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Polyrotaxanes by *In Situ* Self Threading During Polymerization of Functional Macrocycles. Part 2*: Poly(ester crown ether)s.

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ABSTRACT: Poly(ester crown ether)s were synthesized by direct condensation of bis(5-carboxy-m-phenylene)-(3x + 2)-crown-x, x = 6, 8 and 10 (**1a**, **1b** and **1c**) with bisphenols via the Higashi method. The formation of higher molecular weight poly(ester crown ether) **5** from the 32-membered crown ether **1c** and bisphenol-A (**2a**) as compared to polyester **3** from 20-membered crown ether **1a** and bisphenol-A, polyester **4** made from the 26-membered crown ether **1b** and bisphenol-A (**2a**) and polyester **6** derived from 32-membered **1c** and bis(p-t-butylphenyl)-bis(p-hydroxyphenyl)methane (**2b**) under identical conditions is believed to be the result of threading (rotaxane formation) in **5** but no or less threading in **3**, **4** or **6**; indeed polyester **3** provides a control because its macrocyclic component (**1a**) too small to be threaded, even by a polymethylene chain. Threading in **5** was undetectable through NOESY experiments. However, melt polymerization of bis(5-hydroxymethyl-m-phenylene)-32-crown-10 (**7**) with sebacoyl chloride (**8**) gave an insoluble, but swellable elastomeric material **9**, a polyrotaxane network, as a result of more extensive *in situ* threading brought about by hydrogen bonding of the crown ether with the alcohol moieties in the more concentrated medium. © 1997 Elsevier Science Ltd.

INTRODUCTION

A polyrotaxane is a molecular composite comprised of a macromolecule in which macrocycles are threaded by linear segments with no covalent bonds between the two species.[1] Several types of polyrotaxanes are depicted in Figure 1; polypseudorotaxanes such as **A** and **E** do not possess bulky groups to prevent potential diffusional loss of the rotaxane structure, while true polyrotaxanes such as **B**, **C**, **D** and **F** do possess such "stoppers" or "blocking groups." The formation of a main chain polyrotaxane of Type **A** via *in situ* formation of a low molar mass pseudorotaxane is represented in Scheme 1. The macrocycle content, defined as macrocycles per repeat unit (m/n), in the polyrotaxane derived from the pseudorotaxane formed *in situ* depends on the driving force for the threading and the stoichiometry.

Generally there are two synthetic approaches to achieve the threading that leads to the monomeric pseudodrotaxane: statistical and template methods. In the statistical threading approach there is negligible enthalpic driving force and entropy plays a major role. The threading efficiency is affected by several variables such as ring size and ring rigidity, chain length and chain rigidity, ring-chain compatibility, etc. This method produced several low molar mass rotaxanes and catenanes in the early years of topological chemistry;[2] the yields were relatively low, of course. In "statistical threadings" the K values are usually quite small(<1 M^{-1} probably), but in systems of Type A comprised of linear and cyclic poly(dimethylsiloxane)s K values are as high as 500

L/mol for very large (500-membered) rings.[1,3] Thus ring size is indeed a key parameter. For smaller rings, however, as long as they are large enough to be threaded, large excesses of the macrocycle may be used to drive the threading equilibrium through le Chatelier's principle. Vinyl chain growth polymerizations offer a modification of the technique illustrated in Scheme 1, but utilize the same principle of statistical threading. Polystyrene rotaxanes of Type A incorporating cyclic urethanes had m/n values up to 0.14,[1,4] while poly(styrene-*rotaxa*-crown ether)s from free radical and anionic methods had m/n values less than 0.025.[5]

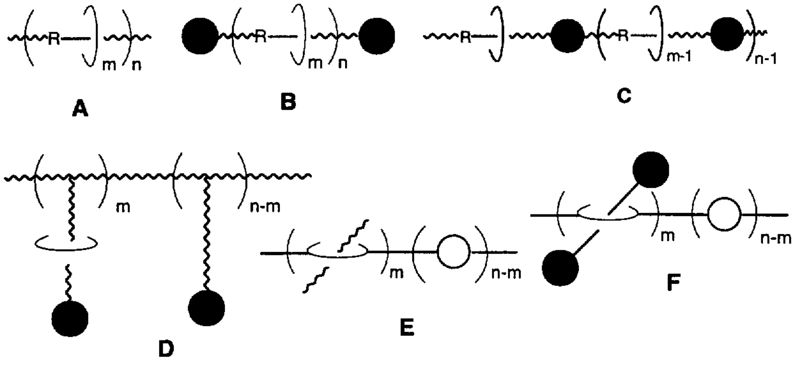
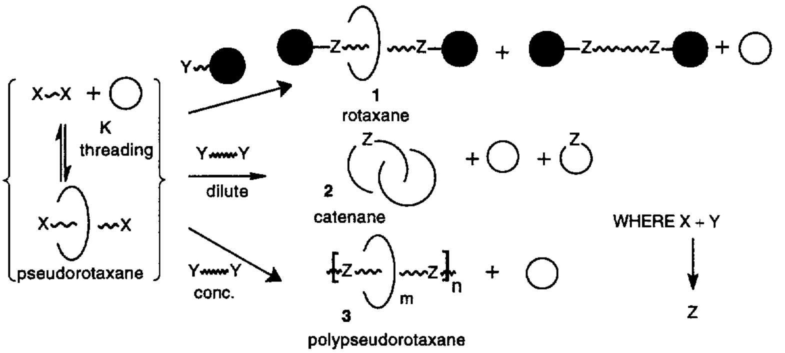


Figure 1. Various types of polyrotaxane architectures.



Scheme 1. Pseudorotaxanes as precursors to rotaxanes, catenanes and polypseudorotaxanes.

On the other hand, the negative enthalpy change for non-covalent bonding is adopted as a threading driving force in the host-guest approach. A nearly quantitative threading efficiency can be obtained with this approach if K is sufficiently high. Since the dominant driving force for this approach is enthalpic (hydrogen bonding, coordination, complexation, electron transfer, etc.), factors associated with the statistical threading method such as ring size, chain length, ring and chain rigidity, ring/chain ratio become less important issues as long as their values satisfy critical requirements for threading.

The host-guest or self assembly approaches can be classified into two categories. First, a species such as a metal ion may be added into the system to serve as a template; the coordination among the metal ion and both cyclic and linear species is the driving force for the formation of an interlocking system, the pseudorotaxane of

Scheme 1. Second, direct host-guest complexation between cyclic and linear species may be used as a driving force. In other words, the cyclic and linear species serve as templates for each other via molecular recognition. We will give examples of both categories.

The first method was used by Sauvage, who in 1984 with coworkers reported the synthesis of a catenane by cyclizing a phenanthroline based bisphenol in the presence of Cu(I) ion via the resultant pseudorotaxane.[6] Many elegant extensions of this concept have been reported.[6,7]

With the enthalpic attraction provided by hydrogen bonding of aliphatic crown ethers with one of the monomers (the diol) in step growth (condensation) polymerizations, we have achieved syntheses of main chain polyrotaxanes of Types **A**, **B** and **C**, namely poly(ester-rotaxane)s with m/n values up to 0.74[8] and polyurethane rotaxaneswith m/n up to 0.87.[9] Other main chain polyrotaxanes of Type **A** prepared in our laboratory with aliphatic crown ethers as the macrocyclic components include polyaramides,[1,10] and liquid crystalline polyesters[1,11] by step growth polymerizations, whose threading is believed to be driven by hydrogen bonding, and a conducting polymer, poly(phenylenevinylene), by a chain growth process, in which pseudorotaxane formation is believed to be facilitated by complexation of the sulfonium ion monomer.[12] Low molar mass rotaxanes and catenanes have been prepared via the corresponding pseudorotaxanes self assembled by hydrogen bonding as reported by Vögtle et al.,[13] Hunter et al., [14] Leigh et al.[15] and Stoddart and coworkers.[16]

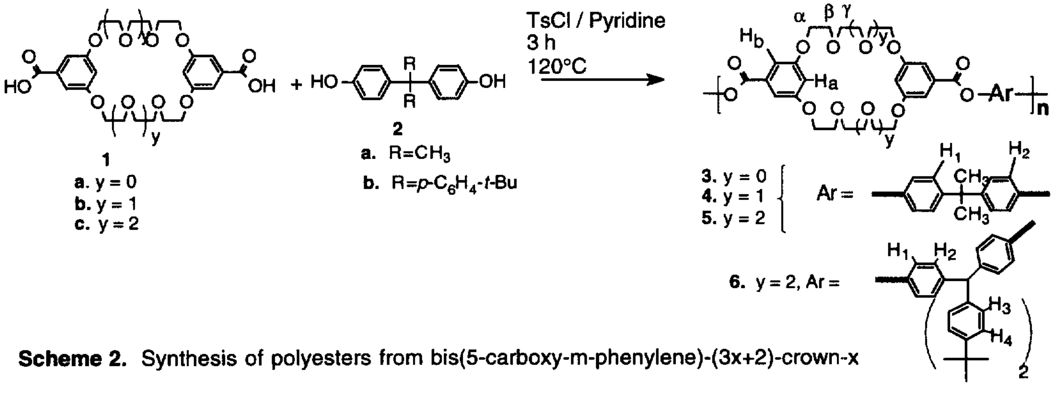
Free radical production of poly[acrylonitrile-rotaxa-(60-crown-20)] (Type **A**), presumably aided by complexation of the monomer in a pseudorotaxane structure analogous to that formed with acetonitrile,[17] provides m/n values up to 0.04, which corresponds to 40% cyclic by mass because of the low repeat unit molar mass.[18]

Cyclodextrin inclusion pseudorotaxane complexes driven by hydrophobic-hydrophilic interactions display formation (threading) constants as high as 10^4 L/mol.[19] A variety of low molar mass rotaxanes based on cyclodextrins as the cyclic species have been reported.[1,20] Indeed in this area the syntheses of polyrotaxanes from cyclodextrin complexes preceded much of the low molar mass activity. Such Type **A** polyrotaxanes include polyamides[21] and homo- and co-polymers of vinylidene chloride.[22] Recently well characterized, main chain polyrotaxanes of Types **A** and **C** were efficiently prepared by threading preformed polyamines through α-cyclodextrin.[23] β-cyclodextrin derivatives have been used to make side chain rotaxanes of Type **D**.[24] Oligomeric rotaxanes of Type **A** have been prepared from cyclodextrins and oligo(ethylene glycol)s, oligo(propylene glycol)s and oligo(isobutylene)s.[25]

Stoddart and coworkers in 1987 reported[26] the synthesis and x-ray structure of a threaded host-guest or pseudorotaxane complex of N,N'-dimethyl-4,4'-bipyridinium ("methyl viologen" or "paraquat") and bis(p-phenylene)-34-crown-10 and have since masterfully applied this technique to "self assembly" processes leading to rotaxanes and catenanes of increasing size and complexity.[27]

Crown ethers are a well known class of molecules.[28] Due to the presence of a hydrophilic cavity and hydrophobic exterior they form stable complexes by metal chelation within the cavity. Their complexation properties make them ideal candidates as receptor molecules in the study of host-guest supramolecular chemistry.[29] Polymeric crown ethers have been known since 1970.[30] The work described so far is basically restricted to crown ethers with ring sizes of 24-membered or less. However, Swager et al. recently demonstrated an elegant method to enhance the sensitivity of a fluorescence based chemosensor via poly(phenyleneethynylene)s by making use of bis(p-phenylene)-34-crown-10 in a Type **E** structure.[31]

Our success in making large functionalized macrocycles[32] gave us the starting materials to investigate the structure-property relationships of poly(crown ether)s. Polyester **5** from polymerization of of bis(5-carboxy-m-phenylene)-32-crown-10 (**1c**) with bisphenol-A (**2a**) (Scheme 2). was soluble,[33] but polycondensation of **1c** with 4,4'-oxydianiline and bis[4-(m-aminophenoxy)phenyl]phenyl phosphine oxide gave insoluble polyamides which swelled in dipolar aprotic solvents.[34] The insolubility was attributed to *in situ* threading, i.e., polyrotaxane network formation of Type **F** (Scheme 1), the driving force being hydrogen bonding of the amine and/or amide moieties with the macrocycles that are part of the backbone and the stoppers being adjacent macrocyclic units. To investigate this phenomenon of "self threading" further in the case of polyesters, therefore, we have explored the use of analogous macrocycles of different ring sizes, bulky bisphenols and the concentration of the polymerization reaction. In this paper we describe the effects of these parameters on threading of polyesters.

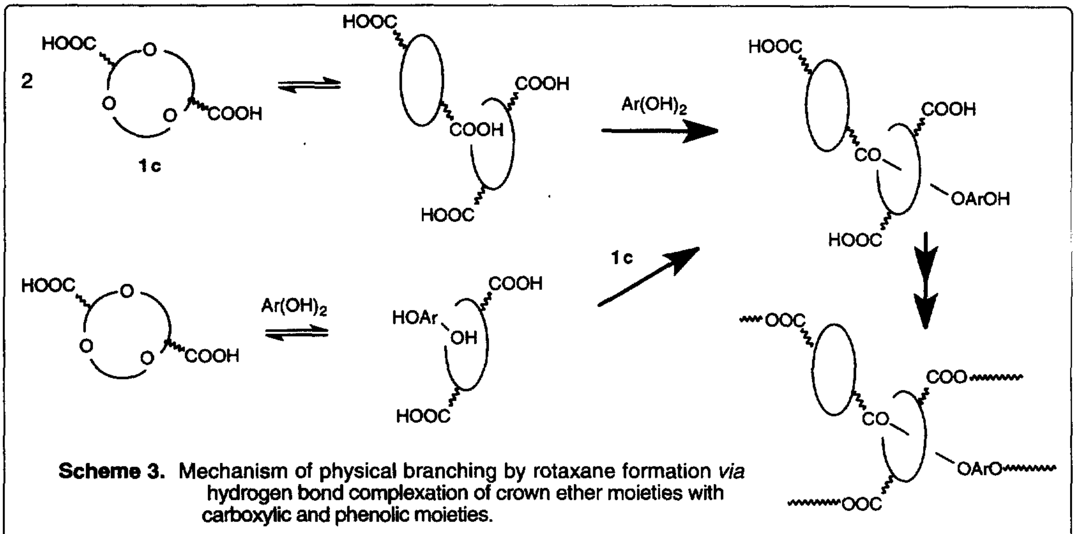


Scheme 2. Synthesis of polyesters from bis(5-carboxy-m-phenylene)-(3x+2)-crown-x

RESULTS and DISCUSSION

A. Poly(ester crown ether)s 5 and 6 Made in Solution by the Higashi Method From Bis(5-carboxy-m-phenylene)-32-crown-10 (1c)

Our previous synthesis of poly(ester crown) **5** gave a high molecular weight polymer (M_w = 133 kg/mol, light scattering) with a molecular weight distribution M_w/M_n = 2.3 (GPC).[33] *In situ* threading during polymerization, even if it were only a few percent, would have a large effect on the molecular weight and also probably broaden the molecular weight distribution above the theoretical maximum of 2.0, as experimentally observed. As shown in Scheme 3threading in this system can occur when an ester bond forms through the cavity of a crown ether of a hydrogen bonded complex with either a carboxylic or phenolic moiety, thus causing permanent entanglements and giving rise to physical crosslinking of Type **E** (Figure 1). This is the same basic mechanism we have proposed for the formation of poly(ester rotaxane)s from diols, diacid chlorides and crown ethers.[8d-8j]



Scheme 3. Mechanism of physical branching by rotaxane formation *via* hydrogen bond complexation of crown ether moieties with carboxylic and phenolic moieties.

In order to re-examine this system and provide more evidence for the proposed polyrotaxane formation, we repeated the synthesis of poly(ester crown) **5** (Scheme 2) via the Higashi method.[35] A white, fibrous, soluble polymer was obtained in quantitative yield. It had somewhat lower molecular weight and distribution than the previous sample.

Analysis of polymer **5** by NOESY (Nuclear Overhauser Effect SpectroscopY) did not reveal any through-space correlation between the protons of the macrocyclic moiety and the biphenol-A moiety, e.g., intra-annular H_a and the methyl groups of the bisphenol-A moiety, which would be expected of a threaded polymer. The absence of NOE was a somewhat surprising result because x-ray studies revealed that the methyl ester of bis(5-carboxy-1,3-phenylene)-32-crown-10 (**1c**) exists in a conformation whose cavity size is 4.9 x 7.8 °A taking into account Van der Waals radii.[32f] This is sufficiently large to permit threading. However, in dilute solution in the highly polar medium perhaps the extent of rotaxane formation is below the detection limit of the NOE experiment.

Therefore, since the absence of NOE in **5** does not rule out the occurence of threading, we thought that by altering the structure of the diphenol we might be able to take the opposite tack and completely suppress the threading during polymerization. Our experience in the use of blocking groups[36] in polyrotaxane formation to prevent the loss of cyclics incorporated on the polymeric backbone led us to use a very bulky monomer for polymerization with BCP32C10 (**1c**). Bis(p-tert-butylphenyl)-bis(p-hydroxyphenyl)methane (**2b**) was synthesized in our laboratory via a multi-step method.[8e] Direct polycondensation of BCP32C10 (**1c**) with **2b** via the Higashi method[35] with tosyl chloride in pyridine gave poly(ester crown ether) **6** in quantitative yield (Scheme 2) as a white, fibrous material. **6** was soluble in chloroform and NMP. The M_n was determined to be

28.5 kg/mol by GPC. **6** showed a glass transition (T_g) at 118°C, much higher than the analogous polymer **5** (T_g = 72°C), probably due to the more rigid character of the backbone. Polymer **6** showed high thermal stability, i.e., 5% weight loss at 386°C and 412°C in air and nitrogen, respectively.

Although the above polymerization reactions were done under identical conditions using the same monomeric diacid (BCP32C10 **1c**), they resulted in quite different molecular weights. We believe that when bisphenol-A (**2a**) was used, threading took place, resulting in a higher molecular weight polymer **5** (M_n = 49.4 kg/mol) as compared to polymer **6**, whose lower molecular weight (M_n = 28.5 kg/mol) was due to the absence of, or diminished, threading by the bulky bisphenol **2b**.

B. Poly(ester crown ether) 4 Made in Solution by the Higashi Method From Bis(5-carboxy-m-phenylene-26-crown-8) (1b)

Experiments by Schill et al.[2d,2k] and Harrison[2e,2f,2i] established that cyclic compounds must contain at least 22 atoms, in order for a methylene chain (cross sectional diameter of 4.5°A) to thread them. X-ray studies of the dimethyl ester of bis(5-carboxy-*m*-phenylene)-26-crown-8 (**1b**)[32c] revealed a puckered structure in which the two aromatic rings are essentially antiparallel to each other with absence of spatial overlap.[32f] The cavity size of 2.6 x 7.0°A, taking into account Van der Waals radii, is much smaller than that of the dimethyl ester of **1c**.[32f] Due to the open but rather small cavity of macrocycle **1b**, it is conceivable but unlikely that the threading can take place unless a very strong driving force is in place.

In order to examine the effect of the ring size on the threading process, we synthesized poly(ester crown ether) **4** by direct polycondensation of the smaller macrocycle BCP26C8[32c] (**1b**) with bisphenol-A (**2a**). The polymer was completely soluble in chloroform and NMP. The M_n was determined to be 16.6 kg/mol by GPC vs. polystyrene standards. **4** showed a glass transition temperature at 100°C as compared to 72°C for analogous polymer **5** based on the more flexible 32-crown-10 diacid **1c**. Polymer **4** exhibited 5% weight loss at 376°C and 385°C in air and nitrogen, respectively .

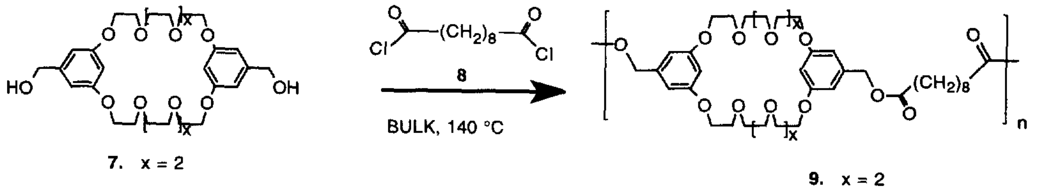
The low molecular weight (M_n = 16.6 kg/mole) of polymer **4** as compared to that of poly(ester crown ether) **5** (M_n = 49.3 kg/mol) suggests the absence of, or diminished, threading in **4**, presumably due to the lack of a strong driving force and the smaller cavity size of **1b**.

C. Poly(ester crown ether) 3 Made in Solution by the Higashi Method From Bis(5-carboxy-m-phenylene)-20-crown-6 (1a)

As noted above it has been shown[2] that the minimum ring size for threading of a polymethylene chain is 22 carbon atoms or the equivalent. Therefore, the 20-membered crown ether diacid **1a** provides a good control experiment, since no threading can take place in its polymerization with bisphenol-A. Indeed this polycondensation produced colorless, fibrous polymer **3** whose M_n was 12.2 kg/mol. The lower molecular weight in this case is taken to indicate that the higher molecular weight obtained in the case of the 32-membered analog **5** was due to branching via rotaxane formation. **3** had a T_g of 150°C; by TGA it underwent 5% weight loss at 428°C in air and 430°C in nitrogen, respectively.

D. Poly(ester crown ether) 9 Made by Bulk Reaction From Bis(5-hydroxymethyl-m-phenylene)-32-crown-10 (7)

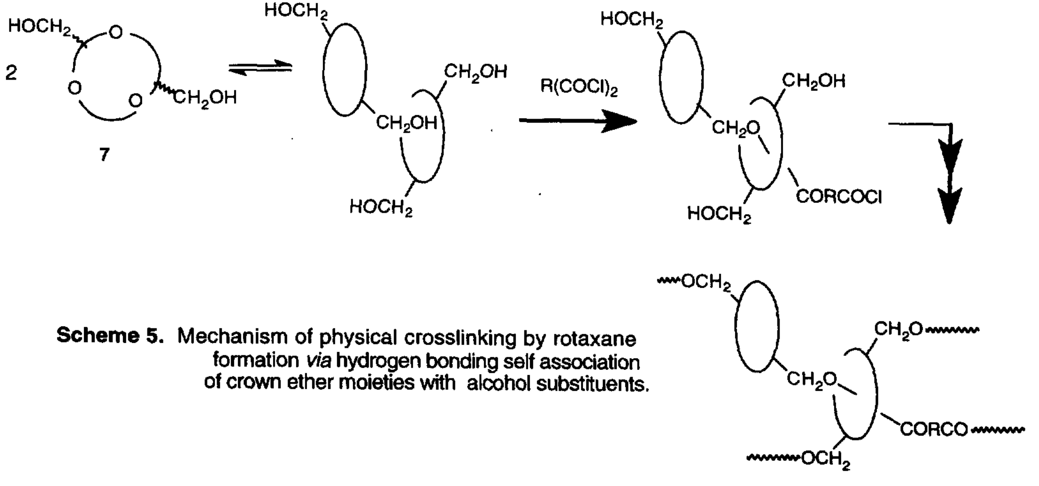
Irrespective of the cavity size poly(ester crown ether)s **3-6** prepared in solution were all soluble. We attribute this to the formation of only a small amount of rotaxane structure during polymerization, even in **5** derived from the 32-membered crown ether. To enhance the proportion of threading we examined polyesterification in the absence of solvent (Scheme 4), i.e., under bulk conditions, in order to increase concentrations and hence the proportion of the hydrogen bonded precursor of the rotaxane structure. Polyesterification of bis(5-hydroxymethylene-1,3-phenylene)-32-crown-10[32a] (**7**) with sebacoyl chloride (**8**) was carried out in the melt state at 140°C. The resultant polymer **9** was obtained quantitatively as an insoluble elastomer which swelled in dipolar aprotic solvents as well as chloroform. We believe that the more efficient *in situ* threading in this system is a result of hydrogen bonding of the hydroxymethyl group with the ethyleneoxy moieties of the macrocycle (Scheme 5). Furthermore due to the smaller cross sectional area of the linear sebacoyl chain the probability of threading is greater than with bisphenols **2**. The result was a physically crosslinked material with a glass transition at 2°C . The polymer exhibited good thermal stability, i.e., 5% weight loss at 386°C and 412°C in air and nitrogen, respectively.



7. x = 2

9. x = 2

Scheme 4. Bulk polyesterification of bis(5-hydroxymethyl-m-phenylene)-32-crown-10 with sebacoyl chloride.



Scheme 5. Mechanism of physical crosslinking by rotaxane formation *via* hydrogen bonding self association of crown ether moieties with alcohol substituents.

CONCLUSIONS

Several novel poly(ester crown ether)s **3**, **4**, **5**, **6** and **9** containing 20-, 26- and 32-membered rings (**1a**,**1b**, **1c** and **7**) in the main chain were synthesized to explore the effect of the cavity size, structure of the comonomers and polymerization process on *in situ* rotaxane formation. Although no NOE correlation between the aromatic protons of the macrocyclic cavity with the protons of the bisphenol-A moiety was evident in **5** derived from the 32-membered crown ether **1c**, this does not rule out the existence of physical crosslinking. A comparison of the molecular weights of polymer **5** with poly(ester crown ether)s **4** made from the 26-membered macrocycle **1b** and **3** derived from the 20-membered crown ether **1a**, which is too small to be threaded, indicates rotaxane formation in **5** but much less in **4** and none in **3**. Indeed, polymer **6** derived from bulky diphenolic monomer **2b** and 32-membered diacid **1c** had a molecular weight much lower than that of polymer **5** synthesized under identical conditions, presumably because of steric inhibition of threading in the case of the bulky phenol **2b**. On the other hand, melt polymerization of 32-membered macrocyclic diol **7** and sebacoyl chloride (**8**) gave an insoluble, swellable gel (**9**) as a result of more extensive *in situ* threading attributable to the higher concentrations and smaller cross section of **8** relative to **2a**.

ACKNOWLEDGMENTS

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EXPERIMENTAL

Materials. Reagent grade reactants and solvents were used as received from chemical suppliers. Pyridine was distilled over CaH_2 prior to its use in polymerization.

Measurements. ^{1}H and ^{13}C NMR spectra were recorded at ambient temperature on a Varian Unity 400 Mhz (100 Mhz for C) spectrometer in deuterated chloroform with TMS (δ = 0) as internal standard unless otherwise noted. TGA was performed on a Perkin-Elmer Model TGA-7 under nitrogen or air at a heating rate of 10°C per minute. DSC was performed on a Perkin-Elmer Series 4 calorimeter or on a Seiko SSC-5200 under dry nitrogen purge using indium and tin as the calibration standards at a heating rate of 10°C per minute and the reported values (midpoints) were obtained from the second heating after cooling. GPC was conducted with a Waters GPC/ALC 150-C chromatograph equipped with a differential refractometer detector. Two columns packed with 10^3 and 10^4Å µStyragel HT were used.

Bis(5-carboxy-m-phenylene)-20-crown-6 (1a): A solution of 1.25g (2.62 mmol) of bis(5-carbomethoxy-m-phenylene)-20-crown-6[32c] and 50 mL of 40% aq. tetrabutylammonium hydroxide was refluxed for 24 h, cooled, acidified with 4M HCl (50 mL), cooled to 0-5°C and filtered. The solid was washed with water, dried and recrystallized from pyridine to afford 822 mg (70%) of colorless solid, mp 310° (dec); ^{1}H NMR [$(CD_3)_2SO$] δ (ppm): 3.79 (β-OCH_2, t, J = 2.0Hz, 8H), 4.13 (α-OCH_2, t, J = 2.0Hz, 8H), 6.67 (H_a, m, 2H), 7.03 (H_b, d, J = 1.0Hz, 4H), 12.4-13.5 (COOH, br s);); ^{13}C NMR [$(CD_3)_2SO$] δ (ppm): 67.7, 68.9, 107.3, 107.6, 132.6, 159.5, 166.8; elemental analysis, calcd. for $C_{22}H_{24}O_{10}$: C 58.93, H 5.39; found: C 58.89, H 5.46.

Poly(ester crown ether) 3 by Polycondensation of BCP20C6 (1a) with 4,4'-Isopropylidenediphenol (Bisphenol-A, 2a): A solution of tosyl chloride (737 mg, 3.87 mmol) in pyridine (5 mL) and DMF (15 drops) was maintained at room temperature for 30 min and added to diacid **1a** (667 mg, 1.49 mmol) in pyridine (5 mL). The mixture was maintained at room temperature for 10 min and then at 120°C for 10 min. A solution of bisphenol-A (**2a**, 339 mg, 1.49 mmol) in pyridine (5 mL) was added over 20 min and the reaction was maintained for 3 h at 120°C. The polymer was isolated by precipitation into methanol, filtered, washed with water and methanol, and dried to afford 888 mg (93%) of colorless polymer. The product was reprecipitated from chloroform solution into methanol twice and then dried under vacuum at 56°C for 24 h. ^{1}H NMR ($CDCl_3$) δ (ppm): 1.70 (CH_3, s, 6H), 3.90 (β-OCH_2, t, J = 4.2Hz, 8H), 4.21 (α-OCH_2, t, J = 4.2Hz, 8H), 6.84 (H_a, t, J = 2.2Hz, 2H), 7.27 (H_1, d, J = 8.4Hz, 4H), 7.09 (H_2, d, J = 8.4Hz, 4H) and 7.32 (H_b, d, J = 2.2Hz, 4H). T_g: 150°C. TGA (5% weight loss): 428°C in air and 430°C in N_2. GPC (polystyrene standards), $CHCl_3$, 30°C: M_n = 12.2 kg/mol; M_w = 29.1 kg/mol, M_w/M_n = 2.37.

Poly(ester crown ether) 4 by Polycondensation of BCP26C8 (1b) with 4,4'-Isopropylidenediphenol (Bisphenol-A, 2a): A solution of tosyl chloride (495.8 mg, 2.600 mmol) in pyridine (2.0 mL) and DMF (6 drops) was maintained at room temperature for 30 min and added to diacid **1b**[32c] (536.6 mg, 1.000 mmol) in pyridine (2 mL). The mixture was maintained at room temperature for 10 min and then at 120°C for 10 min. A solution of bisphenol-A (**2a**, 228.3 mg, 1.000 mmol) in pyridine (2.0 mL) was added over 20 min and the reaction was maintained for 3 h at 120°C. The polymer was isolated by precipitation into methanol, filtered, washed with water and methanol and dried under vacuum at 50°C for 24 h, 710 mg (100%). ^1H NMR ($CDCl_3$) δ (ppm): 1.70 (CH_3, s, 6H), 3.75 (γ-OCH_2, m, 8H), 3.88 (β-OCH_2, t, J = 4.6Hz, 8H), 4.16 (α-OCH_2, t, J = 4.6Hz, 8H), 6.78 (H_a, t, J = 2.2Hz, 2H), 7.09 (H_1, d, J = 8.8Hz, 4H), 7.27 (H_2, d, J = 8.8Hz, 4H) and 7.33 (H_b, d, J = 2.2Hz, 4H). T_g: 100°C. TGA (5% weight loss): 376°C (air), 385°C (N_2). GPC (polystyrene standards), $CHCl_3$, 30°C: M_n = 16.6 kg/mol; M_w = 39.4 kg/mol, M_w/M_n = 2.37.

Poly(ester crown ether) 5 by Polycondensation of BCP32C10 (1c) with 4,4'-Isopropylidenediphenol (Bisphenol-A, 2a): This polymer was synthesized according to the literature procedure.[33] Diacid **1c**[32a] (626.9 mg, 1.004 mmol) in pyridine (2 mL), tosyl chloride (497.9 mg, 2.612 mmol) in pyridine (2 mL) and DMF (6 drops), and bisphenol-A (**2a**, 229.2 mg, 1.004 mmol) in pyridine (2 mL) were used. The polymer was isolated in 100% yield. T_g: 72°C. TGA (5% weight loss): 359°C (air), 408°C (N_2). GPC (polystyrene standards), $CHCl_3$, 30°C: M_n = 49.4 kg/mol; M_w = 100.3 kg/mol, M_w/M_n = 2.03.

Poly(ester macrocycle) 6 by Polycondensation of BCP32C10 (1c) with Bis(p-tert-butylphenyl)-bis(p-hydroxyphenyl)methane (2b): A solution of tosyl chloride (503.3 mg, 2.640 mmol) in pyridine (2.0 mL) and DMF (6 drops) was maintained at room temperature for 30 min and added to diacid **1c**[32a] (633.4 mg, 1.014 mmol) in pyridine (2 mL). The mixture was maintained at room temperature for 10 min and then at 120°C for 10 min. A solution of **2b** (471.2 mg, 1.014 mmol) in pyridine (2.0 mL) was added slowly over 20 min and the reaction was maintained for 3 h at 120°C. The polymer was isolated by precipitation into methanol, filtered, washed with water and methanol and dried under vacuum at 50°C for 24 h, 1.05 g (98%). ^1H NMR ($CDCl_3$) δ (ppm): 1.30 (CH_3, s, 18H), 3.71 (γ-OCH_2, m, 16H), 3.86 (β-OCH_2, t, J = 4.6Hz, 8H), 4.15 (α-OCH_2, t, J = 4.6Hz, 8H), 6.77 (H_a, t, J = 2.4Hz, 2H), 7.08 (H_1, d, J = 8.4Hz, 4H), 7.13 (H_2, J = 8.4Hz, 4H), 7.24-7.28 (H_3, H_4, m, 8H) and 7.32 (H_b, d, J = 2.4Hz, 4H). T_g: 118°C. TGA (5% weight loss): 395°C (air), 427°C (N_2). GPC (polystyrene standards), $CHCl_3$, 30°C: M_n = 28.5 kg/mol, M_w = 60.2 kg/mol, M_w/M_n = 2.11.

Poly(ester crown ether) 9 by Bulk Polycondensation of Bis(5-hydroxymethylene-m-phenylene)-32-Crown-10 (7) with Sebacoyl Chloride (8): A mixture containing bis(5-hydroxymethylene-m-phenylene)-32-crown-10[32a] (**7**, 509.8 mg, 0.8544 mmol) and sebacoyl chloride (**6**, 204.4 mg, 0.8547 mmol) was heated at 140°C for 4 h. The polymer was isolated by pouring the reaction mixture into methanol, filtered, washed with methanol and dried under vacuum at 50°C for 24 h, to give an insoluble, but swellable elastomeric material, 650 mg (100%). T_g: 2°C. TGA: (5% weight loss): 386°C (air), 412°C (N_2).

REFERENCES

* Part 1: reference 34.

1. Reviews: Gibson, H. W. *Large Ring Molecules*, Semlyen, J. A., ed., John Wiley & Sons, New York, 1996, ch. 6, pp. 191-262; Ambalino, D. B.; Stoddart, J. F. *Chem. Revs.*, **1995**, *95*, 2725; Gibson, H. W.; Bheda, M. C.; Engen, P. T. *Prog. Polym. Sci.*, **1994**, *19*, 843; Lipatov, Y. S.; Lipatova, T. E.; Kosyanchuk, L. F. *Adv. Polym. Sci.*, **1989**, *88*, 49.
2. (a) Harrison, I. T.; Harrison S. *J. Am. Chem. Soc.*, **1967**, *89*, 5723; (b) Schill, G.; Zollenkopf, H. *Nachr. Chem. Techn.*, **1967**, *79*, 149; (c) Schill, G.; Zollenkopf, H. *Ann. Chem.*, **1969**, *721*, 53; (d) Schill, G. *Catenanes, Rotaxanes and Knots*, Academic Press, New York, 1971; (e) Harrison, I. T. *J. Chem. Soc., Chem. Commun.*, **1972**, 231; (f) Harrison, I. T. *J. Chem. Soc., Perkin Trans. I.*, **1974**, 301; (g) Agam, G.; Gravier, D.; Zilkha, A. *J. Am. Chem. Soc.*, **1976**, *98*, 5206; (h) Agam, G.; Zilkha, A. *J. Am. Chem. Soc.*, **1976**, *98*, 5214; (i) Harrison, I. T. *J. Chem. Soc., Chem. Commun.*, **1977**, 384; (j) Schill, G.; Schweikert, N.; Fritz, H.; Vetter, W. *Angew. Chem. Int. Ed. Eng.*, **1983**, *22*, 889; (k) Schill, G.; Beckmann, W.; Schweickert, N.; Fritz, H. *Chem. Ber.*, **1986**, *119*, 2647.
3. Joyce, S. J.; Hubbard, R. E.; Semlyen, J. A. *Eur. Polym. J.*, **1993**, *29*, 305; Mark, J. E. *New J. Chem.*, **1993**, *17*, 703; Clarson, S. J. *New J. Chem.*, **1993**, *17*, 711; Clarson, S. J.; Mark, J. E.; Semlyen, J. A. *Polym. Commun.*, **1987**, *28*, 151; DeBolt, L. C.; Mark, J. E. *Macromolecules*, **1987**,

20, 2369.

4. Lipatova, T. E.; Kosyanchuk, L. F.; Gomza, Y. P.; Shilov, V. V.; Lipatov, Y. S. *Dokl. Akad. Nauk S.S.S.R. (Engl. Tr.)*, **1982**, *263*, 140; Lipatova, T. E.; Kosyanchuk, L. F.; Gomza, Y. *Polym. Sci., U.S.S.R. (Engl. Tr.)*, **1985**, *27*, 622.
5. Gibson, H. W.; Engen, P. T.; Lee, S.-H.; Liu, S.; Marand, H.; Bheda, M. C. *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.*, **1993**, *34(1)*, 64. Lee, S.-H.; Engen, P. T.; Gibson, H. W. *Macromolecules*, **1997**, *30*, 337; Lee, S.-H. *Ph. D. Dissertation*, Virginia Polytechnic Institute and State University, 1992.
6. Dietrich-Buchecker, C. O.; Sauvage, J.-P. *J. Am. Chem. Soc.*, **1984**, *106*, 3043; Ambalino, D. B.; Sauvage, J.-P. *J. Chem. Soc., Chem. Commun.*, **1996**, 2441; Carina, R. F.; Dietrich-Buchecker, C. O.; Sauvage, J.-P. *J. Am. Chem. Soc.*, **1996**, *118*, 9110; Weidmann, J.-L.; Kern, J.-M.; Sauvage, J.-P.; Geerts, Y.; Muscat, D.; Müllen, K. *J. Chem. Soc., Chem. Commun.*, **1996**, 1243; Cardenas, D. J.; Livoreil, A.; Sauvage, J.-P. *J. Am. Chem. Soc.*, **1996**, *118*, 11980.
7. Wu, C.; Lecavalier, P. R.; Shen, Y. X.; Gibson, H. W. *Chem. Mater.*, **1991**, *3*, 569.
8. (a) Lecavalier, P. R.; Engen, P. T.; Shen, Y. X.; Joardar, S.; Ward, T. C.; Gibson, H. W. *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.*, **1989**, *30(1)*, 189; (b) Wu, C.; Bheda, M.; Lim, C.; Shen, Y. X.; Sze, J.; Gibson, H. W. *Polymer Commun.*, **1991**, *32*, 204; (c) Gibson, H. W.; Liu, S.; Lecavalier, P.; Wu, C.; Shen, Y. X. *J. Am. Chem. Soc.*, **1995**, *117*, 852; (d) Gibson, H. W.; Liu, S. *Makromol. Chem., Macromol. Symp.*, **1996**, *102*, 55; (e) Gong, C.; Gibson, H. W. *Macromolecules*, **1996**, *29*, 7029; (f) Gong, C; Gibson, H. W. *Macromol. Chem. Phys.*, **1997**, *198*, in press; (g) Gibson, H. W.; Liu, S.; Gong, C.; Joseph, E. *Macromolecules*, **1997**, *30*, in press; (h) Gong, C.; Gibson, H. W. *J. Am. Chem. Soc.*,**1997**, *119*, in press; (i) Gong, C.; Ji, Q.; Glass, T. E.; Gibson, H. W. *Macromolecules*, submitted.
9. Shen, Y. X.; Xie, D.; Gibson, H. W. *J. Am. Chem. Soc.*, **1994**, *116*, 537; Marand, E.; Hu, Q.; Gibson, H. W.; Veytsman, B. *Macromolecules*, **1996**, *29*, 2555; Gong, C.; Gibson, H. W. *Angew. Chem. Int. Ed. Engl.*, submitted. Gong, C.; Gibson, H. W. *J. Am. Chem. Soc.*, submitted. Gong, C.; Gibson, H. W. *Angew. Chem.*, submitted.
10. Bheda, M. C.; Gibson, H. W., unpublished results. Bheda, M. C. *Ph.D. Dissertation*, Virginia Polytechnic Institute and State University, 1992.
11. Sze, J. Y.; Gibson, H. W. *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.*, **1992**, *33(2)*, 331; Sze, J. Y. *M. S. Thesis*, Virginia Polytechnic Institute and State University, 1992.
12. Wang, L. *M. S. Thesis*, Virginia Polytechnic Institute and State University, 1994.
13. Jäger, R.; Schmidt, T.; Karbach, D.; Vögtle, F. *SynLett*, **1996**, 723; Vögtle, F.; Dünnwald, T.; Händel, M.; Jäger, R.; Meier, S.; Harder, G. *Chem. Eur. J.*, **1996**, *2*, 640; Vögtle, F.; Jäger, R.; Händel, M.; Ottens-Hildebrandt, S.; Schmidt, W. *Synthesis*, **1996**, 353.
14. Adams, H.; Carver, F. J.; Hunter, C. A. *J. Chem. Soc., Chem. Commun.*, **1995**, 809; Carver, F. J.; Hunter, C. A.; Shannon, R. J. *J. Chem. Soc., Chem. Commun.*, **1994**, 1277.
15. Johnston, A. G.; Leigh, D. A.; Murphy, A.; Smart, J. P.; Deegan, M. D. *J. Am. Chem. Soc.*, **1996**, *118*, 10662; Leigh, D. A.; Moody, K.; Smart, J. P.; Watson, K. J.; Slawin, A. M. Z. *Angew. Chem. Int. Ed. Engl.*, **1996**, *35*, 306; Leigh, D. A.; Murphy, A.; Smart, J. P.; Slawin, A. M. Z. *Angew. Chem. Int. Ed. Engl.*, **1997**, *36*, 728.
16. Ashton, P. R.; Collins, A. N.; Fyfe, M. C. T.; Glink, P. T.; Menzer, S.; Stoddart, J. F.; Williams, D. J. *Angew. Chem. Int. Ed. Engl.*, **1997**, *36*, 59; Ashton, P. R.; Glink, P. T.; Martinez-Diaz, M.-V.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Angew. Chem. Int. Ed. Engl.*, **1996**, *35*, 1930; *J.* Glink, P. T.; Schiavo, C.; Stoddart, J. F.; Williams, D. J. *Chem. Soc., Chem. Commun.*, **1996**, 1483; Ashton, P. R.; Glink, P. T.; Stoddart, J. F.; Tasker, P.A.; White, A. J. P.; Williams, D. J. *Chem. Eur. J.*, **1996**, *2*, 729.
17. Mosier-Boss, P. A.; Popov, A. I. *J. Am. Chem. Soc.*, **1985**, *107*, 6168; Gold, H. S.; Rice, M. R. *Talanta*, **1982**, *29*, 637.
18. Gibson, H. W.; Engen, P. T. *New J. Chem.*, **1993**, *17*, 723.
19. Szejtli, J. *Cyclodextrins and Their Inclusion Complexes*, Akademiai Kiado, Budapest, 1982, pp. 178-184; Bender, M. L.; Komiyama, M. *Cyclodextrin Chemistry*, Springer, New York 1978; Wenz, G. *Angew. Chem. Int. Ed. Eng.*, **1994**, *33*, 803.
20. Yamanari, K.; Shimura, Y. *Bull. Chem. Soc. Jpn.*, **1983**, *56*, 2283; **1984**, *57*, 1596; Harada, A.; Shimada, M.; Takahashi, S. *Chem. Lett.*, **1989**, *275*; Venkata, T.; Rao, S.; Lawrence, D.S. *J. Am. Chem. Soc.*, **1990**, *90*, 1512; Rao, T. V. S.; Lawrence D. S. *J. Am. Chem. Soc.*, **1990**, *112*, 3614; Manka, J. S.; Lawrence, D. S. *J. Am. Chem. Soc.*, **1990**, *112*, 2440; Isnin, R.; Kaifer, A. E. *J. Am. Chem. Soc.*, **1991**, *113*, 8188; Wylie, R.; Macartney, D. *J. Am. Chem. Soc.*, **1992**, *114*, 3136; Ogino, H. *New. J. Chem.*, **1993**, *17*, 683; Wenz, G.; Bey, E.; Schmidt, L. *Angew. Chem. Int. Ed. Engl.*,

1992, *31*, 783; Wenz, G.; Wolf, F.; Wagner, M.; Kubik, S. *New J. Chem.*, **1993**, *17*, 729; Isnin, R.; Kaifer, A. E. *Pure Appl. Chem.*, **1993**, *65*, 495; Harada, A.; Li, J.; Kamachi, M. *Nature*, **1993**, *364*, 316; Harada, A.; Li, J.; Kamachi, M. *Macromolecules*, **1994**, *27*, 4538.

21. Ogata, N.; Sanui, K.; Wada, J. *J. Polym. Sci. Polym. Lett. Ed.*, **1975**, *14*, 459.
22. Maciejewski, M. *J. Macromol. Sci.-Chem.* **1979**, *A13*, 77; Maciejewski, M.; Gwizdowski, A.; Peczak, P.; Pietrzak, A. *J. Macromol. Sci. -Chem.*, **1979**, *A13*, 87.
23. Wenz, G.; Keller, B. *Angew. Chem. Int. Ed. Engl.*, **1996**, *35*, 2139; Weickenmeier, M.; Wenz, G. *Makromol. Chem., Rapid Commun.*, **1996**, *17*, 731.
24. Born, M.; Ritter, H. *Makromol. Chem., Rapid Commun.*, **1996**, *17*, 197; Born, M.; Ritter, H. *Adv. Mater.*, **1996**, *8*, 149.
25. Harada, A. *Polymeric Materials Encyclopedia*, Salamone, J. C., ed., CRC Press, NY, 1996.
26. Allwood, B. L.; Spencer, N.; Shahriari-Zavareh, H.; Stoddart, J. F.; Williams, D. J. *J. Chem. Soc., Chem. Commun.*, **1987**, 1058.
27. Asakawa, M.; Ashton, P. R.; Ballardini, R.; Balzani, V.; Belohradsky, M.; Gandolfi, M. T.; Kocian, O.; Prodi, L.; Raymo, F. M.; Stoddart, J. F.; Venturi, M. *J. Amer. Chem. Soc.*, **1997**, *119*, 302; Asakawa, M.; Ashton, P. R.; Boyd, S. E.; Brown, C. L.; Gillard, R. E.; Kocian, O.; Raymo, F. M.; Stoddart, J. F.; Tolley, M. S.; White, A. J. P.; Williams, D. J. *J. Org. Chem.*, **1997**, *62*, 26; Ambalino, D. B.; Ashton, P. R.; Balzani, V.; Brown, C. L.; Credi, A.; Fréchet, J. M. J.; Leon, J. W.; Raymo, F. M.; Spencer, N.; Stoddart, J. F.; Venturi, M. *J. Amer. Chem. Soc.*, **1996**, *189*, 12012; Philp, D.; Stoddart, J. F. *Angew. Chem. Int. Ed. Engl.*, **1996**, *35*, 1155.
28. Pedersen, C. J. *J. Am. Chem. Soc.*, **1967**, *89*, 2495; Pedersen, C. J. *J. Am. Chem.. Soc.*, **1967**, *89*, 7017; Pedersen, C. J. *Angew. Chem., Int. Ed. Engl.*, **1988**, *27*, 1021; Laidler, D. A.; Stoddart, J. F. in *Crown Ethers and Analogs*; Patai, S.; Rappoport, Z., Eds.; John Wiley & Sons, New York, 1989, pp 1-58; *Macrocycle Synthesis: A Practical Approach*, Parker, D. B., ed., Oxford University Press, New York, 1996.
29. Lehn, J.-M, *Supramolecular Chemistry*, VCH Publishers, Inc., New York, 1995; Cram, D. J.; Cram, J. M. *Container Molecules and Their Guests*, Royal Society of Chemistry, Cambridge, UK, 1994; Dietrich, B.; Viout, P.; Lehn, J.-M., *Macrocyclic Chemistry*, VCH Publishers, Inc., New York, 1993; *Frontiers in Supramolecular Organic Chemistry and Photochemistry*, Schneider, H.-J and Durr, H., eds., VCH Publishers, New York, 1991; Vogtle, F. *Supramolecular Chemistry*, John Wiley and Sons, New York, 1991.
30. Feigenbaum, W. M.; Michel, R. H. *J. Polym. Sci., Polym. Chem. Ed.* **1971**, *9*, 817; Kopolow, S.; Hogen-Esch, T. E.; Smid, J. *Macromolecules* **1971**, *4*, 359; Varma, A. J.; Majewicz, T.; Smid, J. *J. Polym. Sci.: Polym. Chem. Ed.*, **1979**, *17*, 1573; . Kimura, K.; Maeda, T.; Shono, T. *Anal. Lett.*, **1978**, *A 2*, 821; Yagi, K., Ruiz, J. A.; Scanchez, M. C.; *Makromol. Chem., Rapid Commun.*, **1980**, *1*, 263; Shchori, E.; Jagor-Grodzinski, J. *J. Appl. Polym. Sci.* **1976**, *10*, 1665; Blasius, E.; Klein, W. *Makromol. Chem.*, **1986**, *187*, 2553; Warshawsky, A.; Deshe, A.; Shechtman, L.; Kedem, O. *React. Polym.*, **1990**, *12*, 261; Kurmanaliev, M.; Ergozhin, E. E.; Kalmuratova, A. A. *Dokl. Russ. Akad. Nauk.*, **1992**, *323*, 110; Kakuchi, T.; Kamimura, H.; Matsunami, S.; Yokota, K.; Tsuda, K. *Macromolecules*, **1995**, *28*, 658; Shirai, M.; Ueda, A.; Tanaka, M. *Makromol. Chem.*, **1985**, *186*, 2519; Tokuhisa, H.; Yokoyama, M.; Kimura, K. *Macromolecules*, **1994**, *27*, 1842.
31. Zhou, Q.; Swager, T. M. *J. Am. Chem. Soc.*, **1995**, *117*, 7017.
32. (a) Nagvekar, D. S.; Gibson, H. W. *Can. J. Chem.*, submitted; (b) Nagvekar, D. S.; Yamaguchi, N; Wang, F.; Bryant, W. S.; Gibson, H. W. *J. Org. Chem.*, **1997**, *62*, in press ; (c) Nagvekar, D.; Gibson, H.W. *Org. Prep. Proced. Intern.*, **1997**, *29*, 237; (d) Delaviz, Y. and Gibson, H. W. *Org. Prep. Proc. Int.*, **1991**, *23*, 382; (e) Gibson, H. W. and Delaviz, Y. *Polymer*, **1994**, *34*, 1109; (f) Delaviz, Y.; Merola, J. S.; Berg, M. A. G. and Gibson, H. W. *J. Org. Chem.*, **1995**, *60*, 516; (g) Nagvekar, D.; Delaviz, Y.; Prasad, A.; Merola, J. S.; Srinivasan, S.; Marand, H.; Gibson, H. W. *J. Org. Chem.*, **1996**, *61*, 1211.
33. Delaviz, Y.; Gibson, H. W.; *Macromolecules*, **1992**, *25*, 18.
34. Delaviz, Y.; Gibson, H. W.; *Macromolecules*, **1992**, *34*, 4859; Gibson, H. W.; Nagvekar, D.; Yamaguchi, N.; Bryant, W. S.; Bhattacharjee, S. *Polymer Preprints, Am. Chem. Soc. Div. Polym. Chem.*, **1997**, *38(1)*, 64.
35. Higashi, F.; Akiyama, N.; Takahashi, I.; Koyama, T. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 1653.
36. Lee, S.-H.; Engen, P. T.; Gibson, H. W. *Macromolecules*, **1997**, *30*, 337; Liu, S.; Lee, S. H.; Shen, Y. X.; Gibson, H. W. *J. Org. Chem.*, **1995**, *60*, 3155; Gibson, H. W.; Bheda, M. C. *Polymer*, **1995**, *36*, 2615; Liu, S.; Gibson, H. W. *Tetrahedron Lett.*, **1994**, 35, 8533;Gibson, H. W.; Lee, S. H.; Engen, P. T.; Lecavalier, P.; Sze, J.; Shen, Y. X.; Bheda, M. *J. Org. Chem.*, **1993**, 58, 3748.

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