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Polyrotaxanes Based on Polyurethane Backbones and Crown Ether Cyclics. 1. Synthesis

Ya Xi Shen, Donghang Xie, and Harry W. Gibson*

Contribution from the Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061

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Abstract: Polymeric rotaxanes, consisting of crown ether macrocycles threaded onto a polyurethane backbone, were synthesized by allowing the crown ether to equilibrate with tetrakis(ethylene glycol) prior to its reaction with bis(*p*-isocyanatophenyl)methane (MDI). Use of 18-crown-6, which is too small to be threaded, demonstrated that (1) free macrocycles were easily removed by reprecipitation and (2) no ring opening or other side reactions of the crown ether took place. The threading efficiency, as measured by x/n, the mole ratio of the cyclics per repeat unit, increased linearly with ring size from 36- to 60-membered crown ethers and at constant ring size nonlinearly with the ratio of the cyclic to linear components in neat reactions. Up to 63% by mass of macrocycle was incorporated. The rotaxane structures were demonstrated after repeated precipitation to constant composition as determined by proton NMR using GPC analyses to establish the absence of free macrocycles. The polyrotaxanes have solution and solid-state behaviors that differ from those of the model backbone polyurethane. In solution the interactions of the crown ethers with solvent alter the hydrodynamic volume of the polymers, leading to changes that depend on the size of the crown and the proportion incorporated. In the solid state the glass transition temperature varies with crown content, and at sufficiently high loadings, crystallization of the macrocycle occurs without dethreading. These physically linked analogs of conventional covalent copolymers thus offer new avenues for control of the behavior and properties of polymeric materials.

Introduction

Rotaxanes.[1] The first mention in print of the idea of a stable union of a linear molecule threaded through a cyclic one appeared in 1961.[2] The synthesis of rotaxanes was worked out cursorily by Stetter and Lihotzky in 1962;[3] however, the results were not published. In 1967, the first experimental report was made by Schill and co-workers and the name rotaxane was given.[4] In the same year, Harrison and Harrison reported the synthesis of "hooplane" from 1,10-decanediol, trityl chloride, and a 28-membered acyloin.[5]

The dynamic threading of the linear molecule "L" and the macrocycle "M" to form the rotaxane "R" with equilibrium constant K is depicted in Scheme 1, and eqs 1–3 give the standard expressions relating K to thermodynamic parameters. Two extreme cases are possible: (1) statistical threading in which ΔH is negative (attractive) but close to 0, 0, or positive (repulsive), and entropy changes drive the process, giving low values of K, and (2) directed or template threading, an enthalpically driven process resulting from strong attractive forces (negative ΔH) between the linear species and the cyclic species, resulting in large K values.

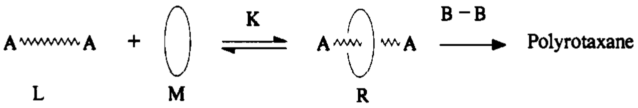
$$K = [\mathrm{R}]/[\mathrm{L}][\mathrm{M}] \qquad (1)$$

$$RT \ln K = -\Delta G = -(\Delta H - T\Delta S) \qquad (2)$$

$$\ln K = -\Delta H/RT + \Delta S/R \qquad (3)$$

Via statistical threading, i.e., equilibration of the linear and cyclic species, Harrison found that rings with less than 22 methylene units cannot be threaded and rings with more than 33 methylene units cannot be retained by trityl-capped chains.[6] Using the statistical threading method, Schill *et al.* prepared rotaxanes whose yields increased as a function of ring size (n = 21–29) and chain length (n = 10–38).[7] Agam *et al* studied the statistical threading method of rotaxane formation from crown ethers, oligomeric ethylene glycols, and trityl chloride.[8] They confirmed that ring size is the most important variable and showed that threading in this case is temperature independent; further, they demonstrated that the yield of rotaxane as a function of linear molecular length passes through a maximum.

Scheme 1. Formation of a Rotaxane and Then a Polyrotaxane



Recently, template-directed syntheses have become actively studied. This method gives the highest yields of rotaxanes. Ogino synthesized and studied some properties of rotaxanes consisting of cyclodextrins threaded by α,ω-diaminoalkanes coordinated to cobalt(III).[9] Lawrence *et al.* reported the self-assembly of a threaded molecular loop in 71% yield from a diammonium chloride salt and heptakis[2,6-di(*O*-methyl)]-β-cyclodextrin in aqueous solution.[10] Stoddart *et al* synthesized a "molecular shuttle" via host–guest complexation of a paraquat tetracationic macrocycle and an oligomeric ethylene glycol chain containing two hydroquinone moieties.[11] Sauvage and co-workers have reported elegant

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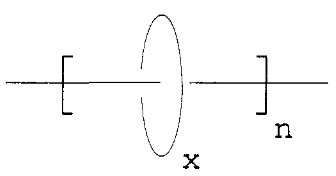
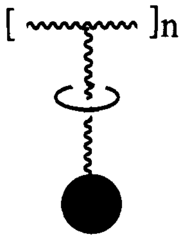
Scheme 2. Schematic Representations of Polyrotaxanes



"Main Chain"



"Side Chain" or "Comb"

syntheses of rotaxanes and catenanes based on complexation of metal ions by 1,10-phenanthroline moieties.[12]

Even though rotaxanes have been synthesized by a variety of synthetic methodologies, the investigation of rotaxane physical properties is still in the primary stage. It has been found that rotaxanes show thin layer chromatographic (TLC) behavior different from that of a mixture of the components.[13] Rotaxanes also show mass spectral (MS) parent ion peaks representing the molecular weight summation of the two components.[14] It seems that the melting points of rotaxanes fall between those of the two components,[6] and so does the solubility. Most rotaxanes, especially when complexation occurs between the linear and cyclic species, show nuclear magnetic resonance (NMR) chemical shift changes for some characteristic peaks.[6,9–12]

Polyrotaxanes. Two generic types of polyrotaxanes, main chain and side chain, are represented in Scheme 2.

Harrison first demonstrated that macrocycles can thread onto polymer chains. He carried out the experiment with gas chromatography.[15] When a macrocycle large enough to be threaded was passed through the column, threading of the macrocycle onto the polymeric stationary phase took place and the vapor pressure of the macrocycle decreased, resulting in greater than expected retention times.

By the addition of naphthalene-1,5-diisocyanate to an equilibrium system of oligomeric ethylene glycols (dp = 3–22) and dibenzo crown ethers (15-, 30-, 44-, and 58-membered rings). Agam *et al.* synthesized the first "main chain" polyrotaxanes (see Scheme 1) in 1976.[16] They studied threading efficiency variation with ring size of the crown ether and chain length of the linear glycol. Unfortunately, the polymers were not completely isolated and purified and molecular weights were not measured. Note that there were no blocking groups used in this polyrotaxane system. Agam *et al.* did use trityl moieties as end blockers to synthesize an oligomeric rotaxane via anionic oligomerization of ethylene oxide in the 58-membered crown ether. The rotaxane was obtained in 11% yield. However, Schill *et al.* have proven that the trityl group cannot block macrocycles larger than 33-membered.[4] Therefore, in the oligomeric rotaxane system, the macrocycle dethreaded upon heating to 150 °C.[16] The molecular weight determined by osmometry presumably reflects considerable dethreading under the dilute solution conditions over the period of time required for the series of measurements.

Maciejewski *et al* synthesized a main chain polyrotaxane from the polymerization of vinylidene chloride and β-cyclodextrin (β-CD).[17] From swollen cyclic urethanes (34–40-membered rings) and neat styrene monomer by thermal polymerization, Lipatova *et al.* also reported the synthesis of main chain polyrotaxanes.[18] Ogata and co-workers[19] made main chain polyrotaxanes by reaction of β-cyclodextrin inclusion complexes of diamines with diacid chlorides; the poly(amide/rotaxanes) were soluble, while the model backbones were not; molecular weights appeared to be low, however.

Recently a comb-like or side chain polyrotaxane (Scheme 2) was synthesized by Born and Ritter.[20] Threading via the self-assembly process of 2,6-dimethyl-β-cyclodextrin and the monofunctional blocking group *p*-triphenylmethyl-4-aminobutananilide produced a so-called semirotaxane. The amino-functionalized semirotaxane was then reacted with a poly(methyl methacrylate) copolymer having reactive carboxylic acid sites along the chain to build a polyrotaxane.

Other workers have also utilized cyclodextrins as the cyclic components of main chain polyrotaxanes. Wenz and Keller threaded preformed protonated polyamines through α-cyclodextrin and the di(*O*-methyl) derivative of β-CD.[21] The larger (35-membered) β-CD threaded more efficiently than the smaller (30-membered) α-CD. The polyamine structure also played a role. Harada and co-workers have threaded oligo(ethylene glycol)s through α-CD and subsequently tied the CD rings together and removed the glycol backbone to produce "nanotubules".[22] In this instance the backbone of the rotaxane was used to hold the rings together so that they could be linked; many exciting possibilities exist for use of such structures.

There have been very few data reported regarding the physical properties of polyrotaxanes. Polyrotaxanes show TLC R_f values between those of the two components.[16] X-ray diffraction patterns of polystyrene rotaxanes derived from cyclic urethanes were identical to those of the cyclic components; these polyrotaxanes were not soluble in benzene or dimethyl sulfoxide (DMSO), while polystyrene is soluble in benzene and the macrocycle is soluble in DMSO.[18] Polyrotaxanes from vinylidene chloride and β-cyclodextrin were soluble in dimethylformamide (DMF), while the simple linear backbone was not.[17b]

The comb polyrotaxane from PMMA and β-CD was soluble in diethyl ether, while the model polymer was not.[20] More solution properties of this system have been studied.[20] For example, chemical shift changes for some protons in the ^{1}H-NMR spectrum were observed; the reduced viscosities of polyrotaxanes were found to be lower than that of the model polymer.

Frisch *et al.* studied a network system which trapped macrocycles by threading onto linear chains between two cross-linking points. They cross-linked polybutadiene containing a cyclic depsipeptide (Valinomycin), a 36-membered ring.[23] Mark,

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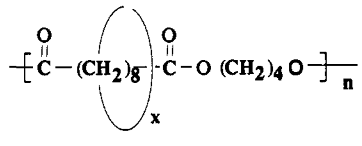
Semlyen, Clarson, *et al.* also studied some cross-linking systems containing cyclic poly(dimethylsiloxane)s.[24–26]

We started research on monomeric and polymeric rotaxanes in 1986. Systems studied include polyester, polyamide, polystyrene, and polyacrylonitrile-based main chain polyrotaxanes and some monomeric rotaxanes.[27] Following the method used by Sauvage *et al.*,[12] a phenanthroline-based rotaxane was synthesized in 42% yield and characterized by ^{1}H-NMR and MS analyses.[28] The polyester-based polyrotaxane **1**, synthesized from dimethyl sebacate, butylene glycol, and crown ethers via the statistical threading approach, showed only one peak by gel permeation chromatography (GPC), while the blend made by physical mixing of the model polymer and the macrocycle showed two peaks corresponding to the two separated components.[29] Also the macrocycle in the blend can be removed easily by reprecipitation, but not in the case of the polyrotaxane system where the macrocycle is threaded; this revealed that reprecipitation is an effective method to remove unthreaded macrocycle from a rotaxane system.



$$-\!\!\left[\overset{\displaystyle O}{\overset{\|}{C}}-(CH_2)_8-\overset{\displaystyle O}{\overset{\|}{C}}-O\,(CH_2)_4\,O\right]_n \quad x$$

1

= 30-Crown-10, 60-Crown-20

Poly(butylene sebacate)-60C20-based polyrotaxanes **1** have shown interesting behavior.[30–32] For example, the polyrotaxanes have lower glass transition temperatures and are more soluble in common solvents than the parent polyester **1**, $x = 0$. Most strikingly, crystallization of 60C20 and the polyester backbone occur, producing two crystalline phases. Kinetics of crystallization in the polyrotaxane system have also been studied, and some potential applications of this new material have been proposed.

We have addressed other polyester/rotaxane systems as well, including liquid crystalline azomethines;[33] these systems display enhanced solubility and lowered phase transition temperatures relative to the parent backbones.

Polyrotaxanes based on styrene and crown ethers have been produced both free radically and anionically.[34] We have demonstrated that these polyrotaxanes form stable emulsions in aqueous media. Indeed, it is possible to carry out emulsion polymerizations without any added surfactant if the crown ether is large enough to thread.[35] Free radical polymerization of acrylonitrile in the presence of 60-crown-20 yields polyrotaxanes whose crown ether content varies systematically with the feed ratio;[34,36] at sufficiently high loadings of the macrocycle the polyrotaxane is soluble in methanol, in contrast to the insolubility of polyacrylonitrile itself.

The essentially complete threading of bisphenylene crown ethers by linear 4,4′-bipyridinium salts reported by Stoddardt[11] has been employed by us to achieve stoichiometric control of structure in ionomeric polyurethane rotaxanes derived from *N,N′*-bis(2-hydroxyethyl)-4,4′-bipyridinium bromide, poly(tetramethylene oxide), and a diisocyanate.[37]

On the basis of previous results, therefore, polyrotaxanes are generally expected to exhibit novel behavior with regard to properties such as glass transition, solubility, viscosity, mechanical behavior, and so on, because their structures result not from covalent bonding of the repeat units but from flexible and movable physical connections of the cyclic and the linear components. This class of materials can be considered as physical analogs of copolymers and true "molecular composites". They are expected to offer wide and special applications in areas such as blend compatibilization, adhesion, controlled processing, engineering materials, etc.

The work reported here was undertaken with two major goals: (1) study of synthetic methodology for polyrotaxanes based on linear polyurethanes and crown ethers, emphasizing the ring size effect on threading efficiency; and (2) preparation of the polyrotaxane samples in quantities sufficient to carry out various characterizations.

Results and Discussion

Polyrotaxanes can generally be synthesized via either the statistical threading method or the template method (Scheme 1) depending on the character of the system. Even though the template method may offer higher threading efficiency for similar sized macrocycles, the statistical threading method is important in principle due to its applicability to any polymer backbone or macrocyclic system. Agam *et al* demonstrated that the threading efficiency (a measure of K) of poly(ethylene glycol)s and dibenzocrown ethers was independent of temperature,[8] i.e., $\Delta H = 0$ (eq 3). In the present work, therefore, we anticipated statistical threading since there would presumably be no additional attractive interactions between the tetrakis(ethylene glycol) and the crown ethers. However, hydrogen bonding between the urethane linkages as they form in the polymerization step (addition of the B–B monomer in Scheme 1) and crown ethers may enhance the threading efficiency in our case, providing an enthalpic attractive force.

Crown Ethers. The key point in the design of macrocycles for polyrotaxane synthesis is, of course, the ring size. The effective cavities of the macrocycles must be larger than the cross sectional area of the linear polymer chain to allow threading to occur. Harrison has demonstrated that hydrocarbon rings with less than 22 methylene units cannot be threaded by 1,11-undecanediol.[6] Agam *et al* pointed out that the size of the ring affects the threading more than any other parameter.[8]

In the statistical threading approach in order to achieve high loadings, macrocycles are used as solvents. Therefore, it is required that the melting point of the macrocycle is below the reaction (polymerization) temperature. To provide a low viscosity for the polymerization system, generally the melting point of the macrocycle is expected to be 30 °C or more below the polymerization temperature. Of course, the macrocycles should be able to dissolve the monomers. Crown ethers with ring sizes of

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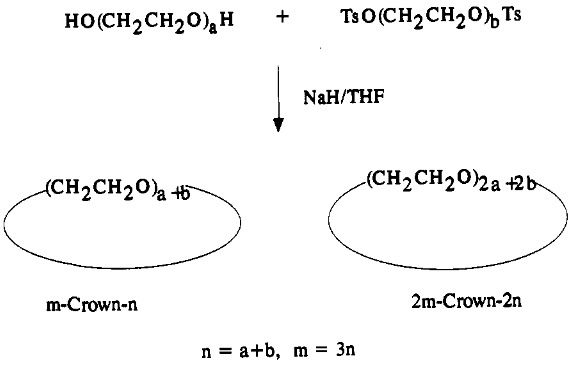
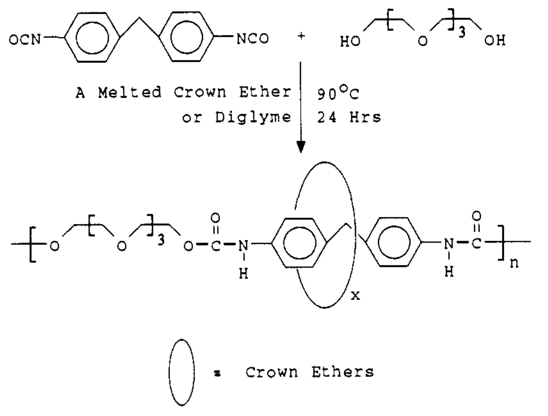
Scheme 3. Systematic Synthesis of Crown Ethers



Scheme 4. Syntheses of Polyrotaxanes and the Model Polymer



2. Polyurethane-rotaxa-36C12 (x /n = 0.16)

3. Polyurethane-rotaxa-42C14 (x/n = 0.29)

4. Polyurethane-rotaxa-48C16 (x/n = 0.52)

5a. Polyurethane-rotaxa-60C20 (x/n = 0.87)

5b. Polyurethane-rotaxa-60C20 (x/n = 0.58)

5c. Polyurethane-rotaxa-60C20 (x/n = 0.34)

6. Model Polyurethane (x/n = 0.00)

Table 1. Monomer Feed Ratios and Polymer Compositions[a]

polymer	feed ratio[b]	1st PPTN	2nd PPTN	3rd PPTN	4th PPTN	final wt % crown	% polymer recovered
2	1.50	0.19	0.15	0.16	0.16	16	81
3	1.50	0.36	0.30	0.29	0.29	29	80
4	1.52	0.69	0.58	0.52	0.52	45	67
5a	1.50	1.05	0.99	0.88	0.87	63	59
5b	0.80	0.69	0.60	0.58	0.58	54	58
5c	0.50	0.44	0.34	0.33	0.34	40	71
6a	0.00	0.00	0.00			0	92
6b	5.41	0.00	0.00	0.00	0.00	0	78

[a] Macrocycles per repeat unit of polymer (x/n) as determined by ^{1}H-NMR spectroscopy. Estimated error in x/n: ±0.02. [b] Molar ratio of crown ether to tetrakis(ethylene glycol).

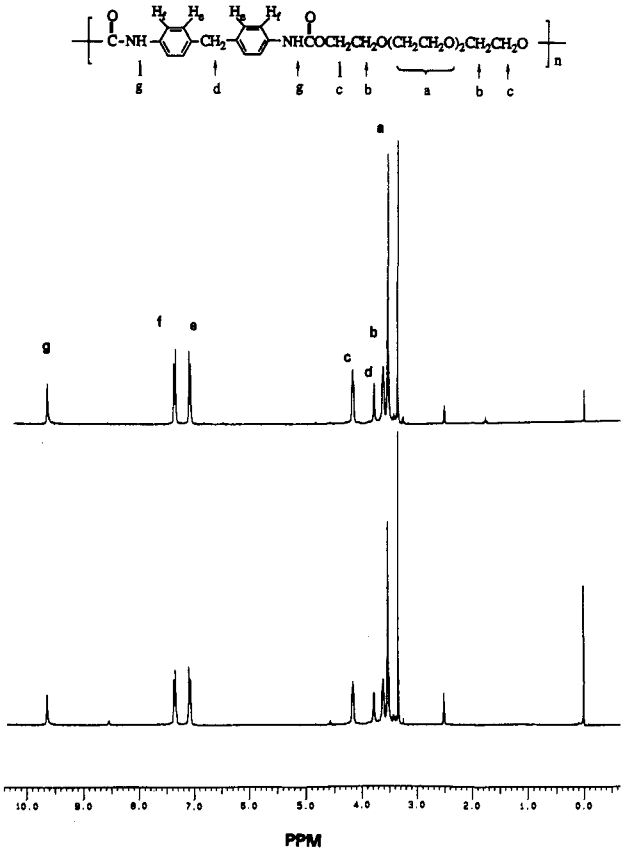


Figure 1. ^{1}H-NMR (270 MHz) spectra of model polyurethanes **6a** (top) and **6b** (bottom) in dimethyl sulfoxide-d_6. The peaks at 2.5 ppm are due to DMSO-d_5; water appears at 3.3 ppm.

30–60-membered are polar in nature, and their melting points are in the range 30–50 °C. They, therefore, are good candidates for many rotaxane and polyrotaxane systems. Macrocycles should be thermally and chemically stable under the reaction conditions; the decomposition temperatures of crown ethers are around 200 °C, so they can be used in polyurethane syntheses at modest temperatures.

Based on our previous work,[27–37] crown ethers with ring sizes of 30–60-membered were expected to thread efficiently. Hence, we selected 36-crown-12 (36C12), 42-crown-14 (42C14), 48-crown-16 (48C16), and 60-crown-20 (60C20) as macrocycles in our polyurethane rotaxane syntheses.

Crown ether syntheses were reported by Chênevert and d'Astous, who used "two-piece combinations" of the corresponding oligo(ethylene glycol)s and oligo(ethylene glycol) ditosylates.[38] For example, 36C12 was synthesized from hexakis(ethylene glycol) and hexakis(ethylene glycol) ditosylate.

However, we used low-molecular-weight glycols and the ditosylates to obtain desired crown ethers by "four-piece combinations". This one-pot systematic synthesis of crown ethers is illustrated in Scheme 3. Two crown ethers were obtained from each reaction. One (m-crown-n) was formed by "two-piece combination", and the other ($2m$-crown-$2n$) was formed by "four-piece combination". The total yield of the two crowns ranged from 30% to 60%. With this method, we prepared large quantities of crown ethers with ring sizes rangeing from 18-membered to 60-membered using only low-molecular-weight glycols and the ditosylates. The reaction of tris(ethylene glycol) and tris(ethylene glycol) ditosylate produced 36-membered and 18-membered crown ethers; tetrakis(ethylene glycol) and tris(ethylene glycol) ditosylate produced 42-membered and 21-membered rings; tetrakis(ethylene glycol) and tetrakis(ethylene glycol) ditosylate produced 48-membered and 24-membered rings; tetrakis(ethylene glycol) ditosylate and hexakis(ethylene glycol) produced 30-membered and 60- membered rings. The two crown ethers were separated and purified mainly by multiple recrystallizations. Their purities and structures were determined by GPC, FTIR, ^{1}H-NMR, and X-ray crystal structure analyses. Details will be reported separately.[39]

Polyrotaxanes and the Model Polyurethane. Scheme 4 illus-

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[38] Chênevert, R.; d'Astous, L. *J. Heterocycl. Chem.* **1986**, *23*, 1785.

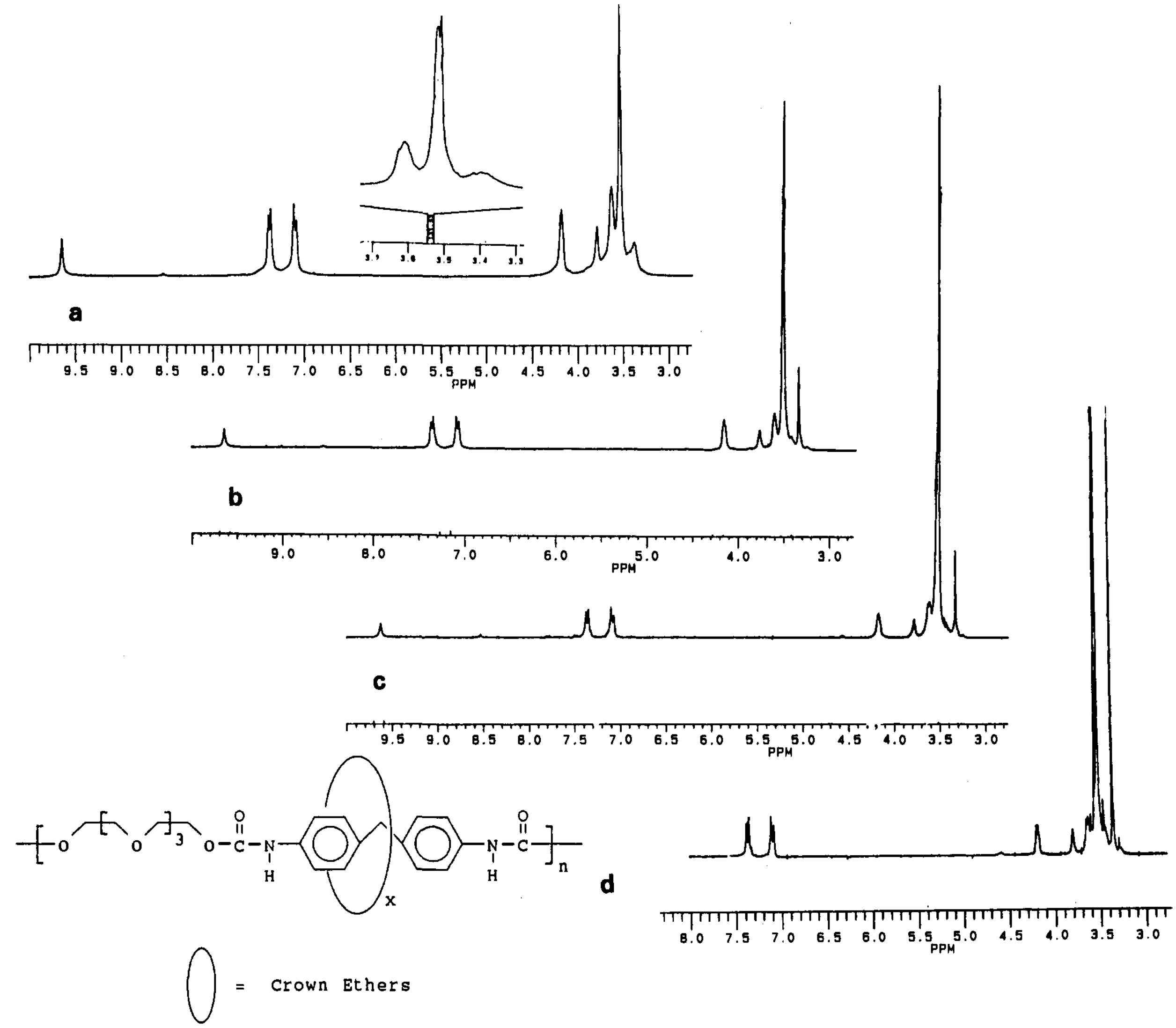

Figure 2. ^{1}H-NMR spectra (270 MHz) of polyrotaxanes: (a) **2** (cyclic = 36C12), (b) **3** (cyclic = 42C14), (c) **4** (cyclic = 48C16), (d) **5a** (cyclic = 60C20) in dimethyl sulfoxide-d_6. The peak at 3.3-3.4 ppm (most upfield signal shown) is due to H_2O. The inset in (a) shows the resolution of the 36-crown-12 peak at 3.54 ppm from the tetraethyleneoxy signal at 3.52 ppm upon scale expansion. A similar but less well resolved separation of signals was observed in (b).

trates the syntheses of the model polyurethane and the polyrotaxanes. The polyrotaxanes (**2–5**) were prepared by carrying out the condensation of tetrakis(ethylene glycol) and bis(*p*-isocyanatophenyl)methane (MDI) using melted crown ethers as solvents; the glycol and the crown ether were stirred in the melt for 1 h to allow threading of the linear species through the macrocycle, as in Scheme 1, prior to the addition of MDI. Model polyurethanes were prepared in two different solvents. Diglyme was used in the synthesis of model polyurethane **6a**, because diglyme has polarity similar to the crown ethers. It is known that rings smaller than 22-membered cannot be threaded even by polymethylene chains.[6] Therefore, 18-crown-6 is an ideal model solvent for the crown ethers because it cannot be threaded. 18-Crown-6 was used as the solvent in the preparation of model polyurethane **6b**. All of the polymerizations were done at 90 °C, approximately 50 °C above the melting points of the crown ethers; at this temperature viscosities were relatively low.

Purification of the Polymers. The polyrotaxanes were purified by multiple reprecipitations from tetrahydrofuran (THF) solutions into a relatively large amount of solvent in which the crown ether is very soluble but the polyrotaxane is not. As a matter of fact, polyrotaxanes have different solubilities when the crown ethers and their contents are different. Different nonsolvents, therefore, were used to precipitate different polyrotaxanes: **2** was reprecipitated into methanol and water; **3** was reprecipitated into methanol, and **4–5c** were reprecipitated into ethyl acetate or ethyl acetate–hexane. The reprecipitation for each polymer was continued until a constant composition (x/n value) of the polymer was reached. Table 1 shows polymer compositions obtained from ^{1}H-NMR analyses after each reprecipitation for each polyrotaxane, including percentages of recoveries from reprecipitations.

It can be seen from Table 1 that a constant ratio of macrocycle to repeat unit (x/n) for all polyrotaxanes was reached after the first or second reprecipitations. Therefore, we expect no free (unthreaded) crown ethers remaining in the systems. Before each reprecipitation, samples were dissolved in THF for 30 min to 1 h. Even though there were no blocking groups at the ends of the polyrotaxane chains, dethreading of macrocycles was not significant after free, unthreaded macrocycle had been removed. The lack of dethreading over these short time frames in solution could result from the random coiling of the chains and the macrocycles coupled with attractive intraannular hydrogen bonding between the crown ethers and the polyurethane chains. Another possible explanation is the "wiggle effect" of the chain

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(39) Gibson, H. W.; Bheda, M. C.; Engen, P.; Shen, Y. X.; Sze, J.; Zhang, H.; Gibson, M. D.; Delaviz, Y.; Lee, S.-H.; Liu, S.; Wang, L.; Rancourt, J.; Taylor, L. T. *J. Org. Chem.*, submitted for publication. Bheda, M. C.; Merola, J. S.; Woodward, W. A.; Vasudevan, V. J.; Gibson, H. W. *J. Org. Chem.*, submitted for publication.

ends as a result of their enhanced mobility relative to the middle of the chain; this would tend to force the macrocycles away from the chain ends toward the middle, in analogy to a button-on-a-string toy. This would also explain the lack of dethreading over similar time scales for poly(ester rotaxane)s **1**,[29] in which no hydrogen bonding is possible.

Table 1 also shows that the percentage of polyrotaxanes recovered from reprecipitations decreases with increasing crown ether ring size and content, because polyrotaxane solubility increases with crown ether ring size and content; this will be discussed later.

The results for model polyurethane **6b** prepared in the presence of 18-crown-6 as solvent are particularly important. First of all, they demonstrate that free, unthreaded crown ethers are readily removed by the purification protocol. Second, the integration ratios for the ethyleneoxy protons to the rest of the protons of the polyurethane backbone are in accord with the simple polyurethane structure, i.e., **6**, $x/n = 0$; this fact eliminates the possibility that the crown ethers of polymers **2–5** are incorporated by some ring-opening process. Moreover, the 18-crown-6 recovered from the filtrates of the precipitations of **6b** showed no evidence of ring opening; that is, the ^{1}H-NMR spectrum contained a single sharp resonance with no extraneous peaks which would have resulted from poly(ethylene glycol) formation.

^{1}H-NMR Analyses. Figure 1 shows the ^{1}H-NMR spectra of the model polyurethanes **6a** and **6b** in dimethyl sulfoxide-d_6. The polyurethane displays a singlet at 3.51 ppm (peak a) due to the eight protons of the two innermost ethyleneoxy units ($\mathrm{OCH_2CH_2(}\mathit{OCH_2CH_2}\mathrm{)_2OCH_2CH_2O}$), a multiplet at 3.62 ppm (peak b) due to the four protons β to the urethane linkage ($\mathrm{OCH_2}\mathit{CH_2}\mathrm{(OCH_2CH_2)_2O}\mathit{CH_2}\mathrm{CH_2O}$), a multiplet at 4.19 ppm (peak c) due to the four protons α to the urethane linkage ($\mathrm{O}\mathit{CH_2}\mathrm{CH_2(OCH_2CH_2)_2OCH_2}\mathit{CH_2}\mathrm{O}$), a singlet at 3.79 ppm (peak d) from the two benzylic methylene protons, a doublet at 7.10 ppm (peak e) due to one set of four aromatic protons), a doublet at 7.38 ppm (peak f) arising from the other four aromatic protons, and a singlet at 9.66 ppm (peak g) corresponding to the two NH protons. The pure crown ethers show singlet resonances at 3.65 ppm in $CDCl_3$.

The ^{1}H-NMR spectra of the polyrotaxanes **2–5** are shown in Figure 2. All the polyrotaxanes have the same spectra as that of the model polymer except that there is a contribution from the crown ether to the signal at 3.5 ppm. The crown ether peak can only be resolved in polyurethane–rotaxa-36-crown-12 (**2**); this is because the chemical shift of 36C12 protons is a little more downfield (at 3.54 ppm) than those of the other crown ethers. In the other systems the crown ether singlet overlaps with the signal for the ethyleneoxy protons in the polymer backbone. Integration of these signals (with correction for the ethyleneoxy protons in the polymer backbone) relative to the aromatic protons enables the crown ether contents of the polyrotaxanes to be determined. Notice that there is a very small singlet at about 8.50 ppm in all ^{1}H-NMR spectra (Figures 1 and 2), indicating that all polymers contain about 1–2% of urea linkage, due to the presence of trace amounts of water, presumably. **5b** was an exception in that the crown ether, which had been exposed to ambient conditions for several days, was not dried before use; integration of the 8.50 ppm signal indicated that 35% of the MDI moieties are involved in urea rather than urethane linkages. Therefore, **5b** is a urea–urethane.

Thus, unlike cyclodextrin-based,[20–22] charge-transfer,[11] or metal complex[12] rotaxanes, these crown ether-based polyrotaxanes do not exhibit any chemical shift changes for the resonances of either the macrocyclic or backbone components.

GPC Analyses. The reprecipitation experiments of Table 1 indicate that there are no free, unthreaded crown ethers in the polyrotaxanes after two precipitations, on the basis of the constancy of x/n and the complete removal of 18-crown-6 in the case of **6b**. In order to confirm the absence of free macrocycles and determine the molecular weights, GPC analyses were carried out under two different sets of conditions: (1) in *N*-methylpyrrolidinone (NMP) containing 6 mM LiBr (0.5% mass/vol) with a differential refractive index detector and a differential viscometric detector and (2) in THF with a differential refractive index detector.

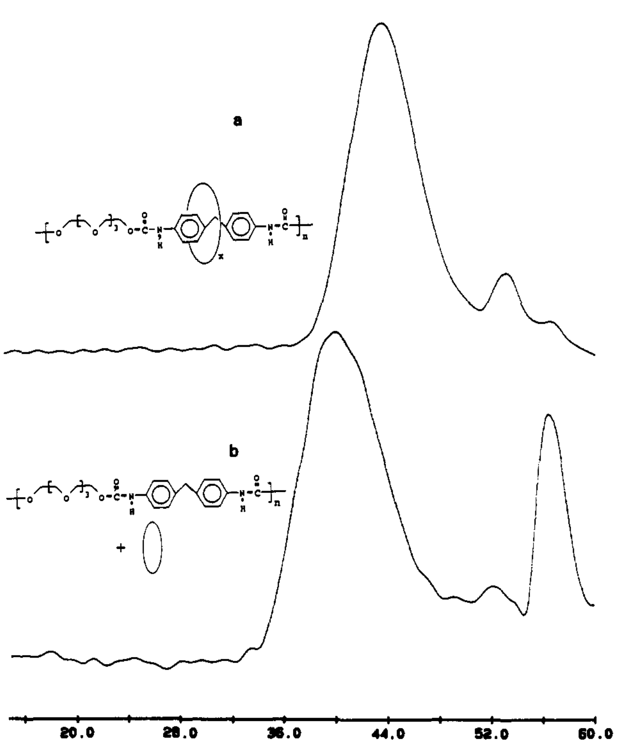

Figure 3. GPC traces of (a) polyurethane–rotaxa-36C12 (**2**) and (b) a blend containing 25 mass % 36C12 in model polyurethane **6a**: solvent, THF. The peak at 52 mL is an impurity in the solvent.

Figure 3 shows GPC traces under condition 2 for two samples: (a) polyrotaxane **2** and (b) a physical blend of 36C12 and **6a** having the same overall composition as the polyrotaxane. The polyrotaxane shows only a single relatively sharp peak; the physical blend displays two peaks, one corresponding to the polyurethane and the other to unthreaded 36C12.

Figure 4 shows GPC traces under condition 1 for three samples: (a) model polyurethane **6a**, (b) a 50:50 mass percent blend of 60C20 and model polyurethane **6a**, and (c) polyrotaxane **5a**. Again, the polyrotaxane is characterized by a relatively sharp peak, while the physical blend produced a broad bimodal peak. Because of the higher molecular weight of 60C20 (880), the resolution in this case is lower than that with the smaller crowns. Nonetheless, the breadth and tailing of the trace for the blend clearly distinguishes it from the polyrotaxane. Similar results are observed with both detectors.

Figure 5 contains the GPC traces under condition 2 for (a) polyrotaxane **5a**, (b) model polyurethane **6a**, (c) 60C20, and (d) a 47:53 mass percent blend of 60C20 and **6a**. As before, the chromatograms for the model system and the polyurethane are relatively sharp, but the trace for the physical blend of macrocycle and model polyurethane is broad and exhibits a pronounced low-molecular-weight (high elution volume) tail due to unthreaded 60-crown-20.

Similar results were obtained for the other systems. Thus, GPC confirms the absence of free, unthreaded macrocycles in the polyrotaxanes and, in view of NMR evidence for their presence and the demonstrated lack of ring opening under the reaction conditions, corroborates the fact that the polymers are indeed physically linked molecular composites.

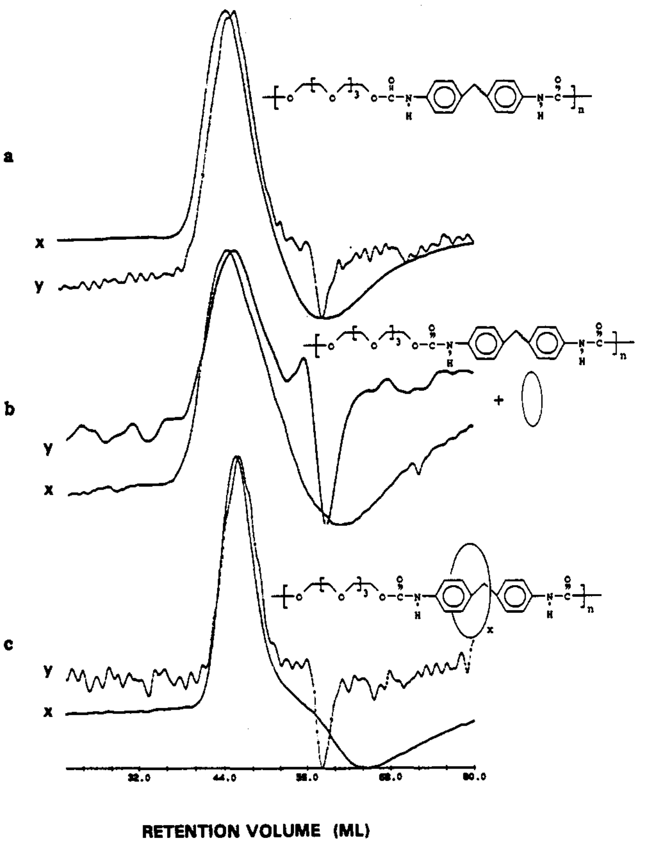

Figure 4. GPC traces of (a) model polyurethane **6a–1**, (b) a blend of model polyurethane **6a–1** and 50 mass % 60-crown-20, and (c) polyrotaxane **5a**: solvent 6 mM LiBr in NMP; detectors, X, differential viscometer; y, differential refractometer.

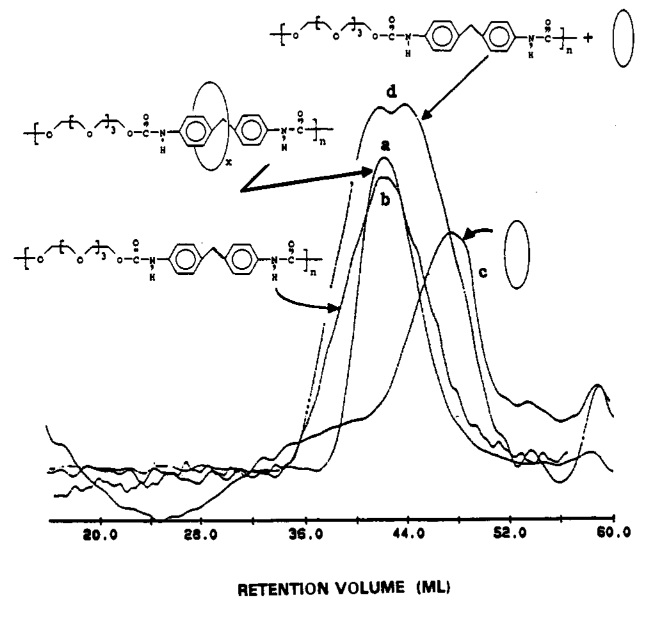

Figure 5. GPC traces of (a) polyrotaxane **5a**, (b) model polyurethane **6a–1**, (c) 60-crown-20, and (d) a blend of model polyurethane **6a–1** and 47 mass % 60-crown-20: solvent, THF; refractive index detector.

Table 2 summarizes the molecular weights determined in THF using polystyrene calibration. Table 3 lists the measured intrinsic viscosities in NMP and molecular weights and polydispersities determined in LiBr–NMP based on polystyrene standards and viscosity average molecular weights, M_v, derived from the data by application of the universal calibration method, whose validity with polyrotaxanes has not been demonstrated.

Table 2. GPC Molecular Weights and Polydispersities in Tetrahydrofuran[a]

polymer	M_n (kg/mol)	M_w (kg/mol)	M_w/M_n
2	7.24	10.8	1.50
3	19.3	37.5	1.95
4	7.01	10.6	1.51
5a	8.03	13.3	1.65
6a–1[b]	12.1	27.0	2.24
6a–2[b]	8.65	26.9	3.11
6b	5.58	11.1	1.98

[a] Molecular weights based on polystyrene standards. [b] Two separate synthetic experiments.

Table 3. Intrinsic Viscosities and GPC Molecular Weights in NMP

polymer	$[\eta]$[a] (dL/g)	M_n[b] (kg/mol)	M_w[b] (kg/mol)	M_v[c] (kg/mol)
2	0.24	11.3	16.6	10.1
3	0.45	29.6	59.7	9.95
4	0.24	13.9	19.5	11.0
5a	0.27	16.5	21.3	13.0
5b		7.5	13.4	6.86
6a–1[d]	0.40	14.8	32.4	15.1
6a–2[d]	0.30			
6b	0.26			

[a] In NMP at 25.8 °C. [b] Determined by GPC in 6 mM LiBr–NMP using a refractive index detector and polystyrene standards for calibration. [c] Determined by GPC in 6 mM LiBr–NMP and differential viscometric detector and universal calibration. [d] Two independent synthetic experiments.

A comparison of the values based on polystyrene standards between the two different solvents reveals reasonable agreement for the model polyurethane **6a–1**. For the polyrotaxanes, although the molecular weight distributions are comparable in Tables 2 and 3, the values of M_n and M_w are considerably higher in NMP (Table 3) than in THF (Table 2). The differences for the polyrotaxanes, we believe, are related to solvation effects, which will vary with the size of the crown ether and its loading. This is discussed below.

The low molecular weights are probably due to the presence of water in the crown ethers and the glycol, even though they were all vacuum dried prior to use; they are quite hygroscopic. Moreover, on a small synthetic scale such as that used in the present work a small amount of moisture has a large effect. The presence of water leads to polyurea formation, as noted in the ^{1}H-NMR spectra and thus causes a stoichiometric imbalance between the diisocyanate and the glycol, which results in lowered molecular weight.

Threading Efficiencies. The threading efficiency is defined as the number of rings per repeat unit in the polyrotaxane backbone, i.e., x/n. Experimental threading efficiencies are listed in Table 1. It is interesting to see that when the crown ether/glycol ratio was kept at 1.5 in the feed, there was a tremendous increase in threading efficiency with increasing ring size. In fact, a plot of x/n versus ring size represented by the number of skeletal atoms in the rings is linear under these conditions, as shown in Figure 6. The amount of threading (x/n) increases linearly with the feed ratio of macrocycle to glycol for these neat reactions, as shown in Figure 7 for **5a**, **5b**, **5c**, which incorporate 60-crown-20, and **6**.

Agam *et al.* derived an equation to describe the threading based on the total volume and the number of moles of linear and cyclic species.[8] However, this equation does not fit our experimental results well. The threading efficiency increases more rapidly with ring size than predicted. Even at constant ring size Agam *et al.*'s equation does not scale according to experimental results for series **5a**, **5b**, and **5c**, in which the feed ratio was varied.

The threading process could be very complicated. There are many possible steps leading to the formation of polyrotaxane macromolecules. The condensation reaction may occur simultaneously with threading. However, the problem is simplified if the threading process is slower than the polymerization reaction.

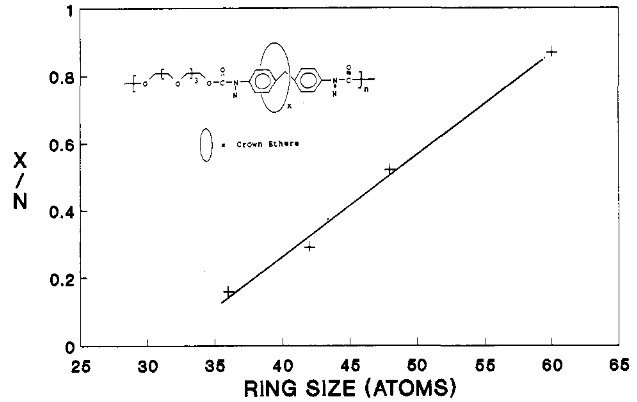

Figure 6. Plot of threading efficiency, defined as x/n, versus the ring size of the crown ether as denoted by the number of skeletal atoms for neat reactions carried out at a crown ether/glycol molar feed ratio of 1.5.

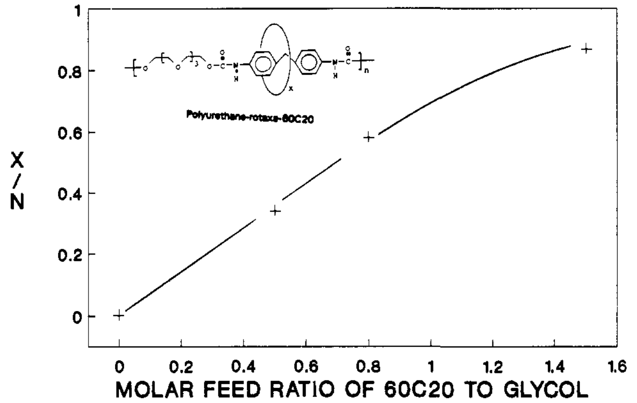

Figure 7. Plot of threading efficiency, defined as x/n, versus the molar feed ratio of 60-crown-20 to tetrakis(ethylene glycol).

Table 4. Equilibrium Constants Calculated from Eq 1[a] for Crown Ethers and Tetrakis(ethylene glycol) at 90 °C

polymer	crown ether	$[L]_0$[b] (M)	[R][c] (M)	K[d] (M^{-1})
2	36C12	1.1	0.18	0.13 ± 0.02
3	42C14	0.98	0.29	0.34 ± 0.05
4	48C16	0.88	0.46	1.2 ± 0.2
5a	60C20	0.73	0.63	15 ± 3
5b	60C20	1.2	0.71	5.1 ± 0.9
5c	60C20	1.7	0.59	1.9 ± 0.4

[a] Assuming all threading occurs prior to polymerization and 100% conversion of glycol to polyurethane. [b] Concentration of linear species, i.e., the glycol. Based on densities of 1.1 g/mL for the crown ether and the glycol and additivity of volumes; total volume refers to only crown ether and glycol. [c] Rotaxane concentration, $[R] = (x/n)[L]_0$. [d] $K = [R]/([L]_0 - [R])([C]_0 - [R])$. Error bars for K are based on estimated errors of ±0.02 in experimental x/n values. $[C]_0$ is the cyclic, i.e., crown ether, concentration.

This essentially means that threading takes place only between one of the monomers (tetrakis(ethylene glycol) in our case) and macrocycle during the prethreading period and no threadings occur during the polymerization. On the basis of this assumption, the simple dynamic equilibrium between a linear, a cyclic, and a rotaxane shown in Scheme 1 can be used to describe the results.

Under the assumptions (1) that all threading occurs prior to polymerization, (2) that 100% conversion of the glycol to the polyurethane takes place, and (3) that there is no fractionation during purification, x/n is equal to $[R]/[L]_0$, where $[L]_0$ is the original concentration of glycol. Equilibrium constants, K, calculated from the experimentally observed x/n values in terms of molar concentrations are given in Table 4. K is quite sensitive to $[R]/[L]_0$, and hence the values of K are quite precisely estimated.

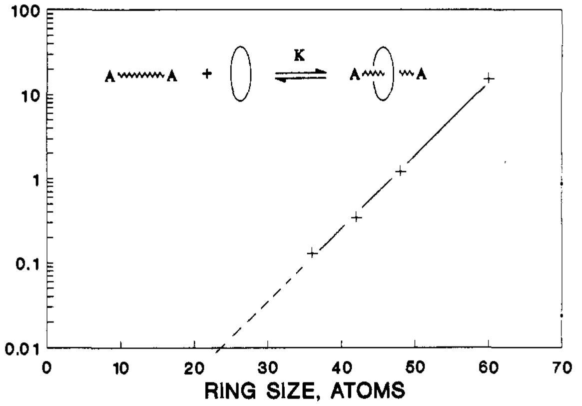

Figure 8. Log of the equilibrium constant, K, for threading of crown ethers by tetrakis(ethylene glycol) versus ring size of the crown ether: neat process, molar feed ratio of cyclic to linear, 1.5; temperature, 90 °C; from results of Table 3.

By examination of the results for **2**–**5a** in Table 4, we see that the values of the equilibrium constants increase rapidly with increasing ring size at constant feed ratio $[C]_0/[L]_0 = 1.5$ This is expected on the following bases. First, for rigid rings the cavity area, to which the equilibrium constant should be related, is proportional to the square of the ring size (circumference). Second, for flexible rings such as the crown ethers the percentage of conformations that are threadable is expected to be an exponential function of the ring size in terms of the number of atoms or rotatable bonds. On this basis the linear relationship between log K and ring size shown in Figure 8 is not surprising. The fact that K approaches 0 at a ring size of ca. 24 atoms is consistent with the experimental findings of Harrison[5] and Schill.[7] A striking prediction of this treatment is the large equilibrium constant extrapolated for larger rings. For example, $K = 100$ for a 69-membered crown ether; this corresponds to an x/n value of 0.972 and a 69 mass % crown in the resultant polyurethane rotaxane for a feed ratio of $[C]_0/[L]_0 = 1.5$

Clarson, Mark, and Semlyen reported the threading of cyclic poly(dimethylsiloxane)s by linear α,ω-dihydroxy poly(dimethylsiloxane) (PDMS) of M_n 18 kg/mol as a function of ring size.[26] They immobilized the threaded rings by cross-linking the linear PDMS; then they extracted the unthreaded rings from the matrix. They reported the results in terms of the percentage of rings threaded for various molar feed ratios ($[C]_0/[L]_0 = 0.19$–16), but approximately 17 mass % cyclic in the feed in all cases. On the basis of densities of 0.98 g/mL for both components, we calculated equilibrium constants from their data in the same manner as we treated our own data, i.e., on a molar basis taking into account the total molar masses of the components; the rotaxane concentration was calculated by multiplying the original cyclic concentration by the percentage of rings that were threaded. The results are shown in Figure 9 in the form log K vs ring size. Although the absolute values of K are different from those of Figure 8, again there is a linear relationship. In this case there are two regimes, one below ca. 100 membered rings and one for larger rings; the two regimes may reflect the fact that below a certain ring size, the ability to be threaded is strongly governed by conformational possibilities, that is, there is a large fraction of unthreadable conformations, while once a certain size is exceeded, there is a diminishing fraction of conformations that are not threadable. The break point of course would depend on the flexibility of the cyclic component and the nature of the linear species. Indeed, recent molecular modeling studies by Semlyen and co-workers indicate that this is the case.[40] Figure 10 shows a plot of the calculated fraction of cyclic PDMS that is threadable by a 7.4-Å-diameter linear species as a function of ring size; note

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

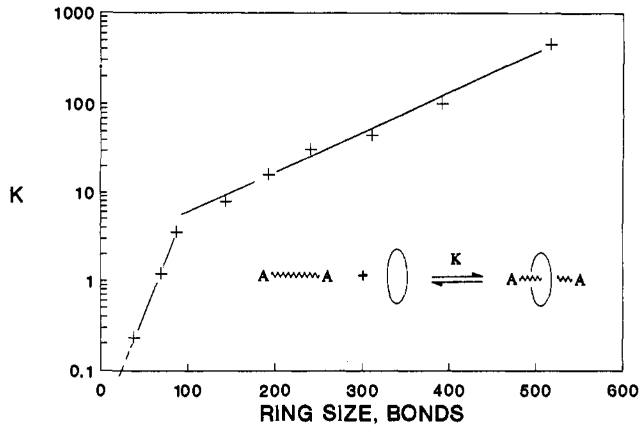

Figure 9. Log of the equilibrium constant, *K*, for threading of cyclic poly(dimethylsiloxane)s by linear poly(dimethylsiloxane) of M_n 18 kg/mol versus ring size of the cyclic species: neat process, molar feed ratio of cyclic to linear, variable; temperature, 25 °C; from results reported in ref 26, assuming densities of 0.90 g/mL for both components.

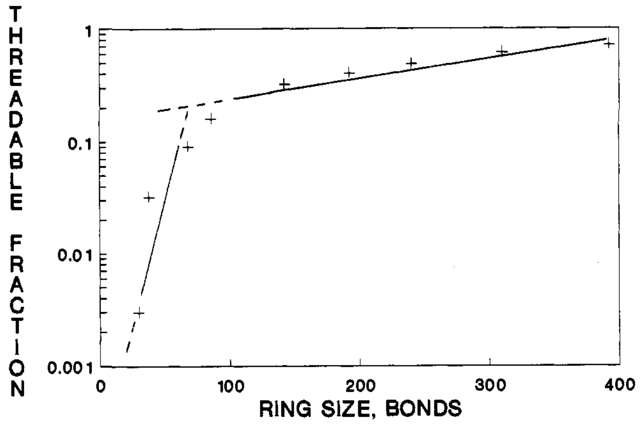

Figure 10. Log of fraction of all conformations of cyclic poly(dimethylsiloxane)s calculated to be threadable by a linear species of cross sectional diameter 7.4 Å as a function of the size of the macrocycle, from results reported in ref 40.

that the break point between the two rather linear regions is again at ca. 100 bonds.

Turning now to the results for polyrotaxane formation from 60-crown-20 at different feed ratios (**5a**–**5c**, Table 4), it can be seen that the calculated *K* values are not constant. The high recovery of polyrotaxanes from the purification process and the invariance of the *x*/*n* values for successive precipitations (Table 1) argue against fractionation as a serious issue. There are several possible explanations. First, the assumption that all threading occurs prior to polymerization may be false and the more complex situation of threading being comparable in rate to polymerization may exist. Second, the assumption that the activity coefficients are unity inherent in calculating *K* on the basis of molar concentrations may be false. Inasmuch as the glycol concentrations vary from 0.7 to 1.7 M, deviation from ideality is not unexpected. Third, in changing the ratio of the two components in a neat system, the nature (polarity, dielectric constant) of the medium changes and this may affect the equilibrium. The mole (volume) fraction of glycol decreases from 0.667 (0.307) to 0.556 (0.217) to 0.400 (0.129) in the series **5a**–**5c**. It is known from simulations that the fraction of threadable 60C20 conformations increases in hydroxylic solvents.[41] However, hydroxyl–hydroxyl hydrogen bonding of the glycol could cause chaining, which would diminish threading at high glycol concentrations, as observed. Further study is required to resolve this issue.

Table 5. Ratios of Molecular Weights[a] and Polydispersities of Polyrotaxanes and Model Polyurethane in LiBr–NMPr[b] and in THF

polymer	$M_{n,NMP}/M_{n,THF}$	$M_{w,NMP}/M_{w,THF}$	MWD_{NMP}/MWD_{THF}[c]
2	1.56	1.54	0.987
3	1.53	1.59	1.04
4	1.98	1.84	0.934
5a	0.939	1.01	1.07
6a–1	1.22	1.20	0.978

[a] Polystyrene equivalents; see Tables 2 and 3. [b] 6 mM. [c] MWD = molecular weight distribution or polydispersity, M_w/M_n.

Solubilities. In the purification processes, we faced the problem of choosing reprecipitation nonsolvents. The polyrotaxanes with smaller crown ethers (**2** and **3**) or lighter loadings of large crown ethers, i.e., as in **5c**, can be reprecipitated into methanol easily. However, those with a greater proportion of larger crown ethers (**4**, **5a**, and **5b**) were very difficult to reprecipitate. They either formed emulsions or were totally soluble in most solvents, even in water. These polyrotaxanes were precipitated from ethyl acetate or hexane–ethyl acetate. Generally speaking, the polyrotaxanes are more soluble than the model polyurethane in common solvents and solubility increases with weight percent of crown ethers in the system. Thus, the model polyurethane is insoluble in acetone, water, and methanol and only slightly soluble in dichloromethane, but **2**–**5c** are also soluble in acetone and dichloromethane. The most interesting observation is that polyrotaxanes **4** and **5a** are water soluble, which could have very important potential applications.[42]

A comparison of the polystyrene equivalent molecular weights and polydispersities in 6 mM LiBr–NMP (Table 3) versus those in THF (Table 2) is presented in Table 5. First, note that the ratios of polydispersities under the two conditions are essentially unity, giving assurance of the individual calibrations. Interestingly, however, the ratios of the molecular weights themselves in the two solvent systems do vary significantly, depending upon the nature of the polymer. The model system **6a** shows a 20% increase in apparent molecular weight in LiBr–NMP relative to THF. That is, the relative elution volume is reduced in LiBr–NMP; this means that there is a larger hydrodynamic volume in LiBr–NMP than in THF, probably as a result of increased intermolecular hydrogen bonding between the solvent and the polymer. However, the polyrotaxanes **2**–**5a** display varying behavior. The polystyrene equivalent molecular weights are essentially unaffected for **5a**, the polyrotaxane involving 60-crown-20. But for those involving 36-crown-12 (**2**) and 42-crown-14 (**3**) the apparent molecular weights in LiBr–NMP are about 55% higher than in THF. And for the polyrotaxane involving 48-crown-16 (**4**) the apparent molecular weights are about 90% higher in LiBr–NMP. These results probably reflect both the nature of the ring components and their loadings.

These results can be interpreted in terms of a combination of two factors: (1) the mutual steric constraints imposed by each of the species on the other, i.e., the cyclic and linear species, and (2) differential solvation of the two species. The steric constraints will tend to increase the end-to-end distances and hydrodynamic volumes for the polyrotaxanes relative to the model polyurethane. The differential solvation effect could in the extremes cause either the macrocycle or the linear backbone to be fully expanded or to collapse into a θ state, as illustrated in Figure 11.

The lack of solvent effect for **5a** could be the result of the large size of the crown ether and its resultant looser connection with the backbone. The higher apparent molecular weights for **2** and **3** and the even larger apparent increase for **4** in LiBr–NMP may reflect the relative intrinsic rigidity of these rings coupled with

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(41) Ha, Y. K.; Chakraborty, A. *J. Phys. Chem.* **1991**, *95*, 10781. Ha, Y. K.; Chakraborty, A. *J. Phys. Chem.* **1993**, *97*, 11291.

(42) Light-scattering studies demonstrate that the solubilization is due to micelle formation: Davis, R. M.; Gibson, H. W.; Shen, Y. X. Unpublished results. Upon raising the temperature of aqueous solutions of **5a** (1–4 mg/mL), cloud points, corresponding to lower critical solution temperatures, ranged from 86–88 °C.

Figure 11. Solvent effects on polyrotaxane: (a) in a good solvent for both the cyclic and linear species, leading to expansion of both components; (b) in a good solvent for the linear macromolecule but a poor solvent for the cyclic species, leading to an expanded backbone but collapsed macrocycles; (c) in a poor solvent for the linear backbone but a good solvent for the macrocycle, providing a collapsed state of the linear component and an expanded state for the rings; (d) in a poor solvent for both the linear and cyclic components, affording collapsed conformations of both. The situation for b could lead to either smaller or larger total hydrodynamic volume than in c depending on the nature of the cyclic and linear species, the relative loading of the latter, and the solvent.

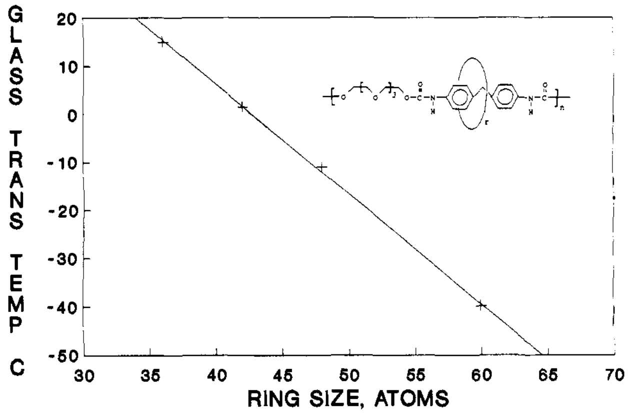

Figure 12. Glass transition temepratures of polyrotaxanes **2**–**5a** prepared from crown ethers at a 1.5 mol ratio of cyclic to glycol in neat reactions as a function of ring size. T_g for model polyurethane **6a** was 51 °C.

their abilities to interact with solvent. The 36- and 42-membered crowns of **2** and **3**, upon solvation in LiBr–NMP perhaps as a result of complexation with the Li ions present, expand the random coil of the backbone; however, their cavities are to a large extent occupied by the backbone, leaving little room for intraannular solvation and complexation. For the larger, more flexible 48-membered rings of **4**, however, more extensive solvation and complexation are possible, leading to a much larger increase in hydrodynamic radius in LiBr–NMP. For the even larger 60-membered rings of **5a** solvation and complexation are even more facile, but do not result in rigidification of the ring because of its larger size and consequent flexibility. The opposing effects of an available cavity for solvation and its effect on rigidifying the resultant system apparently lead to a maximum increase in hydrodynamic volume for polyrotaxane **4**. Obviously, the amount of crown ether incorporated into the polyrotaxane is important also; more detailed studies are required to test these hypotheses.

Physical Behavior of the Polymers. The room temperature physical appearance and state of polyrotaxanes with different ring sizes and ring contents and the model polymer are different, indicating that they have different thermal and morphological properties. Model polyurethane (**6**) is a glassy, brittle transparent solid. Polyurethane–rotaxa-36-crown-12 (**2**) is a hard, amorphous, slightly turbid, ductile solid. Polyurethane–rotaxa-42-crown-14 (**3**) is a soft, amorphous, turbid elastomeric solid. Polyurethane–rotaxa-48-crown-16 (**4**) is a stickly, tar-like material. Polyurethane–rotaxa-60-crown-20 (**5a**) is a wax-like, turbid solid, and **5b** is rubbery.

Figure 12 depicts the experimentally measured glass transition temperatures as a function of ring size for **2**–**5a**, all prepared in neat reactions using 1.5 mol of crown ether per 1 mol of glycol. T_g is a linear function of ring size. Simply by varying the size of the crown, the glass transition can be controlled. Elsewhere, we have described in preliminary fashion the correlation of these results by the Fox equation.[27b,43] More detailed analyses of this behavior will be presented in Part 2.

When there is a sufficiently large proportion of rings of large size in the polyrotaxane, the macrocycle can crystallize without dethreading. Figure 13 shows differential scanning calorimetry traces for **5a**. As can be seen, the first heating of the sample shows a clear melting endotherm at 47 °C in addition to the glass transition. Upon slowly cooling the sample, no crystallization occurs. However, a second heating does bring about crystallization, followed by melting. The crystallization exotherm and melting endotherm are equal, indicating that all of the crystallinity formed upon heating the sample, even though under these conditions only about 60% of the original crystallinity was restored. The melting point coincides closely with that of 60-crown-20 itself, 53 °C. The reproducible, slow recrystallization, however, contrasts with the much faster rate of crystallization observed in a simple physical blend of the model polyurethane **6a** and 60-crown-20 of the same overall composition, indicating that dethreading of the rings of the polyrotaxane does not occur.[44] The polyrotaxane **4** prepared from 48-crown-16 also crystallizes.[44] The slower rate of crystallization of the polyrotaxanes is consistent with the necessity of diffusion of the macrocycles along the backbone in order to aggregate, nucleate, and crystallize. This situation is similar to that observed in poly[(butylene sebacate)-rotaxa-(60-crown-20)] (**1**).[27b,30–32] Detailed studies of the morphological and kinetic aspects of this process will be described in Part 2.

The combination of the ability to control the glass transition temperature and to introduce crystallinity into an amorphous backbone via crystallization of the macrocyclic component means that polyrotaxanes offer a unique way to control systematically the thermal properties of a given polymer backbone. In other words systems based on the same macromolecular backbone can be designed to have different glass transition temperatures. Moreover, new families of thermoplastic elastomers can be designed by use of crystallizable macrocyclic components.

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(43) Gibson, H. W.; Wu, C.; Shen, Y. X.; Bheda, M.; Prasad, A.; Marand, H.; Marand, E.; Keith, D. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1992**, *33* (1), 235.

(44) Marand, H.; Prasad, A.; Marand, E.; Shen, Y. X.; Gibson, H. W. *Prepr. 2nd Polym. Pacific Conf.*, Otsu, Japan **1992**, 839.

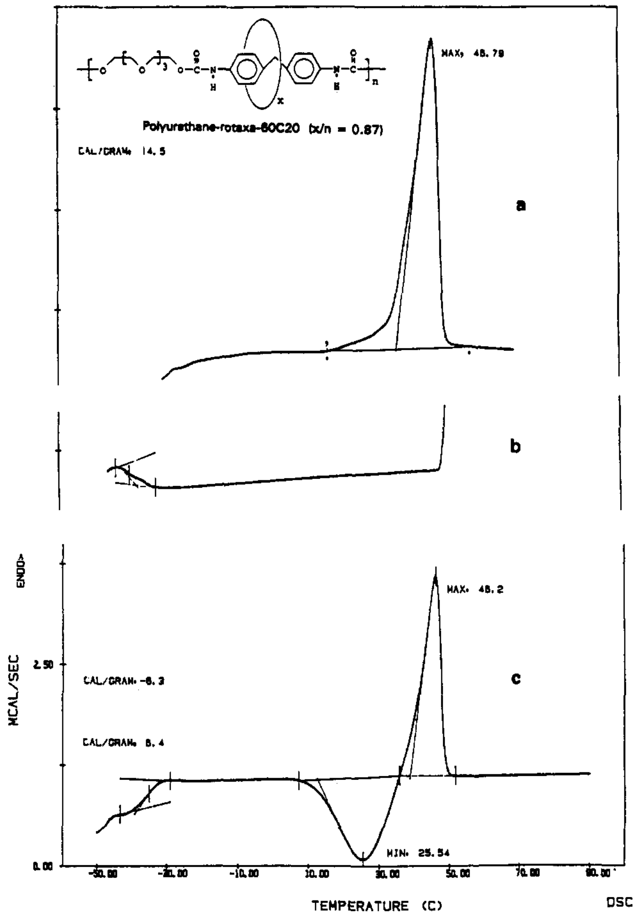

Figure 13. Differential scanning calorimetry (DSC) traces of polyrotaxane **5a**: (a) first heating (10°/min) as made, (b) cooling (5°/min) after first heating, (c) second heating (10°/min).

Conclusions

Polyurethane rotaxanes containing up to 60 (or greater) mass % crown ether can be prepared by equilibration of the macrocycle with tetrakis(ethylene glycol), followed by reaction with MDI. A combination of reprecipitation experiments monitored by proton NMR and GPC provide convincing evidence of the formation of the rotaxane structure. At constant molar ratio of cyclic to glycol in neat reactions the threading efficiency (x/n, the number of cycles per repeat unit of the resulting polyrotaxane) increased linearly with ring size from 36-crown-12 to 60-crown-20. However, attempts to analyze the results for constant ring size at various feed ratios in terms of an equilibrium constant for the threading process gave different values of the "equilibrium constant", for a number of possible reasons which require further study. Physical properties of the polyrotaxanes differ greatly from those of the backbone polyurethane. Solubilities are altered significantly; some of the polyrotaxanes are soluble in water through micelle formation. GPC results in different solvents indicate that the hydrodynamic volume of a given polymer backbone can be altered drastically by rotaxane formation; solvation is shown to be a function of the ring size, but is undoubtedly also dependent upon the amount of crown ether threaded onto the backbone. The glass transition temperatures of the polyrotaxanes prepared at constant molar feed ratio of cyclic to linear monomers change linearly with ring size, offering a unique means of controlling the thermal behavior of a given backbone. At high loadings of the larger crown ethers the macrocycle is able to crystallize without dethreading, offering further options for control of the thermal and associated mechanical behavior of polymeric materials. The thermal and structural properties of these polyrotaxanes will be addressed in detail in Part 2.

Experimental Section

MDI was purchased from Eastman Kodak Co. It was distilled twice under vacuum (bp 188 °C/0.10 Torr) and stored under nitrogen. Tetrakis(ethylene glycol) was purchased from Aldrich Chemical Co. It was also distilled twice under vacuum (bp 170 °C/0.15 Torr) and stored under nitrogen. Diglyme (99+%, anhydrous) and 18-crown-6 were purchased from Aldrich Chemical Co. and used without further purification.

The ^{1}H-NMR spectra were recorded on a Bruker WP270 MHz instrument using tetramethylsilane as the internal standard in DMSO-d_6; all shifts are in parts per million, coupling constants are in hertz, and the following abbreviations are used: s = singlet, d = doublet, m = multiplet. Viscosities of polyurethane-based polyrotaxanes and the model polyurethanes were measured using a Cannon-Ubbelohde semi-micro dilute solution viscometer with a 100 cP inner diameter capillary. GPC analyses were done with a Waters 150C ALC/GPC system with Permagel 10^2–10^6-Å polystyrene–divinylbenzene columns. The instrument was fitted with a refractive index detector (calibrated with polystyrene standards) and Viscotek 100 differential viscometer detector.

All crown ethers larger than 18-crown-6 were synthesized in our laboratories.[39] 36-Crown-12 was obtained as colorless crystals, mp 37.0–37.5 °C (reported[45] mp 36.5–38.0 °C). 42-Crown-14 was obtained as a colorless crystalline solid, mp 49.6–50.4 °C (reported[38] mp 28.5–31.0 °C). 48-Crown-16 was isolated as a colorless crystalline solid, mp 49.6–50.8 °C (reported[45] mp 49.5–50.5 °C). 60-Crown-20 was isolated in pure form as a colorless solid, mp 52.2–53.9 °C (reported[38] mp 46.0–50.5 °C). All crown ethers were dried under vacuum overnight at room temperature before they were used, except for 60C20 used to make **5b**.

Polyurethane–Rotaxa-36-Crown-12 (2). Tetrakis(ethylene glycol) (1.0027 g, 5.1624 mmol) and 36C12 (4.100 g, 7.7436 mmol) were mixed in an oven-dried 15-mL one-necked flask, which was immersed in an oil bath with a temperature of 90 °C. The mixture was magnetically stirred under nitrogen for 1 h. MDI (1.2919 g, 5.1624 mmol) was added. A yellowish-brown color was observed in about 30 min. A viscosity increase was also observed in about 5 h. The reaction was allowed to proceed for a total of 24 h under the same conditions. The polymer was first precipitated into methanol (400 mL) from THF (15 mL). A viscous emulsion was obtained. The second, third, and fourth reprecipitations were done into water (400 mL each) from THF (15 mL each). A yellowish-brown tar-like material (2.21 g) was obtained. Weight percent polymer recovered based on 0.16 threading efficiency: 81%. ^{1}H-NMR: 3.52 (s, $OCH_2CH_2(OCH_2CH_2)_2OCH_2CH_2O$, 8n protons), 3.54 (s, 36C12 0.16 × 48*n* protons), 3.63 (m, $OCH_2CH_2(OCH_2CH_2)_2OCH_2CH_2O$, 4n protons), 4.20 (m, $OCH_2CH_2(OCH_2CH_2)_2OCH_2CH_2O$, 4n protons), 3.80 (s arom-CH_2-arom, 2n protons), 7.10 (d, J = 8.3, aromatic, 4n protons protons), 7.39 (d, J = 8.3, aromatic, 4n protons), and 9.66 (s, NH 2n protons).

Polyurethane–Rotaxa-42-crown-14 (3). Tetrakis(ethylene glycol) (1.0883 g, 5.6032 mmol) and 42C14 (5.1800 g, 8.4048 mmol) were mixed in an oven-dried 15 mL one-necked flask, which was immersed in an oil bath with a temperature of 90 °C. The mixture was magnetically stirred under nitrogen for 1 h. MDI (1.402 26 g, 5.6032 mmol) was added. A yellow color and viscosity increase were observed immediately. The stirring ceased in 5 min. The reaction was allowed to proceed for a total of 24 h under the same conditions without stirring. The polymer was reprecipitated four times into methanol (400 mL each) from THF (20 mL each). A yellow elastomeric solid (2.80 g) was obtained. Weight percent polymer recovered based on 0.29 threading efficiency: 80%. ^{1}H-NMR: 3.52 (s, $OCH_2CH_2(OCH_2CH_2)_2OCH_2CH_2O$, 8n protons; plus 42C14, 0.29 × 56n protons), 3.62 (m, $OCH_2CH_2(OCH_2CH_2)_2OCH_2CH_2O$, 4n protons), 4.19 (m, $OCH_2CH_2(OCH_2CH_2)_2OCH_2CH_2O$, 4*n* protons), 3.80 (s, arom-CH_2-arom, 2n protons), 7.09 (d, J = 8.3, aromatic, 4n protons), 7.38 (d, J = 8.3, aromatic, 4n protons), and 9.65 (s, NH, 2n protons).

Polyurethane–Rotaxa-48-crown-16 (4). Tetrakis(ethylene glycol) (0.991 70 g, 5.1058 mmol) and 48C16 (5.4800 g, 7.749 mmol) were mixed in an oven-dried 15-mL one-necked flask, which was immersed in an oil bath with a temperature of 90 °C. The mixture was magnetically stirred under nitrogen for 1 h. MDI (1.2777 g, 5.1058 mmol) was added. A yellowish-brown color and viscosity increase were observed in 30 min. The reaction was allowed to proceed for a total of 24 h under the same conditions. The polymer was reprecipitated four times into ethyl acetate (400 mL each) from THF (20 mL each). A viscous tar-like substance (2.79 g) was obtained. Weight percent polymer recovered based on 0.52 threading efficiency: 67%. ^{1}H-NMR: 3.52 (s, $OCH_2CH_2(OCH_2CH_2)_2$-

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(45) Vitali, C. A.; Masci, B. *Tetrahedron* **1989**, *45*, 2201.

$\mathrm{OCH_2CH_2O}$, 8n protons; plus 48C16, 0.52 × 64n protons), 3.62 (m, $\mathrm{OCH_2}\mathit{CH_2}\mathrm{(OCH_2CH_2)_2O}\mathit{CH_2CH_2}\mathrm{O}$, 4n protons), 4.19 (m, $\mathrm{O}\mathit{CH_2}\mathrm{CH_2(OCH_2CH_2)_2OCH_2}\mathit{CH_2}\mathrm{O}$, 4n protons), 3.80 (s, arom-$\mathrm{CH_2}$-arom, 2n protons), 7.09 (d, J = 8.3 aromatic, 4n protons), 7.38 (d, J = 8.3, aromatic, 4n protons), and 9.65 (s, NH, 2n protons.

Polyurethane–Rotaxa-60-crown-20 (5a). Tetrakis(ethylene glycol) (1.0275 g, 5.2901 mmol) and 60C20 (6.5000 g, 7.3864 mmol) were mixed in an oven-dried 15-mL one-necked flask, which was immersed in an oil bath with a temperature of 90 °C. The mixture was magnetically stirred under nitrogen for 1 h. MDI (1.3239 g, 5.2901 mmol) was added. A yellow color was observed in a few minutes. A viscosity increase was observed and the stirring ceased in 30 min. The reaction was allowed to proceed for a total of 24 h under the same conditions without stirring. The polymer was first reprecipitated into a mixture of ethyl acetate and *n*-hexane (8:2 v/v, 400 mL) from THF (20 mL). A viscous emulsified liquid was obtained. The second, third, and fourth reprecipitations were done into ethyl acetate (400 mL each) from THF (20 mL each). A slightly yellow, wax-like solid (3.75 g) was obtained. Weight percent polymer recovered based on 0.87 threading efficiency: 59%. ^{1}H-NMR: 3.51 (s, $\mathrm{OCH_2CH_2(O}\mathit{CH_2CH_2}\mathrm{)_2OCH_2CH_2O}$, 8n protons; plus 6OC20, 0.87 × 80n protons), 3.62 (m, $\mathrm{OCH_2}\mathit{CH_2}\mathrm{(OCH_2CH_2)_2O}\mathit{CH_2}\mathrm{CH_2O}$, 4n protons), 4.19 (m, $\mathrm{O}\mathit{CH_2}\mathrm{CH_2)OCH_2CH_2)_2OCH_2}\mathit{CH_2}\mathrm{O}$, 4n protons), 3.80 (s, arom-$\mathrm{CH_2}$-arom, 2n protons), 7.09 (d, J = 8.3 aromatic, 4n protons), 7.38 (d, J = 8.3, aromatic, 4n protons), and 9.65 (s, NH, 2n protons.

Polyurethane–Rotaxa-60-crown-20 (5b) and Polyurethane–Rotaxa-60-crown-20 (5c). These polymerizations were carried out exactly as per the preparation of **5a** using comparable amounts of the glycol and MDI, except that the feed ratio of macrocycle to tetrakis(ethylene glycol) was 0.80 in the case of **5b** and 0.50 in the case of **5c**. The ^{1}H-NMR spectra were the same as **5a** except for the intensities of the 3.5 ppm peak and a larger 8.50 ppm signal in **5b**, indicative of 35% urea linkages relative to urethane moieties; this result was due to the fact that the 60C20 was exposed to ambient conditions for several days but was not vacuum dried.

Model Polyurethane 6a. To an oven-dried 15-mL one-necked flask, tetrakis(ethylene glycol) (1.4012 g, 7.2141 mmol) was added with diglyme (5.00 mL). The flask was immersed in an oil bath with a temperature of 90 °C. MDI (1.8235 g, 7.2864 mmol) was added, and the solution was magnetically stirred under nitrogen. An orange color and increase in viscosity were observed in 20 min. The solution was continuously stirred for 24 h. The polymer was reprecipitated two times into methanol (400 mL each) from THF (20 mL each). A slightly yellow amorphous solid (2.98 g) was obtained. Weight percent polymer recovered 92%. ^{1}H-NMR: 3.51 (s, $\mathrm{OCH_2CH_2(O}\mathit{CH_2CH_2}\mathrm{)_2OCH_2CH_2O}$, 8n protons), 3.62 (m, $\mathrm{OCH_2}\mathit{CH_2}\mathrm{(OCH_2CH_2)_2O}\mathit{CH_2}\mathrm{CH_2O}$, 4n protons), 4.19 (m, $\mathrm{O}\mathit{CH_2}\mathrm{CH_2(OCH_2CH_2)_2OCH_2}\mathit{CH_2}\mathrm{O}$, 4*n* protons), 3.79 (s arom-$\mathrm{CH_2}$-arom, 2n protons), 7.10 (d, J = 8.3, aromatic, 4n protons), 7.38 (d, J = 8.3, aromatic, 4n protons), and 9.66 (s, NH, 2n protons).

Model Polyurethane Prepared in 18-Crown-6 (6b). Exactly the same procedure was used to prepare and purify **6b** as described above for **6a**, except that 6.6994 g (31.3 mmol) of 18-crown-6 was used as solvent. Tetrakis(ethylene glycol) (1.1235 g, 5.7843 mmol) was stirred in the crown ether for 1 h at 90 °C. Then 1.4476 g (5.7843 mmol) of MDI was added, and the solution was stirred for 24 h. NMR (Figure 1): nearly identical to **6a** except for a slightly larger urea peak at 8.5, undoubtedly the result of the hydroscopicity of 18-crown-6. 18-Crown-6 recovered from the filtrate of the reprecitation experiment gave a single sharp ^{1}H-NMR resonance at 3.65 ppm in $\mathrm{CDCl_3}$.

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