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NEW POLYMER ARCHITECTURES: RECENT RESULTS WITH POLYROTAXANES

Harry W. Gibson*, Caiguo Gong, Shu Liu and Devdatt Nagvekar

Department of Chemistry
Virginia Polytechnic Institute & State University
Blacksburg, VA, USA 24061

ABSTRACT

Recent results from our laboratory have shown that the formation of polyester and polyurethane rotaxanes by polymerization in the presence of crown ethers is driven by hydrogen bonding of the OH groups with the oxygen atoms of the macrocycles. Here we summarize these findings. Then we describe the application of this type of self assembly for the production of polyrotaxanes by threading preformed macromolecules and for the controlled synthesis of branched and crosslinked systems. These latter protocols comprise a new and novel way to prepare mechanically linked, elastomeric materials. Rheological properties of main chain polyrotaxanes are compared to simple linear backbones; the rotaxanes display higher intrinsic viscosities and lower melt viscosities, reflecting larger hydrodynamic volumes and less entanglement, respectively; these are potentially useful aspects in terms of processability of this new class of polymeric materials.

INTRODUCTION

A polyrotaxane is a molecular composite comprised of macrocycles threaded onto some portion of a polymer with no covalent bonds between the two species. (Ref.1) Several types of polyrotaxanes are depicted in Figure 1; true polyrotaxanes (B, C, D, F) possess bulky groups to prevent potential diffusional loss of macrocycles, while polypseudorotaxanes (A, E) do not have such "stoppers."

The formation of main chain polyrotaxanes of Types A and B via *in situ* formation of a low molar mass pseudorotaxane is represented in Scheme 1. M/n, defined as macrocycles per repeat unit, in the resultant polyrotaxane depends on the efficiency of formation of the pseudorotaxane and its subsequent capture. Either statistical or host-guest approaches may be employed to achieve the threading that leads to the monomeric pseuodrotaxane. There is

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negligible enthalpic driving force in statistical threading; entropy plays a major role. Other important variables are ring size and rigidity, chain length and rigidity, ring-chain compatibility, etc. The statistical method produced several low molar mass rotaxanes and catenanes in relatively low yields in the early years of topological chemistry (Ref. 2). Large excesses of the macrocycle may be used to drive the threading equilibrium to the right 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. Lipatova made polystyrene rotaxanes by incorporating cyclic urethanes (Refs. 1, 3); m/n values ranged up to 0.14. We later made poly(styrene-*rotaxa*-crown ether)s by free radical and anionic methods; m/n values were less than 0.025. (Refs. 1, 4)

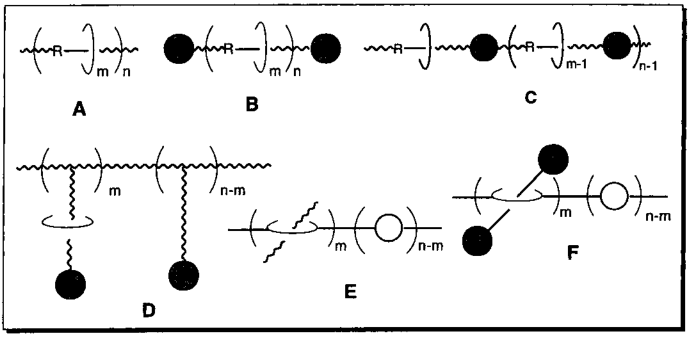
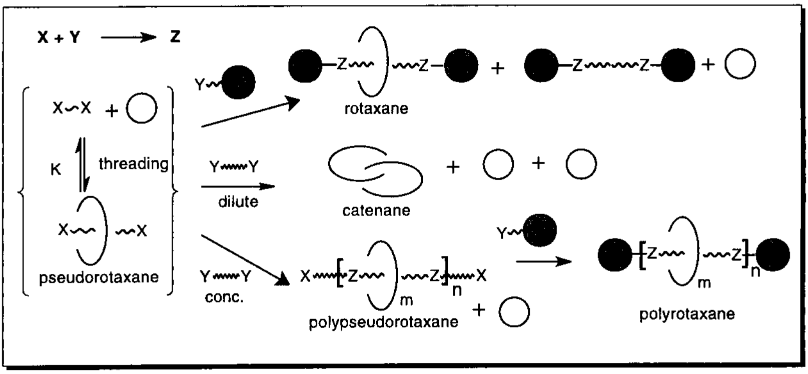


Figure 1. Various types of polyrotaxane architectures.

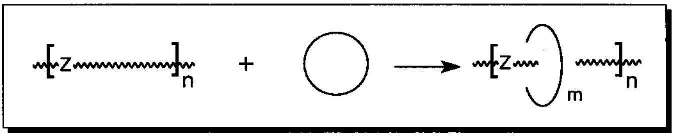


Scheme 1. Pseudorotaxanes as precursors to rotaxanes, catenanes, polypseudorotaxanes and polyrotaxanes.

On the other hand, in the host-guest approach the enthalpy change for non-covalent bonding (hydrogen bonding, coordination, charge transfer complexation, etc.) is used as a threading driving force. As long as their values satisfy critical requirements for threading, factors such as ring size, chain length, ring and chain rigidity and ring/chain ratio become less important.

Metal ions have been used by Sauvage et al. to serve as templates for coordination with both cyclic and linear species, forming the pseudorotaxanes of Scheme 1 and then catenanes by cyclization, specifically using phenanthroline-based bisphenols and macrocycles in the presence of Cu(I) ion. (Ref. 5) We synthesized a rotaxane by the same methodology. (Ref. 6) We used free radical polymerization to make poly[acrylonitrile-*rotaxa*-(60-crown-20)] (Type A) (Ref. 7), presumably aided by complexation of the monomer in a pseudorotaxane structure analogous to that formed with acetonitrile (Ref. 8); m/n values ranged up to 0.04 (40% cyclic). Low molar mass rotaxanes and catenanes have been prepared via the corresponding pseudorotaxanes self assembled by hydrogen bonding as reported by Vögtle et al. (Ref. 9), Hunter et al. (Ref. 10), Leigh et al. (Ref. 11) and Stoddart and coworkers. (Ref. 12)

Formation (threading) constants as high as 10^4 L/mol, driven by hydrophobic-hydrophilic interactions, are observed for cyclodextrin inclusion (pseudorotaxane) complexes. (Ref. 13) A variety of low molar mass rotaxanes based on cyclodextrins as the cyclic species have been reported. (Refs. 1, 14) Indeed the syntheses of polyrotaxanes of Type A from cyclodextrin complexes by application of Scheme 1 preceded much of the low molar mass activity, e.g., polyamides reported by Ogata in 1976 (Ref. 15), and free radical polymers and copolymers of vinylidene chloride made by Maciejewski and coworkers in 1979. (Ref. 16) Recently Wenz and Keller have reported well characterized main chain polyrotaxanes of Types A and C by threading preformed polyamines through α-cyclodextrin according to the generic approach of Scheme 2 and then acylating the in-chain amino groups; m/n values of 0.89 were achieved. (Ref. 17) Side chain polyrotaxanes of Type D were similarly prepared by Ritter and coworkers using β-cyclodextrin derivatives. (Ref. 18) And again by the methodology of Scheme 2, oligomeric rotaxanes of Type A from cyclodextrins with oligo(ethylene glycol)s (Ref. 19), oligo(propylene glycol)s (Ref. 20) and hydrocarbon polymers [oligo(isobutylene)s (Ref. 21a) and polyethylene (Ref. 21b)] have been reported by Harada and coworkers.



Scheme 2. Polyrotaxanes by threading preformed polymers.

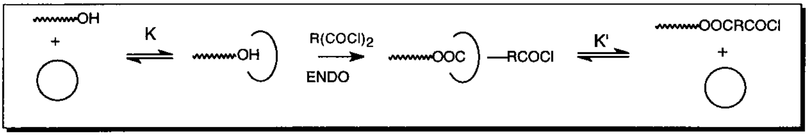
A pseudorotaxane complex of N,N'-dimethyl-4,4'-bipyridinium ("methyl viologen" or "paraquat") and bis(p-phenylene)-34-crown-10, based on charge transfer, hydrogen bonding and dipole-dipole interactions, was reported by Stoddart and coworkers (Ref. 22) and they have extended this technique to structures of increasing size and complexity. (Ref. 23) We both by the methods of Scheme 1 (Ref. 24) and Scheme 2 (Ref. 25) and more recently others by Scheme 2 (Ref. 26) have prepared polyrotaxanes by this approach.

RECENT RESULTS & DISCUSSION

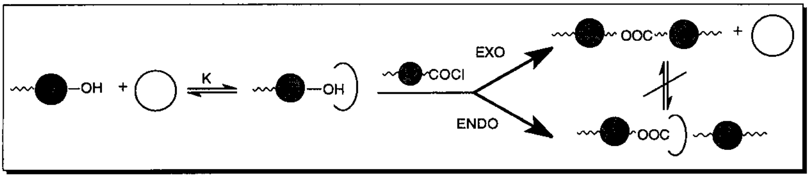
A. Establishment of Hydrogen Bonding as Driving Force in Formation of Polyester Rotaxanes

We have previously reported syntheses of poly(ester-pseudorotaxane)s of Type A with m/n values up to 0.74 (Ref. 27) and analogous polyurethane pseudorotaxanes with m/n up to 0.87 (Ref. 28) using crown ethers and the methodology of Scheme 1. We also reported that all parametric studies were consistent with hydrogen bonding of aliphatic crown ethers with the diol monomers as the driving force, except that no temperature dependence was observed. (Refs. 29, 30) Dethreading from the final polypseudorotaxanes is extremely slow, i.e., half lives of many months! (Ref. 30)

We recently prepared a bulky diol whose steric size disallows passage of rings and used it as a monomer to prepare polyester rotaxanes of Type C. (Ref. 31) We also prepared a similar bulky diacid chloride for the same purpose. (Ref. 32) These systems yielded two very important results. First, for systems with BG's present, m/n was observed to be temperature dependent (Ref. 33), consistent with the involvement of hydrogen bonding. And second, the use of both BG monomers increased m/n 14-fold! (Ref. 32) This indicated that significant (>90%!) dethreading occurs during the polyesterification process in the absence of such "blocking group" (BG) monomers. In the absence of BG's dethreading occurs because, once the OH group is consumed, the resultant ester linkage exerts no restraining force on the crown ether, i.e., 1/K'~0, and the crown ether can dethread from the oligomers (Scheme 3). However, when both monomers are bulky, once an ester bond is formed in an *endo* fashion the ring is trapped (Scheme 4). These new findings mean that the association constant for H-bonding (K, which has not yet been measured) and the proportion of "*endo*"-esterification are much higher than the previous results may have suggested and that with proper design such H-bonding can be utilized in the synthesis of a variety of polyrotaxanes, as we will attempt to demonstrate below.



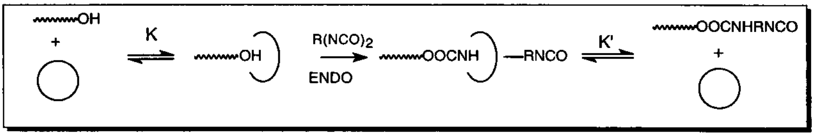
Scheme 3. *Dethreading During Polyesterification of Simple Diols & Diacid Chlorides*



Scheme 4. *Prevention of Dethreading by Use of Bulky Diols & Diacid Chlorides*

B. Identification of Hydrogen Bonding as Driving Force in Formation of Polyurethane Rotaxanes

The above results support the idea that the same hydrogen bond complexation is involved in the formation of polyurethane rotaxanes. And recent studies in which BG monomers were incorporated into polyurethane rotaxanes to give Type C systems corroborate this. However, the intra-annular H-bonding of threaded macrocycles with the N-H groups of the backbone (Scheme 5), which we have studied independently (Ref. 34), reduces the losses from dethreading during the polymerization (Ref. 35), i.e., 1/K'=finite, accounting for the lower degrees of dethreading observed for the polyurethane systems of Type A relative to the analogous polyesters (Scheme 3). Another exciting finding is that it is possible to contol the locus of the crown ether rings in these polyrotaxanes by use of solvent; in $CDCl_3$ hydrogen bonding localizes the rings on the urethane moieties, whereas in DMSO the crown ethers are delocalized over other portions of the backbone. (Ref. 36) These NMR studies thus demonstrate a controllable macromolecular shuttle.



Scheme 5. Dethreading During Polyurethane Formation from Simple Diols & Diisocyanates

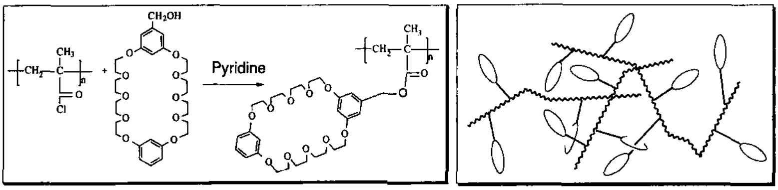
C. Main Chain Polyrotaxanes of Type A By Hydrogen Bond Induced Threading of a Preformed Polyurethane

To demonstrate that hydrogen bonding of N-H groups with crown ethers does provide an efficient means of polyrotaxane formation, recently we used the approach of Scheme 2 to produce for the first time in an efficient manner an aliphatic crown ether-based polyrotaxane. Specifically, a preformed polyurethane derived from tera(ethylene glycol) and 4,4'-bis(isocyanatophenyl)methane (MDI) was mixed in the melt with "42-crown-14" (Ref. 37); this led to the formation of the polyurethane rotaxane with m/n=0.20. (Ref. 36) This corresponds to 22 % by mass crown ether in the polymer. This exciting finding opens the way to facile synthesis of a range of polyrotaxanes by judicious application of the methodology of Scheme 2 and study of the properties of these systems with constant backbone molecular weight.

D. Use of Hydrogen Bonding Driven Self Assembly to Prepare Mechanically Linked Branched and Crosslinked Polymers

1. Polymethacrylates by Polymer Modification

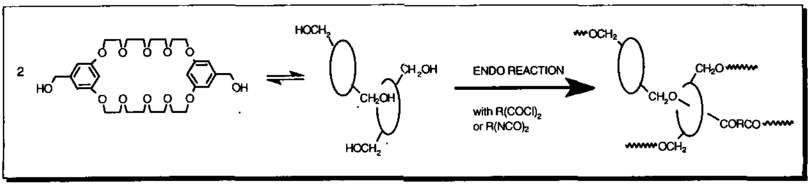
Reaction of preformed poly(methacryloyl chloride) with 5-hydroxymethyl-1,3-phenylene-1,3-phenylene-32-crown-10 at 0.37 M in pyridine produced a highly branched structure (molecular weight distribution=MWD=31. (Ref. 38) Increasing the concentration to 0.71 M yielded a material that was ca. 50% sol and 50% gel. The sol fraction was extremely highly branched (MWD=214). Control experiments with methanol and the analogous 16-membered crown ether, which is too small to thread, showed that there were no chemical side reactions; both polymethacrylates had the same degrees of polymerization and low MWD (ca. 3.6). The self assembled complex of the large macrocyclic alcohol leads to rotaxane formation by endo esterification analogous to Schemes 3, 4 and 5. The proportion of mechanical linkages so generated is therefore related to the concentration and hence the degree of branching is easily controlled.



Scheme 6. Preparation of Branched & Network Polyrotaxanes By Esterification of Poly(acid chloride) with Macrocyclic Alcohol

2. Polyurethanes by Self Threading of Macrocyclic Diols

Self association of a macrocyclic diol prior to reaction with a diisocyanate should bring about rotaxane formation by endo formation of the urethane linkages. We have recently demonstrated this process using MDI and bis(5-hydroxymethyl-*m*-phenylene)-32-crown-10 (Scheme 7). (Ref. 39) By variation of the proportion of macrocyclic diol in copolymers with



Scheme 7. Branched & Crosslinked Polyurethane & Polyester Rotaxanes as a Result of Self Association of Crown Ether Diols

tetra(ethylene glycol) in diglyme solution the extent of branching can be controlled. However, in DMSO rotaxane formation is prevented; thus variation of the solvent also allows control of the topology and, by use of mixtures, the degree of branching. In a bulk polymerization an insoluble elastomer was formed by gelation via the mechanical (rotaxane) linkages; thus, obviously concentration is another experimental variable that can be employed for systematic design of the final polymer's structure.

3. Polyesters by Self Threading of Macrocyclic Diol

Rotaxane units also provide mechanical linkage points for branching in polyesters prepared from macrocyclic diols under appropriate conditions. We demonstrated this by reacting bis(5-hydroxymethyl-*m*-phenylene)-32-crown-10 with sebacoyl chloride in a bulk polymerization to produce an insoluble elastomer (Scheme 7). (Ref. 40) Again self assembly of hydrogen bonded complexes of the macrocyclic diol allows endo esterification, which produces the rotaxane linkages. Furthermore, by control of the concentration and/or solvent in analogous solution polyesterifications it should possible to control the degree of branching .

E. Unique Physical Properties Of Polyrotaxanes

1. Intrinsic Viscosities

Comparison of the intrinsic viscosities of polyesters with those of the poly(ester crown ether rotaxane)s shows that the polyrotaxanes have higher intrinsic viscosities than the simple backbone systems. (Ref.30) This can be ascribed to the increased hydrodynamic volume due to the threaded cyclic species. Differential solvation of the linear and cyclic components of these polyrotaxanes leads to solvent dependent intrinsic viscosities, again reflecting changes in the hydrodynamic volume in response to solvation factors. (Ref. 30) Thus rotaxane formation can be used to increase solution viscosity.

2. Melt Viscosities

Examination of the melt viscosities of series of poly(decamethylene sebacate)s of various molecular weights in comparison to a poly[(decamethylene sebacate)-*rotaxa*-("42-crown-14")] (Figure 2) showed that the polyrotaxane has a melt viscosity that is approximately the same as that of the simple polymer of ~40% its molecular weight. (Ref. 30) In other words the melt viscosity at a given molecular weight is substantially reduced in the polyrotaxane vs. the simple backbone system. The presence of the threaded macrocycles inhibits entanglement in the melt, thereby reducing the viscosity. For enhancement of processability, therefore, rotaxane formation is advantageous.

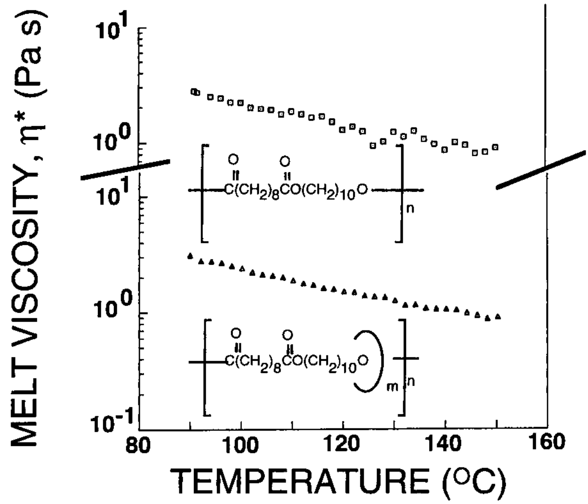


Figure 2. Melt viscosity at an oscillatory shear rate of 1 Hz as a function of temperature for simple polyester (M_n=4.3,M_w=7.0 kg/mol) and polyrotaxane (m/n = 0.13, M_n=10.4, M_w=17.1 kg/mol). MW's by GPC using a viscometer and the universal calibration

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REFERENCES

1. Reviews: H. W. Gibson in *Large Ring Molecules*, J. A. Semlyen, ed., John Wiley & Sons, New York, 1996, ch. 6, pp. 191-262; D. B. Amabilino, J. F. Stoddart, *Chem. Revs.*, **95**, 2725 (1995); H. W. Gibson, M. C Bheda, P. T. Engen, *Prog. Polym. Sci.*, **19**, 843 (1994); Y. S. Lipatov, T. E. Lipatova, L. F. Kosyanchuk, *Adv. Polym. Sci.*, **88**, 49 (1989).
2. I. T. Harrison, S. Harrison *J. Am. Chem. Soc.*, **89**, 5723 (1967); G. Schill, H. Zollenkopf, *Nachr. Chem. Techn.*, **79**, 149 (1967); G. Schill, H. Zollenkopf, *Ann. Chem.*, **721**, 53 (1969); G. Schill, *Catenanes, Rotaxanes and Knots*, Academic Press, New York, (1971); I. T. Harrison, *J. Chem. Soc., Chem. Commun.*, 231 (1972).

3. T. E. Lipatova, L. F. Kosyanchuk, Y. P. Gomza, V. V. Shilov, Y. S. Lipatov, *Dokl. Akad. Nauk S.S.S.R. (Engl. Tr.)*, **263**, 140 (1982); T. E. Lipatova, L. F. Kosyanchuk, Y. Gomza, *Polym. Sci., U.S.S.R. (Engl. Tr.)*, **27**, 622 (1985).
4. H. W. Gibson, P. T. Engen, S.-H. Lee, S. Liu, H. Marand, M. C. Bheda, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **34(1)**, 64 (1993).
5. C. O. Dietrich-Buchecker, J.-P. Sauvage, *J. Am. Chem. Soc.*, **106**, 3043 (1984); D. B. Amabilino, J.-P. Sauvage, *J. Chem. Soc., Chem. Commun.*, 2441 (1996).
6. C. Wu, P. R. Lecavalier, Y. X. Shen, H. W. Gibson, *Chem. Mater.*, *3*, 569 (1991).
7. H. W. Gibson, P. T. Engen, *New J. Chem.*, **17**, 723 (1993).
8. P. A. Mosier-Boss, A. I. Popov, *J. Am. Chem. Soc.*, **107**, 6168 (1985); H. S. Gold, M. R. Rice, *Talanta*, **29**, 637 (1982).
9. R. Jäger, T. Schmidt, D. Karbach, F. Vögtle, *SynLett*, 723 (1996); F. Vögtle, T. Dünnwald, M. Händel, R. Jäger, S. Meier, G. Harder, *Chem. Eur. J.*, **2**, 640 (1996); F. Vögtle, R. Jäger, M. Händel, S. Ottens-Hildebrandt, W. Schmidt, *Synthesis*, 353 (1996).
10. H. Adams, F. J. Carver, C. A. Hunter, *J. Chem. Soc., Chem. Commun.*, 809 (1995); F. J. Carver, C. A. Hunter, R. J. Shannon, *J. Chem. Soc., Chem. Commun.*, 1277 (1994).
11. D. A. Leigh, A. Murphy, J. P. Smart, A. M. Z. Slawin, *Angew. Chem. Int. Ed. Engl.*, **36**, 728 (1997); A. G. Johnston, D. A. Leigh, A. Murphy, J. P. Smart, M. D. Deegan, *J. Am. Chem. Soc.*, **118**, 10662 (1996).
12. P. R. Ashton, A. N. Collins, M. C. T. Fyfe, S. Menzer, J. F. Stoddart, D. J. Williams, *Angew. Chem. Int. Ed. Engl.*, **36**, 735 (1997); P. R. Ashton, A. N. Collins, M. C. T. Fyfe, P. T. Glink, S. Menzer, J. F. Stoddart, D. J. Williams, *Angew. Chem. Int. Ed. Engl.*, **36**, 59 (1997).
13. J. Szejtli, *Cyclodextrins and Their Inclusion Complexes*, Akademiai Kiado, Budapest, pp. 178-184 (1982); M. L. Bender, M. Komiyama, *Cyclodextrin Chemistry*, Springer, New York (1978); G. Wenz, *Angew. Chem. Int. Ed. Eng.*, **33**, 803 (1994).
14. K. Yamanari, Y. Shimura, *Bull. Chem. Soc. Jpn.*, **57**, 1596 (1984); A. Harada; M. Shimada; S. Takahashi, *Chem. Lett.*, 275 (1989); T. V. S. Rao; D. S. Lawrence, *J. Am. Chem. Soc.*, **112**, 3614 (1990); R. Wylie, D. Macartney, *J. Am. Chem. Soc.*, **114**, 3136 (1992); H. Ogino, *New J. Chem.*, **17**, 683 (1993); G. Wenz, F. Wolf, M. Wagner, S. Kubik, *New J. Chem.*, **17**, 729 (1993); R. Isnin, A. E. Kaifer, *Pure Appl. Chem.*, **65**, 495 (1993).
15. N. Ogata, K. Sanui, J. Wada, *J. Polym. Sci. Polym. Lett. Ed.*, **14**, 459 (1975).
16. M. Maciejewski, *J. Macromol. Sci.-Chem.*, **A13**, 77 (1979); M. Maciejewski, A. Gwizdowski, P. Peczak, A. Pietrzak, *J. Macromol. Sci. -Chem.*, **A13**, 87 (1979).
17. G. Wenz, B. Keller, *Angew. Chem. Int. Ed. Engl.*, **35**, 2139 (1996); M. Weickenmeier, G. Wenz, *Makromol. Chem., Rapid Commun.*, **17**, 731 (1996).
18. M. Born, H. Ritter, *Makromol. Chem., Rapid Commun.*, **17**, 197 (1996); M. Born, H. Ritter, *Adv. Mater.*, **8**, 149 (1996).

19. A. Harada, J. Li, M. Kamachi, *Macromolecules*, **27**, 4538 (1994); A. Harada, J. Li, M. Kamachi, *Nature*, **370**, 126 (1994).

20. A. Harada, M. Kamachi, *J. Chem. Soc., Chem. Commun.*, 1322 (1990).

21. (a) A. Harada, J. Li, S. Suzuki, M. Kamachi, *Macromolecules*, 26, 5267 (1993). (b) J. Li, A. Harada, M. Kamachi, *Bull. Chem. Soc. Japan*, **67**, 1 (1994).

22. B. L. Allwood, N. Spencer, H. Shahriari-Zavareh, J. F. Stoddart, D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1058 (1987).

23. M. Asakawa, P. R. Ashton, R. Ballardini, V. Balzani, M. Belohradsky, M. T. Gandolfi, O. Kocian, L. Prodi, F. M. Raymo, J. F. Stoddart, M. Venturi, *J. Amer. Chem. Soc.*, **119**, 302 (1997); M. Asakawa, P. R. Ashton, S. E. Boyd, C. L. Brown, R. E. Gillard, O. Kocian, F. M. Raymo, J. F. Stoddart, M. S. Tolley, A. J. P. White, D. J. Williams, *J. Org. Chem.*, **62**, 26 (1997).

24. Y. X. Shen, P. T. Engen, M. A. G. Berg, J. S. Merola, H. W. Gibson, *Macromolecules*, 25, 2786 (1992); D. Loveday, G. L. Wilkes,Y. X. Shen, M. C. Bheda, H. W. Gibson, *J. Macromol. Sci. Chem.*, **A32**, 1 (1995).

25. H. W. Gibson, S. Liu, Y. X. Shen, M. C. Bheda, S.-H. Lee, F. Wang, *NATO ASI Series*, Kluwer Acad. Pub., Dordrect, the Netherlands, Series C, **456**, 41-58 (1995).

26. P. E. Mason, I. W. Parsons, M. S. Tolley, *Angew. Chem. Int. Ed. Engl., 35*, 2238 (1996); G. J. Owen, P. Hodge, *J. Chem. Soc.,Chem. Commun.*, 11 (1997).

27. H. W. Gibson, S. Liu, P. Lecavalier, C. Wu, Y. X. Shen, *J. Am. Chem. Soc.*, **117**, 852 (1995).

28. Y. X. Shen, D. Xie, Gibson, H. W. *J. Am. Chem. Soc.*, **116**, 537 (1994).

29. H. W. Gibson, S. Liu, *Makromol. Chem., Macromol. Symp.*, **102**, 55 (1996).

30. H. W. Gibson, S. Liu, C. Gong, E. Joseph, *Macromolecules*, **30**, in press (1997).

31. C. Gong, H. W. Gibson, *Macromolecules*, **29**, 7029 (1996); C. Gong, H. W. Gibson, *Macromol. Chem. Phys.*, **198**, in press (1997).

32. C. Gong, Q. Ji, T. E. Glass, H. W. Gibson, *Macromolecules*, submitted

33. C. Gong, H. W. Gibson, Unpublished results.

34. E. Marand, Q. Hu, H. W. Gibson, B. Veytsman, *Macromolecules*, **29**, 2555 (1996).

35. C. Gong, H. W. Gibson, *Macromolecules*, submitted.

36. C. Gong, H. W. Gibson, *Angew. Chem. Int. Ed. Engl.*, submitted.

37. H. W. Gibson, M. C. Bheda, P. Engen, Y. X. Shen, J. Sze, H. Zhang, M. D. Gibson, Y. Delaviz, S.-H. Lee, S. Liu, L. Wang, J. Rancourt, L. T. Taylor, *J. Org. Chem.*, **59**, 2186 (1994). Since the completion of this work we with Prof. Colin Booth et al. (U. of Manchester, UK) discovered that the crown ether with target ring size 42-atoms was a mixture of cyclics and perhaps catenanes. We therefore use quotation marks.

38. C. Gong, H. W. Gibson, *J. Am. Chem. Soc.*, **119**, in press (1997).

39. C. Gong, H. W. Gibson, *J. Am. Chem. Soc.*, submitted.

40. H. W. Gibson, D. S. Nagvekar, J. Powell, C. Gong, W. S. Bryant, *Tetrahedron*, **53**, in press (1997).