

Self-Threading-Based Approach for Branched and/or Cross-linked Poly(methacrylate rotaxane)s

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Abstract: Physically branched and cross-linked polymeric structures were produced for the first time by rotaxane formation during reaction of a pendant group of a preformed macromolecule. The rotaxane structure is believed to form from a hydrogen-bonded bimolecular complex of 5-(hydroxymethyl)-1,3-phenylene-1',3'-phenylene-32-crown-10 (**16**) by esterification of the hydroxy group of one macrocycle through the cavity of the second in its reaction with poly(methacryloyl chloride) (**12**). For esters formed in model reactions of **12** with methanol and with 5-(hydroxymethyl)-1,3-phenylene-16-crown-5 (**14**), which is too small to be threaded, the degrees of polymerization were identical; however, the polymer from reaction of **12** and **16** under the same conditions had a significantly higher degree of polymerization and polydispersity, i.e., was highly branched via rotaxane formation. Increasing the concentration in the reaction of **12** with **16** led to the formation of a gel fraction along with a high molecular weight sol fraction; the gel represents a novel network structure based on mechanical interlocking via rotaxane structures. 2D NOESY NMR experiments clearly demonstrated the rotaxane structure as manifest in the through-space correlation of the benzylic protons of the "thread" with the intra-annular protons of the "bead".

Introduction

Polyrotaxanes, in which rotaxane units are incorporated into macromolecules, because of their novel architectures, have received world-wide attention.^{1–6} Several types of polyrotaxanes as illustrated in Scheme 1 can be constructed by proper procedures. To date, most of the reported polyrotaxanes are of the first and third types. To our knowledge, no examples of the second type, side chain polyrotaxanes formed from polymers with pendant macrocycle units, have been reported! One of the objectives of this work was to explore this class of polyrotaxanes.

The abilities of polyether macrocycles to complex with metal ions and organic cations and to form hydrogen bonds with

hydroxy groups provide the driving forces⁷ necessary for preparation of these new materials, and numerous main chain polyrotaxanes of the first type (Scheme 1) have been prepared with crown ethers as the macrocyclic components.^{1,5,6} In order to prevent the slippage of the cyclic molecule from the linear chain, blocking groups (BG) are often introduced at the chain ends and/or as in-chain units. Recently, it was found that the introduction of difunctional BG can increase the threading efficiency (m/n , the average number of macrocycles per repeat unit in the polyrotaxane) by as much as 15 times!^{6a,c} Hydrogen bonding between hydroxy groups and the crown ether is proposed as a driving force for the threading; an endo esterification of the complexed structure **1** taking place through the cavity of the crown ether yields a main chain polyrotaxane structure (**3**), while an exo esterification yields an unthreaded structure (**2**, Scheme 2).

When this concept is extended, therefore, a crown ether bearing a hydroxy group is expected to self-associate as in structure **8**. Endo esterification of **8** with a poly(acid chloride) (Scheme 3) will lead to a novel rotaxane structure (**9**) along with side chain polymacrocycle units (**10**) via exo esterification. Since a macrocycle will not readily pass through an identical macrocycle, it can play the same role as a BG, and thus, **9** is expected to be stable to dethreading. This process should ultimately yield the branched and/or cross-linked structure **11**. In this work, this novel self-threading method for formation of physically linked networks is investigated

Results and Discussion

I. Preparation of Poly(methacrylate)s. Poly(methacryloyl chloride) (**12**) was prepared by free radical polymerization with 2,2'-azobisisobutyronitrile (AIBN) as initiator in toluene (Scheme 4). **12** was then reacted in pyridine with methanol, 5-(hydroxymethyl)-1,3-phenylene-16-crown-5 (hydroxymethyl-MP-16C5, **14**) and 5-(hydroxymethyl)-1,3-phenylene-1',3'-phenylene-32-crown-10 (hydroxymethyl-BMP32C10, **16**) to afford poly-

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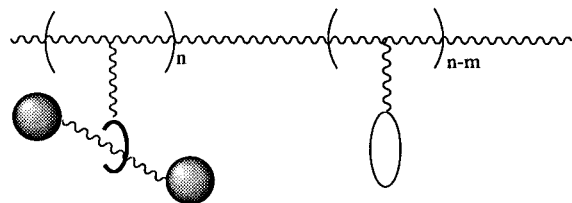
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Scheme 1



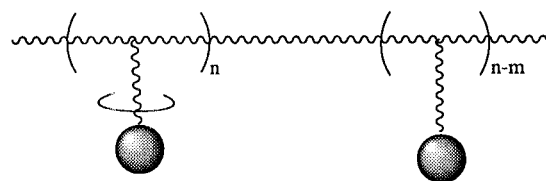
A'. main chain polypseudorotaxanes without blocking group (BG)

A''. main chain polyrotaxane with BGs



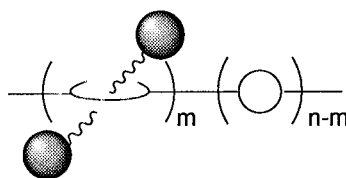
B'. Side chain polypseudorotaxane without BG

B''. Side chain polyrotaxane with BGs



C'. Side chain polypseudorotaxane without BG

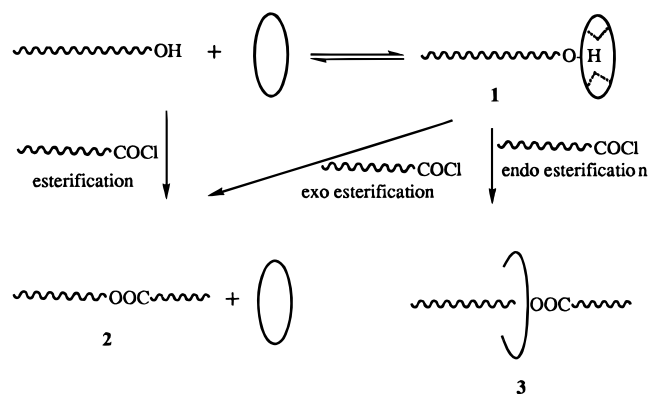
C''. Side chain polyrotaxane with BGs



D'. main chain polypseudorotaxane without BG

D''. main chain polyrotaxane with BGs

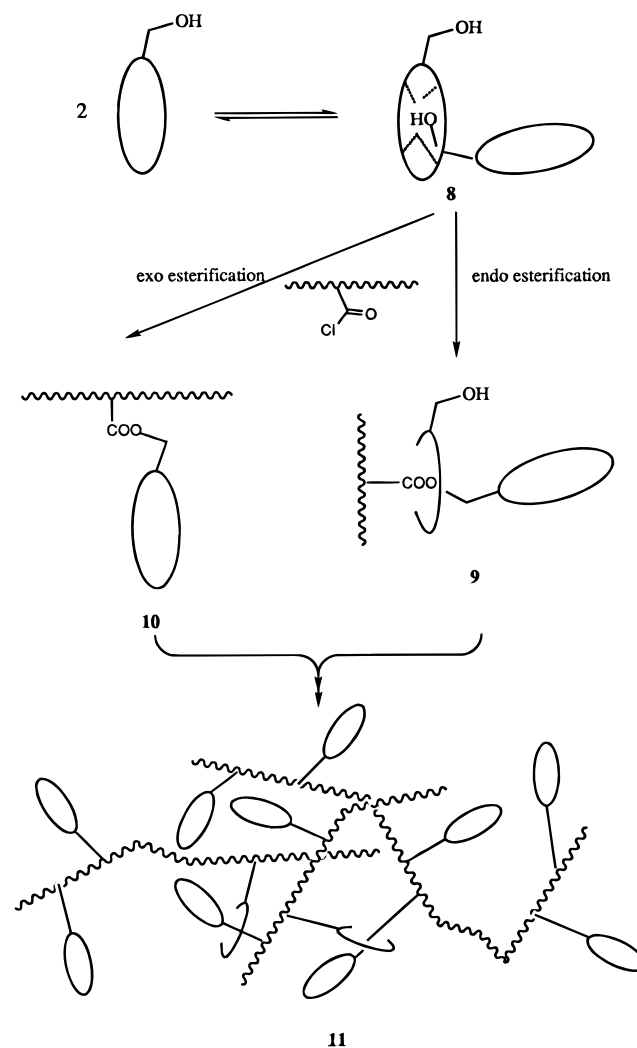
Scheme 2



(methacrylate)s **13**, **15**, and **17a**, respectively. By the same procedure as that for **17a** but increasing the concentrations of both **12** and **16**, both branched **17b** (48%, sol) and cross-linked **18** (52%, gel) were obtained. Proton NMR spectroscopy (see below) demonstrated complete conversions.

II. Characterization by GPC analysis. Since the preformed **12** used for **13**, **15**, **17a**, **17b**, and **18** is from the same batch, the polydispersity (PDI) and the degree of polymerization (number average DP_n or weight average DP_w) of all of these poly(methacrylate)s were expected to be the same, if no branching, cross-linking, or other side reactions occur. Therefore, the absolute molecular weights and PDI were measured by GPC. On the basis of the number and weight average

Scheme 3

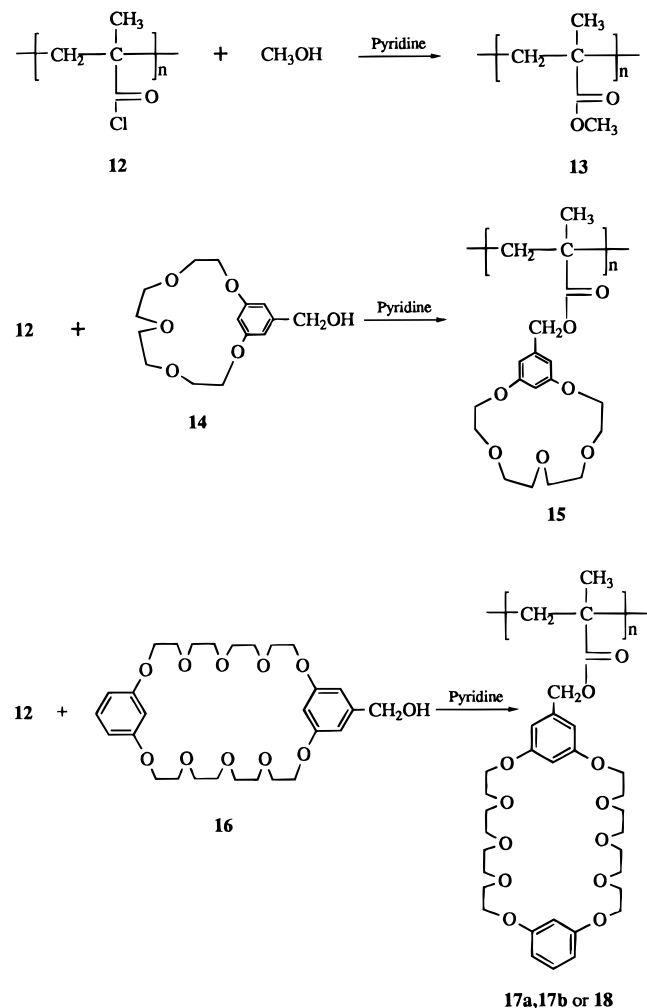


molecular weights (M_n , M_w) of these polymers and the corresponding molecular weights of the repeat units, their degrees of polymerization (DP_n , DP_w) were calculated. As shown in Table 1, poly(methacrylate crown ether) **15** had PDI, DP_n , and DP_w which were almost identical to those of the poly(methyl methacrylate) (PMMA, **13**). Although hydroxymethyl-MP16C5 (**14**) bears both a hydroxy group and polyether units, its cavity size is too small to be penetrated by any linear components to give rotaxane structures.⁸ This result demonstrated that the crown ether moiety does not introduce any side reactions such as ring opening. However, although the poly(methacrylate crown ether) **17a** made under the same conditions is easily and completely soluble in common organic solvents, its PDI, DP_n , and DP_w are much larger than those of both **13** and **15** (Table 1). Since this result can not be attributed to any side reaction, we ascribe the high molecular weight and broad distribution to the formation of a branched polymer, i.e., a rotaxane, by self-threading as demonstrated in Scheme 5. **16** is a 32-membered macrocycle, and thus, it is large enough to be penetrated by a methylene chain.⁸ In addition, the presence of both the hydroxy group and polyether units introduces a driving force (hydrogen bonding) for the formation of the bimolecular complex **19**. The intermediate **19** undergoes an endo esterification with poly(acid chloride) **12** through the cavity of one of the macrocycles to yield rotaxane structure **20**, the branching or cross-linking point for **17** or **18**. An exo esterification gives structure **21**, a normal pendant group modification reaction (Scheme 5).

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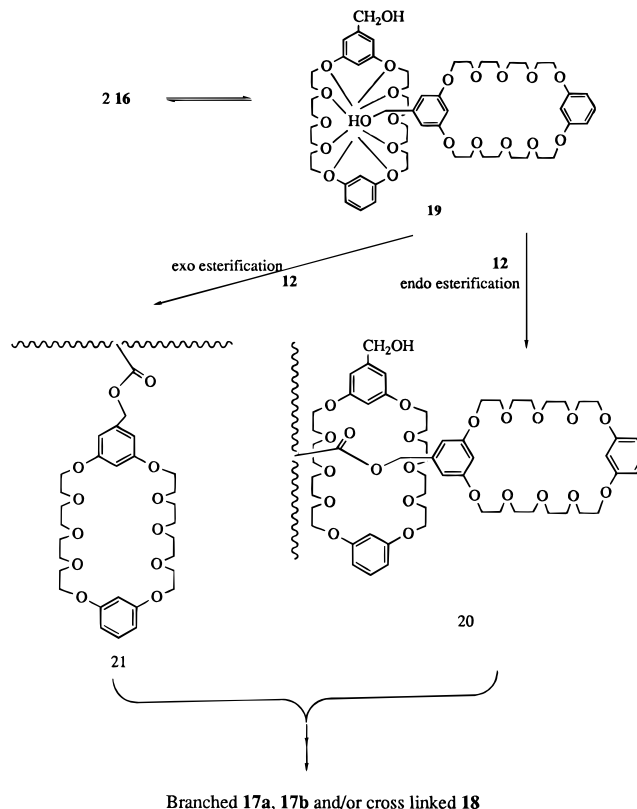
Table 1. Feed Compositions and GPC Results for **13**, **15**, **17a**, **17b**, and **18**

polymeric product	1 (mmol) ^a	pyridine (mL)	ROH/mmol	<i>M_n</i> (kg/mol)	PDI	DP _n	DP _w
13	3.748	10.0	MeOH/excess	9.9	3.4	99	3.4 × 10 ²
15	1.874	5.0	14 /1.874	36.3	3.8	99	3.8 × 10 ²
17a	0.937	2.5	16 /0.937	102.8	30.9	162	5.01 × 10 ³
17b (48%) 18 (52%)	2.116	3.0	16 /2.116	135.5	187.9	214	4.02 × 10 ⁴

^a Repeat unit basis.**Scheme 4**

Since hydrogen bonding is the driving force for the formation of the rotaxane structure **20**, it is expected from Le Chatelier's principle that a higher concentration of hydroxymethyl-BMP32C10 (**16**) will drive this self-threading to a larger extent, and thus, a higher branching degree or cross-linkage can be obtained. When the concentration of **16** was increased from 0.375 to 0.705 M, it was found that only 48% of the product was soluble in CHCl₃, believed to be branched **17b**, and 52% was gel, which was not soluble in any common solvents and believed to be cross-linked **18**. Both facts, that the branched **17b** had PDI, DP_n, and DP_w even higher than those of the branched **17a** (Table 1) and that the gel **18** was formed, confirmed that the threading was increased at higher feed concentration of **16**; this is consistent with the hydrogen-bonding concept and the self-threading process in Scheme 5.

III. NMR Study. The NMR spectra of **15** and **17a** (Figure 1a,b) confirmed their chemical structures. To prove the chemical composition of cross-linked **18**, its proton NMR spectrum was also measured after the sample was ultrasonicated to break the gel to increase the resolution. According to its spectrum (Figure 1c), **18** does have the same chemical composi-

Scheme 5

tion as **17a** and **17b**, although its peaks are very broad. The 2D COSY spectrum (Figure 2) of **17a** also showed couplings consistent with its chemical structure.

As soon as structure **20** (Scheme 5) forms, threaded **16** will be confined to a very short distance between the backbone and the pendant macrocycle. Thus, some protons are expected to interact with each other through space, which can be revealed by 2D NOESY studies. Indeed, several through-space interactions exist (Figure 3). Among them, the most important correlation is proton *i* with protons *e* and *f*; there are no interactions between proton *i* and protons *d*, *g*, and *h*. The results can only be explained by the rotaxane structure **20** (Scheme 5) in which the methylene proton *i* from the pendant cyclic occupies the cavity of a threaded cyclic and thus interacts with those protons inside the cavity (protons *e* and *f*) but not with those protons outside the cavity (protons *d*, *g*, and *h*). It is also worth noting that small new upfield signals for protons *a'*–*c'* arise, although they are overlapped with the main peaks for *a* and *b*. We believe that the minor set of new signals is from the protons of the threaded macrocycle. Interestingly, proton *i* interacts with only the protons of the minor set, *a'*–*c'* of the threaded cyclic, as is most evident for proton *c'*. This fact again is consistent with the structure **20**, since only the protons of the threaded cyclic are sufficiently close to proton *i* to result in such an effect. However, why do the *e* and *f* signals also correlate with protons *a*–*c*, and *c'*? In order to answer this question, we performed a NOESY study of bis(1,3-phenylene)-32-crown-10 (BMP32C10) (Figure 4) which shows

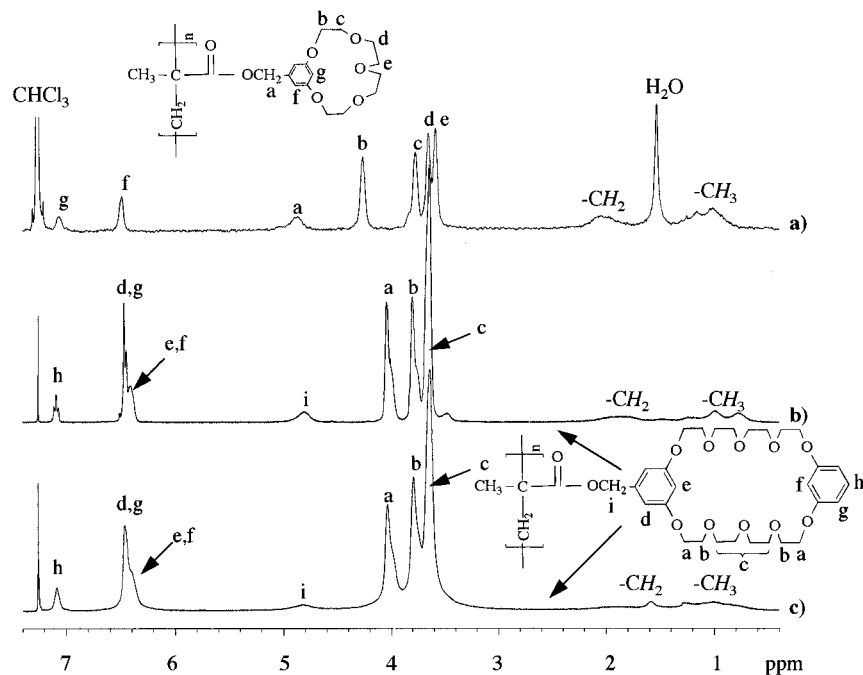


Figure 1. The 400 MHz proton NMR spectra of (a) poly(methacrylate crown ether) **15**, (b) branched poly(methacrylate crown ether) **17a**, and (c) cross-linked **18** (swollen) in CDCl_3 .

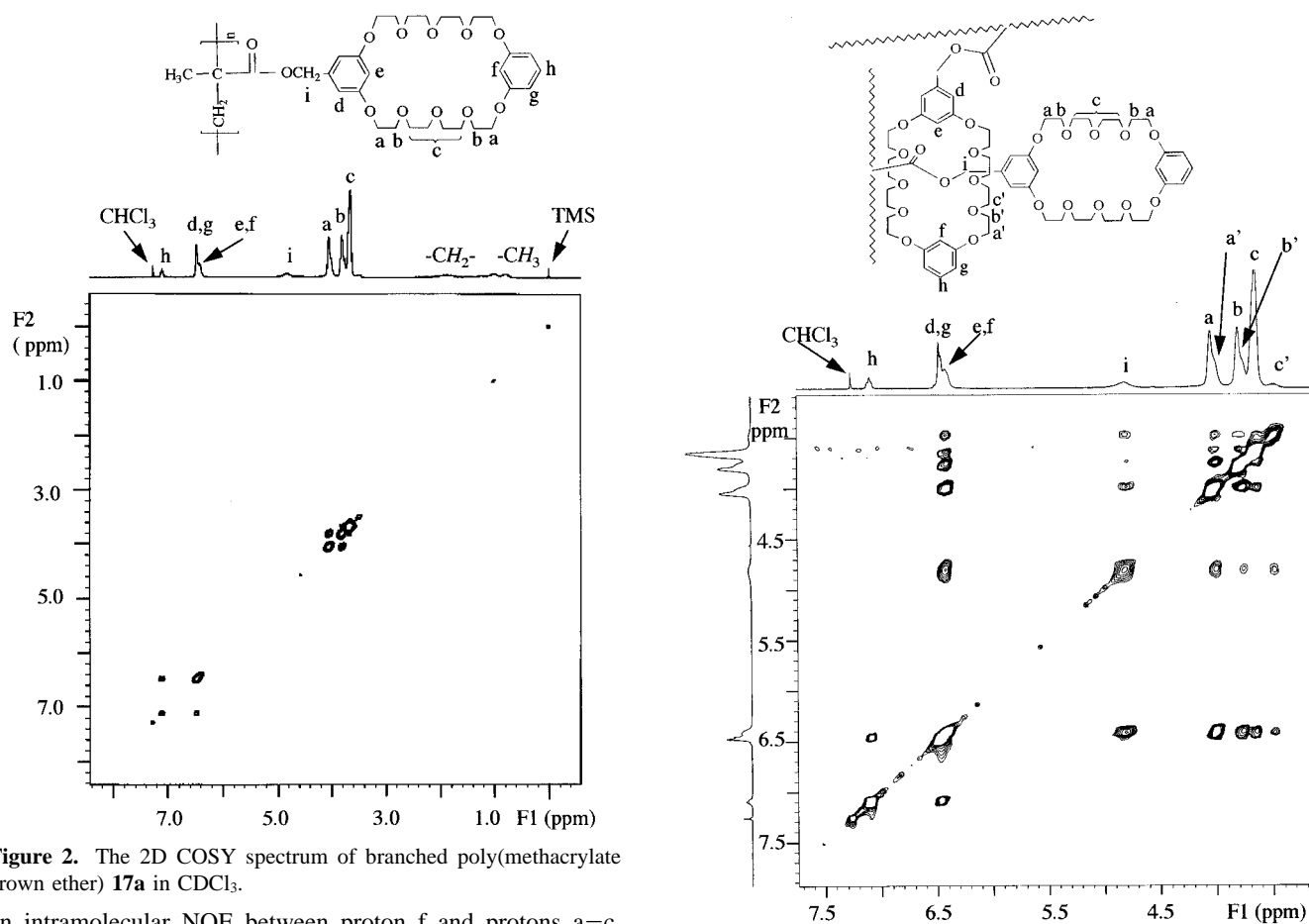


Figure 2. The 2D COSY spectrum of branched poly(methacrylate crown ether) **17a** in CDCl_3 .

an intramolecular NOE between proton f and protons a–c. Therefore, the correlation in **17** arises because the proton e is close enough to correlate intramolecularly with protons a–c and c'. Therefore, the NOESY studies provide compelling evidence for rotaxane structures in the branched **17a** and **17b** and/or cross-linked **18**.

Although we previously reported similar networks from polycondensation of difunctional macrocycles,⁹ the rotaxane structures were inferred based only on solubility or molecular weight changes; NOE did not directly reveal the rotaxane

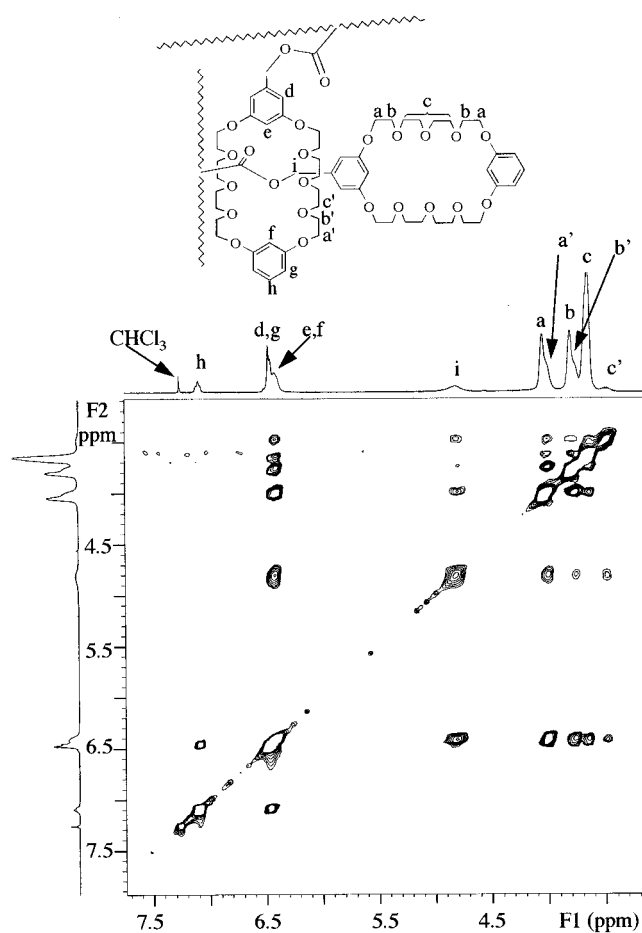


Figure 3. The correlated region of 400 MHz proton–proton 2D NOESY spectrum of branched poly(methacrylate crown ether) **17a** in CDCl_3 .

structures. However, bulk polymerization of the methacrylate ester of **16** provides **17** of high molecular weight, which although not significantly branched did reveal NOE correlations of intraannular protons e and f with backbone (CH_3 and CH_2) and benzylic methylene signals, indicative of statistical threading

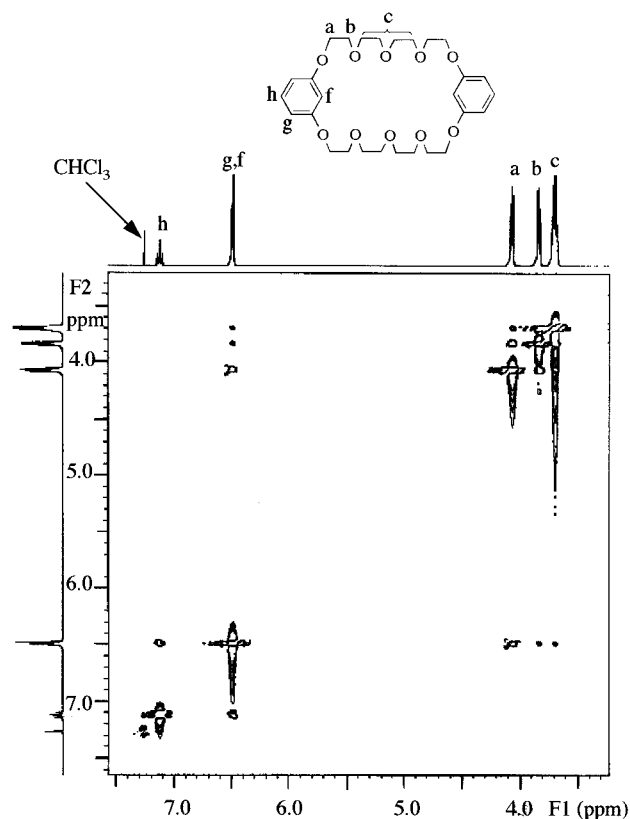


Figure 4. The 400 MHz proton–proton 2D NOESY spectrum of BMP32C10 in CDCl_3 .

to form rotaxanes structures analogous to those formed here and also involving backbone threading as well¹⁰.

IV. DSC Analysis. While PMMA (**13**) is crystalline, poly(methacrylate crown ether)s **15**, **17**, and **18** are amorphous; **15** is a hard material, and both **17** and **18** are transparent rubbery materials. It is believed that the loss of crystallinity in these poly(methacrylate crown ether)s is due to the interference with macromolecular packing by the bulky pendent groups, the crown ethers. Compared to that of **15** ($T_g = 86.2$ °C), the glass transition temperatures for **17a** and **18** are much lower at 22.8 and 25.6 °C, respectively. This is probably because the small macrocycle is more rigid than the large one and/or its smaller size results in less free volume. Therefore, introduction of different types of macrocycles provides a possible method for adjusting glass transition temperatures and/or crystallinity of poly(methacrylate)s.

Conclusions

We developed a novel approach for branched and/or cross-linked polymeric materials by a self-threading process during reaction of a hydroxymethyl macrocycle with a polymeric acid chloride.

The resulting polymers have an original topology in which macromolecules are linked mechanically via rotaxane structures. The polyrotaxanes are novel, belonging to both the second and the third types in Scheme 1; these two species were generated in the same batch reaction. The formation of branching and/or

cross-linking points (rotaxane structures) was proven by 2D NOESY studies.

Experimental Section

General Methods. Reagent grade reactants and solvents were used as received from Aldrich unless otherwise specified. Pyridine and hexane were distilled over sodium hydride. Hydroxymethyl-BMP32C10¹¹ (**16**), hydroxymethyl-MP16C5¹¹ (**14**), and BMP32C10¹² were prepared according to the procedures developed in our laboratory. ¹H NMR spectra were recorded at ambient temperature on a Varian Unity 400-MHz spectrometer. The proton NMR sample of **18** was ultrasonicated for 20 min to break down the gel and increase the resolution. The 2D NOESY and COSY studies were performed at 25 °C with a mixing time of 1 s and a relaxation delay of 5 s. The absolute molecular weights of the polymers were measured by GPC analyses with a Waters 150C ALC/GPC chromatograph equipped with a differential refractometer detector and an online differential viscometric detector (Viscotek 150R) coupled in parallel, and the universal calibration was used. The DSC measurements were done with a Perkin Elmer-B2 at a scan rate of 10 °C per minute, and the data reported here are the midpoints of the transitions in the second heating.

Poly(methacryloyl chloride) (12). Distilled methacryloyl chloride (60.0 g, 0.574 mol) was dissolved in 100 mL of toluene. To the solution was added initiator (AIBN, 0.500 g, 3.04×10^{-3} mol). Polymerization was run for 2 days at 65–70 °C. After it had been cooled down, the solution was precipitated into hexane (800 mL) to afford **12** (57 g, 95%).

General Procedure for Poly(methacrylate)s: Poly(methyl methacrylate) (PMMA, 13). The preformed polymer **12** (391.8 mg, 3.748 mmol of repeat units) was dissolved in pyridine (10 mL). When methanol (1 mL) was added, the reaction proceeded for 24 h at 80 °C. The solution was precipitated into water to afford PMMA (**13**): ¹H NMR (CDCl_3 , ppm) δ 3.60 (s, 3H, OCH_3), 1.70–1.90 (m, 2H, CH_2), 0.84–1.03 (m, 3H, CH_3).

Poly(methacrylate crown ether) 15 and Branched Poly(methacrylate crown ether) 17a. The procedures and reaction conditions were the same as that for PMMA (**13**) except using hydroxymethyl-MP16C5 (**14**) for **15** and hydroxymethyl-BMP32C10 (**16**) for **17a** instead of methanol (Scheme 5). The feed compositions are summarized in Table 1. For **15** (Figure 1a): ¹H NMR (CDCl_3 , ppm) δ 7.06 (br s, 1H, ArH), 6.49 (br s, 2H, ArH), 4.90 (br s, 2H, ArCH_2), 4.27 (br s, 4H, OCH_2), 3.77 (br s, 4H, OCH_2), 3.65 (br s, 4H, OCH_2), 3.58 (br s, 4H, OCH_2), 2.04 (br m, 2H, CH_2), 1.01–1.25 (br m, 3H, CH_3). For **17a** (Figure 1b): ¹H NMR (CDCl_3 , ppm) δ 7.10 (t, $J = 8.0$, 1H, ArH), 6.46 (br m, 6H, ArH), 4.82 (br s, 2H, ArCH_2), 4.05 (br s, 8H, OCH_2), 3.81 (br s, 8H, OCH_2), 3.65 (br s, 16H, OCH_2), 1.08 (br s, 2H, CH_2), 0.78–1.02 (br m, 3H, CH_3). The glass transition temperatures (T_g): 86.2 °C for **15** and 22.8 °C for **17a**.

Branched 17b and Cross-Linked Poly(methacrylate crown ether) 18. The same procedure as that for **17a** was applied except that the feed concentration of macrocycle **16** was increased as specified in Table 1. The product from precipitation was extracted with CHCl_3 , and both branched **17b** (48%, sol) and cross-linked **18** (52%, gel) were obtained. The ¹H NMR (CDCl_3 , ppm) spectra for branched **17b** is the same as that for **17a**. For cross-linked **18** (Figure 1c): ¹H NMR (CDCl_3 , ppm) δ 7.10 (brs, 1H, ArH), 6.46 (br m, 6H, ArH), 4.82 (br s, 2H, ArCH_2), 4.05 (br s, 8H, OCH_2), 3.81 (br s, 8H, OCH_2), 3.65 (br s, 16H, OCH_2), 1.08 (br s, 2H, CH_2), 0.78–1.02 (br m, 3H, CH_3). T_g for cross-linked **18**: 25.8 °C.

Acknowledgment. This work was supported by the Polymers Program, Division of Materials Research, National Science Foundation, through individual investigator grant DMR-93-20196.

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