Synthesis and Characterization of a Polyester/Crown Ether Rotaxane Derived from a Difunctional Blocking Group

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ABSTRACT: A diol with a sterically large core, namely bis(*p-tert*-butylphenyl)bis[*p*-(2-(2-hydroxyethoxy)-ethoxy)phenyl]methane (diol BG **7**), was synthesized by a multiple step method and successfully used for the preparation of a sebacate-based polyester 30-crown-10 (30C10) rotaxane with blocking groups or stoppers along the backbone. It was found that the resulting polyrotaxane had a threading efficiency (*m*/*n* value, the average number of cyclic molecules threaded per repeat unit) 5 times as high as that without BG under the same conditions, which proved that the BG can effectively prevent threaded 30C10 from slipping off the polymeric backbone during the preparation of the polyrotaxane. Additionally, new evidence for the formation of the polyrotaxane was demonstrated, including a chemical shift of threaded 30C10 protons different from that of the unthreaded species, a through-space interaction between 30C10 and the backbone proved by 2D NOESY measurements, and hydrolytic recovery of 30C10.

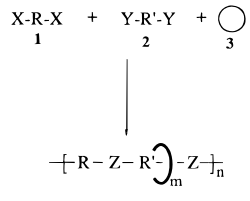
Introduction

Polyrotaxanes are new polymeric materials with novel architectures in which macrocycles are threaded onto a linear polymeric backbone.[1] Upon introduction of different cyclic molecules, the properties of a polymer are expected to be altered on purpose. Two main classes of polyrotaxanes have been widely studied in recent decades: cyclodextrin-based[2−12] and crown ether-based.[13−20]

Preparation of different crown ether-based polyrotaxanes is one of the main goals we are pursuing.[13−20] The most popular method employed in our lab is polycondensation with a crown ether as solvent (Scheme 1).[17,18] By this approach, different polyrotaxanes **4**, e.g., polyester[18] and polyurethane[17] rotaxanes with 30C10, 42C14, and 60C20 as macrocyclic components, were obtained. Since threaded crown ether molecules can move along the polymeric backbone, they can slip off the backbone during the preparation period, especially while the polymer is of low molecular weight. Therefore, different monofunctional bulky "blocking groups" (BGs) were prepared[21] to lower the extent of dethreading and thus increase threading efficiency (*m*/*n* values). Using these BGs, polyrotaxanes of type **6** (Scheme 2) were prepared and had an average *m*/*n* value indeed higher than that without BG.[18] However, the molecular weight of the polymer is limited by introduction of these BGs and dethreading can still occur during the polymerization period because of the existence of some macromolecules with only one end blocked (**6b**) and/or no end blocked (**4**), as shown in Scheme 2. Additionally, in both polyrotaxanes **4** and **6**, threaded macrocycles can accumulate and crystallize to form separate phases.[18]

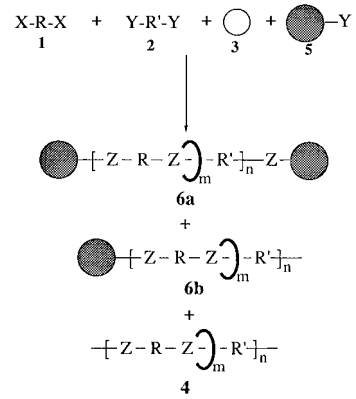
In this paper, we report the synthesis and characterization of a difunctional blocking group (diol BG **7**) and its derived polyrotaxane **8** with a novel architecture, in which threaded macrocycles are confined between stoppers (Scheme 3).

Scheme 1



Where X+Y⟶Z, e.g., X=COCl, Y=OH, Z=COO; **3**: macrocycle, e.g., 30C10; **4**: polyrotaxane

Scheme 2



Where X + Y ⟶ Z, e.g., X=COCl, Y=OH, Z=COO; **3**: macrocycle, e.g., 30C10; **5**: monofunctional blocking group; **6a**, **6b**, and **6c**: polyrotaxane

Experimental Section

Chemical Reagents and Measurements. All chemicals were reagent grade and used directly as received from Aldrich unless otherwise specified. All solvents were HPLC or GC grade. 30C10 was prepared by a well-established procedure.[22] Melting points were taken in capillary tubes and have been corrected. Proton and carbon NMR spectra, reported in ppm, were obtained on a 400 MHz Varian spectrometer using chloroform-*d* solutions with tetramethylsilane as an internal standard. The NOESY study was performed at room temperature with a mixing time of 1 s and relaxation time of 2 s. The following abbreviations have been used in describing NMR spectra: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), and m (multiplet); coupling constants (*J*) are in Hertz. Elemental analyses were performed by Atlantic Microlab of Norcross, GA. GPC analyses were done with a Waters 150CALC/GPC system with polystyrene−divinylbenzene columns, using polystyrene standards. The instrument was fitted with a refractive index detector. The glass transition and melting temperatures of polymers were measured with a Perkin-Elmer thermal analysis system at a rate of 10 °C/min

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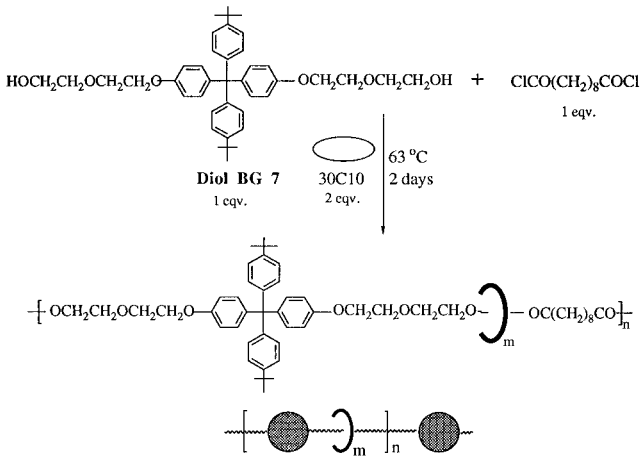
Scheme 3



8: polyrotaxane m/n=0.061
13: model Polymer, m/n=0

for both heating and cooling; all reported values were the centers of transitions from second heatings. TGA data were obtained using a DuPont TGA 951 instrument at a scan rate of 40 °C/min.

Ethyl 4-(Benzyloxy)benzoate (9). After benzyl bromide (86.00 g, 502.8 mmol) and ethyl 4-hydroxybenzoate (56.00 g, 337.0 mmol) had been dissolved in 500 mL of DMF, 75.00 g (584.6 mmol) of potassium carbonate was added. The reaction ran for 18 h at 50−60 °C under the protection of nitrogen. After the system had been cooled, the product was dissolved in toluene (300 mL) and washed with water (4 × 120 mL). A yellow solid was obtained after the solvent in the organic phase had been removed. The crude product was recrystallized in a mixture of hexane and ethyl acetate (250 mL, 1:6) to afford a white solid (68.0 g, 79%), mp 43.3−44.3 °C (lit.[23] 45.5 °C). ^{1}H NMR: 1.37 (t, J = 7.0, 3H), 4.33 (q, J = 7.0, 2H), 5.12 (s, 2H), 6.99 (d, J = 8.4, 2H), 7.34−7.44 (m, 5H), 7.98 (d, J = 8.4, 2H).

Bis(*p*-*tert*-butylphenyl)(*p*-(benzyloxy)phenyl)methanol (10). After 14.5 g (597 mmol) of magnesium turnings had been loaded into a 500 mL flask containing THF (100 mL, Na dried), 4-*tert*-butylbromobenzene (120.6 g, 565.9 mmol) in THF (100 mL) was added to the system dropwise under the protection of nitrogen over 0.5 h. The reaction was initiated by gently heating the mixture. After refluxing for 1 h, the reaction ran for an additional 2 h at room temperature. Then **9** (62.8 g, 245 mmol) in THF (150 mL, Na dried) was added to the system slowly and and it was refluxed overnight. After the system had been cooled, the mixture was neutralized with HCl (10%, 500 mL). The product was extracted with toluene (2 × 250 mL). The combined organic phase was washed with water (3 × 500 mL). After the solvent in the organic phase had been removed, the crude product was recrystallized in a mixture of acetone and methanol (400 mL, 1:1), yielding 73.0 g (62%) of white product, mp 63.0−64.0 °C. ^{1}H NMR: 1.29 (s, 18H), 3.04 (s, 1H), 5.03 (s, 2H), 6.90 (d, J = 6, 2H), 7.25−7.43 (m, 15H). ^{13}C NMR: 31.34, 34.37, 51.91, 69.95, 113.74, 124.51, 127.53, 127.92, 128.24, 128.54, 130.15, 136.80, 137.06, 141.20, 149.34, 157.57 (16 peaks as required). Anal. Calcd for $C_{34}H_{38}O_2$: C, 85.31; H, 8.01. Found: C, 85.35; H, 8.05.

Bis(*p*-*tert*-butylphenyl)bis(*p*-hydroxyphenyl)methane (11) and Bis(*p*-*tert*-butylphenyl)(*p*-hydroxyphenyl)(*p*-(benzyloxy)phenyl)methane (12). 10 (63.00 g, 131.6 mmol) was dissolved in phenol (260.0 g, 2.763 mol) by heating in a 1 L flask. As soon as four drops of 12 M HCl had been added as catalyst, the solution turned deep red immediately. The mixture was refluxed for 24 h. After it had been cooled, the mixture was dissolved in 800 mL of CH_2Cl_2 and was washed with water (8 × 250 mL). After the solvent in the organic phase was removed, the resulting oily residue was boiled in a mixture of hexane and toluene (1 L, 1:1). A slightly yellow solid precipitated from the solution and was further purified by silica gel chromatography with methylene chloride as eluting solvent to afford two fractions. Second fraction (**11**): 17.0 g (28%), mp 270.7−273.0 °C. ^{1}H NMR: 1.29 (s, 18H), 4.85 (s, 2H), 6.79 (d, J = 8.8, 4H), 7.02−7.08 (m, 8H), 7.24 (d, J = 8.8, 4H). ^{13}C NMR: 31.34, 34.27, 70.44, 113.99, 124.08, 130.59, 132.31, 139.78, 144.12, 148.37, 153.31 (11 peaks as required). Anal. Calcd for $C_{33}H_{36}O_2$: C, 85.30; H, 7.81. Found: C, 85.36; H, 7.88. First fraction (**12**): 25.2 g (34%). ^{1}H NMR: 4.70 (s, 1H), 5.02 (s, 2H), 6.70 (d, J = 8.8, 2H), 6.85 (d, J = 8.8, 2H), 7.10−7.03 (m, 8H), 7.22−7.25 (d, J = 8.8, 4H), 7.32−7.44 (m, 5H). ^{13}C NMR: 31.34, 34.27, 69.94, 113.33, 113.97, 124.08, 127.54, 127.91, 128.54, 130.59, 132.13, 132.35, 139.84, 144.12, 148.35, 153.27 (16 peaks, theory: 20). **12** was converted to **11** as follows: 16.00 g (28.84 mmol) of compound **12** was dissolved in THF (200 mL) and 1 g of palladium on carbon (10%) was added as catalyst. The mixture was loaded into a 500 mL high-pressure flask and subjected to deprotection at 60 psi of H_2 for 5 days. After the reaction had been finished, the catalyst was removed by filtration and solvent was evaporated to afford a white solid. The product was recrystallized in toluene (150 mL), 12 g (90%).

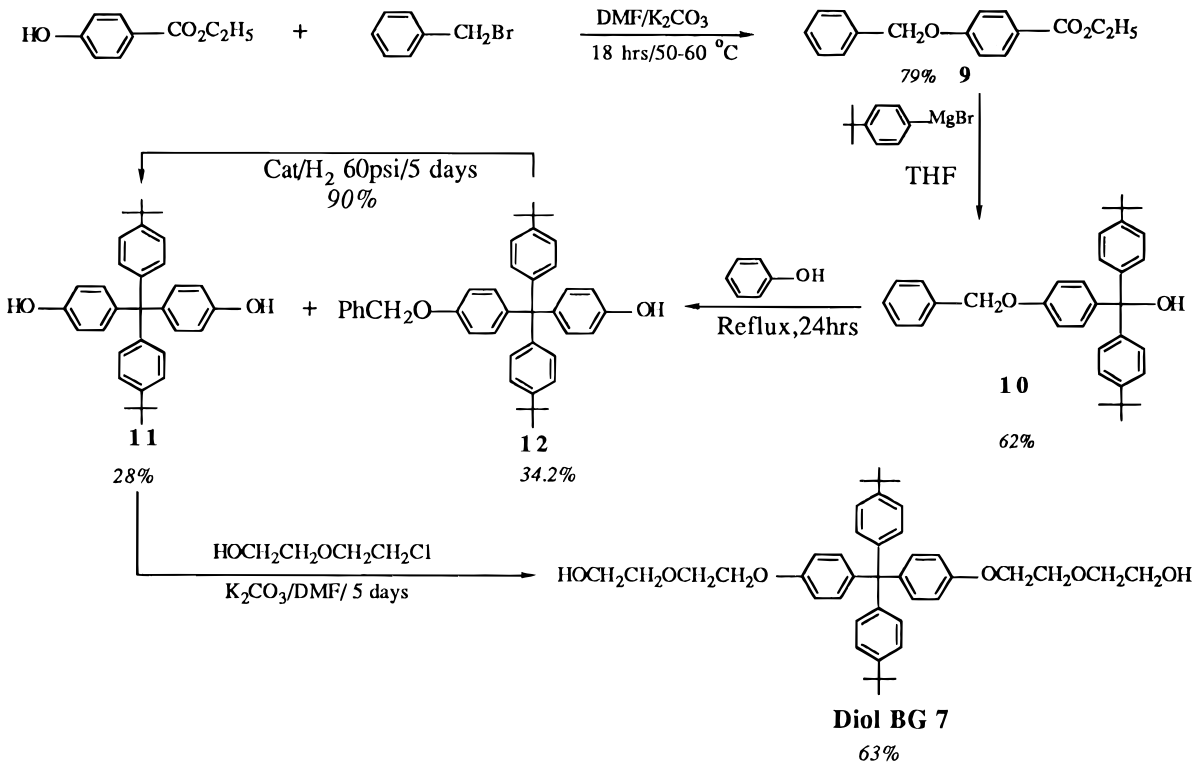
Bis(*p*-*tert*-butylphenyl)bis[*p*-(2-(2-hydroxyethoxy)ethoxy)phenyl]methane (7). After **11** (15.0 g, 32.3 mmol) and 2-(2-chloroethoxy)ethanol (85.0 g, 682 mmol) had been dissolved in DMF (500 mL), K_2CO_3 (15.0 g, 117 mmol) was added. The reaction ran for 5 days at 70−80 °C under the protection of nitrogen. After the system had been cooled, salt was removed by filtration. Upon removal of DMF, the product was dissolved in CH_2Cl_2 (300 mL) and washed with water (2 × 250 mL). After the solvent in the organic phase had been removed, the resulting solid was purified by silica gel chromatography with ethyl acetate as eluting solvent. Yield: 13 g (63%). Mp: 164.7−165.6 °C. ^{1}H NMR (Figure 1): 1.30 (s, 18H), 2.20 (t, J = 6, 2H), 3.67 (t, J = 4.4, 4H), 3.74−3.78 (m, 4H), 3.89 (t, J = 4.4, 4H), 4.12 (t, J = 4.4, 4H), 6.79 (d, J = 8.8, 4H), 7.05−7.09 (m, 8H), 7.22 (d, J = 8.8, 4H). ^{13}C NMR: 31.34, 34.27, 61.69, 67.21, 69.71, 72.51, 113.11, 124.09, 130.58, 132.14, 139.97, 144.09, 148.35, 156.41 (14 peaks, theory: 15). Anal. Calcd for $C_{41}H_{52}O_6$: C, 76.84; H, 8.18. Found: C, 76.86; H, 8.23.

Polyrotaxane 8. Diol BG **7** (399.6 mg, 0.6235 mmol) was dissolved in 30C10 (547.0 mg, 1.242 mmol) at 63 °C. The homogeneous solution was stirred for 0.5 h under the protection of nitrogen to achieve a hydrogen bonding equilibrium between 30C10 and the hydroxyl groups of BG. Then sebacoyl chloride (150.1 mg, 0.6277 mmol) was added to the system. After polymerization had proceeded for 2 days, the product was dissolved in 3 mL of THF and precipitated into water (200 mL); 3 times, 0.47 g (93%). ^{1}H NMR (Figure 2, top): 1.29 (s, 26H), 1.57 (s, broad, H_2O plus 4H of $-OCOCH_2CH_2-$), 2.31 (t, J = 7.6, 4H), 3.52 (s, variable), 3.75 (t, J = 4.8, 4H), 3.83 (t, J = 4.8, 4H), 4.09 (t, J = 4.8, 4H), 4.24 (t, J = 4.8, 4H), 6.77 (major peak) and 6.85 (minor peak) (d, J = 8.8, total 4H), 7.04−7.08 (m, 8H), 7.22 (d, J = 8.8, 4H); m/n: first ppt 0.061, second ppt 0.060, and third ppt 0.061 (3.4 mass % 30C10), based on the integrals of H_d (δ4.09) and 30C10 protons (δ3.52). GPC measurements: $M_n = 16.5 \times 10^3$ and $M_w = 28.8 \times 10^3$ (PS standards). DSC results: T_g = 15.2 °C but no T_m! TGA data: 294 °C; 5% weight loss temperature in air.

Model Polymer 13. Model polymer **13** is the backbone of polyrotaxane **8**. It was prepared by the same procedure as that for **8** except that THF was used as solvent instead of 30C10. ^{1}H NMR (Figure 2, bottom): 1.29 (s, 26H), 1.57 (s, broad, H_2O plus 4H of $-OCOCH_2CH_2-$), 2.31 (t, J = 7.6, 4H), 3.75 (t, J = 4.8, 4H), 3.83 (t, J = 4.8, 4H), 4.09 (t, J = 4.8, 4H), 4.24 (t, J = 4.8, 4H), 6.77 (d, J = 8.8, 4H), 7.04−7.08 (m, 8H), 7.22 (d, J = 8.8, 4H). GPC measurements: $M_n = 18.7 \times 10^3$ and $M_w = 46.1 \times 10^3$ (PS standards). DSC results: T_g = 14.5 °C and T_m = 39.8 °C. TGA data: 444 °C; 5% weight loss temperature in air.

Hydrolysis of Polyrotaxane 8. A 390 mg sample of polyrotaxane **8** (m/n = 0.061) was dissolved in THF (4 mL). After 3 mL of potassium hydroxide aqueous solution (10 mol/L) had been added, the mixture was refluxed for 24 h. Upon the removal of all solvent under reduced pressure, the hydrolysis product was extracted with $CHCl_3$ (3 × 50 mL); $CHCl_3$ was evaporated. It was found that both 30C10 and diol BG **7** were recovered. ^{1}H NMR: Figure 3, middle. Pure 30C10 (10

Scheme 4



mg, 75%) was separated by further extraction using hexane (3 × 50 mL). ^{1}H NMR: Figure 3, top.

Results and Discussion

1. Diol-Functionalized Blocking Group 7. Diol BG **7** was synthesized by a five-step approach shown in Scheme 4. The first step was to protect the hydroxyl group of ethyl 4-hydroxybenzoate with benzyl bromide in DMF solution, using excess potassium carbonate to remove HBr from the reaction. **9** was obtained in 79% yield. **9** was converted to tertiary alcohol **10** by a Grignard reaction. In this case, to initiate the reaction, heating the system is needed due to the low reactivity of *p*-bromo-*tert*-butylbenzene and further refluxing is necessary to increase the reaction rate.[21] **10** was purified by recrystallization with a yield of 62%. Following the approach used by Mikroyannidis in the preparation of bis(*p*-hydroxyphenyl)diphenylmethane[24] and later by us with other difunctional BGs,[25] compound **10** underwent Friedel−Crafts reaction by refluxing in a large excess of phenol with acid as a catalyst. Because of the steric effect, only the para substitution product was formed. Interestingly, in addition to compound **12**, deprotected product **11** was obtained with a fairly high yield (28%). The *in situ* deprotection of the benzyl ether group in this reaction is probably due to an acid-induced ether cleavage and/or ether exchange since a large excess of phenol exists in the system. **12** was quantitatively deprotected by hydrogenation with Pd/C as catalyst.[26] The structure of compound **11** is very similar to that of Bisphenol A. It was successfully used for the preparation of poly(arylene ether rotaxane)s; this will be published later.

We also wish to have an aliphatic hydroxyl-terminated difunctional BG. Therefore, **11** was allowed to react with an excess of 2-(2-chloroethoxy)ethanol in DMF at 70−80 °C, using potassium carbonate as a base, to afford diol BG **7** in 63% yield. Harrison investigated the steric influence of various monofunctional blocking groups and found that tris(*p*-*tert*-butylphenyl)methanol could constrain macrocycles comprised of up to 42 methylene groups.[27−29] Therefore, compound **7** is large enough to block 30C10 and thus its derived polyester rotaxane was studied.

2. Diol BG-based Polyrotaxane 8. Polyrotaxane **8** was synthesized by a polycondensation with 30C10 as solvent (Scheme 3). Unthreaded 30C10 was removed by three reprecipitations from THF solution into water. Surprisingly, compared to that of model polymer **13**, a new signal (δ 3.52) appeared instead of the signal (δ 3.67) of free 30C10 in the ^{1}H NMR spectrum of **8** (Figure 2). Since no chemical shift change has been previously reported for polyrotaxanes based on aliphatic crown ethers,[14−18] how do we explain the new peak? To answer this question, we hydrolyzed the polyrotaxane by refluxing it in a basic solution. The dried reaction products were extracted with chloroform to separate the neutral compounds from sebacic acid potassium salt. As shown in the proton NMR spectrum of neutral hydrolytic products (Figure 3, middle), the free 30C10 signal (δ 3.67) returned and the δ 3.52 signal disappeared, which indicated that the new signal in polyrotaxane **8** was indeed due to threaded 30C10. In addition, by extracting the neutral hydrolytic products with hexane, pure 30C10 was recovered (75%) (Figure 3, top).

What causes the upfield shift of the protons of 30C10 in polyrotaxane **8**? According to the COSY spectrum of polyrotaxane **8**, there is no interaction between the δ 3.52 peak and any peaks of the polymer backbone, which eliminates the possibility that the signal is from the protons of groups chemically bonded to the backbone. Thus the only possible reason is the existence of some through-space interaction. The NOESY spectrum of the polyrotaxane (Figure 4) did show that the signals, a′ and b′ (hidden in the multiplet for b and c) in the aromatic region of the polymer backbone correlate with threaded 30C10. Apparently, the aromatic π electrons in the diol

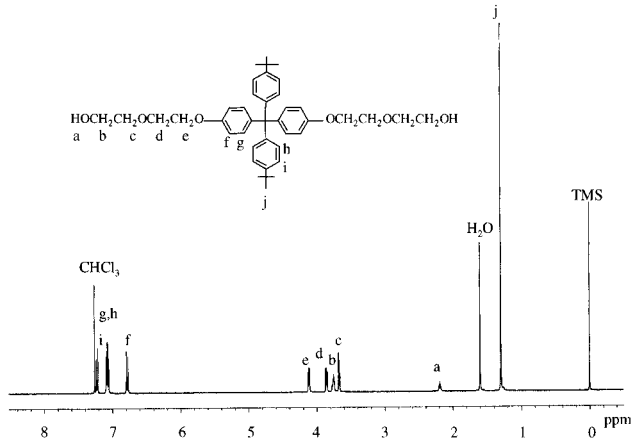


Figure 1. 400 MHz proton NMR spectrum of diol BG **7** in $CDCl_3$ at 25 °C.

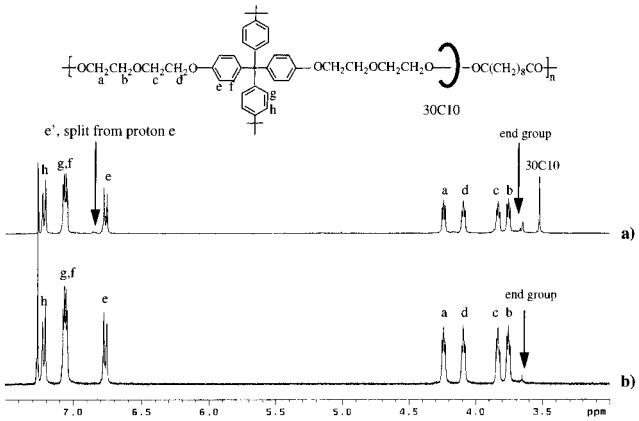


Figure 2. 400 MHz proton NMR spectra of (a) polyrotaxane **8** and (b) model polyester **13** in $CDCl_3$ at 25 °C.

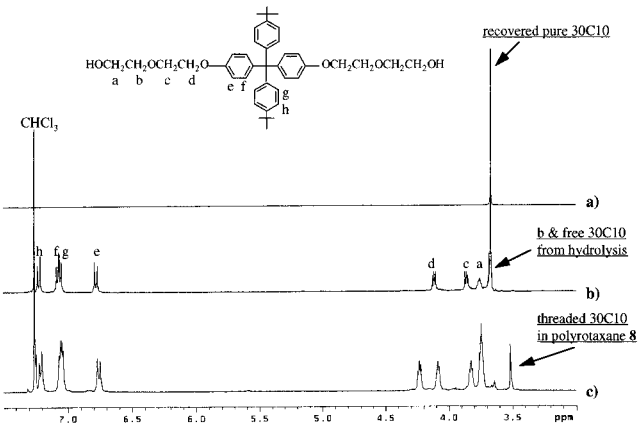


Figure 3. 400 MHz proton NMR spectra of (a) recovered pure 30C10, (b) the neutral hydrolytic products, and (c) polyrotaxane **8** in $CDCl_3$ at 25 °C.

BG unit shield threaded 30C10 protons and the aromatic protons a′ and b′ are deshielded correspondingly. Therefore, the novel structure of the diol BG-based polyrotaxane (Scheme 3) brought us new tools to prove the formation of polyrotaxanes.

To study the constraining ability of diol BG **7**, the threading efficiency (*m*/*n* value) of polyrotaxane **8** was determined by the NMR integrals of the threaded 30C10 protons (δ 3.52) and methylene protons of $-OCH_2-$ (proton d, δ 4.09) in the backbone. It was found that polyrotaxane **8** had an *m*/*n* value (0.061) 5 times as high as that of a polyrotaxane of type **4** without BG (*m*/*n* = 0.012)[30] as well as 4.4 times that (0.014) of a polyrotaxane of type **6** with monofunctional BG in the present work, the latter two systems prepared from 1,10-decanediol, sebacoyl chloride, and 30C10 under the same conditions. This result can be explained by dethreading processes (Schemes 5−7).

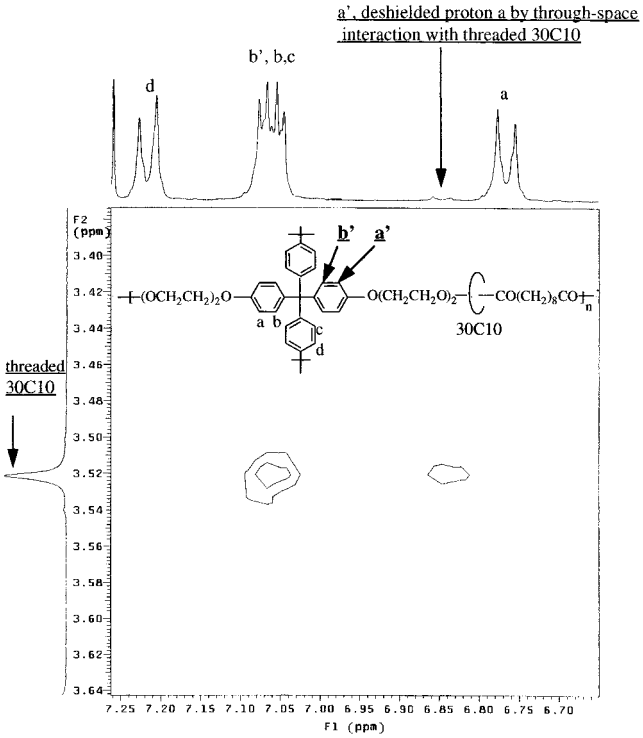
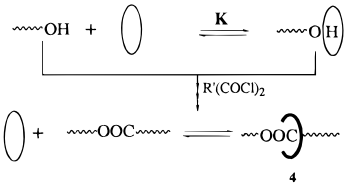
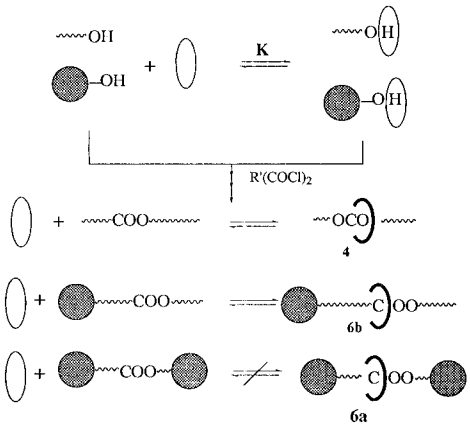


Figure 4. Correlated regions of the 2D NOESY spectrum of polyrotaxane **8** in $CDCl_3$ at 25 °C.

Scheme 5. Proposed Threading and Dethreading Mechanisms during the Formation of Polyrotaxane 4

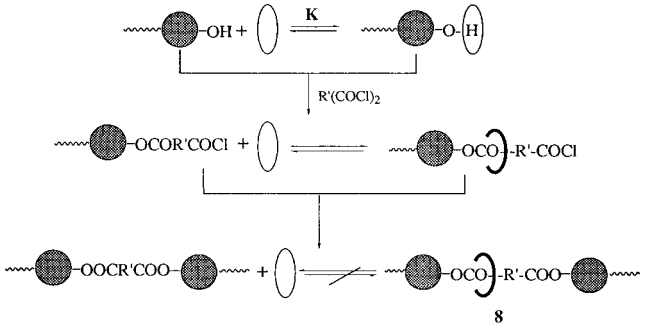


Scheme 6. Proposed Threading and Dethreading Mechanisms during the Formation of Polyrotaxane 6



We believe that hydrogen bonding of −OH end groups with the crown ethers provides the driving force for the threading, formation of ester linkages taking place through the macrocylic cavity in a proportion depending on ring size and other parameters. For polyrotaxane **4** (Scheme 5), there are not any stoppers to keep the cyclic molecules on the backbone. Since the ester groups

Scheme 7. Proposed Threading and Dethreading Mechanisms during the Formation of Polyrotaxane 8



presumably exert no attractive force on the threaded cyclic components, once the OH group has been converted to an ester moiety, the cyclic molecules can move along the polymer backbone and dethread during the polymerization period, especially while the polymer has a molecular weight lower than that of entanglement. Compared to **4**, polyrotaxane **6** with monofunctional BG can diminish the dethreading by the formation of **6a** (Scheme 6). However, dethreading still occurs during the preparation period because at any given time some macromolecules have only one end blocked (**6b**) and/or no ends blocked (**4**). For polyrotaxane **8**, dethreading only happens during a very limited stage, whose extent will be minor compared to the cases for **4** and **6**. As shown in Scheme 7, as soon as 30C10 is located in a BG−ester−ester−BG sequence, it will be restricted between the stoppers and thus cannot slip off the backbone except when the chemical bonds of the backbone are broken. Using a diacid chloride BG together with **7** will eliminate all possible dethreading, once the ester bond is formed. The synthesis of this BG and its derived polyrotaxane are currently under investigation and will be reported later.

Conclusion

A difunctional blocking group (diol BG **7**) was prepared by a five-step approach. Its derived polyester rotaxane **8** had a much higher *m*/*n* value than a corresponding system without BG. Because threaded 30C10 was restricted between stoppers and had a chemical environment different from unthreaded species, new spectral evidence for the formation of the polyrotaxane was demonstrated.

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References and Notes

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