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Interlocked Macromolecules

Françisco M. Raymo and J. Fraser Stoddart*

Department of Chemistry and Biochemistry, University of California, Los Angeles, 405 Hilgard Avenue, Los Angeles, California 90095-1569

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I. From Rotaxanes to Polyrotaxanes

Insertion of an acyclic molecule *(**I**)* inside the cavity of a macrocyclic one *(**II**)* affords (Figure 1) a supramolecular complex *(**III**)*. Dissociation of ***III*** into its components ***I*** and ***II*** can occur, and the equilibrium between the species in solution is controlled by the free energy of complexation. Attachment of two bulky stoppers to the ends of the acyclic component of the *supramolecular* complex ***III*** affords a *molecular* compound ***IV*** which cannot dissociate into its constituent components. A *molecule*, such as ***IV***, is termed a rotaxane,[1,2] while a *supermolecule*, such as ***III***, is called a pseudorotaxane.[3] However, the boundary between rotaxanes and pseudorotaxanes is not well-defined.[4] When size-complementarity between the stoppers and the macrocyclic component is achieved, certain "rotaxanes" behave as pseudorotaxanes and can dissociate into their constituent components under appropriate conditions.[5] Thus, a species which is a rotaxane at ambient temperature might well be a pseudorotaxane at elevated temperatures. Even a solvent change can turn a rotaxane into a pseudorotaxane at the same temperature.

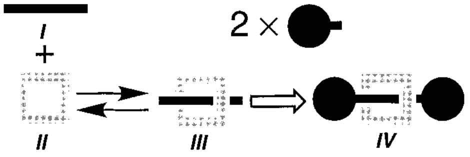

Figure 1. Reversible formation of a pseudorotaxane *(**III**)* from its components *(**I** and **II**)* and its irreversible conversion into a rotaxane *(**IV**)*.

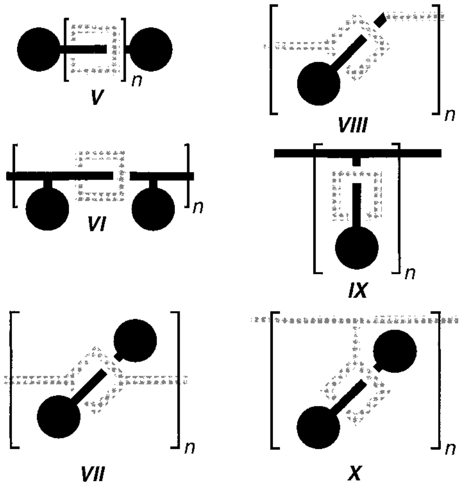

Figure 2. Examples of main-chain *(**V**−**VIII**)* and side-chain *(**IX**−**X**)* polyrotaxanes.

The conceptual transition from a [2]rotaxane into a polyrotaxane can be achieved by a number of different design strategies, half-a-dozen of which are portrayed in Figure 2. By encircling a polymeric dumbbell-shaped component with [$n - 1$] macrocycles, a main-chain polyrotaxane—namely, an [n]-rotaxane *(**V**)*—is obtained. Alternatively, a [2]rotaxane can be transformed into a main-chain polyrotaxane by incorporating either its dumbbell-shaped *(**VI**)* or embedding its macrocyclic *(**VII**)* component into a polymeric backbone. When the macrocyclic and the dumbbell-shaped components are both part of the polymeric backbone, another main-chain polyrotaxane *(**VIII**)*—a so-called daisy-chain polymer—is generated. In a side-chain polyrotaxane, either the dumbbell-shaped *(**IX**)* or the macrocyclic *(**X**)* components of rotaxane subunits are attached covalently to a polymeric backbone. Interestingly, while in the polyrotaxanes ***V***−***VII***, ***IX***, and ***X*** the polymeric backbones are held by covalent bonds, covalent and mechanical bonds alternate along the main axis of a daisy-chain polymer *(**VIII**)*. The relationship that

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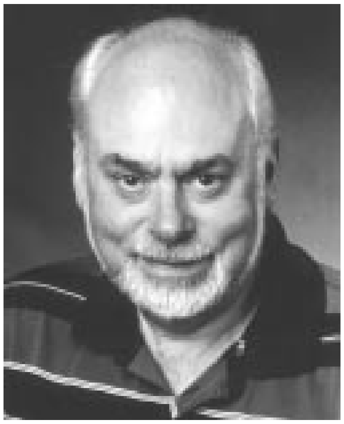
Françisco M. Raymo was born (1969) and educated in Messina (Italy). He obtained his Laurea in Chimica (1992) from the University of Messina (Italy) and his Ph.D. in Chemistry (1996) from the University of Birmingham (U.K.). Since then, he has been a Postdoctoral Research Fellow at the University of Birmingham (1996–1997) and later at the University of California, Los Angeles (1997–1999) working in collaboration with Professors K. N. Houk and J. Fraser Stoddart. In 1998, he was selected as the Marie Curie Success Story for chemistry by the European Commission and obtained the Chancellor's Award for Postdoctoral Research by the University of California, Los Angeles. He is the author of more than 70 publications in the areas of computational chemistry, organic synthesis, and supramolecular chemistry.



J. Fraser Stoddart was born in Edinburgh, Scotland, in 1942. He received all of his degrees from the University of Edinburgh (B.Sc., 1964; Ph.D., 1966; D.Sc., 1980). After a seven-year spell as the Professor of Organic Chemistry at the University of Birmingham in England, Professor Stoddart moved, in 1997, to the Saul Winstein Chair of Organic Chemistry at UCLA. One of his current research interests is the development of new methodology in the area of synthetic supramolecular chemistry. Some of this research effort is focused on the noncovalent synthesis of supramolecular polymers, while other research objectives include the construction of interlocked macromolecules using the concept of supramolecular assistance to molecular synthesis. One of the long-term goals of this research is to uncover a new generation of polymeric materials with novel forms and functions to them.

exists between rotaxanes and pseudorotaxanes extends to their polymeric counterparts—namely, polyrotaxanes and pseudopolyrotaxanes,[6] respectively. Formally, pseudopolyrotaxanes can be derived from polyrotaxanes by removing at least one of the bulky stoppers from the ends of the latter.

II. From Catenanes to Polycatenanes

Two mechanically interlocked macrocycles form (Figure 3) a [2]catenane ***(XI)***. The mechanical bond which holds the two components together cannot be destroyed unless a covalent bond is broken. As a result, a [2]catenane[2,7] is a *molecular* compound which cannot dissociate into its separate macrocyclic components without the cleavage of at least one covalent bond. The transition from a [2]catenane to an [*n*]catenane ***(XII)*** can be realized by simply enlarging the ring component(s), thus enabling the interlocking, in a chainlike manner, of more than two macrocycles. Main-chain polycatenanes can also be constructed by introducing covalent and mechanical bonds into a polymer chain, as in the case of ***XIII*** and ***XIV***, both of which contain [2]catenane units. Side-chain polycatenanes ***(XV)*** are obtained by appending [2]catenane subunits to a polymeric backbone. It is worthy of note that while covalent bonds constitute the polymer chain of ***XIV*** and ***XV***, covalent and/or mechanical bonds comprise the polymeric backbones of ***XII*** and ***XIII***. Interestingly, while synthetic methods for the preparation of macromolecules such ***XII***−***XV*** have been developed only recently, interpenetrating networks,[8,9] held together by covalent and/or noncovalent bonds, had already been discovered accidentally several decades ago.

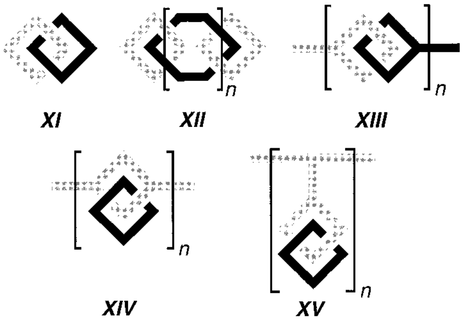


Figure 3. Examples of main-chain ***(XI***−***XIV)*** and side-chain ***(XV)*** polycatenanes.

III. Template-Directed Syntheses of Catenanes and Rotaxanes

The early syntheses of catenanes and rotaxanes relied on either directed[2a,10] or statistical synthetic approaches.[11] The directed approaches involve the multistep syntheses of precatenanes or prerotaxanes in which the interlocked components are linked together temporarily by covalent bonds. Subsequent cleavage of these covalent bonds afford molecular structures in which the interlocked components are held together solely by mechanical bonds. In the statistical syntheses of catenanes and rotaxanes, the formation of a pseudorotaxane ***(III)*** is followed by covalent modification to yield a catenane or a rotaxane. However, noncovalent interactions are not employed consciously to assist in the formation of ***III***, and as a result, it is only obtained in small amounts after using a large excess of one of the two starting components ***(I*** or ***II)***. With the advent of supramolecular chemistry,[12] noncovalently assisted procedures for the efficient assembly of host/guest complexes with pseudorotaxane geometries quickly became available. Thus, template-directed[13] synthetic approaches to catenanes and rotaxanes, relying on the stabilization provided by noncovalent bonds between the recognition sites incorporated within acyclic and macrocyclic precursors, have been developed. A col-

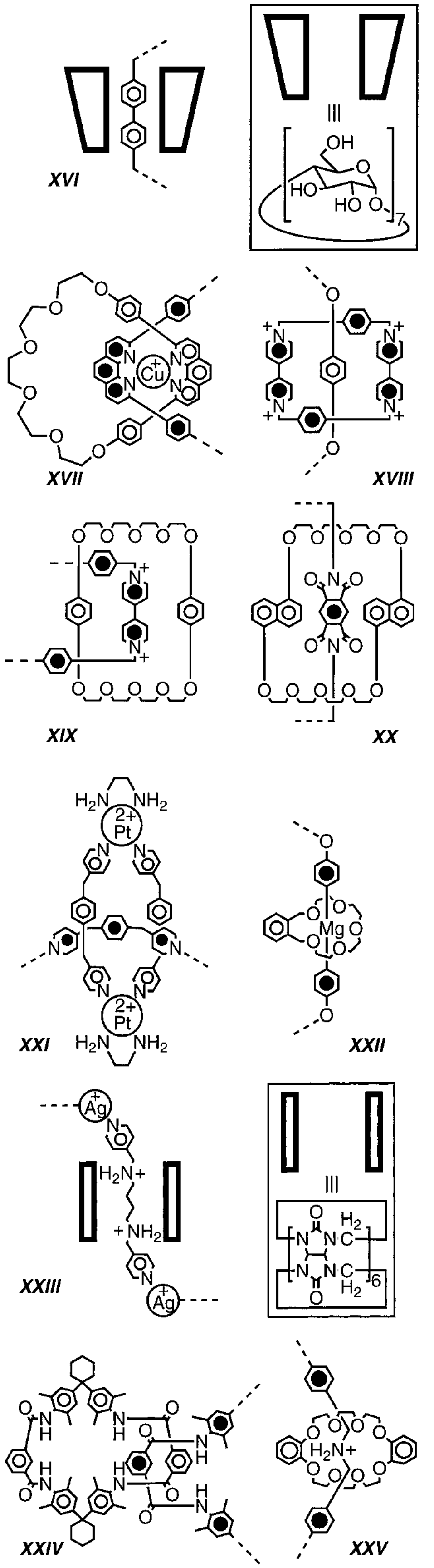


Figure 4. Some of the recognition motifs *(XVI–XXV)* employed to synthesize catenanes and rotaxanes.

lection of some of the more important recognition motifs *(XVI–XXV)* that have been employed to guide the template-directed syntheses of catenanes and/or rotaxanes are illustrated in Figure 4. Cyclodextrins (CDs) bind[14] organic guests in aqueous media as a result of hydrophobic interactions *(**XVI**)*. Metal ions coordinate[15] organic ligands in well-defined geometrical arrangements *(**XVII**)*. [C–H···O] hydrogen bonds and [$\pi\cdots\pi$] stacking interactions control[16,17] the complexation of π-electron-rich guests by π-electron-deficient hosts *(**XVIII**)* and of π-electron-deficient guests by π-electron-rich hosts *(**XIX** and **XX**)*. Hydrophobic interactions and metal coordination induce[18] the threading of organic guests through the cavity of organic hosts in polar media *(**XXI**)*. Metal coordination assists[19] the threading of macrocyclic polyethers onto organometallic guests *(**XXII**)*. Hydrogen bonding interactions and metal coordination sustain[20] the complexation of bis(dialkylammonium) guests by cucurbituril *(**XXIII**)*. Hydrogen bonding interactions between complementary amide functions *(**XXIV**)* and between macrocyclic polyethers and secondary dialkylammonium groups *(**XXV**)* guide[21,22] the self-assembly of catenanes and/or rotaxanes. In most cases, the noncovalent bonds, which assist in the template-directed syntheses, live-on in the final mechanically interlocked structures. Thus, the geometries and the relative motions of the interlocked components—co-conformational changes[23]—in the resulting catenanes and rotaxanes are determined by such intracomponent interactions.

IV. Main-Chain Pseudopolyrotaxanes and Polyrotaxanes Incorporating Cyclodextrins

Pseudopolyrotaxanes *(**XXVI**)* incorporating CDs have been prepared (Figure 5) either *(**A**)* by polymerization of a pseudorotaxane *(**III**)* or *(**B**)* by threading *n* macrocycles *(**II**)* onto a preformed polymer *(**XXVII**)*. Subsequently, ***XXVI*** can be stoppered by attaching covalently bulky groups either at the termini or along the backbone of the acyclic component affording ***V*** or ***VI***, respectively.

The first pseudopolyrotaxanes (**1**–**4**) incorporating CDs (Table 1) were prepared[24] according to route ***A***, wherein solution or interfacial polymerizations of diamines with diacid dichlorides were carried out in the presence of β-CD. However, no direct evidence of threading was provided. Similarly, route ***A*** was

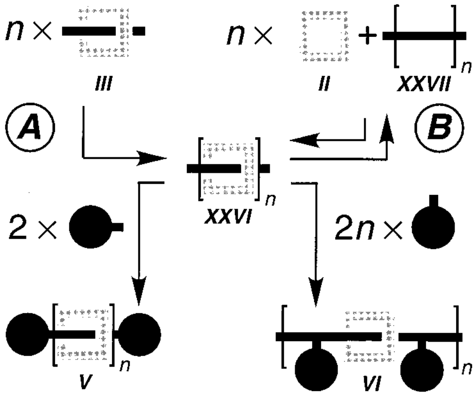


Figure 5. Routes ***A*** and ***B*** starting from the appropriate components *(**III** or **II** and **XXVII**)* to a pseudopolyrotaxane *(**XXVI**)* and its conversion into main-chain polyrotaxanes *(**V** and **VI**)*.

Table 1. Main-Chain Pseudopolyrotaxanes and Polyrotaxanes Incorporating Cyclodextrins

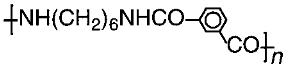
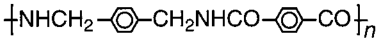
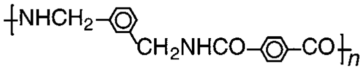
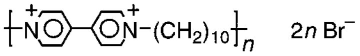
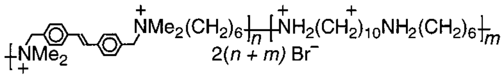
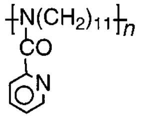
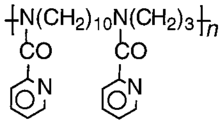
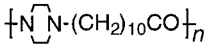
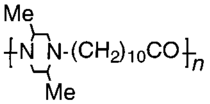
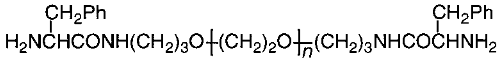
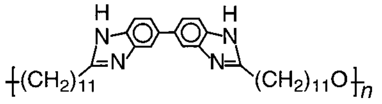
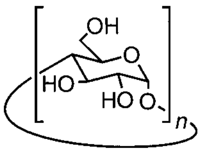
	Acyclic Component	Macrocyclic Component[a]	Ref
1		β-CD	24
2		β-CD	24
3		β-CD	24
4		β-CD	24
5	$[CCl_2CH_2]_n$	β-CD	25a,b,d
6	$[SiMe_2O]_n$	β-CD	25c
7	$[SiPh_2O]_n$	β-CD	25c
8	$[SiMePhO]_n$	β-CD	25c
9	$[NH(CH_2)_{11}]_n$	α-CD	28a,b
10	$[NH(CH_2)_{10}NH(CH_2)_3]_n$	α-CD	28a,b
11		α-CD	28d
12	$[CO(CH_2)_8CO_2[(CH_2)_2O]_{20}]_n$	α-CD	28e
13	$[CO(CH_2)_8CO_2[(CH_2)_2O]_{20}]_n$	β-CD	28e
14	$[\overset{+}{N}Me_2(CH_2)_{10}]_n$ $n\,Br^-$	α-CD	28c,f
15	$[\overset{+}{N}H_2(CH_2)_{11}]_n$ $n\,Br^-$	α-CD	28c,f
16	$[\overset{+}{N}H_2(CH_2)_6\overset{+}{N}H_2(CH_2)_{10}]_n$ $2n\,Br^-$	α-CD	28c,f
17	$[\overset{+}{N}H_2(CH_2)_6\overset{+}{N}H_2(CH_2)_{12}]_n$ $2n\,Br^-$	α-CD	28c,f
18	$[\overset{+}{N}H_2(CH_2)_3\overset{+}{N}H_2(CH_2)_{10}]_n$ $2n\,Br^-$	α-CD	28c,f
19		β-CD	29
20		α-CD	28a,b
21		α-CD	28a,b
26	$[NH(CH_2)_{10}CO]_n$	α-CD	31
27		α-CD	31
28		α-CD	31
29	$[NH(CH_2)_{10}NHCO(CH_2)_8CO]_n$	α-CD	31

Table 1. (Continued)

	Acyclic Component	Macrocyclic Component[a]	Ref
30	$\left[(\mathrm{CH_2})_2\mathrm{O}\right]_n$	α-CD	32
34	$\left[\mathrm{CHMeCH_2O}\right]_n$	β-CD	35
35	$\left[\mathrm{CH_2CMe_2}\right]_n$	β-CD	36
36	$\left[\mathrm{CHMeCH_2O}\right]_n$	γ-CD	35
37	$\left[\mathrm{CH_2CMe_2}\right]_n$	γ-CD	36
38	$\left[\mathrm{CH_2CHOMe}\right]_n$	γ-CD	37
45	 $\mathrm{H_2N\overset{CH_2Ph}{C}HCONH(CH_2)_3O\left[(CH_2)_2O\right]_n(CH_2)_3NHCO\overset{CH_2Ph}{C}HNH_2}$	α-CD	40
46		α-CD	42

[a] Cyclodextrin is abbreviated to CD. The number of α-D-glucopyranose repeating units is indicated by the letters α, β, and γ as shown in the diagram below.



n	
6	α-CD
7	β-CD
8	γ-CD

employed[25,26] to generate **5** by polymerization of adducts of β-CD and vinylidene chloride and to obtain **6**−**8** by hydrolysis and condensation of organosilicon monomers in the presence of β-CD.

Preliminary observations on the unusual diffusion and catalytic behavior of CDs in aqueous solutions containing polymeric solutes suggested[27] that these macrocycles are able to thread (route ***B*** in Figure 5) onto acyclic polymers. Indeed, route ***B*** has been employed[28,29] successfully to prepare **9**−**19** by simply combining appropriate amounts of α- or β-CD and the corresponding acyclic polymer in aqueous solutions.[30] A kinetic investigation on the formation of **14**−**18** revealed[28c,f] that the rate of pseudopolyrotaxane formation is controlled by the rates of migration of the threaded macrocycles along the polymeric backbone as well as by the rates of threading and dethreading. The conversion of some of these pseudopolyrotaxanes into polyrotaxanes, such as ***VI***, was realized by introducing bulky groups along their polymeric backbones. The pseudopolyrotaxanes **9** and **10** were converted[28a,b] into the polyrotaxanes **20** and **21**, respectively, by treatment with nicotinoyl chloride. In these polyrotaxanes, the steric barrier provided by the pyridyl rings traps the α-CD rings mechanically on the acyclic component. The formation of tetraphenylenecyclobutane blocking groups along the backbone of **25** was achieved[29] (Figure 6) by irradiating an aqueous solution of **24** which self-assembles spontaneously from its separate components, **22** and **23**, in the presence of both β- and γ-CD.

Route ***B*** was employed[31] to prepare the water-soluble pseudopolyrotaxanes **26**−**29** by solid-state polycondensations. The pseudopolyrotaxanes **26**−**28** were obtained by heating (240 °C, 0.1 mbar, 5 h) the appropriate monomeric adducts of α-CD and amino acids in the absence of a solvent. The pseudopolyrotaxane **29** was isolated under identical conditions from a mixture of the adducts formed between α-CD and 1,10-decanedioic acid and between α-CD and 1,10-diaminodecane.

The observation that α-CD threads[32] onto poly(ethylene glycol), affording the pseudopolyrotaxane **30**, paved the way for the design and synthesis of CD-based nanotubes. Indeed, threading of α-CD onto poly(ethylene glycol) diamine, followed by reaction with 2,4-dinitrofluorobenzene, afforded[33] **31**, shown in Figure 7. Covalent bridging of the threaded α-CDs was achieved[34] by treatment of **31** with epichlorohydrin under basic conditions to yield **32**. Subsequent removal of the terminal stoppers destroys the mechanical bond between acyclic and macrocyclic components, leading to the release of the CD-based nanotube **33**. However, convincing evidence of its structure still has to be provided.

When acyclic components bulkier than poly(ethylene glycol) are employed as threads, CDs possessing cavities larger than that associated with α-CD are required. Thus, poly(propylene glycol)[35] and poly(*iso*-butylene)[36] thread through β-CD to give **34** and **35**, respectively, and γ-CD to afford **36** and **37**, respectively, while poly(methyl vinyl ether)[37] inserts only through γ-CD, yielding **38**. However, double-stranded pseudopolyrotaxanes (**39**−**44** in Figure 8), in which two acyclic components are inserted through the cavities of the macrocycles, are obtained[38] when γ-CD is mixed with poly(ethylene glycol) derivatives in water.

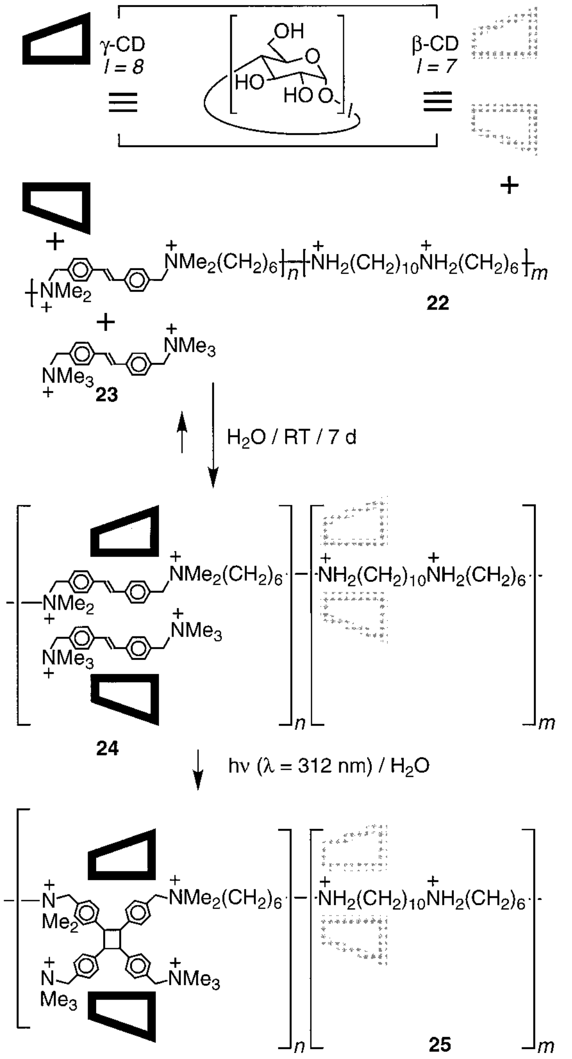


Figure 6. Synthesis of the cyclodextrin-based polyrotaxane **25** incorporating bulky groups along its polymer backbone.

Route ***B*** has been employed[39] to generate several other CD-based pseudopolyrotaxanes. Furthermore, this strategy has also been used to synthesize drug delivery systems in the shape of biodegradable polyrotaxanes. Indeed, threading of α-CD rings onto a poly(ethylene glycol) bisamine, followed by the covalent attachment of L-phenylalanine stoppers, afforded[40,41] the polyrotaxane **45**. When the terminal peptide linkages were hydrolyzed by papain, fast release of the α-CD rings was observed.

Route ***A*** has been used to synthesize[42] polyrotaxane **46** by reacting 3,3′-diaminobenzidine and 1,12-dodecanediol in the presence of α-CD and $RuCl_2(PPh_3)_3$. The aromatic rings incorporated along the polymer backbone of **46** are far too bulky to pass through the relatively small cavities of the α-CDs. As a result, the macrocyclic components are trapped on the aliphatic portions of the polymer and cannot even travel along the backbone of the acyclic component.

V. Main-Chain Pseudopolyrotaxanes Incorporating Cycloalkanes or Cyclourethanes

When poly(ethylene glycol) was employed as the stationary phase, a systematic investigation of the gas–liquid chromatographic behavior of a series of cycloalkanes with 15–35 methylene units revealed[43] a nonlinear correlation between the logarithm of the retention time and the number of methylene units. The retention times, associated with the cycloalkanes incorporating more than 25 methylene units, were surprisingly long. This effect was not observed when comparable acyclic alkanes were investigated under

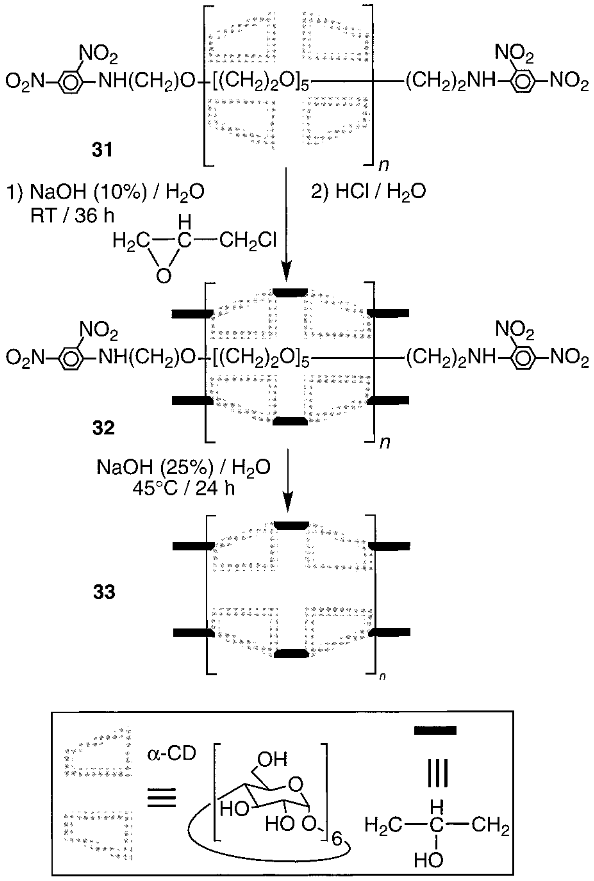


Figure 7. Synthesis of the cyclodextrin-based nanotube **33** from the polyrotaxane **31**.

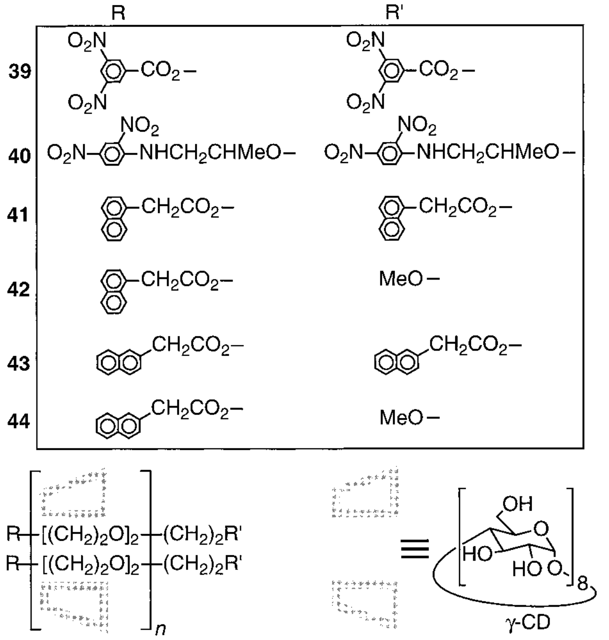


Figure 8. Double-stranded pseudopolyrotaxanes **39**–**44**.

Table 2. Main-chain Pseudopolyrotaxanes Incorporating Cyclourethanes

	Acyclic Component	Macrocyclic Component	Ref
47	$\left[CH_2CHPh \right]_n$	$\left[CONH(CH_2)_6NHCO_2[(CH_2)_2]_2 \right]_2$	44
48	$\left[CH_2CHPh \right]_n$	$\left[CONH(CH_2)_6NHCO_2[(CH_2)_2]_3 \right]_2$	44

otherwise identical conditions. This unusual behavior was ascribed to the threading of the cycloalkanes with more than 25 carbon atoms onto poly(ethylene glycol) to yield pseudopolyrotaxanes.

The pseudopolyrotaxanes **47** and **48** shown in Table 2 were obtained[44] by radical polymerization of styrene in the presence of preformed cyclourethanes. The threading efficiency was enhanced significantly by performing the polymerization in the presence of $ZnCl_2$. It was demonstrated that the production of ordered cluster-like complexes between the cyclourethanes and $ZnCl_2$ facilitates threading and, as a result, the formation of the pseudopolyrotaxanes.

VI. Main-Chain Pseudopolyrotaxanes and Polyrotaxanes Incorporating Crown Ethers

Numerous pseudopolyrotaxanes and polyrotaxanes incorporating crown ethers have also been prepared[45] following the general routes (***A*** and ***B***) shown in Figure 5, with and without the assistance of noncovalent bonding interactions between acyclic and macrocyclic components. The pseudopolyrotaxanes **49**−**51** (Table 3) were obtained[46] as a result of the threading of appropriate crown ethers onto poly(ethylene glycol) followed by treatment with 1,5-diisocyanatonaphthalene. In addition, statistical threading of poly(ethylene glycol) through a crown ether, followed by the covalent attachment of trityl stoppers, has been employed[46] to synthesize the polyrotaxane **52**. Alternatively, **52** was isolated after reacting ethylene oxide with the potassium salt of tetra(ethylene glycol) in the presence of the preformed macrocyclic component. A measure of the number of threaded macrocycles present in **49**−**51** suggested that threading efficiency is influenced by the molar ratios between acyclic and cyclic components, the diameter and length of the acyclic component, the size of the macrocyclic cavity, the volume of the supramolecular system, and the temperature of the medium.

Statistical threading was employed[47] to prepare the pseudopolyrotaxane **53** and the polyrotaxane **54**. In both instances, free-radical polymerization of acrylonitrile or styrene was carried out in the presence of the preformed macrocyclic component. However, in the case of **54**, a free-radical initiator, incorporating tetraarylmethane-based groups, was used in order to terminate the growing polymer with groups large enough to prevent dethreading of the macrocyclic components. Similarly, it has been found that stoppers are required to prevent dethreading during the preparation of polyester polyrotaxanes.[48] In the absence of blocking groups (**55**−**61**), relatively low threading efficiencies were observed[49] when transesterification-based polymerizations were performed using a crown ether as the solvent. However, only a small increase in the number of threaded macrocyclic polyethers (the mass percentage of threaded rings was raised by only 3−9%) was achieved (**62**−**64**) when the polymerizations were carried out in the presence of bulky terminating groups. Thus, to increase the threading efficiency, an alternative synthetic route was developed. To this end, polycondensations of diols and diacid dichlorides were performed[49b,50] using a crown ether as the solvent. When bulky groups were introduced (**65**−**68**) into the diol and/or the diacid dichloride, a significant increase in the number of threaded macrocycles was observed, mainly because the incorporation of stoppers along the acyclic backbone prevents dethreading during polymer growth.[51] To increase further the efficiency of threading, hydrogen bond donors were introduced along the acyclic components. Assistance from hydrogen bonding interactions between these groups and the polyether oxygen atoms of the crown ethers were expected to enhance the formation of pseudopolyrotaxanes and polyrotaxanes. Indeed, polycondensations of diols with bisisocyanates, performed using a crown ether as the solvent, afforded[52,53] pseudopolyrotaxanes **69**−**72** incorporating up to 63% by mass of macrocyclic polyethers. It was found that, in these cases, the threading efficiency increases (i) linearly with the size of the macrocyclic polyether and (ii) nonlinearly with the ratio between the cyclic and acyclic starting materials. Infrared spectroscopic analyses of **69**−**72** confirmed[54] the existence of [N−H···O] hydrogen bonds[55] between the acyclic and cyclic units. To introduce stoppers along the polymeric backbone, diols incorporating bulky groups were employed[56] in the polycondensations. When the resulting polyrotaxane **73** is dissolved in $CHCl_3$, the macrocyclic polyethers are located preferentially around the urethane linkages as a result of intercomponent [N−H···O] hydrogen bonds. By contrast, disruption of these noncovalent bonding interactions occurs in DMSO and the ring components move closer to the stoppers.

The synthesis of polymers incorporating macrocyclic subunits within their backbones—i.e., precursors of ***VII***—has been realized by reacting bisfunctionalized crown ethers with appropriate linking units. In several instances, however, mechanical cross-linking occurred[57] as a result of threading the macrocyclic portions of one polymer chain onto the acyclic segments of another. Nonetheless, polyester **74** could be prepared[58] (Figure 9) by reacting bis(5-hydroxymethyl-1,3-phenylene)-32-crown-10 with sebacoyl chloride in Me_2SO, since this solvent suppresses the formation of hydrogen bonds between the polyether oxygen atoms and the hydroxyl hydrogen atoms. The addition of the bipyridinium-based acyclic compound **75** to a Me_2CO solution of **74** was accompanied by the development of an orange color, indicating pseudopolyrotaxane formation. However, ^1H NMR spectroscopic studies revealed that the binding of **75** by **74** is disfavored relative to a model monomeric bisfunctionalized crown ether. Although the entropic penalties incurred on binding **75** are not so great in

Table 3. Main-Chain Pseudopolyrotaxanes and Polyrotaxanes Incorporating Crown Ethers

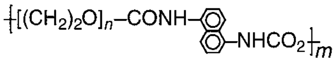
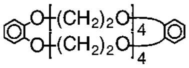
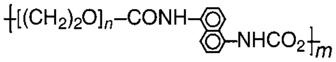
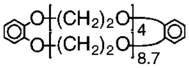
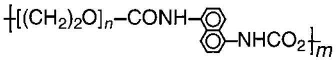
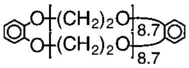
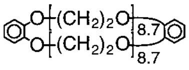
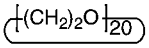
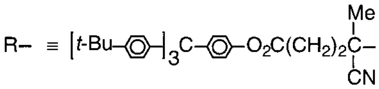
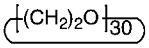
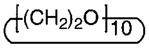
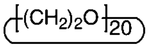
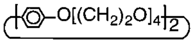
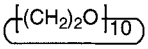
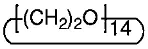
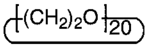
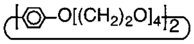
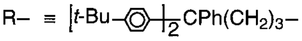
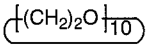
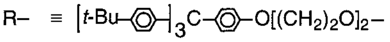
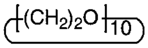
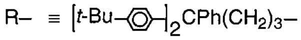
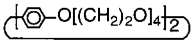
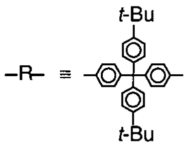
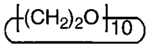
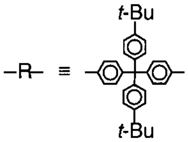
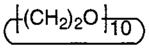
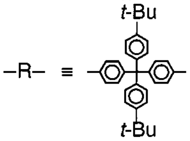
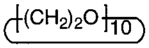
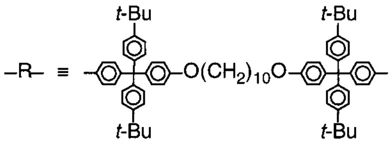
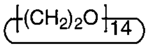
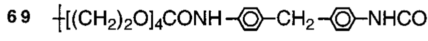
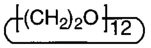
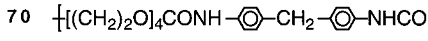
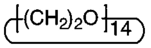
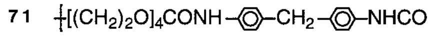
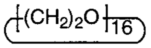
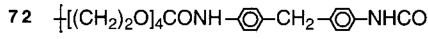
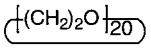
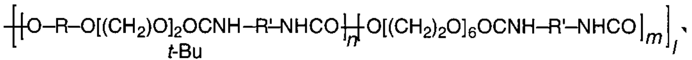
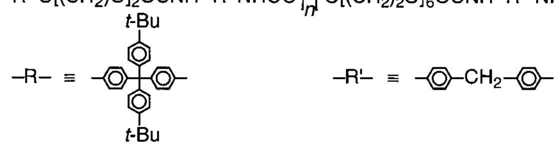
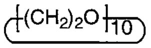
	Acyclic Component	Macrocyclic Component	Ref
49			46
50			46
51			46
52	$Ph_3CO\{(CH_2)_2O\}_nCPh_3$		46
53	$\{CH_2CHCN\}_n$		47c
54	$R\{CH_2CHPh\}_nR$ 		47d
55	$HO\{OC(CH_2)_8CO_2[(CH_2)_2O]_3\}_nCO(CH_2)_8CO_2H$		49
56	$HO\{OC(CH_2)_8CO_2[(CH_2)_2O]_3\}_nCO(CH_2)_8CO_2H$		49
57	$HO\{OC(CH_2)_8CO_2[(CH_2)_2O]_3\}_nCO(CH_2)_8CO_2H$		49
58	$HO\{OC(CH_2)_8CO_2(CH_2)_4O\}_nCO(CH_2)_8CO_2H$		49
59	$HO\{OC(CH_2)_8CO_2(CH_2)_4O\}_nCO(CH_2)_8CO_2H$		49
60	$HO\{OC(CH_2)_8CO_2(CH_2)_4O\}_nCO(CH_2)_8CO_2H$		49
61	$HO\{OC(CH_2)_8CO_2(CH_2)_4O\}_nCO(CH_2)_8CO_2H$		49
62	$R{-}O\{OC(CH_2)_8CO_2[(CH_2)_2O]_3\}_nCO(CH_2)_8CO_2{-}R$ 		49
63	$R{-}O\{OC(CH_2)_8CO_2[(CH_2)_2O]_3\}_nCO(CH_2)_8CO_2{-}R$ 		49
64	$R{-}O\{OC(CH_2)_8CO_2(CH_2)_4O\}_nCO(CH_2)_8CO_2{-}R$ 		49
65	$\{[(CH_2)_2O]_2{-}R{-}O[(CH_2)_2O]_2CO(CH_2)_8CO_2\}_n$ 		50a
66	$\{[(CH_2)_2O]_2{-}R{-}O[(CH_2)_2O]_2CO(CH_2)_8CO_2\}_n\{(CH_2)_{10}O_2C(CH_2)_8CO_2\}_m$ 		50b
67	$\{[(CH_2)_2O]_2{-}R{-}O[(CH_2)_2O]_2CO(CH_2)_5O{-}R{-}O(CH_2)_5CO_2\}_n$ 		50c
68	$\{OC(CH_2)_8CO_2(CH_2)_{10}O[OC(CH_2)_8CO_2{-}R{-}O]_{0.25}\}_n$ 		50d

Table 3. (Continued)

	Acyclic Component	Macrocyclic Component	Ref
69			52a,b
70			52b,53
71			52b
72			52a,b
73	 		56

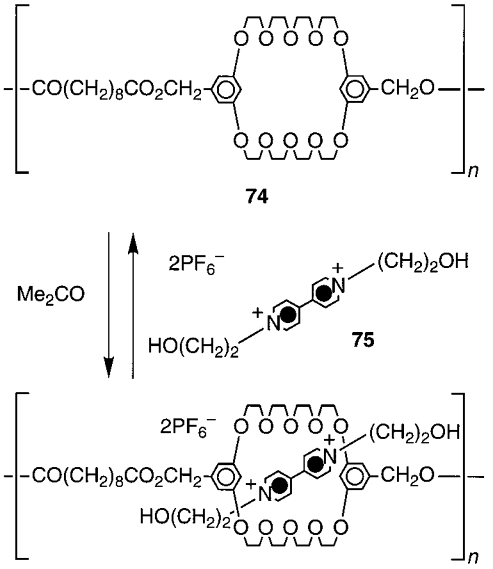


Figure 9. Reversible association of **74** and **75** in Me_2CO.

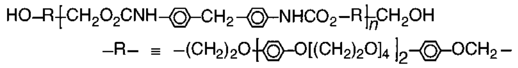
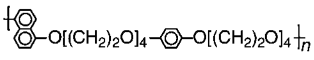
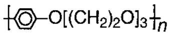
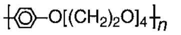
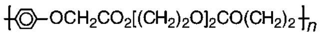
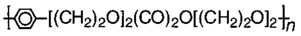
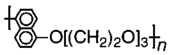
the polymer, the enthalpy gain on complexation is not as large as that in the case of the monomer.

An alternative approach to pseudopolyrotaxanes is based[59] on the amphiphilic character of certain crown ethers. It was found that a 42-membered crown ether bearing an appended hydrophobic tail forms micelles in benzene or toluene in the presence of water. When poly(ethylene glycol) derivatives are added to these aqueous solutions, their diffusion inside the interior of the micelles occurs, presumably as a result of pseudopolyrotaxane formation. It is believed that solvation of the hydrophobic tails of the cyclic components by the nonpolar solvent induces the formation of micelles in which the macrocyclic heads are pointing into the interior of the micelles with their cavities aligned in register. Thus, when a hydrophilic polymer displaying limited solubility in the nonpolar medium is added, its diffusion inside the micelles occurs as a result of threading through the macrocyclic heads.

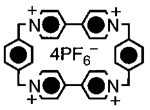
VII. Main-Chain Pseudopolyrotaxanes Incorporating Cyclophanes

The bipyridinium-based tetracationic cyclophane, cyclobis(paraquat-*p*-phenylene), threads[16] onto π-electron-rich guests to form pseudorotaxanes. Thus, the formation of pseudopolyrotaxanes is expected to occur immediately when cyclobis(paraquat-*p*-phenylene) and dioxyarene-based acyclic polymers are mixed together. Indeed, as indicated by the immediate appearance of an orange color, pseudopolyrotaxanes **76**–**82** (Table 4) form[60] spontaneously when cyclobis(paraquat-*p*-phenylene) and the appropriate polymer are combined in solution. ^1H NMR spectroscopic analysis revealed that **77** incorporates one macrocyclic unit for every two repeating units of the acyclic backbone at ambient temperature. However, dethreading occurs at higher temperatures and the number of threaded cyclophanes decreases significantly. In **78**–**82**, the nature of the spacer separating the dioxyarene recognition sites significantly affects significantly the efficiency of threading and maximum loading is achieved for **81** where 94% of the hydroquinone rings are encircled by a tetracationic cyclophane at −40 °C.

Table 4. Main-Chain Pseudopolyrotaxanes Incorporating Cyclophanes[a]

	Acyclic Component	Ref
76		60a,b
77		60c,d
78		60e
79		60e
80		60e
81		60e
82		60e

[a] The hexafluorophosphate salt of cyclobis(paraquat-*p*-phenylene) (shown below) was employed as the macrocyclic component.



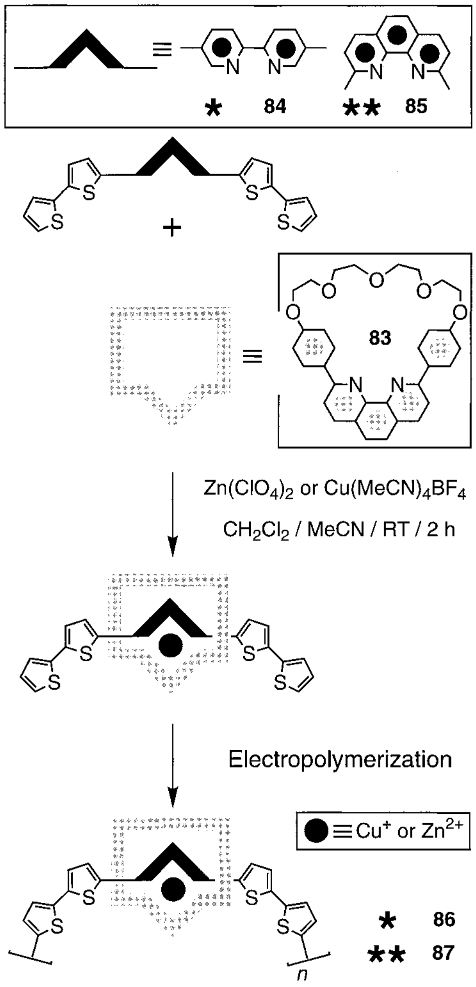


Figure 10. Metal-assisted template-directed synthesis of pseudopolyrotaxanes **84** and **85**.

VIII. Metal-Templated Syntheses of Main-Chain Pseudopolyrotaxanes

The ability of transition metals to impose precise relative orientations on their ligands has been employed[61,62] to thread (Figure 10) the phenanthroline-based macrocycle **83** onto either bipyridine- or phenanthroline-based rods (**84** and **85**, respectively). Electropolymerization of the resulting pseudorotaxanes afforded the corresponding metal-containing pseudopolyrotaxanes **86** and **87** which could be demetalated. Interestingly, while decomplexation/complexation of Zn^{2+} can be achieved reversibly in **86**, the reinsertion of Cu^{+} in **87** is possible only when the original demetalation is performed in the presence of Li^{+}. Presumably, the binding of Li^{+} in the coordination sites vacated by Cu^{+} prevents the irreversible collapse of the polymer.

IX. Side-Chain Pseudopolyrotaxanes and Polyrotaxanes

The synthesis of the first rotaxane was achieved[63] through the formation of a side-chain polyrotaxane. A derivative of 2-hydroxycyclotriacontanone was anchored to a Merrifield resin which was subsequently treated with 1,10-decanediol and triphenylmethyl chloride. Threading of 1,10-decanediol through some of the resin-bound macrocycles occurred to some extent. Reaction of the threaded diol with the bulky triphenylmethyl groups resulted in the formation of resin-bound rotaxanes—i.e., a side-chain polyrotaxane, such as ***X***. After washing unreacted materials and side products off the resin, the rotaxanes were cleaved from the resin and isolated in an overall yield of 6%.

The synthesis of the polyrotaxanes **88**−**92** (Table 5) was realized[64] (Figure 11) by reacting a preformed polymer ***(XXVIII)***, bearing appended side chains, with a semirotaxane[65] ***(XXIX)***. The semirotaxanes were prepared by combining β-CD derivatives with acyclic components carrying a bulky trityl group at one end and a reactive primary amine at the other. Subsequent amide bond formation between the semirotaxanes and the side chains of the comblike polymers afforded **88**−**92**. Interestingly, while in **88**−**91** only one macrocycle can encircle a side chain, more than one can thread onto each side chain of **92**. Polyrotaxane **93** was prepared[66] employing a similar synthetic strategy. It involved the covalent attachment of two semirotaxanes to each side chain of a preformed comblike polymer backbone. An alternative approach was used[67] to synthesize pseudopolyrotaxane **94**. In this instance, a pseudorotaxane, incorporating 2,6-dimethyl-β-cyclodextrin and a cholic acid derivative, was polymerized in water in the presence of a free-radical initiator. Two main fractions containing polymeric materials were isolated. The most abundant one was insoluble in water and contained a ca. 40% molar percentage of threaded CD rings. The less abundant fraction was soluble in water and had nearly all side chains encircled by one CD.

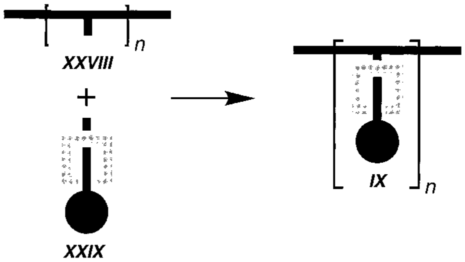


Figure 11. Synthetic strategy for generating side-chain polyrotaxanes ***(IX)*** from appropriate components ***(XXVIII*** and ***XXIX)***.

Polyrotaxanes **95**−**97** were prepared[68] by *N*-alkylation of poly(benzimidazole)s with the appropriate semirotaxanes composed of a trimethyl-β-cyclodextrin encircling an acyclic component bearing a bulky trityl group at one end and a bromide leaving group at the other. It was found that in **95**−**97**, the mass percentage of threaded macrocycles is related to the nature of the spacers separating the bis(benzimidazole) units. Only 21% and 57% of the side chains are encircled by a CD ring in **95** and **96**, respectively, while all side chains of **97** are inserted through a CD ring's cavity.

The syntheses of the linear polymers **98**−**100** bearing appended macrocycles were realized[69,70] by polymerizing the preformed macrocyclic monomers. Insertion (Figure 12) of bipyridinium-based guests

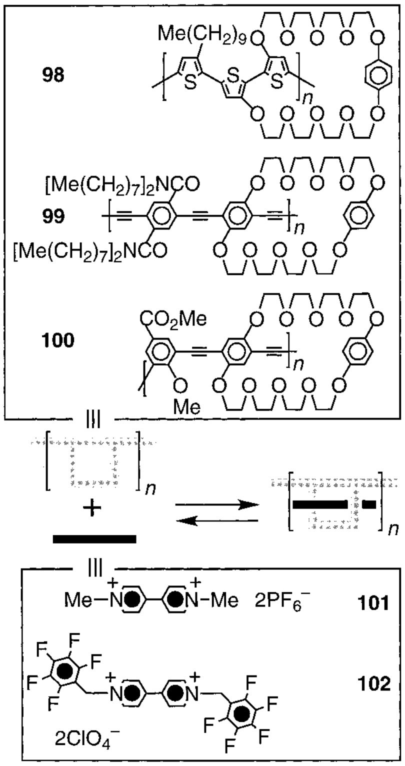


Figure 12. Reversible formation of side-chain pseudopolyrotaxanes.

(**101** or **102**) through the cavities of the appended macrocycles occurs in solution, yielding side-chain pseudopolyrotaxanes. As a result of electrostatic perturbations, lowering of polymer conductivity occurs on pseudopolyrotaxane formation in the case of **98**. Similarly, binding of the bipyridinium guests causes an attenuation of the fluorescence associated with the polymer backbone in **99** and **100**. Interestingly, the response to binding is significantly reduced, or not observed at all, when model monomeric receptors are employed instead of **98**−**100**. These intrinsic properties of the polyreceptors **98**−**100** strongly recommend their potential use as sensory materials.

The synthesis of polymers bearing appended macrocycles has been achieved[71] by reacting poly(methacroyl chloride) with crown ethers having hydroxymethyl groups. However, when a relatively large crown ether was employed, mechanical cross-linking was observed. Presumably, hydrogen bonds between the hydroxymethyl group of one crown ether and the polyether chains of another drive the threading of the side chains of one polymeric backbone through the cavities of the macrocycles appended to another.

X. Daisy-Chain Pseudopolyrotaxanes

The preparation of a daisy-chain pseudopolyrotaxane *(**XXXI*** and ***XXXII**)* requires (Figure 13) the design and synthesis of a self-complementary monomer *(**XXX**)* incorporating a macrocyclic head and an acyclic tail. Threading of the head of one monomer through the tail of another can afford cyclic *(**XXXI**)* and/or acyclic (***XXXII****)* daisy chains, provided that the covalent bridge separating the head and tail of each monomer is rigid enough to prevent a head binding with its own tail. Self-complementary monomers (Table 6), such as ***XXX***, have been prepared by attaching appropriate tails to cyclodextrins, calixarenes, and crown ethers. The monomers **103** and **104** form[72] acyclic daisy chains in the solid state as a result of the insertion of the substituent attached to one of the seven α-D-glucopyranose residues of one CD through the cavity of another CD. Similarly, **105** forms[73] acyclic daisy chains in the solid state upon insertion of one of the two phenoxy ligands of one monomer through the cavity of another. By contrast, monomers **106** and **107** afford[74] dimeric cyclic daisy chains in the solid state. However, **106**−**110** self-assemble into cyclic and/or acyclic daisy chains containing up to five monomeric units in solution. Multicomponent cyclic and/or acyclic daisy chains are also formed[75] by **111** in solution. The concentration dependence of the chemical shifts of selected protons in the ^{1}H NMR spectrum of **111** suggests that aggregates incorporating up to as many as 50 monomeric units are formed in $(CD_3)_2CO$.

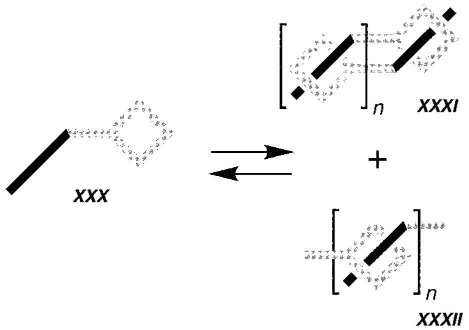


Figure 13. Formation of cyclic *(**XXXI**)* and acyclic *(**XXXII**)* daisy chains from self-complementary monomers *(**XXX**)*.

XI. Polycatenanes

A rather speculative method for the synthesis of polycatenanes, such as ***XII*** in Figure 3, was reported[76] in the early 1970s. Upon spreading alkyl chains terminated by hydrophilic groups (−OH, −COOH, or −COCl) at an interface separating a polar from an apolar phase, a U-shaped conformation is adopted by these amphiphilic molecules. It was claimed that addition of preformed crown ethers or cyclosiloxanes results in threading of the hydrophilic ends through the cavities of the macrocycles. Subsequent ring closure of the U-shaped components was achieved by their reaction with bisfunctionalized alkyl chains bearing terminal reactive groups (−NCO, $-NH_2$, or −COONa). The formation of urethane, amide, anhydride, or ester linkages was confirmed by detailed IR spectroscopic analyses performed on the resulting polymeric materials. On this basis, an interlocked structure reminiscent of ***XII*** was proposed for the products. However, adequate and unequivocal structural proof in support of polycatenanes having been formed has never been reported.

Apart from these early speculative claims, the synthesis of polycatenanes, such as ***XII***, has yet to be achieved. However, an oligocatenane incorporating five interlocked macrocycles has been synthesized[77] following a stepwise approach. The [3]catenane **112** self-assembled (Figure 14) by reacting **114** and **115** in the presence of the crown ether **113**. Subsequent

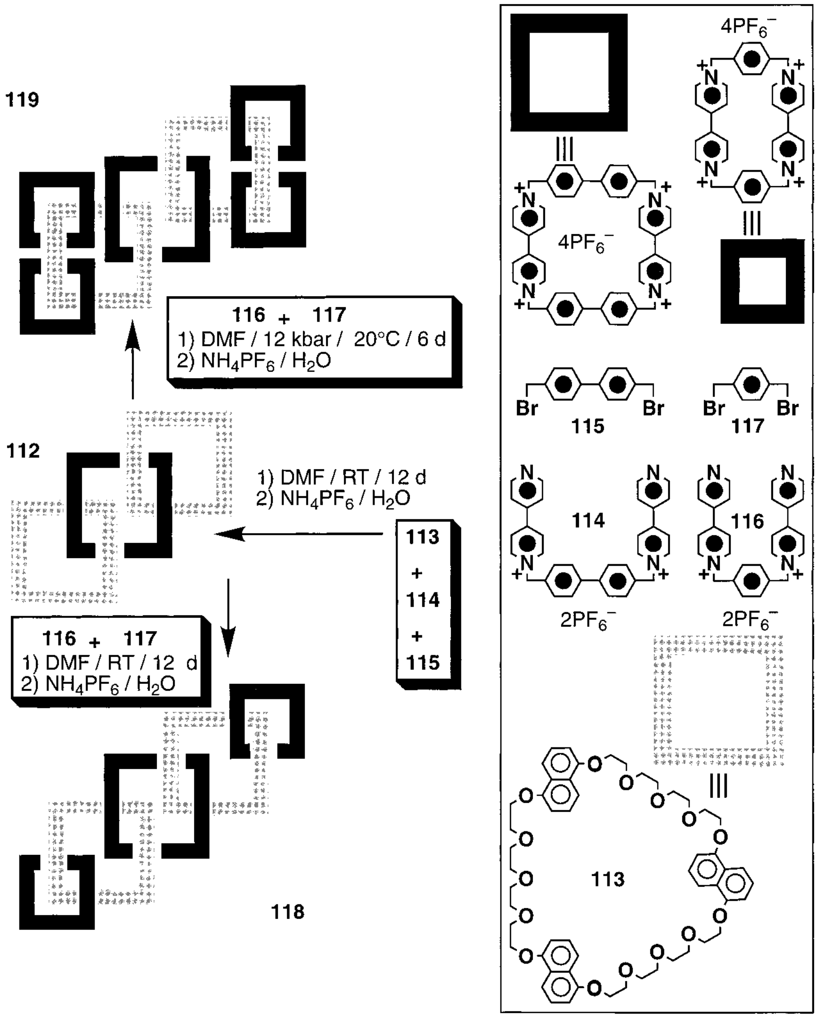
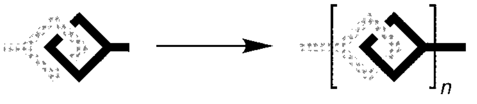


Figure 14. Conversion of the [3]catenane **112** into the [5]catenane **118** and [7]catenane **119**.

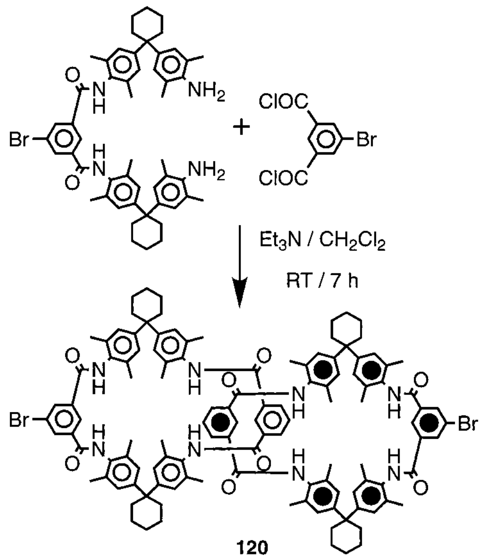


XXXIII *XIII*

Figure 15. Synthetic approach to poly[2]catenanes *(XIII)* from a functionalized [2]catenane *(XXXIII)*.

treatment of **112** with **116** and **117** afforded the [5]catenane **118** which incorporates five interlocked macrocyclic components. When the same starting materials were reacted under high pressure, the [7]catenane **119** was also isolated from the reaction mixture. The interlocking of the five and seven macrocyclic components in **118** and **119**, respectively, was demonstrated unequivocally by single-crystal X-ray structural analyses.

Polycatenanes incorporating [2]catenane subunits *(XIII)*—namely, poly[2]catenanes—have been prepared (Figure 15) by the polymerization or copolymerization of bisfunctionalized [2]catenanes *(XXXIII)*. For this purpose, several bisfunctionalized [2]catenanes incorporating a reactive functional group on each of their two interlocked macrocyclic lactams have been synthesized[78] as described in Figure 16 for **120**. Their copolymerizations with appropriate bridging units afforded (Table 7) poly[2]catenanes **121**–**123** which possess degrees of polymerization ranging from 5 to 11. Bisfunctionalized [2]catenanes have also



120

Figure 16. Hydrogen-bond-assisted template-directed synthesis of the [2]catenane **120**.

been synthesized[79] employing metal templates. For example, **124** was obtained (Figure 17) in two steps from the preformed phenanthroline-based macrocycle **125** and the thread **126** which self-assemble to give **127** in the presence of Cu^+ ions. Polycondensation of such metal-containing [2]catenanes with appropriate

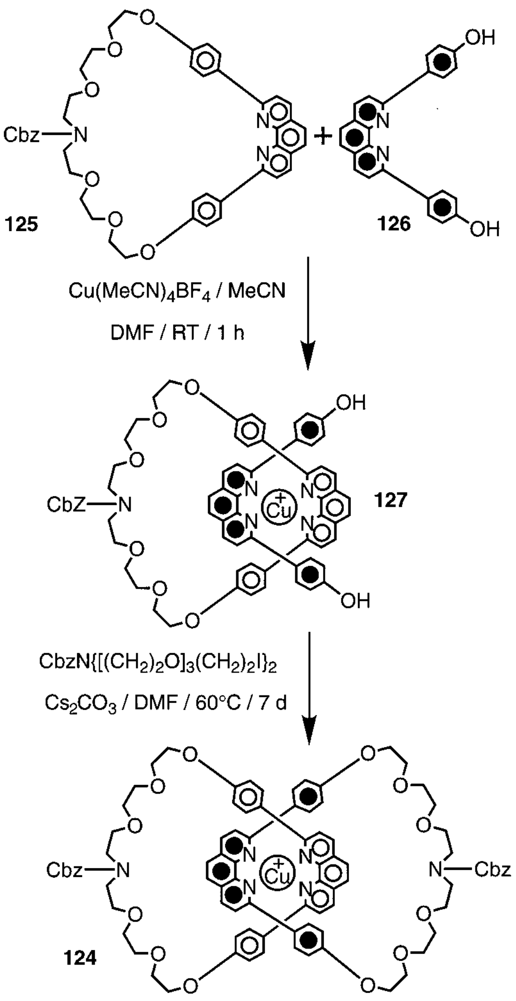


Figure 17. Metal-assisted template-directed synthesis of the [2]catenane **124**.

bisfunctionalized bridging units, followed by demetalation, afforded poly[2]catenanes **128** and **129**. The synthesis of bisfunctionalized [2]catenanes incorporating crown ethers and bipyridinium-based cyclophanes has also been realized with the aim of converting them into poly[2]catenanes. The synthesis of one such [2]catenane is illustrated in Figure 18. Reaction of **116** with **130** in the presence of the functionalized crown ether **131** afforded[80] the bisfunctionalized [2]catenane **132** incorporating one hydroxymethyl group on each of its two macrocyclic components. A similar approach was also employed[81] to prepare a [2]catenane incorporating a bipyridinium-based cyclophane mechanically interlocked with a π-electron-rich crown ether having two hydroxymethyl groups appended to one of its two dioxyarene units. Copolymerization of these [2]catenanes with bis(*p*-isocyanatophenyl)methane afforded the poly[2]catenanes **133** and **134** which incorporate an average of 17 and 20, respectively, repeating units. Similarly, polyesterification of a bisfunctionalized [2]catenane containing a carboxylic function on its crown ether component and a chloromethyl group on the tetracationic cyclophane was realized[81] and afforded the poly[2]catenane **134** incorporating an average of 25 repeating units.

An alternative approach to poly[2]catenanes involves the polymerization or copolymerization of bis-

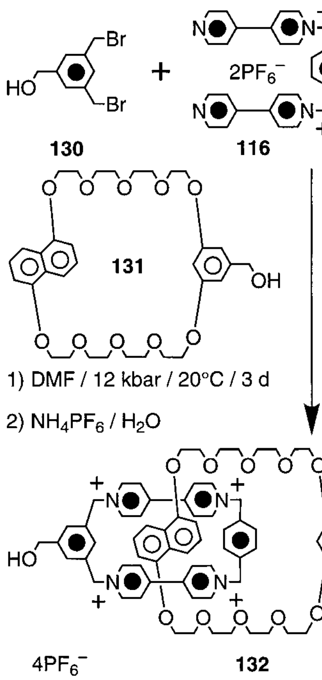


Figure 18. Template-directed synthesis of the [2]catenane **132**.

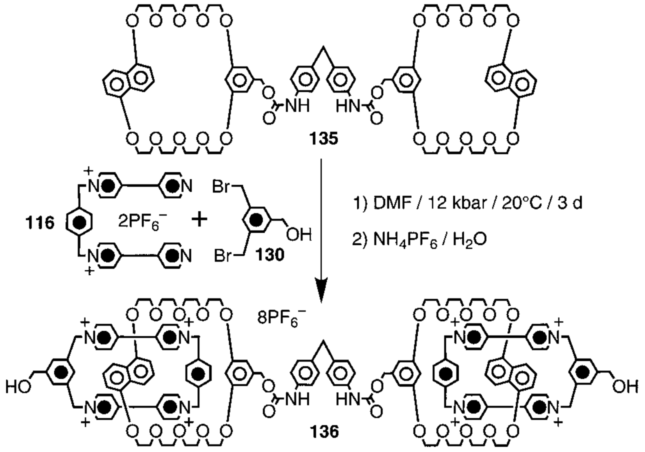
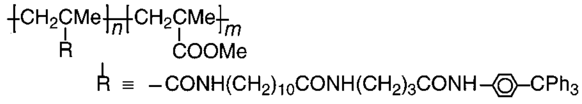
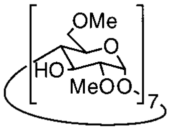
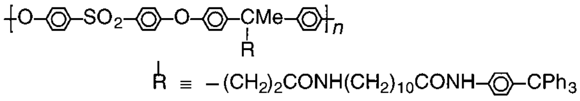
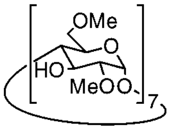
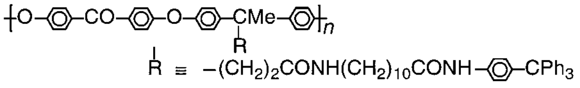
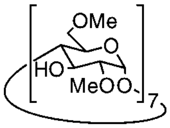
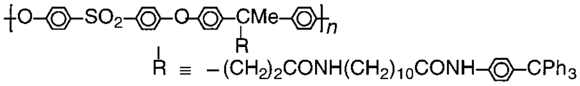
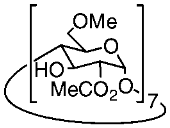
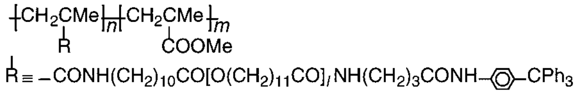
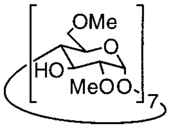
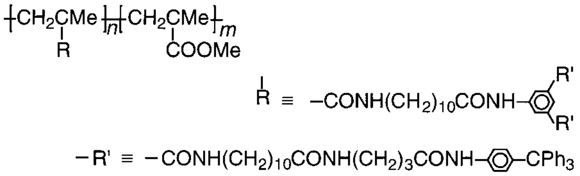
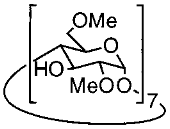
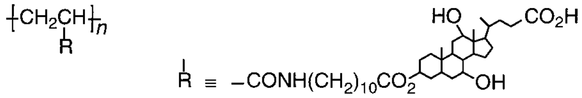
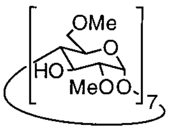
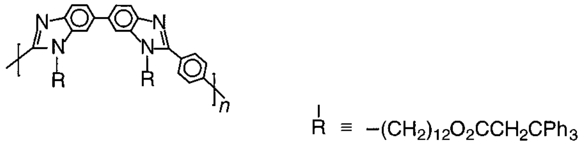
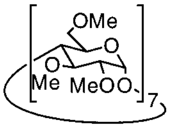
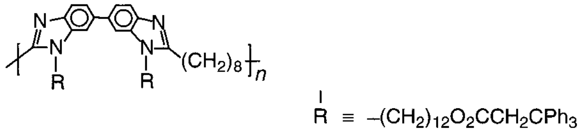
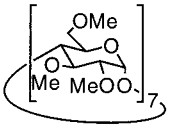
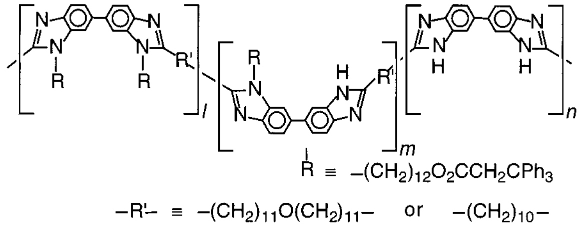
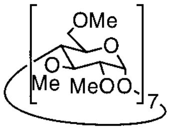


Figure 19. Template-directed synthesis of the bis[2]catenane **136**.

[2]catenanes[82] bearing two reactive groups. The mechanically interlocked molecules are prepared (Figure 19) by reacting **116** with a dibromide, such as **130**, in the presence of an appropriate bis(crown ether), e.g., **135**. The two tetracationic cyclophanes incorporated in the resulting bis[2]catenane **136** are substituted by hydroxymethyl groups, which can be employed in subsequent copolymerizations. Indeed, poly[2]catenanes **136** and **137** were obtained[81] after the polycondensations of hydroxymethyl-containing bis[2]catenanes and bis(*p*-isocyanatophenyl)methane. A similar synthetic strategy was employed[83] to interlock the bis(crown ether) **135** with two tetracationic cyclophanes, each incorporating a 2,2-bipyridine spacer. By exploiting the ability of the 2,2-bipyridine units to coordinate Ag^+ with tetrahedral geometry, the poly[2]catenane **138** containing 40 repeating units on average was generated. Interestingly, in this instance, this poly[2]catenane is held

Table 5. Side-Chain Pseudopolyrotaxanes and Polyrotaxanes

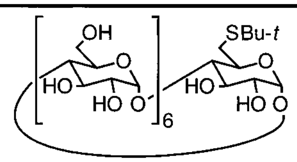
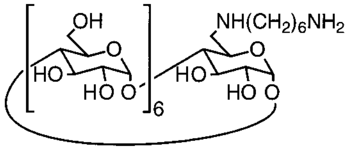
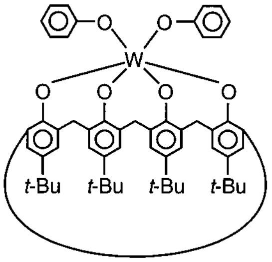
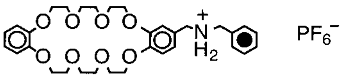
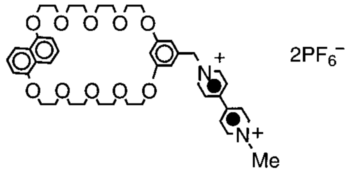
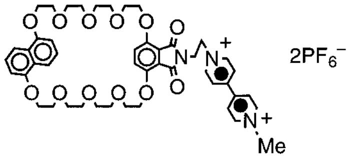
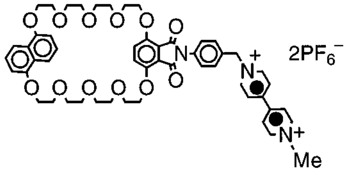
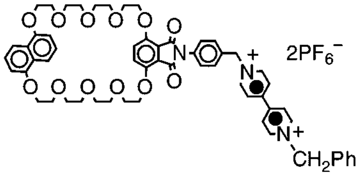
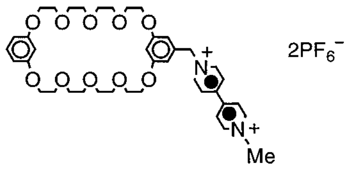
	Acyclic Component	Macrocyclic Component	Ref
88			64a,c
89			64b
90			64d
91			64e
92			64f
93			66
94			67
95			68
96			68
97			68

together by a combination of covalent, mechanical, and coordinative bonds.

XII. Physical Properties

The fundamental difference between interlocked macromolecules and conventional polymers is the nature of the bonding interactions which hold them together. In pseudopolyrotaxanes, polyrotaxanes, and polycatenanes, covalent bonds are supplemented by mechanical links, robust and otherwise, and, in many instances, by noncovalent bonds. This unconventional combination of interactions is responsible for the fundamental differences in properties between interlocked macromolecules and covalent polymers. For example, poly(ethylene glycol)s, as well as α-CD, are soluble[32] in water. However, the pseudopolyrotaxane

Table 6. Daisy-Chain Pseudopolyrotaxanes

	Monomer	Ref
103		72a
104		72b
105		73
106		74a
107		74b
108		74b
109		74b
110		74b
111		75

30, which is obtained by threading α-CD rings onto poly(ethylene glycol), is insoluble in water. Exactly the opposite behavior has been observed[47c] for the poly(acrylonitrile)-based pseudopolyrotaxane **53**. The parent polymer is insoluble in methanol: however, after threading of 60-crown-20, it becomes soluble again. Thus, encircling polymer backbones with macrocyclic components drastically changes their solubilities in comparison with their separate entities. Another interesting phenomenon, which is observed in some instances[32e,52c] on pseudopolyrotaxane formation, is aggregation. Indeed, the formation of micelles and gels has been noted after the threading of crown ethers onto polyurethanes and of α-CD rings onto poly(ethylene glycol)s. When phase mixing of the interlocked components occurs, significant changes of the glass transition temperature (T_g) can result. For example, the T_gs of some polyurethane-based pseudopolyrotaxanes correspond[52c] to a weighted average of those of the separate components. By contrast, the T_gs of side-chain polyrotaxanes are often higher than those of the separate components.[66a] Melting points of polymeric materials are also affected by interlocking. In pseudopolyrotaxanes, where the macrocyclic components have sufficiently high mobilities, aggregation, nucleation, and crystallization have been observed. Thus, two distinct melting points, both slightly lower than those of the separate components, are often associated[52c] with pseudopolyrotaxanes. It is interesting to note that the X-ray diffraction patterns of threaded macrocyclic components are remarkably similar to those obtained by analyzing the same macrocycles in their free form in the solid state.[44] In pseudopolyrotaxanes, gel permeation chromatographic analyses have revealed[45b] that the hydrodynamic volumes increase on threading relative to those associated with the parent components. As a result, intrinsic viscosities also increase. This effect has been exploited[28a] in order to follow pseudopolyrotaxane formation by monitoring viscosity changes with time. In polyester-based polyrotaxanes, the threaded macrocycles inhibit the entanglement of the polymeric backbones in the melt. As a consequence, the melt viscosity is reduced significantly. Comparison of the melt viscosities of a series of polyester-based polyrotaxanes with those of their parent polymers revealed[50c] that the melt viscosities are substantially lower for the polyrotaxanes. Thus, the threading of macrocycles onto polymeric backbones is expected to enhance their processabilities. Another interesting observation relates to the stabilities of pseudopolyrotaxanes relative to pseudorotaxanes. In general, pseudorotaxanes dissociate rapidly into their separate components under equilibrium conditions. By contrast, random coiling of the polymeric backbone in pseudopolyrotaxanes makes[49,50] their dethreading a much more difficult process, thus increasing their stabilities considerably.

XIII. Conclusions

The notion of reproducing the features of mechanical interlocking at the molecular level has fascinated scientists for decades. Molecular-sized abacuses, bearings, chains, gears, and joints could become the components of some of the smallest possible devices in future.[84] In a search for efficient ways for generating interlocked molecules, and hence, eventually, macromolecules, synthetic chemists have made changes in their strategies from complicated directed syntheses, through low yielding statistical approaches, to remarkably efficient and relatively simple supramolecularly assisted procedures. In the past decade or so, a wide variety of recognition motifs have been devised[85] and used to assist the threading of

Table 7. Poly[2]catenanes

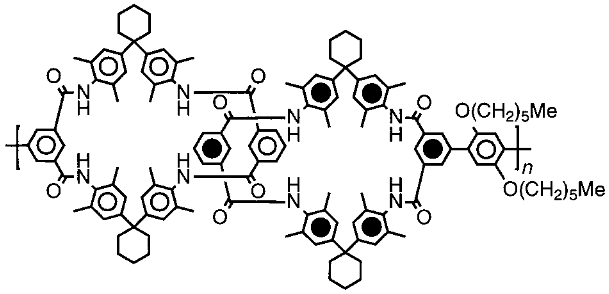
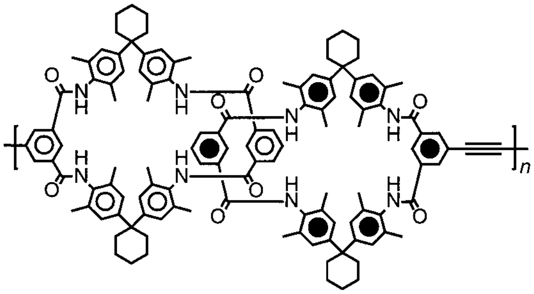
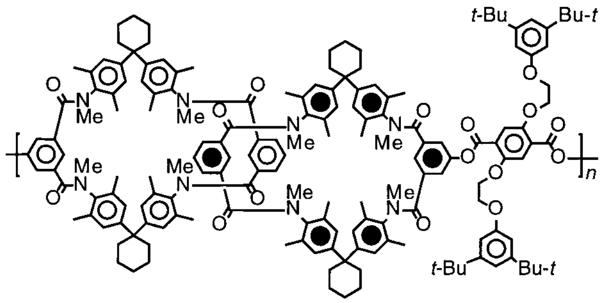
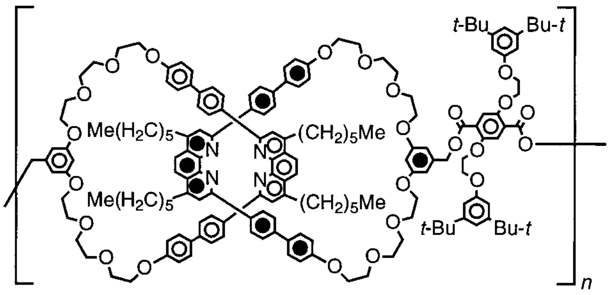
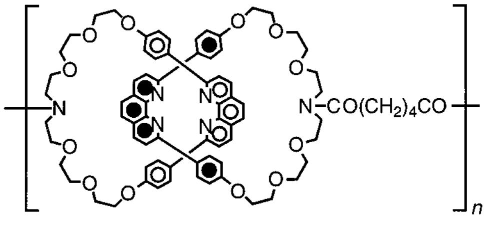
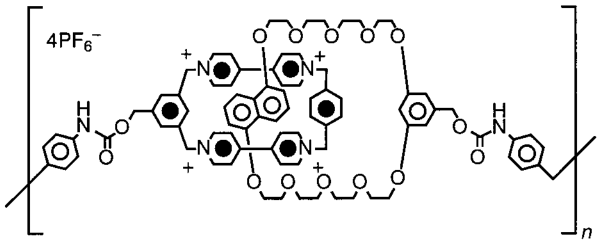
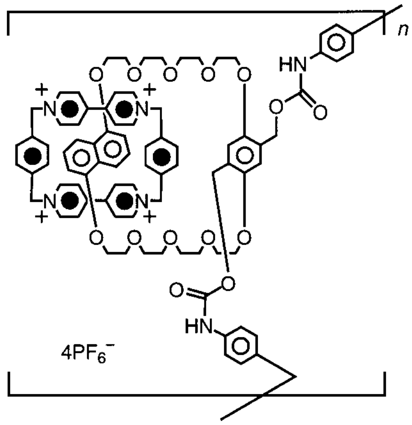
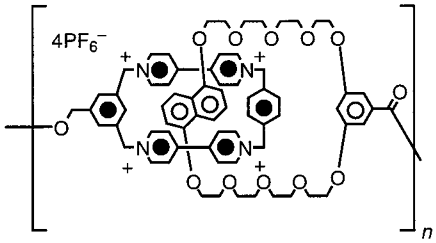
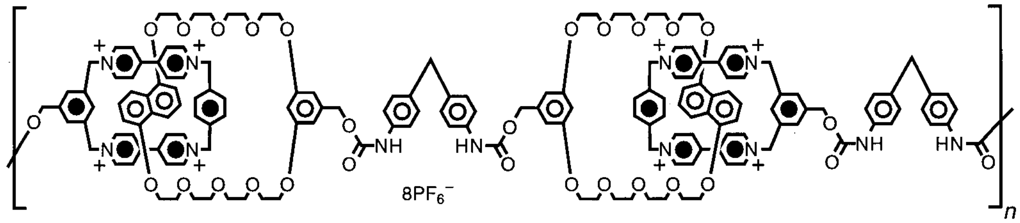
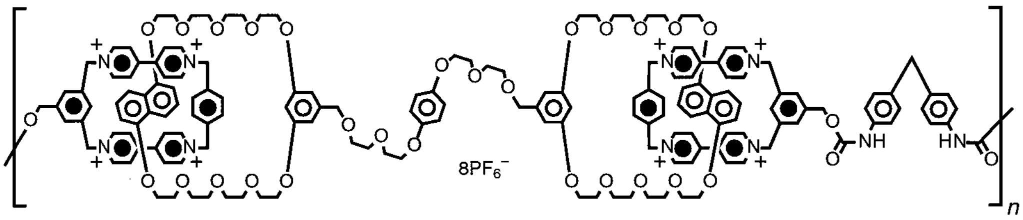
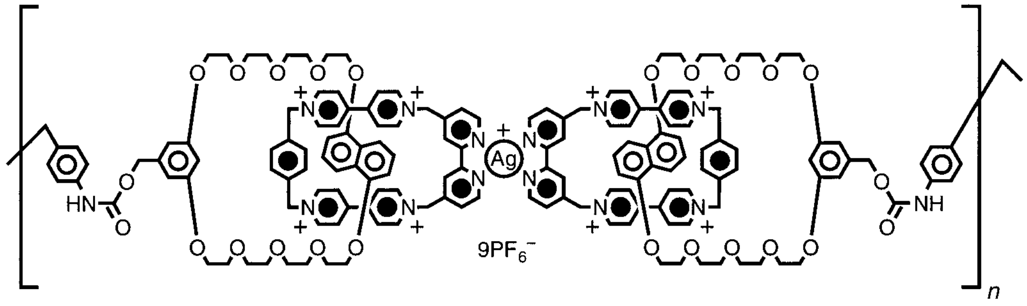
	Poly[2]catenane	Ref
121		78a
122		78a
123		78b
128		79a
129		79b
133		80

Table 7. (Continued)

	Poly[2]catenane	Ref
134		81
135		81
136		81
137		81
138		83

chemical beads onto chemical strings, paving the way for the generation of catenanes and rotaxanes and their macromolecular counterparts—i.e., polycatenanes and polyrotaxanes, respectively. Thus, main-chain and side-chain pseudopolyrotaxanes and polyrotaxanes are not chemical curiosities anymore but, rather, relatively easy synthetic targets which can often be prepared in few steps from commercially available starting materials. Nonetheless, main-chain polycatenanes, incorporating interlocked macrocycles disposed in linear arrays, are still a considerable challenge, even although synthetic methods for the preparation of so-called poly[2]catenanes are now well-established. The properties of these interlocked macromolecules are just starting to be investigated and understood. Preliminary studies have already revealed that the fundamental differences which exist between conventional covalent polymers and unconventional interlocked macromolecules are reflected dramatically in their physical properties.

Indeed, mechanical interlocking influences solubilities, phase-transition behaviors, hydrodynamic volumes, and stabilities, offering the opportunity to the synthetic chemist of being able to construct a new generation of exotic polymeric materials.

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