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Studies of the Formation of Poly(ester rotaxane)s from Diacid Chlorides, Diols, and Crown Ethers and Their Properties

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ABSTRACT: The formation of poly(alkylene sebacate−crown ether pseudorotaxane)s by condensation of linear alkylene diols and sebacoyl chloride in the presence of crown ethers in the neat state has been studied. It was found that the average number of crown ether molecules per repeat unit in the polypseudorotaxane was a function of (a) the ring size and (b) the stoichiometric ratio of macrocycle to diol but independent of (i) the equilibration time of the diol and crown ether prior to addition of the diacid chloride, (ii) the length of the diol, and (iii) the temperature of equilibration and polycondensation. All of these observations are consistent with the involvement of hydrogen bonding between the diol and the crown ether as a driving force for threading, except the lack of temperature dependence. Dethreading of the isolated polypseudorotaxanes was shown to be extremely slow. Therefore, it was reasoned that the lack of temperature dependence was due to dethreading during the polymerization, inasmuch as once the ester bond has formed there is no strongly attractive force between the linear and cyclic species and the low molecular weights of the growing oligomeric esters would permit relatively facile dethreading. Based on this idea, a bulky tetraphenylmethane-based bisphenol was employed to make a copolymer (1:4) with 1,10-decanediol; indeed, the purified polyrotaxane contained more than twice as much crown ether as the polypseudorotaxane from the linear diol, confirming that dethreading does occur during the polymerization process. The polyrotaxanes all were capable of extracting metal ions from aqueous solutions. In the cases with high loadings of crown ether two distinct crystalline phases were detected by DSC: one due to the polyester backbone and one due to the crown ether; glass transitions were also observed for the crown ether component of the polyrotaxanes. Polyrotaxanes possess higher intrinsic viscosities than the backbone polymers of the same molecular weight due to increased hydrodynamic volume brought about by the macrocyclic components. However, differential solvation of the backbone and cyclic components of the polyrotaxanes was demonstrated; the intrinsic viscosity of the polyrotaxane decreased in a good solvent for the crown ether. The temperature dependence of the melt viscosity of a polyrotaxane was essentially the same as that of the polyester model backbone, but the absolute melt viscosity was much lower due to reduced chain entanglement.

Introduction

In the last 10 years the study of rotaxanes and polyrotaxanes has yielded significant progress from the early studies of pioneers like Harrison,[1] Schill,[2] and coworkers. Because these fields have been recently reviewed extensively,[3,4] only brief mention of the various classes of polyrotaxanes will be noted here. These include the early work of Maciejewski et al. with vinyl monomers and cyclodextrins,[5] Lipatova et al. with polystyrene and cyclic urethanes,[6] Zilkha et al. with poly(ethylene glycol)s and crown ethers,[7] the more recent efforts of the groups of Wenz,[8] Ritter,[9] Harada,[10] and Ooya[11] on other cyclodextrin-containing polyrotaxanes, and the work of Swager et al. on crown ether-based polyrotaxanes.[12] In our laboratory we have reported a variety of polyrotaxanes based on crown ethers as the cyclic moieties; these have included polyesters,[13] polyamides,[14] polyurethanes,[15] and polystyrene,[16] among others.[3]

Our approach has been to carry out polymerizations in the presence of macrocycles and thus to capture the pseudorotaxane[17] structure in the polymeric product. This concept is illustrated in general in Scheme 1. Since the special properties of polyrotaxanes arise from the

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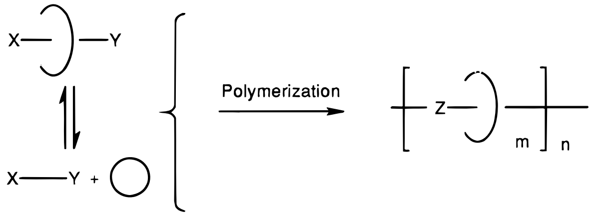
Scheme 1. Generic Approach to Polyrotaxanes via Polymerization of *in Situ* Generated Pseudorotaxanes



physical linkage of linear and cyclic molecules, a high degree of threading of macrocycles onto the linear species has been diligently pursued. The key step in the construction of a rotaxane is to create conditions that allow the threading of the linear chain through the cyclic component to take place. Therefore, it is necessary to understand the nature of the threading process. Parameters of interest are the size of the macrocycles, the length and nature of the linear monomers, the molar ratio of cyclic to linear species, temperature, time, and most importantly, the nature of the interaction between the linear and cyclic species, which can often be deduced from study of the other variables noted and by other means as well, including spectroscopy and X-ray crystallography.

The acid chloride method, a well-known polymerization technique for the syntheses of polyesters,[18] allows us to ascertain the effects of these parameters in the threading process. Although some such studies were carried out earlier,[13c,f] here we report a systematic study of the variables mentioned above.

Results and Discussion

I. Model Polymerizations. In order to optimize the reaction conditions for the synthesis of poly(decamethylene sebacate) (**9**), in model reactions (Scheme 2) sebacoyl chloride was reacted with 1,10-decanediol (**3**) in diglyme. Diglyme was chosen as a model for the crown ethers.

The polymerization of diacid chlorides with diols is a typical step growth polymerization of an A−A monomer with a B−B monomer.[18] High molecular weight polymers can be produced by using pure starting monomers, by choosing appropriate reaction conditions to reduce side reactions, and by controlling the precise stoichiometry of monomers.[18] Therefore, all monomers and the solvent were carefully purified before use.

During the reactions, a nitrogen flow was passed through the reaction system to remove the hydrogen chloride generated in the reactions. An attempt to use pyridine as an acid capturer was not successful because the polymer is not soluble in the mixure of pyridine and diglyme.

Two important reaction parameters, temperature and time, were optimized by a series of reactions under different reaction conditions. The results are listed as experiments 1−4 in Table 1. The conditions of experiment 2, 80 °C and 48 h, gave the highest molecular weight.

The precise stoichiometry of the two monomers is another important factor in achieving high molecular weight polymers. Polyrotaxanes are usually synthesized on a small scale because the supply of crown ethers is limited. Unfortunately, the exact equivalent ratio of monomers is very difficult to attain on a small scale because of relatively large measurement errors. Precisely weighing the liquid monomer, sebacoyl chloride, in small quantities is especially difficult. Therefore, even when temperature and reaction time had been optimized, the molecular weight was still relatively low. The situation is more complicated in syntheses of polyrotaxanes in which the diol monomer and crown ether are mixed in the melt prior to the addition of liquid sebacoyl chloride. The acid chloride needs to be weighed in a separate vessel instead of in the reaction flask directly. The problem was circumvented by using a two-chambered reaction flask; the two monomers were weighed directly into separate chambers. Liquid sebacoyl chloride was weighed first so that the quantity of solid diol monomer could be adjusted to maintain the exact 1:1 molar ratio of the two monomers. After the diol monomer was melted in chamber 1, the two monomers were mixed directly inside the flask at the reaction temperature under nitrogen. Using this method, the molecular weight was greatly increased, as shown in Table 1, experiment 5.

In the ^{1}H NMR spectrum of poly(decamethylene sebacate) (**9**) (Figure 1), the various protons are readily assigned. The ^{13}C NMR spectrum of **9** is shown in Figure 2 and displays nine of ten possible signals, assigned as indicated.

Another model polymerization of 1,10-decanediol and sebacoyl chloride was carried out under exactly the same conditions except that 18-crown-6 was substituted for diglyme. The resultant polymer after purification by reprecipitation from CH_2Cl_2 into methanol as described below for the polyrotaxanes displayed NMR spectra identical to those shown in Figures 1 and 2. 18-Crown-6 is too small to be threaded.[1−4] The lack of ethyleneoxy signals in the ^{1}H and ^{13}C NMR spectra demonstrate two important facts: (1) nonthreaded or free crown ethers can be effectively removed by the reprecipitation protocols, and (2) no ring opening of the crown ether takes place under the reaction conditions; incorporation of ethyleneoxy units covalently can be ruled out.

II. Parametric Studies of Threading Processes in Poly(ester rotaxane) Syntheses From Diols and Diacid Chlorides. A. General Methods. Our studies were performed with poly[(alkylene sebacate)-*rotaxa*-(crown ether)]s. As depicted in Scheme 2, the polyrotaxanes were prepared by the condensation of alkylene diols and sebacoyl chloride using melted crown ethers[19] as solvents. The diol and the crown ether were stirred in the melt to allow threading of the linear species through the macrocycle prior to the addition of sebacoyl chloride. This threading process is termed “prethreading” (Scheme 1).

The polyrotaxanes were purified by multiple reprecipitations from CH_2Cl_2 solution into methanol, which is a good solvent for the crown ether but not for the polyrotaxane. After each precipitation, the polymer composition was determined by quantitative ^{1}H NMR, affording a measure of the m/n value, the molar ratio of macrocycle to repeat units of polymer backbone. All the polyrotaxanes synthesized reached a constant m/n value after three precipitations, indicating the complete removal of free macrocycles.

The ^{1}H and ^{13}C NMR spectra of poly[(decamethylene sebacate)-*rotaxa*-(“42-crown-14”)] (**14**) are shown in Figures 3 and 4. These spectra are the same as those of their linear counterpart **9** shown in Figures 1 and 2, except for the signals of the crown ethers. The ^{1}H NMR spectrum of **14** contains only one additional peak at 3.7 δ (**e**) due to the crown ether. Likewise, the ^{13}C NMR

Scheme 2. Synthesis of Poly(alkylene sebacate)s and Poly(alkylene sebacate rotaxane)s

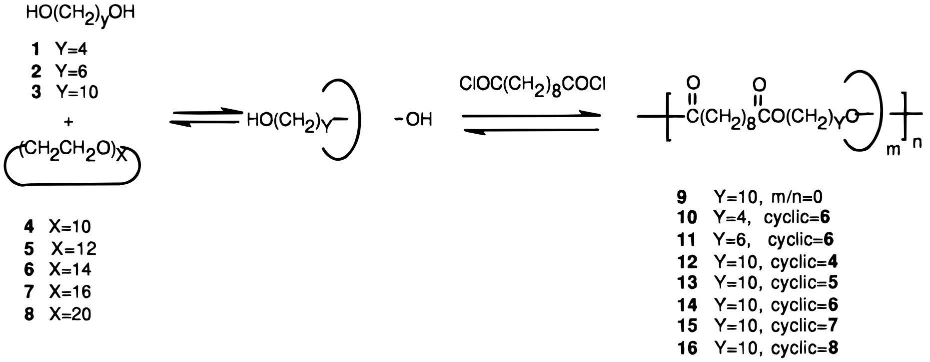


Table 1. Optimization of the Synthesis of Poly(decamethylene sebacate) (9)

experiment	temp (°C)	time (h)	$10^{-3} M_n$	$10^{-3} M_w$	M_w/M_n
1[a]	80	24	7.9[c]	16.1[c]	2.02
2[a]	80	48	8.9[c]	15.2[c]	1.55
3[a]	110	48	7.7[c]	12.9[c]	1.66
4[a]	140	48	5.2[c]	7.1[c]	1.38
5[b]	80	48	13.9[d]	23.5[d]	1.69

[a] Reactions were done in a single-chambered flask. [b] The reaction was done in a double-chambered flask. [c] Measured by GPC in chloroform at 25 °C with polystyrene standards. [d] Measured by GPC in toluene at 25 °C with polystyrene standards.

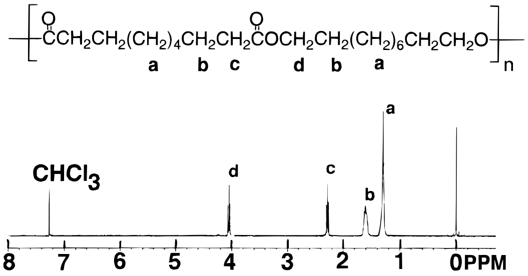


Figure 1. 400 MHz ^{1}H NMR spectrum of poly(decamethylene sebacate) (**9**) in $CDCl_3$.

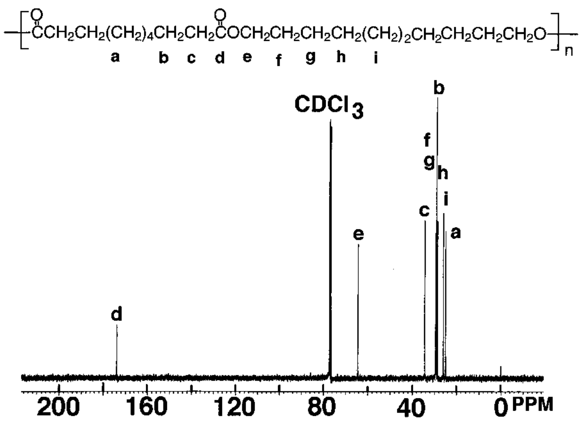


Figure 2. 100 MHz ^{13}C NMR spectrum of poly(decamethylene sebacate) (**9**) in $CDCl_3$.

spectrum of **14** differs from that of the model polymer **9** only by the resonance at 70.5 δ (**j**), easily assigned to the carbons of the "42-crown-14" component of the polyrotaxane.

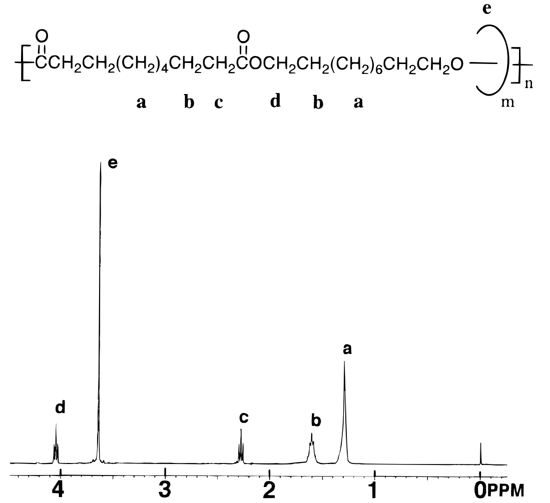


Figure 3. 400 MHz ^{1}H NMR spectrum of poly[(decamethylene sebacate)-*rotaxa*-("42-crown-14")] (**14**, m/n = 0.29) in $CDCl_3$.

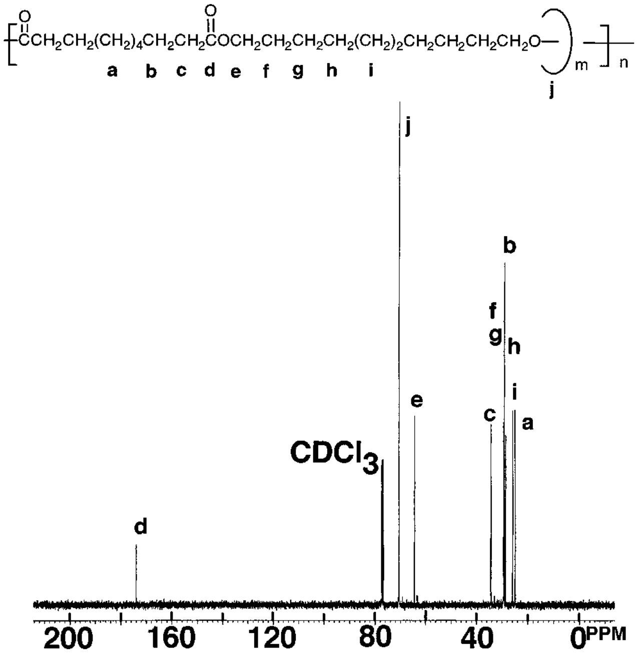


Figure 4. 100 MHz ^{13}C NMR spectrum of poly[(decamethylene sebacate)-*rotaxa*-("42-crown-14")] (**14**, m/n = 0.29) in $CDCl_3$.

Copolyester **17** was prepared from decanediol, poly(ethylene glycol) (PEG) (M_n = 600) and sebacoyl chloride as a reference for comparison of the spectral and thermal properties of the polyrotaxanes. The polymer contains 35% by mass of ethyleneoxy moieties, essentially the same as the ethyleneoxy content of polyrotaxane **14**, m/n = 0.29 (34%). However, the ^{1}H NMR spectrum of **17** (Figure 5) is more complex than that of **14**. In polyrotaxane **14** all of the crown ether protons are equivalent and yield only a single resonance, at 3.65 ppm (Figure 3). In copolymer **17**, because of their magnetic nonequivalence, the ethyleneoxy units yield

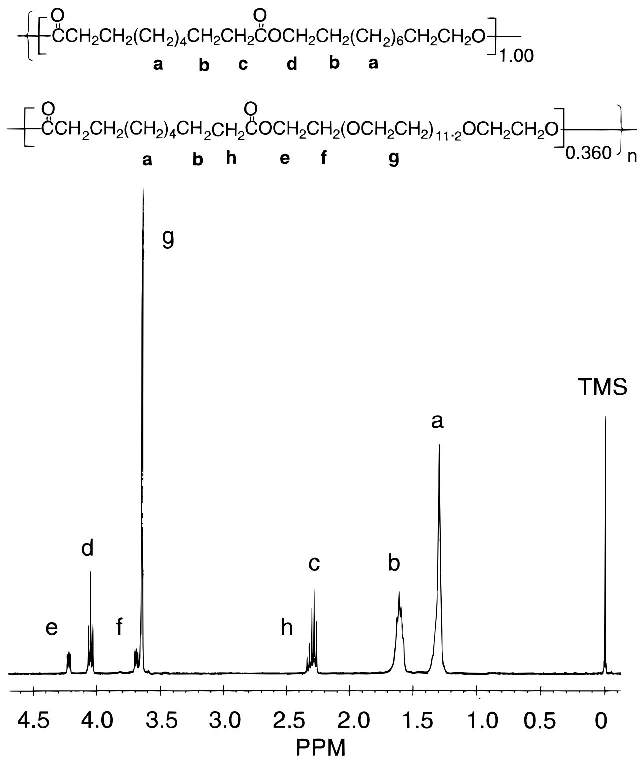


Figure 5. 400 MHz ^{1}H NMR spectrum of poly[(decamethylene sebacate)-*co*-(oligo(ethyleneoxy) sebacate)] (**17**) in CDCl$_3$.

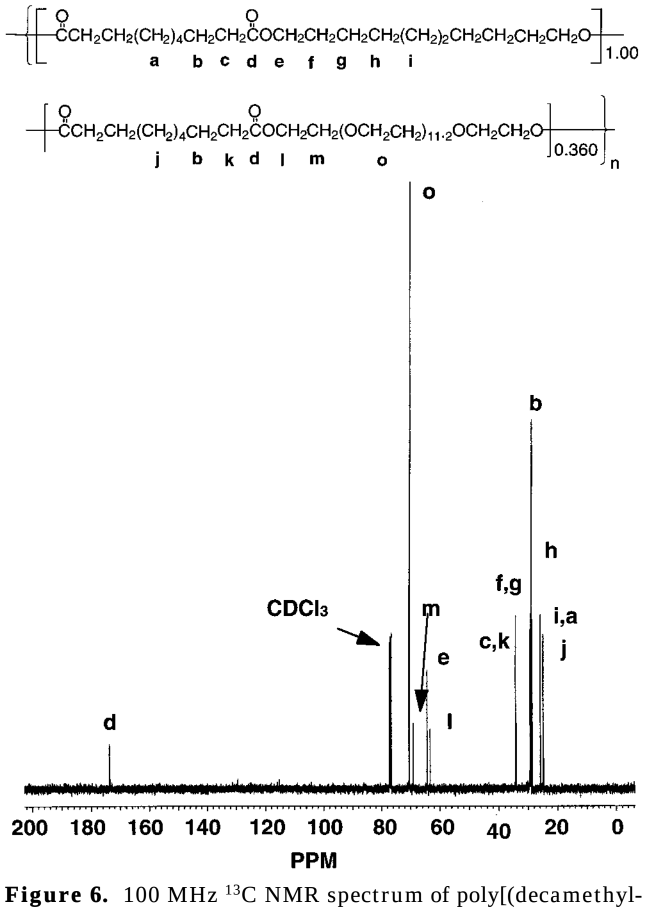


Figure 6. 100 MHz ^{13}C NMR spectrum of poly[(decamethylene sebacate)-*co*-(oligoethyleneoxy sebacate)] (**17**) in CDCl$_3$.

a total of four distinct new resonances, at 2.35, 3.64, 3.69, and 4.22 ppm. Similarly, the ^{13}C NMR spectrum of **17** (Figure 6) is more complex; by comparison to Figure 2 new signals attributable to the PEG sebacate unit can be identified as 24.8, 34.1, 63.3, 69.1, and 70.5; note that in polyrotaxane **14**, as indicated above, the only new signal is for the crown ether carbon atoms, all equivalent, at 70.5 ppm (Figure 4). These results further demonstrate, as did the control experiment with 18-crown-6 described above, that a true polyrotaxane has been prepared; the crown was incorporated intact and did not undergo ring opening and subsequent covalent copolymerization. Elsewhere, we have further proved the polyrotaxane architecture by hydrolysis of the polyester backbone and recovery of the crown ether.[13a−c,e]

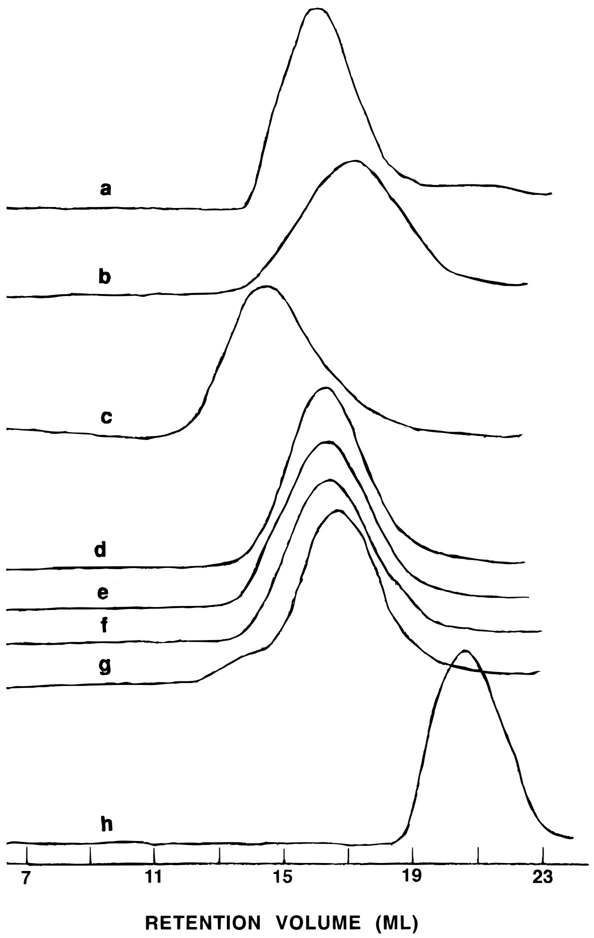
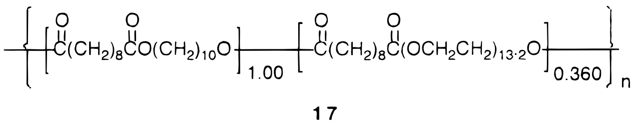


Figure 7. GPC traces (THF at 30 °C, refractive index detector): (a) poly[(butylene sebacate)-*rotaxa*-("42-crown-14")] (**10**, *m*/*n* = 0.32); (b) poly[(hexamethylene sebacate)-*rotaxa*-("42-crown-14")] (**11**, *m*/*n* = 0.30); (c) poly[(decamethylene sebacate)-*rotaxa*-(30-crown-10)] (**12**, *m*/*n* = 0.012); (d) poly-[(decamethylene sebacate)-*rotaxa*-("36-crown-12")] (**13**, *m*/*n* = 0.22); (e) poly[(decamethylene sebacate)-*rotaxa*-("42-crown-14")] (**14**, *m*/*n* = 0.29); (f) poly[(decamethylene sebacate)-*rotaxa*-("48-crown-16")] (**15**, *m*/*n* = 0.34); (g) poly[(decamethylene sebacate)-*rotaxa*-("60-crown-20")] (**16**, *m*/*n* = 0.36); and (h) "42-crown-14" (**6**).



$$\left[\left[\overset{O}{\overset{\|}{C}}(CH_2)_8\overset{O}{\overset{\|}{C}}O(CH_2)_{10}O \right]_{1.00} \left[\overset{O}{\overset{\|}{C}}(CH_2)_8\overset{O}{\overset{\|}{C}}(OCH_2CH_2)_{13.2}O \right]_{0.360} \right]_n$$

17

The single peak in the GPC diagrams of the polyrotaxanes also demonstrated the absence of free macrocycles, as shown for **14** in Figure 7e. The number average molecular weight of polyrotaxane **14** determined by GPC with polystyrene standards was 8.3K. Also shown in Figure 7h is the GPC trace for "42-crown-

Table 2. Errors of Determination of the *m*/*n* Value from the Sampling of Poly[(decamethylene sebacate)-*rotaxa*-(“42-crown-14”)] (14) (20 Data Sets)

method[a]	mean	spread	100σ (std dev)
1	0.356	0.029	0.719
2	0.340	0.018	0.443
3	0.325	0.036	0.754
4	0.326	0.013	0.344

[a] See text, eqs 1−4.

14” alone. In Figure 7e note the absence of the free crown ether. This sample of polyrotaxane **14** ($m/n = 0.29$) was shown by NMR spectroscopy to contain 34 mass % of “42-crown-14”.

Although there were no blocking groups at the ends of the polymer chains, no free macrocycles were found in the polyrotaxanes, as demonstrated by both constant m/n values after the second and third reprecipitations and by GPC measurements.

The threading process may be very complicated. In order to simplify the situation, the studies began in neat systems so that solvent effects did not come into play.

B. Determination of Measurement Error for *m*/*n* Values. The m/n values, the molar ratios of the macrocycle to the repeat unit of the polymer backbone, were determined by quantitative ^{1}H NMR measurements. Indeterminate errors of the method, arising form sampling and measuring, were statistically treated. Each treatment dealt with 20 data sets to obtain the populational results.

(1) Sampling Error. Twenty samples were taken from a poly[(decamethylene sebacate)-*rotaxa*-(“42C14”)] (**14**) sample which had been thoroughly stirred. These samples were then measured by ^{1}H NMR spectroscopy and m/n values were calculated by four methods based on different protons of the polysebacate backbone (Figure 3).

Method 1 is based on protons **d** compared to protons **e**:

$$m/n = A_{3.6}/[14A_{4.1}] \tag{1}$$

where A represents the integration of signals whose chemical shifts in ppm are indicated by subscripts.

Method 2 uses protons **c** and **d** compared to protons **e**:

$$m/n = A_{3.6}/[7(A_{4.1} + A_{2.3})] \tag{2}$$

Method 3 depends on the comparison of protons **a**, **c**, and **d** to protons **e**:

$$m/n = A_{3.6}/[2(A_{4.1} + A_{2.3} + A_{1.3})] \tag{3}$$

and protons **c** are compared to protons **e** in method 4:

$$m/n = A_{3.6}/[14A_{2.3}] \tag{4}$$

Protons **b** were not taken into account because the peak is overlapped by that of water.

Results are summarized in Table 2. Among the four methods, method 4 is the best with respect to both the spread and the standard deviation.

(2) Measurement Error. One NMR sample of **14** was measured 20 times, and m/n values were calculated using methods 1 and 4. Results are listed in Table 3. Method 4 again appears to be the better one, having a smaller standard deviation (3.46×10^{-3}). Therefore, method 4 was used in subsequent calculations. The resultant overall error is 6.90×10^{-3}. It is concluded that the error in m/n is ≤ 0.01.

Table 3. Errors of Determination of the *m*/*n* Value from the Measurement of a Single Sample of Poly[(decamethylene sebacate)-*rotaxa*-(“42-crown-14”)] (14) (20 Data Sets)

method[a]	mean	spread	100σ (std dev)
1	0.369	0.017	0.395
4	0.329	0.013	0.346

[a] See text, eqs 1−4.

Table 4. Effect of Macrocycle Size on the Threading of Crown Ethers 4−8 by 1,10-Decanediol (3) To Form Polypseudorotaxanes 12−16[a]

ring size	30C10	“36C12”	“42C14”	“48C16”	“60C20”
m/n[b]	0.012	0.22	0.29	0.34	0.36
wt % ring	1.5	25	34	41	48

[a] Neat process; temperature: 80 °C; molar feed ratio of cyclic to linear, 1.0; prethreading time, 30 min. [b] Final molar ratio of macrocycle to repeat unit of the polymer backbone in polyrotaxanes **12**−**16** measured by ^{1}H NMR.

C. Ring Size. Crown ethers with different ring sizes[19] were involved in the study. The following conditions were adopted in the syntheses of poly(decamethylene sebacate) rotaxanes with different crown ethers: the prethreading time was 0.5 h, the reaction temperature was 80 °C and the molar ratio of crown ether[19] to diol was 1. The results are shown in Table 4. The m/n values increase nonlinearly with ring size, as did previous other systems.[1,2,7,13−16]

Harrison studied the influence of macrocycle size on rotaxane yields.[1] His procedure consisted of equilibrating a mixture of cyclic alkanes with ring sizes of 14−42 atoms and 1,13-bis[tris-(*p*-*tert*-butylphenyl)methoxy]tridecane, with an acid catalyst. He found a monotonic increase in the yield of rotaxane as the size of the macrocycle increased from 24 to 33 atoms. Schill and his colleagues carried out similar studies to address the issue of ring size.[2] The yield of rotaxane was found to increase with macrocycle size. Zilkha synthesized oligomeric rotaxanes by threading crown ether macrocycles onto poly(ethylene glycol)s.[7] The proportion of threading was found to increase with increasing ring size of the crown ethers. Similar observations were also obtained in polyurethane−crown ether rotaxanes synthesized by Shen et al.[15] Clarson, Mark, and Semlyen threaded narrow molecular weight distribution cyclic poly(dimethylsiloxane)s with linear α,ω-dihydroxypoly(dimethylsiloxane)s (PDMS) of M_n 18K to form siloxane homopolyrotaxanes.[20] They immobilized the threaded rings by cross-linking the linear PDMS. The unthreaded rings were then extracted from the matrix. They found that the mass percentage of cyclics in the cured polyrotaxane increased with ring size. Gibson et al. calculated equilibrium constants from Clarson’s data on a molar basis by taking into account the total molar masses of the components.[3a] The results in the form log K vs ring size display two linear regions.[3a]

As defined previously,[3a] homorotaxanes are composed of cyclic and linear species which are chemically equivalent. Heterorotaxanes, on the other hand, involve cyclic and linear species having different chemical structures. In the literature cited above, the results are all from homorotaxane systems, except for polyurethane rotaxanes, which are a semihomorotaxane system because of the chemical equivalence of crown ethers and tetra(ethyleneoxy) units in the polymeric backbones.[15]

Table 5. Effect of Feed Ratio on the Threading of "42C14" (6) by 1,10-Decanediol (3) (0.5 h, 80 °C) To Form Polyrotaxanes 14

M_o/D_o[a]	m/n[b]	wt % "42C14"
1.00	0.29	34
1.45	0.33	37
2.00	0.41	43
4.00	0.42	43

[a] Molar feed ratio of "42-crown-14" to 1,10-decanediol. [b] Final molar ratio of macrocycle to repeat unit of the polymer backbone in polyrotaxane **14** measured by ^{1}H NMR.

The ring size effects of macrocycles in the homorotaxane systems can be divided into two regions. In the small ring size region, the repulsive interaction between the cyclic and linear species may be the most important factor that affects threading. Therefore, the degree of threading is an exponential function of ring size, following perhaps the Lennard-Jones potential.[21] For large rings, repulsive interaction is less important. Above the small ring region, the plot of threading constant vs ring size also shows a logarithmic pattern. The overall semilog curve can be roughly treated as two straight lines, one in the small ring size region and one in the large ring size region. The two regions may also reflect the fact that below a certain ring size, the ability to be threaded is strongly governed by conformational possibilities; that is, up to a certain size, there is a large fraction of unthreadable conformations, but once that size is exceeded, the fraction of unthreadable conformations diminishes. Therefore, the increase of threading yield with increasing ring size in the large ring size region is slower (smaller slope) than that in the small ring size region. The break point would depend on the flexibility of the cyclic component and the nature of the linear species. Indeed, recent molecular modeling studies by Semlyen and co-workers indicated that such is the case.[22]

Although the poly[(decamethylene sebacate)−crown ether rotaxane]s are heterorotaxanes and the threading process is more complicated than those in homorotaxane systems, the principles discussed above are still applicable. Therefore, the semilog curve can be divided into two straight lines with the break point at about 38 atoms. "36-Crown-12" differs greatly from 30-crown-10 in terms of degree of threading, probably due to the great differences in repulsive interaction and threadable conformations.

In a separate experiment, 1 mol of 1,10-decanediol was stirred with 0.5 mol of 30-crown-10 and 0.5 mol of "42-crown-14" before the addition of sebacoyl chloride. 30-Crown-10 can be differentiated from "42-crown-14" because it shows a singlet at δ 3.671 and "42-crown-14" displays a singlet at δ 3.647 in ^{1}H NMR spectra in $CDCl_3$. After three precipitations into methanol, no 30-crown-10 molecules were found in the polyrotaxane. This experiment again demonstrated the important effect of ring size on degree of threading.

D. Feed Ratio. The next parameter studied was the feed ratio of crown ether to diol monomer. The polyrotaxanes were prepared by the polymerization of sebacoyl chloride with 1,10-decandiol at 80 °C. "42-crown-14" (**6**) was stirred with 1,10-decanediol in the melt for 0.25 h before the addition of sebacoyl chloride. The macrocycle content increases with increasing molar feed ratio up to 2. After that, the macrocycle content becomes constant. These results are listed in Table 5.

Zilkha et al. found that the proportion of the threaded cyclic species can be maximized by using an excess of macrocycle.[7] The same phenomenon was observed in polyurethane−crown ether rotaxanes.[15] All these results demonstrate that the formation of polyrotaxanes follows le Chatelier's principle.

Table 6. Effect of the Diol Length on the Threading of "42C14" (6) by HO(CH$_2$)$_x$OH (1−3) To Form Polypseudorotaxanes 10, 11, and 14 (0.5 h, 80 °C)

length (x)	m/n[a]	wt % "42C14"
4	0.32	43
6	0.30	39
10	0.29	34

[a] Final molar ratio of macrocycle to repeat unit of the polymer backbone in polyrotaxanes **10**, **11**, and **14** measured by ^{1}H NMR.

The fact that the equivalence point was about 2 initially suggested that one diol molecule was "saturated" by two crown ether molecules during the prethreading process.[13f] However, since we now know that the "42C14" actually consists of a mixture of cyclics,[19] this observation must now be considered coincidental.

E. Length of the Diol. If the hydrogen bonding between the diol monomers and crown ethers plays an important role in the threading, the degree of the threading, m/n, should not be significantly affected by the length of the diol monomers, although at the extremes changes in the polarity of the medium could have an influence. A study of the effect of the length of diols on threading yield was performed by the preparation of polyrotaxanes by the condensation of sebacoyl chloride with 1,4-butanediol (**1**), 1,6-hexanediol (**2**), and 1,10-decanediol (**3**), respectively, in the presence of "42-crown-14" (**6**). Again, the prethreading time was 0.5 h, the temperature was 80 °C and the molar feed ratio of cyclic to linear monomer in the prethreading process was 1. The results (Table 6) revealed that the m/n values did not change with increasing length of the alkylenediol. Because increasing the length of the diol does not increase the degree of threading but does increase the molecular weight of the repeat unit of the polymer backbone, the mass percentage of macrocycle in the polyrotaxane decreases with increasing diol length.

The above result is different from the results obtained for *homorotaxane* formation, in which threading increased with the length of the linear species. For example, Schill and co-workers studied the effect of the length of linear alkane chains of 10−38 carbons blocked by trityl groups on their threading into a 29-carbon cycloalkane.[2] The yield of rotaxane increased from 4.5% to 11.3% when the chain length increased from 10 carbons to 38 carbons. Here the threading equilibrium is statistically determined by the length of the linear species.

Zilkha and co-workers found from their synthesis of poly[(ethylene glycol)−crown ether rotaxane]s that the degree of threading was nearly independent of linear species length.[7] In this case the hydroxyl groups of the linear oligo(ethylene glycol)s can hydrogen bond with the crown ethers, just as in the present systems.

The ^{1}H and ^{13}C NMR spectra of poly[(butylene sebacate)-*rotaxa*-("42-crown-14")] were previously reported.[13b] ^{1}H and ^{13}C NMR spectra of poly[(hexamethylene sebacate)-*rotaxa*-("42-crown-14")] (**11**) are completely analogous.

Figure 7 shows the GPC traces for polyrotaxanes **10**−**16**. Note that all the polyrotaxanes display single symmetrical signals and no free crown signals were observed at high elution volumes.

Table 7. Effect of Equilibration Time on the Threading of "42-Crown-14" (6) by 1,10-Decanediol (3) To Form Polypseudorotaxane 14[a]

time (h)	<0.02	0.5	1	2	24	8
m/*n*[b]	0.32	0.29	0.30	0.31	0.31	0.31

[a] Neat process; molar feed ratio of cyclic to linear, 1.0; temperature, 80 °C. [a] Final molar ratio of macrocycle to repeat unit of the polymer backbone in polyrotaxane **14** measured by ^{1}H NMR.

Table 8. Prethreading of "42-Crown-14" (6) by Sebacoyl Chloride (Molar Ratio of Cyclic and Linear; 1.0; Temperature; 80 °C; 0.5 h) and by 1,10-Decanediol (3) (Molar Ratio of Cyclic and Linear, 1.0; Temperature, 80 °C; 0.5 h) To Form Polypseudorotaxane 14

	double prethreading	monoprethreading of 1,10-decanediol	
M_o/L_o[a]	1.00	1.00	2.00
M_o/S_o[b]	1.00	0.00	0.00
m/*n*[c]	0.35	0.29	0.41

[a] Molar ratio of "42-crown-14" to 1,10-decanediol in the monomer feed. [b] Molar ratio of "42-crown-14" to sebacoyl chloride in the monomer feed. [c] Final molar ratio of macrocycle to repeat unit of the polymer backbone in polyrotaxane **14** measured by ^{1}H NMR.

F. Prethreading Time. Zilkha and his colleagues observed that the equilibrium for threading of linear poly(ethylene glycol) into dibenzo crown ethers was established within 30 min.[7] Similarly, here we found that the threading yield of 1,10-decanediol with "42-crown-14" did not increase with equilibration time from <1 min to 48 h, as shown in Table 7. This result is attributed to the very rapid formation of hydrogen bonds between the cyclic and linear species during the prethreading process.

G. "Double" Prethreading. The importance of prethreading invites consideration of "double" prethreading, that is, separately prethreading both monomers through macrocycles prior to reaction. An experiment was performed in which both sebacoyl chloride and 1,10-decanediol had been mixed with an equivalent of "42C14" independently and separately prior to the polymerization, at 80 °C for 0.5 h. The final *m*/*n* value was 0.35, higher than that of diol monoprethreading with $M_o/L_o = 1$ ($m/n = 0.29$) but lower than that with $M_o/L_o = 2$ ($m/n = 0.41$) (Table 8). As expected, the hydrogen bond-driven threading yield of the diol is higher than that of the diacid chloride. Dipole−dipole interactions of the chlorocarbonyl and ethyleneoxy units may provide some driving force in this case, however. It may be that pseudorotaxane formation from the diacid chloride reduces its reactivity, enabling more dethreading to occur during the retarded esterification process (see below).

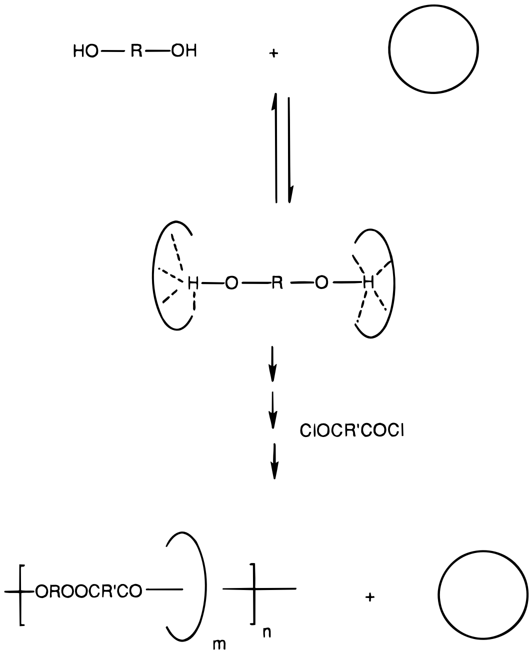
On the basis of the above results (sections C−G), it is believed that initially one diol molecule hydrogen bonds with two crown ether molecules during the prethreading process. The polymerization takes place after the threading equilibrium has been established. This concept is depicted in Scheme 3. It is possible that hydrogen bonding of crown ether with protonated OH groups, derived from liberated HCl, or *vice versa* could also contribute.

H. Temperature. Because hydrogen bonding is a favorable interaction between the cyclic and linear species, the term for the enthalpy change ($\Delta H°$) in the free energy equation:

$$\Delta G° = \Delta H° - T\Delta S° \qquad (5)$$

was expected to be negative. Since

Scheme 3. Hydrogen Bonding between the Diol and Crown Ether in the Prethreading Process



$$\Delta G° = -RT \ln K = \Delta H° - T\Delta S° \qquad (6)$$

the natural log of the equilibrium constant for threading is a function of the reciprocal of temperature:

$$\ln K = -(\Delta H°)/(RT) + \Delta S°/R \qquad (7)$$

Therefore, the temperature dependence of the degree of the threading was expected. Prethreading of 1,10-decanediol with "42-crown-14" (1:1 molar ratio, 0.5 h) was performed at different temperatures followed by polymerization at those temperatures. However, the similarity of all *m*/*n* values in the temperature range of 80−160 °C, as shown in Table 9, suggested that threading is independent of temperature, i.e., statistical (ΔS driven) in nature. The temperature independence of the threading was also observed by Zilkha et al.[7] They suggested that due to the chemical similarity between the macrocycle and linear polymer, the chain ends show no preferred interaction with any element in the system.

However, several factors need to be taken into account in our heterorotaxane systems:

(1) Not all crown ethers hydrogen bonding with OH groups will be threaded onto the polymer backbones since ester bond formation can also occur in an *exo* manner. Whether the rings can be threaded onto polymer chains depends on their conformations. Conformational changes of the linear species will also affect the degree of threading, although they may not be as significant as conformational changes of the macrocycles. Unfortunately, the influence of temperature on threadable conformations is not well understood at this time.

(2) Molecular weights of polyrotaxanes might also influence the dethreading of macrocycles from polymer chains due to the differences in numbers of chain ends. However, as shown in Table 9, *m*/*n* values do not vary significantly with molecular weight.

(3) An unfavorable interaction of the nonpolar linear chain and the polar cyclic species may contribute a positive enthalpy component once the ester bond is formed.

Table 9. Effect of Temperature on the Threading of "42C14" (6) by 1,10-Decanediol (3) to form Polypseudorotaxane 14[a]

temp. (°C)	80	110	115	140	160
m/n^b	0.29	0.30	0.29	0.33	0.32
10^{-3} M_n	8.3[c]	12.8[d]	10.9[d]	6.3[d]	11.6[d]
M_w/M_n	1.68[c]	1.74[d]	1.62[d]	1.75[d]	1.69[d]

[a] Neat process; molar feed ratio of cyclic to linear, 1.0; prethreading time, 30 min. [b] Final molar ratio of macrocycle to repeat unit of the polymer backbone in polyrotaxane **14** measured by ^{1}H NMR. [c] Determined by GPC with polystyrene standards in THF. [d] Determined by GPC with polystyrene standards in chlorofrom.

Scheme 4. Dethreading of "42-Crown-14" (6) from Poly[(decamethylene sebacate)-rotaxa-("42-crown-14")] (14)

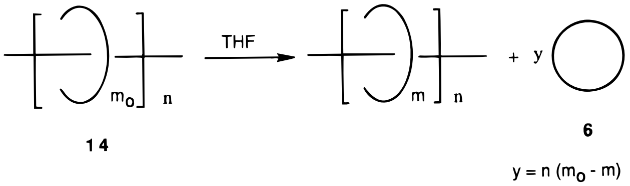


Table 10. Dethreading Experiments of "42C14" (6) from Poly[(decamethylene sebacate)-*rotaxa*-("42-crown-14")] (14)

experiment	1	2	3	4
temp (°C)	50	65	65	65/25
concn (g/L)	42	4.8	4.8	4.8
time (days)	7	11	35	311/172
initial m/n	0.34	0.18	0.18	0.18
initial wt % cyclic	35	25	25	25
initial 10^{-3} M_n	8.3[a]	11.3[b]	11.3[b]	11.3[b]
initial 10^{-3} M_w	14[a]	20.5[b]	20.5[b]	20.5[b]
final m/n^c	0.27	0.17	0.15	0.09
final wt % cyclic	30	24	21	14
final 10^{-3} M_n		9.1[b]	12.7[b]	
final 10^{-3} M_w		17.9[b]	22.3[b]	

[a] Determined by GPC with polystyrene standards in toluene. [b] Determined by GPC with polystyrene standards in THF. [c] Determined by ^{1}H NMR.

(4) Thus, the threaded macrocycles can be lost after formation of the ester linkage because the hydrogen-bonding driving force is then no longer operative; during the polymerization process, depending on a number of factors, significant dethreading could occur. This hypothesis was supported as the most plausible explanation of the lack of temperature dependence by the synthesis of a polyrotaxane with bulky spacers on its backbone, which will be discussed below.

I. Dethreading Experiments. The lack of dethreading during purification is supported by the results from long term experiments in which poly[(decamethylene sebacate)-*rotaxa*-("42-crown-14")] (**14**) was heated in tetrahydrofuran solution (Scheme 4). Table 10 summarizes the results.

In experiment 1, **14** ($m/n = 0.34$, 35 wt % "42C14") was dissolved in THF and the solution was stirred at 50 °C for 7 days. After the purification, the m/n value was reduced to 0.27 (30 wt % "42-crown-14"). The dethreading rate was 1.0×10^{-2} day^{-1}.

In experiment 2, **14** with lower mass percent of "42-crown-14" ($m/n = 0.18$) was treated in refluxing THF for 11 days. Sampling the solution showed a lack of dethreading, as the m/n value only decreased by 0.01, about the limit of error of the measurement (see above). The rest of the solution was then stirred for another 24 days under the same conditions, but only a small change of the m/n value was observed (experiment 3). Figure 8 is the plot of the m/n value against time, the results of experiments 2 and 3. The dethreading rate derived from the slope was 8.5×10^{-4} per day.

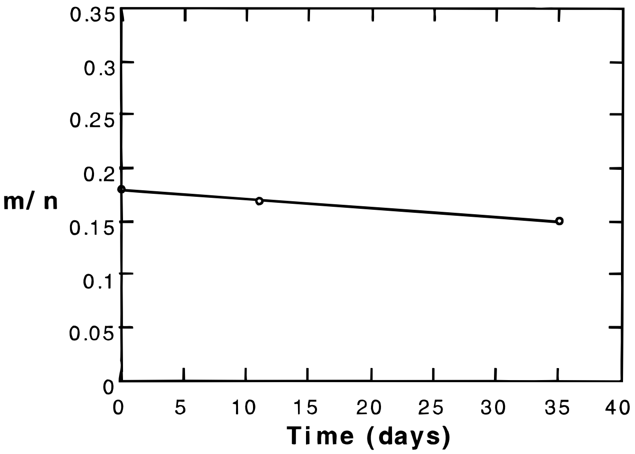


Figure 8. m/n value of poly[(decamethylene sebacate)-*rotaxa*-("42-crown-14")] (**14**) as a function of dethreading time (conditions: in THF; concentration of **14**, 4.8 g/L, temperature, 65 °C).

The above results demonstrate that the dethreading rate is significantly affected by the initial macrocycle content, as expected from kinetic and thermodynamic considerations. The initial m/n value in experiment 1 was 1.9 times higher and the molecular weight was lower than that of the polyrotaxane in experiment 2. Although the conditions in experiment 1 are less favorable for the dethreading of macrocycles than those of experiment 2, with lower temperature, shorter dethreading time, and higher concentration, the dethreading rate of the former is 10-fold higher than the latter.

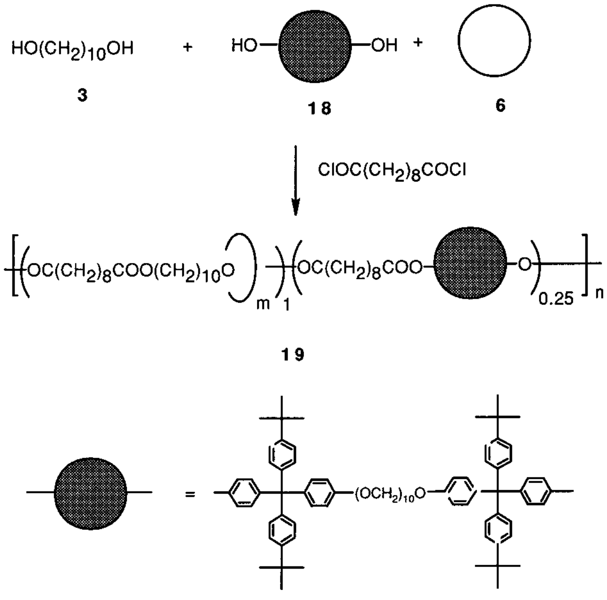
A longer term experiment was also carried out (experiment 4) at 65 °C for 311 days and then at 25 °C for 172 days; m/n was reduced over this time to 50% of its initial value. In other words the half-life of the polyrotaxane is quite long!

These results support the hypothesis that loss of threaded macrocycles is hindered by the random coiling of both linear and cyclic species and the "wiggle effect" of the chain ends which enhances the movement of macrocycles toward the middle of the chains. Two other factors arise from the OH and COOH end groups, which act as blocking groups not via steric interaction but by attractive interactions; first, these will H-bond with the terminal crown ether molecules, hindering their departure, and second, H-bonding to solvent molecules or other macromolecules or the crown ethers threaded onto other macromolecules will give the same result. It must also be pointed out that macrocycles can only dethread one at a time at each end of the linear macromolecule; i.e., it is a stochastic process. In any event, although thermodynamically favorable, the loss of crown ether molecules from these polypseudorotaxanes is kinetically very slow.

J. Molecular Strings of Beads with Stoppers from Difunctional Blocking Groups. Loss of macrocycles during the polymerization can lead to a reduced m/n value. In order to prevent macrocycles from dethreading, blocking groups are needed. Since the end-capping of polymer chains by monofunctional blocking groups is often not efficient in the cases of high molecular weight polymers,[13c] difunctional bulky monomers are desirable.

Therefore, a bisphenolic blocking group, 1,10-bis{*p*-[bis(*p*′-*tert*-butylphenyl)(*p*″-hydroxyphenyl)methyl]-

Scheme 5. Synthesis of Polyrotaxane 19

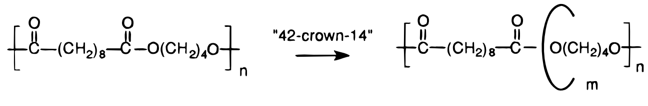


phenoxy}decane (**18**), was used in polyrotaxane synthesis, as depicted in Scheme 5. In the reaction, the molar ratio of **18** to 1,10-decanediol (**3**) was 1:4 and the molar ratio of "42-crown-14" to sebacoyl chloride was 1. After three precipitations, the m/n value, the molar ratio of macrocycle to the decamethylene sebacate unit of the polymer backbone, was 0.74, as determined by the proton NMR spectroscopy. The macrocycle content in polyrotaxane **19** was 2.4-fold higher than that of **14** made under comparable conditions. This result, coupled with the demonstrated very slow dethreading of crown ethers from isolated polyrotaxanes, revealed the fact that for polypseudorotaxanes (without blocking groups), significant loss of threaded macrocycles does indeed occur during the polymerization process. Subsequent work has corroborated this fact by reaction of another bulky diol with sebacoyl chloride in the presence of 30C10,[13b] preparation of a series of copolymeric rotaxanes from the bulky diol and 1,10-decanediol with sebacoyl chloride[13a] and finally polymerization of a bulky diol and a bulky diacid chloride to produce a 30C10 polyrotaxane with an m/n value of 0.172,[13h] i.e., >14 times higher than in **12** prepared here (Table 4). In the case of the bulky diol sebacate rotaxane, as anticipated, the m/n value was indeed temperature dependent.[13j]

III. Threading of Preformed Polyester. To test the efficiency of formation of polyrotaxanes by threading of preformed polymers, poly(butylene sebacate) was mixed in the melt with "42-crown-14" at 120 °C for 3 days, as summarized in Scheme 6. This led to the formation of polyrotaxane **10** with $m/n = 2.0 \times 10^{-2}$, corresponding to 4.6 mass % crown ether. The polyrotaxane was treated again with crown ether, this time in THF solution at 55 °C for 3 days; this led to **10**, $m/n = 1.7 \times 10^{-2}$ (4.0 mass %). And, finally, a third treatment in THF−acetonitrile afforded **10**, $m/n = 1.3 \times 10^{-2}$ (3.0 mass %). Thus, a conclusion from these studies is that it is possible to form polypseudorotaxanes from preformed polymers in this way, but it is not very efficient.

In a control experiment poly(butylene sebacate) with both ends blocked with tris(*p*-*tert*-butylphenyl)methyl groups[13c] and comparable molecular weight was mixed with "42-crown-14" in THF at 60 °C for 11 days; the resultant polyrotaxane **10** had an m/n value of only 3.0×10^{-4} (0.07 mass %), indicating that the blocking groups effectively prevent threading by "42-crown-14", probably both sterically and by the lack of hydrogen-bonding sites.

Scheme 6. Threading of Preformed Poly(butylene sebacate) through "42-Crown-14"



exp no.	polymer mass (g)	crown mass (g)	solvent (mL)	temp (°C)	time (days)	mass % "42-crown-14" 1st ppt	2nd ppt	3rd ppt
1	1.00[a]	4.80	none	120	3	23	4.9	4.6
2	0.80[b]	4.60	THF (10)	55	3	10	4.4	4.0
3	0.59[b]	3.65	M[c] (60)	62	16	5.8	4.4	3.0[d]

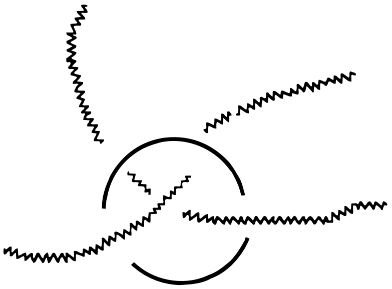
[a] Poly(butylene sebacate), $M_n = 18.8$ kg/mol, $M_w = 35.7$ kg/mol by GPC with universal calibration; $[\eta] = 0.847$ dL/g ($CHCl_3$, 30 °C). [b] Polymer from previous experiment. [c] THF:CH_3CN, 3:1 v/v. [d] $M_n = 44.8$ kg/mol, $M_w = 198$ kg/mol by GPC with universal calibration; $[\eta] = 1.654$ dL/g ($CHCl_3$, 30 °C).

IV. Properties of Poly(ester rotaxane)s. A. Double (or Multiple) Threading of Preformed Polymer. The 3.0 mass % of crown ether in polypseudorotaxane **10**, $m/n = 0.013$ corresponds to ca. one macrocycle per macromolecule based on the molecular weight of the starting polyester. However, as shown by GPC measurements using the universal calibration, the molecular weight increased significantly ($M_n = 44.8$K, $M_w = 198$K, MWD = 4.42 by GPC with universal calibration) vs the starting polyester ($M_n = 18.8$K, $M_w = 35.7$K by GPC with universal calibration). Moreover, the intrinsic viscosity of the polyrotaxane was twice that of the parent polyester: 1.654 vs 0.847 dL/g ($CHCl_3$, 30 °C); this measurement indicates that the hydrodynamic volume of the polypseudorotaxane is about twice that of the polyester itself.

The question is: how can the presence of one (actually less than one, given that the crown ether is a mixture whose average size is larger than 42-membered[19]) crown ether per macromolecule have such a large effect on the molecular weight and hydrodynamic volume?

The threaded crown ethers are expected to increase the hydrodynamic volume as a result of their exclusion of volume from occupation by the backbone because of the conformational mobility of the macrocycles. However, this is not expected to be a large effect at this low level of macrocycle content and, moreover, it should not have a measurable effect on the molecular weight. Examination of molecular models indicates that 42-crown-14 has a large enough cavity to undergo double threading. Since the crown ether sample in reality contained on average rings larger than this, double (or multiple) threading is the most plausible explanation; double threading, as shown in **20,** would result in branching, as observed by GPC, and also the observed increase of hydrodynamic volume, deduced from the solution viscosity data.

This raises the question of double or multiple threading and branching in the polyrotaxanes made by polymerization in the presence of the large crown ethers. However, the molecular weight data given in the Experimental and Table 9 do not indicate the increase in distribution that this would cause; it is possible that fractionation removes the branched material during



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purification and indeed in some cases, particularly with “60-crown-20”, some gel was noted.

B. Intrinsic Viscosity as a Function of Solvent. The solution behavior of polyrotaxanes depends on the differential solvation of the cyclic and linear species of the polymers. The differential solvation effect could in the extreme case cause either the macrocycle or the linear backbone to be fully expanded or to collapse into a θ state. A good solvent for both the cyclic and linear species would lead to expansion of both components. A good solvent for the linear macromolecule but a poor solvent for the cyclic species should lead to an expanded backbone but collapsed macrocycle. A poor solvent for the linear backbone but a good solvent for the macrocycle should provide a collapsed state of the linear component and an expanded state for the rings. A poor solvent for both the linear and cyclic components affords collapsed conformations of both. It should be noted that for polypseudorotaxanes these factors will be very important in determining the rates of threading and dethreading.

In order to address this issue, the intrinsic viscosities of poly(decamethylene sebacate) (**9**) and poly[(decamethylene sebacate)-*rotaxa*-(“42-crown-14”)] (**14**) were measured in pure THF and in mixtures of THF and methanol with different ratios (Table 11). THF is a good solvent for both linear and cyclic species of the polyrotaxane, while methanol is a good solvent for the crown ether but a poor solvent for poly(decamethylene sebacate). In fact, methanol can form complexes with crown ethers.[23] Thus, a change in the intrinsic viscosity of the polyrotaxane with the ratio of THF:methanol is expected. Indeed, the intrinsic viscosity of **14** was reduced from 0.331 to 0.248 dL/g as the solvent was changed from pure THF to a mixture of THF and methanol (100:10, v:v). On the other hand, the [η] value of polymer **9** does not change much as the ratio of THF:methanol changes from 100:0 to 100:20, regardless of its molecular weight. Nor is there a significant change in the intrinsic viscosity of the PEO copolymer **17** with solvent; since the ethyleneoxy content of **17** matches that of polyrotaxane **14**, this result rules out a simple differential solvation as the explanation for the observed results with **14** and indicates that the effect is truly of topological origin. Clearly, the better solvating power of methanol for the crown ether leads to a lowering of the hydrodynamic volume of **14**, presumably by loosening the macrocycles’ grip on the backbone, allowing more chain folding.

It is also noteworthy that in a given solvent the intrinsic viscosity of the polyrotaxane is higher than that of the model polyester **9** of about the same molecular weight, indicating a significant increase in hydrodynamic volume in the rotaxane. Thus, rotaxanation has the potential to increase the intrinsic viscosity of linear macromolecules; this could be advantageous in some applications.

Table 11. Intrinsic Viscosities[a] ([η], dL/g) of the Model Polymer 9, Copolymer 17, and the Polyrotaxane 14, *m*/*n* = 0.29 as Functions of Solvents

			(THF−methanol; v:v)		
polymer	10^{-3} M_n	10^{-3} M_w	(100:0)	(100:10)	(100:20)
9	5.2,[b] 5.0[c]	7.1,[b] 7.3[c]	0.141	0.147	0.146
9	8.9,[b] 5.4[c]	15.2,[b] 8.8[c]		0.160	0.157
9	17.1[c]	32.8[c]	0.543	0.549	pi[e]
14	8.3[d]	14[d]	0.331	0.248	pi[e]
17	15.6[c]	39.8[c]	0.414	0.403	pi[e]

[a] Measured in a Cannon-Fenske type viscometer at 25 °C. [b] Determined by GPC with polystyrene standards in chloroform. [c] Determined by GPC with universal calibration (viscosity detector) in chloroform. [d] Determined by GPC with polystyrene standards in toluene. [e] Partly insoluble.

Table 12. Thermal Properties of Model Polymers and Polyrotaxanes Measured by DSC at 10 °C/min

polymer	T_g[a] (°C)	T_m[b] (°C)	ΔH_f[b] (cal/g)	T_c[c] (°C)
9		77	30.8	62.1
10	−55	44, 62	5.7, 12.0	23, 46
11	−55	39, 67	5.6, 15.8	22, 49
12		80	25.8	63
13	−54	42, 69, 71	5.0, 16.8[d]	21, 56
14[e]	−56	42, 70, 74	4.1, 20.9[d]	25, 59
15	−58	43, 71, 75	5.7, 23.3[d]	25, 60, 62
16	−58	44, 63, 70	5.4, 18.6[d]	26, 55, 57
17	−54	66	15.3	49
19	−56	45, 67	5.0, 5.0	8, 47

[a] Data from the second heating. [b] Data from the second heating, except the data of **10**, which were from the third heating. [c] Crystallization exotherm data from the second cooling. [d] Heat of fusion of two partially overlapped endotherms. [e] *m*/*n* = 0.29.

C. Thermal Properties of Polyrotaxanes. Polyrotaxanes show different phase transition behavior compared to the parent polyesters (Table 12). Melting temperatures were changed and in some cases the macrocycles were able to crystallize without dethreading.

a. Poly(decamethylene sebacate) Systems. The model system poly(decamethylene sebacate) (**9**) is a highly crystalline polymer. It shows a melting transition at 77 °C upon heating and a crystallization exotherm at 62 °C during cooling. T_g was not observed by DSC. The T_m of **9** has been reported to be 70−78 °C,[24−27] heat of fusion 33.7−39.9 cal/g,[25,27] and T_g −58 to −75 °C.[26,27] Poly[(decamethylene sebacate)-*rotaxa*-(30-crown-10)] (**12**), a polyrotaxane containing only 1.5 mass % macrocycle, demonstrates nearly the same thermal properties: $T_m = 80$ °C, $T_c = 63$ °C, and no T_g was observed. A crown ether crystalline phase was not observed due the low proportion of macrocycles present.

However, for poly(decamethylene sebacate) rotaxanes containing larger macrocycles and larger macrocycle contents, glass transitions were observed and three melting temperatures appeared. Poly[(decamethylene sebacate)-*rotaxa*-(“36-crown-12”)] (**13**), as shown in Figure 9a, displayed a glass transition signal at −54 °C, in the vicinity of the glass transition of “36-crown-12” (−73 °C), a melting endotherm at 42 °C, which was somewhat below the melting point of “36-crown-12” (57 °C, Figure 10a), and two other partially overlapped endotherms at 69 and 71 °C, which were somewhat below the melting point of polymer **9** (77 °C). Upon cooling, a crystallization exotherm appeared at 56 °C and another exotherm was shown at 21 °C (Figure 9b). Figure 10 illustrates the phase transition behavior of

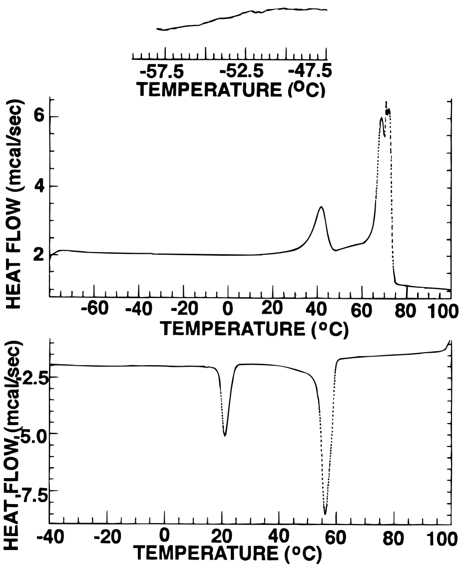


Figure 9. DSC traces for poly[(decamethylene sebacate)-*rotaxa*-(“36-crown-12”)] (**13**, $m/n = 0.22$): (a) second heating scan (top); (b) second cooling scan (bottom); 10 °C/min. Inset: low-temperature region.

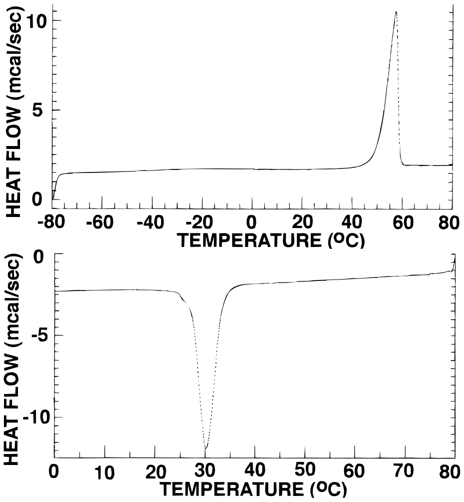


Figure 10. DSC traces for “36-crown-12” (**5**): (a) second heating scan (top); (b) second cooling scan (bottom); 10 °C/min.

“36-crown-12” (**5**), which underwent melting at 57 °C (Figure 10a) and upon slow cooling crystallized at 31 °C (Figure 10b); after rapid cooling, the glass transition was observed at −73 °C. It is apparent that the glass transition of polyrotaxane **13** corresponds to “36-crown-12” (**5**). In view of the fact that the melting transition of “36-crown-12” (**5**) is lower than that of poly(decamethylene sebacate) (**9**) and the mass percent of macrocycle in polyrotaxane **13** is lower than that of the polymer backbone, the lowest melting transition with the lowest heat of fusion is due to the macrocyclic component of the polyrotaxane. Likewise, the lowest crystallization exotherm with the lowest enthalpy of crystallization comes from the crown ether in the polyrotaxane. The two partially overlapped melting endotherms and exotherms at high temperatures are attributed to the polymer backbone.

The presence of two melting transitions for the polymer backbone is not unusual for aliphatic polyesters; it reflects either polymorphism or different lamellar thicknesses arising during different stages of the crystallization process.[28]

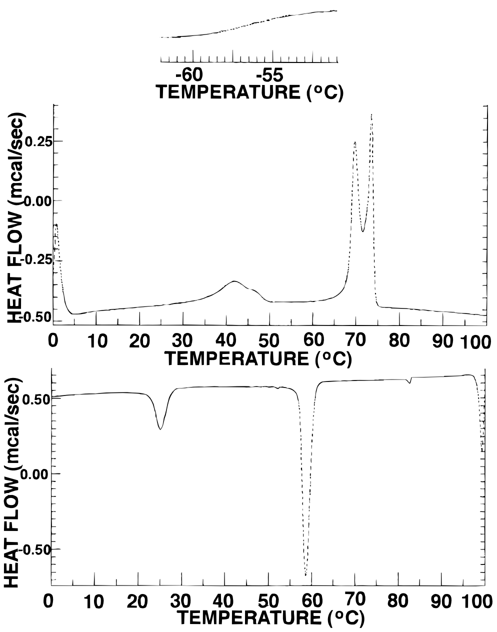


Figure 11. DSC traces for poly[(decamethylene sebacate)-*rotaxa*-(“42-crown-14”)] (**14**, $m/n = 0.29$): (a) second heating scan (top); (b) second cooling scan (bottom); 10 °C/min. Inset: low-temperature region.

Taking into account the fact that polyrotaxane **13** was 25 mass % macrocycle, comparison of the heats of fusion of the backbone, macrocycle, and polyrotaxane indicates that ~57% of the macrocycle and ~73% of the linear component of **13** crystallized with respect to components **5** and **9**.

Polyrotaxane **14**, $m/n = 0.29$, showed similar phase transition behavior, as demonstrated in Figure 11 and Table 12: on heating (Figure 11a), a glass transition signal at −56 °C, in the vicinity of the glass transition of “42-crown-14” (−68 °C), a melting endotherm at 42 °C, which was somewhat below the melting point of “42-crown-14” (59 °C), and two partially overlapped endotherms at 70 and 74 °C, which were somewhat below the melting point of poly(decamethylene sebacate) (77 °C). Upon cooling, a crystallization exotherm appeared at 59 °C and another exotherm at 25 °C (Figure 11b). It is apparent that the glass transition of the polyrotaxane corresponds to “42-crown-14”. In view of the fact that the melting transition of 42-crown-14 is lower than that of poly(decamethylene sebacate) and the mass percent of macrocycle in the polyrotaxane is lower than that of the polymer backbone, the lowest melting transition with the lowest heat of fusion is due to the macrocyclic component of the polyrotaxane. Likewise, the lowest crystallization exotherm with the lowest enthalpy of crystallization comes from the crown ether in the polyrotaxane. The two partially overlapped melting endotherms and exotherms at high temperatures are attributed to the polymer backbone. Comparison of the heats of fusion of polyrotaxane **14** with those of pure components **6**[13c] and **9** indicated that ~32% of the macrocycle and ~100% of the backbone species of **14** crystallized.

Comparison of polyrotaxanes and covalent analogs of the same compositions enables a determination of the topological effects extant in the former systems. Thus, comparison of the thermal behavior of covalent copolymer **17** vs that of polyrotaxane **14** is of interest (Table 12). Poly[(decamethylene sebacate)-*co*-oligo(ethyleneoxy)-sebacate)] (**17**) in the second heating displayed a glass

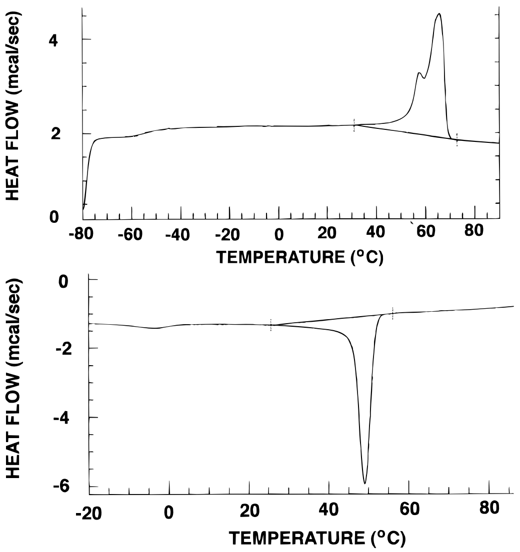


Figure 12. DSC traces for poly[(decamethylene sebacate)-*co*-(oligo(ethyleneoxy) sebacate)] (**17**): (a) second heating scan (top); (b) second cooling scan (bottom); 10 °C/min.

transition signal at −54 °C and a melting endotherm at 66 °C with a shoulder at 57 °C (Figure 12a). Upon the second cooling, a crystallization exotherm appeared at 49 °C with a small exotherm at −5 °C (Figure 12b). Comparison of the heats of fusion of the copolymer with that of the backbone polymer, poly(decamethylene sebacate), indicates that ∼76% of the decamethylene sebacate component of the copolymer crystallized with respect to the homopolymer. Therefore, polyrotaxane **14** displays some special thermal properties compared to copolymer **17**, even though the two polymers have similar mass percentages of ethyleneoxy units: (1) Due to its mobility along the backbone, the macrocyclic component of the polyrotaxane can aggregate and crystallize, unlike the covalently linked ethyleneoxy units of the copolymer. (2) Accordingly, the crystallinity of the decamethylene sebacate component of the polyrotaxane is higher than that of the copolymer, as shown by the lower melting and crystallization temperatures and the lower heat of fusion of **17** vs **14**. This is due to the shorter length of the decamethylene sebacate segments in the copolymer backbone and the diminished ability of these units to separate themselves spatially from the ethyleneoxy segments.

Polyrotaxane **15** showed a T_g at −58 °C, a melting endotherm at 43 °C, and two other partially overlapped endotherms at 71 and 75 °C (Table 12). Upon cooling, two overlapped crystallization exotherms appeared at 62 and 60 °C and another exotherm was shown at 25 °C. "48-Crown-16" (**7**) underwent melting at 55 °C and upon slow cooling crystallized at 25 °C; after rapid cooling, the glass transition was observed at −73 °C. About 45% of the macrocyclic species of **15** crystallized with respect to the component **7**. Comparison of the heats of fusion of **9** and **15** indicates that the crystallinity of the linear chain of **15** is 28% higher than that of model polymer **9**. This may due to the fact that molecular weight of the backbone of **15** is lower than **9** and thus it crystallizes more readily. Indeed, the heat of fusion of **15**'s backbone is the same as the reported value for the low molecular weight polymer **9** (M_v = 5.2K).[27]

The same phenomenon was observed in poly[(decamethylene sebacate)-*rotaxa*-("60-crown-20")] (**16**) (Table 12). While ∼39% of the macrocyclic species of **16** crystallized compared to "60-crown-20" (**8**), the crystallinity of the backbone of **16** was 16% higher than model polymer **9** but 10% lower than that reported for low molecular weight polymer.[27]

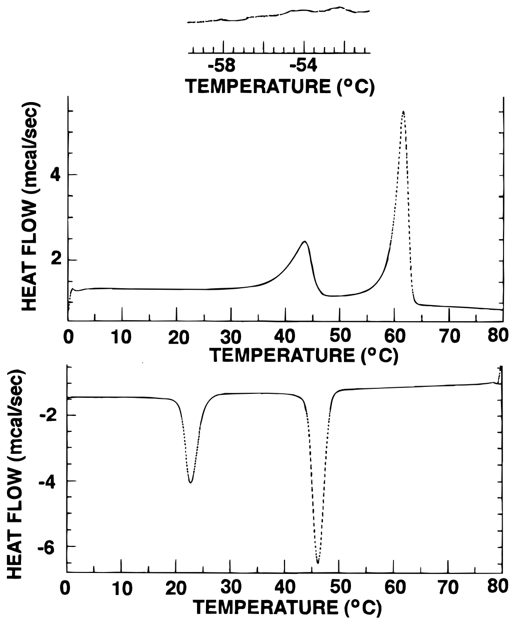


Figure 13. DSC trace for poly[(butylene sebacate)-*rotaxa*-("42-crown-14")] (**10**, m/n = 0.32): (a) third heating scan (top); (b) second cooling scan (bottom); 10 °C/min. Inset: low-temperature region.

b. Poly(butylene sebacate) and Poly(hexamethylene sebacate) Systems. Poly(butylene sebacate) displayed T_m = 67 °C and T_c = 48 °C, and T_g was not observed by DSC. T_m of the polymer has been reported as 63−65 °C,[26,27,29] the heat of fusion as 37.0 cal/g,[27] and T_g as −57 to −75 °C.[26,27,29] Poly[(butylene sebacate)-*rotaxa*-("42-crown-14")] (**10**) displayed a melting endotherm at 46 °C, and two overlapped endotherms at 58 and 63 °C upon first heating, similar to the results shown in Figures 9 and 11 for the decamethylene systems. In the second heating after rapid cooling, the glass transition was observed at −55 °C. Although three endotherms were observed during the second heating, the lower melting peak of the two overlapped endotherms was greatly reduced. This transition disappeared upon the third heating (Figure 13a). **10** shows two crystallization exotherms at 46 and 23 °C during the second cooling (Figure 13b). The crystallinity of the cyclic component of **10** is 57% lower than that of "42-crown-14" (**6**), but the crystallinity of polyrotaxane **10**'s backbone is 14% higher with respect to the model polymer. The heat of fusion of the linear component of **10** (21.1 cal/g) is lower than the reported value (37.0 cal/g) for low molecular weight model poly(butylene sebacate) (M_v = 2.5K).[27]

Similarly, poly[(hexamethylene sebacate)-*rotaxa*-("42-crown-14")] (**11**) shows three endotherms upon first heating. In the second heating after rapid cooling, the lower endotherm for the backbone nearly disappeared (Table 12). Two crystallization exotherms were observed upon the second cooling. About 39% of the macrocyclic species of **11** was crystallized with respect to **6**. The model polymer, poly(hexamethylene sebacate), was not synthesized, but its T_m has been reported to be 65−71 °C,[25−27] heat of fusion 33.7−37.0 cal/g,[25,27] and T_g −60 to −70 °C.[26,27] Note that the heat of fusion of the polyrotaxane **11** backbone (25.9 cal/g) is lower than the reported values for the backbone polymer itself.

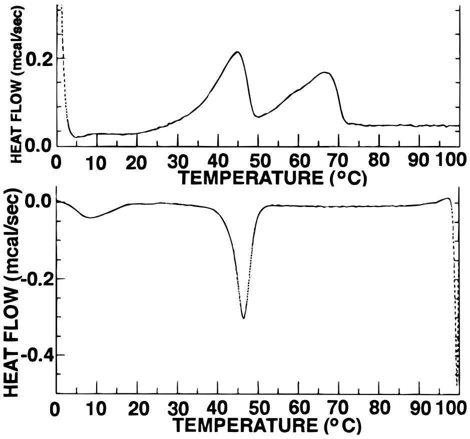
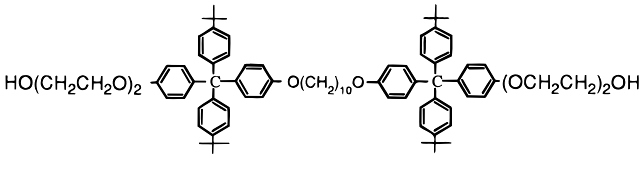


Figure 14. DSC traces for polyrotaxane **19**, $m/n = 0.74$: (a) second heating scan (top); (b) second cooling scan (bottom); 10 °C/min.

c. Polyrotaxane 19 with Bulky Spacers. Due to the lower reactivity of the bisphenolic blocking group **18** toward the sebacoyl chloride compared to the alkylene diol monomer, the blocking groups in **19** are expected to be separated by irregular sequences of alkylene sebacate units. Therefore, macrocyles are still able to move along the polymer backbones, resulting in two crystalline phases: macrocycle and polymer backbone. The DSC measurements showed that indeed this is the case. **19** shows two broad melting endotherms at 45 and 67 °C upon heating (Figure 14a) and two crystallization exotherms at 47 and 8 °C upon cooling (Figure 14b). Because the bulky group **18** disturbs the packing of the polymer chain and the chain length between two bulky groups is not regular, the crystallinity of the polymer chain is greatly reduced. The broad melting endotherm and crystallization exotherm of macrocyclic species of **19** are due to the difference in the numbers of macrocycles between irregularly spaced bulky groups.

The bisphenolic blocking group **18** has been converted to a corresponding diol blocking group **21**.[30] Because of its equal reactivity with diol monomers, 2**1** is expected to be included in polymer chains more randomly, resulting in a random separation of the threaded macrocycles. In this situation, the crystallization of macrocycles may not occur, depending on the ability of aggregates of critical nucleation size to form. Other simpler difunctional blocking group monomers of this type have now also been prepared and used to synthesize poly(ester rotaxane)s.[13a,b,h]



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D. Metal Complexation of Crown Ether Components of Polyrotaxanes. It is a well-known fact that crown ethers can form complexes with metal ions.[23] If the crown ether components of polyrotaxanes are capable of forming complexes with metal ions, changes in thermal and mechanical properties of the complexed polymer compared to the native polyrotaxanes should be observed. The presence of the metal ion should stiffen the chains, increasing the glass transition temperature and modulus. The complexed polyrotaxanes may find some applications in ionic and electronic conduction, separations, and so on.

Table 13. Metal Complexation Tests of Crown Ethers (4–8), Poly(decamethylene sebacate) (9), and Poly[(decamethylene sebacate)-*rotaxa*-(crown ether)]s (12–16) in Which the Toluene Solutions Containing Organic Compounds Were Shaken with an Aqueous Solution of Metal Picrate[a]

compd	Na	K	Ca	Cs
blank	no	no	no	no
4	yes	yes	yes	yes
5	yes	yes	yes	yes
6	yes	yes	yes	yes
7	yes	yes	yes	yes
8	yes	yes	yes	yes
9	no	no	no	no
12	yes	yes	yes	yes
13	yes	yes	yes	yes
14	yes	yes	yes	yes
15	yes	yes	yes	yes
16	yes	yes	yes	yes

[a] Complexations were determined by the color changes in the organic phases.

A series of experiments was done to determine qualitatively the metal complexation capability of threaded crown ethers in poly(decamethylene sebacate) rotaxanes **12–16**. The metal ions investigated were sodium, potassium, calcium, and cesium. In the experiments the polyrotaxane was dissolved in methylene chloride. Metal picrates (the salts of picric acid, 2,4,6-trinitrophenol) were prepared by dissolving picric acid and the metal hydroxide in water. The picrate anion is intensely yellow. The two solutions were then shaken together in a test tube. A blank methylene chloride solution, methylene chloride solutions of crown ethers, and a methylene chloride solution of poly(decamethylene sebacate) were also tested as references. While the blank solution and poly(decamethylene sebacate) solution did not show any color changes after being shaken with the aqueous solutions containing metal picrates, all the crown ether solutions and polyrotaxane solutions displayed a visible yellow color after being shaken, indicating that metal complexation of crown ethers had taken place (Table 13). Note that poly[(decamethylene sebacate)-*rotaxa*-(30-crown-10)] can also form complexes with metal ions even though 30-crown-10 has a relatively small cavity size, and the crown ether content in the polyrotaxane is low. The internal diameter of a fully opened 30-crown-10 molecule is about 7 Å.[31] It does not have enough room to accommodate a polymer chain (4.5 Å)[1] and a cesium cation (3.6 Å).[32] However, its flexibility apparently allows it to form a noncircular conformation to contain both the polymer chain and the cesium cation. 30-Crown-10 molecules in the polyrotaxanes, after they form complexes with cesium ions, may not be able to move along the polymer backbone because of steric hindrance. On the other hand, large crown ethers in polyrotaxanes, after they form complexes with small metal ions, may have enough room in their cavity to allow them to move along the polymer backbone. This movement can probably be hindered by the complexation of the metal ions in the crown ether and carbonyl groups in polymer backbones. Therefore, the movement of threaded macrocycles can probably be controlled by adjusting the size of the macrocycles, the size and the nature of metal ions, and the nature of the polymer chains. Since the macrocycles may thus be locked by complexation with metal ions, blocking groups may become unnecessary.

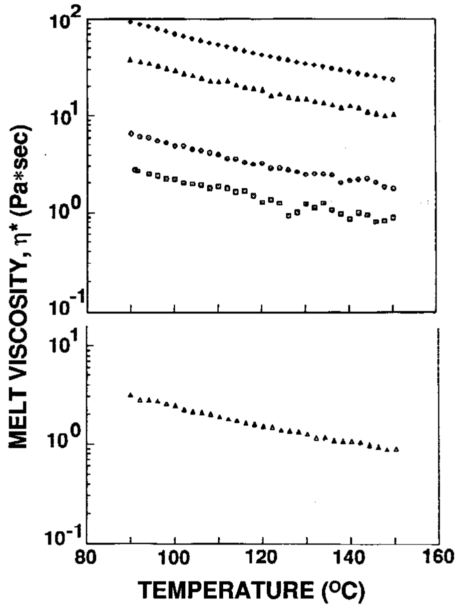

Figure 15. Melt viscosity at an oscillatory shear rate of 1 Hz as a function of temperature. (a) (Top panel) poly(decamethylene sebacate)s [M_n/M_w values from top to bottom: 18.6K/46.2K; 16.7K/36.0K; 7.8K/18.2K; 6.5K/15.9K (polystyrene standards; see Experimental Section)]; the lowest molecular weight sample had M_n = 4.3K, M_w = 7.0K by GPC using a viscometer and the universal calibration. (b) (Bottom panel) poly[(decamethylene sebacate)-*rotaxa*-("42-crown-14")] (**14**, *m*/*n* = 0.13), M_n = 8.3K, M_w = 14.9K with polystyrene standards; M_n = 10.4K, M_w = 17.1K by GPC using a viscometer and the universal calibration.

E. Melt Viscosity. The melt viscosity of polyrotaxane **14**, *m*/*n* = 0.13 was determined as a function of temperature in comparison to that of poly(decamethylene sebacate) (**9**) of various molecular weights (Figure 15). The temperature dependence of the two polymers is the same within experimental error. The curve for the polyrotaxane (M_n = 10.4K) is superimposable on that of the lowest molecular weight **9** (M_n = 4.3K). Even if the 19 mass % of crown ether is subtracted, the polyrotaxane still has a higher molecular weight. The lower viscosity of the polyrotaxane can be attributed to the deleterious effect of the cyclic species on entanglement. Thus, in contrast to intrinsic viscosity, a measure of the hydrodynamic volume and stiffness of a single chain, which is higher for the polyrotaxane than for model polymers as noted above, "rotaxanation" lowers the melt viscosity, a measure of intermolecular interactions, by diminishing the degree of chain entanglement, increasing the free volume, and perhaps repelling other backbones. This feature of rotaxanes could improve the processability of high molecular weight polymers.

Conclusions

The processes of threading/dethreading of macrocycles onto/from polymer chains were studied in poly(alkylene sebacate−crown ether rotaxane) systems using the acid chloride polymerization method. For polyrotaxanes without blocking groups, i.e., polypseudorotaxanes, the macrocycle content is independent of time, temperature, and length of diol monomer used in the polymerization. The macrocycle content is significantly affected by the feed ratio of the macrocycle to linear monomers, indicating that the formation of polyrotaxanes follows le Chatelier's principle. The macrocycle content of polyrotaxanes increases nonlinearly with the size of the macrocycles, presumably due to changes in the fraction of threadable conformations of the macrocycles. Dethreading from isolated polypseudorotaxanes is not significant on experimental purification time scales, as demonstrated by long term dethreading experiments.

In order to constrain macrocycles onto polymer chains completely, a difunctional bulky compound was copolymerized into polyester backbones. The high macrocycle content of the blocked polyrotaxane compared to those of unblocked polyrotaxanes (polypseudorotaxanes) revealed the dethreading of macrocycles during the latter polymerization. This is believed to be the origin of the lack of temperature dependence, since once the ester bond is formed, there is no (or very little) attractive force to prevent dethreading. Indeed, subsequent studies have shown dramatic increases in the threading yield (*m*/*n* value) and its temperature dependence when bulky blocking group monomers are used.[13a,b,h,j]

The polyrotaxanes with high macrocycle contents displayed multiphase behavior in DSC; for both the cyclic and backbone components crystalline phases exist and a glass transition was observed for the cyclic component. The intrinsic viscosity of the polyrotaxanes, which is higher than that of the backbone species due to increased hydrodynamic volume, has been shown to be a function of the solvent, increasing significantly in a good solvent for the crown ether component because of changes in conformational mobility. All of the polyrotaxanes are able to complex metal ions and extract them from aqueous solutions by interactions of the crown ether components. The melt viscosity of polyrotaxanes is lower than that of simple backbone polymers of equivalent molecular weight; the presence of the threaded macrocycles reduces the degree of chain entanglement.

Overall then, the polyrotaxane architecture provides polymer scientists with the ability to (1) alter solubility properties, (2) control the solid state phase behavior, including the introduction of crystalline phases derived from the cyclic species, (3) increase and manipulate through differential solvation the intrinsic viscosity, (4) reduce the melt viscosity, and (5) bring about metal complexation of linear macromolecules.

Experimental Section

Measurements. ^{1}H nuclear magnetic resonance (NMR) spectra were recorded with chloroform-*d* solutions (unless otherwise noted) with tetramethylsilane as an internal standard on a Bruker 270 MHz instrument and a Hewlett Packard 7550A graphics plotter or on a Varian Unity 400 MHz instrument. The following abbreviations have been used in describing the NMR spectra: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), and m (multiplet); coupling constants are represented by *J* in Hz. ^{13}C NMR spectra were recorded on chloroform-*d* solutions (unless otherwise noted) using a Varian Unity 400 MHz instrument; chemical shifts are relative to the center line of the $CDCl_3$ triplet at 77.0 ppm. Transition temperatures (T_g, T_m) were determined by a dual-cell Perkin-Elmer DSC 2 at a heating rate of 10 °C/min or less. Gel permeation chromatography (GPC) measurements were done using a Waters 590 instrument fitted with refractive index, UV, and viscometric detectors and calibrated with polystyrene standards; Permagel 10^2−10^6 Å poly(styrene−divinylbenzene) columns were employed.

Starting Materials. Sebacoyl chloride was purified by vacuum distillation. 1,4-Butanediol (**1**) was distilled before use. 1,6-Hexanediol (**2**) and 1,10-decanediol (**3**) were recrystallized twice from water and dichloroethane, respectively, and were vacuum dried at 45 °C. Diglyme was dried by first refluxing it with sodium and then distilled. Crown ethers **4**−**8**

were prepared using literature procedures[33,34] and were vacuum dried in the melt before use. 1,10-Bis{*p*-[bis(*p*′-*tert*-butylphenyl)-(hydroxyphenyl)methyl]phenoxy}decane (**18**) was synthesized using the literature method[30] and vacuum dried at 100 °C before use. The other chemicals were used without purification as obtained from commercial sources.

Poly(decamethylene sebacate) (9). To chamber one of a two-bulb one-necked flask equipped with magnetic stirring and nitrogen inlet was added distilled sebacoyl chloride (1.1212 g, 4.6885 mmol) via a pipet. Recrystallized 1,10-decanediol (0.8168 g, 4.687 mmol) (with a spatula) and dried diglyme (Na) (6 mL) (with a pipet) were added into chamber 2 of the flask and stirred at 80 °C under nitrogen until the diol was dissolved. The contents of the two bulbs were then mixed in chamber two, and the polymerization was allowed to proceed for 2 days at 80 °C. During the reaction, the flask was continuously flushed with a nitrogen stream to remove HCl. After it had been cooled to room temperature, the product was dissolved in CH_2Cl_2 (15 mL) and precipitated into methanol (400 mL). The solid was filtered and dried under vacuum, 1.4588 g (91%). $M_n = 13.9$K and $M_w = 23.5$K (GPC, polystyrene standards, in toluene). ^{1}H NMR: δ 1.32 (m, 20 H, $-(CH_2)_6(CH_2)_2OOCCH_2CH_2(CH_2)_4-$), 1.64 (t, $J = 7$ Hz, 8 H, $-OCH_2CH_2-$, $-OOCCH_2CH_2-$), 2.30 (t, $J = 8$ Hz, 4 H, $-OOCCH_2-$), 4.05 (t, $J = 8$ Hz, 4 H, $-OCH_2-$). ^{13}C NMR: δ 24.9, 25.8, 28.6, 29.0, 29.1, 29.4, 34.3, 64.35, 173.8 (9 signals; theory, 10). (DSC traces are in the Supporting Information.)

Control Reaction: Synthesis of Poly(decamethylene sebacate) in the Presence of 18-Crown-6. The polymerization was carried out as noted above using 0.8252 g (4.734 mmol) of decanediol, 2.330 g (8.826 mmol) of 18-crown-6, and 1.132 g (4.734 mmol) of sebacoyl chloride. The product was precipitated three times from CH_2Cl_2 into methanol. ^{1}H NMR: identical to that above. ^{13}C NMR: identical to that above.

General Procedure for the Syntheses of Poly(alkylene sebacate rotaxane)s Using the Acid Chloride Method: Poly[(decamethylene sebacate)-*rotaxa*-("42-crown-14")] (14). To chamber 1 of a two-bulb one-necked flask equipped with magnetic stirring and nitrogen inlet was added distilled sebacoyl chloride (1.2165 g, 5.0869 mmol) via a pipet. Recrystallized 1,10-decanediol (0.8866 g, 5.087 mmol) and "42C14" (4.5499 g, 7.3773 "mmol") were added with spatulas into chamber 2 of the flask, and the mixture was stirred at 80 °C under nitrogen for 0.5 h. The contents of the two bulbs were then mixed in chamber 2, and the polymerization was allowed to proceed at 80 °C for 2 days. During the reaction, the flask was continuously flushed with a nitrogen stream to remove HCl. After it had been cooled to room temperature, the product was dissolved in CH_2Cl_2 (15 mL) and precipitated into methanol (600 mL). The precipitation was performed three times. After each precititation, the polymer was checked by ^{1}H NMR to determine the macrocycle content. After three precipitations, the polymer was dried under vacuum and 0.9479 g (36%) of polymer was obtained. $M_n = 8.3$K and $M_w = 14.0$K (GPC, polystyrene standards, in toluene). ^{1}H NMR: δ 1.32 (m, 20 H, $-(CH_2)_6(CH_2)_2OOCCH_2CH_2(CH_2)_4-$), 1.64 (t, $J = 7$ Hz, 8 H, $-OCH_2CH_2-$, $-OOCCH_2CH_2-$), 2.30 (t, $J = 8$ Hz, 4 H, $-OOCCH_2-$), 3.65 (s, 42C14), 4.05 (t, $J = 8$ Hz, 4 H, $-OCH_2-$); $m/n = 0.29$. ^{13}C NMR: δ 24.9, 25.8, 28.6, 29.0, 29.1, 29.4, 34.3, 64.3, 70.5 (42C14), 173.8 (10 signals; theory, 11).

A. Ring Size. Poly[(decamethylene sebacate)-*rotaxa*-(30-crown-10)] (**12**), poly[(decamethylene sebacate)-*rotaxa*-("36-crown-12")] (**13**), poly[(decamethylene sebacate)-*rotaxa*-("48-crown-16")] (**15**), and poly[(decamethylene sebacate)-*rotaxa*-("60-crown-20")] (**16**) were prepared from sebacoyl chloride (0.2391 g, 1.000 mmol), 1,10-decanediol (0.1743 g, 1.000 mmol), and crown ethers (1.000 "mmol"). M_n and M_w values determined by GPC with polystyrene standards in THF: **12** 32.8, 58.9; **13** 14.3, 22.5; **15** 11.4, 19.5 (DSC traces in Supporting Information); and **16**: 10.7, 20.7.

B. Feed Ratio. Poly[(decamethylene sebacate)-*rotaxa*-("42-crown-14")]s (**14**) were prepared from sebacoyl chloride (0.2391 g, 1.000 mmol), 1,10-decanediol (0.1743 g, 1.000 mmol), and "42-crown-14" (0.6167*n* g, *n* "mmol"). The molecular weights of the resultant polyrotaxanes were not measured.

C. Equilibration Time. Poly[(decamethylene sebacate)-*rotaxa*-("42-crown-14")]s (**14**) were prepared from sebacoyl chloride (0.2391 g, 1.000 mmol), 1,10-decanediol (0.1743 g, 1.000 mmol), and "42-crown-14" (0.6167 g, 1.000 "mmol"). Before the polymerization, 1,10-decanediol and "42-crown-14" were stirred in chamber 2 at 80 °C under nitrogen for 0, 0.5, 1, 2, and 13 h, respectively. The molecular weights of the resultant polyrotaxanes were not measured.

D. "Double" Prethreading. To chamber one of a two-bulb one-necked flask equipped with magnetic stirring and nitrogen inlet were added distilled sebacoyl chloride (0.5816 g, 2.432 mmol) and "42C14" (1.5000 g, 2.4321 "mmol"). Recrystallized 1,10-decanediol (0.4238 g, 2.432 mmol) and "42C14" (1.5000 g, 0.4321 "mmol") were added into chamber 2 of the flask. The two mixtures were stirred separately at 80 °C under nitrogen for 0.5 h prior to the polymerization of the diacid chloride and the diol by mixing the contents of the two chambers. The molecular weight of the resultant polyrotaxane was not measured.

E. Temperature. Poly[(decamethylene sebacate)-*rotaxa*-("42-crown-14")]s (**14**) were prepared from sebacoyl chloride (0.2391 g, 1.000 mmol), 1,10-decanediol (0.1743 g, 1.000 mmol), and "42-crown-14" (0.6167 g, 1.000 "mmol") by equilibration and reaction at 110, 115, 140, and 160 °C, respectively. The M_n and M_w values (GPC, polystyrene standards, in THF) were as follows: 110 °C 12.8, 22.3; 115 °C 10.9, 17.8; 140 °C 6.3, 11.0; 160 °C 11.6, 19.7.

Poly[(hexamethylene sebacate)-*rotaxa*-("42C14")] (11). **11** was prepared from sebacoyl chloride (0.2391 g, 1.000 mmol), 1,6-hexanediol (0.1182 g, 1.000 mmol), and "42C14" (0.6167 g, 1.000 "mmol"). Before the polymerization, 1,6-hexanediol and "42-crown-14" were stirred at 80 °C under nitrogen for 0.5 h. $M_n = 8.3$K and $M_w = 16.1$K (GPC, polystyrene standards, in THF). ^{1}H NMR: δ 1.30 (s, 8 H, $-(CH_2)_4(CH_2)_2COO-$), 1.38 (t, $J = 7$ Hz, 4 H, $-OCH_2(CH_2)_2-$), 1.62 (m, 8 H, $-CH_2CH_2COOCH_2CH_2-$), 2.29 (t, $J = 8$ Hz, 4 H, $-CH_2COO-$), 3.65 (s, 42C14), 4.06 (t, $J = 7$ Hz, 4 H, $-OCH_2-$); $m/n = 0.30$. ^{13}C NMR: δ 24.8, 25.5, 28.5, 29.0, 64.1, 70.5 (42C14), 173.8 (7 signals; theory, 9). (NMR spectra are in the Supporting Information.)

Poly[(butylene sebacate)-*rotaxa*-("42C14")] (10). **10** was prepared from sebacoyl chloride (0.2391 g, 1.000 mmol), 1,4-butanediol (0.0901 g, 1.000 mmol), and "42C14" (0.6167 g, 1.000 "mmol"). Before the polymerization, 1,4-butanediol and "42C14" were stirred at 80 °C under nitrogen for 0.5 h. $M_n = 29.5$K and $M_w = 42.5$K (GPC, polystyrene standards, in THF). ^{1}H NMR: δ 1.31 (br s, 8 H, $-(CH_2)_4(CH_2)_2COO-$), 1.61 (m, 4 H, $-CH_2CH_2COO-$), 1.71 (m, 4 H, $-(CH_2)_2CH_2O-$), 2.29 (t, $J = 7.0$ Hz, 4 H, $-CH_2COO-$), 3.65 (s, 42C14), 4.09 (t, $J = 5.5$ Hz, 4 H, $-CH_2O-$); $m/n = 0.32$. ^{13}C NMR: δ 24.8, 25.3, 29.0, 34.2, 63.6, 70.5 (42C14), 173.7 (7 signals; theory, 8).

Poly[(decamethylene sebacate)-*co*-(oligo(ethyleneoxy) sebacate] (17). To a 20 mL one-necked flask equipped with magnetic stirrer and nitrogen inlet were added 1,10-decanediol (1.7689 g, 10.150 mmol) and poly(ethylene glycol) with $M_n = 600$ (2.1900 g, 3.6500 mmol), and the mixture was stirred at 80 °C until 1,10-decanediol was dissolved. Sebacoyl chloride (3.3001 g, 13.800 mmol) was added and its glass ampule was crushed in the reaction. The magnetic stirring stopped because of the high viscocity of the reaction mixture. Triglyme (3.5 mL) was then added, and the stirring was resumed. The temperature was increased to 105 °C and the reaction was allowed to proceed for 96 h. During the reaction, the flask was continuously flushed with a nitrogen stream to remove HCl. After it had been cooled to room temperature, the product was dissolved in THF (25 mL) and precipitated into water (1200 mL). After the polymer had been dried under vacuum at room temperature for 2 days, it was dissolved in CH_2Cl_2 (25 mL) and precipitated into hexane (1500 mL) twice. The polymer was then dried under vacuum with P_2O_5; 5.68 g (91%) of white polymer was obtained. $T_g = -54$ °C, $T_m = 57$ and 66 °C, and $T_c = 49$ °C. ^{1}H NMR: δ 1.30 (s, 63 H), 1.60 (m, 26 H), 2.30 (m, 15 H), 3.64 (m, 45 H), 3.69 (t, $J = 5$ Hz, 4 H), 4.05 (t, $J = 7$ Hz, 11 H), 4.22 (t, $J = 5$ Hz, 4 H). ^{13}C NMR: δ 24.8, 24.9, 25.8, 28.7, 29.0, 29.2, 29.4, 34.1, 34.3, 63.3, 64.3, 69.1, 70.5, 173.9 (14 signals; theory, 28). For MW and intrinsic viscosity data see Table 11.

Threading of Preformed Poly(butylene sebacate) through "42-Crown-14". a. Control Process with End-Capped Polyester. Poly(butylene sebacate) end-capped with tris(*p-tert*-butylphenyl)methyl moieties (M_n = 19.9K, M_w = 33.3K by GPC with polystyrene standards[13c]), 1.0 g, 4.0 g of "42-crown-14", and 10 mL of THF were heated and stirred at 55 °C under nitrogen for 11 days. Three precipitations from CH_2Cl_2 into methanol gave **10**, $m/n = 3.0 \times 10^{-4}$ by ^1H NMR spectroscopy.

b. Non-End-Capped Polyester. Poly(butylene sebacate) (M_n = 19.6K, M_w = 41.7K by GPC with polystyrene standards;[13c] M_n = 18.8K, M_w = 35.7K by GPC with universal calibration), 1.0 g, 4.8 g of "42-crown-14", and 20 mL of THF was stirred at 60 °C under nitrogen, and when everything had dissolved, the temperature was raised to evaporate the THF. The mixture was heated at 120 °C for 3 days and then dissolved in CH_2Cl_2 and precipitated into methanol three times to give polyrotaxane **10**, $m/n = 2.0 \times 10^{-2}$. This polymer (0.8 g) along with the crown ether recovered from the methanol was dissolved in 20 mL of THF and stirred at 55 °C under nitrogen for 3 days and reprecipitated thrice as before to give polyrotaxane **10**, $m/n = 1.7 \times 10^{-2}$. This polymer (0.59 g) and 3.65 g of recovered "42-crown-14" were stirred in 45 mL of THF and 15 mL of acetonitrile under nitrogen at 55 °C for 16 days and precipitated as before to afford **10**, $m/n = 1.3 \times 10^{-2}$, M_n = 44.8, M_w = 198K by GPC with universal calibration.

Poly{(decamethylene sebacate)-*co*-(1,10-bis{*p*-[bis(*p′*-*tert*-butylphenyl)-(4-oxyphenyl)methyl]phenoxy}-decamethylene sebacate)-*rotaxa*-("42-crown-14")} (19). To chamber 1 of a two-bulb one-necked flask equipped with magnetic stirring and nitrogen inlet was added distilled sebacoyl chloride (0.2396 g, 1.002 mmol) via a pipet. Recrystallized 1,10-decanediol (0.1393 g, 0.7993 mmol), 1,10-bis{*p*-[bis(*p-tert*-butylphenyl)-(4-hydroxyphenyl)methyl]phenoxy}-decane (**18**) (0.2135 g, 0.200 mmol), and "42C14" (0.6165 g, 0.9996 "mmol") were added with spatulas to chamber 2 of the flask, and the mixture was stirred under nitrogen for 0.5 h at 130 °C. The contents of the two bulbs were then mixed in chamber 2, and the polymerization was allowed to proceed for 2 days at 130 °C. During the reaction, the flask was continuously flushed with a nitrogen stream to remove HCl. After it had been cooled to room temperature, the product was dissolved in CH_2Cl_2 (10 mL) and precipitated into methanol (250 mL). The precipitation was performed three times. After each precipitation, the polymer was checked by ^1H NMR to determine the macrocycle content. M_n = 18.7K and M_w = 29.3K (GPC, polystyrene standards, in chloroform). ^1H NMR: δ 1.29 (m, 28 H, protons **a**), 1.61 (m, 10 H, protons **c**), 2.29 (t, J = 7.6 Hz, 5 H, protons **d**), 3.64 (s, 42C14), 3.91 (t, J = 6.8 Hz, 1 H, protons **b**), 4.05 (t, J = 6.8 Hz, 4 H, protons **e**), 6.68−7.23 (m, 8 H, arom); final m/n = 0.74. (The NMR spectrum is in the Supporting Information.)

Poly(decamethylene sebacate)s (9) for Melt Rheology. These polymers were made essentially as described above, but on a larger scale, e.g., using 4.4041 g (18.416 mmol) of sebacoyl chloride, 3.1998 g (18.416 mmol) of 1,10-decanediol, and 11.358 g of diglyme, and the temperature was briefly raised to 110 °C and then held at 90 °C for 48 h. GPC ($CHCl_3$, polystyrene standards): M_n = 16.7K, M_w = 36.0K, M_{z+1} = 75.7K. Similarly three other samples were prepared with M_n values of 6.5K, 7.8K, and 18.6K; M_w values of 15.9, 18.2 and 46.2K; and M_{z+1} values of 43.5K, 44.5K, and 95.6K, respectively (GPC, $CHCl_3$, polystyrene standards). The lowest molecular weight sample was also examined by GPC using viscometry and the universal calibration ($CHCl_3$): M_n = 4.3K, M_w = 7.0K, M_z = 10.6K.

Poly[(decamethylene sebacate)-*rotaxa*-("42-crown-14")] (14) for Melt Rheology. This polyrotaxane was made as described above using 4.6513 g (19.45 mmol) of sebacoyl chloride, 3.3897 g (19.45 mmol) of 1,10-decanediol, and 12.0344 g (19.51 "mmol") of "42-crown-14". The polyrotaxane was purified by three reprecipitations from THF into water; the m/n value (0.13, 19 mass %) remained the same from the second to the third precipitation (3.54 g). GPC (toluene, polystyrene standards): M_n = 8.3K, M_w = 14.0K, M_{z+1} = 31.0K. The sample was also examined by GPC using viscometry and the universal calibration ($CHCl_3$): M_n = 10.4K, M_w = 17.1K, M_z = 28.1K.

Rheology Measurements. The model polyesters **9** described above were mixed with a stabilizer/antioxidant (Irganox 1010, 6.6 mg/5.00 g of polymer). The polyrotaxane **14** described above was also mixed with the stabilizer (3.7 mg/3.54 g). The stabilized polymers were then examined on a Rheometrics dynamic analyzer with a 25 mm parallel plate attachment. The sample was loaded at room temperature and a temperature sweep experiment (2 deg steps, soak time 1 min) was carried out from 90 to 150 °C in an oscillatory mode at 1 Hz.

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Supporting Information Available: 400 MHz ^1H NMR spectrum of poly[(hexamethylene sebacate)-*rotaxa*-("42-crown-14")] (**11**, m/n = 0.30) in $CDCl_3$; 100 MHz ^{13}C NMR spectrum of poly[(hexamethylene sebacate)-*rotaxa*-("42-crown-14")] (**11**, m/n = 0.30) in $CDCl_3$; 270 MHz ^1H NMR spectrum of polyrotaxane **19**, m/n = 0.74 in $CDCl_3$; DSC traces for poly(decamethylene sebacate) (**9**), heating and cooling scans, 10 °C/min and the low-temperature region; DSC traces for poly[(decamethylene sebacate)-*rotaxa*-("48-crown-16")] (**15**, m/n = 0.34), heating and cooling scans, 10 °C/min and the low-temperature region; DSC traces for "48-crown-16" (**7**), heating and cooling scans, 10 °C/min (7 pages). Ordering information is available on any current masthead page.

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(17) A *pseudorotaxane* is defined[3,4] as a macrocycle threaded by a linear molecule without bulky end blocking groups. Thus, technically, all of the polyrotaxanes described here with the exception of **19** are *polypseudorotaxanes*.

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(19) Since the completion of this work we, in collaboration with Prof. Colin Booth and his colleagues at the University of Manchester, U.K., have discovered by GPC, HPLC, and mass spectroscopy that the crown ethers with target ring sizes of 36, 42, 48, and 60 atoms are not pure, single-sized macrocycles. Rather, they are mixtures of cyclics and perhaps catenanes. By NMR spectroscopy there are no detectable amounts of the linear tosylate or glycol starting materials, nor vinyl ether moieties in the samples; this was confirmed by elemental analyses. In a separate publication we will describe the results of these studies. The 30-crown-10 is a pure compound, however. In this paper we will use quotation marks around the name to designate the size of the crown ether that was the target of the synthesis, but generally speaking, the average size of the macrocycle is larger.

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(31) The internal diameter of a fully opened 30-crown-10 was calculated by the equation $D = (10/\pi)[(1.52)\sin(108.95/2) + (2)(1.42)\sin(107.00/2)] - 4.5$, where 1.52 Å is the length of the carbon−carbon bond, 1.42 Å is the length of the carbon−oxygen bond, 108.95° is the C−C−C bond angle, and 107.00° is the C−O−C bond angle. 4.5 Å is the cross sectional diameter of a poly(ethylene oxide) chain.

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