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A Strategy To Eliminate Dethreading during the Preparation of Poly(ester/crown ether rotaxane)s: Use of Difunctional Blocking Groups

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ABSTRACT: A novel strategy to completely eliminate dethreading of captured cyclics during the preparation of polyrotaxanes has been developed. A new difunctional blocking group (BG), namely bis(*p*-*tert*-butylphenyl)bis[*p*-((5-(chlorocarbonyl)pentyl)oxy)phenyl]methane (diacid chloride BG **14**), was prepared in an overall yield of 63% by a three-step method. BG **14** polymerized with bis[*p*-((2-hydroxyethoxy)ethoxy)phenyl]bis(*p*-*tert*-butylphenyl)methane (diol BG **15**) using 30-crown-10 (30C10) as solvent to afford poly(ester rotaxane)s **17** with unique architectures having two BGs per repeat unit. The formation of the polyrotaxanes was proved by a chemical shift of threaded 30C10 different from that of unthreaded species, hydrolytic recovery of 30C10, and a 2D NOESY study and supported by the GPC analysis. It was found that the resulting polyrotaxanes **17** had threading efficiencies (*m*/*n* values, average number of cyclic molecules per repeat unit) 2 times as high as those of poly(ester rotaxane)s **16** made under the same conditions from diol BG **15** and sebacoyl chloride. By optimizing the conditions, the threading efficiency was increased to 0.172 in polyrotaxane **17c**, almost 14 times as high as that (0.012) of the polyrotaxane of type **1** made from decanediol and sebacoyl chloride.

Introduction

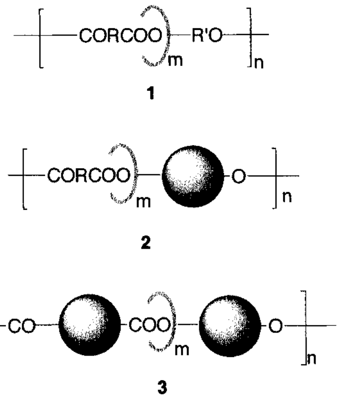
Compared to the conventional polymeric materials, polyrotaxanes, prepared by threading macrocycles onto linear polymeric backbones, bear novel architectures and show many interesting properties.[1] Cyclodextrins (CD)[2−4] and crown ether molecules[1,5−16] have been the most common macrocycles used in the preparation of polyrotaxanes. The formation of CD-derived polyrotaxanes is well understood to result from inclusion complexation between CD and linear components, and polyrotaxanes with high threading efficiencies have been obtained.[2−4] However, the driving force for the formation of crown ether-based poly(ester rotaxane)s and related systems has not been clearly established and the threading efficiency is not so high. Since the *m*/*n* value is directly related to the properties of polyrotaxanes, we urgently need to identify the driving force for the formation of these polyrotaxanes and design a method to increase the *m*/*n* values.

While most of our early work was with poly(ester pseudorotaxane)s of type **1** (Chart 1), different blocking groups (BGs) were designed recently in order to achieve higher *m*/*n* values.[13−18] Indeed, blocking groups can prevent threaded cyclic molecules from slipping off the backbone and the *m*/*n* value of a poly(ester rotaxane) of type **2** using a bulky diol as the only diol monomer was 5 times as high as that of a poly(ester pseudorotaxane) of type **1** without a BG (Chart 1).[13]

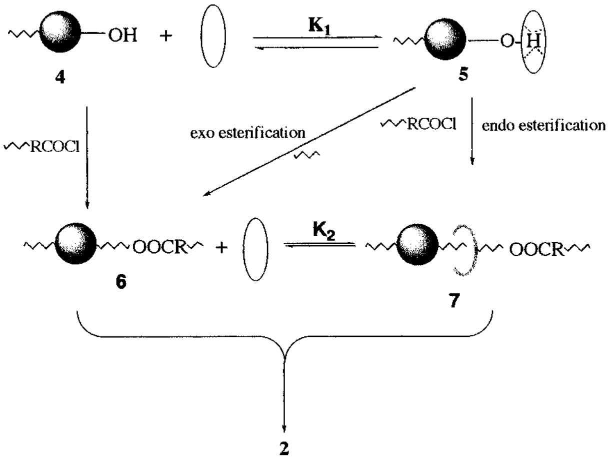
We proposed[12−15] that the hydrogen bonding of the hydroxyl group of **4** with the crown ether to form **5** provides the driving force for threading in poly(ester rotaxane)s; i.e., K_1 is significant (Scheme 1). For polyrotaxanes of type **2**, dethreading still occurs during the reaction period because once the ester bond forms in an endo fashion to capture the ring (structure **7**), there is no or minimal retaining force unless the cyclic is trapped between two BGs and thus loss of the cyclic can occur from **7**, leading to **6** plus free cyclic; i.e., K_2 is very small (Scheme 1). Experimentally, the degree of dethreading in the preparation of the polyrotaxanes of type **2** increased linearly as the proportion of diol BG in the total diol decreased.[14]

It is expected that dethreading during the polyesterification period can be eliminated by using two bulky

Chart 1. Various Main Chain Polyrotaxanes



Scheme 1. Proposed Mechanisms for Threading and Dethreading during the Preparation of Polyrotaxanes 2



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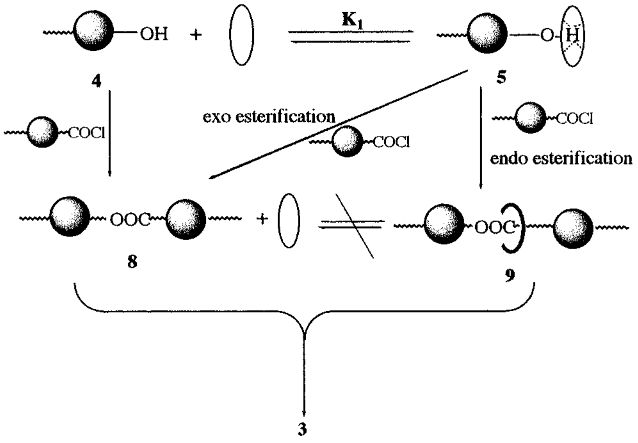
Scheme 2. Proposed Mechanisms for Threading and Dethreading during the Preparation of Polyrotaxanes 3



monomers, a diacid chloride BG and a diol BG, to form polyrotaxanes of type **3** (Chart 1), because the threaded cyclic is mechanically confined between two BG units as soon as the ester bond (structure **9**) forms and there can be no dethreading equilibrium leading to **8** (Scheme 2). Here, we report the preparation of a diacid chloride BG and derived polyrotaxanes of type **3** to test this idea.

Results and Discusion

1. Diacid Chloride-Functionalized Blocking Group 14. Diacid chloride BG **14** was synthesized by a three-step method with an overall yield of 63% (Scheme 3). By reacting **10**[13] with a large excess of bromide **11** in a basic solution, diester BG **12** was obtained in 80% yield. Ester **12** was easily converted to diacid BG **13** by refluxing its basic solution in ethanol followed by neutralization with acid. Although the reaction was quantitative, recrystallization lowered the yield to 90%. Finally, diacid chloride BG **14** was prepared by reacting the diacid BG with thionyl chloride. Since **14** was to be used as a monomer for polyesters, it was purified by recrystallization in hexane twice to afford needle crystals. The structure of **14** was confirmed by its proton NMR spectrum (Figure 1) and elemental analysis.

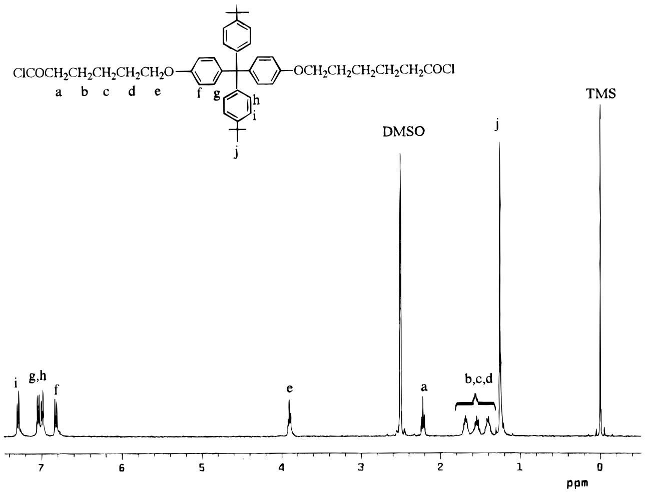


Figure 1. 400 MHz proton NMR spectrum of diacid chloride BG **14** in DMSO-d_6.

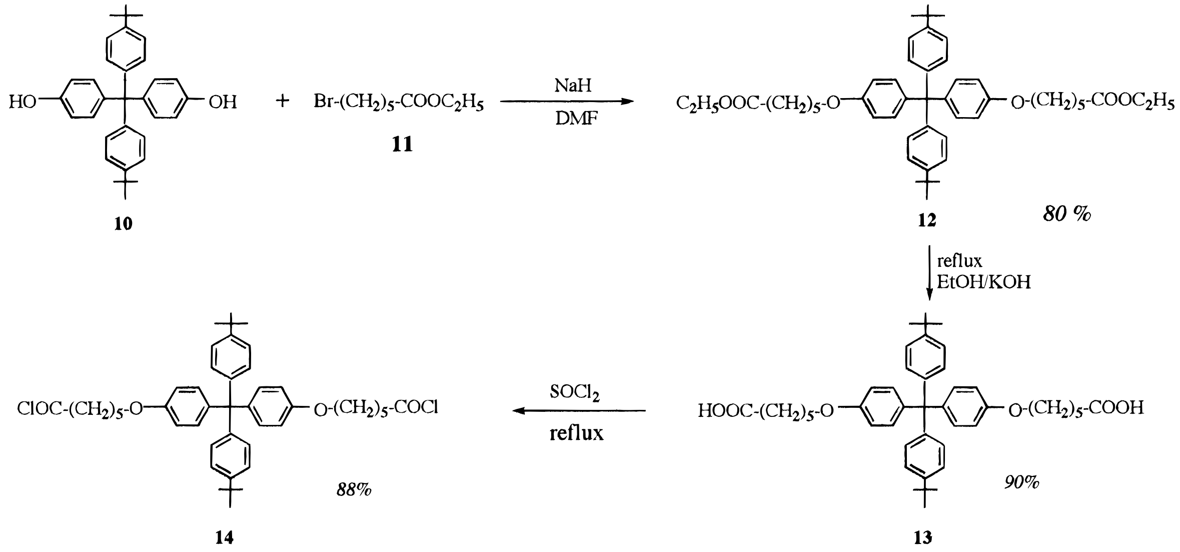
It was reported that tris(*p*-*tert*-butylphenyl)methanol could block macrocycles up to 42 methylene groups.[19] Thus **14** is bulky enough to constrain 30C10 and can be used to provide stoppers along the polymeric chain as well as the diol BG **15** we previously used.[13] By using **14** as the acid chloride monomer and **15** as the diol monomer, polyrotaxanes of type **3** (Chart 1) were successfully prepared; this provides a novel strategy to eliminate dethreading during the polyesterification reaction.

2. Polyrotaxanes 16a and 16b. For comparison purposes, polyrotaxanes **16a** and **16b** were prepared by polycondensation of diol **15** with sebacoyl chloride using 30C10 as solvent (Scheme 4).[13,14] Formation of the polyrotaxanes was previously proved by hydrolytic recovery of 30C10, a NOESY study, and a chemical shift of threaded 30C10 protons different from that of the unthreaded species.[13] The conditions and results are summarized in Table 1.

3. Polyrotaxanes 17a–17c and Model Polymer 17d. A. Synthesis. Polyrotaxanes **17a–17c** were prepared by polycondensation of diacid chloride BG **14** with diol BG **15** using 30C10 as solvent (Scheme 5). Reaction conditions and results are specified in Table 1. The polymers were purified by reprecipitation from THF solution into water. Model polyester **17d** was prepared by using diglyme as solvent instead of 30C10.

B. Characterization. I. GPC Analysis. 30C10 is a monodisperse small molecule. It has its own specific retention volume in GPC with a certain column, which

Scheme 3. Preparation of Diacid Chloride BG 14



Scheme 4. Preparation of Polyrotaxanes 16a and 16b

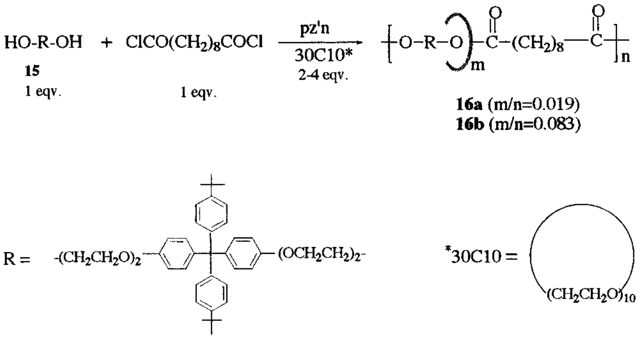
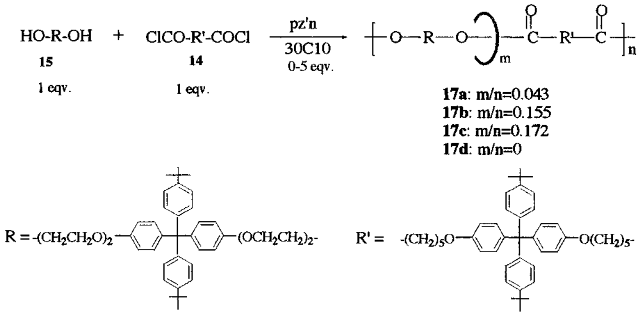


Table 1. Reaction Conditions and Results for Polyrotaxanes 16 and 17

			m/n^b				
poly-rotaxane	feed ratio (30C10/diol)	temp (°C)[a]	1st ppt	2nd ppt	3rd ppt	$10^{-3}M_n$	$10^{-3}M_w$
16a	2	153	0.020	0.020	0.019	6.0[c]	11.3[c]
16b	4	63	0.085	0.084	0.083	12.0[c]	22.1[c]
17a	2	153	0.044	0.044	0.043	9.0[d]	18.2[d]
17b	4	63	0.156	0.157	0.155	8.9[d]	31.0[d]
17c	5	63	0.175	0.173	0.172	25.2[d]	87.3[d]
17d	0[e]	90	0			18.5[d]	37.5[d]

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

Scheme 5. Preparation of Polyrotaxanes 17a–17c and Model Polymer 17d



is far separated from that of the polymers (Figure 2). The excellent resolution provides a reliable tool to prove the absence of free crown ether and the formation of polyrotaxanes. It was found that the GPC trace of polyrotaxane **17c** has no 30C10 peak while that (Figure 2b) of the mixture of **17c** and free 30C10 (5%) has two well-resolved peaks at 28.4 and 19.1 mL, corresponding to those of polyrotaxane **17c** (Figure 2c) and free 30C10 (Figure 2a), respectively. This result directly proved that no free 30C10 existed in polyrotaxanes **17a**–**17c** and that they are not simple mixtures; it also demonstrated that precipitation is an effective method to remove the unthreaded 30C10.

II. Proton NMR Spectroscopy. After three precipitations, no signal (3.67 ppm) of free 30C10 was present in the proton NMR spectrum (Figure 3a) of polyrotaxanes **17a**–**17c**; instead, a new signal at 3.50 ppm appeared, compared to that (Figure 3b) of model polymer **17d**. Is the new signal from threaded 30C10, and if so, why does it have a different chemical shift from that (3.52 ppm) of threaded 30C10 in polyrotaxane **16**?[20] To answer these questions, the same characterization techniques were applied to polyrotaxanes **17** as were used for **16**.[13,14]

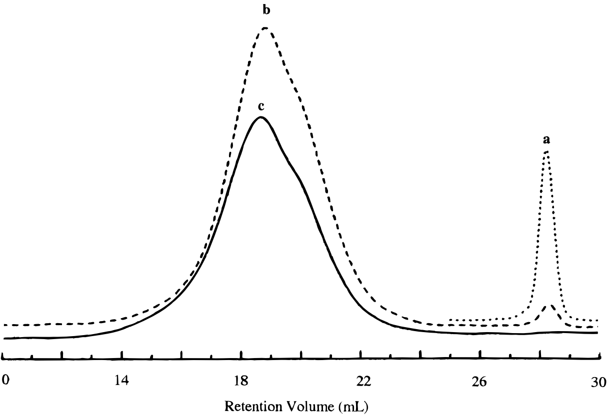


Figure 2. GPC traces of (a) 30C10, (b) a mixture of **17c** and 5% free 30C10, and (c) polyrotaxane **17c** in chloroform.

First, polyrotaxane **17c** was hydrolyzed by refluxing its basic solution in THF. It was found that the 3.50 ppm signal disappeared and that (3.67 ppm) of free 30C10 returned in the neutral hydrolytic products (Figure 4b) and by extracting with hexane, pure 30C10 was recovered (Figure 4a). This degradation experiment directly proved that the signal at 3.50 ppm in polyrotaxanes **17a**–**17c** is indeed from the protons of the threaded 30C10 and, furthermore, that the crown ether retained its integrity in the polyrotaxanes.

A 2D COSY study of **17c** revealed that the 3.50 ppm signal is not coupled with any protons in the backbone (Figure 5); this ruled out the possibility that the signal is from protons chemically bonded to the backbone. Thus the only possible reason for the change of chemical shift of 30C10 before and after threading is the existence of a through-space interaction, which was well demonstrated in our previous work.[13,14] The 2D NOESY spectrum of polyrotaxane **17c** (Figure 6) indeed shows a correlation similar to that observed in polyrotaxane **16**.[13,14] The protons of threaded 30C10 (3.50 ppm signal) are correlated with the aromatic protons e′, f′, g′, h′, i′, and j′. Therefore, the upfield shift for threaded 30C10 in **17** is due to shielding by the aromatic π electrons in the BG units, the same reason as that for **16**,[13,14] and the corresponding aromatic protons (e, f, g, h, i, and j) were shifted downfield to e′, f′, g′, h′, i′, and j′; the protons e′ and j′ are distinguished from the mother protons, but the protons f′, g′, and i′ are merged with their major peaks. The shielding of 30C10 molecules depends on the distance between BG units because the signal is time averaged.[14] In polyrotaxanes **16** and **17**, there are 22 atoms and 13 atoms between BG units, respectively. Thus threaded 30C10 in **17** experiences stronger shielding than that in **16** and thus its signal shifted upfield further (3.50 vs 3.52 ppm).[20]

4. Threading and Dethreading Mechanisms in the Formation of Polyrotaxanes. Because diacid chloride BG **14** was difficult to dissolve in small amounts of 30C10 at low temperatures, polyrotaxane **17a** was initially prepared at 153 °C with a feed ratio of 30C10 vs diol BG **15** of 2. In order to increase the threading efficiency, a lower temperature and higher feed ratio were applied for **17b**. To understand the effect of introduction of diacid chloride BG **14** on threading efficiency, the corresponding polyrotaxanes **16a** and **16b** were prepared under the same conditions with sebacoyl chloride instead of **14**. As the results in Table 1 show, **17a** and **17b** had threading efficiencies, *m*/*n* values, twice as high as those of **16a** and **16b**. The higher *m*/*n* values for **17** can be easily understood by the proposed threading and dethreading processes (Schemes 1 and 2).

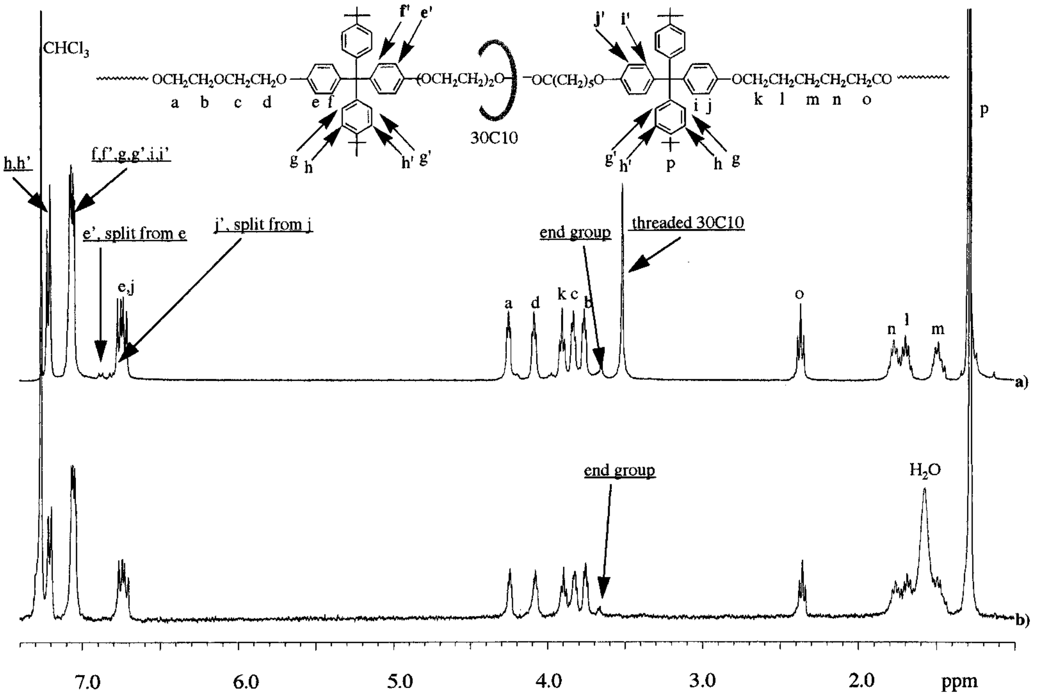


Figure 3. 400 MHz proton NMR spectra of (a, top) polyrotaxane **17c** (*m*/*n* = 0.172) and (b, bottom) model polyester **17d** (*m*/*n* = 0) in $CDCl_3$.

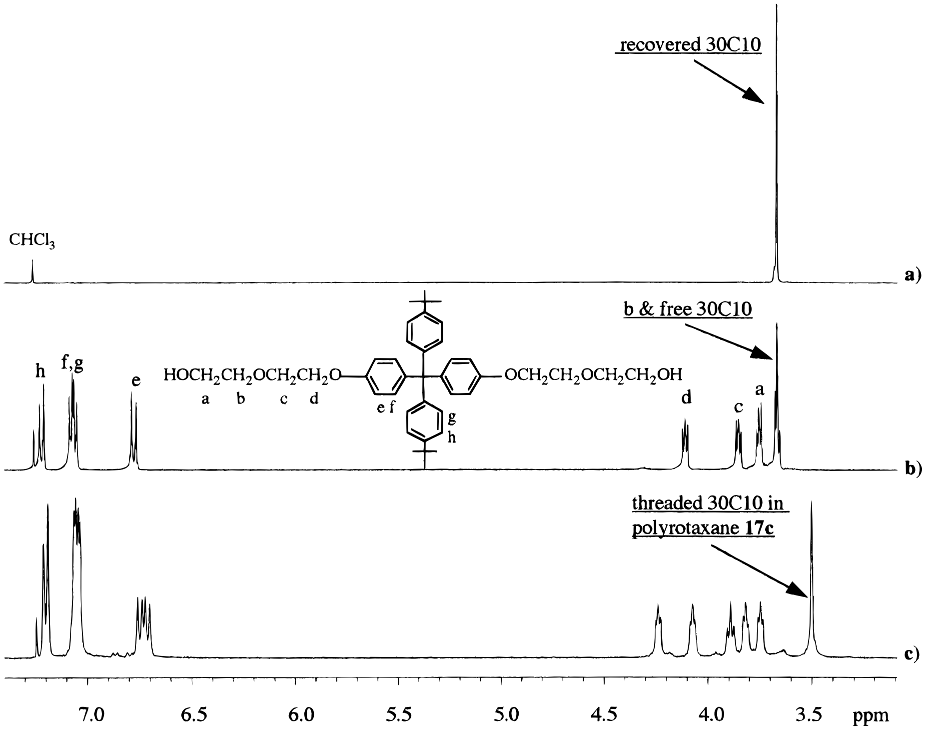


Figure 4. 400 MHz proton NMR spectra of (a, top) recovered 30C10, (b, middle) the neutral hydrolytic products, (c, bottom) polyrotaxane **17c** in $CDCl_3$.

For polyrotaxanes **16**, dethreading occurs during the stage of structure **7** from the endo esterification of the hydrogen-bonded structure **5**, leading to unthreaded **6** before reaction with another diol **15** (Scheme 1), since the ester backbone presumably exerts no retaining force for threaded 30C10 molecules.[13,14] During the preparation of polyrotaxanes **17**, as soon as 30C10 is threaded via the endo esterification of **5**, it is confined between two BG units (structure **9**) and no dethreading can occur to form unthreaded **8** and free crown ether (Scheme 2). Thus by using diacid chloride BG **14** and diol BG **15**, a novel approach to eliminate dethreading during the polycondensation was introduced. Therefore, polyrotaxanes **17** will have the highest *m*/*n* values among the three types of main chain polyrotaxanes, **1**–**3**, made under the same conditions.

The threading efficiencies of **17b** (0.155) and **17c** (0.172) are much larger than the value that can be obtained by a statistical threading for a 30-membered macrocycle.[21] Therefore, the data also indicate that some driving force for threading must exist in the preparation of these polyrotaxanes. Since the ester backbone of the poly(ester rotaxane)s has no strong attractive force for 30C10, hydrogen bonding between the crown ether and the hydroxy groups of diol monomers is a most plausible driving force for threading;[22]

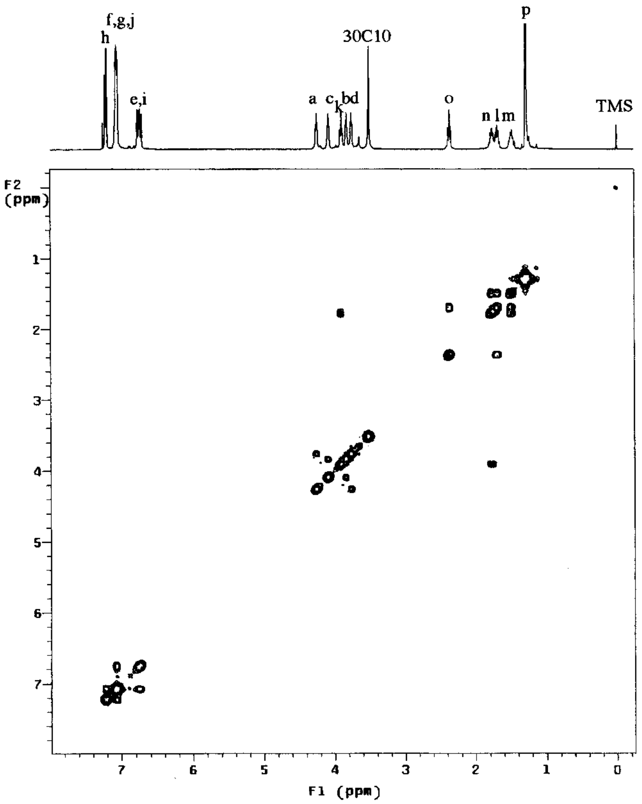


Figure 5. 400 MHz proton NMR 2D COSY spectrum of polyrotaxane **17c** in $CDCl_3$ (for peak assignments, see Figure 3).

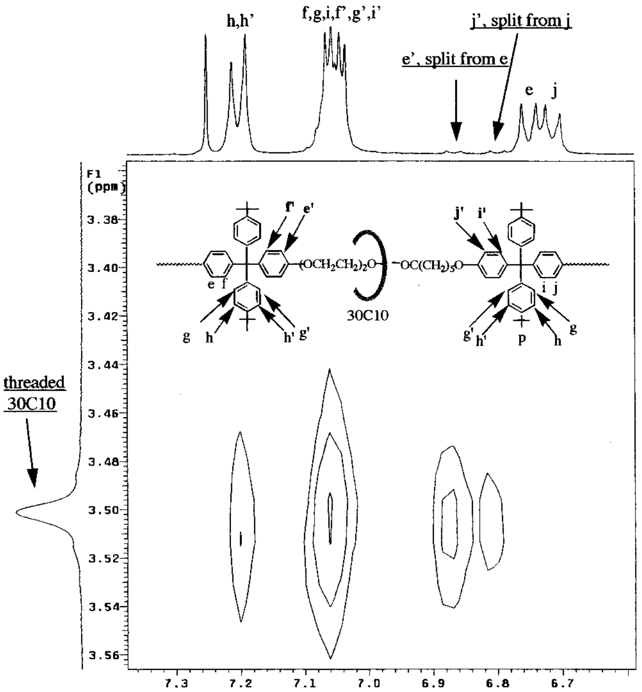


Figure 6. Correlated region of 400 MHz proton 2D NOESY spectrum of polyrotaxane **17c** in $CDCl_3$ at 25 °C.

a fraction of endo esterification of **5**, which depends on the cavity size and other factors, takes places through the macrocycle, leading to **9**, while exo ester bond formation produces unthreaded **8** (Scheme 2).

In addition, it is worth mentioning that by decreasing the polymerization temperature from 153 to 63 °C and increasing the feed ratio of crown ether to diol from 2 to 4, the *m*/*n* values of both polyrotaxanes **16** and **17** were increased about 4-fold (Table 1). The huge dependence of threading efficiencies on these conditions is again consistent with the proposed H-bonding theory. Since a negative change of entropy is involved in H-bonding, lower temperatures will favor H-bond formation, a higher fraction of structure **5**, and enhanced threading (Schemes 1 and 2). When more crown ether is applied, the equilibrium will be driven in the same direction. Therefore, both factors combine to result in a large influence: higher feed ratio and lower temperature, higher *m*/*n* values of the resulting polyrotaxanes.

Since reacting diacid chloride **14** with diol **15** can eliminate all dethreading, we believe that an accurate fundamental study can now be performed and crown ether-based poly(ester rotaxane)s can be fully understood. More detailed study of the temperature dependence of the threading efficiency is in progress and the association constant for the hydrogen bonding between 30C10 and diol **15** will be measured. From these results it should be possible to ascertain the capture efficiencies of the hydrogen-bonded prerotaxanes, i.e., the ratio of structure **9** vs structure **8** resulting from endo and exo esterification of the complexed **5**, respectively, and other factors that control the threading and dethreading processes.

Conclusions

A new difunctional BG (diacid chloride BG **14**) was prepared, and it was successfully used in the preparation of the polyrotaxanes of type **3**. A novel strategy to eliminate dethreading during the preparation of poly(ester crown ether) rotaxanes was thus demonstrated by using both diol BG **15** and diacid chloride BG **14** as the only monomers. Thus polyrotaxanes with the highest threading efficiencies were obtained, compared to both the polypseudorotaxanes of type **1** and the polyrotaxanes of type **2** made under the same conditions. A dethreading mechanism is proposed. In addition, the results of this research are consistent with the H-bonding theory proposed previously, although more detailed study has to be done to directly prove it.

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.[23] Diphenolic BG **10** and diol BG **15** were synthesized by a reported method.[13] Proton NMR spectra, reported in ppm, were obtained on a 400 MHz Varian Unity spectrometer using chloroform-*d* solutions or DMSO-d_6 solutions as specified in the text and with tetramethylsilane as an internal standard. The NOESY studies were performed at room temperature with a mixing time of 1 s and a 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. The *m*/*n* values of the polyrotaxanes were measured by proton NMR spectroscopy and calculated from the integrals of threaded 30C10 vs the methylene protons of diol BG units in the backbone. Absolute molecular weights were measured by GPC analyses with a Waters 150C ALC/GPC chromatograph with polystyrene–divinylbenzene columns equipped with a differential refractometer detector and an on-line differential viscometric detector (Viscotek 150R) coupled in parallel and using the universal calibration. Relative molecular weights were measured by GPC analyses with a Waters 150C ALC/GPC system with polystyrene–divinylbenzene columns, using polystyrene standards; the instrument was fitted with a refractive index detector.

Bis(*p*-*tert*-butylphenyl)bis[*p*-((5-carbethoxypentyl)oxy)phenyl]methane (12). Bis(*p*-*tert*-butylphenyl)bis(*p*-hydroxyphenyl)methane (**10**) (5.00 g, 10.8 mmol) in DMF (50 mL) was added to a suspension of sodium hydride (1.30 g, 60%, 32.5 mmol) in 50 mL of DMF over 10 min at room temperature. After the mixture had been stirred for 1 h, ethyl 6-bromohexanoate (**11**, 12.0 g, 53.8 mmol) in DMF (50 mL) was added to the system. After reaction for 8 h at 60 °C, TLC showed that all starting materials disappeared and only one product was formed. After the system had been cooled to room temperature, the salt was removed by suction filtration and DMF by vacuum evaporation. The residue was taken up in CH_2Cl_2/H_2O (150 mL/50 mL). Separation of the organic layer and removal of the solvent afforded a white solid. The crude product was recrystallized in methanol (80%, mp 89.2−90.4 °C). ^{1}H NMR in $CDCl_3$: δ 1.25 (t, J = 7.2, 6H), 1.29 (s, 18H), 1.49 (m, 4H), 1.69 (m, 4H), 1.78 (m, 4H), 2.33 (t, J = 7.2, 4H), 3.93 (t, J = 6.4, 4H), 4.13 (q, J = 7.2, 4H), 6.74 (d, J = 9.2, 4H), 7.08−7.05 (m, 8H), 7.22 (d, J = 9.2, 4H). ^{13}C NMR in $CDCl_3$: δ 14.23, 25.69, 29.00, 31.35, 34.25, 60.21, 62.73, 67.43, 112.93, 124.04, 130.60, 132.09, 139.49, 144.25, 148.24, 156.79, 173.63 (18 peaks; theory, 21 peaks). Anal. Calcd for $C_{49}H_{64}O_6$: C, 78.57; H, 8.61. Found: C, 78.63; H, 8.66.

Bis(*p*-*tert*-butylphenyl)bis[*p*-((5-carboxypentyl)oxy)phenyl]methane (13). Diester BG **12** (7.00 g, 9.34 mmol) was added to a mixture of EtOH (500 mL) and KOH solution (4 M, 120 mL). The mixture was refluxed for 20 h. After it had been cooled, the mixture was acidified with concentrated HCl solution. Extraction with methylene chloride (2 × 150 mL) and removal of the organic solvent afforded a white solid. The crude product was recrystallized in hexane/ethyl acetate twice (1:1, 150 mL) (5.8 g, 90%, mp 184.5−186.0 °C). ^{1}H NMR in DMSO-d_6: δ 1.25 (s, 18H), 1.40 (m, 4H), 1.55 (m, 4H), 1.69 (m, 4H), 2.22 (t, J = 7.2, 4H), 3.90 (t, J = 6.2, 4H), 6.82 (d, J = 9.2, 4H), 6.98−7.05 (m, 8H), 7.29 (d, J = 9.2, 4H), 12.02 (s, 2H). ^{13}C NMR in DMSO-d_6: δ 24.25, 25.19, 28.49, 31.11, 33.60, 34.02, 62.23, 67.10, 113.28, 124.27, 129.93, 131.33, 138.82, 144.06, 147.70, 156.37, 174.40 (17 peaks as required). Anal. Calcd for $C_{45}H_{56}O_6$: C, 78.00; H, 8.15. Found: C, 78.12; H, 8.11.

Bis(*p*-*tert*-butylphenyl)bis[*p*-((5-(chlorocarbonyl)pentyl)oxy)phenyl]methane (14). Diacid BG **8** (4.70 g, 6.78 mmol) was dissolved in $SOCl_2$ (50 mL), and the solution was refluxed for 3 h. Upon the removal of excess $SOCl_2$, a yellow solid was obtained, which was recrystallized in hexane (150 mL) to give needle crystals (4.3 g, 88%), mp 138.6−140.0 °C. ^{1}H NMR in DMSO-d_6 (Figure 1): δ 1.25 (s, 18H), 1.38 (m, 4H), 1.52 (m, 4H), 1.66 (m, 4H), 2.19 (t, J = 7.2, 4H), 3.87 (t, J = 6.4, 4H), 6.82 (d, J = 9.2, 4H), 6.98−7.05 (m, 8H), 7.29 (d, J = 9.2, 4H). ^{13}C NMR in DMSO-d_6: δ 24.25, 25.19, 28.48, 31.11, 33.60, 34.02, 62.22, 67.11, 113.28, 124.27, 129.93, 131.33, 138.82, 144.06, 147.71, 156.36, 174.37 (17 peaks as required). Anal. Calcd for $C_{45}H_{54}O_4Cl_2$: C, 74.14; H, 7.47. Found: C, 74.11; H, 7.41.

General Procedure for Polyrotaxanes 16. Diol BG **15** (399.6 mg, 0.6235 mmol) was dissolved in 30C10 (2−4 equiv) at 140 °C. Then the temperature was adjusted according to Table 1. After the homogeneous solution was stirred for 0.5 h under the protection of nitrogen, sebacoyl chloride (150.1 mg, 0.6277 mmol) was added to the system. The polymerization proceeded for 2 days. The polymer was purified by precipitation from THF solution (2.5 mL) into water (200 mL). ^{1}H NMR in $CDCl_3$: δ 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).

General Procedure for Polyrotaxanes 17a−17c. Diol BG **15** (250 mg, 0.391 mmol) was dissolved in 30C10 (2−5 equiv) at 140 °C. Then the temperature was adjusted as specified in Table 1 and the solution was stirred for 0.5 h. After diacid chloride BG **14** (284 mg, 0.390 mmol) had been added to the system, the polymerization ran for 2 days at the same temperature. After it had been cooled, the product was precipitated into water (3 × 150 mL) from THF solution (2 mL). ^{1}H NMR in $CDCl_3$ (Figure 3a): δ 1.25 (s, 36H), 1.48 (m, 4H), 1.69 (m, 4H), 1.76 (m, 4H), 2.36 (t, J = 7.2, 4H), 3.50 (broad s, variable), 3.75 (t, J = 4.6, 4H), 3.82 (t, J = 4.6, 4H), 3.90 (t, J = 6.8, 4H), 4.09 (t, J = 4.6, 4H), 4.25 (t, J = 4.6, 4H), 6.07-6.78 (m, 8H), 7.04−7.08 (m, 16H), 7.20−7.23 (m, 8H).

General Procedure for Model Polyester 17d, *m*/*n* = 0. Diol BG **15** (250 mg, 0.391 mmol) and diacid chloride BG **14** (284 mg, 0.390 mmol) were dissolved in 2 mL of diglyme (anhydrous). The system was heated to 90 °C. Polymerization ran for 2 days at this temperature. After it had been cooled, the product was precipitated into methanol (2 × 150 mL) from THF (2 mL). ^{1}H NMR in $CDCl_3$ (Figure 3b): δ 1.25 (s, 36H), 1.48 (m, 4H), 1.69 (m, 4H), 1.76 (m, 4H), 2.36 (t, J = 7.2, 4H), 3.75 (t, J = 4.6, 4H), 3.82 (t, J = 4.6, 4H), 3.90 (t, J = 6.8, 4H), 4.09 (t, J = 4.6, 4H), 4.25 (t, J = 4.6, 4H), 6.07−6.78 (m, 8H), 7.04−7.08 (m, 16H), 7.20-7.23 (m, 8H).

Hydrolysis of Polyrotaxane 17c. Polyrotaxane **17c** (100 mg, m/n = 0.172) was dissolved in THF (3 mL). After 1.5 mL of aqueous potassium hydroxide (10 M) had been added, the mixture was refluxed for 8 h. Upon the removal of all solvent under reduced pressure, the hydrolysis product was extracted with $CHCl_3$ (3 × 50 mL) and $CHCl_3$ was evaporated. It was found that both 30C10 and diol BG **15** were recovered. ^{1}H NMR: Figure 4b. Pure 30C10 was recovered by further extraction of the neutral hydrolytic products using hexane (3 × 50 mL); ^{1}H NMR: Figure 4a.

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

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