
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Controlling Polymeric Topology by Polymerization Conditions: Mechanically Linked Network and Branched Poly(urethane rotaxane)s with Controllable Polydispersity

Caiguo Gong and Harry W. Gibson*

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

Received April 30, 1997[®]

Abstract: Compared to that of model polyurethane **8** from the reaction of tetra(ethylene glycol) (**6**) and 4,4'-methylenebis(*p*-phenyl isocyanate) (**7**) under the same polymerization conditions, polydispersities (PDI) of copolyurethanes **9–11** incorporating bis(5-(hydroxymethyl)-1,3-phenylene)-32-crown-10 (**5**) as comonomer were significantly higher; for these branched polymers, the PDI increased with feed ratio of **5** vs **6** up to $M_w/M_n = 24$ for 75% of **5**. This constitutes an original method to control branching. The branching units in **9–11** are main chain rotaxanes formed with H-bonding between the ether moieties of macrocycle **5** and –OH groups as a driving force and thus are mechanically linked, as directly proven by ¹H NMR spectra, NOESY, and complexation studies with a bipyridinium salt. The cavity of **5** acts as a “topological functionality”. Since solvent can either allow or disfavor such H-bonding, polymeric topology, branched or linear, can be controlled by the proper choice of solvent. Indeed, although homopolyurethanes were prepared from the reaction of **5** and **7** under the same conditions otherwise, **12a** made in diglyme had very high PDI and was highly branched, while the PDI of **12b** made in DMSO was low, close to that of model polyurethane **8**, and thus it was linear. In addition, **12c** from melt polymerization of **5** and **7** is believed to be physically cross-linked since it is not soluble in common solvents for **12a** and **12b**. Therefore, a novel strategy for controlling polymeric topology simply by reaction conditions to afford mechanically linked network and branched polymeric materials with controllable PDI, which are essentially three-dimensional main chain polyrotaxanes, is demonstrated.

Introduction

Compared to linear counterparts, branched polymers often show new properties such as high solubility, low melt viscosity, and low density and thus bring about many new applications. Hyperbranched materials can easily be prepared by one-step reactions of AB_x monomers, in which functional groups A and B can react with each other and *x* is 2 or greater.^{1–12} However, there are some limitations in this classical approach. First, the

final product is always highly functional, i.e., contains lots of unreacted B, and an additional step is required to decrease or terminate such end-functional groups if necessary. Second, groups A and B cannot be too reactive. For example, polyurethanes cannot be constructed directly from monomers with

[®] Abstract published in *Advance ACS Abstracts*, September 1, 1997.

(1) For reviews, see: (a) Dvornic, P. R.; Tomalia, D. A. *Curr. Opinion Coll. Interface Sci.* **1996**, *1*, 221–235. (b) Newkome, G. R.; Moorefield, C. N.; Vogtle, F. *Dendritic Molecules*; VCH Publishers: Weinheim, Germany, 1996. (c) Fréchet, J. M. J. *Science* **1994**, *263*, 1710–1715. (d) Fréchet, J. M. J. *J. Macromol. Sci., Pure Appl. Chem.* **1994**, *A31*, 1627.

(2) Massa, D. J.; Shriner, K. A.; Turner, S. R.; Voit, B. I. *Macromolecules* **1995**, *28*, 3214–3220.

(3) Turner, S. R.; Walter, F.; Voit, B. I.; Mourey, T. H. *Macromolecules* **1994**, *27*, 1611–1616.

(4) Wooley, K. L.; Hawker, C. J.; Lee, R.; Fréchet, J. M. J. *Polym. J.* **1994**, *26*, 187–197.

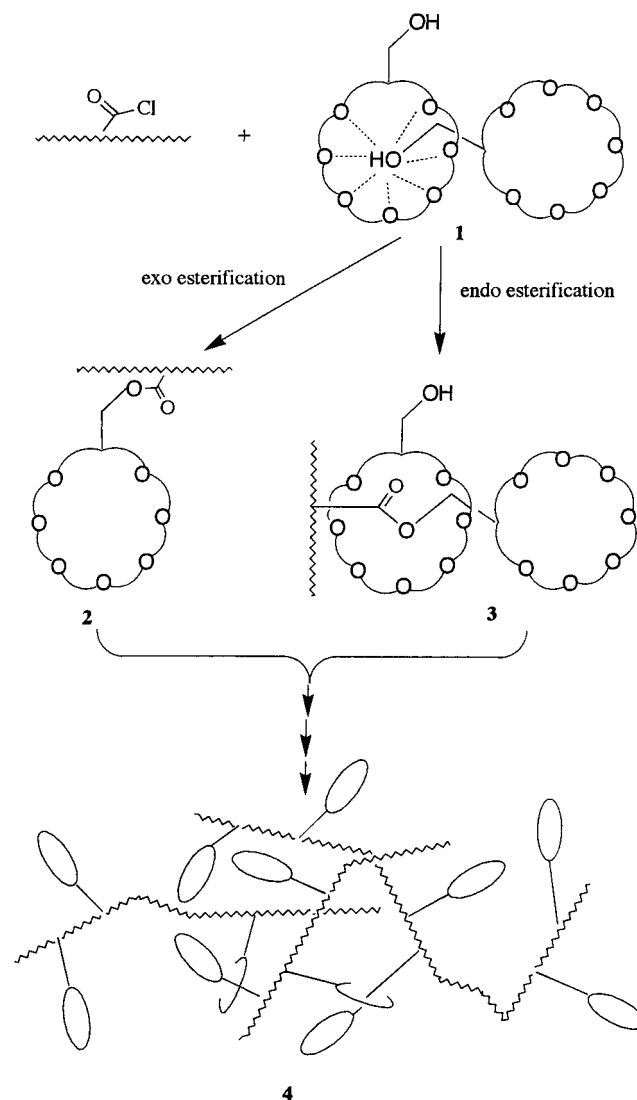
(5) Turner, S. R.; Voit, B. I.; Mourey, T. H. *Macromolecules* **1993**, *26*, 4617–4623.

(6) Ralph, P.; Hawker, C. J.; Fréchet, J. M. J. *Macromolecules* **1993**, *26*, 4809–4813.

hydroxy and isocyanate groups and a protective group has to be introduced.¹¹ Finally, the degree of branching or polydispersity (PDI) and the degree of polymerization (DP) are difficult to control because they are mainly decided by statistics, accessibility of functional groups and reaction rate. Overcoming these limitations remains a great challenge to chemists.

Polyrotaxanes, in which rotaxane units (cyclics threaded by linear species) are incorporated into macromolecules, also have received world-wide attention.^{13–22} Numerous main chain polyrotaxanes have been prepared with crown ethers as cyclic components.^{13,17–19} Recently, hydrogen bonding between hydroxy groups and the crown ether was proposed as a driving force for the threading.^{18–20} Therefore, a crown ether bearing a hydroxy functional group brings about a driving force for the formation of a self-complexed structure (**1**), which can lead to a novel rotaxane structure (**3**) by an endo esterification with a poly(acid chloride) (Scheme 1), as we demonstrated by the formation of a branched and/or cross-linked polymer (**4**).²⁰ In the present work, this concept is extended and used as a novel

Scheme 1. Mechanism for the Formation of Branched and Network Polymers with a Side Chain Rotaxane Structure



(7) Miller, T. M.; Neenan, T. X.; Kwock, E. W.; Stein, S. M. *J. Am. Chem. Soc.* **1993**, *115*, 356.

(8) Uhrich, K. E.; Hawker, C. J.; Fréchet, J. M. J.; Turner, S. R. *Macromolecules* **1992**, *25*, 4583–4587.

(9) Kim, Y. H. *J. Am. Chem. Soc.* **1992**, *114*, 4947.

(10) Kim, Y. H.; Webster, O. W. *Macromolecules* **1992**, *25*, 5561–5572.

(11) Hawker, C. J.; Lee, R.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4583–4595.

(12) Mathias, L. J.; Carothers, T. W. *J. Am. Chem. Soc.* **1991**, *113*, 4043.

(13) For reviews, see: (a) Gibson, H. W. In *Large Ring Molecules*; Semlyen, J. A., Ed.; J. Wiley and Sons: New York, 1996; pp 191–262. (b) Philp, D.; Stoddart, J. F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1154–1196. (c) Ambalino, D. B.; Stoddart, J. F. *Chem. Rev. Rev.* **1995**, *95*, 2725–2828. (d) Gibson, H. W.; Bheda, M. C.; Engen, P. T. *Prog. Polym. Sci.* **1994**, *19*, 843–945.

(14) (a) Steinbrunn, M. B.; Wenz, G. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2139–2142. (b) Weickenmeier, M.; Wenz, G. *Macromol. Rapid Commun.* **1996**, *17*, 731–736. (c) Wenz, G. *Macromol. Symp.* **1994**, *87*, 11–16. (d) Wenz, G.; Wolf, F.; Wagner, M.; Kubik, S. *New J. Chem.* **1993**, *17*, 729–738. (e) Wenz, G.; Keller, B. *Angew. Chem., Int. Ed. Engl.* **1992**, *104*, 201–204. (f) Wenz, G.; Keller, B. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 197–199.

(15) (a) Born, M.; Ritter, H. *Macromol. Rapid Commun.* **1996**, *17*, 197–202. (b) Born, M.; Ritter, H. *Adv. Mater.* **1996**, *8*, 149–151. (c) Born, M.; Ritter, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *107*, 342–345. (d) Born, M.; Ritter, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 309–311. (e) Born, M.; Ritter, H. *Acta Polym.* **1994**, *45*, 68–72.

(16) (a) Harada, A.; Okada, M.; Li, J.; Kamachi, M. *Macromolecules* **1995**, *28*, 8406–8411. (b) Harada, A.; Li, J.; Kamachi, M. *Macromolecules* **1994**, *27*, 4538–4543. (c) Harada, A.; Li, J.; Kamachi, M. *Nature* **1994**, *370*, 126–129; **1993**, *364*, 516–518. (d) Harada, A.; Li, J.; Kamachi, M. *Macromolecules* **1993**, *26*, 5698–5703.

(17) (a) Gibson, H. W.; Liu, S.; Lecavalier, P.; Wu, C.; Shen, Y. X. *J. Am. Chem. Soc.* **1995**, *117*, 852–874. (b) Shen, Y. X.; Xie, D.; Gibson, H. W. *J. Am. Chem. Soc.* **1994**, *116*, 537–548. (c) Gibson, H. W.; Marand, H. *Adv. Mater.* **1993**, *5*, 11–21.

(18) (a) Gibson, H. W.; Liu, S.; Shen, Y. X.; Bheda, M. C.; Lee, S.-H.; Wang, F. *NATO ASI Series*; Kluwer: Dordrecht, The Netherlands, 1995; Series C, Vol. 456, pp 41–58. (b) Gong, C.; Gibson, H. W. *Macromol. Chem. Phys.* **1997**, *198*, 2331–2342. (c) Gibson, H. W.; Liu, S.; Gong, C.; Ji, Q.; Joseph, E. *Macromolecules* **1997**, *30*, 3711–3727. (d) Gong, C.; Gibson, H. W. *Macromolecules* **1996**, *29*, 7029–7033. (e) Gong, C.; Gibson, H. W. *Macromolecules* In press. (f) Gibson, H. W.; Liu, S. *Macromol. Symp.* **1996**, *102*, 55–59. (g) Gibson, H. W.; Gong, C.; Liu, S.; Nagvekar, D. *Macromol. Symp.* In press.

(19) Gong, C.; Gibson, H. W. *Angew. Chem.* Accepted for publication.

(20) Gong, C.; Gibson, H. W. *J. Am. Chem. Soc.* **1997**, *119*, 5862–5866.

(21) (a) Gibson, H. W.; Nagvekar, D.; Yamaguchi, N.; Bryant, W. S.; Bhattacharjee, S. *Am. Chem. Soc., Div. Polym. Chem., Polym. Prepr.* **1997**, *38* (1), 64–65. (b) Gibson, H. W.; Nagvekar, D.; Bryant, W. S.; Powell, J.; Bhattacharjee, S. *Am. Chem. Soc., Div. Polym. Chem., Polym. Prepr.* **1997**, *38* (1), 115–116. (c) Nagvekar, D.; Gibson, H. W. *Am. Chem. Soc., Div. Polym. Chem., Polym. Prepr.* **1996**, *37* (2), 299–300. (d) Delaviz, Y.; Gibson, H. W. *Macromolecules* **1992**, *25*, 18–21. (e) Delaviz, Y.; Gibson, H. W. *Macromolecules* **1992**, *25*, 4859–4862. (f) Gibson, H. W.; Nagvekar, D. S.; Powell, J.; Gong, C.; Bryant, W. S. *Tetrahedron* In press. (g) Delaviz, Y.; Gibson, H. W. *Polym. Commun.* **1991**, *32*, 103–105.

(22) Gong, C.; Gibson, H. W. Submitted for publication.

strategy to overcome the limitations of classical methods for the preparation of branched and network polymers, demonstrated by the syntheses of mechanically linked branched and network polyurethanes.

Results and Discussion

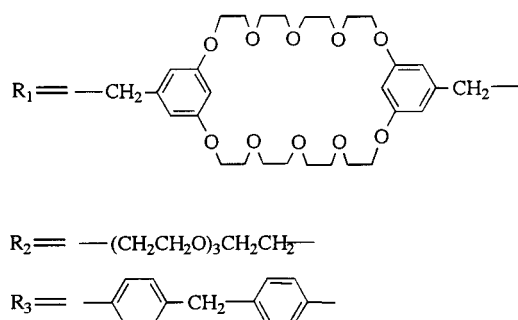
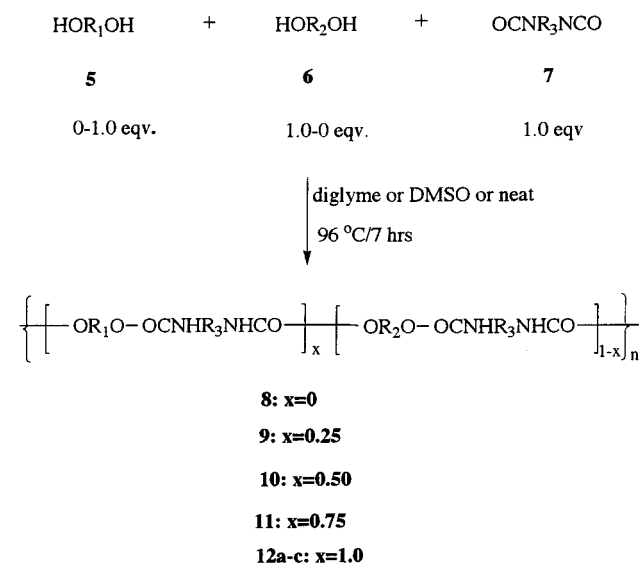
A. Syntheses of Polyurethanes 8–11 and 12a–c. To establish the conditions to achieve high molecular weight polymers, model polyurethane **8** was prepared from tetra-(ethylene glycol) (**6**) and 4,4'-methylenebis(*p*-phenyl isocyanate) (MDI) (**7**) by solution polymerization using diglyme as solvent (Scheme 2). According to gel permeation chromatography (GPC) measurements (Table 1), high molecular weight **8** can be obtained within 7 h at 96 °C. Therefore, the same conditions were applied for copolyurethanes **9–11**, which were made from the reaction of bis(5-(hydroxymethyl)-1,3-phenylene)-32-crown-10²³ (**5**) and **6** with MDI (**7**) (Scheme 2). To study the influence of the feed percentage of **5** on the PDI of the resulting polyurethanes, the ratio of macrocyclic diol **5** vs **6** was increased in the syntheses of **8–11** while the concentration of total hydroxy groups (**5** plus **6**) was kept at the same value (Table 1). To test the effect of solvent on polymer topology,

(23) Gibson, H. W.; Nagvekar, D. S. *Can. J. Chem.* Accepted for publication.

Table 1. The Feed Compositions, Polymerization Conditions,^a and GPC and DSC Results for Polyurethanes **8–11** and **12a–c**

polymer	solvent (mL)	5 (mmol)	6 (mmol)	7 (mmol)	M_n (kg/mol) ^b	M_w (kg/mol) ^b	PDI ^b	T_g (°C) ^c
8	diglyme (58.0)	0.00	18.95	18.95	16.6	58.7	3.54	54.0
9	diglyme (2.0)	0.1629	0.4865	0.6493	8.5	46.4	5.54	55.0
10	diglyme (2.0)	0.3250	0.3244	0.6493	8.0	109	13.6	57.4
11	diglyme (1.9)	0.4689	0.1565	0.6254	6.6	161	24.2	59.5
12a	diglyme (1.5)	0.4890	0	0.4890	11.3	267	23.6	66.4
12b	DMSO (1.5)	0.4890	0	0.4890	13.2	53.9	4.0	66.2
12c	no solvent	0.5392	0	0.5392				73.9

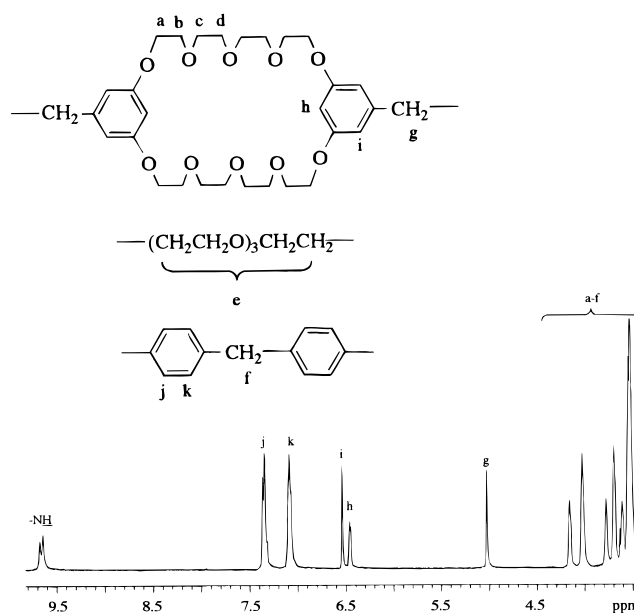
^a Polymerization temperature, 96 ± 2 °C; time, 7 h. ^b Measured by GPC using universal calibration in NMP at 60 °C. ^c Measured by DSC at a scan rate of 10 °C/min.

Scheme 2. Preparation of Polyurethanes **8–11** and **12a–c**

homopolyurethanes **12a** and **12b** were prepared from the reaction of macrocyclic diol **5** with MDI (**7**) using different solvents, diglyme for **12a** and DMSO for **12b**. Finally, **12c** was prepared by melt polymerization of **5** and **7**. The chemical compositions of these polymers were confirmed by proton NMR measurements, exemplified by the spectrum of **10** (Figure 1).

B. GPC Measurements and Mechanism for Branching and Cross-linking. As the GPC results in Table 1 show, copolyurethanes **9–11** have much higher PDI than model polymer **8**. Such a high PDI directly indicates that these polymers are essentially branched materials. It is well-known that branched polymers and networks can only be generated from starting monomers with functionality greater than 2. How can we explain the branching structures of polyurethanes **9–11**, since from the point of view of reactive groups only difunctional monomers were used (Scheme 2)?

For the preparation of polyester rotaxanes, we proposed that H-bonding of the crown ethers with ---OH groups provides the driving force for threading.¹⁸ Therefore, macrocyclic moieties described as structure **13**, macrocyclic diol **5** initially and in-chain macrocyclic units during the polymerization, are expected

**Figure 1.** Proton (400 MHz) NMR spectrum of polyurethane **10** in $\text{DMSO-}d_6$ at room temperature.

to form various intermediates simplified as structure **15** by H-bonding with ---OH groups of **14**, another macrocyclic diol **5**, or glycol **6** at the start and the terminal ---OH groups of polymeric chains during the polymerization (Scheme 3). Hydrogen-bonded complex **15** can undergo endo reaction with the isocyanate group of **16**, with that of MDI (**7**) initially, and with unreacted ---NCO groups during the polymerization to give rotaxane structure **17**, a branching or cross-linking point for polyurethanes **9–11**. Compound **15** may also undergo exo reaction to yield normal linear backbone units (structures **18** and **19**). Ultimately, a novel three-dimensional main chain polyrotaxane structure (**20**) is derived. Thus, the branching topology of **9–11** is produced by the formation of rotaxane units via a physical functionality, the cavity of the macrocycle, i.e., macrocyclic diol **5** is trifunctional, having two chemically reactive moieties and a physical linking site, a “topological functionality”.

More interestingly, the PDI of the final polymers increased with the feed ratio of **5** vs **6** (Table 1) and the relationship is plotted in Figure 2. This relationship is consistent with the above hypothesis. First, as more **5** and less **6** are applied as diol monomers, the concentration of **13** increases and thus more intermediate **15** and branching units **17** are expected (Scheme 3). Second, it is believed that a macrocycle cannot pass through another identical cyclic; thus, in the rotaxanes, macrocycles essentially serve as blocking groups (BG) to prevent dethreading.^{18,20} Therefore, as more **5** is applied, there is less dethreading, and consequently a higher branching degree is achieved.

It was reported that the strength of H-bonding of crown ethers with ---OH moieties is dependent on the polarity of the solvent.²⁴ Recently, we found that DMSO is very good solvent to depress

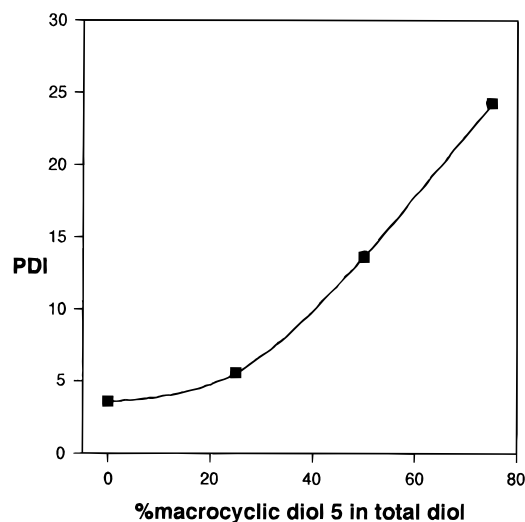
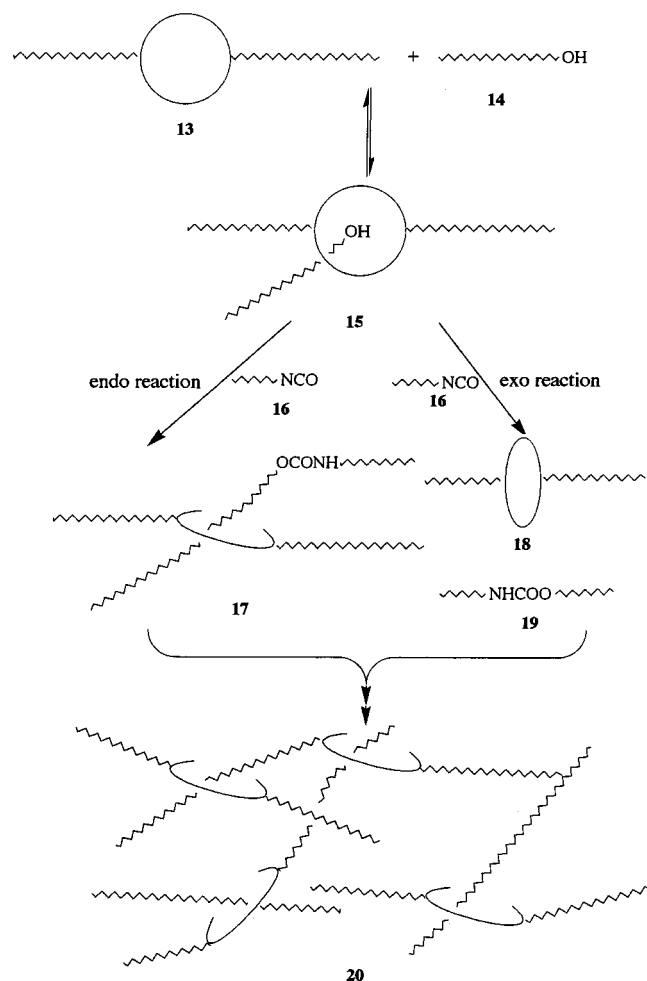


Figure 2. The relationship of the polydispersity of polyurethanes 8–11 vs the feed percentage of macrocyclic diol 5.

Scheme 3. Mechanism for the Formation of Branched Polyurethanes 9–11 and 12a and Network Polyurethane 12c



or prevent the formation of such H-bonding structures.¹⁹ Therefore, the complex **15** and branching points **17** (Scheme 3) are not expected to form effectively in this solvent. According to GPC analysis, polyurethane **12b** prepared with DMSO as solvent indeed has a low PDI (Table 1 and Figure 3), close to that of model polyurethane **8**, and thus, it is believed

(24) Izatt, R. M.; Bradshaw, J. S.; Pawlak, K.; Bruening, R. L.; Tarbet, B. *J. Chem. Rev.* **1992**, *92*, 1261–1354.

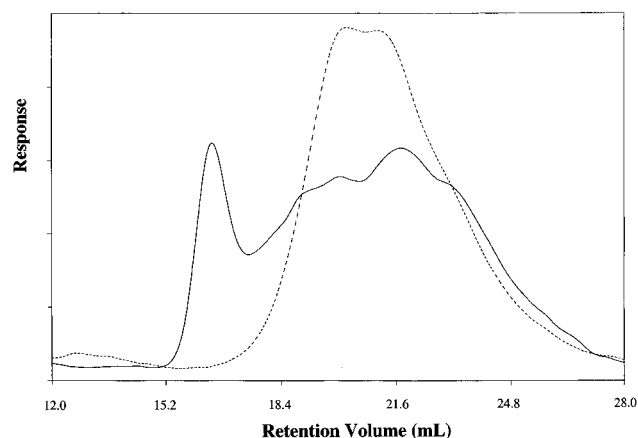


Figure 3. The GPC traces of (a) polyurethane **12a** (solid line) and (b) polyurethane **12b** (dashed line) with viscosity detector using *N*-methylpyrrolidinone as solvent.

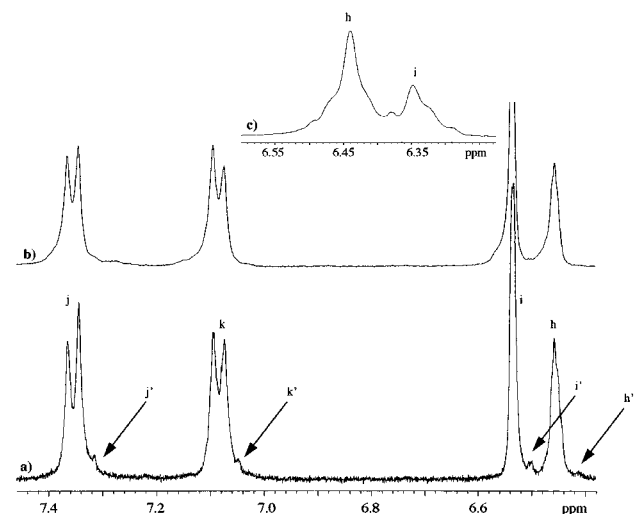


Figure 4. The expanded 400 MHz proton NMR spectra of (a) **12a** in DMSO-*d*₆, (b) **12b** in DMSO-*d*₆, and (c) **12a** in CDCl₃ (for peak assignments, see Figure 1 and Scheme 4).

to be linear or to contain only very small amounts of branching rotaxane units, although both PDIs were above 2 due to the formation of small amounts of allphonate as detected by proton NMR. This result also rules out the possibility that side reactions are responsible for the formation of the branched and/or network polyurethanes. As expected, **12a** prepared in diglyme has a very high PDI (Table 1 and Figure 3). These results further support the proposed mechanism for the formation of branched and network polymers (Scheme 3).

Additionally, **12c** was prepared by melt polymerization and thus had the highest concentration of H-bonded complex **15**. This produced the highest degree of branching as expected; indeed, an insoluble network was formed.

C. NMR Studies. It is well-known that threaded macrocycles or backbones can show different chemical shifts from their parent protons because of through-space interactions in the rotaxane structures, especially for macrocycles restricted between blocking groups^{18b,d,e} or other macrocycles.²⁰ In polyurethane **12a**, the branching points are main chain rotaxane structures, and the threaded macrocycles are confined between other macrocyclic moieties (structures **21** and/or **22** in Scheme 4), since a macrocycle usually cannot pass through another identical moiety.²⁰ New signals appear in the spectrum of **12a** (Figure 4a); this is because of the existence of the rotaxane units (**21** and **22**), the branching points. The lack of these new signals for **12b** (Figure 4b) indicates that it contains no rotaxane

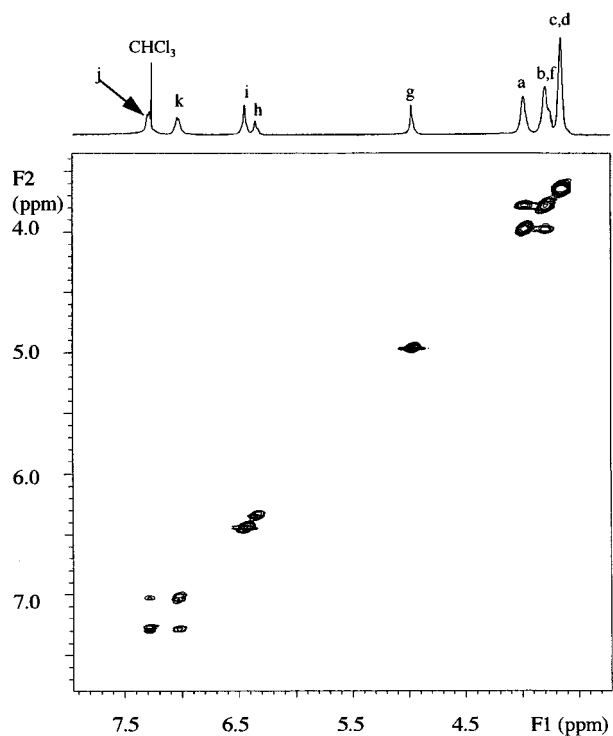


Figure 5. The 400 MHz COSY spectrum of **12a** in CDCl_3 at 26°C (for peak assignments, see Figure 1 and Scheme 4).

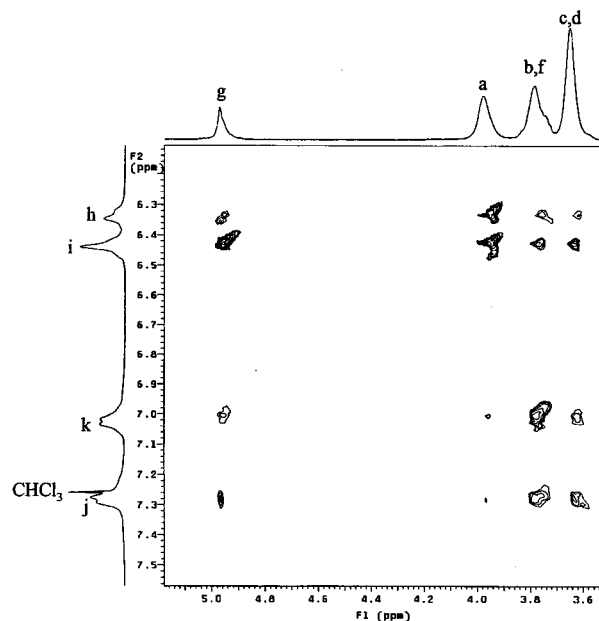


Figure 6. The correlated region of 400 MHz NOESY spectrum of **12a** in CDCl_3 at 26°C (for peak assignments, see Scheme 4).

structures but rather is a linear polymer; this agrees with the GPC results. In addition, the signals h and i of **12a** became even more complicated and broader in CDCl_3 (Figure 4c) than in $\text{DMSO}-d_6$. We believe that H-bonding between the threaded macrocycle and the in-chain NH group¹⁹ restricts the motion of the macrocycle and thus leads to signal broadening (Scheme 4).

The COSY spectrum of **12a** shows the couplings consistent with its structure (Figure 5); this rules out the possibility that side reactions may cause branching. As expected, the NOESY spectrum (Figure 6) of **12a** in CDCl_3 indeed showed some through-space interactions. Since proton h is close to protons a–d even in the unthreaded cyclic (Scheme 4), the correlation

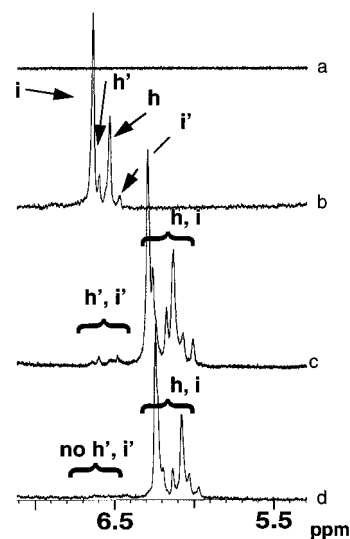


Figure 7. The expanded (5.5–7.0 ppm region) 400 MHz proton NMR spectra of (a) **23**, (b) **12a**, (c) **12a** with excess **23**, and (d) **12d** with excess **23** in $\text{THF}-d_5/\text{CD}_3\text{CN}$ (1:1 by volume) (for peak assignments, see Scheme 4).

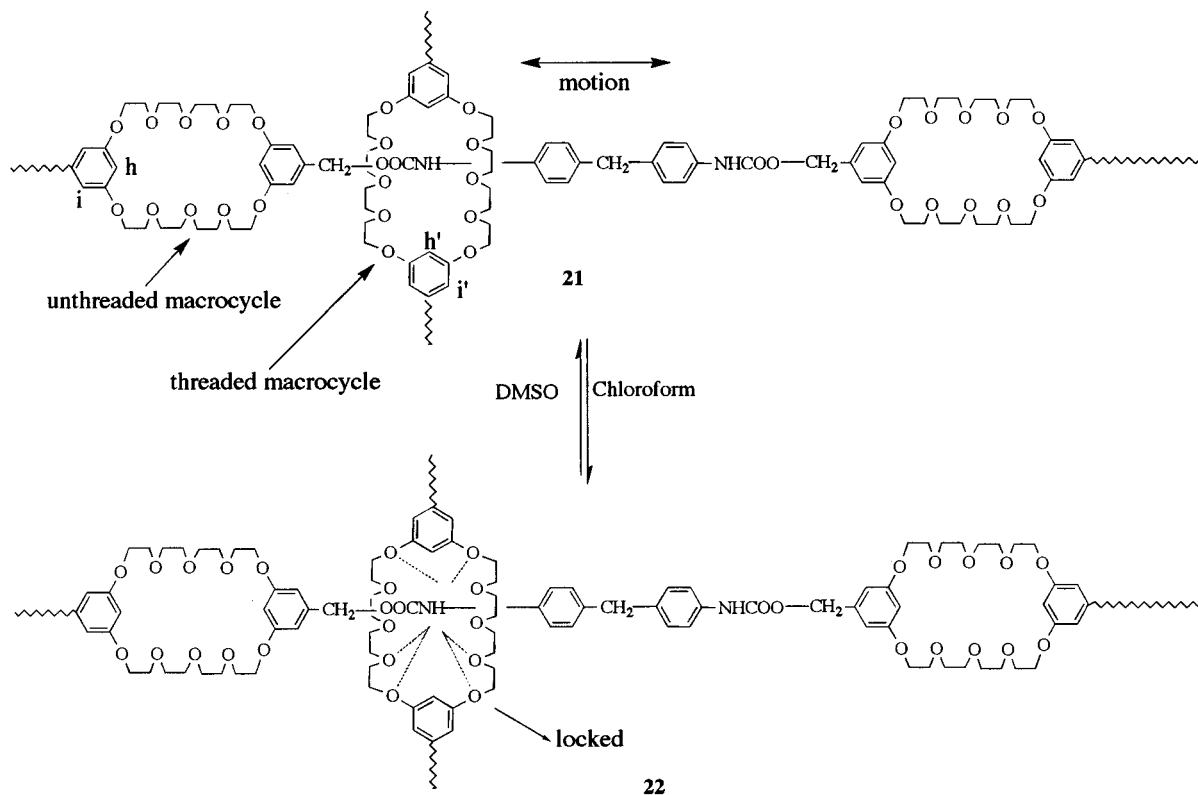
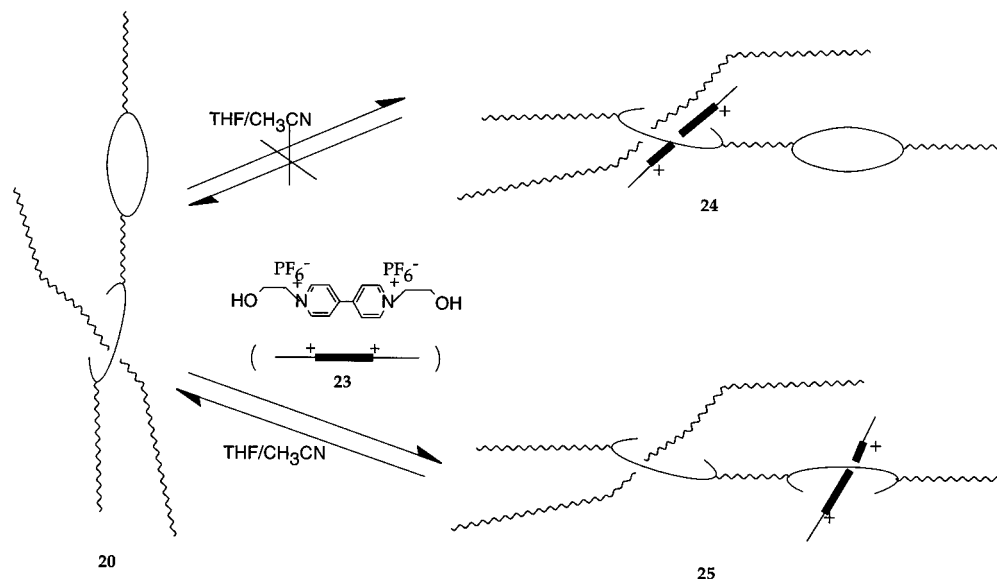
does not directly prove the rotaxane structure, although it does agree with it. However, the correlations between proton i and the protons a–d as well as those of protons k and j with a–d do indicate the formation of the rotaxane topology for **9–11** and **12a** (Schemes 3 and 4), since they do not correlate with each other in unthreaded structures.²⁰ It is necessary to point out that the evidence is still fragile because these correlations were relatively weak and they only showed up after 10 h of data collection at a high concentration; this can be ascribed to the low degree of threading. Therefore, the following study was performed to augment the NOESY results.

It is well demonstrated that 4,4'-bipyridinium salts complex with bisphenylene-based crown ethers by charge transfer accompanied by hydrogen bonding and dipole–dipole interactions.^{13,25} Since the complexation between these two components is a fast exchange process, both components display time-averaged signals in the proton NMR spectrum.^{25,26} Recently we prepared new main chain polyrotaxanes by threading *N,N'*-(hydroxyethoxy)ethyl-4,4'-bipyridinium dihexafluorophosphate (**23**) through the cavity of in-chain **5** units of a poly(ester crown ether).²² Indeed, in this system, the aromatic protons h and i of **5** show time-averaged signals shifted upfield relative to the starting polymer.

Therefore, the unthreaded macrocyclic moieties of polyurethane rotaxanes **9–11** and **12a** are expected to complex with **23** to afford a pseudorotaxane structure (**25**), while the threaded units will not have enough room to accommodate **23** to produce doubly threaded structure **24** (Scheme 5). There are no signals from **23** in the region of interest (Figure 7a). In a solution of **12a**, a branched rotaxane polymer, and excess **23** (Figure 7c), major signals h and i were shifted upfield while minor signals h' and i' remained at their original positions relative to **12a** itself (Figure 7b). Therefore, the signals h' and i' are indeed from self-threaded cyclic units, directly proving the formation of mechanically linked (rotaxane) structures of type **20** (Scheme 3). As expected, **12b**, a linear polyurethane containing

(25) (a) Allwood, B. L.; Spencer, N.; Shahriari-Zavareh, H.; Stoddart, J. F.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1987**, 106–109. (b) Asakawa, M.; Ashton, P. R.; Ballardini, R.; Balzani, V.; Belohradsky, M.; Gandolfi, M. T.; Kocian, O.; Prodi, L.; Raymo, F. M.; Stoddart, J. F.; Venturi, M. *J. Am. Chem. Soc.* **1997**, *119*, 302–310.

(26) Mason, P. E.; Parsons, I. W.; Tolley, M. S. *Angew. Chem.* **1996**, *108*, 2405–2408; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2238–2241.

Scheme 4. Branching Structure in Polyurethanes **12a** and **12c****Scheme 5.** Complexation Mechanisms of **12a** and **12b** with Bipyridinium Salt **23**

no rotaxane branching, i.e., no or only a very small amount of threaded macrocyclic moieties, showed no h' or i' signals after complexation with excess bipyridinium salt (Figure 7d).

D. Thermal Properties. All of the polyurethanes **8–11** and **12a–c** are amorphous and transparent materials. Since only one glass transition temperature (T_g) (Table 1) was observed for each copolyurethane, they are all believed to be random copolymers. The T_g values of copolyurethanes **9–11** were between that of homopolyurethane **8** (54 °C) and that of homopolymer **12a** (66.4 °C). The higher T_g of **12a** is attributed to the greater rigidity of macrocycle **5** relative to glycol **6**. In addition, cross-linked **12c** has a T_g higher than those of **12a** and **12b** because of restricted chain flexibility.

Conclusions

The present study demonstrates a novel method for the preparation of mechanically linked branched or cross-linked polymers, three-dimensional main chain polyrotaxanes. The rotaxane structures were directly proven by complexation studies. More importantly, an approach to control polymeric topology (linear, branched, or cross-linked) simply by reaction conditions (solvent or bulk) is provided, i.e., a method to control PDI; this cannot be achieved by a classical approach for hyperbranched polymers. In principle, the degree of polymerization can also be adjusted by the feed ratio and the final product may contain no functional groups if monofunctional

end-capping agents are used; this level of structural control is again difficult to achieve by a one-step approach from AB_x monomers.

The above concept can be used for other condensation polymers, i.e., branched polyesters can be easily prepared by reaction of diacid chlorides with macrocyclic diol **5**.^{21,b,f} Since polymer melt viscosity is closely related to topology, i.e., a branched polymer has lower melt viscosity,¹ the present work potentially provides a method to control rheology by adjusting the PDI simply by changing the amount of macrocycle **5**. In addition, the threaded macrocycle probably can move along the backbone induced by external forces, and thus these polymers are expected to have different mechanical properties, e.g., a higher elongation compared to chemically bonded branched polymers from classical methods.

Experimental Section

General Methods. Reagent grade reactants and HPLC or GC grade solvents were used as received from Aldrich except DMSO and diglyme, which were dried over sodium hydride and distilled. Bis(5-(hydroxymethyl)-1,3-phenylene)-32-crown-10 (**5**) was prepared by a well-established procedure.²³ ¹H NMR spectra were recorded at ambient temperature on a Varian Unity 400 MHz spectrometer. The NOESY study was performed with a degassed sample at 26 °C with a mixing time of 1 s and relaxation delay of 2 s. 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 universal calibration was used. The differential scanning calorimetry (DSC) measurements were done with a Perkin Elmer DSC-4 at a scan rate of 10 °C per minute, and the data reported here are the midpoints of the transitions in the second heating.

Polyurethane 8. To a 100 mL flask were added tetra(ethylene glycol) (oven dried at 100 °C) (**6**), freshly distilled MDI (**7**), and diglyme (Table 1). The solution was heated at 96 °C in an oil bath for 7 h. The product was precipitated into a solution of methanol and water (1 L, 1:1) to give a light yellow solid. For **8**: ¹H NMR (DMSO-*d*₆, ppm) δ 9.66 (s, 2H, NH), 7.38 (d, 4H, *J* = 8.3 Hz, ArH), 7.10 (d, *J* = 8.3 Hz, 4H, ArH), 4.19 (br s, 4H, OCH₂CH₂(OCH₂CH₂)₂-OCH₂CH₂O), 3.79 (s, 2H, ArCH₂Ar), 3.62 (br s, 4H, OCH₂CH₂(OCH₂-CH₂)₂OCH₂CH₂O), 3.51 (br s, 8H, OCH₂CH₂(OCH₂CH₂)₂OCH₂CH₂O).

General Procedure for Copolyurethanes 9–11. Macrocyclic diol **5** and glycol **6** were dissolved in anhydrous diglyme (Table 1). After the solution was stirred for 0.5 h at 96 °C under the protection of nitrogen, MDI (**7**) was added as a solid, and the reaction proceeded for an additional 7 h. The polymer was precipitated into a mixture of methanol and water (120 mL, 1:1). For **9**: ¹H NMR (DMSO-*d*₆, ppm)

δ 9.66 (s, 1.5H, NH), 9.44 (s, 0.5H, NH), 7.35 (br s, 4H, ArH), 7.07 (br s, 4H, ArH), 6.52 (br s, 1H, ArH), 6.44 (br s, 0.5H, ArH), 5.00 (s, 1H, ArCH₂O), 4.19 (br s, 3H, OCH₂CH₂(OCH₂CH₂)₂OCH₂CH₂O), 4.0 (br s, 2H, ArOCH₂CH₂(OCH₂CH₂)₂OCH₂CH₂OAr), 3.78 (br s, 2H, ArCH₂Ar), 3.67 (br s, 2H, ArOCH₂CH₂(OCH₂CH₂)₂OCH₂CH₂OAr), 3.62 (br s, 3H, OCH₂CH₂(OCH₂CH₂)₂OCH₂CH₂O), 3.51 (br m, 10H, OCH₂CH₂(OCH₂CH₂)₂OCH₂CH₂O plus ArOCH₂CH₂(OCH₂CH₂)₂-OCH₂CH₂OAr). For **10**: ¹H NMR (DMSO-*d*₆, ppm) (Figure 1) δ 9.66 (s, 1H, NH), 9.44 (s, 1H, NH), 7.35 (br s, 4H, ArH), 7.07 (br s, 4H, ArH), 6.52 (br s, 2H, ArH), 6.44 (br s, 1H, ArH), 5.00 (s, 2H, ArCH₂O), 4.19 (br s, 4H, OCH₂CH₂(OCH₂CH₂)₂OCH₂CH₂O), 4.0 (br s, 4H, ArOCH₂CH₂(OCH₂CH₂)₂OCH₂CH₂OAr), 3.78 (br s, 2H, ArCH₂Ar), 3.67 (br s, 4H, ArOCH₂CH₂(OCH₂CH₂)₂OCH₂CH₂OAr), 3.62 (br s, 2H, OCH₂CH₂(OCH₂CH₂)₂OCH₂CH₂O), 3.51 (br m, 12H, OCH₂-CH₂(OCH₂CH₂)₂OCH₂CH₂O plus ArOCH₂CH₂(OCH₂CH₂)₂OCH₂CH₂-OAr). For **11**: ¹H NMR (DMSO-*d*₆, ppm) δ 9.66 (s, 0.5H, NH), 9.44 (s, 1.5H, NH), 7.35 (br s, 4H, ArH), 7.07 (br s, 4H, ArH), 6.52 (br s, 3H, ArH), 6.44 (br s, 1.5H, ArH), 5.00 (s, 3H, ArCH₂O), 4.19 (br s, 1H, OCH₂CH₂(OCH₂CH₂)₂OCH₂CH₂O), 4.0 (br s, 6H, ArOCH₂-CH₂(OCH₂CH₂)₂OCH₂CH₂OAr), 3.78 (s br, 2H, ArCH₂Ar), 3.67 (br s, 6H, ArOCH₂CH₂(OCH₂CH₂)₂OCH₂CH₂OAr), 3.62 (br s, 1H, OCH₂CH₂(OCH₂CH₂)₂OCH₂CH₂O), 3.51 (br m, 16H, OCH₂CH₂- (OCH₂CH₂)₂OCH₂CH₂O plus ArOCH₂CH₂(OCH₂CH₂)₂OCH₂CH₂OAr).

Polyurethanes 12a and 12b. Macrocyclic diol **5** was dissolved in anhydrous diglyme for **12a** and anhydrous DMSO for **12b** (Table 1). After the solution was stirred for 0.5 h at 96 °C under the protection of nitrogen, MDI (**7**) was added slowly as a solid and polymerization was allowed to proceed for 7 h. The polymer solution was precipitated into a mixture of methanol and water (120 mL, 1:1). For **12b**: ¹H NMR (DMSO-*d*₆, ppm) δ 9.64 (s, 2H, NH), 7.35 (d, 2H, *J* = 8.3 Hz, ArH), 7.07 (d, *J* = 8.3 Hz, 2H, ArH), 6.52 (br s, 4H, ArH), 6.44 (br s, 2H, ArH), 5.00 (s, 4H, ArCH₂O), 4.0 (br s, 8H, ArOCH₂CH₂(OCH₂-CH₂)₂OCH₂CH₂OAr), 3.76 (s, 2H, ArCH₂Ar), 3.67 (br s, 8H, ArOCH₂CH₂(OCH₂CH₂)₂OCH₂CH₂OAr), 3.51 (br m, 16H, OCH₂-CH₂(OCH₂CH₂)₂OCH₂CH₂O).

Polyurethane 12c. Macrocyclic diol **5** was melted at 120 °C and then cooled to 96 °C. Before **5** solidified, MDI (**7**) was added as a solid (Table 2), and after the transparent solution had stirred for 2 h at this temperature, stirring had stopped. Polymerization was continued for 5 h, and the polymer was poured out before it solidified. No detectable amount of soluble product was obtained by extracting with DMF.

Acknowledgment. The present work was supported by the Division of Materials Research, National Science Foundation, through individual investigator grant DMR-93-20196. We also thank Prof. J. McGrath and Dr. Q. Ji for the GPC measurements.

JA971385X