308 *Macromolecules* **1998,** *31,* 308−313

Poly(urethane/crown ether rotaxane)s with Solvent Switchable Microstructures

Caiguo Gong, Thomas E. Glass, and Harry W. Gibson*

Department of Chemistry, Virginia Polytechnic Institute & State University
Blacksburg, Virginia 24061

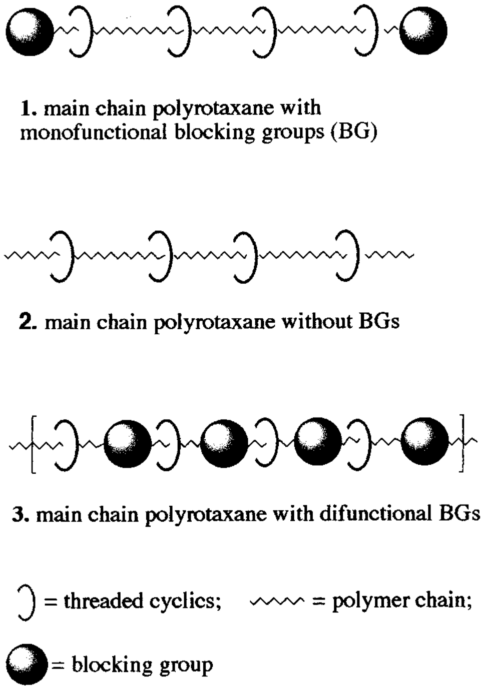
Received June 9, 1997; Revised Manuscript Received October 31, 1997

ABSTRACT: Poly(urethane/crown ether rotaxane)s **7c−g** were prepared from bis(*p*-*tert*-butylphenyl)-bis[*p*-(2-(2′-hydroxyethoxy)ethoxy)phenyl]methane (diol BG **4**), tetrakis(ethylene glycol) (**5**) and 4,4′-methylenebis(phenyl isocyanate) (MDI) (**6**) using 30-crown-10 (30C10) as solvent. It was found that threading efficiencies (*m*/*n* value, average number of cyclics per repeat unit) of **7c−g** increased with the feed proportion of diol BG **4**. Compared to poly(ester rotaxane)s in which the crown ethers can freely move along the backbone, the dethreading rate during polymerization is slow due to the H-bonds between in-chain NH groups and threaded crown ethers. In poly(urethane rotaxane)s, crown ethers are localized at the NH sites by H-bonding in chloroform, locked translationally and perhaps rotationally, to afford a well-defined microstructure. However, the cyclics tend to be in the vicinity of BG units in DMSO, which disrupts the H-bonding. Induction of shuttling between the two sites is caused by the use of mixtures of DMSO and $CHCl_3$. Therefore, **7c−g** are considered to be the first polymeric molecular switches reported so far. Threaded 30C10 has much shorter relaxation time than its free counterpart; this is a novel and easy method to characterize the formation of polyrotaxanes. The glass transition temperatures of **7c−g** increase with the amount of BG units in the polymers, an easy approach to adjust T_g's of polyurethanes.

Introduction

Polyrotaxanes consisting of linear backbone and cyclics, in which these two components are mechanically linked with each other, are formed by threading macrocycles onto polymeric chains for main chain polyrotaxanes or side chains for side chain polyrotaxanes.[1−9] There are three types of main chain polyrotaxanes (Scheme 1) including polypseudorotaxane **2**, in which the cyclics can slip off the backbone, and true polyrotaxanes **1** and **3**, in which the cyclics are confined between blocking groups (BG) and are thus thermally stable. Two general methods are used for preparation of these materials: threading the cyclics onto preformed polymers (approach I, Scheme 2)[1−4,5e,5f,10] or threading during polymerization using the cyclics as solvent (approach II, Scheme 2).[1,5a−e,6−8] In both **1** and **2**, the cyclics can translate along the backbone to form a separate phase if there is no strong backbone/cyclic interaction, e.g., poly(ester rotaxane)s,[5c,5d] while cyclics in **3** are separated by BG and have a diminished ability to aggregate and crystallize.[5d] It was 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; the use of difunctional BG mechanically prevented dethreading, thus increasing the *m*/*n* value 13-fold compared to that without BG.[6a−c] Since the crown ethers can H-bond with NH groups,[8,9] the threaded crown ethers should not dethread or do so only to a limitted extent with polyurethane or polyamide backbones. In addition, in low polarity media the crown ethers could be localized at the NH sites by H-bonding to afford a well-defined microstructure. We tested this idea by the preparation of poly(urethane/crown ether rotaxane)s and report the results here.

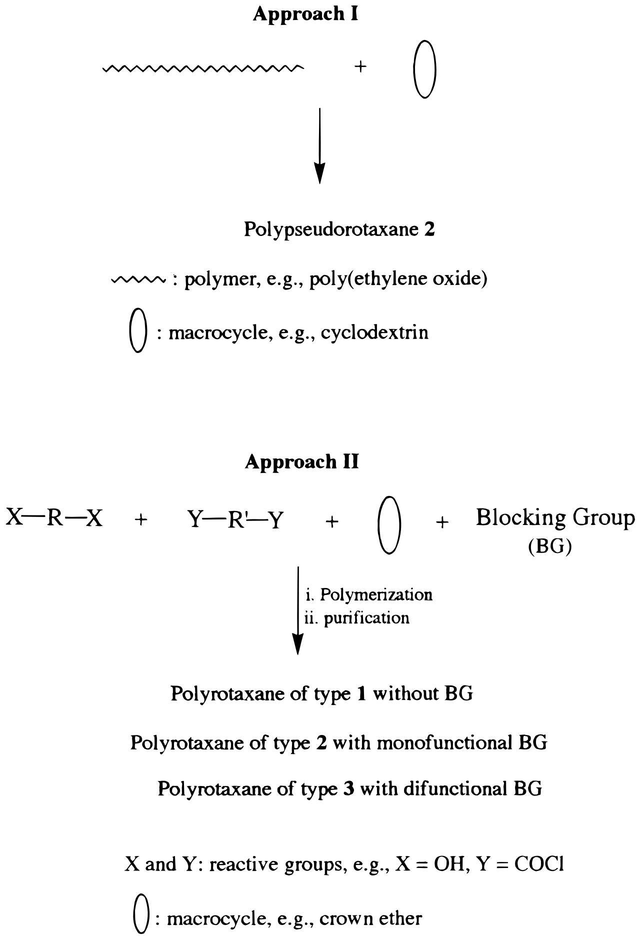
Scheme 1. Various Main Chain Polyrotaxanes



Results and Discussion

I. Synthesis of Model Polyurethanes 7a,b and Poly(urethane rotaxane)s 7c−g. High molecular weight model homopolyurethane **7a** was prepared from glycol **5** and MDI (**6**), and copolyurethane **7b** from diol BG **4**, **5**, and MDI by solution polymerization using DMF as solvent (Scheme 3) at 95 °C for 7 h (Tables 1 and 2). The same polymerization conditions were applied for the syntheses of poly(urethane rotaxane)s **7c−g** except that 30C10 was used as solvent instead of DMF. Un-

Scheme 2. Preparation Methods for Main Chain Polyrotaxanes



Scheme 3. Preparation of Model Polyurethanes 7a,b and Poly(urethane rotaxane)s 7c–g

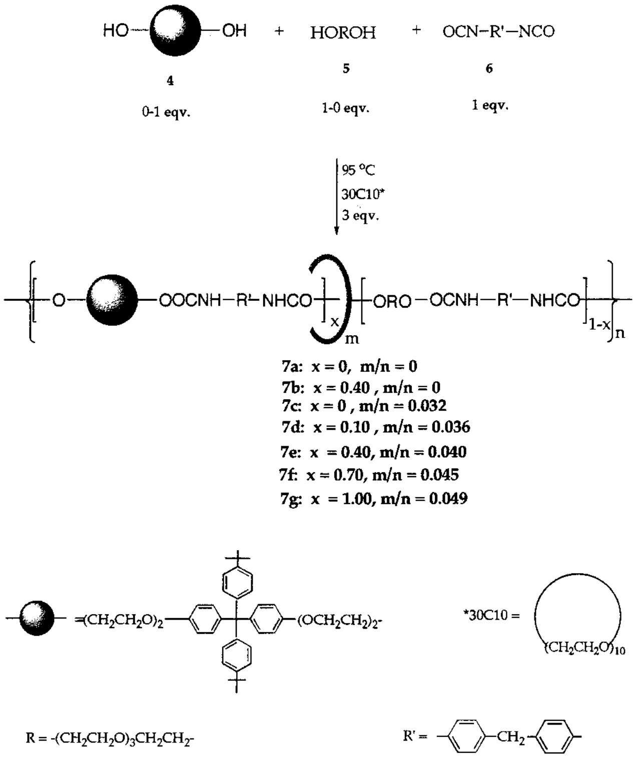


Table 1. Feed Compositions and Polymerization Conditions for Polyurethanes 7a,b and Poly(urethane rotaxane)s 7c–g[a]

product	BG diol **4** (mg/mmol)	glycol **5** (mg/mmol)	MDI **6** (mg/mmol)	30C10 (g/mmol)
7a	0/0	194.2/1.000	250.3/1.000	0[b]
7b	255.5/0.400	116.5/0.600	250.3/1.000	0[b]
7c	0/0	194.2/1.000	250.3/1.000	1.321/3.000
7d	63.9/0.100	174.8/0.900	250.3/1.000	1.321/3.000
7e	255.5/0.400	116.5/0.600	250.3/1.000	1.321/3.000
7f	447.2/0.700	58.3/0.300	250.3/1.000	1.321/3.000
7g	638.8/1.000	0/0	250.3/1.000	1.321/3.000

[a] Temperature, 96 °C; time, 7 h. [b] DMF as solvent (2 mL).

threaded 30C10 was removed by precipitation from DMF into methanol, a good solvent for 30C10 but a poor solvent for the backbone.[5c]

II. Characterization of Polyrotaxanes. The formation of poly(urethane rotaxane)s was proven by procedures well-established with the poly(ester rotaxane)s.[6a–c] First, the removal of free 30C10 was confirmed by both GPC[6c] and proton NMR. The free 30C10 peak was absent in the GPC traces of polyrotaxanes **7c–g**. In ^{1}H NMR spectra of **7c–f** the integrations of the ethyleneoxy protons (a–d) and benzylic proton (p) were in proper proportion to the aromatic signals (e–h, l, m) (Figure 1), confirming the absence of the free 30C10 (3.67 ppm). Likewise this signal was clearly absent in the proton NMR spectrum of **7g** (Figure 2d). Compared to that (Figure 1b) of model polymer **7b**, the spectrum (Figure 1a) of the corresponding polyrotaxane **7e** has a new signal at 3.50 ppm which is due to threaded 30C10, consistent with the formation of the polyrotaxane.

III. Microstructures of Polyrotaxanes 7c–g. For copoly(ester rotaxane)s made from diol BG **4**, 1,10-decanediol, and sebacoyl chloride, threaded 30C10 had a range of chemical shifts in $CDCl_3$,[6b] while in copoly(urethane rotaxane)s **7d–f** it has only one signal in the same solvent (Figure 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. 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.[6b] With polyurethane as the backbone, however, H-bonding between the in-chain NH groups and the crown ethers is known to take place.[8,9] Such H-bonding induces a well-defined polymer microstructure **8** (Scheme 4), in which 30C10 is confined near the phenyl groups of MDI units and thus the upfield shift for threaded 30C10 in the polyurethanes is caused by these phenyl rings. Therefore, in $CDCl_3$ threaded 30C10 in **7d–g** displays the same chemical shift even in different sequence structures. In fact the chemical shifts and breadths of the signals for the threaded crown ethers were insensitive to an increase of temperature up to 60 °C, indicating that the H-bonding is rather strong.

To confirm the above hypothesis, proton NMR studies of poly(urethane rotaxane)s **7d–g** were also performed using DMSO-d_6 as solvent. As shown in Figure 3, threaded 30C10 in copolyurethanes **7d–f** indeed displays a range of chemical shifts from 3.33 to 3.38 ppm, while free 30C10 and the threaded 30C10 in **7c** appear at 3.52 ppm. DMSO is a very good solvent for disruption of H-bonding between the NH groups and the crown ethers[7,8] and thus the macrocycles in the polyurethane

Table 2. Threading Efficiencies, Dethreading Degrees, GPC and DSC Results for Polyurethanes 7a–g

product	% BG diol **4**	molar ratio (30C10/diol)	*m*/*n*	dethreading[a] degree (%)	M_n/M_w[b] ($\times 10^{-3}$)	T_g[c] (°C)
7a	0	0	0	-	16.8/30.0	54.0
7b	40	0	0	-	13.9/24.0	80.9
7c	0	3	0.032	34.7	17.8/31.0	56.0
7d	10	3	0.036	26.5	22.6/39.4	65.4
7e	40	3	0.040	18.4	12.4/18.0	80.6
7f	70	3	0.045	8.16	18.7/52.9	101.7
7g	100	3	0.049	0	23.4/37.8	125.3

[a] Degree of dethreading (%) = $\{[(m/n)_{\max} - (m/n)_{co}]/(m/n)_{\max}\} \times 100$. $(m/n)_{\max}$: threading efficiency of diol BG-based homopoly(urethane rotaxane) **7g**. $(m/n)_{co}$: threading efficiency of poly(urethane rotaxane)s **7c**–**g**. [b] Measured by GPC with universal calibration in NMP at 60 °C. [c] Measured by DSC at scan rate 10 °C/min.

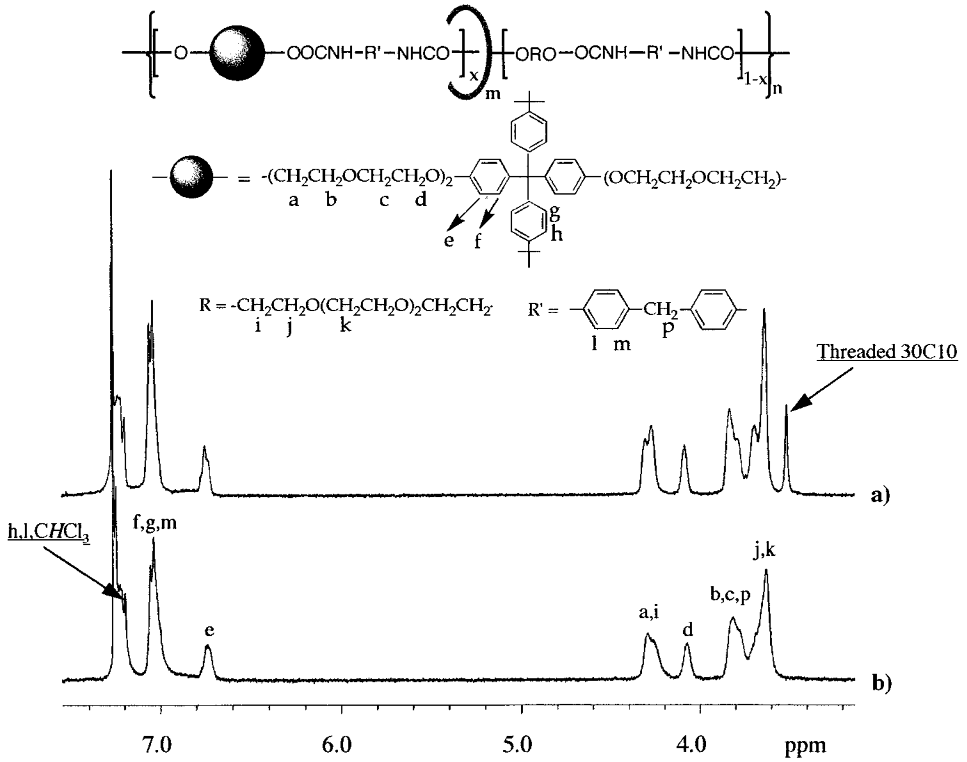


Figure 1. 400 MHz proton NMR spectra of (a) polyrotaxane **7e** and (b) model polymer **7b** in CDCl3 at 30 °C.

rotaxanes are located in the vicinity of the BG units (Scheme 4) and the 30C10 signal is shifted upfield as noted above for polyesters.[6b] Since the copolyurethanes have different sequence structures with different lengths between the BG units, a range of chemical shifts for threaded 30C10 was observed (Figure 3).

All the above observations are supported by the measurements of spin-lattice relaxation times (T_1). Threaded 30C10 in **7g** in chloroform and DMSO has T_1 values of 0.178 and 0.542 s, respectively; the smaller T_1 in chloroform confirms the restriction of ring movement (both translation and rotation) because of H-bonding (**8**), while the larger T_1 in DMSO indicates the relatively free movement of macrocycle, i.e., translation and rotation. The macrocycle in **7g** is still restricted even in DMSO to a large extent since its T_1 is small compared to that (1.78 s) 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.[6a–c]

Since the solvent has a large effect on the locus of the rings in these polyrotaxanes, as shown in Figures 2 and 3, manipulation of the solvent should allow control

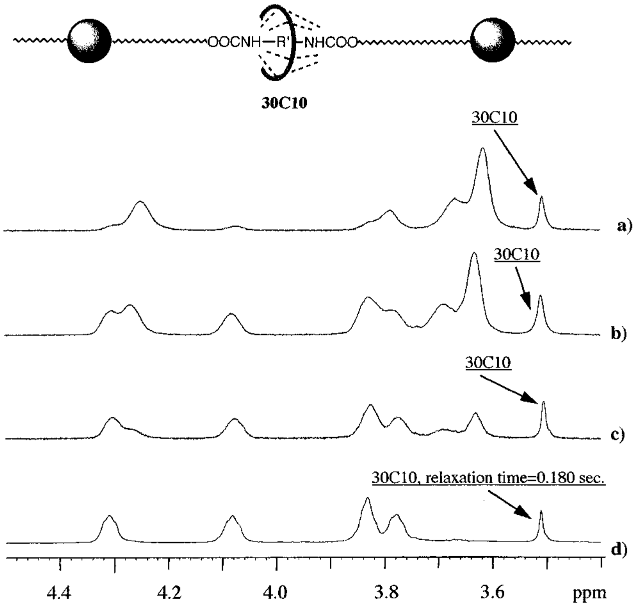
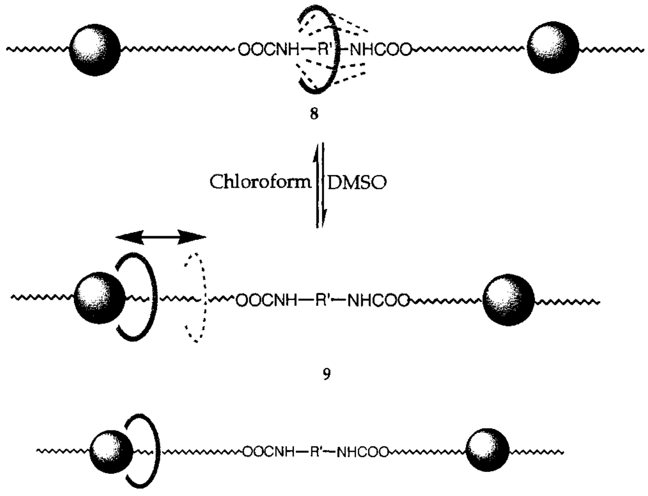


Figure 2. Expanded aliphatic region of the 400 MHz proton NMR spectra of poly(urethane rotaxane)s (a) **7d**, (b) **7e**, (c) **7f** and (d) **7g** in CDCl3 at 30 °C.

Scheme 4. Solvent-Induced Switching of Crown Ether in Polyrotaxanes 7c−g



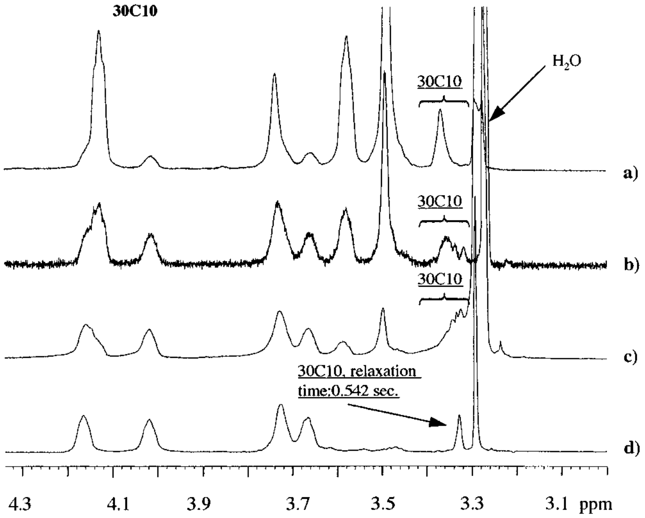


Figure 3. Expanded aliphatic region of the 400 MHz proton NMR spectra of poly(urethane rotaxane)s (a) **7d**, (b) **7e**, (c) **7f** and (d) **7g** in DMSO-d_6 at 30 °C

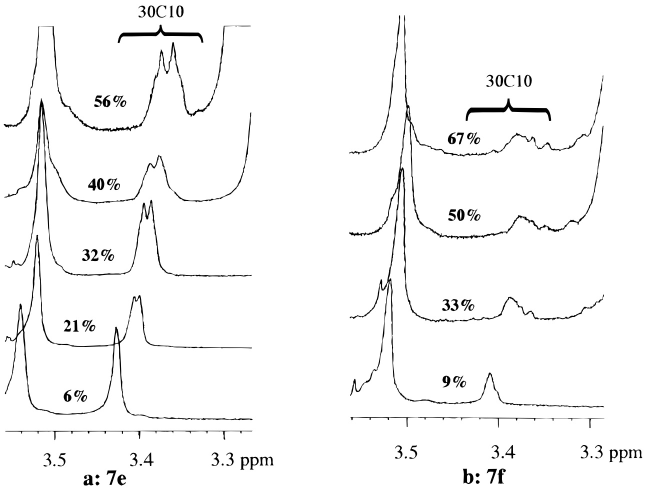


Figure 4. Effect of incremental addition of DMSO-d_6 to CDCl$_3$ solutions of polyrotaxanes (a) **7e** and (b) **7f** on the position and shape of the 400 MHz ^{1}H NMR signal for threaded 30C10 (%DMSO by volume).

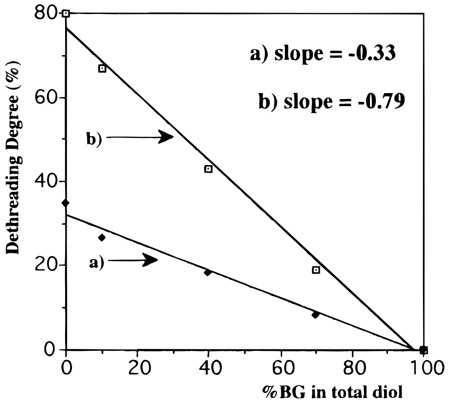


Figure 5. Dependence of dethreading degree on the feed percentage of diol BG **4** (a) for poly(urethane rotaxane)s and (b) for poly(ester rotaxane)s.[6b]

over the microstructure. Indeed, as shown in Figure 4, incremental addition of DMSO to CDCl$_3$ solutions of polyrotaxanes **7e** and **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 **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.

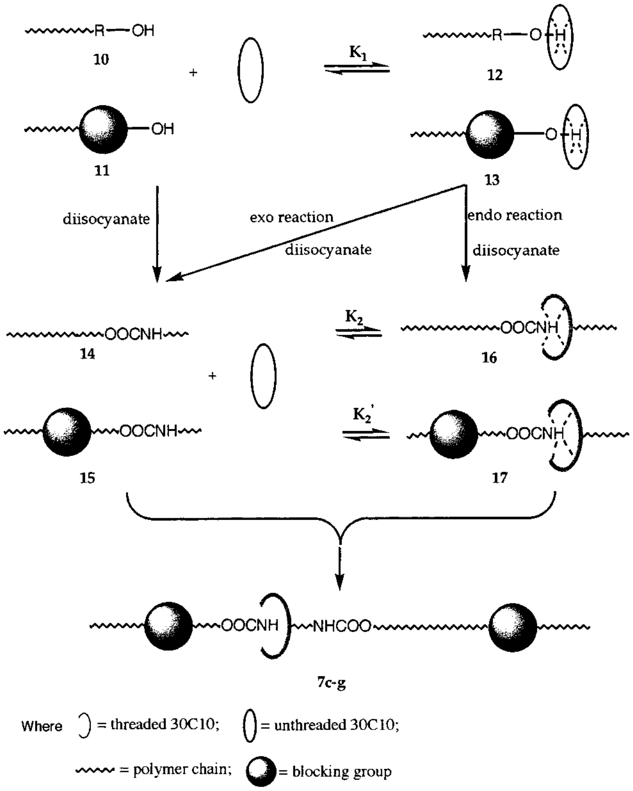
IV. Threading and Dethreading. The threading efficiencies of polyrotaxanes **7c**−**g** were measured by the integrals of 30C10 signals vs the backbone protons.[6a−c] It was found that m/n values decreased with decreasing feed percentage of diol BG **4** (Table 2). However, compared to that during the preparation of poly(ester rotaxane)s (Figure 5b),[6b] the extent of dethreading during the preparation of poly(urethane rotaxane)s was small (Figure 5a). It is believed that the decreased dethreading is due to the introduction of in-chain NH groups (Scheme 5). In the polyurethane, as soon as the crown ether is threaded, with formation of structures **16** and **17** by an endo reaction (taking place through the cavity of the cyclic), it will H-bond with the −NH groups. Thus dethreading, leading to structures **14** and **15** plus free macrocycles, occurs at a slower rate than that in the polyester because the ester linkage has no strong retaining force.[6a,b,c] In other words K_2 and K_2' are larger for the polyurethanes than for the polyesters. The difference between K_2 and K_2' will be smaller than that with polyester backbone. This means the dependence of m/n on %BG is less for poly(urethane rotaxane)s. Therefore, higher m/n can simply be achieved by choosing the proper backbone and using larger crown ethers even without any BG. Theoretically, the method is also applicable for other polyrotaxanes with similar in-chain functional groups, i.e., polyamides.

V. DSC Analyses. Model polyurethanes **7a**,**b** and poly(urethane rotaxane)s **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. The T_g's of model polymers **7a** and **7b** are almost identical to those of corresponding polyrotaxanes **7c** and **7e** (Table 2), probably because of the low loading of 30C10. The T_g does change with the amount of BG units; the more BG moieties, the higher is T_g. This is because of the bulkiness and rigidity of the BG linkage.

Conclusions

Crown ether-based poly(urethane rotaxane)s were prepared by solution polymerization using 30C10 as

Scheme 5. Threading and Dethreading Mechanisms in the Formation of Poly(urethane rotaxane)s 7c−g



solvent. The extent of dethreading during their preparation is 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 be in the vicinity of the BG moiety in DMSO; these are the first solvent-responsive polymeric molecular switches reported. The glass transition temperatures of the polyurethanes depend on the amount of BG units. 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.

Experimental Section

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[11] and diol BG **4**[6a] were prepared by well-established procedures. Proton NMR spectra, reported in ppm, were obtained on a 400 MHz Varian spectrometer using $CDCl_3$ solutions or DMSO-d_6 with Me_4Si as an internal standard. The relaxation times (T_1) were measured by standard $180-\tau-90-$acquisition techniques. 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. T_g's were measured with a Perkin-Elmer thermal analysis system at a rate of 10 °C/min for both heating and cooling; all reported values were the centers of transitions from second heatings.

Model Polyurethanes 7a,b. To a 10 mL flask were added tetrakis(ethylene glycol) (**5**) (194.2 mg, 1.000 mmol) (oven dried at 100 °C), freshly distilled MDI (**6**) (250.3 mg, 1.000 mmol) for **7a** or diol BG **4** (255.5 mg, 0.400 mmol), **5** (116.5 mg, 0.600 mmol), and MDI (**6**) (250.3 mg, 1.000 mmol) for **7b** in DMF (2 mL). The solution was heated at 96 °C in an oil bath under N_2 for 7 h. The product was precipitated into MeOH to give a transparent material. ^1H NMR (DMSO-d_6) for **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). ^1H NMR ($CDCl_3$) for **7b**: 7.19−7.31 (m, 5.6H plus $CHCl_3$), 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 7c−g. Diols (**4** plus **5**, total 1 mmol) (Table 1) were dissolved in 30C10 (3 mmol) at 96 °C. After the solution had been stirred for 0.5 h at this temperature, MDI (**6**) (1 mmol) was added slowly and polymerization proceeded for 7 h under N_2. The reaction product was dissolved in DMF and precipitated into MeOH (five times) to remove free 30C10. ^1H NMR (DMSO-d_6) for **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). ^1H NMR ($CDCl_3$) for **7d**: 7.19−7.31 (m, 4.4H plus $CHCl_3$), 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). ^1H NMR ($CDCl_3$) for **7e**: 7.19−7.31 (m, 5.6H plus $CHCl_3$), 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). ^1H NMR ($CDCl_3$) for **7f**: 7.19−7.31 (m, 6.8H plus $CHCl_3$), 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).

Acknowledgment. This work was supported by the National Science Foundation, Division of Materials Research, Grant No. DMR-93-20196 and DMR-97-06909.

References and Notes

(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. Ed. Engl.* **1996**, *35*, 1154. (d) Gibson, H. W. In *Large Ring Molecules*, Semlyen, J. A., Ed.; J. Wiley and Sons: New York, 1996; pp 191−262.

(2) (a) Wenz, G.; Keller, B. *Angew. Chem., Int. Ed. Engl.* **1992**, *104*, 201. (b) Wenz, G.; Keller, B. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 197. (c) Wenz, G.; Wolf, F.; Wagner, M.; Kubik, S. *New J. Chem.* **1993**, *17*, 729. (d) Wenz, G. *Macromol. Symp.* **1994**, *87*, 11. (e) Weickenmeier, M.; Wenz, G. *Macromol. Rapid. Commun.* **1996**, *17*, 731. (f) Steinbrunn, M. B.; Wenz, G. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2139. (g) Herrmann, W.; Keller, B.; Wenz, G. *Macromolecules* **1997**, *30*, 4966.

(3) (a) Born, M.; Ritter, H. *Acta Polym.* **1994**, *45*, 68. (b) Born, M.; Ritter, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *107*, 342. (c) Born, M.; Ritter, H. *Angew. Chem., Int. Ed. 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. (f) Noll, O.; Ritter, H. *Macromol. Rapid Commun.* **1997**, *18*, 53.

(4) (a) Harada, A.; Li, J.; Kamachi, M. *Nature* **1993**, *364*, 516. (b) Harada, A.; Li, J.; Kamachi, M. *Nature* **1994**, *370*, 126. (c) Harada, A.; Li, J.; Kamachi, M. *Macromolecules* **1993**, *26*, 5698. (d) Harada, A.; Li, J.; Kamachi, M. *Macromolecules* **1994**, *27*, 4538. (e) Harada, A.; Okada, M.; Li, J.; Kamachi, M. *Macromolecules* **1995**, *28*, 8406. (f) Harada, A.; Li, J.; Kamachi, M. *J. Chem. Soc., Chem. Commun.* **1997**, 1413.

(5) (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*, **1997**, *30*, 3711. (e) Gibson, H. W.; Liu, S. *Macromol. Symp.* **1996**, *102*, 55. (f) Gong, C.; Ji, Q.; Subramanium, C.; Gibson, H. W. *Macromolecules*, in press.

(6) (a) Gong, C.; Gibson, H. W. *Macromolecules* **1996**, *29*, 7029. (b) Gong, C.; Gibson, H. W. *Macromol. Chem. Phys.* **1997**,

198, 2321. (c) Gong, C.; Ji, Q.; Glass, T. E.; Gibson, H. W. *Macromolecules*, in press.

(7) (a) Gong, C.; Gibson, H. W. *J. Am. Chem. Soc.* **1997**, *119*, 5862. (b) Gong, C.; Gibson, H. W. *J. Am. Chem. Soc.* **1997**, *119*, 85.

(8) Gong, C.; Gibson, H. W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2331.

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

(10) (a) Gibson, H. W.; Liu, S.; Shen, Y. X.; Bheda, M. C.; Lee, S.-H.; Wang, F *NATO ASI Series*, Kluwer Acad. Pub., Dordrect, the Netherlands, Series C, Vol. 456 **1995**, pp. 41–58. (b) Mason, P. E.; Parsons, I. W.; Tolley, M. S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2238. (c) Owen, J.; Hodge, P. *J. Chem. Soc., Chem. Commun.* **1997**, 11. (d) Mason, P.; Gibson, H. W., unpublished observations.

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

MA970812O