Cartoon representation of two types of main-chain polypseudorotaxanes.

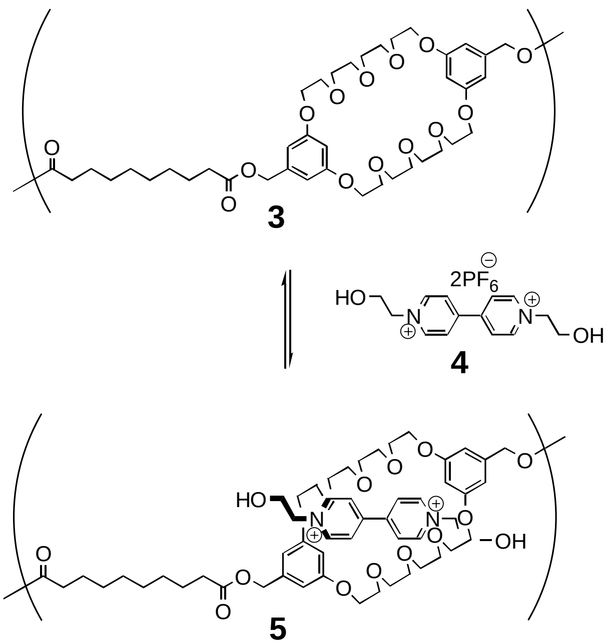


Figure 13.2. Self-assembly approach to construct a main-chain polypseudorotaxane of type **1**.[1]

13.2. Synthesis and Characterization

Following the method developed in our laboratories two different main-chain polymacrocycles were synthesized.[7-9] The synthesis of bis(5-hydroxymethyl-1,3-phenylene)-32-crown-10 was previously described in section 2.2.3.

13.2.1. Poly(ester crown ether) (10)

In a control reaction we synthesized polyester **8** in solution by reacting 1,4-benzenedimethanol (**6**) and isophthaloyl dichloride (**7**) in the presence of pyridine (Figure 13.3). **8** is a crystalline polymer with melting transition at 114-134°C (DSC) and is soluble in common organic solvents. The ^{1}H NMR spectrum of **8** is in good agreement with the polymer structure. In addition, the IR spectrum indicated the formation of ester bonds at 1720 cm^{-1}. The polyester had M_n=3.2 and M_w=4.9 kg/mol as determined by GPC. Despite the low molecular weight of the model polyester obtained by this protocol, we decided to proceed to synthesize poly(ester crown ether) **10** under the same reaction conditions.

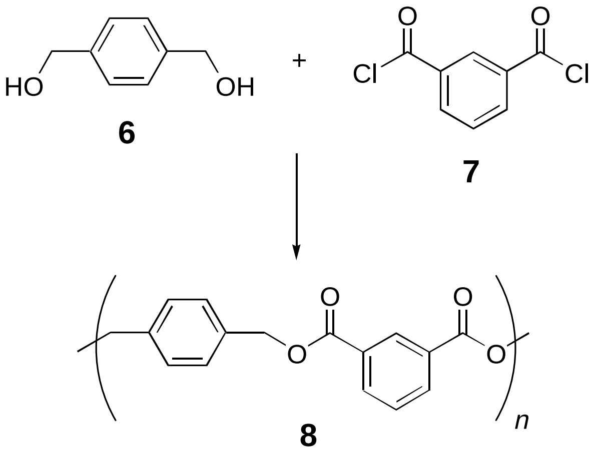


Figure 13.3. Synthesis of model polyester **8**.

The step growth polymerization between bis(5-hydroxymethyl-1,3-phenylene)-32-crown-10 (**9**) and **7** yielded main-chain poly(ester crown ether) **10** (Figure 13.4). As for the poly(ester crown ether) **5**, **10** is an amorphous polymer with M_n and M_w 4.1 and 5.8 kg/mol (GPC in chloroform), respectively. The polymer is soluble in organic solvents. The IR spectrum of the polyester shows a characteristic band at 1740 cm^{-1} for C=O stretching of the ester group. The ^{1}H NMR spectrum of **10** is simple and consistent with the polymer structure and shows no evidence of thermally induced and/or acid catalyzed ring open reactions of the crown ether, which would consequently form chemically cross-linked networks. It has been demonstrated in our laboratories that crown ethers containing more than 23 atoms with homodifunctionality of primary alcohol groups undergo *in situ* threading during polymerizaiton to form physically cross-linked structures when reacted with diacid chloride monomers.[10,11] As shown in Figure 13.5, the *in situ* threading is facilitated by intermolecular hydrogen bonding of crown ether monomers. However, a combination of the low polydispersity (PDI=1.4) obtained from the GPC analysis and excellent solubility in common organic solvents suggests that the extent of cross-linking in **10** is relatively low.

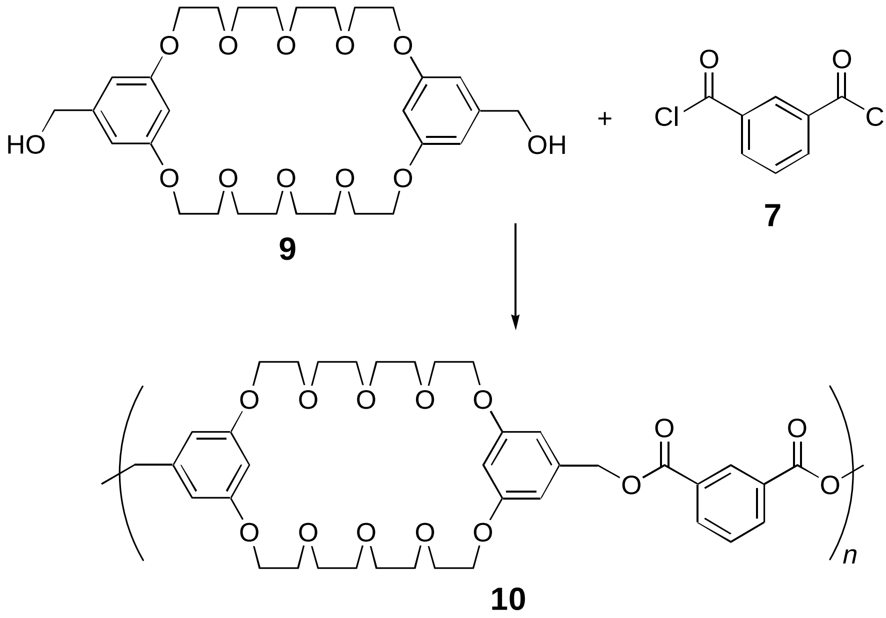


Figure 13.4. Synthesis of poly(ester crown ether) **10**.

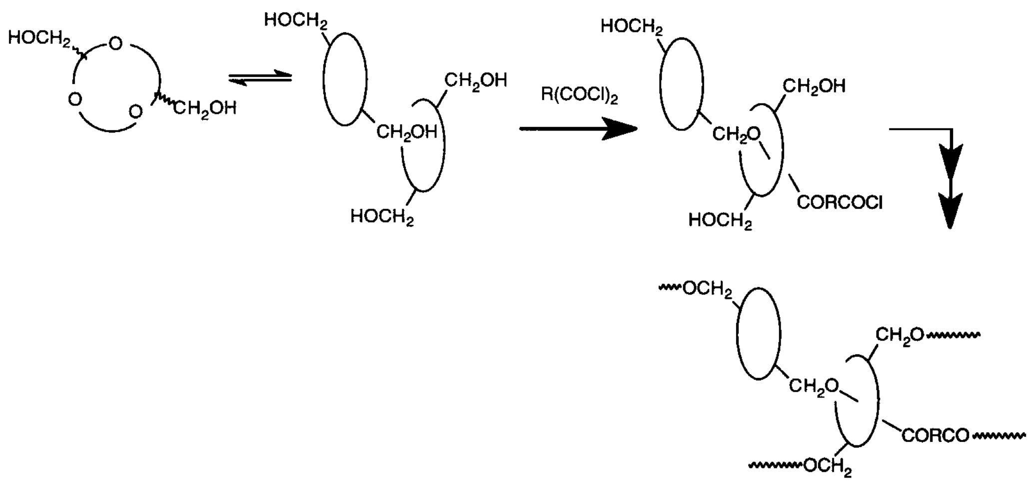


Figure 13.5. Mechanism of physical cross-linking *via* intermolecular hydrogen bonding between crown ether monomer molecules.[10]

13.2.2. Poly(urethane crown ether) (13)

The synthesis of polyurethane **12** is represented in Figure 13.6. **12** was prepared in solution from 1,4-benzenedimethanol (**6**) and MDI (**11**). The model polyurethane **12** is insoluble in most nonpolar solvents and only sparingly soluble in polar aprotic solvents such as DMSO. The ^{1}H NMR spectrum of **12** is consistent with the formation of polyurethane structure. The IR spectrum indicates a stretching band typical for the N-H bonds of urethane linkage at 3320 cm^{-1}.

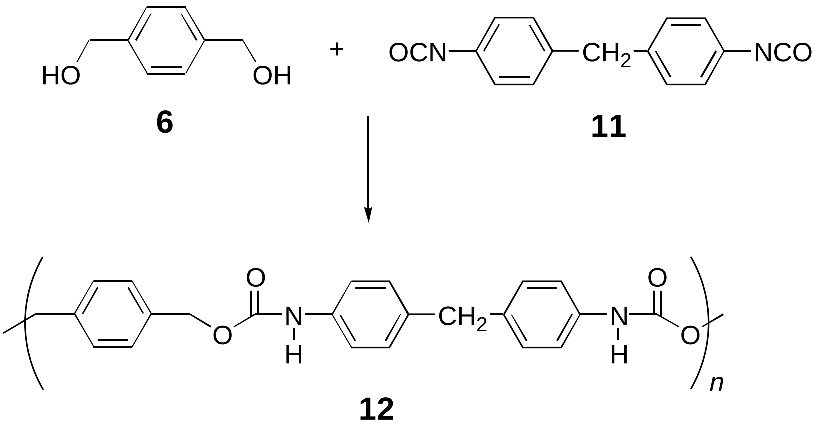


Figure 13.6. Synthesis of model polyurethane.

Similarly, poly(urethane crown ether) **13** was prepared in solution from **9** and **11** (Figure 13.7). The resulting polyurethane is soluble in common organic solvents unlike the model polyurethane **12**. The ^{1}H NMR spectrum of **13** shows all the signals required for the structure of the polymer. Also, the N-H stretch band appears at 3210 cm^{-1} in the IR spectrum of **13**, indicating the presence of the urethane linkage. The good solubility of the polyurethane allowed the molecular weight determination by GPC (chloroform, PS standard) which revealed the number and weight average molecular weight of 2.4 and 3.0 kg/mol, respectively. Because of the low molecular weight polyurethane obtained for this polymerization we decided to carry out the same reaction in melt. The monomers were heated to 110^{o}C and the melt reaction mixture was stirred vigorously. Within 5 min the stirrer came to a complete stop due to the significant increase in viscosity. The resulting polyurethane was insoluble in any organic solvents and only swelled in polar aprotic solvents. As stated in section 13.2.1, the swelling of the polymer suggests that the network system may have been formed through rotaxane formation (Figure 13.5). Similar observations were reported for polyesterification reaction between **9** and sebacoyl chloride in the melt.[10]

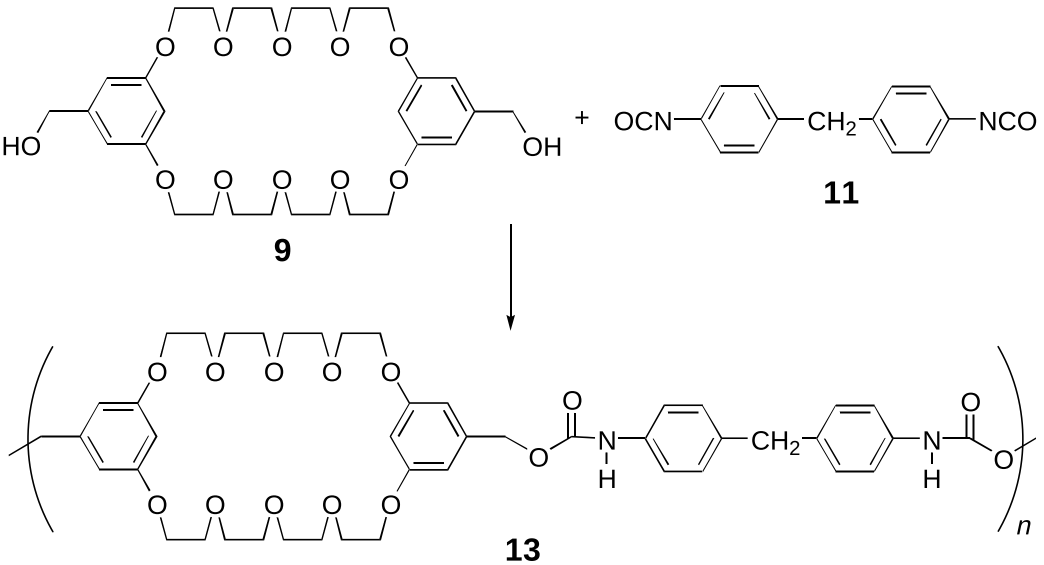


Figure 13.7. Synthesis of poly(urethane crown ether).

13.3. Conclusions

Two low molecular weight main-chain polymacrocycles were synthesized *via* step-growth polymerization. The polymacrocycles prepared by solution polymerization have excellent solubility, indicating a relatively low extent of physical cross-linking in these polymers. Thus, they can be used as building components to construct main-chain polypseudorotaxanes of type **1**. In contrast, the poly(urethane crown ether) prepared in the melt indicated the formation of a network system due a high extent of *in situ* threading during the polymerizaiton.

13.4. Experimental

Pyridine was stirred with CaH_2 overnight and distilled and 4,4'-methylenebis(phenyl isocyanate) (MDI) was distilled twice *in vacuo* (bp 163-165^{o}C @1.0 mmHg) prior to the use. 1,4-Benzenedimethanol was recrystallized twice from acetone prior to the polymerization reactions. Tetrahydrofuran (THF) was distilled from Na and benzophenone. All other solvents were used as received. Melting points were taken on a Mel-Temp II melting point apparatus and are uncorrected. The 400 MHz ^{1}H NMR spectra were recorded on a Varian Unity with tetramethylsilane (TMS) as an internal standard. The following abbreviations are used to denote splitting patterns: s (singlet), d (doublet), t (triplet), and m (multiplet). The IR spectra were taken on a Nicolet Impact 400 infrared spectrometer using pulverized KBr as the medium. Gel permeation chromatography (GPC) was performed with an ISCO model 2300, coupled with an ISCO UV detector, using PLgel 5 mm MIXED-D (300 x 7.5 mm) columns and chloroform as solvent and calibrated with PS standards. Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer Series-4 calorimeter under a nitrogen purge using indium as the calibration standard. Scanning electron microscopy (SEM) was performed on a Philips 420T. The copper substrate was sputtered with gold after sample deposition and before exposure to the electron beam. Elemental analyses were obtained from Atlantic Microlab, Norcross, GA. Mass spectra were provided by the Washington University Mass Spectrometry Resource, an NIH Research Resource (Grant No. P41RR0954).

Polyester 8 (model reaction). To a 25 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet were added 1,4-benzenedimethanol (**6**) (1.33 g, 9.67 mmol) and pyridine (15 mL). To this was added a solution of isophthaloyl dichloride (**7**) (1.96 g, 9.65 mmol) in THF (4 mL) at 0^{o}C. The reaction mixture was gradually warmed to room temperature and vigorously stirred for 12 h. The mixture was then precipitated into methanol twice to afford a white solid (1.98 g, 77% yield), mp 114-134^{o}C. GPC (chloroform, PS standards, kg/mol): M_n=3.2, M_w=4.9, PDI=1.5. ^{1}H NMR (400 MHz, chloroform-*d*, 22^{o}C): δ=5.38 (4H, s), 7.46 (4H, s), 7.49 (1H, t, J = 8.0 Hz), 8.23 (2H, d, J = 8.0 Hz), and 8.73 (1H, s). IR (cm^{-1}): 1720 (C=O stretch) and 1225 (C-O stretch).

Poly(ester crown ether) 10. To a 10 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet were added bis(5-hydroxymethyl-1,3-phenylene)-32-crown-10 (**9**) (0.2144 g, 0.3593 mmol) and pyridine (1.5 mL). To this was added a solution of **7** (0.0730 g, 0.3596 mmol) in THF (2 mL) at 0^{o}C. The reaction mixture was gradually warmed to room temperature and vigorously stirred for 12 h. The mixture was then precipitated into methanol twice to afford a colorless gummy material (0.18 g, 70% yield). ^{1}H NMR (400 MHz, chloroform-*d*, 22^{o}C): δ=3.67 (16H, s), 3.81 (8H, s), 4.05 (8H, s), 5.23 (4H, s), 6.35-6.55 (6H, m), 7.49 (1H, t, *J* = 7.6 Hz), 8.21 (2H, d, *J* = 7.6 Hz), and 8.71 (1H, s). GPC (chloroform, PS standards, kg/mol): M_n=4.1, M_w=5.8, PDI=1.4. IR (cm^{-1}): 1740 (C=O stretch) and 1235 (C-O stretch).

Polyurethane 12 (model reaction). To a 10 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet were added **6** (0.1594 g, 1.154 mmol) and THF (1.5 mL). To this was added MDI (**11**) (0.2887 g, 1.154 mmol) and the reaction mixture was warmed to 70^{o}C. A noticeable viscosity change was observed after 1 h and within 5 h the polymer precipitated out of the solution. The precipitate was filtered, redissolved in DMSO, and reprecipitated into methanol twice to afford a white solid (0.42 g, 93% yield), mp 308-310^{o}C (capillary). IR (cm^{-1}): 3320 (CON-H stretch), 3040 (aromatic C-H stretch), 1710 (C=O stretch) and 1595 (C=C stretch). ^{1}H NMR (400 MHz, DMSO-d_6, 22^{o}C): δ=3.76 (2H, s), 5.11 (4H, s), 7.07 (4H, d, *J* = 8.0 Hz), 7.34 (4H, d, *J* = 8.0 Hz), and 7.41 (4H, s).

Poly(urethane crown ether) 13 (in solution). To a 10 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet were added **9** (0.1107 g, 0.1855 mmol) and THF (1.5 mL). To this was added **11** (0.0464 g, 1.854 mmol) and the reaction mixture was vigorously stirred at 60^{o}C for 2 days. The mixture was precipitated into methanol to afford a yellowish gummy material (0.10 g, 64% yield). GPC (chloroform, PS standards, kg/mol): M_n=2.4, M_w=3.0, PDI=1.3. ^{1}H NMR (400 MHz, chloroform-*d*, 22^{o}C): δ=3.65 (16H, s), 3.73 (2H, s), 3.78 (8H, s), 3.97 (8H, s), 4.96 (4H, s), 6.31-6.43 (6H, m), 7.03 (4H, d, *J* = 8.0 Hz), and 7.27 (4H, d, *J* = 8.0 Hz). IR (cm^{-1}): 3330 (CON-H stretch), 2900 (aromatic C-H stretch), 1740 (C=O stretch) and 1615 (C=C stretch).

Poly(urethane crown ether) 13 (in neat). To a 5 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet were added **9** (0.2804 g, 0.4699 mmol) and **11** (0.1176 g, 0.4699 mmol). The flask was immersed in a preheated oil bath at 110^{o}C and the reaction mixture was vigorously stirred until the stirrer came to a complete stop. The crude product was washed with methanol to give a colorless solid (0.37 g, 93% yield), which was insoluble in any common organic solvents. IR (cm^{-1}): 3210 (CON-H stretch), 2900 (aromatic C-H stretch), 1715 (C=O stretch) and 1610 (C=C stretch).

13.5. References

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