

Chapter 5

Diacid chloride blocking group and its derived polyester rotaxanes: a strategy to eliminate dethreading

5.1 Introduction

Compared to the conventional polymeric materials, polyrotaxanes, prepared by threading macrocycles onto linear polymeric backbones, bear novel architectures and show many interesting properties.¹ Cyclodextrins (CD)²⁻⁴ and crown ether molecules^{1,5-11} have been the most common macrocycles used in the preparation of polyrotaxanes. The formation of CD-derived polyrotaxanes is well understood to result from inclusion complexation between CD and linear components and polyrotaxanes with high threading efficiencies have been obtained.²⁻⁴ However, the driving force for the formation of crown ether-based poly(ester rotaxane)s and related systems has not been clearly established and the threading efficiency is not so high. Since the m/n value is directly related to the properties of polyrotaxanes, we urgently need to identify the driving force for the formation of these polyrotaxanes and design a method to increase the m/n values.

¹ Reviews: a) Gibson, H. W.; Marand, H. *Adv. Mater.* **1993**, *5*, 11. b) Gibson, H. W.; Bheda, M. C.; Engen, P. T. *Prog. Polym. Sci.* **1994**, *19*, 843. c) Ambalino, D. B.; Stoddart, J. F. *Chem. Rev.*, **1995**, *95*, 2725. d) Gibson, H. W. in *Large Ring Molecules*, Semlyen, J. A. ed., J. Wiley and Sons, New York, **1996**, pp. 191.

² a) Steinbrunn, M. B.; Wenz, G. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2139. b) Weickenmeier, M.; Wenz, G. *Macromol. Rapid Commun.* **1996**, *17*, 731

³ a) Born, M.; Ritter, H. *Angew. Chem.* **1995**, *107*, 342. b) Born, M.; Ritter, H. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 309. c) Born, M.; Ritter, H. *Macromol. Rapid Commun.* **1996**, *17*, 197; d) Born, M.; Ritter, H. *Adv. Mater.* **1996**, *8*, 149.

⁴ a) Harada, A.; Li, J.; Kamachi, M. *Macromolecules* **1994**, *27*, 4538 b) Harada, A.; Okada, M.; Li, J.; Kamachi, M. *Macromolecules* **1995**, *28*, 8406.

⁵ Shen, Y. X.; Xie, D.; Gibson, H. W. *J. Am. Chem. Soc.* **1994**, *116*, 537.

⁶ Gibson, H. W.; Liu, S.; Lecavalier, P.; Wu, C.; Shen, Y. X. *J. Am. Chem. Soc.* **1995**, *117*, 852.

⁷ Marand, E.; Hu, Q.; Gibson, H. W.; Veytsman, B. *Macromolecules*, **1996**, *29*, 2555.

⁸ Gibson, H. W.; Liu, S. *Macromol. Symp.* **1996**, *102*, 55.

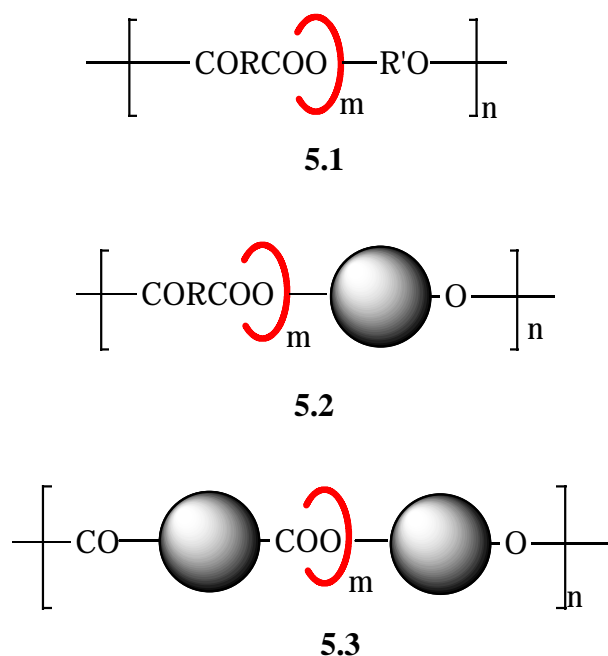
⁹ a) Chapter 3. b) Gong, C.; Gibson, H. W. *Macromolecules* **1996**, *29*, 7029.

¹⁰ a) Chapter 4. b) Gong, C.; Gibson, H. W. *Macromol. Chem. Phys.* **1997**, *198*, 2321.

¹¹ Gibson, H. W.; Liu, S.; Gong, C.; Ji, Q.; E. Joseph, Q. *Macromolecules*, **1997**, *30*, 3711.

While most of our early work was with poly(ester pseudorotaxane)s of type **5.1** (Scheme 5.1),^{5,8-11} different blocking groups (BGs) were designed recently in order to achieve higher m/n values.⁹⁻¹³ Indeed, blocking groups prevented threaded cyclic molecules from slipping off the backbone and the m/n value of a poly(ester rotaxane) of type **5.2** using a bulky diol as the only diol monomer was 5 times as high as that of a poly(ester pseudorotaxane) of type **5.1** without BG (Scheme 5.1).⁹

Scheme 5.1



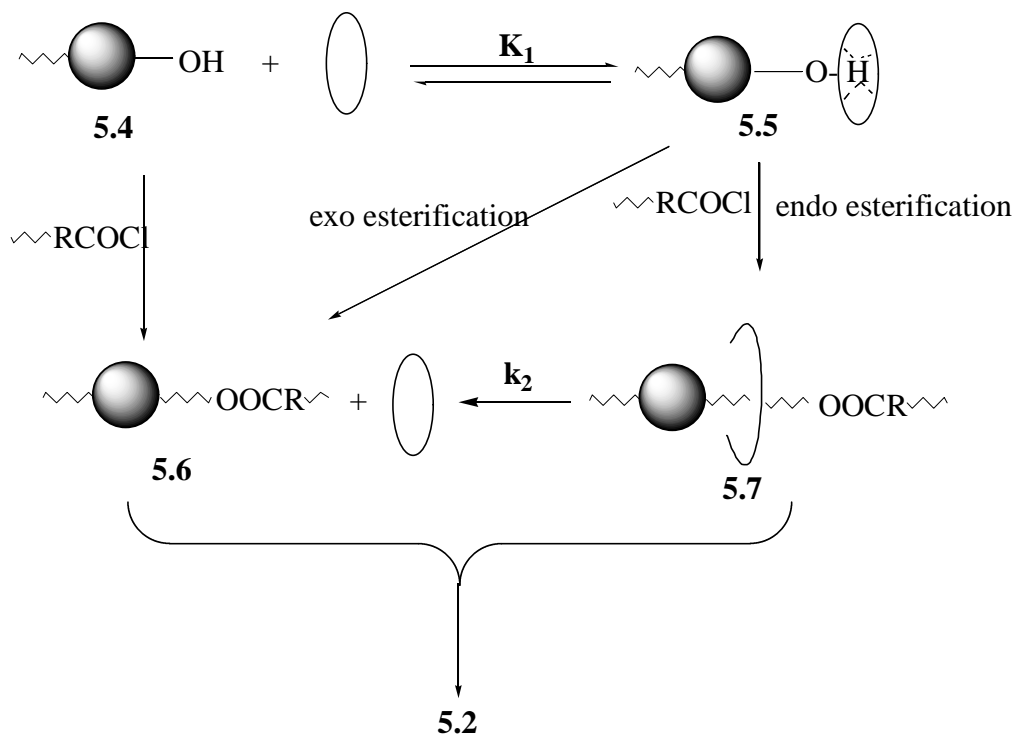
We proposed⁸⁻¹¹ that the hydrogen bonding of the hydroxyl group with the crown ether to form **5.5** provides the driving force for threading in poly(ester rotaxane)s, i.e., K_1 is significant (Scheme 5.2). For polyrotaxanes of type **5.2**, dethreading still occurs during the reaction period because once the ester bond forms in an endo fashion to capture the ring (structure **5.7**), there is no or minimal retaining force unless the cyclic is trapped between two

¹² Gibson, H. W.; Lee, S.-H.; Engen, P. T.; Lecavalier, P.; Sze, J.; Shen, Y. X.; Bheda, M. *J. Org. Chem.* **1993**, *58*, 3748.

¹³ Liu, S.; Shen, X. Y.; Gibson, H. W. *J. Org. Chem.* **1995**, *60*, 3155.

BGs; thus loss of the cyclic can occur from **5.7**, leading to **5.6** plus free cyclic, i.e., $k_2 > 0$ (Scheme 5.2). Experimentally the degree of dethreading in the preparation of the polyrotaxanes of type **5.2** increased linearly as the proportion of diol BG in the total diol decreased.¹⁰

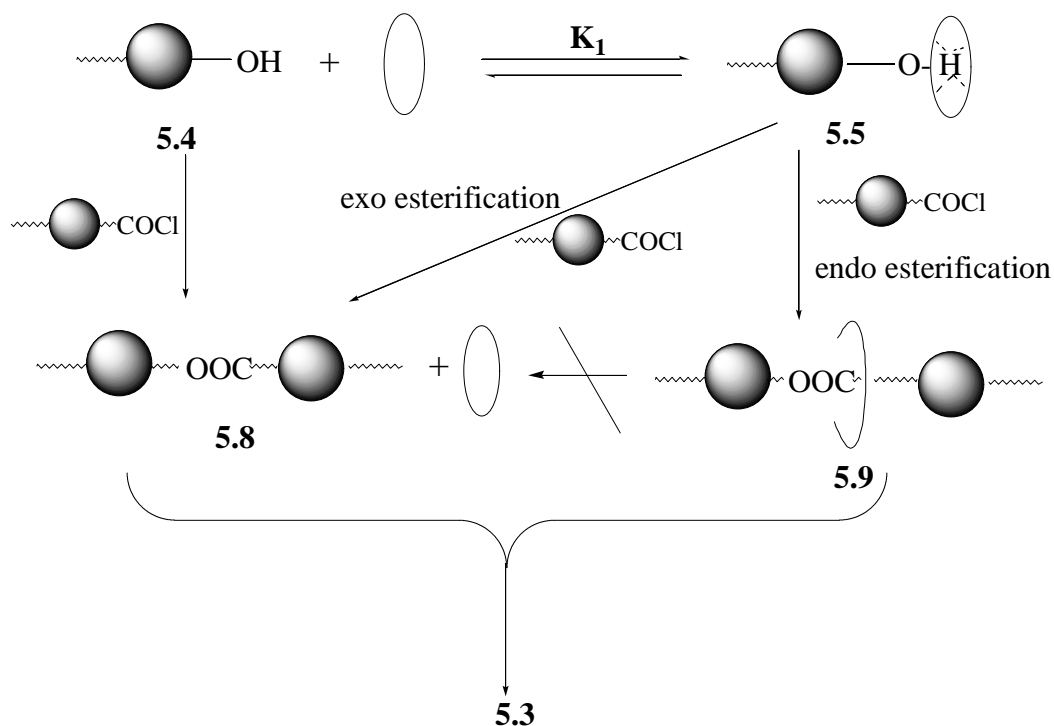
Scheme 5.2 The Proposed Mechanisms for Threading and Dethreading During the Preparation of Polyrotaxanes **5.2**



It is expected that dethreading during the polyesterification period can be eliminated by using two bulky monomers, a diacid chloride BG and a diol BG, to form polyrotaxanes of type **5.3** (Scheme 5.1), because the threaded cyclic is mechanically confined between two BG units as soon as the ester bond (structure **5.9**) forms and there can be no dethreading equilibrium leading to **5.8** (Scheme 5.3). Here, we report the preparation of a diacid chloride BG and derived polyrotaxanes of type **5.3** to test this idea. Since the dethreading can be eliminated by this approach, the threading abilities of different macrocycles can be compared by polymerization in the presence of a mixture of different macrocycles. These results are

also reported in this chapter. In addition, the relationship of threading efficiency vs. temperature was explored in the present system.

Scheme 5.3: The Proposed Mechanisms for Threading and Dethreading During the Preparation of Polyrotaxanes **5.3**



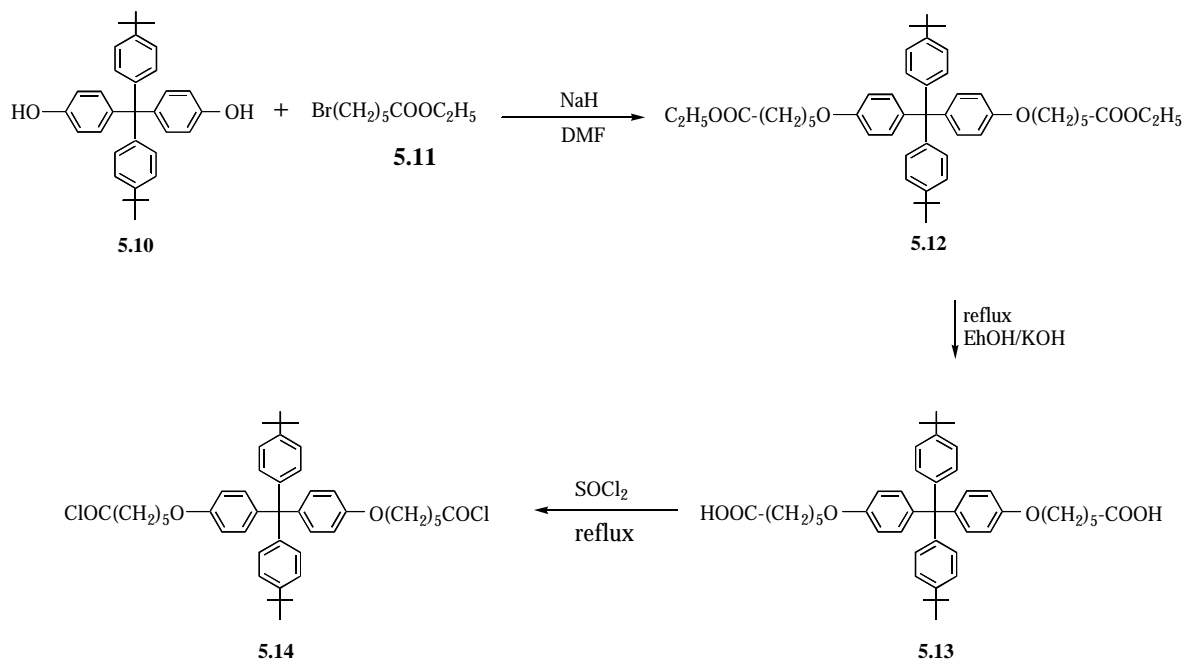
5.2 Results and discussion

5.2.1. Diacid Chloride-functionalized Blocking Group **5.14**.

Diacid chloride BG **5.14** was synthesized by a three-step method with an overall yield of 63 % (Scheme 5.4). By reacting **5.10**⁹ with a large excess of bromide **5.11** in a basic solution, diester BG **5.12** was obtained in 80 % yield. Ester **5.12** was easily converted to diacid BG **5.13** by refluxing its basic solution in ethanol followed by neutralization with acid. Although the reaction was quantitative, recrystallization lowered the yield to 90 %. Finally, diacid chloride BG **5.14** was prepared by reacting the diacid BG with thionyl chloride. Since **5.14** was to be used as a monomer for polyesters, it was purified by recrystallization in

hexane twice to afford needle crystals. The structure of **5.14** was confirmed by its proton NMR spectrum (Figure 5.1) and elemental analysis.

Scheme 5.4 Preparation of diacid chloride BG **5.14**



It was reported that tris(*p-tert*-butylphenyl)methanol could block macrocycles up to 42 methylene groups.¹⁴ Thus **5.14** is bulky enough to constrain 30C10 and can be used to provide stoppers along the polymeric chain as well as diol BG **5.15** we previously used.⁹ By using **5.14** as the acid chloride monomer and **5.15** as the diol monomer, polyrotaxanes of type **5.3** (Scheme 5.1) were successfully prepared.

¹⁴ a) Harrison, I. T.; Harrison, S. *J. Am. Chem. Soc.* **1967**, 89, 5723. b) Harrison, I. T. *J. Chem. Soc. Chem. Commun.* **1972**, 231. c) Harrison, I. T. *J. Chem. Soc., Perkin Trans. 1* **1974**, 301.

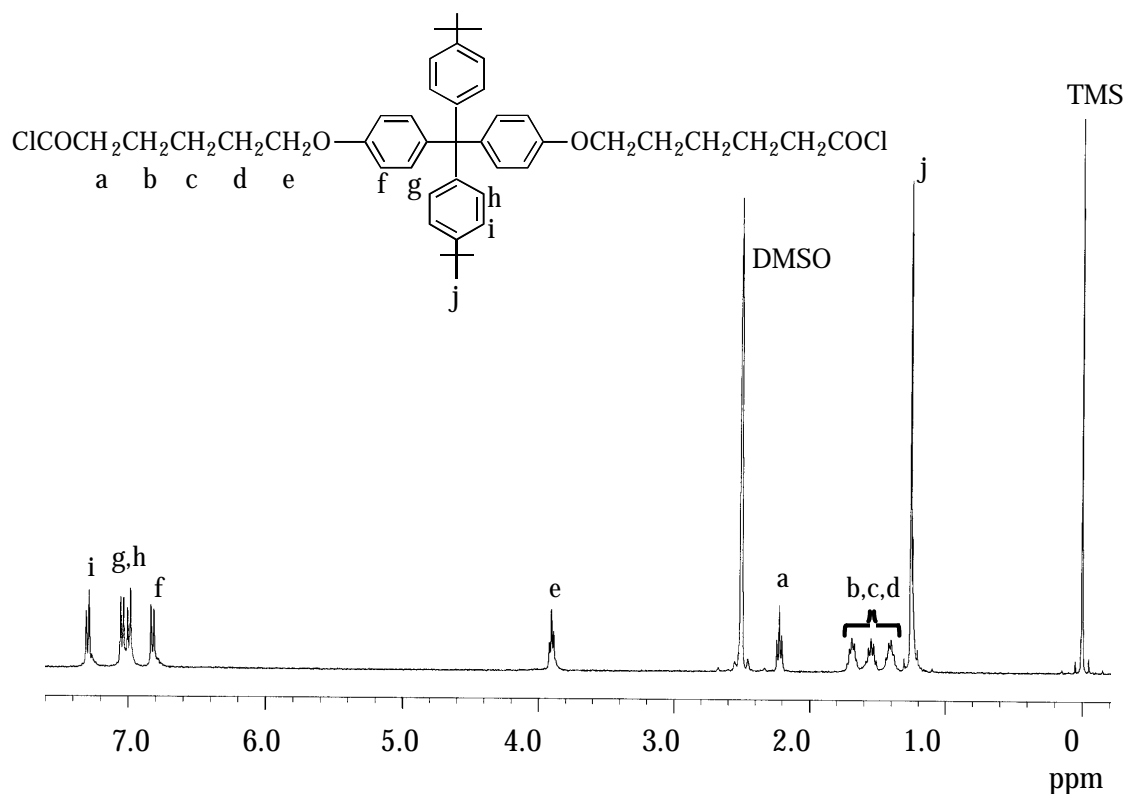


Figure 5.1 The 400 MHz proton NMR spectrum of diacid chloride BG 5.14 in DMSO- d_6

5.2.2 Polyrotaxanes 5.16a and 5.16b.

For comparison purposes, polyrotaxanes **5.16a** and **5.16b** were prepared by polycondensation of diol **5.15** with sebacoyl chloride using 30C10 as solvent (Scheme 5.5).⁹ Formation of the polyrotaxanes was previously proved by hydrolytic recovery of 30C10, NOESY study and a chemical shift of threaded 30C10 protons different from that of the unthreaded species.⁹ The conditions and results are summarized in Table 5.1.

5.2.3 Polyrotaxanes 5.17a, 5.17b and 5.17c and Model Polymer 5.17d.

i. Synthesis.

Polyrotaxanes **5.17a**, **5.17b** and **5.17c** were prepared by polycondensation of diacid chloride BG **5.14** with diol BG **5.15** using 30C10 as solvent (Scheme 5.6). Reaction conditions and results are specified in Table 5.1. The polymers were purified by precipitation

from THF solution into water. Model polyester **5.17d** was prepared by using diglyme as solvent instead of 30C10.

Scheme 5.5 Preparation of polyrotaxanes **5.16a** and **5.16b**

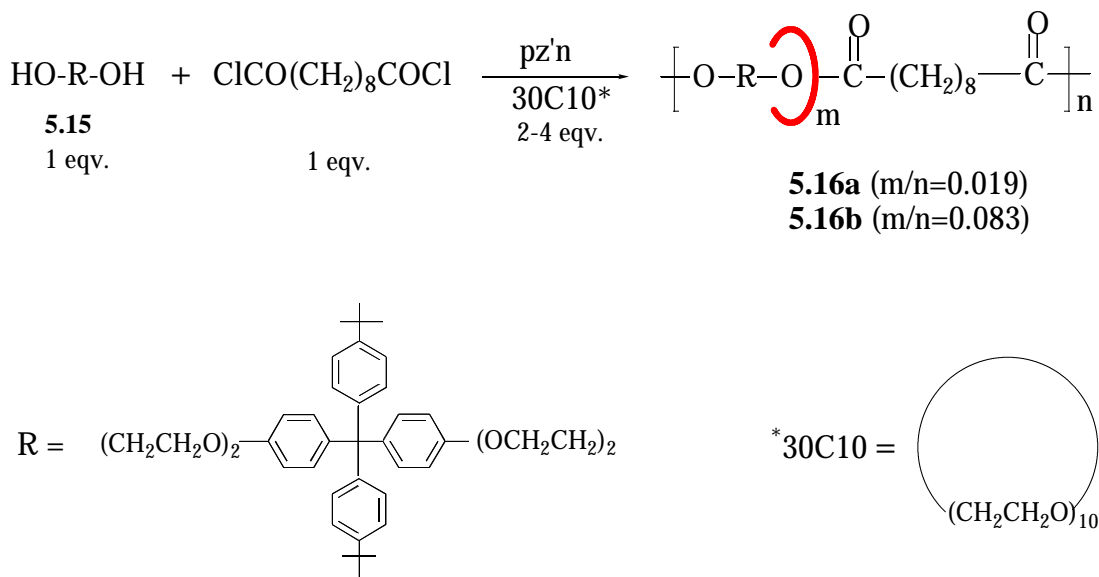


Table 5.1: Reaction conditions and results for polyrotaxanes **5.16** and **5.17**

polyrotaxan	feed ratio (30C10/diol)	Temp. (°C) ^a	m/n ^b	M _n (x10 ⁻³)	M _w (x10 ⁻³)
5.16a	2	153	0.019	6.0 ^c	11.3 ^c
5.16b	4	63	0.083	12.0 ^c	22.1 ^c
5.17a	2	153	0.043	9.0 ^d	18.2 ^d
5.17b	4	63	0.155	8.9 ^d	31.0 ^d
5.17c	5	63	0.172	25.2 ^d	87.3 ^d
5.17d	0 ^e	90	-	18.5 ^d	37.5 ^d

a) ±2.0 °C; b) Estimated error: ±5% relative; c) Determined by GPC with polystyrene standards in chloroform; d) Determined by GPC with universal calibration in chloroform; e) Diglyme used as solvent.

Scheme 5.6: Preparation of Polyrotaxanes **5.17a-17c** and Model Polymer **5.17d**

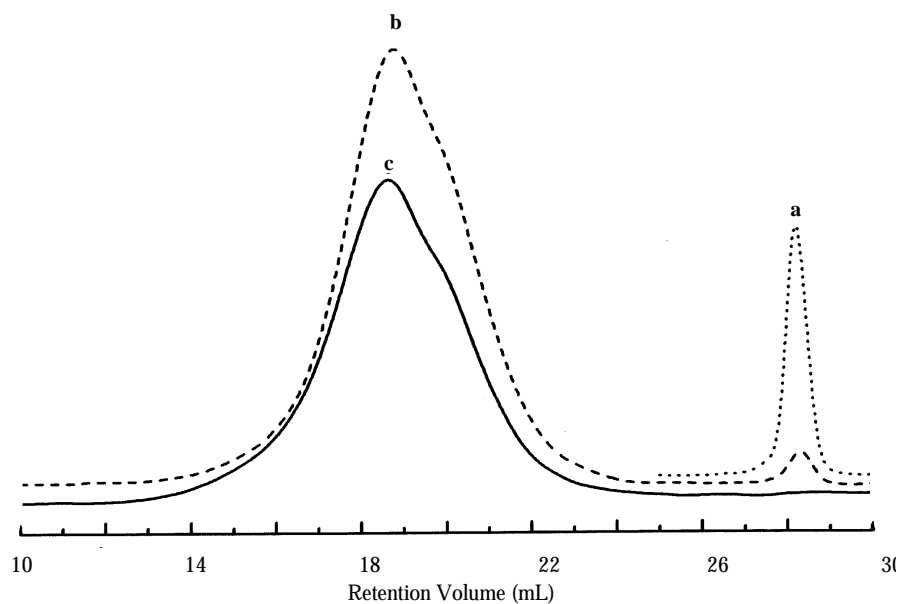
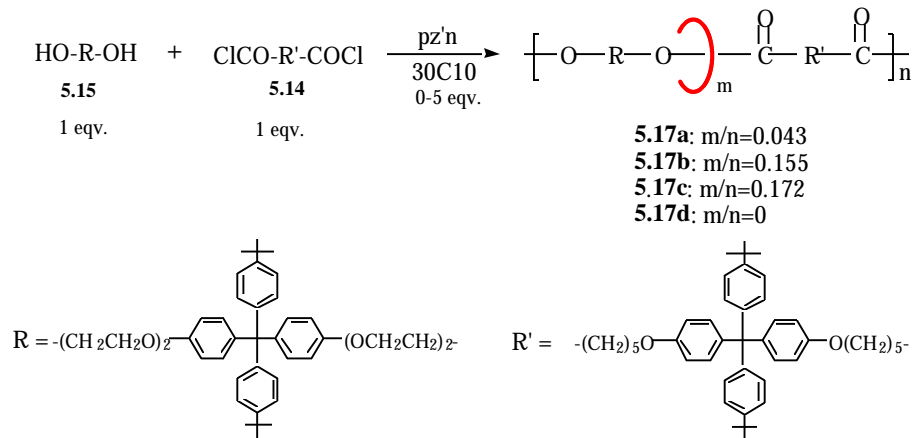


Figure 5.2 The GPC traces of a) 30C10, b) a mixture of **5.17c** and 5% 30C10 and c) **5.17c** (eluting solvent: CHCl_3)

ii. Characterization.

a) GPC analysis.

30C10 is a monodisperse small molecule. It has its own specific retention volume in GPC with a certain column, which is far separated from that of polymers (Figure 5.2). The excellent resolution provides a reliable tool to prove the absence of free crown ether and the formation of polyrotaxanes. It was found that the GPC trace of polyrotaxane **5.17c** has no

30C10 peak while that (Figure 5.2b) of the mixture of **5.17c** and free 30C10 (5%) has two well resolved peaks at 28.4 ml and 19.1 ml, corresponding to those of polyrotaxane **5.17c** (Figure 5.2c) and free 30C10 (Figure 5.2a), respectively. This result directly proved that no free 30C10 existed in polyrotaxanes **5.17a-17c** and that they are not simple mixtures; it also demonstrated that precipitation is an effective method to remove the unthreaded 30C10.

b) Proton NMR spectroscopy.

After three precipitations, no signal (3.67 ppm) of free 30C10 was present in the proton NMR spectrum (Figure 5.3a) of polyrotaxanes **5.17a-17c**; instead a new signal at 3.50 ppm appeared, compared to that (Figure 3b) of model polymer **5.17d**. Is the new signal from that threaded 30C10 and if so, why does it have a different chemical shift from that (3.52 ppm) of threaded 30C10 in polyrotaxane **5.16**?¹⁵ To answer these questions, the same characterization techniques were applied to polyrotaxanes **5.17** as were used for **5.16**.^{9,10}

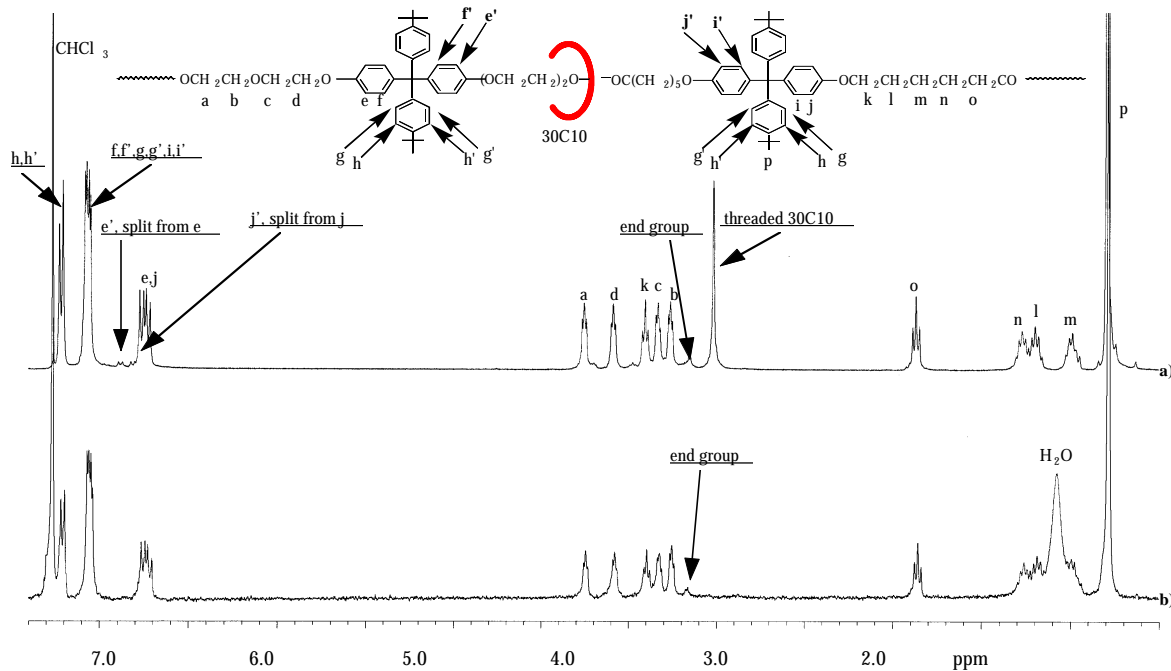


Figure 5.3 The 400 MHz proton NMR spectra of a) top, polyrotaxane **5.17a** and b) bottom, model polymer **5.17d** in CDCl_3

¹⁵ Although the difference of the signals for threaded 30C10 protons was very small, 3.50 ppm in **17** and 3.52 ppm in **16**, they each have excellent reproducibility.

First, polyrotaxane **5.17c** was hydrolyzed by refluxing its basic solution in THF. It was found that the 3.50 ppm signal disappeared and that (3.67 ppm) of free 30C10 returned in the neutral hydrolytic products (Figure 5.4b) and by extracting with hexane, pure 30C10 was recovered (Figure 5.4a). This degradation experiment directly proved that the signal at 3.50 ppm in polyrotaxanes **5.17a-c** is indeed from the protons of the threaded 30C10 and furthermore that the crown ether retained its integrity in the polyrotaxanes.

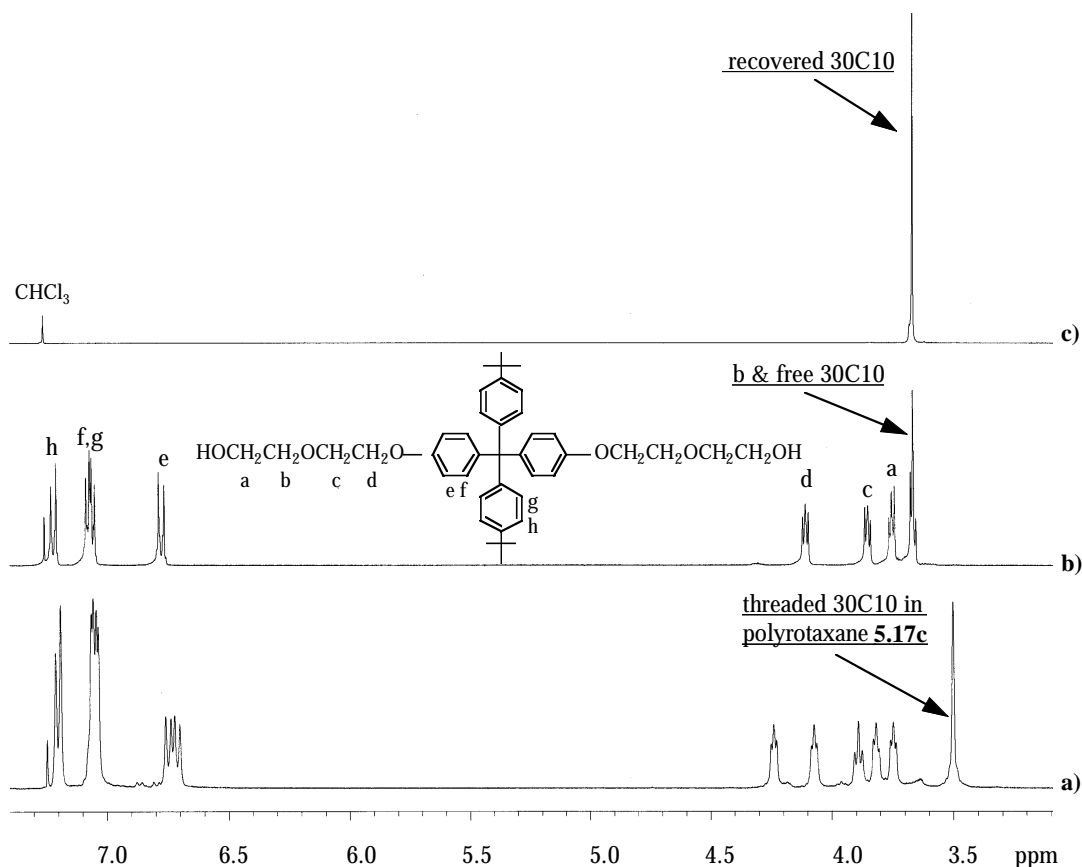


Figure 5.4 The 400 MHz proton NMR spectra of a) polyrotaxane **5.17c**, b) the neutral hydrolytic products and c) recovered 30C10 in CDCl₃

A 2D COSY study of **5.17c** revealed that the 3.50 ppm signal is not coupled with any protons in the backbone (Figure 5.5); this ruled out the possibility that the signal is from protons chemically bonded to the backbone. Thus the only possible reason for the change of chemical shift of 30C10 before and after threading is the existence of a through-space interaction, which was well demonstrated in our previous work.^{9,10}

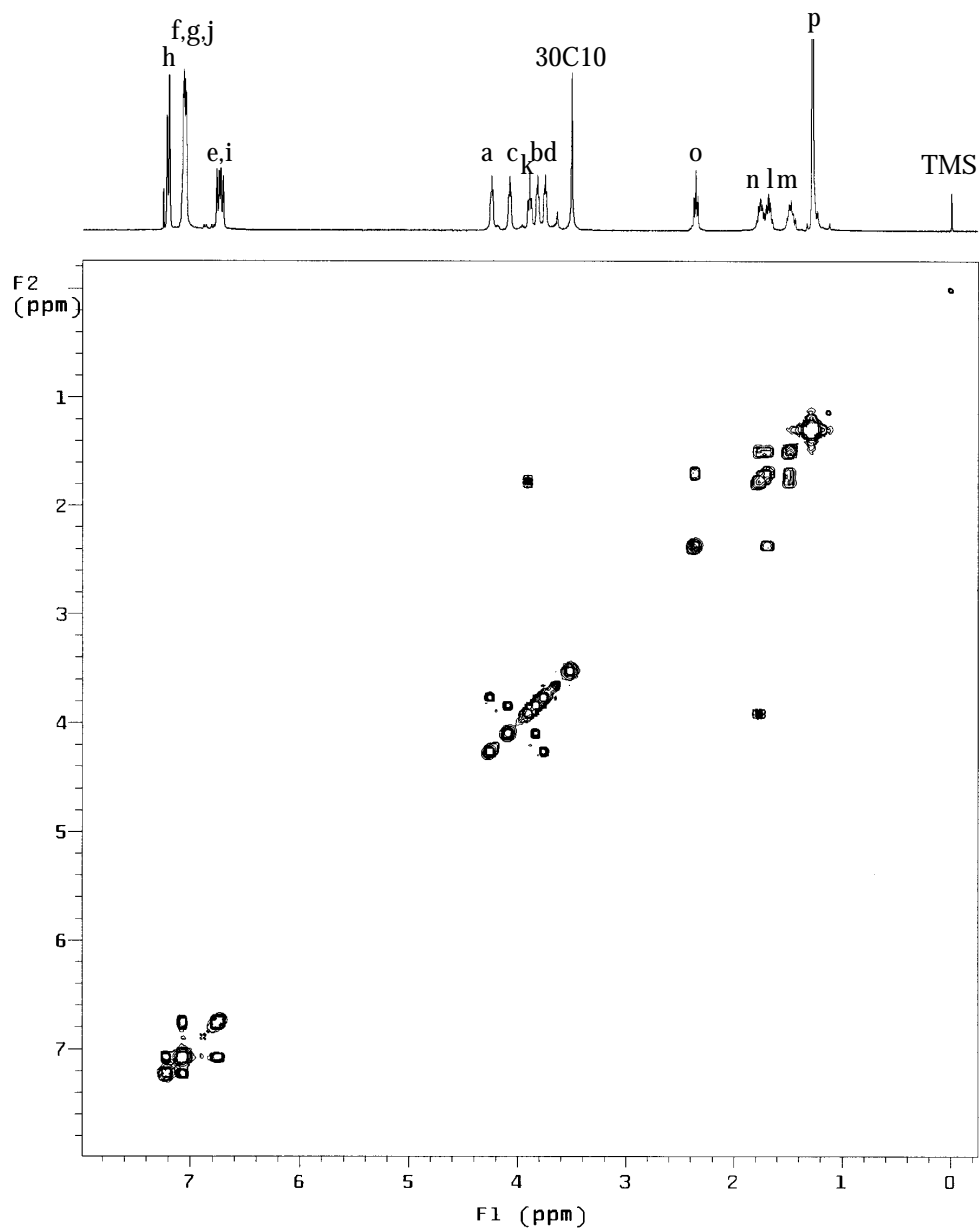


Figure 5.5 The 400 MHz proton NMR 2D COSY spectrum of **5.17c** in CDCl_3 (for peak assignments, see Figure 5.3)

The 2D NOESY spectrum of polyrotaxane **5.17c** (Figure 5.6) indeed shows a correlation similar to that observed in polyrotaxane **5.16**.^{9,10} The protons of threaded 30C10 (3.50 ppm signal) are correlated with the aromatic protons e', f', g', h', i' and j'. Therefore, the upfield shift for threaded 30C10 in **5.17** is due to through-space interaction with aromatic protons because of the ring current effect as that for **5.16**,^{13,14} and the corresponding aromatic

protons (e, f, g, h, i and j) were shifted downfield to e', f', g', h', i' and j'; the protons e' and j' are distinguished from the mother protons but the protons f', g' and i' are merged with their major peaks. The shielding of 30C10 molecules depends on the distance between BG units because the signal is time averaged.^{9,10} In polyrotaxanes **5.16** and **5.17**, there are 22 atoms and 13 atoms between BG units, respectively. Thus threaded 30C10 in **5.17** experiences stronger shielding than that in **5.16** and thus its signal shifted upfield further (3.50 vs. 3.52 ppm).

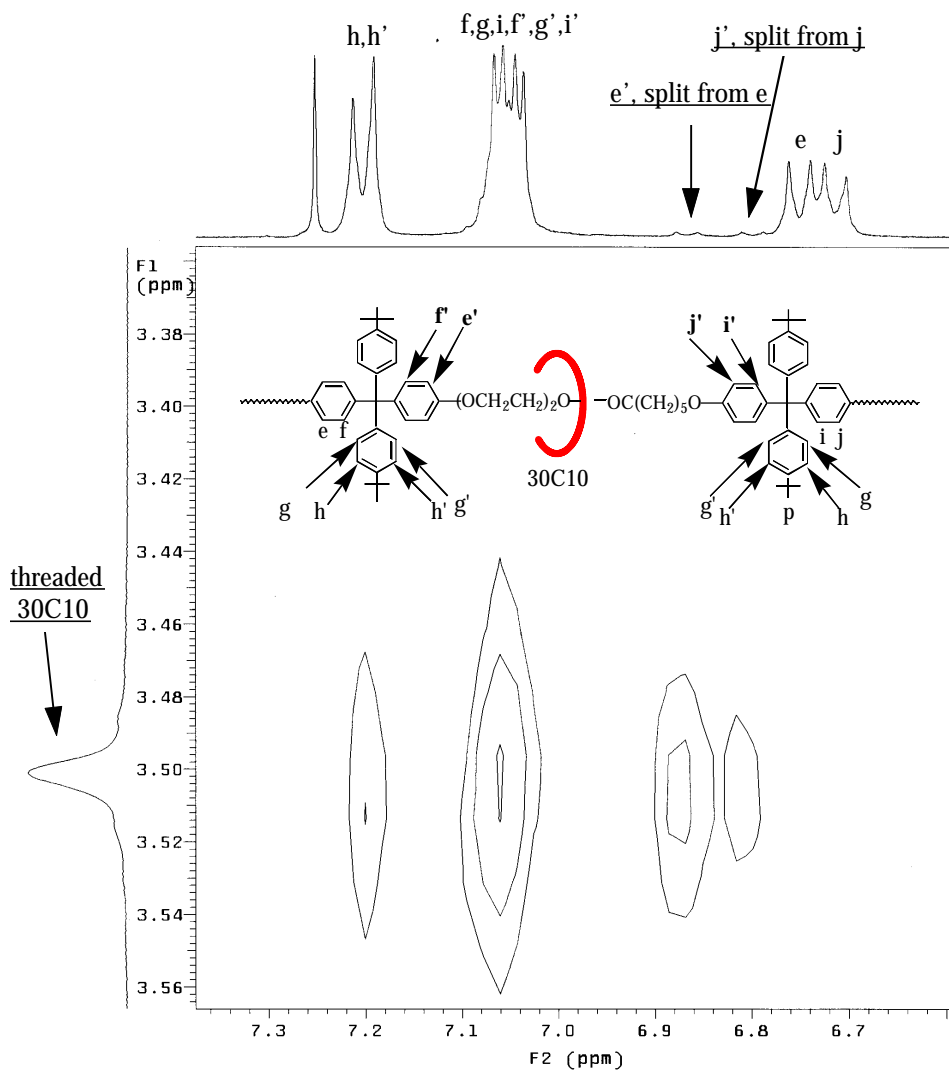


Figure 5.6 The correlated region of 400 MHz proton 2D NOESY spectrum of polyrotaxane **5.17c** in CDCl₃ at 25 °C

5.2.4 Threading and dethreading mechanisms

Because diacid chloride BG **5.14** was difficult to dissolve in small amounts of 30C10 at low temperatures, polyrotaxane **5.17a** was initially prepared at 153 °C with a feed ratio of 30C10 vs. diol BG **5.15** of 2. In order to increase threading efficiency, a lower temperature and higher feed ratio were applied for **5.17b**. To understand the effect of introduction of diacid chloride BG **5.14** on threading efficiency, the corresponding polyrotaxanes **5.16a** and **5.16b** were prepared under the same conditions with sebacoyl chloride instead of **5.14**. As the results in Table 5.1 show, **5.17a** and **5.17b** had threading efficiencies, m/n values, twice as high as those of **5.16a** and **5.16b**. The higher m/n values for **5.17** can be easily understood by the proposed threading and dethreading processes (Scheme 5.2 and 5.3).

For polyrotaxanes **5.16**, dethreading occurs during the stage of structure **5.7** from the endo esterification of hydrogen bonded structure **5.5**, leading to unthreaded **5.6** before reaction with another diol **5.15** (Scheme 5.2), since the ester backbone presumably exerts no retaining force for threaded 30C10 molecules.^{9,10} During the preparation of polyrotaxanes **5.17**, as soon as 30C10 is threaded via the endo esterification of **5.5**, it is confined between two BG units (structure **5.9**) and no dethreading can occur to form unthreaded **5.8** and free crown ether (Scheme 5.3). Thus by using diacid chloride BG **5.14** and diol BG **5.15**, a novel approach to eliminate dethreading during the polycondensation was introduced. Therefore, polyrotaxanes **5.17** will have the highest m/n values among the three types of main chain polyrotaxanes, **5.1**, **5.2** and **5.3**, made under the same conditions.

Harrison^{14c} reported that a neat reaction of cyclodotriacontane (2.2 mol), tris(*p*-*tert*-butylphenyl)methanol (2.4 mol) and 1,13-tridecanediol (1.0 mol) afforded an 0.6% yield of the rotaxane by a “statistical” process. Schill et al.¹⁶ reported that heating equimolar amounts of cyclononacosane and 1,1,1,12,12,12-hexaphenyldodecane neat at 125 °C for 2 hrs produced a rotaxane in 2.3% yield. DeBolt and Mark¹⁷ reported that a 30-membered cyclic dimethylsiloxane was not threaded by linear siloxane, but 38-membered rings were to the

¹⁶ Schill, G.; Beckman, W.; Schweickert, N.; Fritz, H. *Chem. Ber.* **1986**, *119*, 2647.

¹⁷ DeBolt, L. C.; Mark, J. E. *Macromolecules*, **1987**, *20*, 2369.

extent of 5.0% (neat, molar ratio cyclic/linear = 43). Joyce et al.¹⁸ reported that the calculated percentage of cyclic PDMS threaded onto linear siloxane is between 0.2-0.3 for a 30-membered ring and up to 74.3 for a 392-membered ring.

Therefore, the threading efficiencies of **5.17b** (0.155) and **5.17c** (0.172) are much larger than the value which can be obtained by a statistical threading for a 30-membered macrocycle. The data indicates that some driving force for threading must exist in the preparation of these polyrotaxanes. Since the ester backbone of the poly(ester rotaxane)s has no strong attractive force for 30C10, hydrogen bonding between the crown ether and the hydroxy groups of diol monomers is a most plausible driving force for threading;¹⁹ a fraction of endo esterification of **5.5**, which depends on the cavity size and other factors, takes place through the macrocycle leading to **5.9** while exo ester bond formation produces unthreaded **5.8** (Scheme 5.3).

In addition, it is worth mentioning that by decreasing the polymerization temperature from 153 °C to 63 °C and increasing the feed ratio of crown ether to diol from 2 to 4, the m/n values of both polyrotaxanes **5.16** and **5.17** were increased about four-fold (Table 5.1). The huge dependence of threading efficiencies on these conditions is again consistent with the proposed H-bonding theory. Since a negative change of entropy is involved in H-bonding, lower temperature will favor H-bond formation, a higher fraction of structure **5.5** and enhanced threading (Schemes 5.2 and 5.3). When more crown ether is applied, the equilibrium will be driven in the same direction. Therefore, both factors combine to result in a large influence; higher feed ratio and lower temperature, higher m/n values of the resulting polyrotaxanes.

¹⁸ Joyce, S. J.; Hubbard, R. E.; Semlyen, J. A. *Eur. Polym. J.* **1993**, 29, 305.

¹⁹ Yakshin, V. V.; Abashkin, V. M.; Laskprin, B. N. *Dokl. Chem. Proc. Acad. Sci. USSR (Engl. Trans.)* **1979**, 224, 27, reported that ΔH values for the H-bonding of 15-crown-5, 18-crown-6, dibenzo-18-crown-6 and dibenzo-24-crown-8 with methanol in CCl_4 at 25 °C are -15.1, -14.6, -10.5 and -14.2 kJ/mol, respectively, but no ΔS values were reported.

5.2.5 Temperature dependence of threading efficiency

No temperature dependence of threading efficiency was observed for polyrotaxanes of type **5.1** because of the interference of dethreading.^{8,11} Using diol BG for **5.2** effectively decreased degree of dethreading and a temperature dependence of m/n was found.⁹ However, the dethreading still occurs in the preparation of **5.2** and thus its dependence was still affected by dethreading. As shown in the above section, dethreading was eliminated using the approach in Scheme 5.3 for **5.17**; this will insure accurate results in terms of hydrogen bond involvement. Therefore, **5.17** was prepared at different temperatures with the same feed ratio of 30C10 vs. diol BG to measure such dependence. As expected from hydrogen bonding theory, the lower the temperature was, the higher m/n was (Table 5.2). The relationship is plotted in Figure 5.7. These results further consolidated the hydrogen bonding theory.

Table 5.2 The threading efficiency of polyrotaxane **5.17**
prepared at different temperatures^a

Products	T (K) ^b	m/n			M _n ^d (x10 ⁻³)	M _w ^d (x10 ⁻³)
		1st ppt ^c	2nd ppt ^c	3rdd ppt ^c		
5.17e	358	0.129	0.131	0.130	15.4	58.0
5.17f	378	0.106	0.104	0.105	15.6	54.4
5.17g	400	0.074	0.076	0.075	12.9	34.3
5.17h	428	0.051	0.052	0.053	12.8	33.6

a) the ratio of 30C10 vs. diol BG **5.4** is constant at 5.

b) +/- 2 °C

c) precipitated from chloroform into methanol

d) measured by GPC with universal calibration.

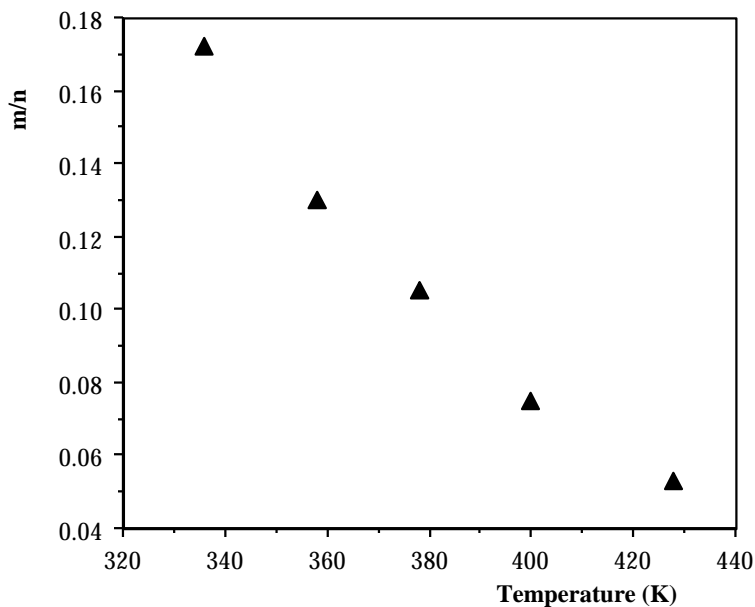


Figure 5.7 The relationship of threading efficiency of polyrotaxane 5.17 vs. temperature

As described in Chapter 3, the m/n values can be used to estimate the hydrogen bonding equilibrium constants (K). As shown in scheme 5.7, the hydroxy group of diol monomer H-bonds with the crown ether to achieve an equilibrium upon mixing. It is believed that the equilibrium process is much faster than the esterification and thus the rates of products **R** and **P** are determined by the rate constants, k_{endo} , k_{exo} and k_{free} .

Because there is no dethreading ($k_{\text{dethr}} = 0$), $d[\mathbf{R}]/dt = k_{\text{endo}}[\mathbf{H}][\mathbf{Cl}]$ <1>

$d[\mathbf{P}]/dt = k_{\text{free}}[\mathbf{L}][\mathbf{Cl}] + k_{\text{exo}}[\mathbf{H}][\mathbf{Cl}]$ <2>

where $[\mathbf{R}]$, $[\mathbf{H}]$, $[\mathbf{Cl}]$, $[\mathbf{P}]$ and $[\mathbf{L}]$ are the instantaneous concentrations of the rotaxane structure (**R**), the hydroxy group H-bonded with crown ether (**H**), acid chloride group (**Cl**), normal ester linkage (**P**), and the hydroxy group not H-bonded with crown ether (**L**).

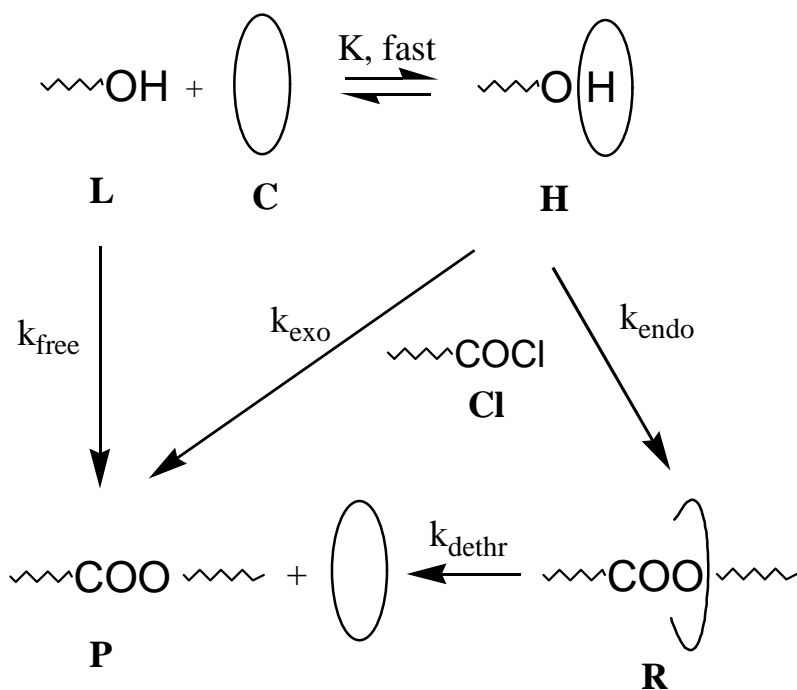
Because $[\mathbf{H}] = K[\mathbf{L}][\mathbf{C}]$: $d[\mathbf{R}]/dt = k_{\text{endo}}K[\mathbf{L}][\mathbf{Cl}][\mathbf{C}]$ <3>

$d[\mathbf{P}]/dt = k_{\text{free}}[\mathbf{L}][\mathbf{Cl}] + k_{\text{exo}}K[\mathbf{L}][\mathbf{Cl}][\mathbf{C}]$ <4>

Thus <3>/<4> gives:

$d[\mathbf{R}]/d[\mathbf{P}] = \{k_{\text{endo}}K[\mathbf{C}]\}/\{k_{\text{free}} + k_{\text{exo}}K[\mathbf{C}]\}$ <5>

Scheme 5.7



Because m/n is very low and H-bonding is weak, $[C]$ can be treated as a constant, the feed concentration ($[C]_0$). Because no variables except for R and P exist in equation <5>, its integration affords: $[R]/[P] = \{k_{\text{endo}}K[C]_0\}/\{k_{\text{free}} + k_{\text{exo}}K[C]_0\}$ <6>

$$m/n = 2[R]/\{[P] + [R]\} = \{2k_{\text{endo}}K[C]_0\}/\{k_{\text{free}} + k_{\text{exo}}K[C]_0 + k_{\text{endo}}K[C]_0\} \quad <7>$$

According to equation <7>, m/n will increase with higher concentration of crown ether and/or larger K value; this agrees with the experimental results; polyrotaxanes prepared with higher feed ratio of 30C10 to diol monomer and/or at lower polymerization temperature had higher m/n values. Apparently, without the kinetic data, the relationship between K and m/n can precisely not be defined. However, assuming that $k_{\text{free}} = k_{\text{exo}} = k_{\text{endo}}$, equation <7> can be further simplified as

$$m/n = (2K[C]_0)/(1 + 2K[C]_0) \text{ or } K = (m/n)/\{2[C]_0(1-m/n)\} \quad <8>$$

Thus the m/n values at different temperatures (Table 5.2) were converted into K (Table 5.3). $\ln K$ was then plotted against $1/T$ to afford the van't Hoff plots (Table 5.4) and thus ΔH and ΔS values. The obtained ΔH and ΔS values, -17 kJ/mol and -72 J/mol.K, respectively, are very close to the results from Chapter 3. The ΔH value is also close to those reported for the H-bonding of 15-crown-5, 18-crown-6, dibenzo-18-crown-6 and dibenzo-24-

crown-8 with methanol in CCl₄ at 25 °C (-15.1, -14.6, -10.5 and -14.2 kJ/mol, respectively, but no ΔS values were reported),^{20,21} this consolidates the obtained results. These values provide a basis to understand and design polyrotaxanes because one can predict m/n. The negative ΔH term confirmed the existence of a strong interaction between the diol and the crown ethers, hydrogen bonding. The negative ΔS terms is easy to understand since H-bonding restricts the motions of both diol monomer and the crown. In conclusion, the ultimate m/n values are governed by these two factors, the ΔH term favors threading while the ΔS term disfavors it.

Table 5.3. K and lnK values calculated from m/n values (Table 5.2) at different t temperatures and different assumed values of k^{a,b}

Temp	428 K	400 K	378 K	358 K	336 K
K (M ⁻¹)	0.021	0.030	0.044	0.056	0.078
lnK	-3.9	-3.5	-3.1	-2.9	-2.6

a) [C]₀ is 1.34 M corresponding to b = 5.

b) Van't Hoff plot: slope = 2.0x10³, intercept = -8.6 and R² = 0.98.

Because i) k' is probably not independent of temperature, ii) [C] is not totally constant and iii) k_{free}, k_{endo} and k_{exo} may not equal to one another, the above calculated results clearly are not exact. However, they indicate a general trend and afford approximate values for the parameters involved in threading process.

5.2.6 Comparison of threading ability of different macrocycles

Since their properties are closely related to the macrocycle content (m/n value, average number of cyclics per repeat unit), the threading efficiency of a polyrotaxane is of critical importance and a rapid, simple method to measure such values for different macrocycles would be very valuable to the field.

²⁰ R. M. Izatt, J. S. Bradshaw, K. Pawlak, R. L. Bruening, B. J. Tarbet, *Chem. Rev.* **1992**, 92, 1261.

²¹ Yakshin, V. V.; Abashkin, V. M.; Laskprin, B. N. *Dokl. Chem. Proc. Acad. Sci. USSR (Engl. Trans.)* **1979**, 224, 27.

The above-addressed trapping method using bulky monomers precludes the loss of threaded cyclics during polymerization and makes it possible for us to compare the m/n values for different macrocycles in an accurate manner. Since the threading process is controlled by a hydrogen bonding equilibrium (Scheme 5.3), the threading efficiency of crown ether-based polyrotaxanes is always related to the polymerization conditions, e.g., temperature, feed composition and concentration as manifested in Chapters 3 and 4 and the above section in this Chapter. Therefore, an internal standard, 30C10, was used; a mixture of 30C10 and another macrocycle was used as solvent for polyrotaxane syntheses to eliminate the external conditional interference. Using this competitive threading methodology, the measured threading efficiencies of different macrocycles depend only on their true threading abilities, e.g., ring size, hydrogen bonding strength with hydroxy groups and ring conformations.

In practice, hybrid polyrotaxanes²² **5.18** and **5.19** were prepared by solution polycondensation using a mixture of 30C10 and bisphenylene 34-crown-10 (BPP34C10), and a mixture of 30C10 and dibenzo-24-crown-8 (DB24C8) as solvent, respectively (Scheme 5.8). The unthreaded macrocycles were removed by five precipitations from THF solution into methanol.

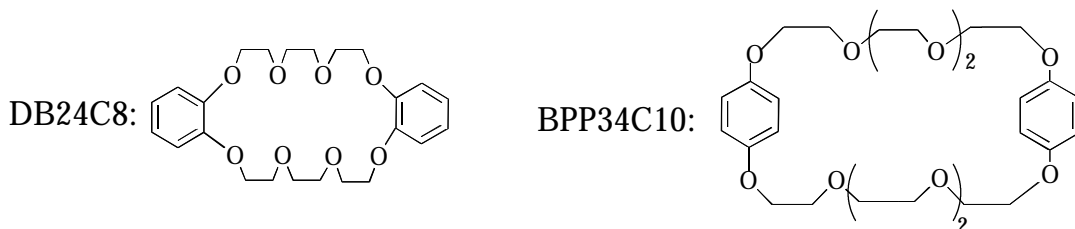
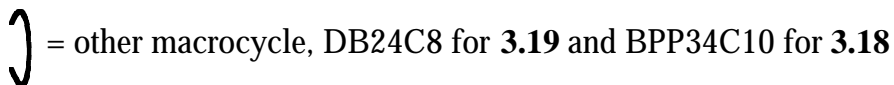
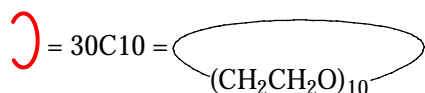
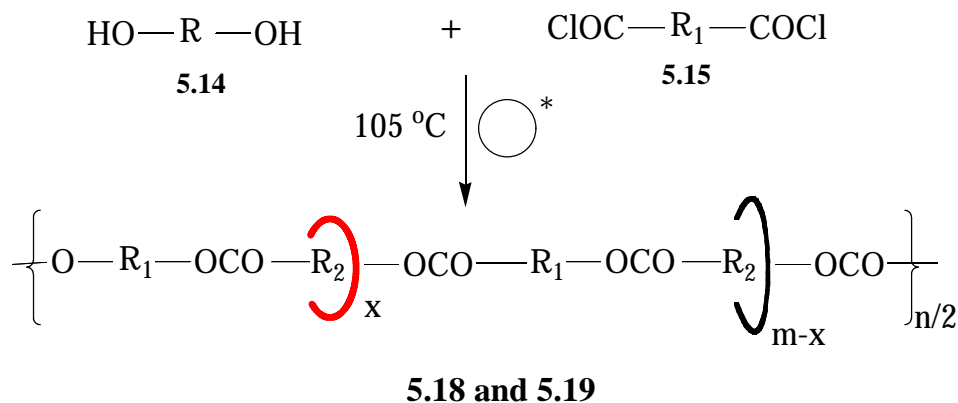
It is well understood that threaded 30C10 in polyrotaxane **5.17** has an upfield chemical shift compared to its free counterpart because of its through-space interaction with the electron rich aromatic rings of the BG units.^{9,10} Interestingly, in hybrid polyrotaxane **5.18**, that (Figure 5.8b) of threaded BPP34C10 is also different from its free counterpart (Figure 5.8a). The ethyleneoxy protons b, c, and d are shifted upfield, surely because of the same reason as that for 30C10.^{9,10} The downfield shift of aromatic proton a is because of i) the loss of free rotation of the aromatic rings upon threading²³ as observed previously for the poly(ester pseudorotaxane) of Type **5.1**⁶ or ii) its through-space interaction with the in-chain

²² We define a polyrotaxane threaded with two or more different macrocycles as a hybrid polyrotaxane to distinguish it from a polyrotaxane threaded with one type of cyclic.

²³ Out of phase rotation of the phenylene rings of BPP34C10 places proton a of one ring in the shielding zone of the other ring. In polyrotaxane not only is rotation prevented but the space between the rings is occupied and the aromatic proton a appears at nearly the same chemical shift (6.83 ppm) as those in *p*-dimethoxybenzene (6.85 ppm).

ethyleneoxy moiety as in poly(ester rotaxane)s of Type **5.3** discussed in early chapter. As expected, the same observation was made for DB24C8 in polyrotaxane **5.19**. Therefore, the proton NMR study directly proved the rotaxane structures of **5.18** and **5.19**.

Scheme 5.8 Preparation of hybrid polyrotaxanes **5.18** and **5.19**



As the results in Table 5.4 show, by referring to 30C10 as the standard, BPP34C10 had a relative threading efficiency of 1.35 and DB24C8, however, only 0.837 under these conditions. The threading efficiency consists of two factors: the hydrogen bonding association constant K and the capture constant, the fraction of hydrogen bonded “prerotaxanes” that are threaded by endo esterification (Scheme 5.8). The better threading ability of BPP34C10 can be attributed to its larger ring size or possibly its higher rigidity

which leads to a more open cavity, probably increasing the association and capture constants. The small ring size probably lowers both association and capture constants of DB24C8.

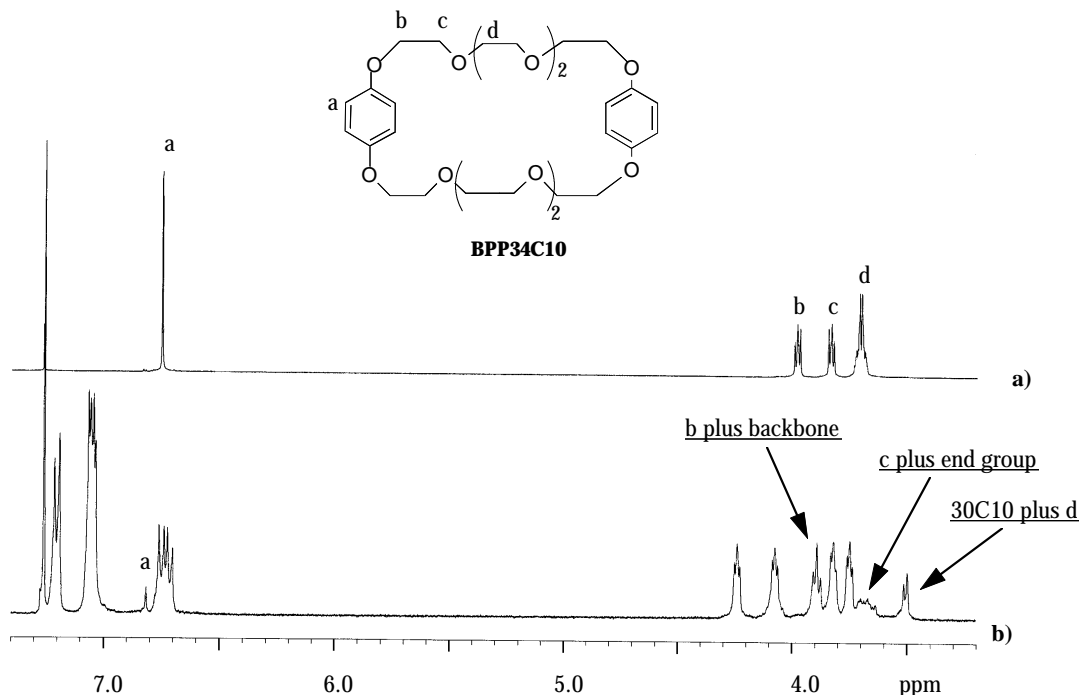


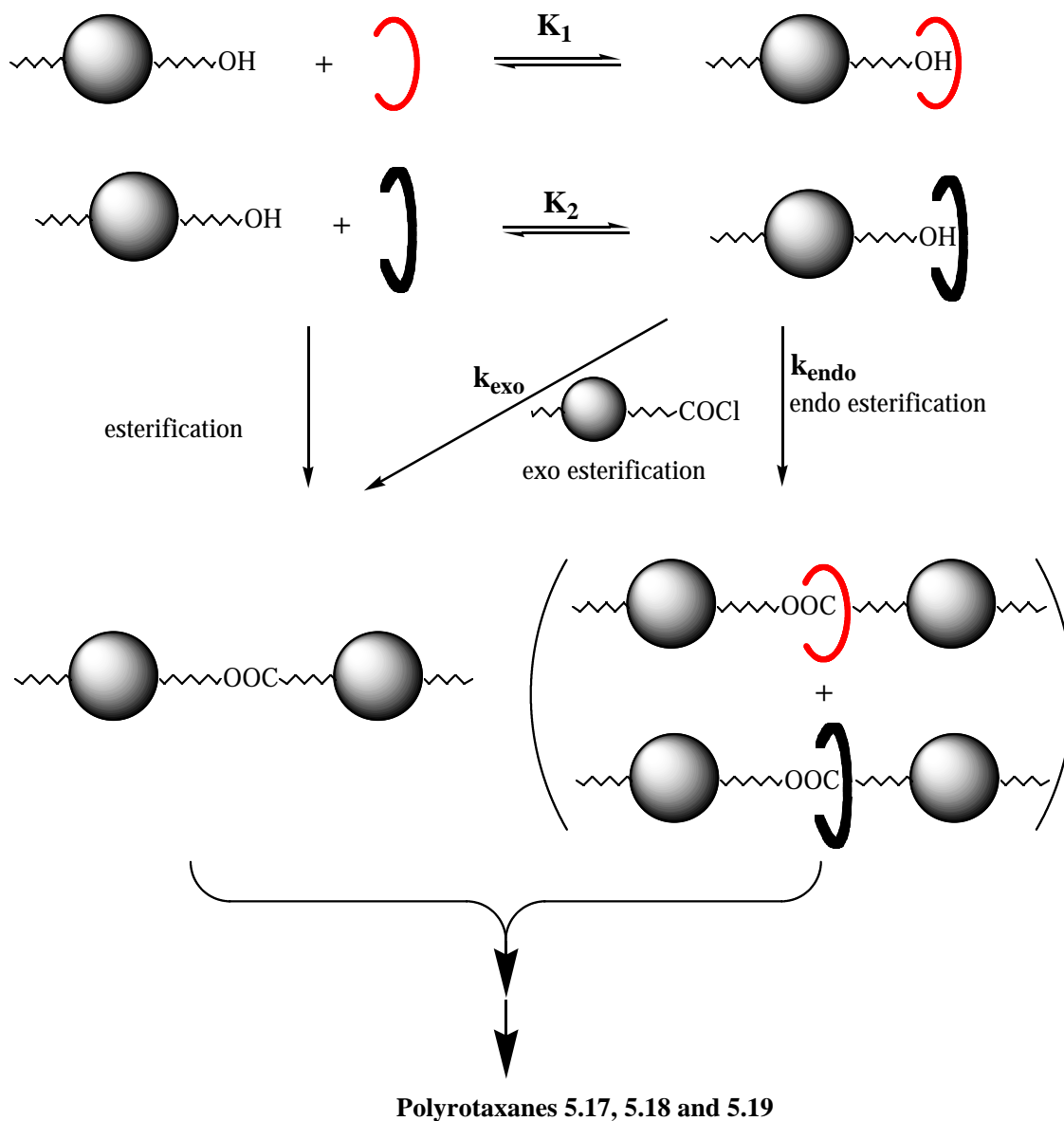
Figure 5.8 The 400 MHz proton NMR spectra of a) top, BPP34C10 and b) bottom, polyrotaxane **5.18** in CDCl₃

Table 5.4. Polymerization conditions^a and threading efficiencies for polyrotaxanes **5.17c**, **5.18** and **5.19**

polyrotaxane ^b	feed ratio of cyclic vs. diol 5.15	x/n, (m-x)/n ^c	relative threading efficiency ^d
5.17c	30C10 (5.00)	0.106, 0	1.00
5.18^e	30C10 (2.50), BPP34C10 (2.50)	0.0513, 0.0690	1.35
5.19^e	30C10 (2.50), DB24C8 (2.50)	0.0546, 0.0457	0.837

a) temperature: 105 °C; time: 2 days. b) unthreaded cyclic removed by precipitation into methanol five times.⁶ c) measured by proton NMR.⁶ d) the ratio of threading efficiency of the cyclic vs. that of 30C10. e) relative molecular weights measured by GPC with PS standards: M_w = 36 k and 42 k for **5.18** and **5.19**, respectively (PDI~2.5).

Scheme 5.8 Competitive threading mechanism



$$\text{Capture constant} = [k_{endo}/(k_{endo}+k_{exo})]$$

It is worth mentioning that the smallest macrocycle successfully used previously in polyrotaxanes was 30C10.^{9,10} Therefore, this is the first time that a 24-membered macrocycle has been successfully threaded onto a polymer backbone while it has been used for

preparation of low MW rotaxanes.²⁴ We believe the result is important to the field as well as encouraging to scientists. First, DB24C8 is commercially available and using it as the cyclic component for polyrotaxanes will save lots of precursor preparation time. In addition, since the ring movement on and/or around the backbone and the properties of polyrotaxanes are related to its size¹, using such a small cyclic will probably induce more interesting as well as important behaviors in these species.

5.3 Conclusions

A new difunctional BG (diacid chloride BG **5.14**) was prepared and it was successfully used in the preparation of the polyrotaxanes of type **5.3**. A novel strategy to eliminate dethreading during the preparation of poly(ester crown ether) rotaxanes was thus demonstrated by using both diol BG **5.15** and diacid chloride BG **5.14** as the only monomers. Thus polyrotaxanes with highest threading efficiency were obtained, compared to both the polyseudorotaxanes of type **5.1** and the polyrotaxanes of type **5.2** made under the same conditions. The threading efficiency depended on temperature; the lower the temperature was, the higher the m/n was. Detailed threading and dethreading mechanisms were proposed. The results of this research are consistent with the H-bonding theory proposed previously, although more detailed study has to be done to directly prove it. All the results pointed to hydrogen bonding and thus a detailed threading and dethreading mechanism was provided. The enthalpy and entropy changes for the H-bonding are estimated to be -17 kJ/mol and -70 J/mol.K, respectively.

Moreover, a feasible and accurate method is provided to determine the relative threading abilities of different macrocycles for polyrotaxane synthesis; this is done using 30C10 as co-solvent along with the studied macrocycle in competitive experiments.

²⁴ Amabilino, D. B.; Ashton, P. R.; Brown, C. L.; Cordova, E.; Godinez, L. A.; Goodnow, T. T.; Kaifer, A. E.; Newton, S. P.; Pietraszkiewicz, M.; Philip, D.; Raymo, F. M.; Reder, A. S.; Rutland, M. T.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Williams, D. J. *J. Am. Chem. Soc.* **1995**, *117*, 1271.

5.4 Experimental

Chemical Reagents and Measurements

All chemicals were reagent grade and used directly as received from Aldrich unless otherwise specified. All solvents were HPLC or GC grade. 30C10²⁵ and BPP34C10²² were prepared by well-established procedures. Diphenolic BG **5.14** and diol BG **15** were synthesized by a reported method.⁹ Proton NMR spectra, reported in ppm, were obtained on a 400 MHz Varian Unity spectrometer using chloroform-*d* solutions or DMSO-*d*₆ solutions as specified in the text and with tetramethylsilane as an internal standard. The NOESY studies were performed at room temperature with a mixing time of one second and a relaxation time of two seconds. The following abbreviations have been used in describing NMR spectra: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), and m (multiplet); coupling constants (J) are in Hertz. The m/n values of the polyrotaxanes were measured by proton NMR spectroscopy and calculated from the integrals of threaded 30C10 vs. the methylene protons of diol BG units in the backbone. Absolute molecular weights were measured by GPC analyses with a Waters 150C ALC/GPC chromatograph with polystyrene-divinylbenzene columns equipped with a differential refractometer detector and an on-line differential viscometric detector (Viscotek 150R) coupled in parallel and using the universal calibration. Relative molecular weights were measured by GPC analyses with a Waters 150C ALC/GPC system with polystyrene-divinylbenzene columns, using polystyrene standards; the instrument was fitted with a refractive index detector.

Bis(*p*-*tert*-butylphenyl)bis[*p*-(5-carbethoxypropyloxy)phenyl]methane (5.12).

Bis(*p*-*tert*-butylphenyl)bis(*p*-hydroxyphenyl)methane (**5.10**) (5.00 g, 10.8 mmol) in DMF (50 mL) was added to a suspension of sodium hydride (1.30 g, 60%, 32.5 mmol) in 50 mL of DMF over 10 minutes at room temperature. After the mixture had been stirred for one hour, ethyl 6-bromohexanoate (**5.11**, 12.0 g, 53.8 mmol) in DMF (50 mL) was added to the system. After reaction for 8 hrs at 60 °C, TLC showed that all starting materials disappeared

²⁵ Bheda, M. C.; Merola, J. S.; Woodward, W. A.; Vasudevan, V. J.; Gibson, H. W. *J. Org. Chem.* **1994**, *59*, 1684.

and only one product was formed. After the system had been cooled down to room temperature, the salt was removed by suction filtration and DMF by vacuum evaporation. The residue was taken-up in CH₂Cl₂/H₂O (150 mL/50 mL). Separation of the organic layer and removal of the solvent afforded a white solid. The crude product was recrystallized in methanol (80 %, mp 89.2-90.4 °C). ¹H NMR in CDCl₃: 1.25 (t, J=7.2, 6H); 1.29 (s, 18H); 1.49 (m, 4H); 1.69 (m, 4H); 1.78 (m, 4H); 2.33 (t, J=7.2, 4H); 3.93 (t, J=6.4, 4H); 4.13 (q, J=7.2, 4H); 6.74 (d, J=9.2, 4H); 7.08-7.05 (m, 8H); 7.22 (d, J=9.2, 4H). ¹³C NMR in CDCl₃: 14.23; 25.69; 29.00; 31.35; 34.25; 60.21; 62.73; 67.43; 112.93; 124.04; 130.60; 132.09; 139.49; 144.25; 148.24; 156.79; 173.63 (18 peaks, theory: 21 peaks). Anal. Calcd for C₄₉H₆₄O₆: C, 78.57; H, 8.61. Found: C, 78.63; H, 8.66.

Bis(*p*-*tert*-butylphenyl)bis[*p*-(5-carboxypentyloxy)phenyl]methane (5.13).

Diester BG 5.12 (7.00 g, 9.34 mmol) was added to a mixture of EtOH (500 mL) and KOH solution (4M, 120 mL). The mixture was refluxed for 20 hrs. After it had been cooled down, the mixture was acidified with con. HCl solution. Extraction with methylene chloride (2x150 mL) and removal of the organic solvent afforded a white solid. The crude product was recrystallized in hexane/ethyl acetate twice (1:1, 150 mL) (5.8 g, 90%, mp 184.5-186.0 °C). ¹H NMR in DMSO-*d*₆: 1.25 (s, 18H); 1.40 (m, 4H); 1.55 (m, 4H); 1.69 (m, 4H); 2.22 (t, J=7.2, 4H); 3.90 (t, J=6.2, 4H); 6.82 (d, J=9.2, 4H); 6.98-7.05 (m, 8H); 7.29 (d, J=9.2, 4H); 12.02 (s, 2H). ¹³C NMR in DMSO-*d*₆: 24.25; 25.19; 28.49; 31.11; 33.60; 34.02; 62.23; 67.10; 113.28; 124.27; 129.93; 131.33; 138.82; 144.06; 147.70; 156.37; 174.40 (17 peaks as required). Anal. Calcd for C₄₅H₅₆O₆: C, 78.00; H, 8.15. Found: C, 78.12; H, 8.11.

Bis(*p*-*tert*-butylphenyl)bis[*p*-(5-chlorocarbonylpentyloxy)phenyl]methane (5.14).

Diacid BG 5.13 (4.70 g, 6.78 mmol) was dissolved in SOCl₂ (50 mL) and refluxed for 3 hrs. Upon the removal of excess SOCl₂, a yellow solid was obtained, which was recrystallized in hexane (150 mL) to give needle crystals (4.3 g, 88%), mp 138.6-140.0 °C. ¹H NMR in DMSO-*d*₆ (Figure 1): 1.25 (s, 18H); 1.3.8 (m, 4H); 1.52 (m, 4H); 1.66 (m, 4H); 2.19 (t, J=7.2, 4H); 3.87 (t, J=6.4, 4H); 6.82 (d, J=9.2, 4H); 6.98-7.05 (m, 8H); 7.29 (d, J=9.2,

4H). ^{13}C NMR in $\text{DMSO-}d_6$: 24.25; 25.19; 28.48; 31.11; 33.60; 34.02; 62.22; 67.11; 113.28; 124.27; 129.93; 131.33; 138.82; 144.06; 147.71; 156.36; 174.37 (17 peaks as required). Anal. Calcd for $\text{C}_{45}\text{H}_{54}\text{O}_4\text{Cl}_2$: C, 74.14; H, 7.47. Found: C, 74.11; H, 7.41.

General Procedure for Polyrotaxanes 5.16.

Diol BG **5.15** (399.6 mg, 0.6235 mmol) was dissolved in 30C10 (2-4 eqv.) at 140 °C. Then temperature was adjusted according to Table 5.1. After the homogeneous solution was stirred for half hour under the protection of nitrogen, sebacoyl chloride (150.1 mg, 0.6277 mmol) was added to the system. The polymerization proceeded for two days. The polymer was purified by precipitation from THF solution (2.5 mL) into water (200 mL). ^1H NMR in CDCl_3 : 1.29 (s, 26H); 1.57 (s, broad, H_2O plus 4H of $-\text{OCOCH}_2\text{CH}_2-$); 2.31 (t, $J=7.6$, 4H); 3.52 (s, variable); 3.75 (t, $J=4.8$, 4H); 3.83 (t, $J=4.8$, 4H); 4.09 (t, $J=4.8$, 4H); 4.24 (t, $J=4.8$, 4H); 6.77 (major peak) and 6.85 (minor peak) (d, $J=8.8$, total 4H); 7.04-7.08 (m, 8H); 7.22 (d, $J=8.8$, 4H).

General Procedure for Polyrotaxanes 5.17a-17c.

Diol BG **5.15** (250 mg, 0.391 mmol) was dissolved in 30C10 (2-5 eqv.) at 140 °C. Then the temperature was adjusted as specified in Table 1 and the solution was stirred for half hour. After diacid chloride BG **5.14** (284 mg, 0.390 mmol) had been added to the system, the polymerization ran for two days at the same temperature. After it had been cooled down, the product was precipitated into water (3x150 mL) from THF solution (2 mL). ^1H NMR in CDCl_3 (Figure 5.3a): 1.25 (s, 36H), 1.48 (m, 4H), 1.69 (m, 4H), 1.76 (m, 4H), 2.36 (t, $J = 7.2$, 4H), 3.50 (broad s, variable), 3.75 (t, $J = 4.6$, 4H), 3.82 (t, $J = 4.6$, 4H), 3.90 (t, $J = 6.8$, 4H), 4.09 (t, $J = 4.6$, 4H), 4.25 (t, $J = 4.6$, 4H), 6.07-6.78 (m, 8H), 7.04-7.08 (m, 16H), 7.20-7.23 (m, 8H).

The same procedure was applied for polyrotaxanes **5.17e-17h** using 30C10 as solvent. The detailed conditions are specified in Table 5.2. Hybrid polyrotaxanes **5.18** and **5.19** were also prepared by similar approach except that the solvent was a mixture of two different macrocycles. The start feed compositions and polymerization conditions are indicated in

Table 5.4. The reaction scale is about ca. 1 g of product (recovery: >90 %).

Procedure for Model Polyester 5.17d, m/n=0.

Diol BG **5.15** (250 mg, 0.391 mmol) and diacid chloride BG **5.14** (284 mg, 0.390 mmol) were dissolved in 2 mL of diglyme (anhydrous). The system was heated to 90 °C. Polymerization ran for two days at this temperature. After it had been cooled down, the product was precipitated into methanol (2x150 mL) from THF (2 mL). ¹H NMR in CDCl₃ (Figure 5.3b): 1.25 (s, 36H); 1.48 (m, 4H); 1.69 (m, 4H); 1.76 (m, 4H); 2.36 (t, J=7.2, 4H); 3.75 (t, J=4.6, 4H); 3.82 (t, J=4.6, 4H); 3.90 (t, J=6.8, 4H); 4.09 (t, J=4.6, 4H); 4.25 (t, J=4.6, 4H); 6.07-6.78 (m, 8H); 7.04-7.08 (m, 16H); 7.20-7.23 (m, 8H).

Hydrolysis of polyrotaxane 5.17c

Polyrotaxane **5.17c** (100 mg, m/n=0.172) was dissolved in THF (3 mL). After 1.5 mL of aqueous potassium hydroxide (10 M) had been added, the mixture was refluxed for 8 hrs. Upon the removal of all solvent under reduced pressure, the hydrolysis product was extracted with CHCl₃ (3x50 mL) and CHCl₃ was evaporated. It was found that both 30C10 and diol BG **5.15** were recovered; ¹H NMR: Figure 5.4b. Pure 30C10 was recovered by further extraction of the neutral hydrolytic products using hexane (3x50 mL); ¹H NMR: Figure 5.4a.

Chapter 6

Poly(urethane/crown ether rotaxane)s with controlled microstructures

6.1 Introduction

Polyrotaxanes are macromolecular structures consisting of linear species and cyclics, mechanically linked with each other.¹ There are three types of main chain polyrotaxanes (Scheme 6.1) including polypseudorotaxane **6.2**, in which the cyclics can slip off the backbone,^{2,3,4} and true polyrotaxanes **6.1**^{4c} and **6.3**,^{4d,5} in which the cyclics are confined between blocking groups (BG) and which thus are thermally stable. In both **6.1** and **6.2**, the cyclics can translate along the backbone to form a separate phase if there is no strong interaction between the backbone and the cyclics, e.g., poly(ester rotaxane)s,^{4c,4d} while the cyclics in **6.3** are separated by BG and have a diminished ability to aggregate and crystallize.⁵ It was also found that dethreading occurs during the preparation of poly(ester rotaxane)s because the ester linkage can not retain threaded cyclics at the stage of low MW and the use of difunctional BG mechanically prevented dethreading and thus increased the m/n value by 13-fold compared to that without BG.⁵ Since the crown ethers can hydrogen bond with -OH or NH groups,^{5,6} the threaded crown ethers should not dethread or do so only to small extent with polyurethane or polyamide backbones; in-chain NH groups tend to retain the threaded

¹ a) Gibson, H. W.; Bheda, M. C.; Engen, P. T. *Prog. Polym. Sci.* **1994**, *19*, 843. b) Amabilino, D. B.; Stoddart, J. F. *Chem. Rev.*, **1995**, *95*, 2725. c) Philp, D.; Stoddart, J. F. *Angew. Chem. Int. Engl.* **1996**, *35*, 1154. d) Gibson, H. W. in *Large Ring Molecules*, Semlyen, J. A., ed., J. Wiley and Sons, New York, **1996**, 191-262.

² a) Wenz, G. *Macromol. Symp.* **1994**, *87*, 11. b) Weickenmeier, M.; Wenz, G. *Macromol. Rapid Commun.* **1996**, *17*, 731. c) Steinbrunn, M. B.; Wenz, G. *Angew. Chem. Int. Engl.* **1996**, *35*, 2139.

³ a) Harada, A.; Li, J.; Kamachi, M. *Macromolecules* **1994**, *27*, 4538. b) Harada, A.; Okada, M.; Li, J.; Kamachi, M. *Macromolecules* **1995**, *28*, 8406.

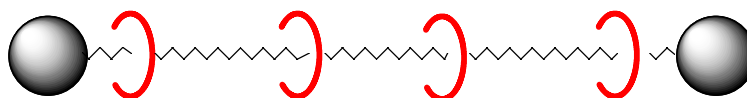
⁴ a) Gibson, H. W.; Marand, H. *Adv. Mater.* **1993**, *5*, 11. b) Shen, Y. X.; Xie, D.; Gibson, H. W. *J. Am. Chem. Soc.*, **1994**, *116*, 537. c) Gibson, H. W.; Liu, S.; Lecavalier, P.; Wu, C.; Shen, Y. X. *J. Am. Chem. Soc.* **1995**, *117*, 852. d) Gibson, H. W.; Liu, S.; Gong, C.; Ji, Q.; Joseph, E. *Macromolecules*, 3711. e) Gibson, H. W.; Liu, S. *Macromol. Symp.* **1996**, *102*, 55.

⁵ a) Gong, C.; Gibson, H. W. *Macromolecules* **1996**, *29*, 7029 and chapter 3. b) Gong, C.; Gibson, H. W. *Macromol. Chem. Phys.* **1997**, *198*, 2321 and chapter 4. c) Gong, C.; Ji, Q.; Glass, T. E.; Gibson, H. W. *Macromolecules*. **1997**, *30*, 4807.

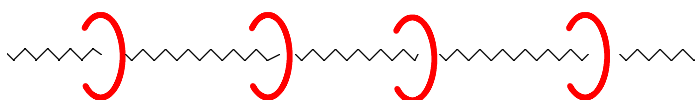
⁶ Marand, E.; Hu, Q.; Gibson, H. W.; Veytsman, B. *Macromolecules* **1996**, *29*, 2555.

cyclics. In addition, the crown ethers could be localized at the NH sites by H-bonding to afford a well-defined microstructure. I tested this idea by the preparation of poly(urethane/crown ether rotaxane)s and the results are reported in this chapter.

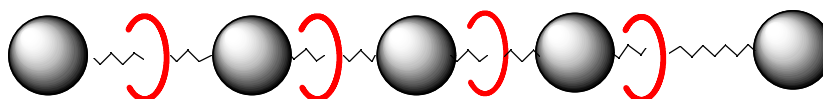
Scheme 6.1 Various main chain polyrotaxanes



6.1. main chain polyrotaxanes with monofunctional blocking groups (BG)



6.2. main chain polyrotaxane without BGs



6.3. main chain polyrotaxane with difunctional BGs

Moreover, the aliphatic crown ether-based polyrotaxanes have only successfully been prepared by threading macrocycles onto linear components during polymerization using the cyclics as solvents^{1,4,5} (Approach II, Scheme 6.2). For CD-based polyrotaxanes,^{2,3,7} the driving force is well understood to be inclusion complexation between CD and the linear molecule and rotaxanes are always constructed by threading CD onto the preformed backbone for main chain polyrotaxanes^{2,3} or side chain units for side chain polyrotaxanes⁷ (Approach I, Scheme 6.2). Similarly by Approach I, threading of a bisphenylene crown ether

⁷ a) Born, M.; Ritter, H. *Acta Polym.* **1994**, *45*, 68. b) Born, M.; Ritter, H. *Angew. Chem. Int. Engl.* **1995**, *107*, 342. (c) Born, M.; Ritter, H. *Angew. Chem. Int. Engl.* **1995**, *34*, 309. (d) Born, M.; Ritter, H. *Adv. Mater.* **1996**, *8*, 149. (e) Born, M.; Ritter, H. *Macromol. Rapid Commun.* **1996**, *17*, 197.

onto a polymer containing 4,4'-bipyridinium units was successful,⁸ as was polypseudorotaxane formation from a cyclic bis(4,4'-bipyridinium) macrocycle and polymers containing electron rich aromatic moieties.⁹ However, because of the high melting points of CD's and the bipyridinium macrocycle and the thermal instability of the bipyridinium moieties, application of Approach II to these systems requires the use of solvents, typically water for the CD's and a polar solvent such as acetone for the bipyridinium systems.

In contrast, aliphatic crown ethers have low melting points (<55 °C)¹⁰ and possess both hydrophilic and hydrophobic character, making them reasonably good solvents. Therefore, it occurred to us that it might be possible to synthesize polypseudorotaxanes in a melt process using approach I, thus enabling the preparation of this new architecture in a straightforward manner easily adaptable to normal polymer processing techniques. Indeed, we previously attempted to prepare aliphatic crown ether-based polyrotaxanes by Approach I. However, very little cyclic ($m/n = 2 \times 10^{-2}$, threading efficiency, average number of cyclics per repeat unit) was threaded using "42-crown-14" ("42C14")¹² as solvent with a polyester backbone.^{4d}

Since threaded crown ethers form H-bonds with in-chain NH groups in polyurethane rotaxanes,⁶ crown ethers are expected to thread onto preformed polymers containing NH groups, i.e., polyurethanes and polyamides, by hydrogen bonding (Scheme 6.3); this has now

⁸ (a) Gibson, H. W.; Liu, S.; Shen, Y. X.; Bheda, M. C.; Lee, S.-H.; Wang, F. *NATO ASI Series*, Kluwer Acad. Pub., Dordrecht, the Netherlands, Series C, Vol. 456 **1995**, pp. 41-58.

⁹ a) Mason, P. E.; Parsons, I. W.; Tolley, M. S. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2238. b) Owen, J.; Hodge, P. *J. Chem. Soc., Chem. Commun.* **1997**, 11.

¹⁰ Chenevert, R.; D'Astous L. *J. Heterocyclic Chem.* **1986**, *23*, 1785.

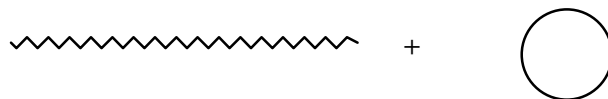
¹¹ This material was prepared by the procedure we reported for the synthesis of 42-crown-14 (Gibson, H. W.; Bheda, M. C.; Engen, P. T.; Shen, Y. X.; Sze, J.; Zhang, H.; Gibson, M. D.; Delaviz, Y.; Lee, S.-H.; Wang, F.; Nagverkar, D.; Rancourt, J.; Taylor, L. T. *J. Org. Chem.* **1994**, *59*, 2186). Subsequent detailed GPC study in collaboration with Prof. Colin Booth and colleagues at the University of Manchester (U.K.) and HPLC study by Dr. Xie and Gibson, showed this material was a mixture of different sized macrocycles but rather pure 42C14. We thus use quotation marks around the name to designate the size of the crown ether that was the target of the synthesis, rather than its true size.

¹² a) Johnston, A. G.; Leigh, D. A.; Nezhat, L.; Smart, J. P.; Deegan, M. D. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1212. b) Johnston, A. G.; Leigh, D. A.; Pritchard, R. J.; Deegan, M. D. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1209. c) Leigh, D. A.; Murphy, A.; Smart, J. P.; Slawin, A. M. Z. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 728-731.

been demonstrated for the first time by the preparation of main chain poly(urethane/crown ether rotaxane)s in the present work.

Scheme 6.2 Preparation methods for main chain polyrotaxanes

Approach I

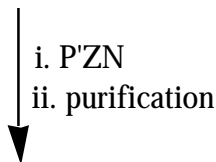
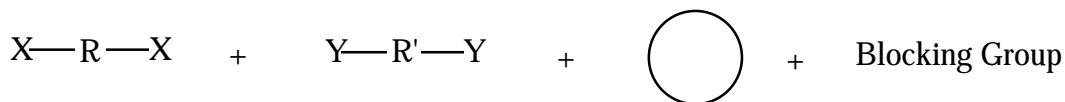


Polypseudorotaxanes **6.2**

~~~~~ : polymer, e.g., poly(ethylene oxide)

○ : macrocycles, e.g., cyclodextrin

**Approach II**



Polyrotaxanes of type **6.1** without BG

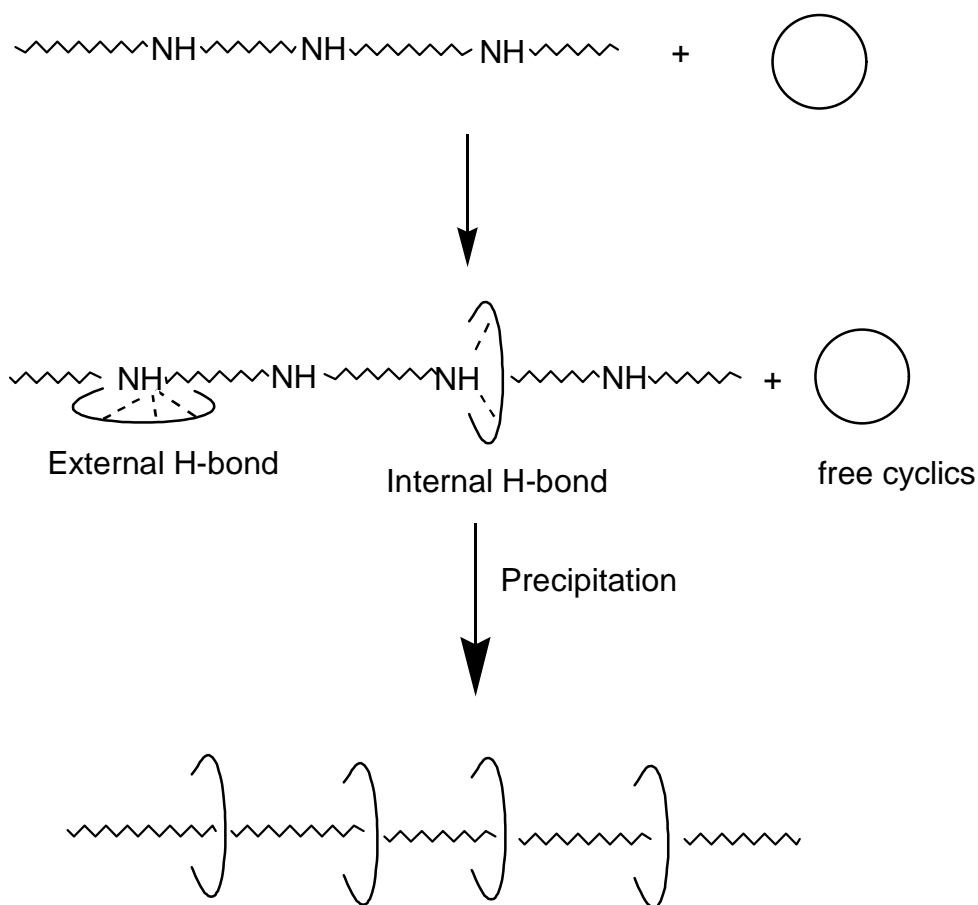
Polyrotaxanes of type **6.2** with monofunctional BG

Polyrotaxanes of type **6.3** with difunctional BG

X and Y: reactive groups, e.g., X = OH, Y = COCl

○ : macrocycles, e.g., crown ethers

Scheme 6.3



## 6.2 Results and Discussion

### 6.2.1 Polyrotaxanes prepared by approach II

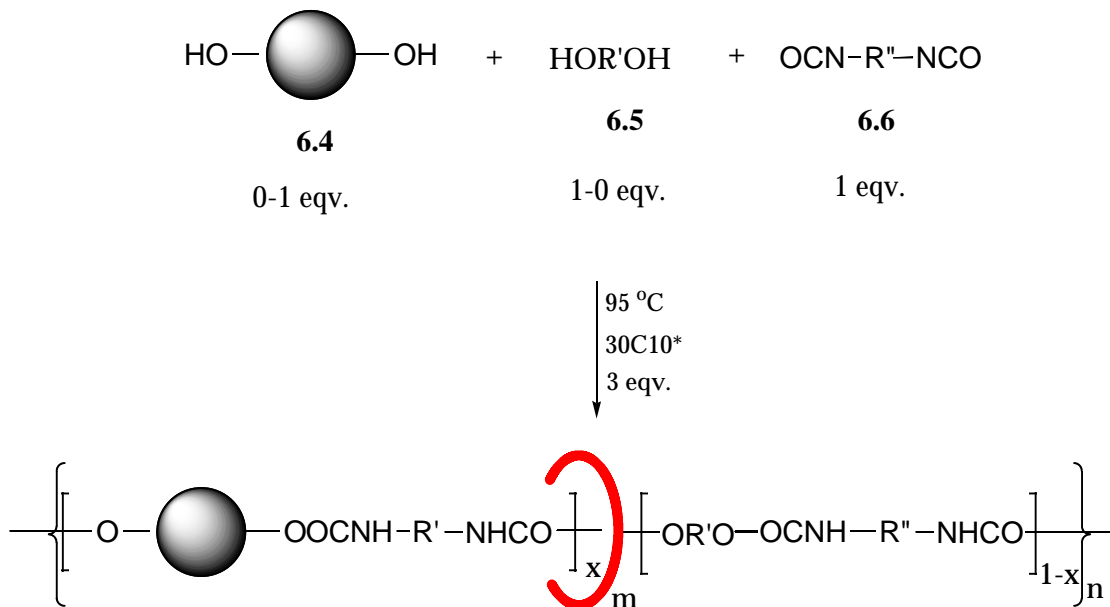
#### i. Synthesis of model polyurethane **6.7a-b** and poly(urethane rotaxane)s **6.7c-g**.

To establish the conditions for production of high molecular weight polymer, model homopolyurethane **6.7a** was prepared from glycol **6.5** and MDI (**6.6**) and copolyurethane **6.7b** from diol BG **6.4**, **6.5**, and MDI by solution polymerization using DMF as solvent (Scheme 6.4) at 95 °C for 7 hours (Table 6.1). It was found that these reaction conditions afforded high MW polymers (Table 6.2). Therefore, the same polymerization conditions were applied for the syntheses of poly(urethane rotaxane)s **6.7c-g** except that 30C10 was used



as solvent instead of DMF. Unthreaded 30C10 was removed by precipitation from DMF into methanol, a good solvent for 30C10 but a poor solvent for the backbone.<sup>4c</sup>

**Scheme 6.4**



- 6.7a:**  $x = 0, m/n = 0$
- 6.7b:**  $x = 0.40, m/n = 0$
- 6.7c:**  $x = 0, m/n = 0.032$
- 6.7d:**  $x = 0.10, m/n = 0.036$
- 6.7e:**  $x = 0.40, m/n = 0.040$
- 6.7f:**  $x = 0.70, m/n = 0.045$
- 6.7g:**  $x = 1.00, m/n = 0.049$

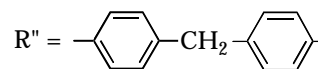
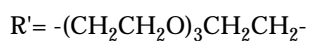
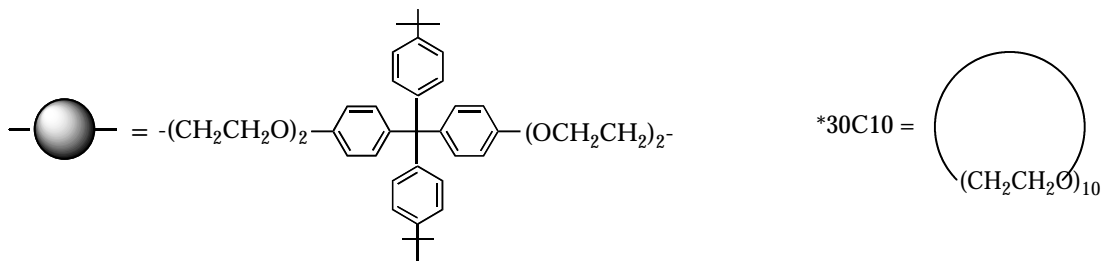


Table 6.1 The feed compositions and polymerization conditions for polyurethanes **6.7a-b** and poly(urethane rotaxane)s **6.7c-ga**

| products    | BG diol <b>6.4</b><br>(mg,mmol) | glycol <b>6.5</b><br>(mg,mmol) | MDI <b>6.6</b><br>(mg,mmol) | 30C10<br>(g,mmol) |
|-------------|---------------------------------|--------------------------------|-----------------------------|-------------------|
| <b>6.7a</b> | 0.00/0.00                       | 194.2/1.000                    | 250.3/1.000                 | 0 <sup>b</sup>    |
| <b>6.7b</b> | 255.5/0.400                     | 116.5/0.600                    | 250.3/1.000                 | 0 <sup>b</sup>    |
| <b>6.7c</b> | 0.00/0.00                       | 194.2/1.000                    | 250.3/1.000                 | 1.321/3.000       |
| <b>6.7d</b> | 63.9/0.100                      | 174.8/0.900                    | 250.3/1.000                 | 1.321/3.000       |
| <b>6.7e</b> | 255.5/0.400                     | 116.5/0.600                    | 250.3/1.000                 | 1.321/3.000       |
| <b>6.7f</b> | 447.2/0.700                     | 58.3/0.300                     | 250.3/1.000                 | 1.321/3.000       |
| <b>6.7g</b> | 638.8/1.000                     | 0.00/0.00                      | 250.3/1.000                 | 1.321/3.000       |

a) temperature: 96 °C, time: 7 h.

b) DMF as solvent (2 mL).

Table 6.2. Threading Efficiencies, dethreading degree, GPC and DSC results for polyurethanes **6.7a-g**

| products    | %BG<br><b>6.4</b> | molar <sup>a</sup><br>ratio | m/n   | dethreading <sup>b</sup><br>degree (%) | M <sub>n</sub> /M <sub>w</sub> <sup>c</sup><br>(kg/mol) | T <sub>g</sub> <sup>d</sup><br>(°C) |
|-------------|-------------------|-----------------------------|-------|----------------------------------------|---------------------------------------------------------|-------------------------------------|
| <b>6.7a</b> | 0                 | 0                           | 0     | -                                      | 16.8/30.0                                               | 54.0                                |
| <b>6.7b</b> | 40                | 0                           | 0     | -                                      | 13.9/24.0                                               | 80.9                                |
| <b>6.7c</b> | 0                 | 3                           | 0.032 | 34.7                                   | 17.8/31.0                                               | 56.0                                |
| <b>6.7d</b> | 10                | 3                           | 0.036 | 26.5                                   | 22.6/39.4                                               | 65.4                                |
| <b>6.7e</b> | 40                | 3                           | 0.040 | 18.4                                   | 12.4/18.0                                               | 80.6                                |
| <b>6.7f</b> | 70                | 3                           | 0.045 | 8.16                                   | 18.7/52.9                                               | 101.7                               |
| <b>6.7g</b> | 100               | 3                           | 0.049 | 0                                      | 23.4/37.8                                               | 125.3                               |

a) molar ratio of 30C10 vs. BG diol **6.4**.

b) Degree of dethreading (%) =  $\{[(m/n)_{\max} - (m/n)_{\text{co}}] / (m/n)_{\max}\} \times 100\%$ <sup>5b</sup>

(m/n)<sub>max</sub>: threading efficiency of diol BG-based homopoly(urethane rotaxane) **6.7g**

(m/n)<sub>co</sub>: threading efficiency of poly(urethane rotaxane)s **6.7c-g**.

c) Measured by GPC with universal calibration in NMP at 60 °C.

d) Measured by DSC at scan rate 10 °C/minute.

## ii. Characterization of polyrotaxanes 6.7c-g.

The formation of poly(urethane rotaxane)s was proven by well-established procedures used for the poly(ester rotaxane)s.<sup>5</sup> First, the removal of free 30C10 was confirmed by proton NMR, i.e., the matching of the integrals of the backbone signals with their chemical compositions for **6.7c-6.7f** in which the free 30C10 signal (3.67 ppm) overlaps with protons b, c, and p (Figure 6.1a) or the disappearance of the signal (3.67 ppm) of free 30C10 for **6.7g** (Figure 6.2d).

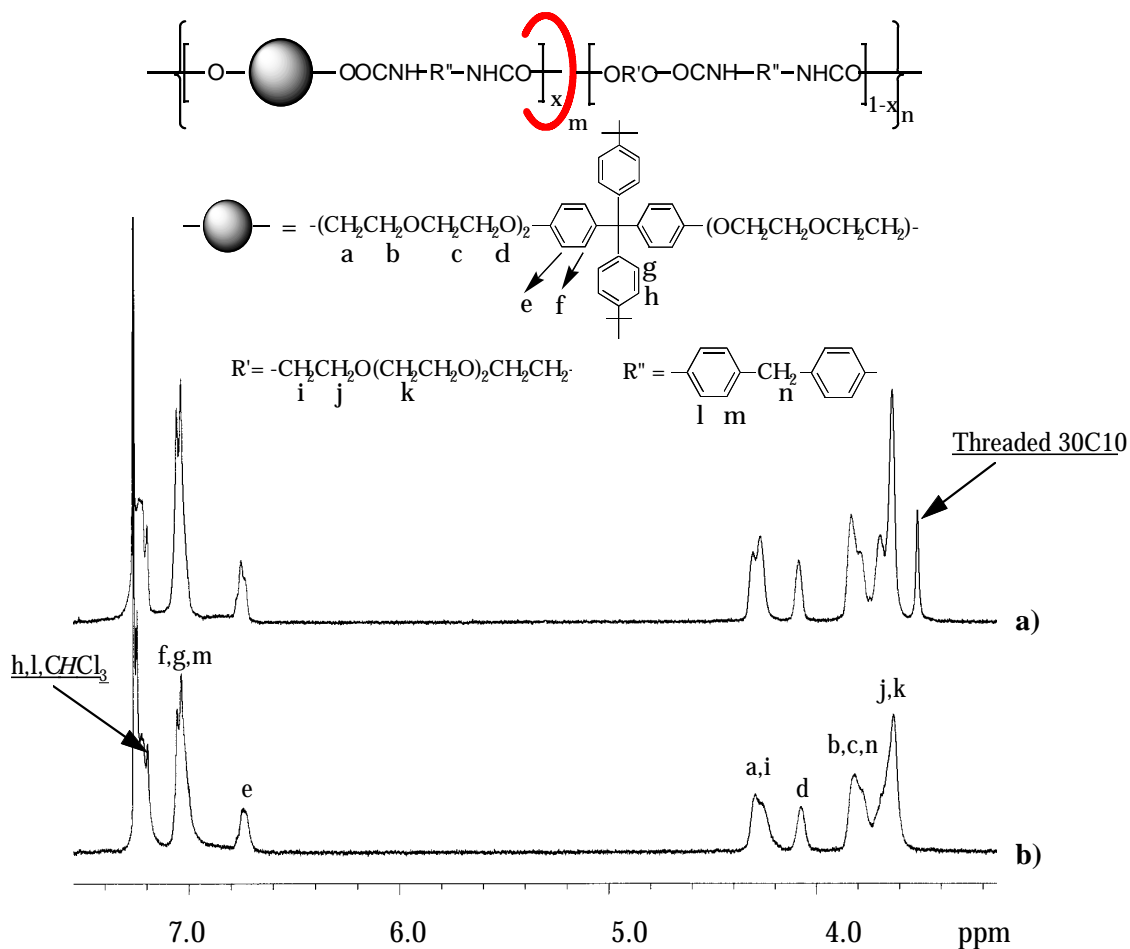
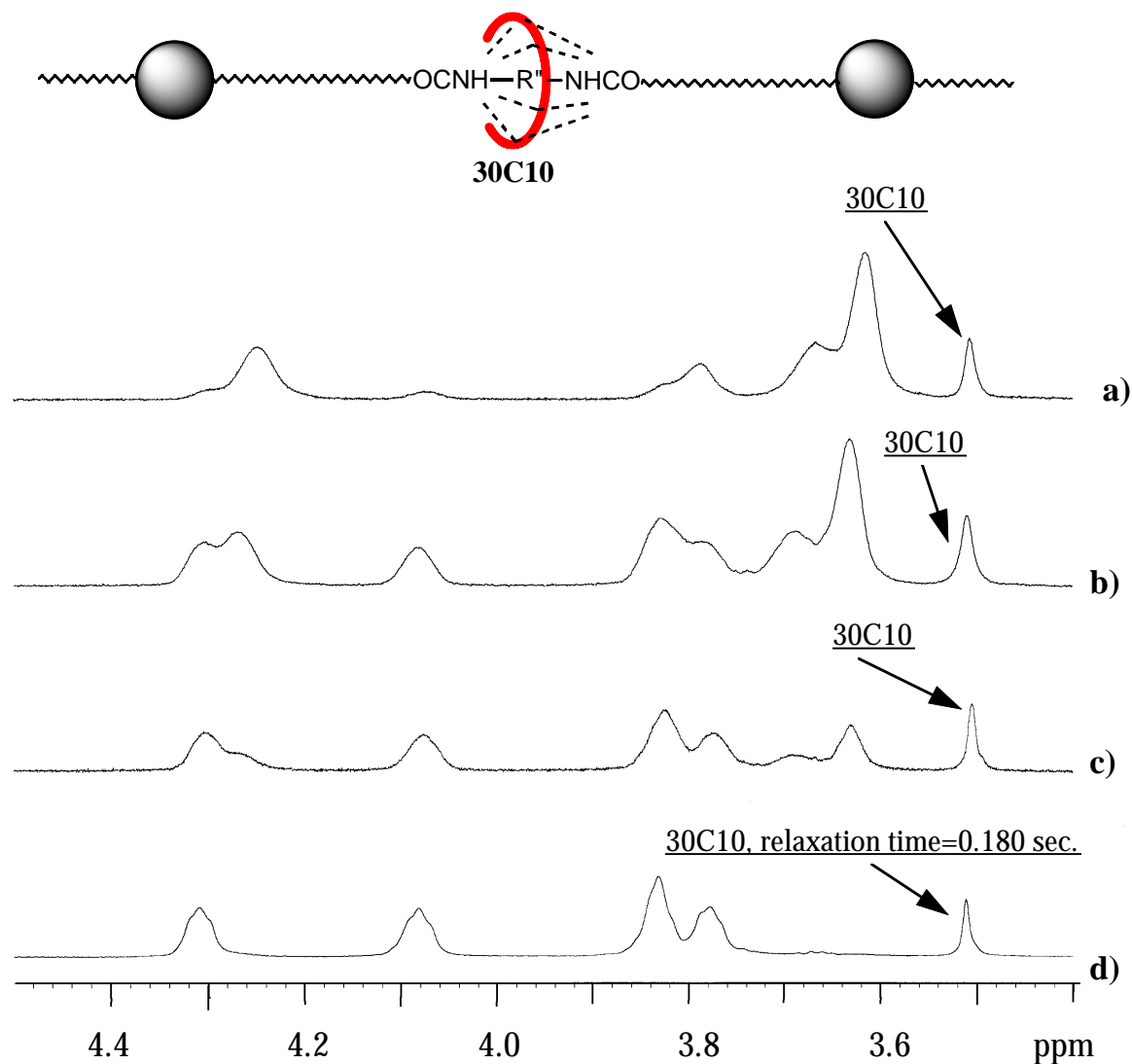


Figure 6.1. 400 MHz proton NMR spectra of a) polyrotaxane 6.7e and b) model polymer 6.7b in CDCl<sub>3</sub> at 30 °C



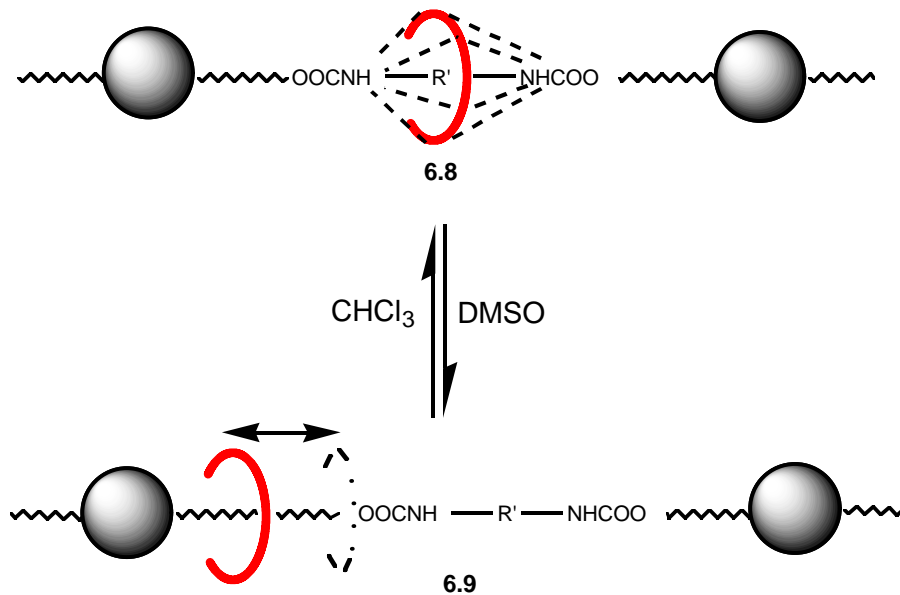
**Figure 6.2.** The expanded aliphatic region of the 400 MHz proton NMR spectra of poly(urethane rotaxane)s a) **6.7d**, b) **6.7e**, c) **6.7f** and d) **6.7g** in  $\text{CDCl}_3$  at  $30^\circ\text{C}$

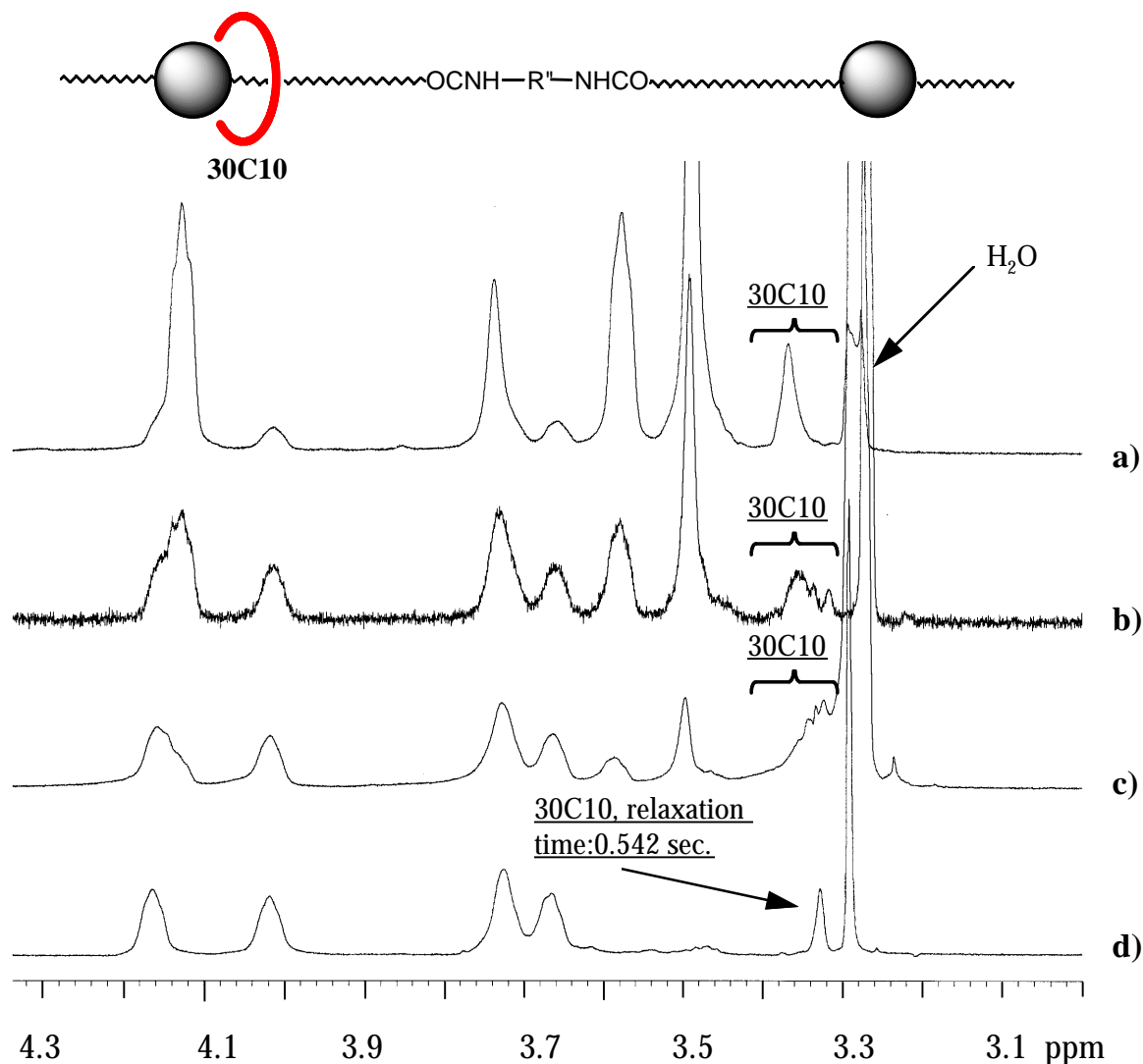
Compared to that (Figure 6.1b) of model polymer **6.7b**, the spectrum (Figure 6.1a) of the corresponding polyrotaxane **6.7e** has a new signal at 3.50 ppm which is due to threaded 30C10, while free 30C10 has a chemical shift at 3.67 ppm. Therefore, the formation of polyrotaxanes is directly proved by the proton NMR spectra.

### iii. Microstructures of polyrotaxanes 6.7c-6.7g

For copoly(ester rotaxane)s made from diol BG **6.4**, 1,10-decanediol and sebacoyl chloride, threaded 30C10 had a range of chemical shifts in  $\text{CDCl}_3$ ,<sup>5b</sup> while in copoly(urethane rotaxane)s **6.7d-f** it has only one signal in the same solvent (Figure 6.2). What causes the different proton NMR observations between these two polyrotaxanes? In the polyesters, threaded 30C10 is shielded by the phenyl groups of the BG units and thus shifted upfield. It displays different time averaged chemical shifts corresponding to the various sequence structures in which it is constrained; in the sequences with longer distances between the BG units, the crown ether is less shielded.<sup>5b</sup> With polyurethane as the backbone, however, hydrogen bonding between the in-chain NH groups and the crown ethers is known to take place<sup>6</sup> and thus 30C10 is localized at the NH groups. Such hydrogen bonding induces a well-defined polymer microstructure **6.8** (Scheme 6.5), in which 30C10 is confined near the phenyl groups of MDI units. Thus, the upfield shift for threaded 30C10 in the polyurethanes is caused by these phenyl rings. Therefore, in  $\text{CDCl}_3$  threaded 30C10 in **6.7d-g** displays the same chemical shift even in different sequence structures.

**Scheme 6.5. Solvent controlled microstructures in polyrotaxane 6.7c-g**





**Figure 6.3.** The expanded aliphatic region of the 400 MHz proton NMR spectra of poly(urethane rotaxane)s a) **6.7d**, b) **6.7e**, c) **6.7f** and d) **6.7g** in DMSO- $d_6$  at 30 °C

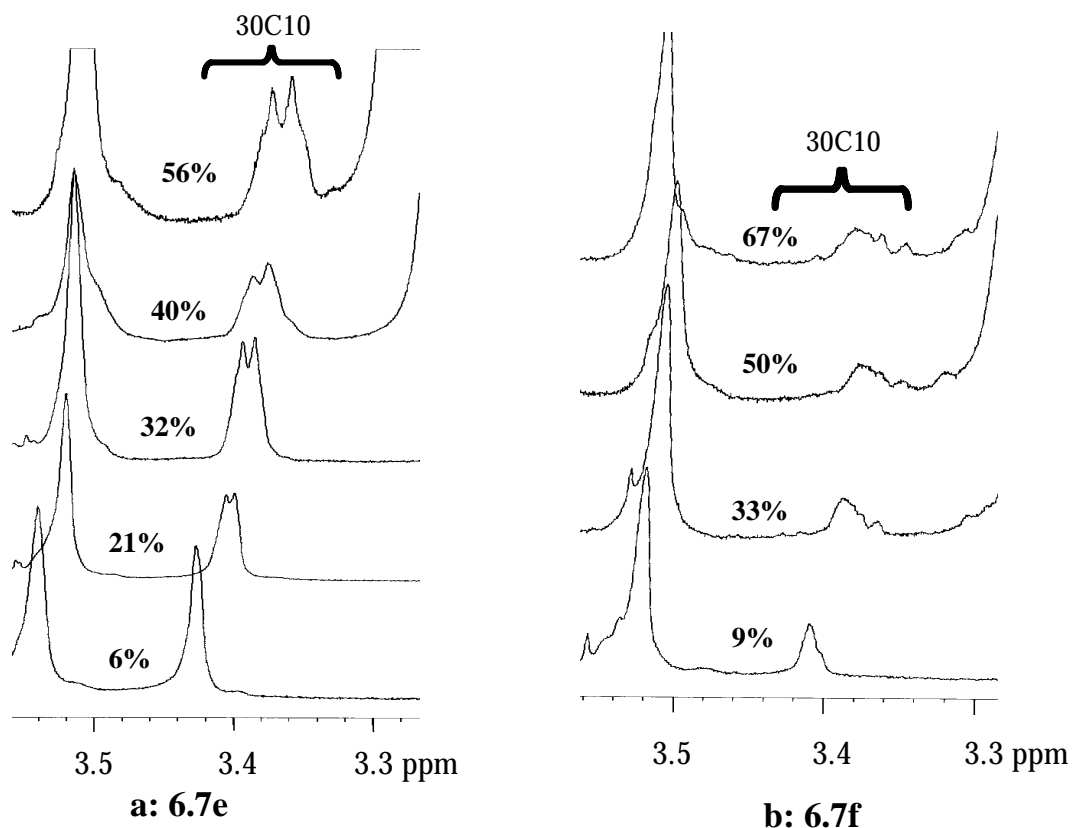
To confirm the above hypothesis, proton NMR studies of poly(urethane rotaxane)s **6.7d-g** were also performed using DMSO- $d_6$  as solvent instead of  $CDCl_3$ . As shown in Figure 6.3, threaded 30C10 in copolyurethanes **6.7d-f** indeed displays a range of chemical shifts from 3.33 to 3.38 ppm, while free 30C10 and the threaded 30C10 in **6.7c** appear at 3.52 ppm. DMSO is very good solvent for displacement of hydrogen bonding between the NH groups and the crown ethers and thus the macrocycles in polyurethanes are no longer localized at NH sites but are located in the vicinity of the BG units (structure **6.9** in Scheme

6.5). Therefore, the 30C10 signal is shifted upfield because it is shielded by the phenyl groups of the BG units, the same reason as that for polyesters.<sup>5</sup> Since copolyurethanes have different sequence structures with different lengths between the BG units, a range of chemical shifts for threaded 30C10 reflecting these sequence structures of copolyurethanes was observed (Figure 6.3). Therefore, in DMSO, although its signal is time averaged, 30C10 is inhibited from H-bonding with the NH group and thus is near the BG unit for a significant fraction of time, resulting in several signals corresponding to different sequence structures.

All the above observations are supported by the measurements of spin-lattice relaxation times ( $T_1$ ). Threaded 30C10 in **6.7g** in chloroform and DMSO has  $T_1$  values of 0.178 and 0.542 seconds, respectively; the smaller  $T_1$  in chloroform confirms the restriction of ring movement (both translation and rotation) because of hydrogen bonding (**6.8**), while the larger  $T_1$  in DMSO indicates the relatively free movement of macrocycle, i.e., translation and rotation. It is necessary to point out that the macrocycle in **6.7g** is still restricted even in DMSO to a large extent since its  $T_1$  is still small compared to that (1.78 seconds) of unthreaded 30C10. The large  $T_1$  differences between threaded and unthreaded macrocycles provide an additional novel, easy and reliable method for characterization of the formation of polyrotaxanes, augmenting chemical shift changes and nuclear Overhauser effects.<sup>5</sup>

Since the solvent has a large effect on the locus of the rings in these polyrotaxanes, as shown in Figures 6.2 and 6.3, manipulation of the solvent should allow control over the microstructure. Indeed as shown in Figure 6.4 incremental addition of DMSO to  $\text{CHCl}_3$  solutions of polyrotaxanes **6.7e** and **6.7f** results in 1) incremental upfield shifts based on the solvent induced displacement of the crown ethers away from the NH groups and nearer to the blocking groups and 2) the appearance of several signals due to the sensitivity of the degree of shift to the sequence length between blocking groups with the most upfield signals arising from units having homopolymer **6.7g** units. In the mixed solvent systems, then, the signals are time averaged because the rings are indeed shuttling between the two types of sites. Because hydrogen bonding involves a negative enthalpy change, increasing temperature tends to depress such bonding. However, for polyrotaxanes **6.7e** and **6.7f**, no signal breadth or

chemical shift changes were observed up to 60 °C in their proton NMR spectra using CDCl<sub>3</sub> as solvent, indicating H-bonding between crown ether and NH groups is fairly strong.



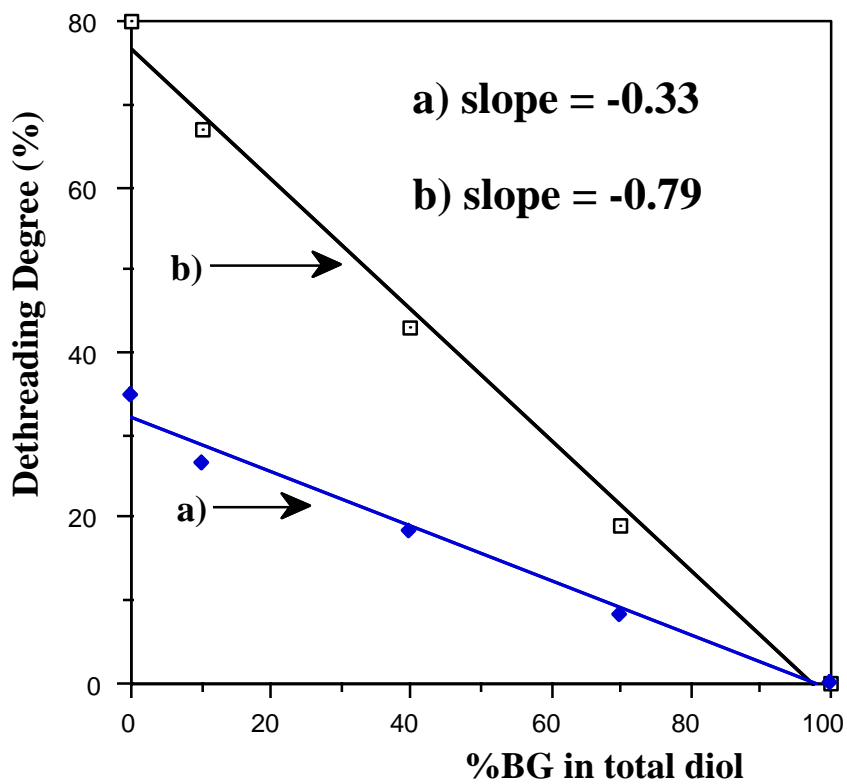
**Figure 6.4** The expanded 30C10 region of the 400 MHz proton NMR spectra of poly(urethane rotaxane)s a) 6.7e and b) 6.7f in the mixtures of DMSO-*d*<sub>6</sub> (relative percentage shown) and CDCl<sub>3</sub> at 30 °C.

Therefore, these poly(urethane rotaxane)s are essentially polymeric shuttles and the microstructures of the polymeric materials in solution are controlled by the solvent; the crown ethers are localized at the NH groups by hydrogen bonding in chloroform, in which both rotation and translation are restricted, while they are time averaged but tend to be in the vicinity of the BG units in DMSO. In principal, this concept can be used for other polymers, i.e., polyamides, bearing similar functional groups.



#### iv. Threading and Dethreading.

The threading efficiencies of polyrotaxanes **6.7c-g** were measured by the integrals of  $^{30}\text{C}10$  signals vs. the backbone protons.<sup>4,5</sup> It was found that  $m/n$  values decreased with decreasing feed percentage of diol **6.4** (Table 6.2). However, compared to that during the preparation of poly(ester rotaxane)s (Figure 6.4b),<sup>5b</sup> the extent of dethreading during the preparation of poly(urethane rotaxane)s was small (Figure 6.4a).

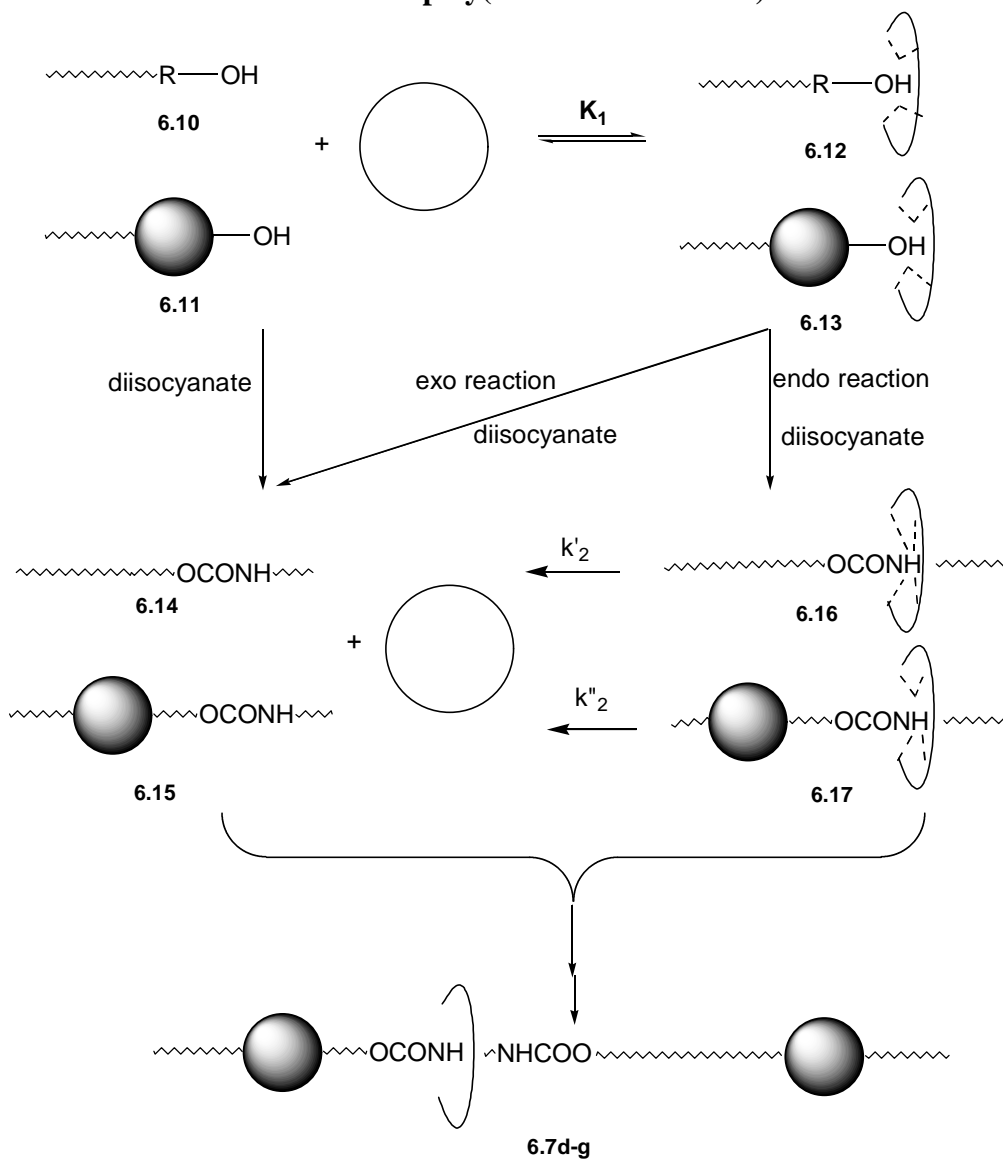


**Figure 6.5.** The dependence of dethreading degree on the feed percentage of diol **6.4** a) for poly(urethane rotaxane)s and b) for poly(ester rotaxane)s<sup>5b</sup>

It is believed that the decreased dethreading is due to the introduction of in-chain NH groups (Scheme 6.6). In the polyurethane, as soon as the crown ether is threaded, the formation of structures **6.16** and **6.17** by endo reaction, it will be H-bonded with the -NH groups and thus dethreading of the macrocycle in **6.16** and/or **6.17**, leading to structures **6.14** and **6.15** plus free macrocycles, occurs at a slower rate than that in the polyester because the ester linkage has no such retaining force.<sup>5</sup> In other words  $k'_2$  and  $k''_2$  are smaller for the

polyurethanes than for the polyesters. In addition, the difference between  $k'_2$  and  $k''_2$  will be smaller than that with polyester as backbone; this means the dependence of  $m/n$  on %BG is less for poly(urethane rotaxane)s as proved in the present study. Therefore, this implies that higher  $m/n$  can simply be achieved by choosing the proper backbone and using larger crown ethers even without any BG. Theoretically, the method can also be applied for other polyrotaxanes with similar in-chain functional groups, i.e., polyamides.

**Scheme 6.6. Threading and dethreading mechanism for the formation of poly(urethanes rotaxane)s**



## v. DSC analyses of model polyurethanes and poly(urethane rotaxane)s

Model polyurethanes **6.7a-b** and poly(urethane rotaxane)s **6.7c-g** are transparent and amorphous. They each display a single glass transition temperature ( $T_g$ ) and thus are believed to be single phase materials. Surprisingly, the  $T_g$ 's of model polymers **6.7a** and **6.7b** are almost identical to those of corresponding polyrotaxanes **6.7c** and **6.7e** (Table 6.2); this means that threaded 30C10 does not significantly change the thermal properties of the polymers because of its low loading. However,  $T_g$  does change with the amount of BG units; the more BG moieties, the higher  $T_g$ . This is because of the bulkiness and rigidity of the BG linkage.

### 6.2.2 Polyrotaxanes prepared by approach I

While similar hydrogen-bonds between amide and amide<sup>12,13</sup> and between ammonium and bisphenylene-based crown ethers<sup>14,15</sup> have successfully been used for the construction of different monorotaxanes, to our best knowledge, no polyrotaxanes have been prepared by Approach I via hydrogen bonding mechanism.

### i. Synthesis of model polymer **6.18** and polyrotaxanes **6.19a-f**

Polyurethane **6.18** was synthesized by solution polymerization of tetra(ethylene glycol) with 4,4'-methylenebis(*p*-phenyl isocyanate) (MDI) in DMF for 7 hrs at 96 °C. Polyrotaxanes **6.19a-f** were prepared simply by stirring solutions of “42C14”<sup>11</sup> or 30C10 and polyurethane **6.18** (Scheme 6.7) with or without cosolvent at 80 °C for three days. The detailed feed compositions are specified in Table 6.3. The unthreaded “42C14” or 30C10 was removed by precipitation from THF solution into water, a good solvent for the cyclics but a poor solvent for the polymer.<sup>4,5</sup>

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<sup>14</sup> Kolchinski, A. G.; Busch, D. H.; Alcock, N. W. *J. Chem. Soc., Chem. Commun.* **1995**, 1289.

<sup>15</sup> a) Ashton, P. R.; Glink, P. T.; Martinez-Diaz, M.-V.; Stoddart, J. F.; White, A. J.P.; Williams, D. J. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1930. b) Glink, P. T.; Schiavo, C.; Stoddart, J. F.; Williams, D. V. *J. Chem. Commun.* **1996**, 1483. c) Ashton, P. R.; Chrystal, E. J. T.; Glink, P. T.; Menzer, S.; Schiavo, C.; Spencer, N.; Stoddart, J. F.; Tasker, P. A.; White, A. J.P.; Williams, D. J. *Chem. Eur. J.* **1996**, *2*, 709.

**Scheme 6.7**

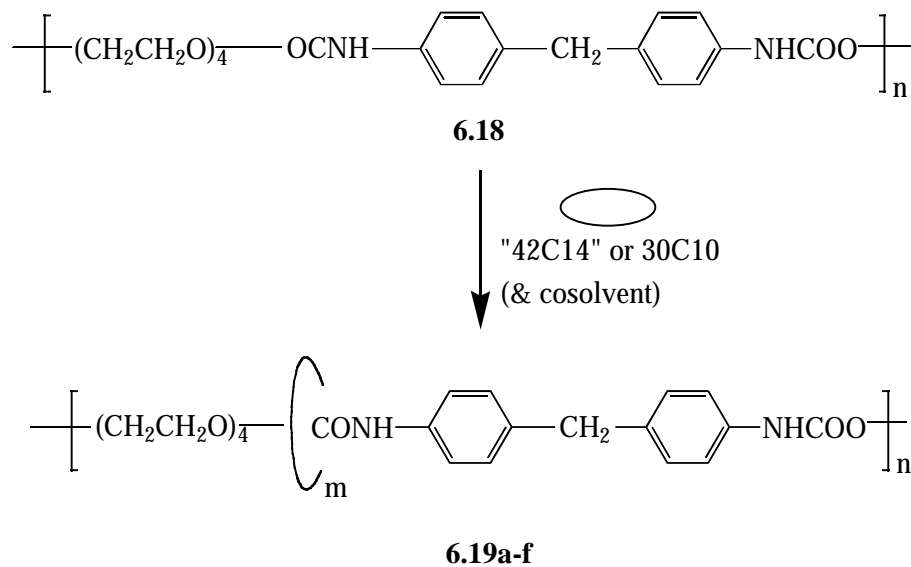


Table 6.3. The feed compositions and threading efficiencies of polyrotaxanes **6.19a-f** and model studies.

| product      | <b>6.18</b> <sup>a</sup><br>(mmol) | "42C14" <sup>b</sup><br>(mmol) | solvent<br>(ml)   | m/n <sup>c</sup> | mass %<br>crown ether |
|--------------|------------------------------------|--------------------------------|-------------------|------------------|-----------------------|
| <b>6.19a</b> | 1.00                               | 1.00                           | 0                 | 0.092            | 11.3                  |
| <b>6.19b</b> | 1.00                               | 3.00                           | 0                 | 0.178            | 19.8                  |
| <b>6.19c</b> | 1.00                               | 5.00                           | 0                 | 0.192            | 21.0                  |
| <b>6.19d</b> | 1.00                               | 6.00                           | 0                 | 0.201            | 21.8                  |
| <b>6.18</b>  | 1.00                               | 3.00                           | 2.00 <sup>d</sup> | 0                | 0                     |
| <b>6.19e</b> | 1.00                               | 3.00                           | 2.00 <sup>e</sup> | 0.085            | 10.5                  |
| <b>6.19f</b> | 1.00                               | 5.00 <sup>f</sup>              | 0                 | 0.065            | 6.04                  |
| <b>6.18</b>  | 1.00                               | 5.00 <sup>g</sup>              | 0                 | 0                | 0                     |
| <b>6.18</b>  | 1.00                               | 5.00 <sup>h</sup>              | 0                 | 0                | 0                     |

a) repeat unit basis. b) based on MW = 616 for "42C14". c) +/- 5 %

d) DMSO. e) diglyme. f) 30C10. g) PEO (MW=600). h) 18C6

## ii. Model studies

18-Crown-6 (18C6), too small to thread,<sup>4</sup> and linear poly(ethylene glycol) (PEO) (dihydroxy terminated, MW=600) were used as substitutes for “42C14” following the same procedure as that for polyrotaxanes **6.19a-e**. It was found that no 18C6 or PEO was left in the polymer after five precipitations; this proves that no side reactions, ring opening of crown ether or the reaction of -OH groups with polyurethane **6.18**, take place and that reprecipitation is an effective method to remove unthreaded cyclics.

## iii. Threading mechanism and threading efficiency

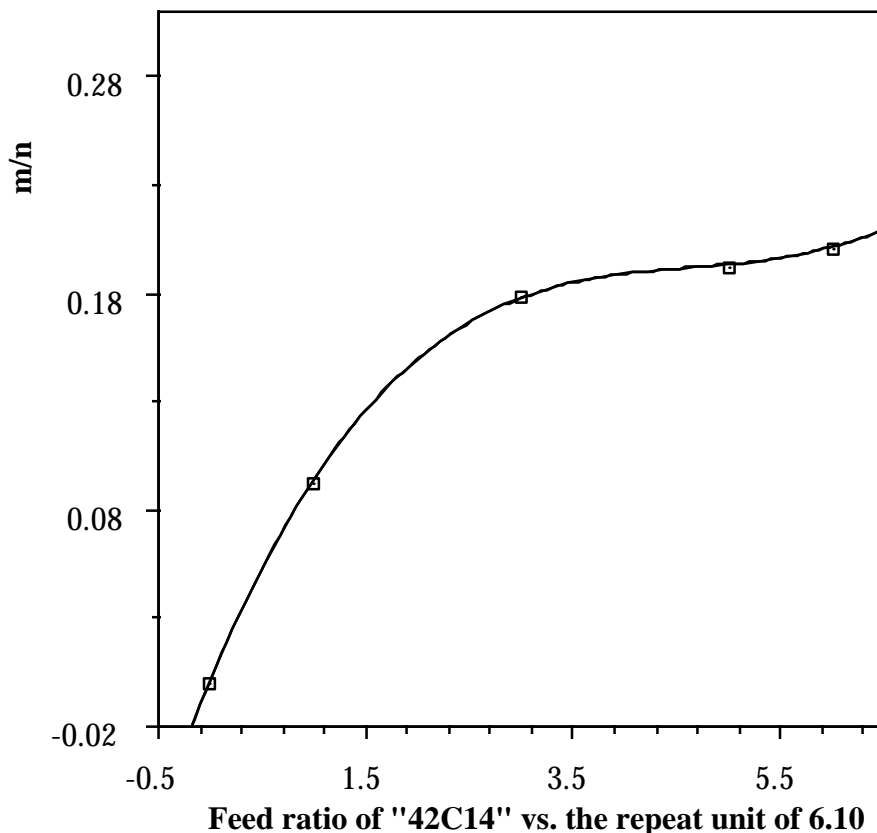
Threading efficiencies of polyrotaxanes **6.19a-f** were measured based on the integral of the “42C14” or 30C10 signal vs. that of the methylene protons of the backbone by proton NMR.<sup>4b</sup> It was found that the m/n values of all these polyrotaxanes (Table 6.3) are much higher than that ( $2 \times 10^{-2}$ ) with a polyester as preformed polymer and “42C14” as the cyclic.<sup>4d</sup> We believe that the lower threading with the polyester is because there is no strongly attractive force between the ester linkages and the crown ether<sup>5</sup> and thus the threading process is essentially statistical. However, the existence of hydrogen bonding between the NH groups of the polyurethane and the crown ether brings about a significant thermodynamic driving force for threading and thus the resulting polyrotaxanes have higher m/n values. As expected for equilibrium process, to a certain limit the higher the molar ratio of cyclics vs. NH groups is, the more cyclics that are threaded (Figure 6.6 and Table 6.3). As much as 22 % by mass of the crown ether is incorporated (Table 6.3).

The number average degree of polymerization of **6.18** was 37.4. The number average of crown ether molecules threaded onto each macromolecule ranged from 2.4 to 7.5. Based on the measured m/n values, the association constant ( $K_{\text{int H-bond}}$ ) for threading was estimated to  $7.23 \pm 1.18 \times 10^{-2}$ .<sup>16</sup> It should be pointed out that this value may depend on the molecular

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<sup>16</sup> Assuming that 1) densities are 1.00 g/mL for **6.18** and “42C14” and 2) that no threaded crown ethers are lost during purification;  $K_{\text{int H-bond}}$  was calculated by the equation:  $K = [R]/\{[NH][\text{“42C14”}]\}$ , in which [R], [NH] and [“42C14”] are the equilibrium concentrations of the rotaxane unit, the NH group and free “42C14”. [R] was calculated from m/n value as  $(m/n)[NH]_0/2$ . Because of possible dethreading during purification especially for cyclics near chain ends, the obtained K is a minimum value.

weight of the polyurethane as result of the stochastic or queuing nature of the threading process, as observed for other systems.<sup>1</sup>



**Figure 6.6. The relationship of m/n values for 6.19a-d vs. the molar feed ratios of "42C14" to the repeat unit of 6.18.**

The m/n values of polyrotaxanes **6.19b-d** in the present work are lower than that (0.29) of the same polyrotaxane prepared at a higher temperature (90 °C) and a lower molar feed ratio of "42C14" per repeat unit (1.5) by Approach II.<sup>4b</sup> But this is not contrary to the proposed mechanism in Scheme 6.3. In approach I, the crown ether can form both external H-bonds, disfavoring threading, and internal H-bonds, leading to polyrotaxane, and thus the m/n value of the polyrotaxane is a result of this competition. In approach II, however, the initial driving force is H-bonding between the crown ether and the -OH groups of the diol monomer<sup>5</sup> and once the urethane bond is formed the threaded cyclics tend not to slip off the

backbone because of H-bonding with in-chain NH groups<sup>6</sup> and random coil conformations of the polymer chain.<sup>8</sup> Therefore, the m/n value of the resulting polyrotaxane via Approach II is mainly determined by the strength of H-bonding of the crown ether with -OH groups but NH groups of the polymer help to retain them.

Since DMSO can dissociate hydrogen bonds between NH or -OH groups and crown ethers, in this solvent no threading is expected.<sup>6</sup> Indeed, no “42C14” was threaded onto the polymer using DMSO as the solvent and only polymer **6.18** was recovered (Table 6.3). **6.19e** with m/n = 0.085 was obtained with diglyme as the solvent; relative to **6.19b** this reduced value upon dilution again agrees with the H-bonding hypothesis.

On the other hand, 30C10 because of less hydrogen bonding sites, oxygen atoms, and smaller ring size was less favored to be threaded. Therefore, compared to **6.19c** its derived polyrotaxane **6.19f** had a lower m/n value (Table 6.3).

The present study also implies a new method for other main chain polyrotaxanes or side chain polyrotaxanes by incorporating H-bonding moieties and threading them with crown ethers. The melt blending approach is adaptable to normal polymer processing techniques.

#### **iv. Some properties of polyrotaxanes.**

The present approach for preparation of polyrotaxanes allows an accurate study of the relationship of the properties of polyrotaxanes with threading efficiency (m/n) because the backbones of all derived polyrotaxanes in terms of molecular weight and polydispersity are identical to the corresponding model (starting) polymer.

##### **a) Intrinsic viscosity**

To study the effect of the formation of polyrotaxanes on polymeric chain conformation, the intrinsic viscosity of both model polymer and polyrotaxanes were measured in THF under an identical condition.

Based on the measured specific viscosities at different concentrations (C), the plot of  $\eta_{sp}/C$  vs. C afforded the intrinsic viscosity and the shape dependent factor (Huggins constant

k') for the model polymer **6.18** and polyrotaxanes **6.19** via equation  $\eta_{sp}/C = [\eta] + k'[\eta]^2C$  (Table 6.4). Interestingly, Huggins constants (k') for the polyrotaxanes were much smaller than that of the starting polyurethane under the same conditions (THF as solvent at 25 °C), but the intrinsic viscosities of the polyrotaxanes were higher. I believe that these differences were caused by the conformational changes of the backbone upon threading as shown in scheme 6.8. Relative to the model polymer, the polyrotaxanes tend to adopt a more expanded form because of the bulkiness of the threaded cyclics and thus had a higher hydrodynamic volume; this explains their higher intrinsic viscosities. As expected, the model polymer was a random coil and became more and more expanded upon dilution; this resulted in a higher Huggins constant k'. However, the backbone in polyrotaxanes was already expanded even at higher concentration and thus the dependence of chain conformation on the concentration was less and thus a smaller k'.

Table 6.4. Intrinsic viscosities and glass transition temperatures of model polymer **6.18** and polyrotaxanes **6.19**

| polymer      | T <sub>g1</sub> <sup>a</sup><br>(°C) | T <sub>g2</sub> <sup>b</sup><br>(°C) | T <sub>g3</sub> <sup>c</sup><br>(°C) | [η] <sup>d</sup><br>(dL/g) | k' <sup>e</sup> |
|--------------|--------------------------------------|--------------------------------------|--------------------------------------|----------------------------|-----------------|
| <b>6.18</b>  | 54.0                                 | 54.0                                 | -                                    | 0.299                      | 0.491           |
| <b>6.19a</b> | 43.1                                 | 33.4                                 | -23.0                                | 0.351                      | 0.350           |
| <b>6.19b</b> | 35.5                                 | 19.5                                 | -22.1                                | 0.361                      | 0.259           |
| <b>6.19d</b> | 34.1                                 | 16.5                                 | -21.2                                | 0.369                      | 0.250           |

a) The measured glass transition temperatures by DSC

b) The calculated glass transition temperatures by the Fox equation based on T<sub>g</sub>'s of crown ether and backbone, -68 °C and 54 °C, respectively.

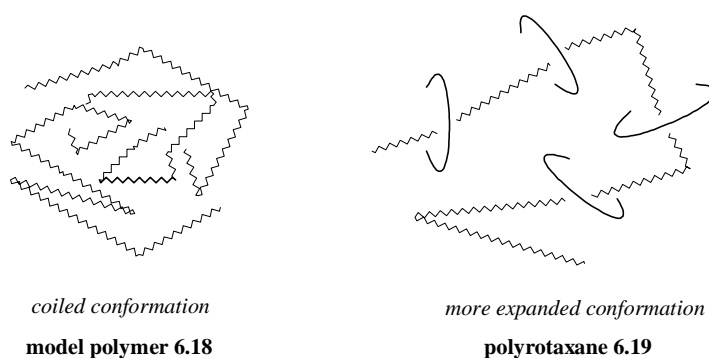
c) The calculated glass transition temperatures of threaded crown ethers by the Fox equation based on the measured T<sub>g</sub>'s of polyrotaxanes and model polymer.

d) measured with a Cannon L12 viscometer in THF at 25 °C

e) calculated by Huggins equation.



**Scheme 6.8**

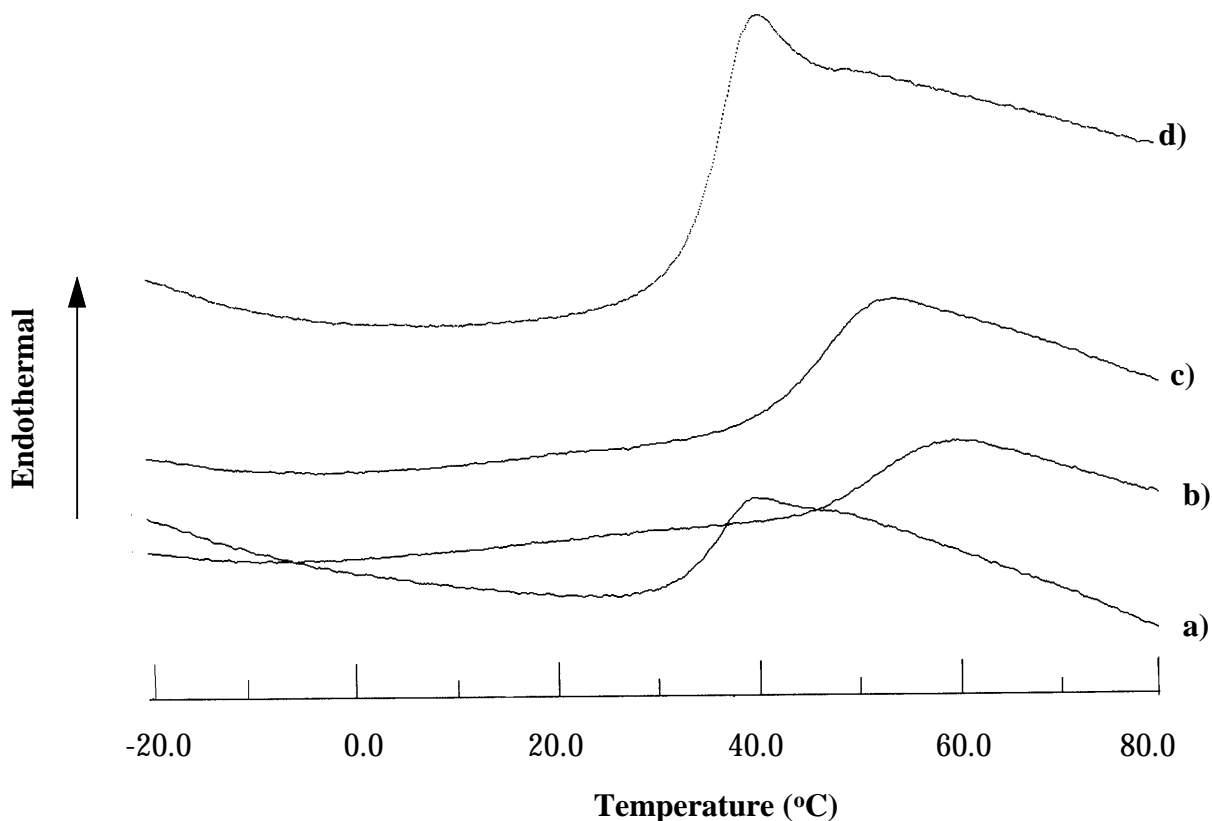


### b) Thermal properties

In poly(ester rotaxane)s, crown ethers can move along the backbone and accumulate into a separate phase; this gives melting points roughly corresponding to those of the pure crown ether and backbone, respectively, in DSC traces.<sup>4c,4d</sup> Recently, it was demonstrated that in polyurethane rotaxanes, threaded crown ether can form hydrogen bonds with in-chain NH groups.<sup>6</sup> Such hydrogen bonding will retard aggregation of the crown ethers. Indeed, no melting corresponding to the crown ethers was observed for the present polyrotaxanes **6.19**; only one glass transition temperature exists (Table 6.4 and Figure 6.6). Therefore, these poly(urethane rotaxane)s were one phase materials and the crown ethers lost crystallinity. As expected, the more crown ether that was threaded, the lower  $T_g$  the polyrotaxane had (Table 6.2).

According to the Fox equation, the glass transition temperature ( $T_g$ ) for the polyrotaxanes, one phase materials, were calculated (Table 6.4) based on weight fractions of the crown ether and the backbone (Table 6.3) and the  $T_g$ 's of free crown ether and the backbone at  $-68$  °C and  $54$  °C, respectively. Surprisingly, the measured value was much higher than that calculated from the Fox equation. What causes this deviation? As discussed earlier and demonstrated in earlier work<sup>6</sup>, the crown ethers form hydrogen bonds with in-chain NH groups in the polyrotaxanes and are not free in motion anymore. Thus restricted motion surely decreases the flexibility of the crown ether; this results in a higher glass transition temperature for threaded crown ether. Therefore,  $T_g$  for the crown ether in the polyrotaxanes should not be  $-68$  °C but a much higher value. Reversibly, based on the

measured  $T_g$  of polyrotaxanes, the weight fraction of the crown ethers and the  $T_g$  of the backbone, the corresponding  $T_g$  of threaded “42C14” was calculated to be  $-22 \pm 1$  °C; this clearly supported the rigidification theory about threaded crown ethers.



**Figure 6.7.** The DSC traces of a) 6.19b, b) 6.18; c) 6.19a and d) 6.19d

### 6.3 Conclusions

Crown ether-based poly(urethane rotaxane)s were prepared by solution polymerization using 30C10 as solvent. The extent of dethreading during their preparation is much less than that with polyesters because of H-bonding of the NH groups with the threaded crown ethers. In these polyrotaxanes, the crown ethers are localized at NH sites in chloroform to give a well-defined polymeric microstructure, but they tend to in the vicinity of the BG moiety in DMSO. In the mixtures of DMSO and  $CDCl_3$ , 30C10 shuttles between sites and thus these are the first polymeric molecular shuttles reported so far. The glass transition temperatures of the polyurethanes depend on the amount of BG units, as expected.

The measurement of spin-lattice relaxation times provides an easy and effective method for characterization of the formation of polyrotaxanes; the threaded cyclic has a much shorter  $T_1$  than its free counterpart.

In addition, a new method for crown ether-based polyrotaxanes was demonstrated; this was preparation of poly(urethane rotaxane)s by threading crown ether onto a preformed polyurethane in both solution and melt states. The threading extent was easily controlled by the feed ratio of the two components, concentration and solvent. Interestingly, polyrotaxanes had higher intrinsic viscosity but a smaller shape constant; this indicates that polyrotaxanes adopted a more expanded chain conformation. Because of intra-annular hydrogen bonding, polyrotaxanes were one phase materials whose glass transition temperatures were related to the loading of crown ether.

## 6.4 Experimental

### Chemical reagents and measurements

All chemicals were reagent grade and used directly as received from Aldrich unless otherwise specified. All solvents were HPLC or GC grade. 30C10<sup>16</sup>, “42C14”<sup>11</sup> and diol BG 6.4<sup>5</sup> were prepared by well-established procedures. Proton NMR spectra, reported in ppm, were obtained on a 400 MHz Varian spectrometer using chloroform-*d* solutions or DMSO-*d*<sub>6</sub> with tetramethylsilane as an internal standard. The relaxation time ( $T_1$ ) was measured by standard 180- $\tau$ -90-acquisition techniques. The following abbreviations have been used in describing NMR spectra: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), and m (multiplet); coupling constants (J) are in Hertz. The absolute molecular weights of the polymers were measured by GPC analyses with a Waters 150C ALC/GPC chromatograph equipped with a differential refractometer detector and an on-line differential viscometric detector (Viscotek 150R) coupled in parallel and the universal calibration was used. The glass transition temperatures of polymers were measured with a Perkin-Elmer thermal analysis system at a rate of 10 °C/minute for both heating and cooling; all reported

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<sup>16</sup> Bheda, M. C.; Merola, J. S.; Woodward, W. A.; Vasudevan, V. J.; Gibson, H. W. *J. Org. Chem.* **1994**, *59*, 1684.

values were the centers of transitions from 2nd heating. The intrinsic viscosities were measured with a Cannon L12 viscometer in THF at 25 °C.

### **Model polyurethanes 6.7a and 6.7b**

To a 10 mL flask were added tetra(ethylene glycol) (**6.5**) (194.2 mg, 1.000 mmol) (oven dried at 100 °C), freshly distilled MDI (**6.6**) (250.3 mg, 1.000 mmol) for **6.7a** or diol BG **6.4** (255.5 mg, 0.400 mmol), **6.5** (116.5 mg, 0.600 mmol) and MDI (**6**) (250.3 mg, 1.000 mmol) for **6.7b** in DMF (2 mL). The solution was heated to 96 °C in an oil bath for 7 h and precipitated into methanol to give a transparent material. <sup>1</sup>H NMR in DMSO-d<sub>6</sub> for **6.7a**: 9.66 (s, 2H), 7.38 (d, 4H, *J* = 8.3), 7.10 (d, *J* = 8.3, 4H), 4.19 (s br, 4H), 3.79 (s, 2H), 3.62 (s br, 4H), 3.51 (s br, 8H). <sup>1</sup>H NMR in CDCl<sub>3</sub> for **6.7b**: 7.19-7.31 (m, 5.6H plus CHCl<sub>3</sub>), 7.03-7.05 (m, 7.2H), 6.74 (d, *J* = 8.4, 1.6H), 4.25-4.30 (m br, 4H), 4.07 (s br, 1.6H), 3.3.78-2.80 (m br, 5.2H), 3.61-3.67 (m br, 7.2H), 1.27 (s, 7.2H).

### **General procedure for poly(urethane rotaxane)s 6.7c-6.7g.**

Diols (**6.4** plus **6.5**, total 1 mmol) (Table 6.1) were dissolved in 30C10 (3 mmol) at 96 °C. After the solution had stirred for 0.5 h at this temperature, MDI (**6.6**) (1 mmol) was added slowly and polymerization proceeded for 7 h under the protection of nitrogen. The reaction product was redissolved in DMF and precipitated into methanol 5 times to remove free 30C10. <sup>1</sup>H NMR in DMSO-d<sub>6</sub> for **6.7c**: 9.66 (s, 2H), 7.38 (d, 4H, *J* = 8.3), 7.10 (d, *J* = 8.3, 4H), 4.19 (s br, 4H), 3.79 (s, 2H), 3.62 (s br, 4H), 3.51-3.50 (s br, 8H plus 30C10). <sup>1</sup>H NMR in CDCl<sub>3</sub> for **6.7d**: 7.19-7.31 (m, 4.4H plus CHCl<sub>3</sub>), 7.03-7.05 (m, 4.8H), 6.74 (s br, 0.4H), 4.25-4.30 (m br, 4H), 4.07 (s br, 0.4H), 3.78-3.80 (m br, 2.8H), 3.61-3.67 (m br, 12.8H), 3.50 (s br, variable), 1.27 (s, 1.8H). <sup>1</sup>H NMR in CDCl<sub>3</sub> for **6.7e**: 7.19-7.31 (m, 5.6H plus CHCl<sub>3</sub>), 7.03-7.05 (m, 7.2H), 6.74 (d br, 1.6H), 4.25-4.30 (m br, 4H), 4.07 (s br, 1.6H), 3.3.78-2.80 (m br, 5.2H), 3.61-3.67 (m br, 7.2H), 3.50 (s br, variable) 1.27 (s, 7.2H). <sup>1</sup>H NMR in CDCl<sub>3</sub> for **6.7f**: 7.19-7.31 (m, 6.8H plus CHCl<sub>3</sub>), 7.03-7.05 (m, 9.6H), 6.74 (d br, 2.8H), 4.25-4.30 (m br, 4H), 4.07 (s br, 2.8H), 3.3.78-2.80 (m br, 7.6H), 3.61-3.67 (m br, 3.6H), 3.50 (s br, variable), 1.27 (s, 12.6H).

### **Model polyurethane 6.18**

To a 50 mL flask were added tetra(ethylene glycol) (1.94 g, 10.0 mmol) (oven dried at 100 °C), freshly distilled MDI (2.50 g, 10.0 mmol) in DMF (10 mL). The solution was heated to 96 °C in an oil bath under the protection of nitrogen for 7 h and precipitated into methanol to give a transparent material. <sup>1</sup>H NMR in DMSO-d<sub>6</sub>: 9.66 (s, 2H), 7.38 (d, 4H, *J* = 8.3), 7.10 (d, *J* = 8.3, 4H), 4.19 (s br, 4H), 3.79 (s, 2H), 3.62 (s br, 4H), 3.51 (s br, 8H). *M<sub>n</sub>* = 16.6 kg/mol (*DP<sub>n</sub>* = 37.4) and *M<sub>w</sub>* = 58.7 kg/mol (*DP<sub>w</sub>* = 132); measured by GPC with universal calibration in NMP at 60 °C.

### **General procedures for poly(urethane rotaxane)s 6.19a-f.**

Polyurethane **6.18** and crown ethers were dissolved in the crown ethers at 80 °C with or without cosolvent as specified in Table 6.3. After the solution had stirred for 3 days at this temperature under the protection of nitrogen, the reaction product was dissolved in THF and precipitated into water 5 times to remove free crown ether. <sup>1</sup>H NMR in DMSO-d<sub>6</sub>: 9.66 (s, 2H), 7.38 (d, 4H, *J* = 8.3), 7.10 (d, *J* = 8.3, 4H), 4.19 (s br, 4H), 3.79 (s, 2H), 3.62 (s br, 4H), 3.51-3.50 (s br, 8H plus “42C14” or 30C10).

### **General procedures for model study by approach I.**

Polyurethane **6.18** (Table 6.3) was dissolved in 18C6 or PEO-600 at 80 °C. After the solution had stirred for 3 days at this temperature under the protection of nitrogen, the reaction product was dissolved in THF and precipitated into water 5 times. <sup>1</sup>H NMR in DMSO-d<sub>6</sub>: 9.66 (s, 2H), 7.38 (d, 4H, *J* = 8.3), 7.10 (d, *J* = 8.3, 4H), 4.19 (s br, 4H), 3.79 (s, 2H), 3.62 (s br, 4H), 3.51-3.50 (s br, 8H).

## Chapter 7

### Branched and/or cross-linked poly(methacrylate rotaxane)s derived from self-threading

#### 7.1 Introduction

Polyrotaxanes, in which rotaxane units are incorporated into macromolecules, because of their novel architectures have received world-wide attention.<sup>1-6</sup> Two types of side chain polyrotaxanes as illustrated in Scheme 7.1 can be constructed by proper procedures. To date all of the reported side chain polyrotaxanes are of type B. No examples of type A, side chain polyrotaxanes formed from polymers with pendant macrocycle units, have been reported! One of the objectives of this work was to explore this class of polyrotaxanes.

The abilities of polyether macrocycles to complex with metal ions, organic cations and form hydrogen bonds with hydroxy groups provide driving forces<sup>7</sup> necessary for preparation of these new materials and lots of main chain polyrotaxanes have been prepared with crown ethers as the macrocyclic components.<sup>1,5,6</sup> In order to prevent the slippage of the cyclic molecule from the linear chain, blocking groups (BG) are often introduced at the chain

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<sup>1</sup> a) Gibson, H. W.; Bheda, M. C.; Engen, P. T. *Prog. Polym. Sci.* **1994**, *19*, 843. b) Ambalino, D. B.; Stoddart, J. F. *Chem. Rev.*, **1995**, *95*, 2725. c) Philp, D.; Stoddart, J. F. *Angew. Chem. Int. Engl.* **1996**, *35*, 1154. d) Gibson, H. W. In *Large Ring Molecules*, Semlyen, J. A. ed., J. Wiley and Sons, New York, **1996**, 191.

<sup>2</sup> a) Weickenmeier, M.; Wenz, G. *Macromol. Rapid. Commun.* **1996**, *17*, 731. b) Steinbrunn, M. B.; Wenz, G. *Angew. Chem. Int. Engl.* **1996**, *35*, 2139.

<sup>3</sup> a) Born, M.; Ritter, H. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 309. b) Born, M.; Ritter, H. *Adv. Mater.* **1996**, *8*, 149. c) Born, M.; Ritter, H. *Macromol. Rapid Commun.* **1996**, *17*, 197.

<sup>4</sup> a) Harada, A.; Li, J.; Kamachi, M. *Macromolecules* **1994**, *27*, 4538. b) Harada, A.; Okada, M.; Li, J.; Kamachi, M. *Macromolecules* **1995**, *28*, 8406.

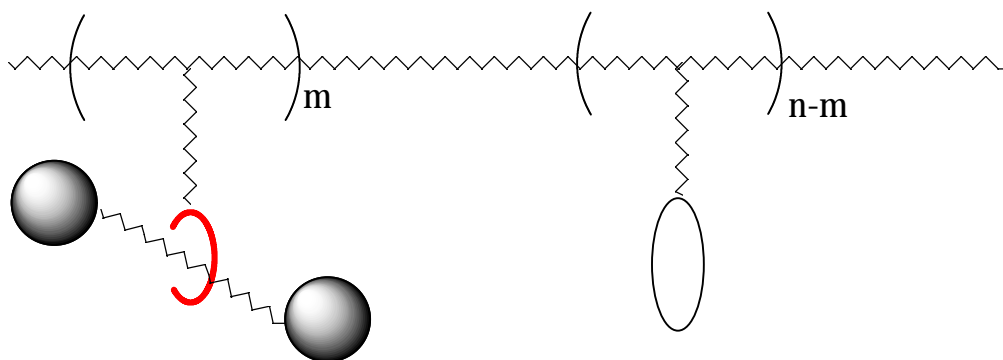
<sup>5</sup> a) Gibson, H. W.; Marand, H. *Adv. Mater.* **1993**, *5*, 11. b) Shen, Y. X.; Xie, D.; Gibson, H. W. *J. Am. Chem. Soc.*, **1994**, *116*, 537. c) Gibson, H. W.; Liu, S.; Lecavalier, P.; Wu, C.; Shen, Y. X. *J. Am. Chem. Soc.*; **1995**, *117*, 852.

<sup>6</sup> a) Gong, C.; Gibson, H. W. *Macromolecules* **1996**, *29*, 7029 and chapter 3. (b) Gong, C.; Gibson, H. W. *Macromol. Chem. Phys.* **1997**, 2321 and chapter 4. c) Gong, C.; Ji, Q.; Glass, T. E.; Gibson, H. W. *Macromolecules*, in press and chapter 5. d) Gibson, H. W.; Liu, S.; Gong, C.; Ji, Q.; Joseph, E. *Macromolecules*, **1997**, *31*, 3711. <sup>7</sup> Izatt, R. M.; Bradshaw, J. S.; Pawlak, K.; Bruening, R. L.; Taret, B. *Chem. Rev.* **1992**, *92*, 1261.

<sup>7</sup> Izatt, R. M.; Bradshaw, J. S.; Pawlak, K.; Bruening, R. L.; Taret, B. *Chem. Rev.* **1992**, *92*, 1261.

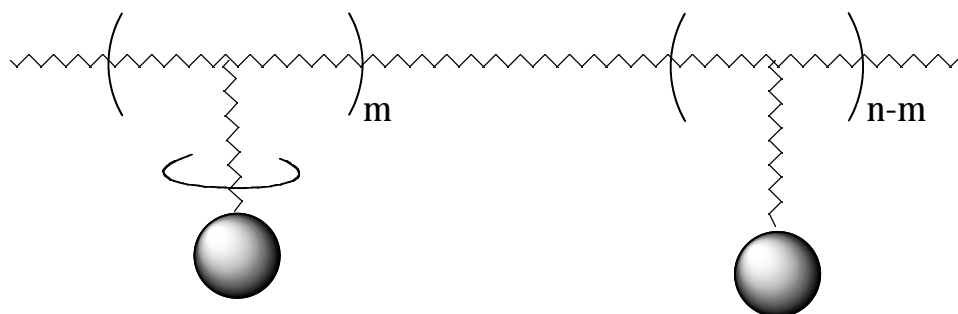
ends and/or as in-chain units. Recently, it was found that the introduction of difunctional BG can increase the threading efficiency ( $m/n$ , the average number of macrocycles per repeat unit in polyrotaxane) by as much as thirteen times!<sup>6a,c</sup> The hydrogen bonding between hydroxy groups and the crown ether is proposed as a driving force for the threading; an endo esterification of the complexed structure **7.1** taking place through the cavity of the crown ether yields a main chain polyrotaxane structure **7.3**, while an exo esterification yields an unthreaded structure **7.2** (Scheme 7.2).

**Scheme 7.1. Different side chain polyrotaxanes**



**A'**. Side chain polypseudoroataxne without BG

**A''**. Side chain polyroataxne with BGs

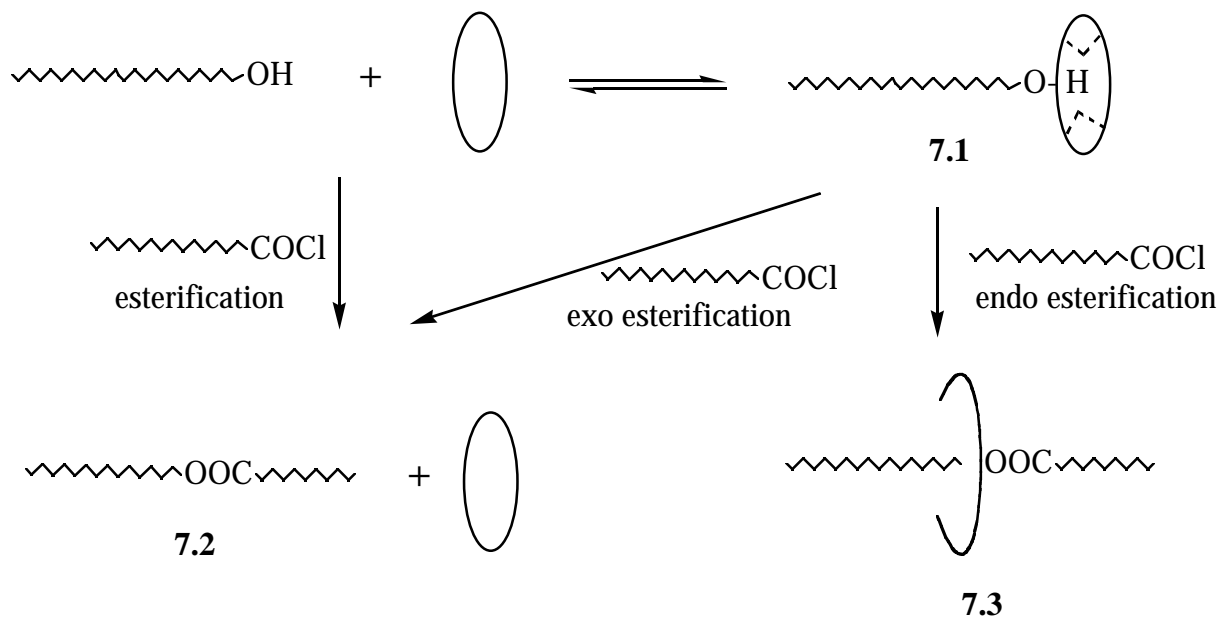


**B'**. Side chain polypseudoroataxne without BG

**B''**. Side chain polyroataxne with BGs

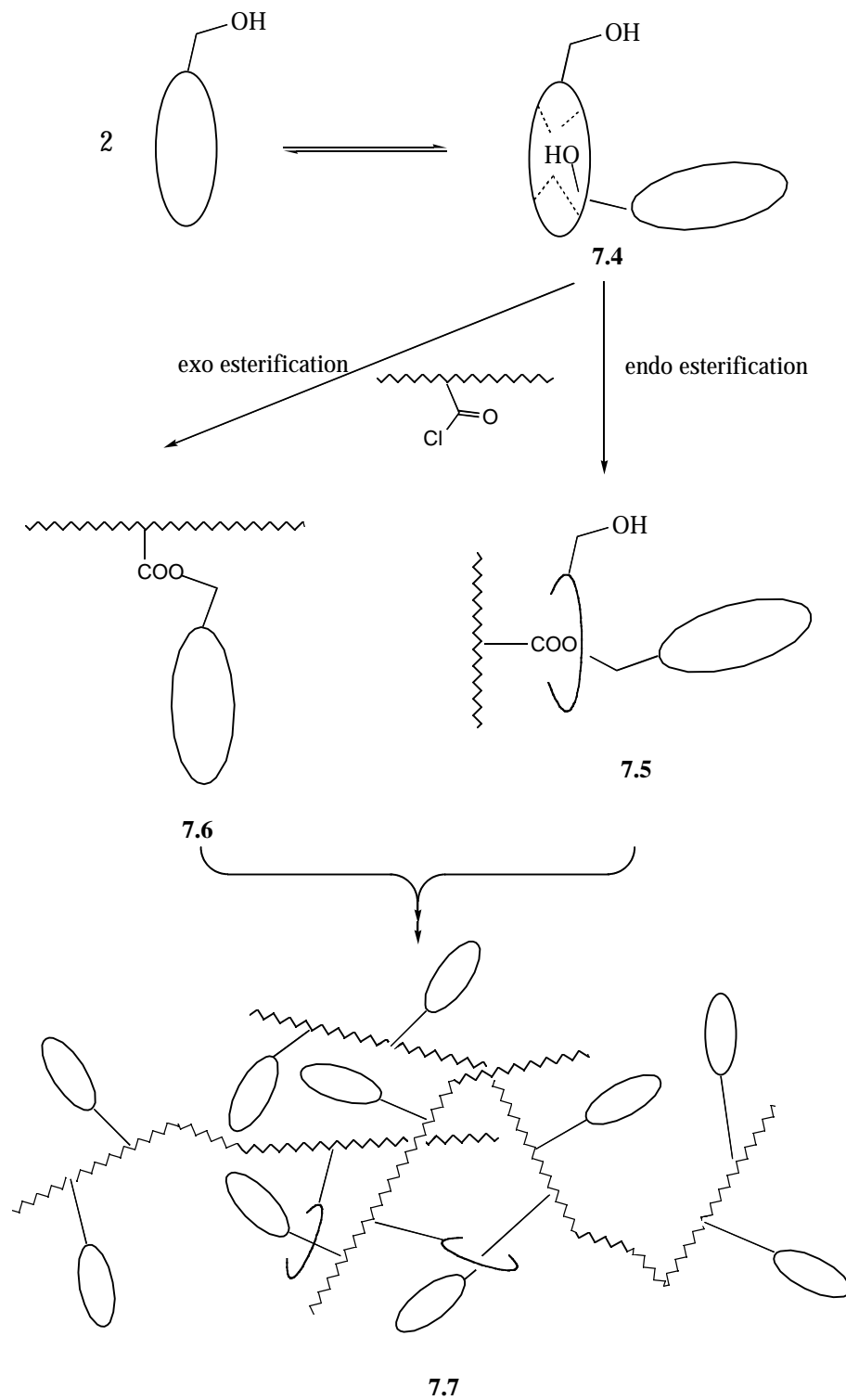
By extension of this concept, therefore, a crown ether bearing a hydroxy group is expected to self associate as in structure **7.4**. Endo esterification of **7.4** with a poly(acid chloride) (Scheme 7.3) will lead to a novel rotaxane structure **7.5** along with side chain polymacrocycle **7.6** units via exo esterification. Since a macrocycle will not readily pass through an identical macrocycle, it can play the same role as a BG and thus **7.5** is expected to be stable toward dethreading. This process should ultimately yield branched and/or crosslinked structure **7.7**. I investigated this novel self-threading method for formation of physically linked networks and the results are reported in this chapter.

**Scheme 7.2. Threading mechanism for poly(ester/crown ether rotaxane)s**





Scheme 7.3 Possible approach for construction of branched polymer  
by self-threading process

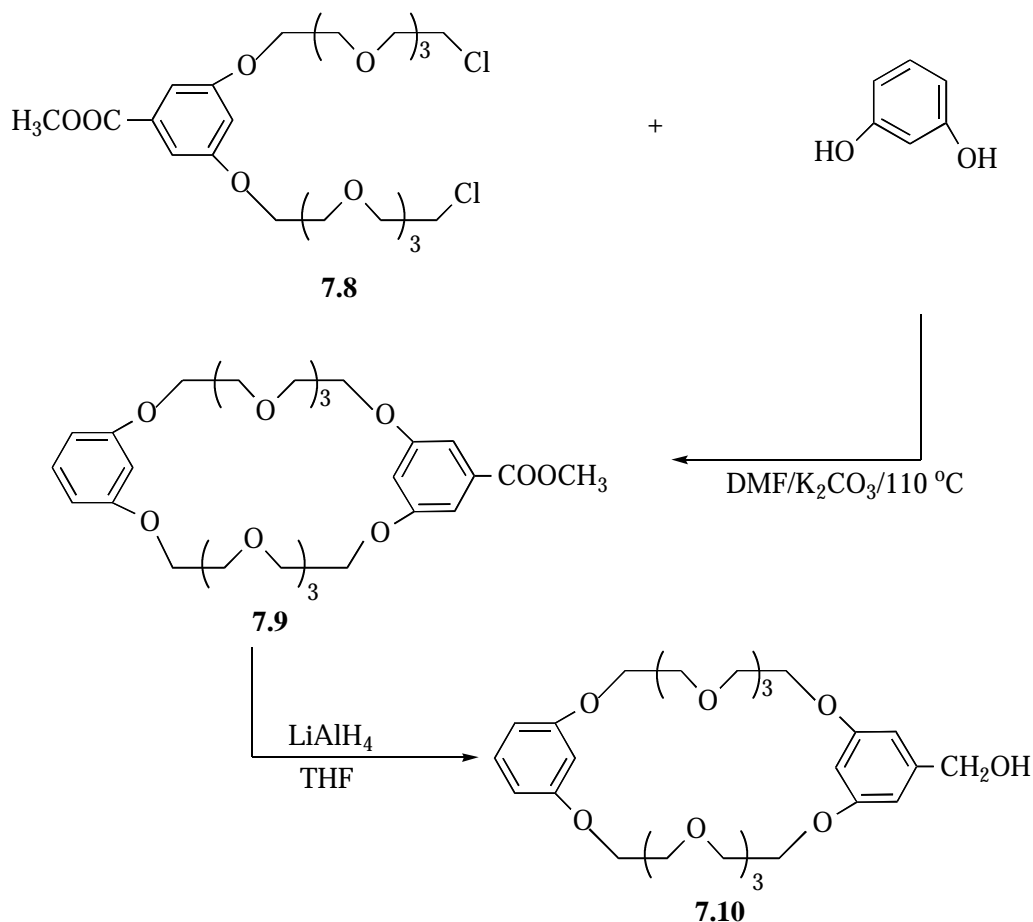


## 7.2 Results and discussion

### 7.2.1 Preparation of hydroxymethyl BMP32C10 (7.10)

In order to test the idea outlined in Scheme 7.3, a crown ether bearing a hydroxy group is essential. Hydroxymethyl BMP32C10 **7.10** is a perfect choice for this study. Thus **7.10** was prepared according to a reported procedure as shown in Scheme 7.4.<sup>8</sup>

Scheme 7.4 Preparation of hydroxymethyl BMP32C10 (**7.10**)



In practice, monoester BMP32C10 **7.9** was synthesized using the two piece combination approach. An equimolar solution of dichloride **7.8** and resorcinol in DMF was

<sup>8</sup> Gibson, H. W.; Nagvekar, D. S.; Yamaguchi, N.; Wang, F.; Bryant, W. S. *J. Org. Chem.* **1997**, *62*, 4798.

added to a suspension of base ( $K_2CO_3$ ) in a large volume of DMF very slowly to keep high pseudo-dilute conditions to favor cyclization rather than chain growth. However, the yield (37 %) was 9 % lower than that by a reported procedure.<sup>8</sup> In the purification of the crude product by chromatography, it was found that there was a small amount of impurity whose  $R_f$  was higher than that of **7.9**, which was discarded. In the literature, **7.9** was separated with ether as eluting solvent and no impurity was mentioned.<sup>8</sup> The yield difference is possibly due to this impurity. Compound **7.9** was reduced to **7.10** by  $LiAlH_4$  in THF according to a reported procedure.<sup>8</sup> Although the reaction was quantitative, recrystallization in ethanol lowered the yield to 87 %.

### 7.2.2 Preparation of poly(methacrylate)s

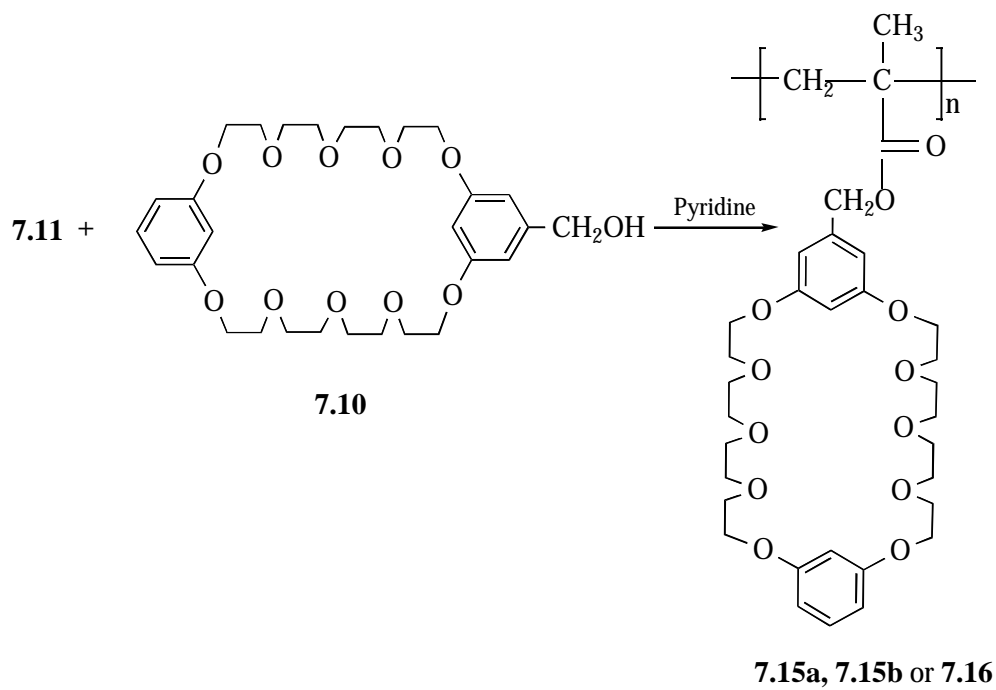
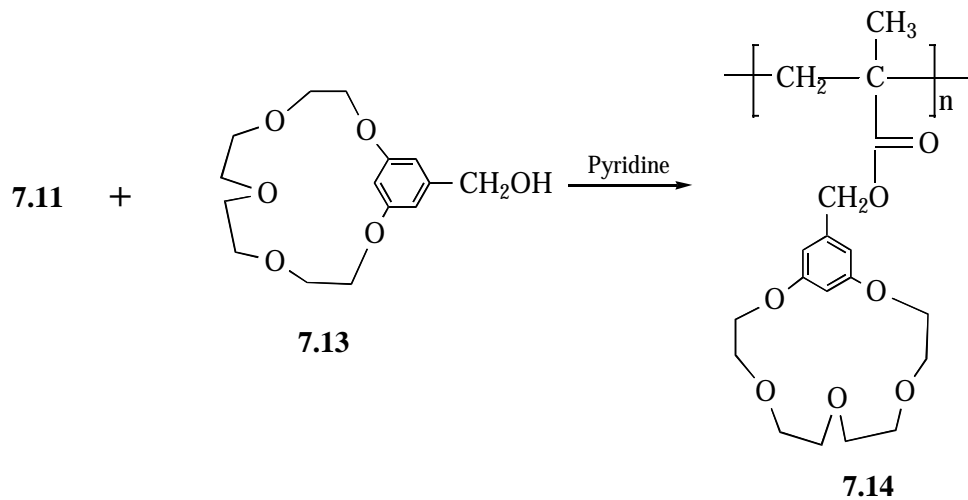
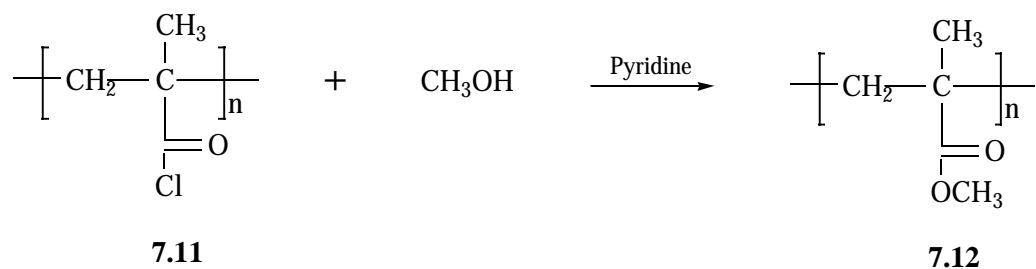
Poly(methacryloyl chloride) (**7.11**) was prepared by free radical polymerization with AIBN as initiator in toluene. **7.11** was then reacted in pyridine with methanol, 5-hydroxymethyl-1,3-phenylene-16-crown-5 (hydroxymethyl-MP16C5, **7.13**) and 5-hydroxymethyl-1,3-phenylene-1,3-phenylene-32-crown-10 (hydroxymethyl-BMP32C10, **7.10**) to afford poly(methacrylate)s **7.12**, **7.14** and **7.15a**, respectively (Table 7.1 and Scheme 7.5). By the same procedure as for **7.15a** but increasing the concentrations of both **7.11** and **7.10**, both branched **7.15b** (48 %, sol) and cross-linked **7.16** (52 %, gel) were obtained. The detailed feed compositions are summarized in Table 7.1. Proton NMR (Figure 7.1) demonstrated complete conversions.

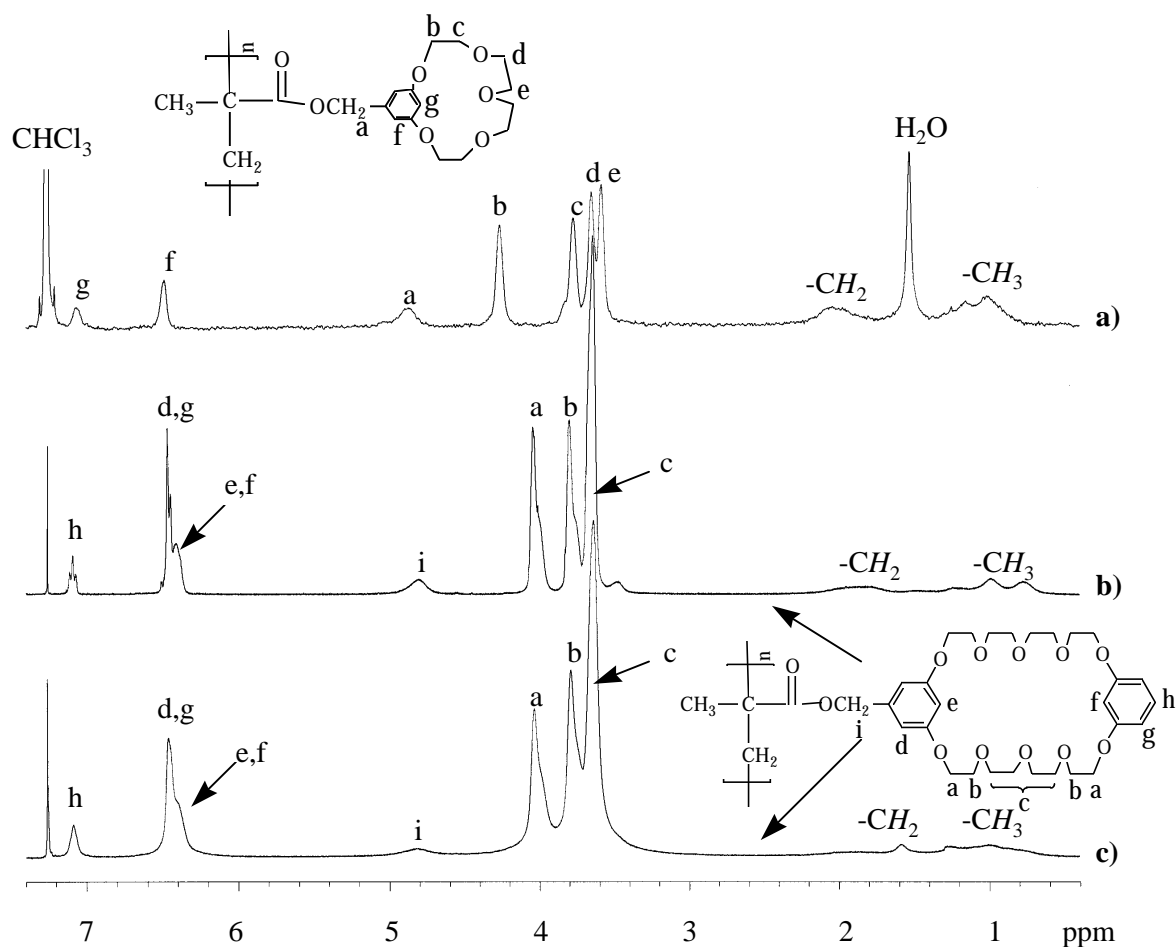
Table 7.1 Feed compositions for **7.12**, **7.14**, **7.15a**, **7.15b** and **7.16**

| Polymeric product   | <b>7.11</b> (mmol) <sup>a</sup> | Pyridine (mL) | ROH/mmol    |
|---------------------|---------------------------------|---------------|-------------|
| <b>7.12</b>         | 3.748                           | 10.0          | MeOH/excess |
| <b>7.14</b>         | 1.874                           | 5.0           | 14/1.874    |
| <b>7.15a</b>        | 0.937                           | 2.5           | 16/0.937    |
| <b>7.15b</b> (48 %) | 2.116                           | 3.0           | 16/2.116    |
| <b>7.16</b> (52%)   |                                 |               |             |

a. repeat unit basis.

Scheme 7.5 Preparation of poly(methacrylate)s **7.12**, **7.14**, **7.15** and **7.16**





**Figure 7.1** 400 MHz proton NMR spectra of a) poly(methacrylate crown ether) **7.14**, b) branched poly(methacrylate crown ether) **7.15a** and c) cross-linked **7.16** (swollen) in  $\text{CDCl}_3$ .

### 7.2.3 Characterization of **7.15** and **7.16**

#### i. GPC analysis

Since the preformed **7.11** used for **7.12**, **7.14**, **7.15a**, **7.15b** and **7.16** is from the same batch, the polydispersity (PDI) and the degree of polymerization (number average  $\text{DP}_n$  or weight average  $\text{DP}_w$ ) of all these poly(methacrylate)s were expected to be the same if no branching, cross-linking or other side reactions occur. Therefore, their absolute molecular

weights and PDI's were measured by GPC. Based on the number and weight average molecular weights ( $M_n$ ,  $M_w$ ) of these polymers and the corresponding molecular weights of the repeat units, their degrees of polymerization ( $DP_n$ ,  $DP_w$ ) were calculated. As shown in Table 7.2, poly(methacrylate crown ether) **7.14** had PDI,  $DP_n$ , and  $DP_w$ , which were almost identical to those of the poly(methyl methacrylate) (**7.12**). Although hydroxymethyl-MP16C5 (**7.13**) bears both a hydroxy group and polyether units, its cavity size is too small to be penetrated by any linear components to give rotaxane structures.<sup>9</sup> This result demonstrated that the crown ether moiety does not introduce any side reaction such as ring opening. However, although the poly(methacrylate crown ether) **7.15a** made under the same conditions is easily and completely soluble in common organic solvents, its PDI,  $DP_n$  and  $DP_w$  are much larger than those of both **7.12** and **7.14** (Table 7.2). Since this result can not be attributed to any side reaction, we ascribe the high molecular weight and broad distribution to the formation of a branched polymer, i.e., a rotaxane, by self-threading.

Table 7.2 GPC results for **7.12**, **7.14**, **7.15a**, **7.15b** and **7.16**

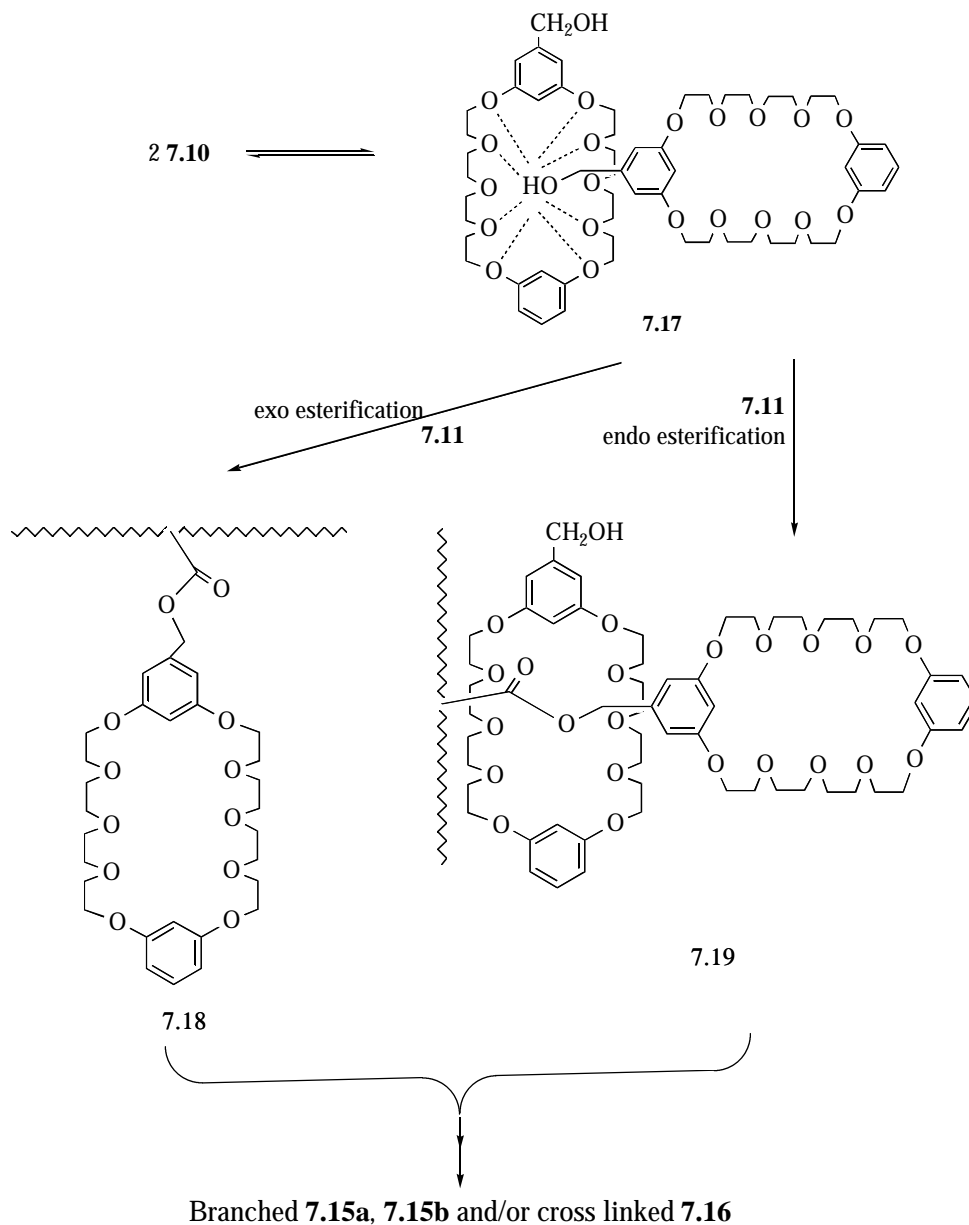
| Polymeric product   | $M_n$ (kg/mol) | PDI   | $DP_n$ | $DP_w$             |
|---------------------|----------------|-------|--------|--------------------|
| <b>7.12</b>         | 9.9            | 3.4   | 99     | $3.4 \times 10^2$  |
| <b>7.14</b>         | 36.3           | 3.8   | 99     | $3.8 \times 10^2$  |
| <b>7.15a</b>        | 102.8          | 30.9  | 162    | $5.01 \times 10^3$ |
| <b>7.15b</b> (48 %) | 135.5          | 187.9 | 214    | $4.02 \times 10^4$ |
| <b>7.16</b> (52%)   | --             | --    | --     | --                 |

The threading process is demonstrated in Scheme 7.6. **7.10** is a 32-membered macrocycle and thus it is large enough to be penetrated by a methylene chain.<sup>8</sup> In addition, the presence of both the hydroxy group and polyether units introduces a driving force (hydrogen bonding) for the formation of the bimolecular complex **7.17**. The intermediate **7.17**

<sup>9</sup> a) Harrison, I. T. *J. Chem. Soc., Chem. Commun.*, **1972**, 231. b) Harrison, I. T. *J. Chem. Soc., Perkin Trans. I*, **1974**, 301.

undergoes an endo esterification with poly(acid chloride) **7.11** through the cavity of one of the macrocycles to yield rotaxane structure **7.19**, the branching or crosslinking point for **7.15** or **7.16**. An exo esterification gives structure **7.18**, a normal pendant group modification reaction.

Scheme 7.6 Mechanism of the formation of branched and crosslinked **7.15** and **7.16**



Since hydrogen bonding is the driving force for the formation of the rotaxane structure **7.19**, it is expected from Le Chatelier's principle that a higher concentration of hydroxymethyl-BMP32C10 (**7.10**) will drive such self-threading to a larger extent and thus a higher branching degree or cross-linkage can be obtained. When the concentration of **7.10** was increased from 0.375 M to 0.705 M, it was found that only 48 % of the product was soluble in CHCl<sub>3</sub>, believed to be branched **7.15b**, and 52 % was gel, which was not soluble in any common solvents and believed to be cross-linked **7.16**. Both facts, that the branched **7.15b** had PDI, DP<sub>n</sub> and DP<sub>w</sub> even higher than those of the branched **7.15a** (Table 7.2) and the gel **7.16** was formed, confirmed that the threading was increased at higher feed concentration of **7.10**; this is consistent with the hydrogen bonding concept and the self-threading process in Scheme 7.6.

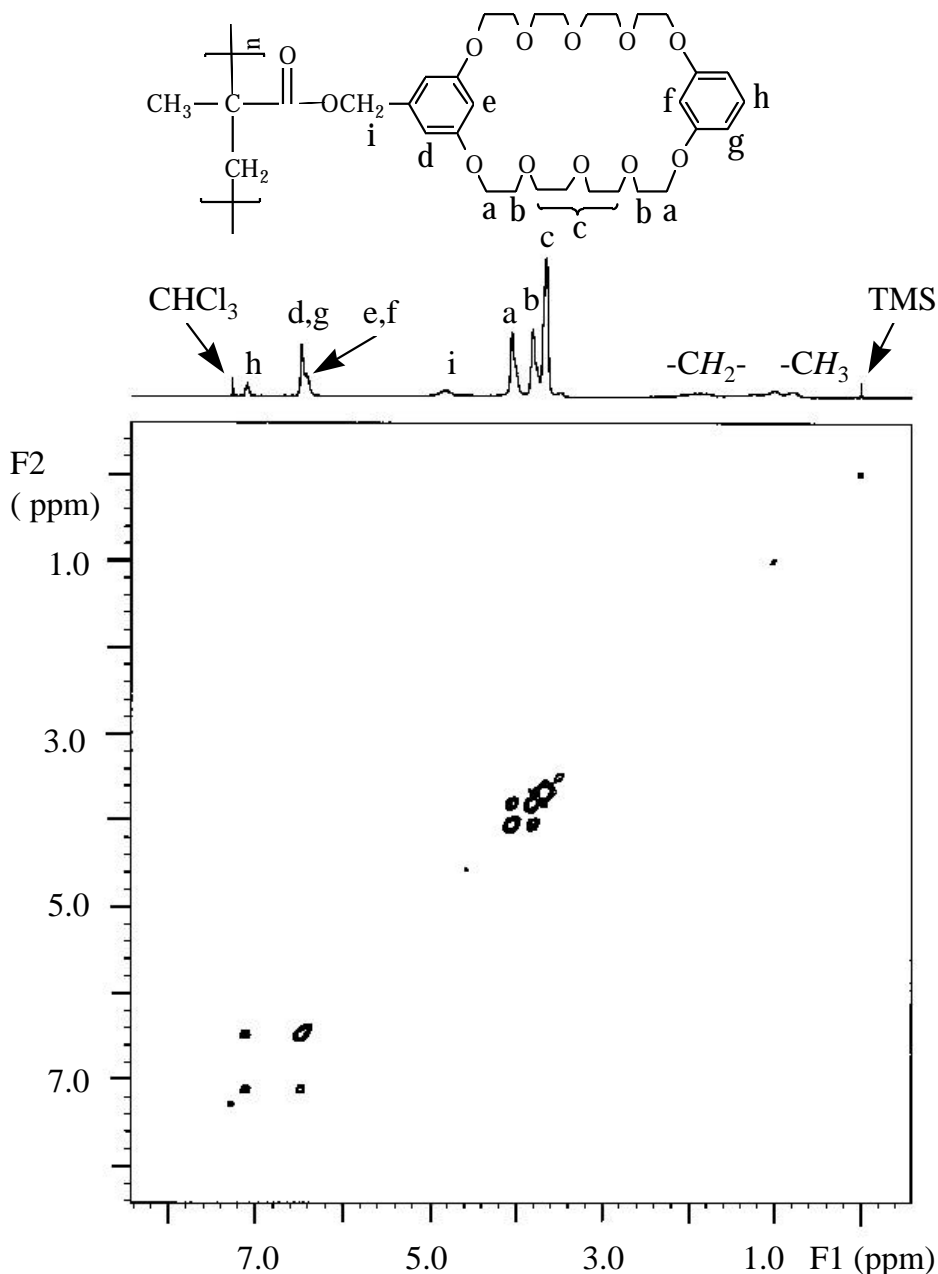
## ii. NMR study

The NMR spectra of **7.14** and **7.15a** (Figure 7.1a, 7.1b) confirmed their chemical structures. To prove the chemical composition of cross-linked **7.16**, its proton NMR was also measured after the sample was ultrasonicated to break the gel to increase the resolution. According to its spectrum (Figure 7.1c), **7.16** does have the same chemical composition as **7.15a** and **7.15b**, although its peaks are very broad. The 2D COSY spectrum (Figure 7.2) of **7.15a** also showed the couplings consistent with its chemical structure.

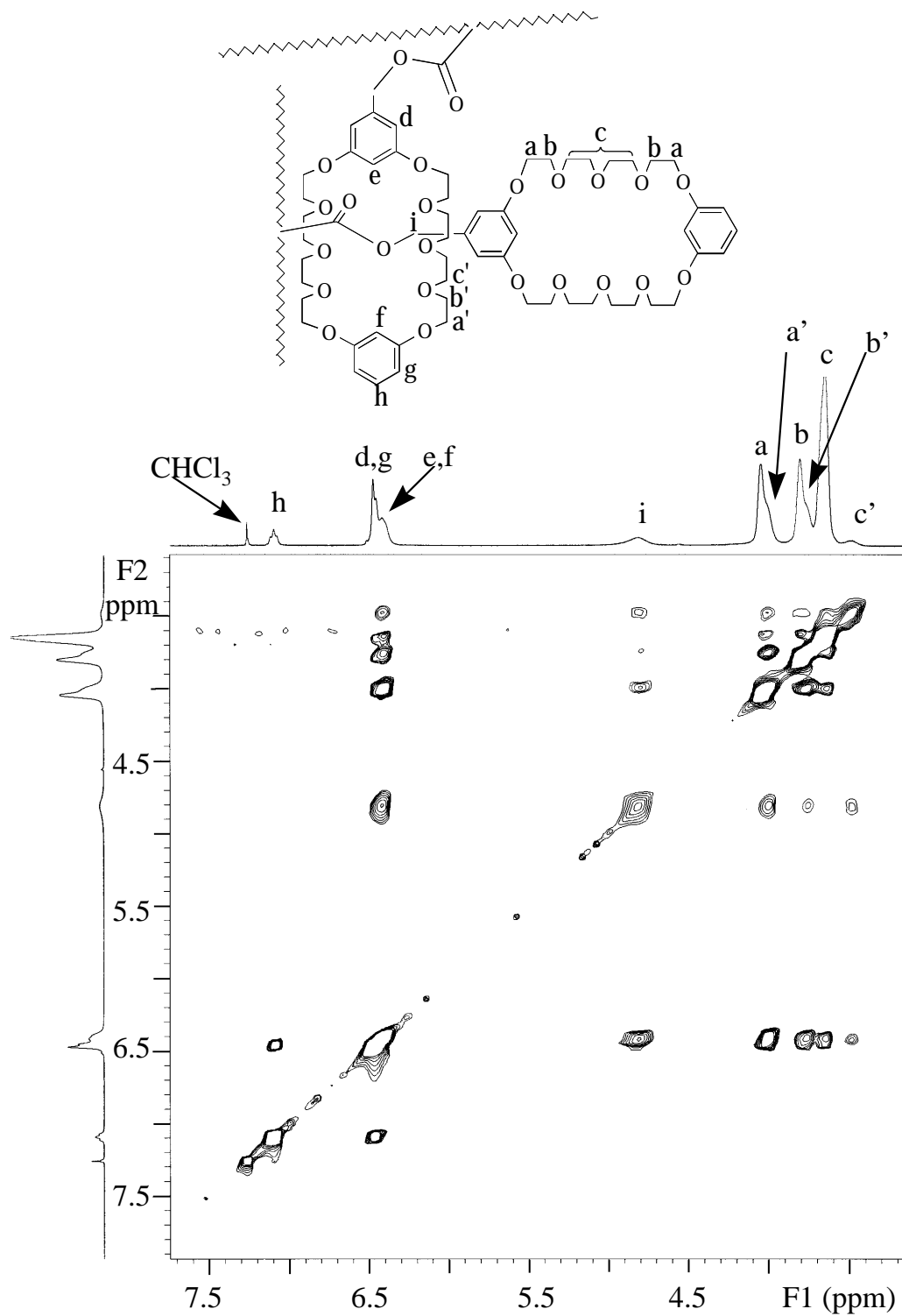
As soon as structure **7.19** (Scheme 7.6) forms, threaded **7.10** will be confined to a very short distance between the backbone and the pendant macrocycle. Thus some protons are expected to interact with each other through space, which can be revealed by 2D NOESY studies. Indeed, several through-space interactions exist (Figure 7.3). Among them, the most important correlation is proton i with protons e and f'; there are no interactions between proton i and protons d, g and h. The results can be only explained by the rotaxane structure **7.19** (Scheme 7.6) in which the methylene proton i from the pendant cyclic occupies the cavity of a threaded cyclic and thus interacts with those protons inside the cavity (protons e and f) but not with those protons outside the cavity (protons d, g and h). It is also worth noting that small new upfield signals for protons a', b' and c' arise, although they are



overlapped with the main peaks for a and b. We believe that the minor set of new signals is from the protons of the threaded macrocycle. Interestingly, proton i interacts with only the protons of the minor set, a', b' and c' of the threaded cyclic as is most evident for proton c'. This fact again is consistent with the structure **7.19**, since only the protons of the threaded cyclic are sufficiently close to proton i to result in such an effect.



**Figure 7.2** 2D COSY spectrum of branched poly(methacrylate crown ether) **7.15a** in CDCl<sub>3</sub>.



**Figure 7.3.** The correlated region of 400 MHz proton-proton 2d NOESY spectrum of branched poly(methacrylate crown ether) 7.15a in CDCl<sub>3</sub>.

However, why do the e and f signals also correlate with protons a, b, c and c'? In order to answer this question, we performed a NOESY study of bis(1,3-phenylene)-32-crown-10 (BMP32C10) (Figure 7.4) which shows an intramolecular NOE between proton f and protons a, b and c. Therefore, the correlation in **7.15** arises because the proton e is close enough to correlate intramolecularly with protons a, b, c and c'. Therefore, the NOESY studies provide compelling evidence for rotaxane structures in the branched **7.15a**, **7.15b** and/or cross-linked **7.16**.

Although we previously reported similar networks from polycondensation of difunctional macrocycles,<sup>10</sup> the rotaxane structures were inferred based only on solubility or molecular weight changes; NOE did not directly reveal the rotaxane structures. However, bulk polymerization of the methacrylate ester of **7.10** provides **7.15** of high molecular weight, which although not significantly branched did reveal NOE correlations of intraannular protons e and f with backbone (CH<sub>3</sub> and CH<sub>2</sub>) and benzylic methylene signals, indicative of statistical threading to form rotaxanes structures analogous to those formed here and also involving backbone threading as well.<sup>11</sup>

### iii. DSC analysis

While PMMA (**7.12**) is crystalline, poly(methacrylate crown ether)s **7.14**, **7.15**, and **7.16** are amorphous; **7.14** is a hard material and both **7.15** and **7.16** are transparent rubbery materials. It is believed that the loss of crystallinity in these poly(methacrylate crown ether)s is due to the interference with macromolecular packing by the bulky pendent groups, the crown ethers. Compared to that of **7.14** (T<sub>g</sub> = 86.2 °C), the glass transition temperatures for **7.15a**, **7.16** are much lower, 22.8 °C and 25.6 °C, respectively. This is probably because the

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<sup>10</sup> a) Delaviz, Y. and Gibson, H. W. *Macromolecules*, **1992**, *25*, 4859. b) Nagvekar, D. and Gibson, H. W. *Am. Chem. Soc. Div. Polym. Chem. Polym. Prep.* **1996**, *37(2)*, 299. c) Gibson, H. W.; Nagvekar, D.; Yamaguchi, N.; Bryant, W. S.; Bhattacharjee, S. *Am. Chem. Soc. Div. Polym. Chem. Polym. Prep.* **1997**, *38(1)*, 64. d) Gibson, H. W.; Nagvekar, D.; Bryant, W. S.; Powell J.; Bhattacharjee, S. *Am. Chem. Soc. Div. Polym. Chem. Polym. Prep.* **1997**, *38(1)*, 115. e) Gibson, H. W.; Nagvekar, D. S.; Powell, J.; Gong, C.; Bryant, W. S. *Tetrahedron*, in press.

<sup>11</sup> Gibson, H. W.; Nagvekar, D.; Bhattacharjee, S. *Am. Chem. Soc. Div. Polym. Chem. Polym. Prep.*, **1997**, *38(1)*, 481.

small macrocycle is more rigid than the large one and/or its smaller size results in less free volume. Therefore, introduction of different types of macrocycles provides a possible method for adjusting glass transition temperatures and/or crystallinity of poly(methacrylate)s.

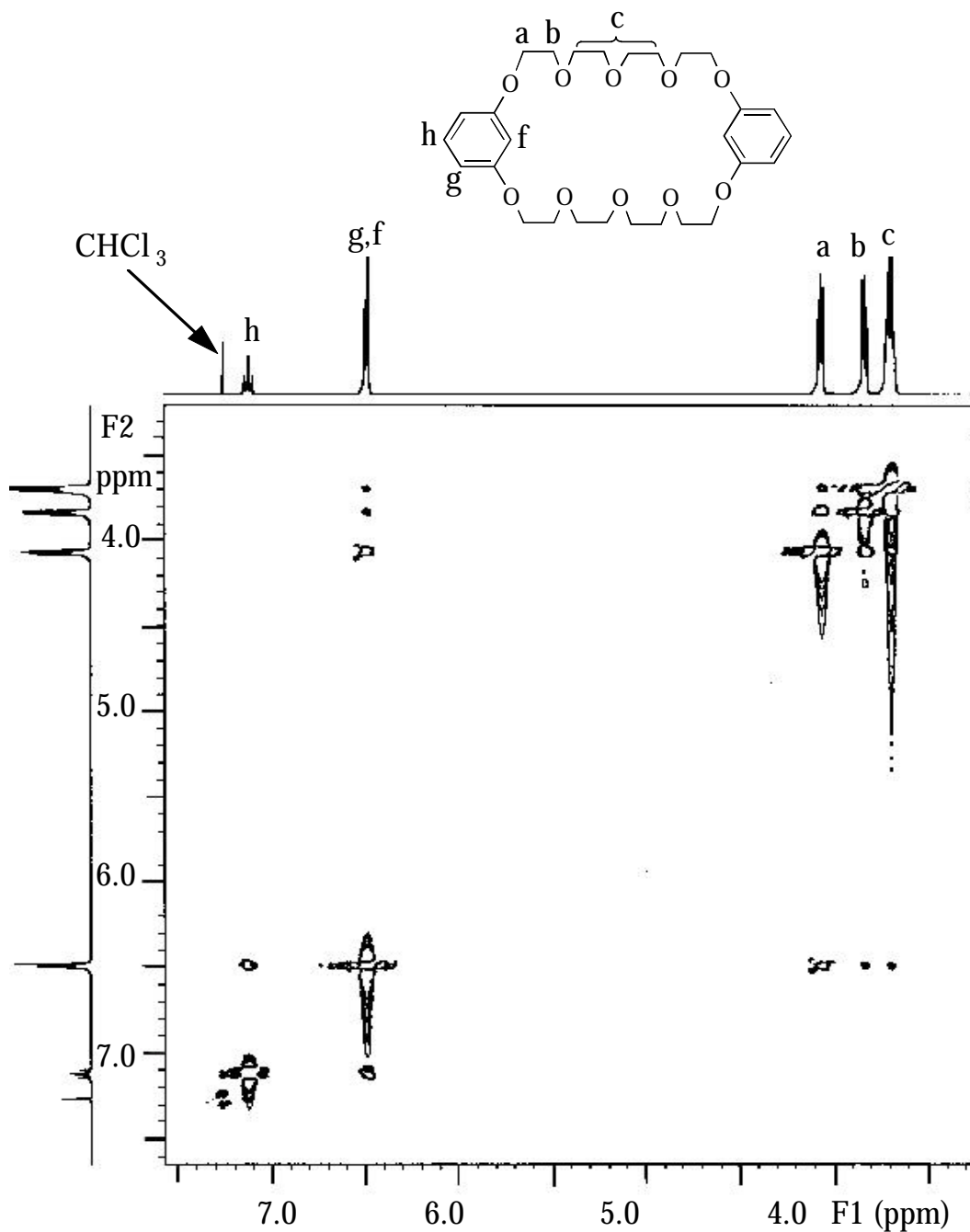


Figure 7.4. 400 MHz proton-proton 2D NOESY spectrum of BMP32C10 in CDCl<sub>3</sub>.

### 7.3 Conclusions

I developed a novel approach for branched and/or cross-linked polymeric materials by a self-threading process during reaction of a hydroxymethyl macrocycle with a polymeric acid chloride.

The resulting polymers have an original topology in which macromolecules are linked mechanically via rotaxane structures. The polyrotaxanes are novel, belonging to both types A and B in Scheme 7.1; these two species were generated in the same batch reaction. The formation of branching and/or crosslinking points, rotaxane structures, was proved by 2D NOESY studies.

### 7.4 Experimental

#### General methods

Reagent grade reactants and solvents were used as received from Aldrich unless otherwise specified. Pyridine and hexane were distilled over sodium hydride. Hydroxymethyl-MP16C5<sup>8</sup> (**7.13**) and BMP32C10<sup>12</sup> were prepared according to the procedures developed in our laboratory. <sup>1</sup>H NMR spectra were recorded at ambient temperature on a Varian Unity 400-MHz spectrometer. The proton NMR sample of **7.16** was ultrasonicated for 20 minutes to break down the gel and increase the resolution. The 2D NOESY and COSY studies were performed at 25 °C with a mixing time of one second and a relaxation delay of five seconds. The absolute molecular weights of the polymers were measured by GPC analyses with a Waters 150C ALC/GPC chromatograph equipped with a differential refractometer detector and an on-line differential viscometric detector (Viscotek 150R) coupled in parallel and the universal calibration was used. The DSC measurements were done with Perkin Elmer-B2 at a scan rate of 10 °C per minute and the data reported here are the midpoints of the transitions in the second heating.

#### 5-Carbomethoxy-1,3-phenylene-1',3'-phenylene-32-crown-10 (**7.9**)

A solution of methyl 3,5-bis(11-chloro-3,6,9-trioxaundecyloxy)benzoate (**7.8**) (7.66 g,

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<sup>12</sup> Delaviz, Y; Gibson, H. W. *Polym. Commun.* **1991**, 32, 103.

13.7 mmol) and resorcinol (1.52 g, 13.8 mmol) in DMF (25 mL) was added to a suspension containing  $K_2CO_3$  (38.048g, 275.4 mmol) and  $n-Bu_4NI$  (50 mg) in DMF (800 ml) via syringe at the rate of 0.521 ml/hr at 110 °C. After the addition was completed, the mixture was stirred for three days. Then the same amounts of dichloride and resorcinol were added to the mixture at the same addition rate and the reaction was run for five more days. After the system was cooled to room temperature, the salt was removed by filtration and solvent by vacuum evaporation. The residue was separated by chromatography with ethyl acetate as eluting solvent. The first fraction was found to be an impurity and the second fraction was desired product **7.9**, a white solid (6.1 g, 37%, mp: 76.5-77.8 °C, lit.<sup>8</sup> 74.8-75.4 °C, 46%).  $^1H$  NMR in  $CDCl_3$ : 3.63-3.70 (m, 16H); 3.82-3.85 (m, 8H); 3.88 (s, 3H); 4.05-4.11 (m, 8H), 6.47-6.49 (m, 3H); 6.83 (t, J = 2.4, 1H); 7.11 (t, J = 6.4, 1H); 7.17 (d, J = 2.4, 2H).  $^{13}C$  NMR in  $CDCl_3$ : 52.16; 67.83; 69.55; 70.84; 70.91; 106.82; 107.98; 131.79; 159.72; 166.71 (ten peaks as required).

#### **5-Hydroxymethyl-1,3-phenylene-1',3'-phenylene-32-crown-10 (7.10)**

To a 150 ml flask was added a solution of 5-carbomethoxy-1,3-phenylene-1,3-phenylene-32-crown-10 (**7.9**) (5.6 g, 9.4 mmol) in THF (60 mL).  $LiAlH_4$  (13 mL, 1 M in THF, 13 mmol) was added dropwise at room temperature. The reaction was run for 14 hrs. The excess hydride was destroyed by addition of ethyl acetate and the solution was diluted with water (40 mL). The product was extracted with  $CH_2Cl_2$  (2x80 mL). Crude product from the removal of solvent was recrystallized in ethanol to afford clear crystals (4.38 g, 82 %, mp: 86.4-87.2 °C, lit.<sup>8</sup> 84 %, mp: 88.4-88.9 °C.  $^1H$  NMR in  $CDCl_3$ : 3.68-3.72 (m, 16H); 3.82-3.84 (m, 8H); 4.04 (t, J = 4.9, 4H); 4.08 (t, J = 4.8, 4H); 6.40 (t, J = 2.4, 1H); 6.44 (t, J = 2.4, 1H); 6.48-6.52 (m, 4H); 7.13 (t, J = 8.2, 1H).  $^{13}C$  NMR in  $CDCl_3$ : 65.26; 67.47; 67.63; 69.68; 69.69; 70.84; 100.92; 101.61; 105.51; 107.11; 129.74; 143.41; 159.93; 160.09 (total 14 peaks, theoretical 17 peaks).

### **Poly(methacryloyl chloride) (7.11)**

Distilled methacryloyl chloride (60.0 g, 0.574 mol) was dissolved in 100 mL of toluene. To the solution was added initiator (AIBN, 0.500 g,  $3.04 \times 10^{-3}$  mol). Polymerization was run for 2 days at 65-70 °C. After it had been cooled down, the solution was precipitated into hexane (800 mL) to afford **7.11** (57 g, 95 %).

### **General procedure for poly(methacrylate)s: poly(methyl methacrylate) (PMMA, 7.11)**

The preformed polymer **11** (391.8 mg, 3.748 mmol of repeat units) was dissolved in pyridine (10 mL). Upon the addition of methanol (1 mL), the reaction proceeded for 24 hours at 80 °C. The solution was precipitated into water to afford PMMA (**7.12**). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm) δ 3.60 (s, 3H, OCH<sub>3</sub>), 1.70-1.90 (m, 2H, CH<sub>2</sub>), 0.84-1.03 (m, 3H, CH<sub>3</sub>).

### **Poly(methacrylate crown ether) 7.14 and branched Poly(methacrylate crown ether) 7.15a**

The procedures and reaction conditions were the same as that for PMMA (**7.12**) except using hydroxymethyl-MP16C5 (**7.13**) for **7.14** and hydroxymethyl-BMP32C10 (**7.10**) for **7.15a** instead of methanol (Scheme 7.5). The feed compositions are summarized in Table 7.1. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm) for **7.14** (Figure 7.1a) δ 7.06 (br s, 1H, ArH), 6.49 (br s, 2H, ArH), 4.90 (br s, 2H, ArCH<sub>2</sub>), 4.27 (br s, 4H, OCH<sub>2</sub>), 3.77 (br s, 4H, OCH<sub>2</sub>), 3.65 (br s, 4H, OCH<sub>2</sub>), 3.58 (br s, 4H, OCH<sub>2</sub>), 2.04 (br m, 2H, CH<sub>2</sub>), 1.01-1.25 (br m, 3H, CH<sub>3</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm) for **7.15a** (Figure 7.1b) δ 7.10 (t,  $J = 8.0$ , 1H, ArH), 6.46 (br m, 6H, ArH), 4.82 (br s, 2H, ArCH<sub>2</sub>), 4.05 (br s, 8H, OCH<sub>2</sub>), 3.81 (br s, 8H, OCH<sub>2</sub>), 3.65 (br s, 16H, OCH<sub>2</sub>), 1.08 (br s, 2H, CH<sub>2</sub>), 0.78-1.02 (br m, 3H, CH<sub>3</sub>). The glass transition temperatures ( $T_g$ ): 86.2 °C for **7.14** and 22.8 °C for **7.15a**.

### **Branched 7.15b and cross-linked poly(methacrylate crown ether) 7.16**

The same procedure as that for **7.15a** was applied except that the feed concentration of macrocycle **7.10** was increased as specified in Table 7.1. The product from precipitation was extracted with CHCl<sub>3</sub> and both branched **7.15b** (48%, sol) and cross-linked **7.16** (52%,

gel) were obtained.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm) for branched **7.15b**: same as for **7.15a**.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm) for crosslinked **7.16** (Figure 7.1c)  $\delta$  7.10 (s br, 1H, ArH), 6.46 (br m, 6H, ArH), 4.82 (br s, 2H, ArCH<sub>2</sub>), 4.05 (br s, 8H, OCH<sub>2</sub>), 3.81 (br s, 8H, OCH<sub>2</sub>), 3.65 (br s, 16H, OCH<sub>2</sub>), 1.08 (br s, 2H, CH<sub>2</sub>), 0.78-1.02 (br m, 3H, CH<sub>3</sub>). T<sub>g</sub> for crosslinked **7.16**: 25.8 °C.