Chapter 9

Non-Covalent Chemical Modification of Crown Ether Side-Chain Polymethacrylates with a Secondary Ammonium Ion: A New Family of Polypseudorotaxanes

9.1. Introduction

Supramolecular chemistry has increasingly been applied to prepare polymeric materials such as liquid crystalline polymers,[1-4] dendrimers,[5-7] linear and cross-linked "smart" polymers,[8-18] and polypseudorotaxanes of various types.[19-26] As elegantly demonstrated in numerous recent reports, the use of strong non-covalent interactions in constructing such polymeric structures provides efficiency and versatility. Moreover, the reversible nature of the bonding in these supramolecular polymers, unlike in the conventional counterparts, ensures thermodynamic stability in the final polymers, *i.e*., the formation of kinetically induced side products is eliminated.

Previously, we reported successful synthesis of main-chain polypseudorotaxanes of type **1a** (Figure 9.1) based on poly(ester-32-crown-10) and *N*,*N*'-dialkyl-4,4'-bipyridinium salts, "paraquats", by taking advantage of the enthalpic driving forces of hydrogen bonding and electrostatic interaction.[19,20] Physical properties of the main-chain polypseudorotaxanes were shown to be tunable by adjusting the fraction of the crown ether receptors threaded with paraquat. Main-chain polypseudorotaxanes of type **1b** (Figure 9.1) from linear polymers containing aromatic guest units and a tetracationic cyclophane host with two paraquat units have also been reported by us and others.[21-24] Swager et al. synthesized polythiophenes and poly(phenyleneethynylene) containing crown ether receptors that are capable of forming side-chain polypseudorotaxanes with paraquat (type **2** in Figure 9.1) as sensory materials.[26] However, no thermal or morphological properties of these materials of type **2** were reported.
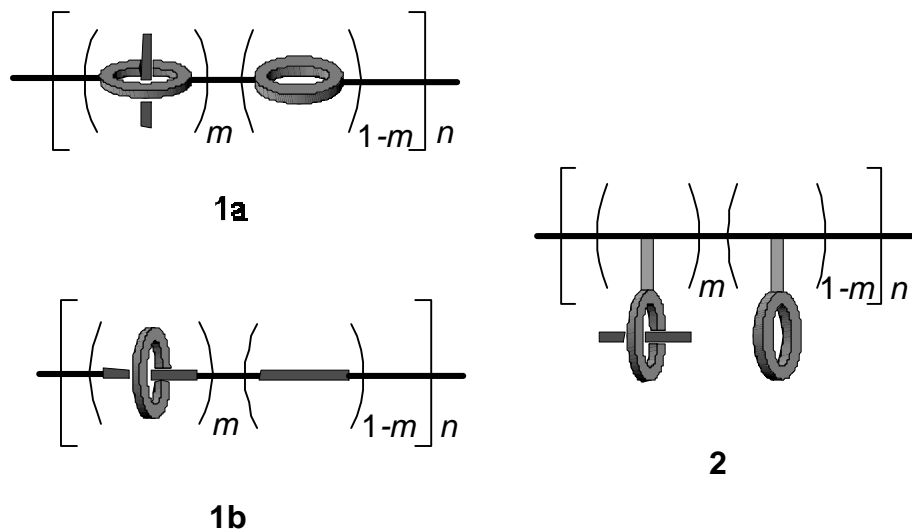
1a

1b

2

Figure 9.1. Illustration of three types of polypseudorotaxanes. **1a** and **1b**: linear main-chain polypseudorotaxanes, **2**: linear side-chain polypseudorotaxanes.

Herein we describe the preparation of side-chain polypseudorotaxanes of type **2** in solution where poly(methyl methacrylate) copolymers bearing randomly distributed dibenzo-24-crown-8 (DB24C8) units (76.7, 32.3, 21.2, and 6.29 mole %) are the polytopic hosts and dibenzylammonium hexafluorophosphate is the guest unit. We also demonstrate how the solid state physical properties can be altered by this simple molecular recognition between the crown ether receptors and the ammonium salt. These systems are based on the extensive work of Stoddart et al. with monomeric DB24C8 and secondary ammonium ions.[27-31]

9.2. Results and Discussion

9.2.1. Synthesis

A crown ether side-chain polymethacrylate with $m/n=0.767\pm0.010$ (**5a**) was prepared by reacting poly(methacryloyl chloride) (**3**) with an excess of 4-hydroxymethylbis(1,2-phenylene)-24-crown-8 (**4**) for an extended period of time (Figure 9.2) and then quenching with methanol to ensure total esterification. The IR spectrum of **5a** revealed no –OH stretching band, ruling out the possibility of carboxylic acid formation. To minimize "self-threading" of **5** *in situ*, the esterification reaction of **3** was run in a substantially dilute condition.[32-38] A low PDI (1.3) obtained by GPC indicates

that **5** contains predominately linear chains. **5a** is an amorphous polymer with $T_g=66^{\circ}$C as indicated by DSC measurement. The considerably lower T_g with respect to that of poly(methyl methacrylate) (**6**) ($T_g=85^{\circ}$C), prepared by quantitative esterification of **3** with MeOH, is presumably due to the flexible and bulky crown ether pendant groups, giving rise to ineffective packing of the polymer chains in the solid state. In addition, three other crown ether side-chain polymethacrylates (**5b**, **5c**, and **5d**) with lower m/n values were synthesized by appropriately adjusting the molar ratio of **4** to **3**.
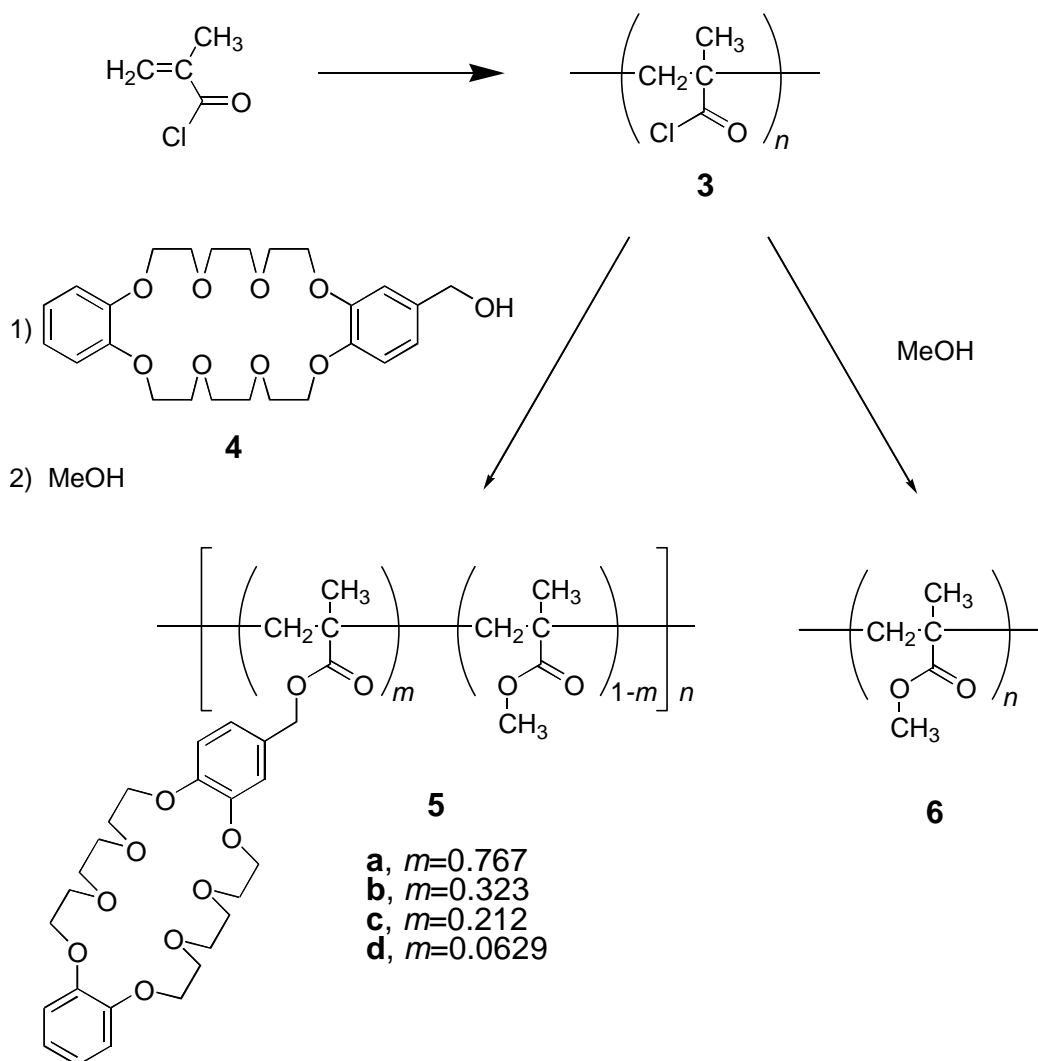

Figure 9.2. Synthesis of the crown ether side-chain polymethacrylate **5** and PMMA (**6**) *via* polymer precursor **3**.

Stereochemical information (tacticity) on **5** was successfully obtained from spectroscopic analysis of **6**. The ^{1}H NMR spectrum of **6** in the aliphatic region exhibited the principle resonance (a singlet) corresponding to the methylene protons (-CH_2-) at 1.81 ppm, showing that polymers **5** are predominately syndiotactic, as generally observed for vinyl polymers synthesized with free radical intiators.[39]

The chemical compositions of **5** were determined by analyzing the corresponding ^{1}H NMR spectrum, *e.g.*, Figures 9.3a and b, which revealed a broad resonance corresponding to the H_α protons of the crown ether pendant group at 4.1 ppm along with another broad resonance corresponding to the methyl ester group (CH_3O-) at 3.5-3.6 ppm, indicating that **5** are copolymers. From careful integration of these two resonances in Figure 9.3a, it is calculated that **5a** contains 76.7 mole % of the crown ether pendant methacrylate repeat unit and 23.3% of methyl methacrylate repeat unit (m/n=0.767). For the analysis of polymer **5a**, the ^{1}H NMR spectrum (Figure 9.3a) was expanded vertically and a deconvolution technique was utilized since the resonance corresponding to the CH_3O- protons is weak in intensity and partially overlapped with the resonance of H_γ protons. Alternatively, integration of the resonance corresponding to the CH_3O- protons obtained by subtracting integration of well-resolved resonance for H_α protons (X 3) from entire integration of resonances for H_α, H_β, H_γ, and CH_3O- protons (3.4-4.4 ppm) gave similar results in determination of m/n values. The incomplete esterification of **3** with excess **4** is presumably due to steric crowding at the remaining reaction sites after a certain conversion is achieved. The ^{1}H NMR spectrum of **5a** did not exhibit the principle resonance for the methylene protons (-CH_2-) at 1.81 ppm, suggesting that **5a** does not contain substantially long blocks of poly(methyl methacrylate).[39] Thus we conclude that **5a** is a random copolymer. The single T_g observed for **5a** is also consistent with random arrangement of the two repeat units in the polymer chain. By the same analogy, **5b**, **5c**, and **5d** are random copolymers with m/n values of 0.323, 0.212, and 0.0629, respectively.
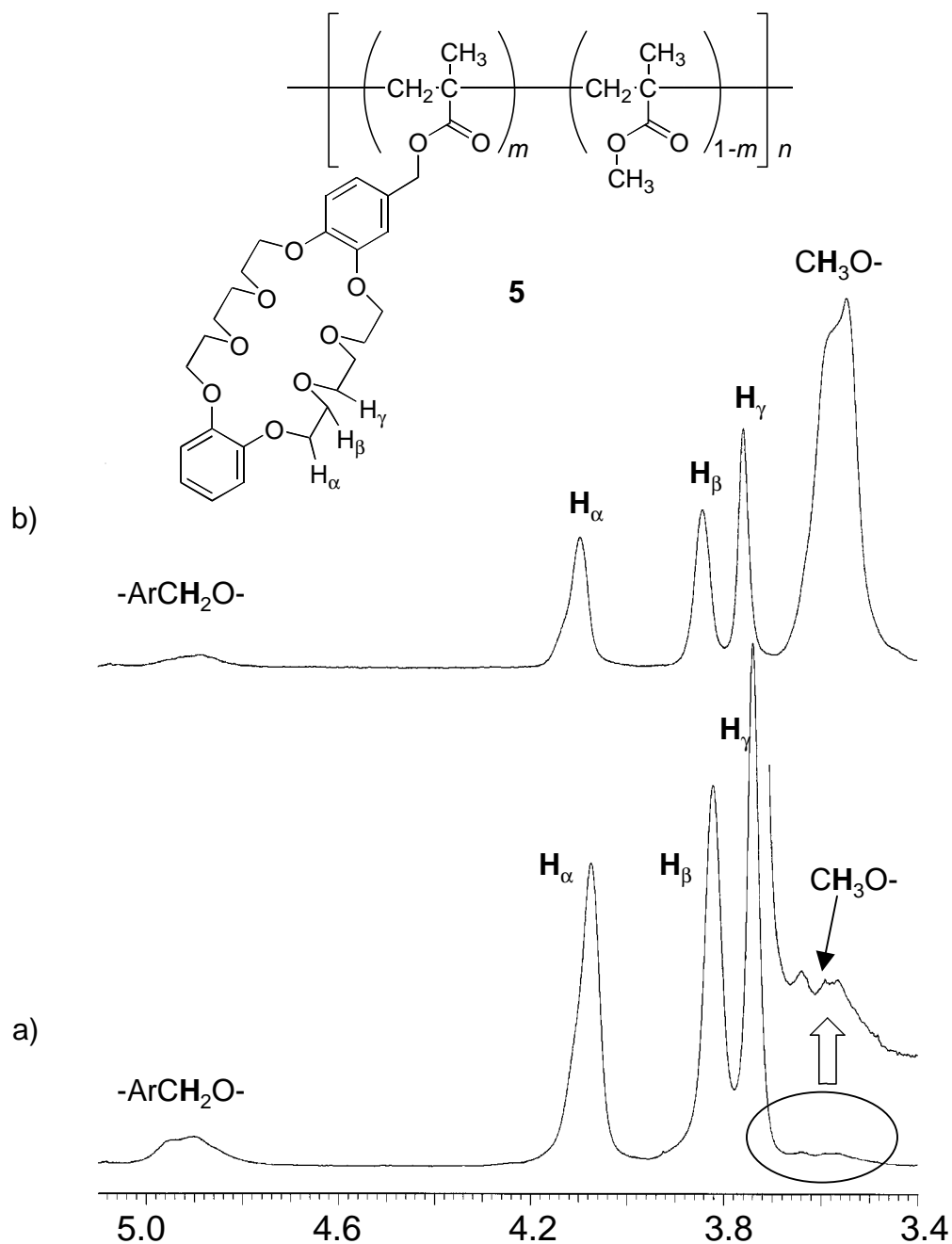
Figure 9.3. The ^{1}H NMR spectra in the aliphatic region of solutions (10 mL) of a) **5a** with an insert of the vertically enlarged CH$_3$O- signal and b) **5d** (400 MHz, acetone-d_6/chloroform-d (1/1, v/v), 22°C).

9.2.2. Complexation studies

Interaction of polytopic hosts **5** and dibenzylammonium salt **7** was expected to yield side-chain polypseudorotaxanes **8** (Figure 9.4). As for other supramolecular assemblies based on pseudorotaxane complexes formed between dibenzylammonium salt

7 and dibenzo-24-crown-8 (DB24C8) moieties in solution,[6,14,15,27-31,40] the ^{1}H NMR spectra recorded for solutions of **5** and **7** (*e.g.*, Figures 9.5c and d) revealed four sets of signals corresponding to free crown ether moieties in **5,** free **7**, complexed crown ether moieties in **8**, and complexed **7**, due to slow exchange of host-guest moieties on the ^{1}H NMR time scale. Since the concentration of each species at equilibrium can be determined from the initial concentrations of the crown ether methacrylate repeat unit of **5** and **7** and integration of the appropriate signals (the benzylic protons of free and complexed **7**) in the ^{1}H NMR spectra, the association constants were calculated by the standard expression K_a=[complexed **7**]/[free crown ether moieties in **5**][free **7**].
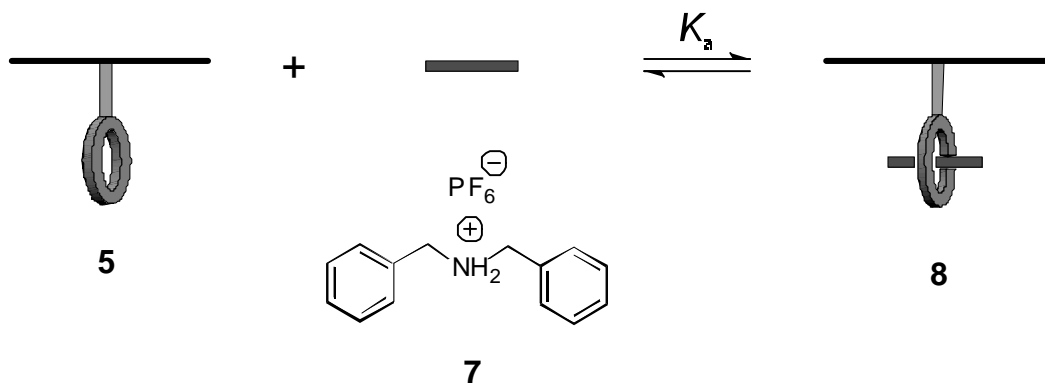

Figure 9.4. Cartoon representation of construction of **8** from **5** and **7**.
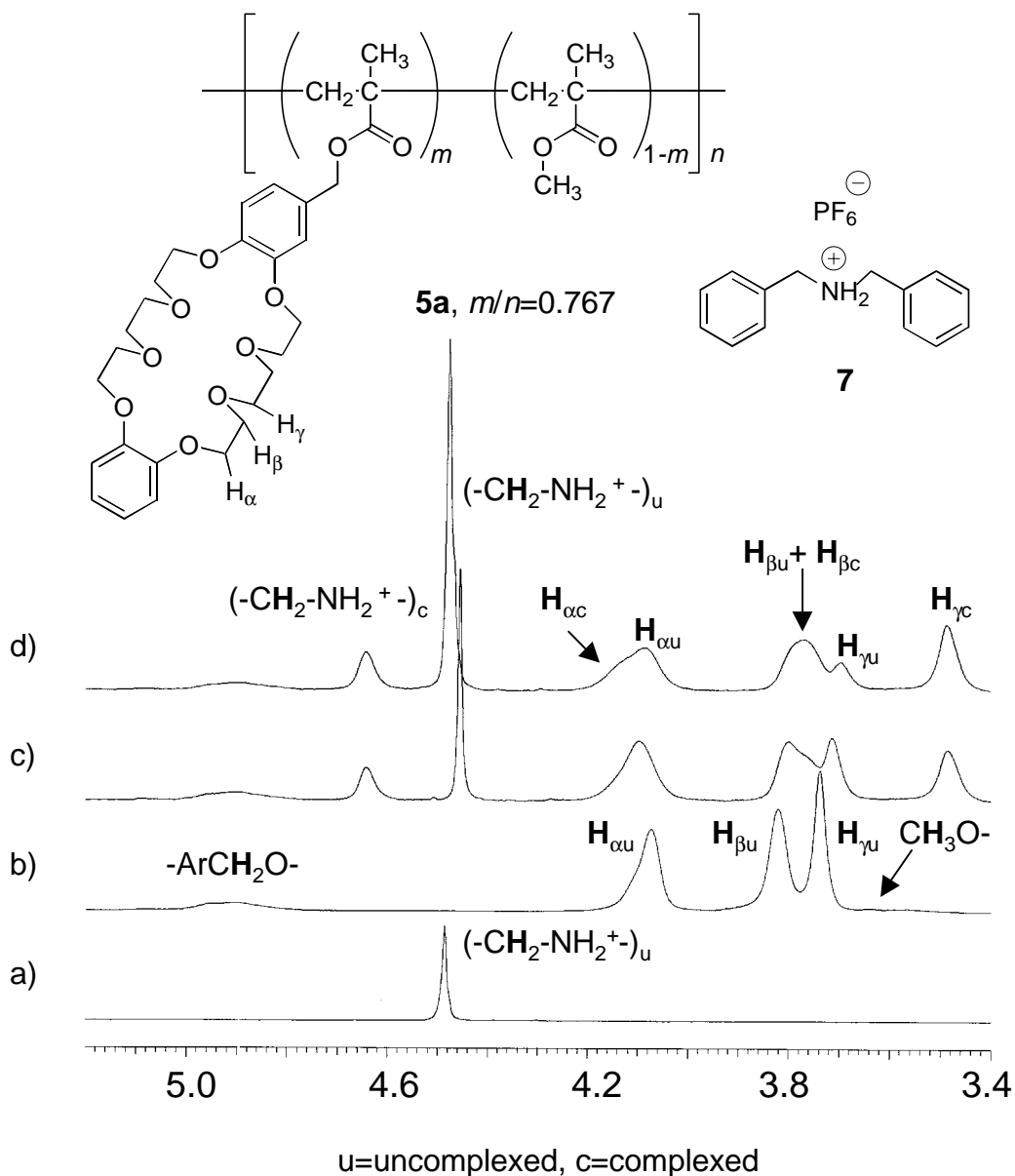
Figure 9.5. The stacked ^1H NMR spectra in the aliphatic region of solutions **5a** and **7** at a) 0/10, b) 10/0, c) 10/20, and d) 10 mM/40 mM (400 MHz, acetone-d_6/chloroform-d (1/1, v/v), 22°C).

Not only does Table 1 show that the apparent "K_a" values obtained for complexation of **5** and **7** are significantly lower than that for monomeric DB24C8 and **7**, but it also shows that they are dependent on the relative initial concentrations of **7** (varied from 10 to 80 mM) to **5** (fixed at 10 mM for **5a-c** and 12 mM for **5d**) and decrease non-linearly with increasing concentration of **7**. The word "apparent" is used to denote that the K_a values determined for complexation of **5** and **7** are concentration dependent under

our experimental conditions. Moreover, the crown ether moieties in **5** with smaller m/n values are shown to accommodate the guest unit more efficiently (Table 2), *e.g.*, the fraction of crown ether moieties complexed is 0.84 with **5d** ($m/n=0.0629$) vs. 0.60 with **5a** ($m/n=0.767$) at 80 mM of **7**; however, in all cases there seem to be limits as to what fraction of crown ether moieties in **5** can be loaded. Figure 9.6 shows that fraction complexed gradually reaches a plateau at higher concentrations of **7**.

Table 9.1. The apparent "K_a" values for complexation of **5** and **7** as a function of [**7**]

[**7**](mM)	apparent "K_a" $(M^{-1})^{a,b}$			
	5a	**5b**	**5c**	**5d**
10	76	180	220	300
20	58	120	130	160
40	38	71	77	90
60	26	54	68	71
80	20	42	62	63

a)The apparent "K_a" was calculated by using the expression "K_a"=[complexed **7**]/[free crown ether moieties in **5**][free **7**] (relative error $\leq \pm 14\%$).
b)The initial concentrations of crown ether moieties in **5** were maintained at 10 mM in acetone-d_6/chloroform-d, 1/1, v/v except for **5d** (12 mM).

Table 9.2. Fraction of complexed crown ether moieties **8** as a function of [**7**]

[**7**](mM)	fraction complexed^{a,b}			
	5a	**5b**	**5c**	**5d**
10	0.34	0.48	0.52	0.59
20	0.47	0.62	0.64	0.71
40	0.57	0.70	0.72	0.78
60	0.58	0.73	0.78	0.82
80	0.60	0.75	0.82	0.84

a)Fraction of complexed crown ether moieties was calculated from [complexed crown ether moieties in **8**]/[crown ether moieties in **5**] (relative error $\leq \pm 6\%$).
b)The initial concentrations of crown ether moieties in **5** were maintained at 10 mM in acetone-d_6/chloroform-d, 1/1, v/v except for **5d** (12 mM).
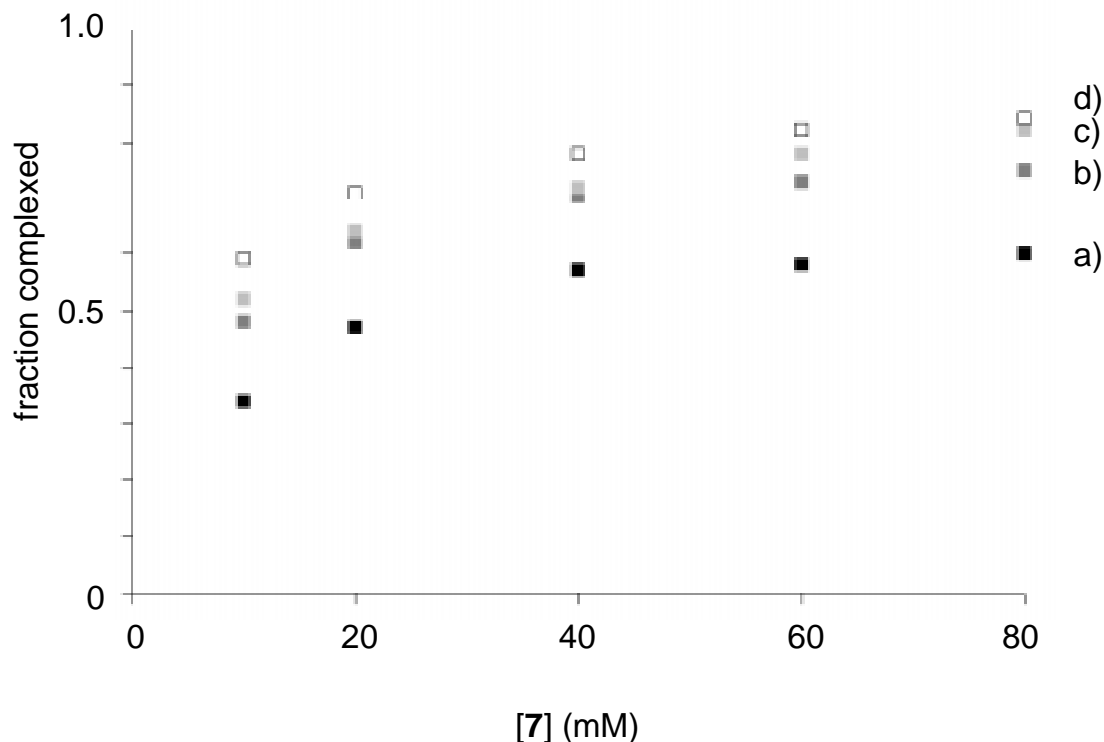
Figure 9.6. Plots of fraction complexed in **8** versus concentration of **7**: a) **5a**, b) **5b**, c) **5c**, and d) **5d** vs. **7** (relative error ≤ ±6%). The initial concentrations of crown ether moieties of polymers **5a**-**c** and **5d** were 10 mM and 12 mM, respectively.

These phenomena reflect the following points: 1) the mobility of the crown ether moieties in **5** is reduced because of their covalent attachment onto the polymethacrylate backbone,[19,20] giving rise to the lower apparent "K_a" than the monomeric model system; 2) steric effects caused by crown ether moieties and pseudorotaxane structures in **8** contribute negatively to pseudorotaxane formation at adjacent available crown ether moieties as % loading increases. In other words, the available crown ether host sites in **5** do not act independently.

To further investigate steric effects between crown ether receptors of neighboring repeat units on % loading, molecular modeling of a syndiotactic crown ether side-chain oligomethacrylate with 7 repeat units was performed and one possible configurational sequence of this heptamer (Figure 9.7) revealed that crown ether moieties of every other, but not adjacent, repeat units are situated in close proximity for potential interference upon complexation with the guest unit. In Figure 9.8 are represented planar zigzag projections of pentad sequences and their frequencies of occurrence as a function of *m/n*

values are listed in Table 3. The probability of a crown ether at position 3 having crown ether neighbors at both positions 1 and 5 is expressed by $P_{ccc}=P_{cycyc}=$(*m/n* for **5**) x $(1)^3$ x (*m/n* for **5**), where c is crown ether, m is methyl ester, and y is either c or m. For mcc and ccm sequences, their total probability is determined by solving $P_{mcc}+P_{ccm}=P_{mycyc}+P_{cycym}=2[($*n-m/n* for **5**) x $(1)^3$ x (*m/n* for **5**)]. Likewise, $P_{mcm}=P_{mycym}=($*n-m/n* for **5**) x $(1)^3$ x (*n-m/n* for **5**). Intuitively, a crown ether at position 3 of pentads with mcm sequences should be most favorable for complexation due to the least steric crowding from positions 1 and 5. Pentads with mcc and ccm sequences should present more steric obstacles at position 3 than mcm, but not as much as with ccc sequences (*i.e.*, $K_{mcm}>K_{mcc}=K_{ccm}>K_{ccc}$ in Figure 9.9). Thus, we postulate that a crown ether at position 3 with m (methyl ester) neighboring groups at both positions 1 and 5 will preferentially accommodate the guest unit and then a crown ether at position 3 with m at either position 1 or 5 will be occupied.
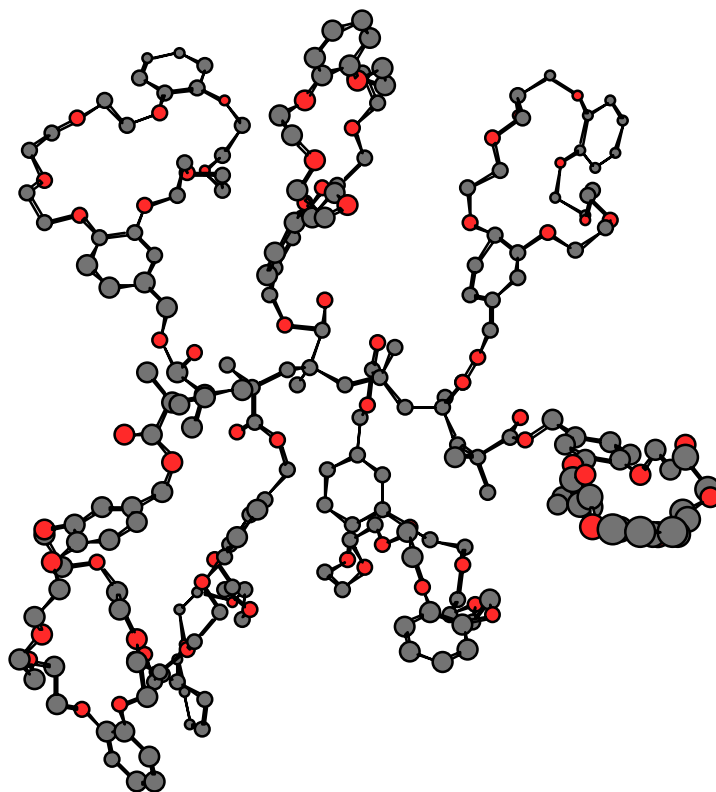

Figure 9.7. Representation of one possible configurational structure of syndiotactic crown ether side-chain heptamer. The hydrogen atoms are omitted for clarity.
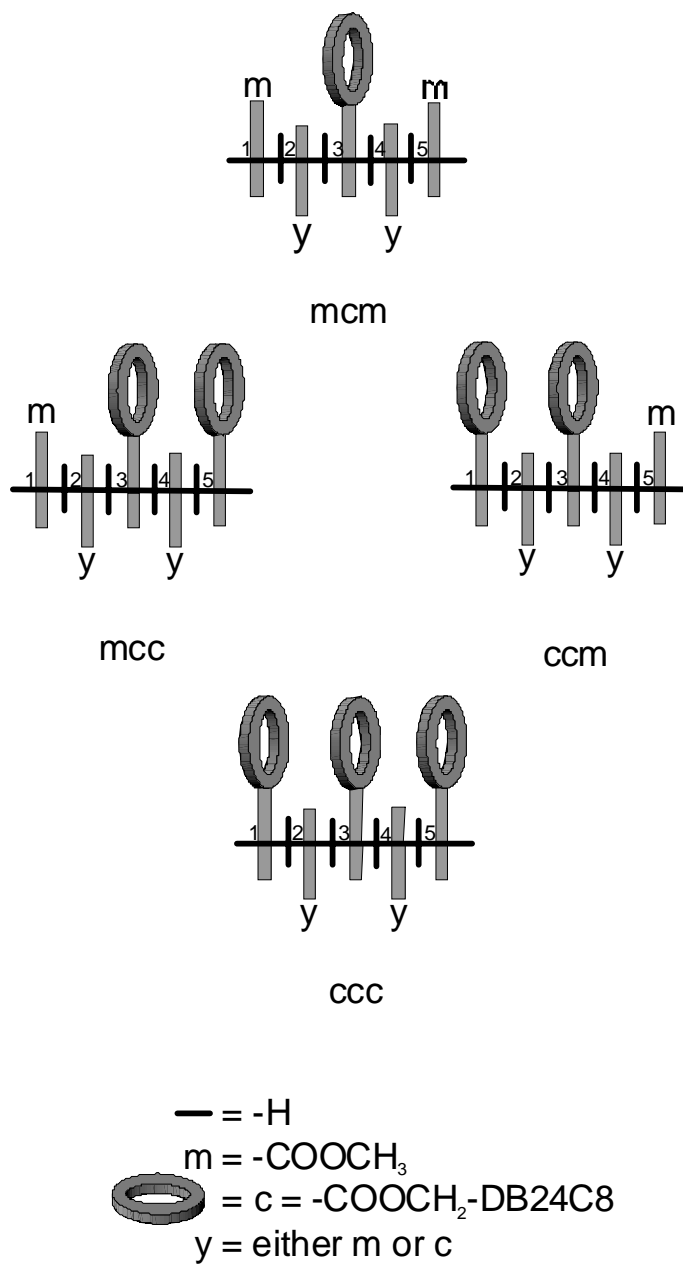
Figure 9.8. Representation of planar zigzag projections of syndiotactic pentad sequences.

Table 9.3. The probability of pentads of **5** having mcm, mcc or ccm, and ccc sequences

Polymer	m/n	P_{mcm}	$P_{mcc}+P_{ccm}$	P_{ccc}
5a	0.767	0.05	0.36	0.59
5b	0.323	0.46	0.44	0.10
5c	0.212	0.62	0.33	0.04
5d	0.0629	0.88	0.12	0.00

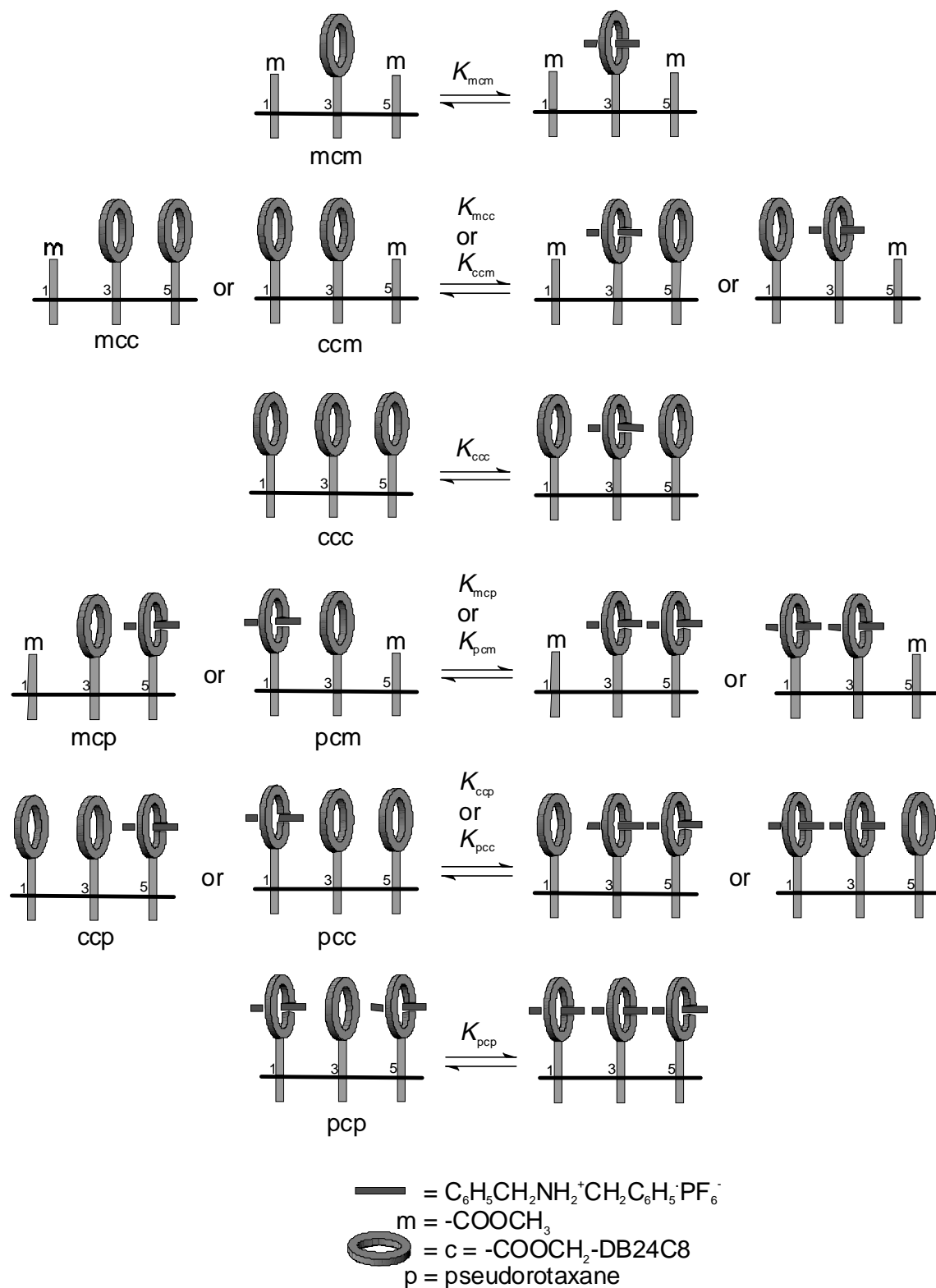**Figure 9.9.** Possible complexation equilibria of crown ether (at position 3 of pentad structures) with **7**.

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For **5a**, $m/n=0.767$, since the sum of P_{mcm}, P_{mcc}, and P_{ccm} (0.41) is less than the observed values for fraction complexed (0.60) at 80 mM of **7**, the crown ether at position 3 of ccc or mcp and pcm pentad sequences must then be occupied, assuming $K_{ccc}>K_{mcp}=K_{pcm}>K_{ccp}=K_{pcc}>K_{pcp}$ (Figure 9.9). This analysis is based on the assumption that complexation of the crown ether at position 3 with two adjacent pseudorotaxane complexes (pcp pentad sequence) is most inhibited due to steric effects. A lesser inhibition than the former case is assumed for complexation of the crown ether at position 3 with adjacent free crown and pseudorotaxane complex (ccp and pcc pentad sequences).

For **5b**, **5c**, and **5d**, the maximum observed values for fraction complexed are less than the sums of P_{mcm}, P_{mcc}, and P_{ccm}. In these cases, a crown ether at position 3 with at least one m neighboring group is occupied. Combined with steric effects along with a number of possible conformations in pentad structures, the large number of possible equilibria (Figure 9.9) conspire to make this a very complex system. It is not amenable to quantitative analysis with the data in hand. Nonetheless, the trend of the observed values for fraction complexed with probabilities of these pentads seems to hold.

This is the first time steric effects have been so dramatically observed in side-chain polymeric pseudorotaxane systems. In crown-paraquat systems of type **1a** the K_a values were found to be 1/5 to 1/2 those of the model monomeric systems, depending on the temperature, but independent of the site occupancy.[19,20] In systems of type **1b** with paraquat guest sites in the backbone and monomeric cyclic hosts, the K_a values were lower than those of the model systems by a factor of up to 2,[21,23] and site occupancy was limited to 50-94%, depending upon the spacer length between guest sites in the polymer and the temperature.[24]

It is noteworthy that the apparent "K_a" value of **5d** is most sensitive to the concentration of **7**; the value undergoes a 5-fold reduction as [**7**] increases from 10 to 80 mM. In contrast, "K_a's" for **5a-c** undergo only a 4-fold decrease over this range. We believe that these decreases, in addition to the "negative cooperativity" discussed above, are in part due to changes in the medium; as more salt is added the medium becomes a poorer solvent for the polymer, causing contraction of the random coil.[41] This contraction, of course, is expected to diminish the accessibilty of the host crown ether moieties to the ammonium salt guests. The effect is larger for **5d** for two reasons: 1)

since the crown ether concentration is kept relatively constant, the total polymer concentration is highest for **5d** relative to the other samples and 2) the poly(methyl methacrylate) segments of the copolymers are expected to be contracted more by the presence of the ammonium salt than the more polar crown ether moieties and **5d** contains the largest proportion of these units.

9.2.3. Physical properties

To investigate the effect of populations of the occupied sites in side-chain polypseudorotaxanes **8a** on the solid state properties, four different films, with 0 to 60% loading of **7** in the crown ether moieties of **5a**, were prepared by freeze drying 100 mM solutions of **5a** with a series of solutions of **7** (from 20 to 60 mM) and their thermal behaviors were investigated by DSC. The ^{1}H NMR spectra of these solutions at -40°C displayed signals corresponding only to complexed **7** but not to free **7**, assuring the quantitative complexation of **7** with the crown ether receptor sites in each sample. The solutions were slowly cooled to -95°C and frozen with an acetone-ethanol/liquid nitrogen bath. The solvents were then removed via high vacuum to afford slightly yellowish transparent films. To eliminate any thermal history of the freeze-dried samples, they were initially heated to 130°C and cooled to 25°C at the rate of 10°C/min. They were then heated to 130°C and the DSC thermograms were recorded. The results are summarized in Table 4. The increase in T_g is apparent as % loading increases. Similar observations have been reported for other main-chain polypseudorotaxanes[19,20] and side-chain polyrotaxanes.[42,43] To understand this T_g increase conceptually, we postulate that pseudorotaxane complexes in the side-chains aggregate "intra-" and "intermolecularly" in which one of somewhat electron poor benzene rings of **7** interacts through $\pi-\pi$ stacking with a somewhat electron rich benzo ring of crown ether to introduce rigidity and also chain stiffening occurs via a Coulombic effect,[19,20] as a result raising T_g almost 40°C for the case of side-chain polypseudorotaxane with 60% loading. The X-ray crystal structure of the [2]pseudorotaxane complex from DB24C8 and dibenzylammonium hexafluorophosphate revealed that the crown ether units pack, presumably due to $\pi-\pi$ stacking, to form channels.[27,29] In all samples, the T_g's were reproducible in the heating

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range of 25-130°C. It is noteworthy that physical blends of the two species, **5a** and **7**, at any ratio we examined, indicated no noticeable change in T_g, presumably due to phase separation. Three physical blend samples were prepared by slow evaporation of DMF solutions of **5** (100 mM) and **7** (20, 40, and 60 mM) at ambient temperature. The ^{1}H NMR spectrum recorded for solutions of DB24C8 and **7** (10 mM each in DMF-d_7) revealed no sign of [2]pseudorotaxane formation, presumably because of competitive hydrogen bonding of DMF with **7**.

Table 9.4. Effect of population of crown ether moieties occupied in polypseudorotaxane from **5a** on T_g (heating rate: 10°C/min)

% crown ether occupied	$T_g(^{\circ}C)^a$
0	66
20	91
40	99
60	103

a)Error ≤ ±1°C

To observe physical effects of the formation of pseudorotaxane complexes in the side-chains, SEM images of freeze-dried films of **5a** and side-chain polypseudorotaxane of 20% loading were recorded. Figure 9.10a suggests that the surface of **5a** is fragile. The considerable morphological change, resulting from the addition of **7** to form **8**, is shown in Figure 9.10b. As for the T_g increase, we reason that "intra-" and "intermolecular" interactions between pseudorotaxane complexes give additional supramolecular integrity and reinforce the side-chain polypseudorotaxane as a whole.
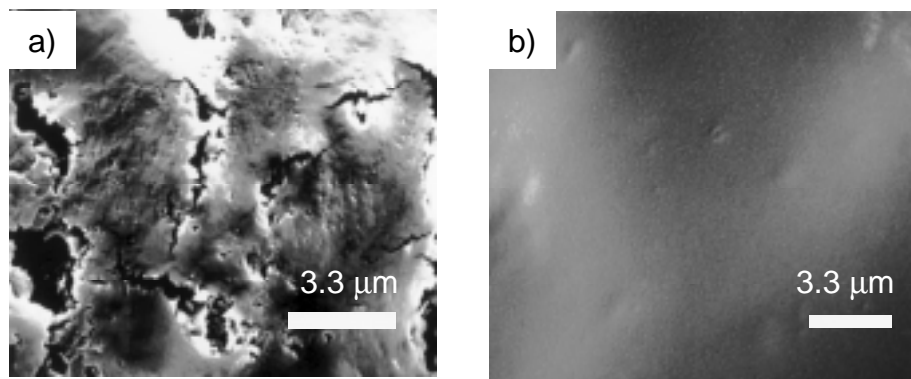
Figure 9.10. Longitudinal views of scanning electron micrographs of films prepared by freeze-drying solutions of **5a** and **7** at a) 100/0 and b) 100 mM/20 mM.

9.3. Conclusions

We have synthesized polymethacrylates bearing DB24C8 receptor sites that can accommodate secondary ammonium salts to form side-chain polypseudorotaxanes. The chemical modification of the side-chain polymers achieved by spontaneous complexation with a dibenzylammonium salt was studied in solution using ^{1}H NMR spectroscopy. The solid state samples of the side-chain polypseudorotaxanes prepared by freeze-drying revealed pronounced differences in thermal behavior and morphology with respect to the individual building blocks.

9.4. Experimental

Tetrahydrofuran (THF) was distilled from Na and benzophenone. Pyridine and hexanes were stirred with CaH_2 overnight and distilled. All other solvents were used as received. Methacryloyl chloride was distilled *in vacuo* just before use. The 400 MHz ^{1}H NMR spectra were recorded on a Varian Unity with tetramethylsilane (TMS) as an internal standard. 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. Molecular modeling was performed on a Dell 200 computer using *Chem3D Pro*^{TM} by Cambridge Scientific Computing, Inc. The heptamer was first drawn

in *ChemDraw Pro*^{TM} and pasted onto *Chem3D Pro*^{TM}. The structure was then minimized using MM2 parameters until the root mean square (RMS) gradient was below 0.05. 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).

Poly(methacryloyl chloride) (3). To a 250 mL two necked round bottom flask equipped with a condenser and N_2 inlet were added methacryloyl chloride (40.58 g, 388.2 mmol), AIBN (0.34 g, 2.1 mmol), and toluene (60 mL) and the reaction mixture was vigorously stirred at 65°C for 3 days. The solution was precipitated into dry hexanes (600 mL) to afford an off-white solid (38.44 g, 95% yield). ^{1}H NMR (400 MHz, DMSO-d_6, 22°C): δ=0.80-1.27 (br m, -CH_3) and 1.52-2.05 (br m, -CH_2-). This polymer was used in the subsequent step without further purification.

Poly{[4-methylenebis(1,2-phenylene)-24-crown-8-methacrylate]-ran-[methyl methacrylate]}s

Procedure for 5a (*m/n*=0.767). To a 100 mL two necked round bottom flask equipped with a magnetic stirrer, condenser, and N_2 inlet were added poly(methacryloyl chloride) (**3**) (0.22 g, 2.1 mmol), pyridine (0.8 mL), and dry THF (35 mL). To this solution was added a solution of 4-hydroxymethylbis(1,2-phenylene)-24-crown-8 (**4**) (1.08g, 2.27 mmol) in dry THF (5 mL) via syringe and the reaction mixture was vigorously stirred for 5 days at reflux. After the salt was filtered, the filtrate was precipitated into MeOH (250 mL) to afford a white solid, 0.79 g (70% yield). M_n=6.1 and M_w=8.2 kg/mol (GPC). IR (KBr): ν=3020 (Ar-H str.), 2870 (CH$_2$, CH$_3$ str.), and 1760 (C=O str.). ^{1}H NMR (400 MHz, acetone-d_6/chloroform-d (1/1, v/v), 22°C): δ=0.82-2.20 (br m, –CH_3 and -CH_2-), 3.62 (br s, -OCH_3), 3.74 (br s, ArOCH$_2$CH$_2$OCH_2-), 3.82 (br s, ArOCH$_2$CH_2OCH$_2$-), 4.07 (br s, ArOCH_2CH$_2$OCH$_2$-), 4.90 (br s, ArCH_2-), and 6.80-6.97 (br m, ArH).

General procedure for 5b, 5c, and 5d (*m*/*n*=0.323, 0.212, and 0.0629, respectively). To a two necked round bottom flask equipped with a magnetic stirrer, condenser, and N_2 inlet were added **3**, pyridine, and dry THF. To this solution was added a solution of an appropriate molar amount of **4** dissolved in dry THF via syringe and the reaction mixture was vigorously stirred for 2 days at reflux. The reaction was quenched with MeOH and the precipitate was filtered to afford a white solid.

Poly(methyl methacrylate) (6). The same reaction and purification procedures as those for the syntheses of **5** were utilized except that **3** was reacted with MeOH instead of **4** in the presence of pyridine: 88% yield, M_n=3.3 and M_w=4.0 kg/mol (GPC). ^{1}H NMR (400 MHz, DMSO-d_6, 22°C): δ =0.79-1.42 (br m, –CH_3), 1.78-2.03 (br m, -CH_2-), and 3.55 (br s, -OCH_3).

General methods for determination of m/n values for 5. Three different sets of ^{1}H NNR spectra were recorded independently for each polymer (**5a**-**d**) and *m*/*n* values were generally determined using the average of six integration ratios of the signals for the CH_3O- protons to H$_\alpha$ protons and to the benzylic protons (ArCH_2O-) of the crown ether pendant group in each spectrum. The results (with standard deviations) are as follows: *m*/*n* = 0.767±0.010 for **5a**, 0.323±0.007 for **5b**, 0.212±0.005 for **5c**, and 0.0629±0.001 for **5d**.

General methods for preparation of solutions of 5 and 7. The number of moles of crown ether methacrylate repeat unit in each polymer was determined by using the molecular weights of crown ether methacrylate and methyl methacrylate repeat units (MW=546.61 and 100.12 g/mol, respectively) and the *m*/*n* values. In general, crown ether side-chain polymers **5** were directly weighed into volumetric flasks and diluted with acetone-d_6/chloroform-*d* (1/1, v/v) to appropriate volumes to achieve desired concentrations. Similarly, the calculated moles of the ammonium salt **7** were weighed into volumetric flasks and diluted with the same solvent system to appropriate volumes. They were then mixed to record the corresponding ^{1}H NMR spectrum.

9.5. References

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