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Main Chain Polyrotaxanes by Threading Crown Ethers onto A Preformed Polyurethane: Preparation and Properties

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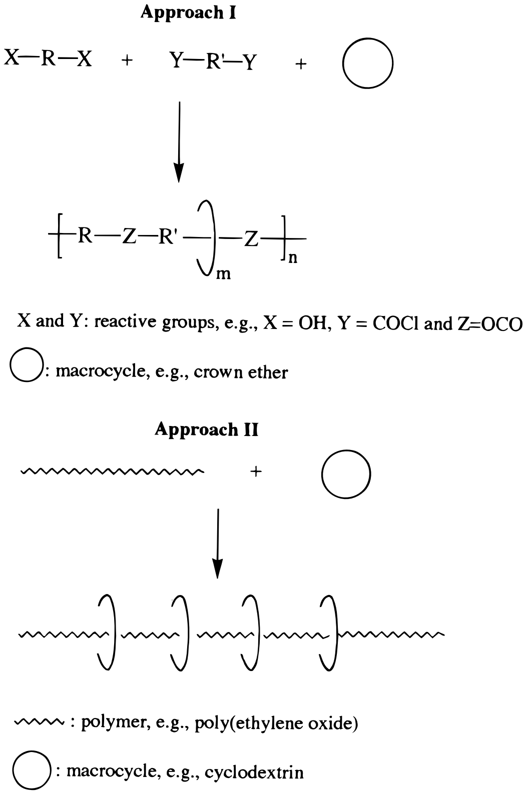
ABSTRACT: A new method for preparation of crown ether-based polyrotaxanes is described; stirring a solution of the melt of an aliphatic crown ether and a polyurethane afforded the corresponding polypseudorotaxane with hydrogen bonding between the NH groups of the polymer and the ether oxygen atoms of the cyclic species as the driving force. The degree of threading (m/n, the average number of cyclics per repeat unit) increased with increasing molar feed ratio of crown ether to polymeric NH groups. The degree of threading was reduced by simple dilution with a cosolvent, or threading was prevented by use of a competitive hydrogen-bonding solvent such as DMSO. The polyrotaxanes had higher intrinsic viscosities but lower shape-dependent Huggins constants than the backbone; this was attributed to their greater hydrodynamic volumes and more expanded chain conformations. Moreover, all the polyrotaxanes had only one glass transition temperature; the values depending on m/n agreed with the Fox equation using a T_g of −22 °C for threaded crown ether instead of using the T_g (−68 °C) of the free counterpart.

Introduction

Polyrotaxanes, in which rotaxane structures (mechanically linked cyclic and linear moieties) are incorporated into macromolecules, are a new class of polymeric materials.[1] Cyclodextrins (CDs)[2−4] and aliphatic crown ethers[5−8] are the most common cyclics used for preparation of these materials. Until now, aliphatic crown ether-based polyrotaxanes have been successfully prepared only by threading macrocycles onto linear components during polymerization using the cyclics as solvents[1,5−7] (Approach I, Scheme 1). For CD-based polyrotaxanes,[2−4] the driving force is well-understood to be inclusion complexation between CD and the linear molecule, and rotaxanes are always constructed by threading CD onto the preformed backbone for main chain polyrotaxanes[2,4] or onto the side chain units for side chain polyrotaxanes[3] (Approach II, Scheme 1). Similarly by Approach II, threading of a bisphenylene crown ether onto a polymer containing 4,4′-bipyridinium units was successful,[9] as was polypseudorotaxane formation from a cyclic bis(4,4′-bipyridinium) macrocycle and polymers containing electron-rich aromatic moieties.[10,11] However, because of the high melting points of CDs and the bipyridinium macrocycle and the thermal instability of the bipyridinium moieties, application of Approach II to these systems requires the use of solvents, typically water for the CDs and a polar solvent such as acetone for the bipyridinium systems.

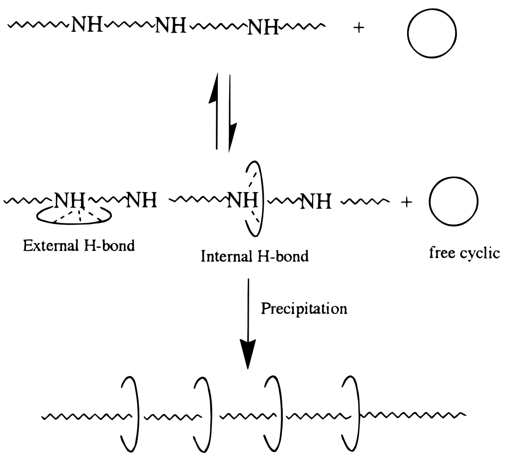
In contrast, aliphatic crown ethers have low melting points (<55 °C)[12] and possess both hydrophilic and hydrophobic characters, making them reasonably good solvents. Therefore, it occurred to us that it might be possible to synthesize polypseudorotaxanes in a melt process using Approach II, thus enabling the preparation of this new architecture in a straightforward manner easily adaptable to normal polymer-processing techniques. However, very little of the cyclic moiety ($m/n = 2 \times 10^{-2}$) was threaded by this approach using “42-crown-14” (“42C14”)[13] as solvent and a polyester backbone.[5d]

Scheme 1

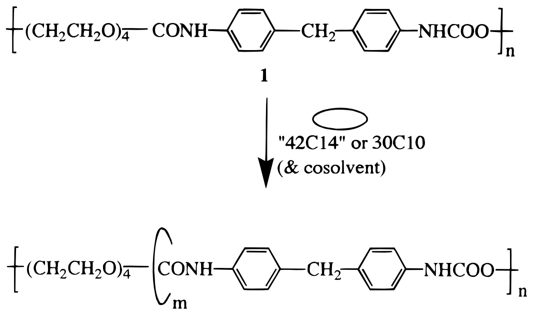


Recent results indicate that hydrogen bonding between crown ethers and OH groups of diol monomers is the driving force for threading during formation of polyester and polyurethane rotaxanes by Approach I.[6,7] It was also found that threaded crown ethers form H-bonds with in-chain NH groups in polyurethane rotaxanes in chloroform.[7,8] Therefore, crown ethers are expected to thread onto preformed polymers containing NH groups, that is, polyurethanes and polyamides, by hydrogen bonding (Scheme 2); this has now been

Scheme 2



Scheme 3



2a-f

Table 1. Feed Compositions and Threading Efficiencies of Polyrotaxanes 2a−f and Model Studies

product	repeat units of **1** (mmol)	cyclics (mmol)	cosolvent (mL)	m/n[b]	mass % crown ether
2a	1.00	“42C14”, 1.00[a]	0	0.092	11.3
2b	1.00	“42C14”, 3.00[a]	0	0.178	19.8
2c	1.00	“42C14”, 5.00[a]	0	0.192	21.0
2d	1.00	“42C14”, 6.00[a]	0	0.201	21.8
1	1.00	“42C14”, 3.00[a]	DMSO, 2.00	0	0
2e	1.00	“42C14”, 3.00[a]	diglyme, 2.00	0.085	10.5
2f	1.00	30C10, 5.00	0	0.065	6.04
1	1.00	PEO, 5.00[c]	0	0	0
1	1.00	18C6, 5.00	0	0	0

[a] Based on MW = 616. [b] +/−5% relative. [c] Based on MW = 600, dihydroxy terminated.

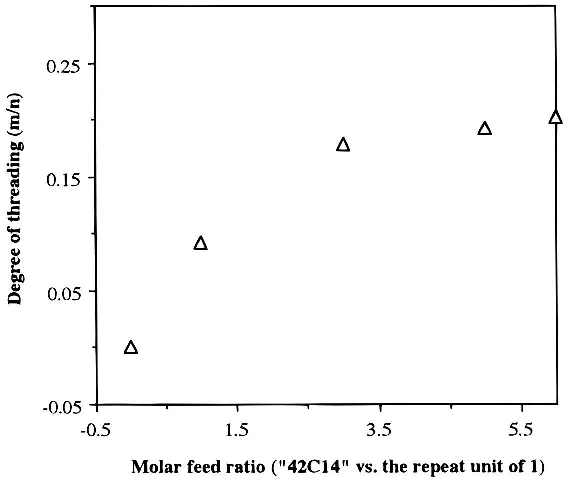


Figure 1. Relationship of m/n values for **2a**−**d** versus the molar feed ratios of “42C14” to the repeat unit of **1**.

demonstrated for the first time by the preparation of main chain poly(urethane/crown ether rotaxane)s in the present work, while similar hydrogen bondings between amide and amide[14,15] and between secondary ammonium ions and bisphenylene-based crown ethers[16,17] have successfully been used for the construction of low-molecular-weight rotaxanes.

Results and Discussion

Syntheses of Model Polymer 1 and Polyrotaxanes 2a−f. Polyurethane **1** was synthesized by solution polymerization of tetra(ethylene glycol) with 4,4′-methylenebis(*p*-phenyl isocyanate) (MDI) in DMF for 7 h at 96 °C. Polyrotaxanes **2a**−**f** were prepared simply by stirring solutions of “42C14”[13] or 30C10 and polyurethane **1** (Scheme 3) with or without cosolvent at 80 °C for 3 days. The detailed conditions are specified in Table 1. The unthreaded “42C14” or 30C10 was removed by precipitation from THF solution into water, a good solvent for the cyclics but a poor solvent for the polymer.[5,6]

Model Studies. 18-Crown-6 (18C6), too small to thread,[5] and linear poly(ethylene glycol) (PEO) (dihydroxy terminated, MW = 600) were used as substitutes for “42C14”, following the same procedure as that for polyrotaxanes **2a**−**e**. It was found that no 18C6 or PEO was left in the polymer after five precipitations, proving that no side reactions, ring opening of the crown ether or the reaction of OH groups with polyurethane **1**, take place and that reprecipitation is an effective method to remove unthreaded cyclics.

Threading Mechanism and Degree of Threading Efficiency. The m/n values of polyrotaxanes **2a**−**f** were measured by proton NMR via the integrals of the crown ether signal and the methylene protons of the backbone.[5b] It was found that the m/n values of all these polyrotaxanes (Figure 1 and Table 1) are much higher than that (2×10^{-2}) with a polyester as preformed polymer.[5d] We believe that the lower threading efficiency with the polyester is because there is no strongly attractive force between the ester linkages and the crown ether,[6] and thus the threading process is essentially statistical. However, the existence of hydrogen bonding between the NH groups of the polyurethane and the crown ether brings about a significant thermodynamic driving force for threading, and thus the resulting polyrotaxanes have higher m/n values. As expected for an equilibrium process, up to a certain limit, the higher the molar feed ratio of the cyclics versus the repeat unit of **1**, the more cyclics are threaded (Figure 1 and Table 1). The leveling-off (Figure 1) at higher ratios is due to approach to saturation. As much as 22% by mass of the crown ether is incorporated (Table 1). On the other hand, probably due to fewer hydrogen bonding sites, oxygen atoms, and/or the small ring size, polyrotaxane **2f** with 30C10 as the cyclic moiety had a lower m/n (0.065) than that (0.192) of **2c** (Table 1).

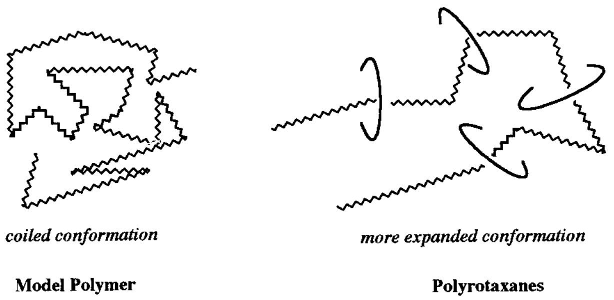
The number-average degree of polymerization of polyurethane **1** was 37.4. The number-average number of crown ether molecules threaded onto each macromolecule ranged from 2.4 for **2f** to 7.5 for **2d**. On the basis of the measured m/n values for **2a**−**d**, the association constant ($K_{\text{int H-bond}}$) for threading was estimated to be $(7.23 \pm 1.18) \times 10^{-2}$ M^{-1}.[18] It should be pointed out that this value may depend on the molecular weight of

Table 2. Intrinsic Viscosities and Glass Transition Temperatures of the Model Polymer and Polyrotaxanes

polymer	measured T_g (°C)	calcd T_g^a (°C)	calcd T_g^b (°C)	$[\eta]$ (dL/g) (THF, 25 °C)	calcd k'
1	54	54		0.299	0.491
2a	43	33	−23	0.351	0.350
2b	36	20	−22	0.361	0.259
2d	34	17	−21	0.369	0.250

[a] Calculated by the Fox equation based on the T_g's of the free crown ether (−68 °C) and the backbone (54 °C). [b] Glass transition temperature of the threaded crown ether calculated with the Fox equation based on the measured T_g's of polyrotaxanes.

Chart 1



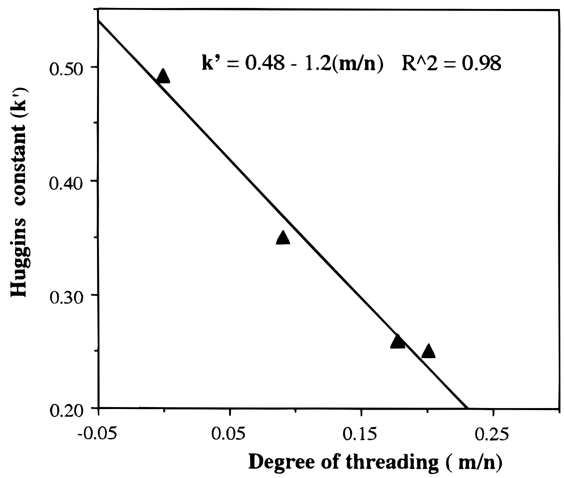


Figure 2. Relationship of the Huggins constant (k') versus the degree of threading efficiency (m/n) for model polymer **1** and polyrotaxanes **2a**, **2b**, and **2d**.

the polyurethane as a result of the stochastic or queuing nature of the threading process, as observed in other systems.[10]

The m/n values of polyrotaxanes **2a**−**d** in the present work are lower than that (0.29) of the same polyrotaxane but with higher molecular weight prepared at a higher temperature (90 °C) and a lower molar feed ratio of "42C14" to the repeat unit (1.5) by Approach I.[5b] In Approach II, the crown ether can form both external H-bonds, disfavoring threading, and internal H-bonds, leading to polyrotaxane, and thus the m/n value of the polyrotaxane is a result of this competition. In Approach I, however, the initial driving force is H-bonding between the crown ether and the OH groups of the diol monomer,[6] and once the urethane bond is formed, the threaded cyclics tend not to slip off the backbone because of H-bonding with in-chain NH groups[7] and the random coil conformations of the polymer chain.[5] Therefore, the m/n value of the resulting polyrotaxane via Approach I is mainly determined by the strength of H-bonding of the crown ether with OH groups, but the NH groups of the polymer help to retain them.

2e with $m/n = 0.085$ was obtained with diglyme as the solvent; this lower value compared to that (0.178) for **2b** again agrees with the H-bonding hypothesis, a dilution effect, and the $K_{\text{int H-bond}}$ was estimated[18] to be 6.48×10^{-2} M^{-1}, in agreement with results for **2a**−**d**. Since DMSO can dissociate hydrogen bonds between NH or OH groups and crown ethers, in this solvent no threading is expected.[6d,7] Indeed, no "42C14" was detected in the product after purification when DMSO was the solvent (Table 1).

Some Properties of Polyrotaxanes. The present approach for preparation of polyrotaxanes allows an accurate study of the relationship of the properties of polyrotaxanes to m/n because the backbones of all derived polyrotaxanes in terms of molecular weights and polydispersity are identical to the corresponding model (starting) polymer.

(i) Intrinsic Viscosity. To study the effect of the polyrotaxane architecture on polymeric chain conformation, the intrinsic viscosities of model polymer **1** and some polyrotaxanes **2** were measured under identical conditions (THF as solvent at 25 °C).

On the basis of the measured intrinsic viscosity (η_{sp}'s) at different concentrations (C's), the plot of η_{sp}/C versus C afforded the intrinsic viscosities and shape-dependent factors (Huggins constant k') for the model polymer **1** and polyrotaxanes **2** (Table 2) via the Huggins equation: $[\eta_{sp}/C] = [\eta] + k'[\eta]^2C$. Interestingly, the Huggins constants (the k' values) for the polyrotaxanes were much smaller than that of the starting polyurethane, but the intrinsic viscosities of the polyrotaxanes were higher, as demonstrated previously for polyesters.[5d] The Huggins constant is related to (i) the molecular weight distribution or (ii) the branching of the macromolecule.[19] Although the molecular weight distribution of the polyrotaxanes may increase as m/n increases, we believe these differences may be caused by conformational changes of the backbone upon threading, as shown in Chart 1. Relative to the model polymer, the polyrotaxanes probably tend to adopt a more expanded form because of the bulkiness of the threaded cyclics, and thus they have a greater hydrodynamic volume and higher intrinsic viscosity. The model polymer was a random coil which became more and more expanded upon dilution; this resulted in a higher Huggins constant k'. However, the backbone in polyrotaxanes was already expanded even at higher concentrations, and thus the dependence of chain conformation on the concentration was less. As shown in Figure 2, k' decreased linearly with increasing m/n; this is taken to mean that threading more rings onto a polymer does not result in any higher order chain stiffening.

(ii) Thermal Properties. In poly(ester rotaxane)s, crown ethers can move along the backbone and accumulate into a separate crystalline phase; this gives melting points roughly corresponding to those of the pure crown ether and the semicrystalline backbone in DSC traces.[5c,d] In polyurethane rotaxanes, threaded crown ethers can H-bond with in-chain NH groups.[7,8] Such H-bonding should prevent aggregation of the crown ethers. Indeed, no melting corresponding to the crown ethers was observed for the present polyrotaxanes. Only one glass transition temperature exists (Table 2); that is, these poly(urethane rotaxane)s were one-phase materials. As expected, the more crown ether that was threaded, the lower the T_g of the polyrotaxane (Table 2).

According to the Fox equation, the glass transition temperatures (T_g's) for the polyrotaxanes were calculated (Table 2) on the basis of the weight fractions of the crown ether and the backbone (Table 1) and the T_g's of the free crown ether and the backbone at −68 and 54 °C, respectively. Surprisingly, the measured value was much higher than the calculated one. What causes this deviation? The H-bonding restricts motion of the threaded crown ether,[7,8] which results in a higher glass transition temperature for "42C14" relative to that of the free counterpart. Indeed, on the basis of the measured T_g's of the polyrotaxanes, the weight fraction of the crown ethers, and the T_g of the backbone, the corresponding T_g of threaded "42C14" was estimated to be -22 ± 1 °C in all the polyrotaxanes (Table 2).

Conclusions

A new method for the synthesis of crown ether-based polyrotaxanes was demonstrated: threading crown ethers onto a preformed polyurethane in both solution and melt states. The threading extent was controlled by the feed ratio of the two components, the concentration, and the solvent. Interestingly, the polyrotaxanes had higher intrinsic viscosities but smaller shape-dependent constants than the starting polyurethane, indicating that polyrotaxanes adopted an expanded chain conformation. Because of intra-annular hydrogen bonding, the polyrotaxanes were one-phase materials and the glass transition temperature was related to the loading of the crown ether. Moreover, the melt-blending approach is adaptable to normal polymer-processing techniques.

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[20] and "42C14"[13] were prepared by well-established procedures. Proton NMR spectra, reported in ppm, were obtained on a 400-MHz Varian spectrometer using DMSO-d_6 with Me_4Si as an internal standard. The absolute molecular weight of the polyurethane was measured by GPC in *N*-methylpyrrolidinone (NMP) at 60 °C with a Waters 150C ALC/GPC chromatograph equipped with a differential refractometer detector and an on-line differential viscometric detector (Viscotek 150R) coupled in parallel, and the universal calibration was used. The T_g values were measured with a Perkin-Elmer DSC-B2 system at a rate of 10 °C/min for both heating and cooling from −30 °C to +80 °C; all reported values were the centers of transitions from second heatings. The intrinsic viscosities were measured with Cannon L12 50 viscometers in THF at 25 °C.

Model Polyurethane 1. To a 50-mL flask were added tetra(ethylene glycol) (1.94 g, 10.0 mmol) (oven dried at 100 °C for 4 h under vacuum) and freshly distilled MDI (2.50 g, 10.0 mmol) in DMF (10 mL). The solution was heated at 96 °C in an oil bath under N_2 for 7 h. The product was precipitated into MeOH to give a transparent material. ^1H NMR in DMSO-d_6, δ: 9.66 (s, 2H), 7.38 (d, 4H, $J = 8.3$), 7.10 (d, $J = 8.3$, 4H), 4.19 (s br, 4H), 3.79 (s, 2H), 3.62 (s br, 4H), 3.51 (s br, 8H). $M_n = 16.6$ kg/mol ($DP_n = 37.4$), and $M_w = 58.7$ kg/mol ($DP_w = 132$).

General Procedures for Poly(urethane rotaxane)s 2a−f. Polyurethane **1** was dissolved in the crown ether at 80 °C with or without cosolvent, as specified in Table 1. After the solution had been stirred for 3 days at this temperature under N_2, the mixture was dissolved in THF and precipitated into H_2O (5×) to remove free crown ether.

General Procedures for Model Study. Polyurethane **1** was dissolved in 18C6 or PEO-600 at 80 °C. After the solution had been stirred for 3 days at this temperature under N_2, the mixture was dissolved in THF and precipitated into H_2O (5×).

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(18) It was assumed (1) that densities are 1.00 g/mL for **1** and “42C14” and (2) that no threaded crown ethers are lost during purification; on the basis of the data for **2a**−**d**, the association constant for threading ($K_{\text{int H-bond}}$) was calculated by the equation $K = [\text{R}]/\{[\text{NH}][\text{“42C14”}]\}$, in which [R], [NH], and [“42C14”] are the equilibrium concentrations of the rotaxane unit, the NH group, and free “42C14”. [R] was calculated from the measured m/n value as $(m/n)[\text{NH}]_0/2$. For example for **2b**, 1 mmol of **1** = 0.416 mL, 3 mmol of “42C14” = 1.85 mL, $[\text{NH}]_0 = 0.883$ M, $[\text{“42C14”}]_0 = 1.32$ M, and $[\text{R}] = (0.178)(0.883)/2 = 0.0786$ M; thus, $K = 7.81 \times 10^{-2}\ \text{M}^{-1}$. Because of possible dethreading during precipitations especially for cyclics near chain ends, the obtained K is a minimum value.

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