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Polycatenanes

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1. Introduction

1.1. Overview

Over the past few decades, the increasing uses and requirements of synthetic polymers in different fields of our life have stimulated research to produce more novel polymers, especially polymers with versatile structures which could provide a wider range of properties. It has been well-known that the fundamental properties of polymers are not only closely related to the chemical composition of the polymer chains but also depend on the architectural aspects, such as chain conformations and chain interactions. One of the interesting architectural features which can be introduced into polymer chains is mechanically interlocked cyclic molecules—catenanes. Catenanes are compounds consisting of two or more mechanically interlocked macrocycles that cannot be destroyed without breaking at least one of the covalent bonds of the macrocycles, e.g., the [*n*]catenane (type **A** in Figure 1; *n* describes the number of cyclic components participating in mechanical bonding[1]). The interlocked macrocycles of catenanes can rotate and move within each other. Therefore, the molecular components of catenanes have high degrees of freedom and mobility compared with other conventional covalently connected molecules. The name "catenane" is derived from the Latin *catena,* meaning "chain". Pseudorotaxanes[2−9] are generally precursors to catenanes (Scheme 1). A pseudorotaxane is a supramolecular species consisting of a linear molecule (guest) threaded through a macrocylclic ring (host), like thread through the eye of a needle. Because the linear molecule can dethread and rethread, the pseudorotaxane is in equilibrium with its two components—host and guest. A ring closure reaction of the linear component of a pseudorotaxane will afford a catenane. By incorporating catenane structures into polymers, polycatenanes, consisting of chainlike mechanically interlocked component structures, are constructed. Due to the high flexibility and mobility of the catenane structures, polycatenanes are expected to have more flexibility and different chain conformations compared to conventional polymers that have covalent linkages only. Therefore, the rheological,[10,11] dynamic,[12−14] mechanical,[15,16] and thermal properties[17] of the polycatenanes will be dramatically changed accordingly. As a result, polycatenanes obviously will have some unique properties. For this reason, polycatenanes have received considerable attention during the past decade or so. Since several reviews on polycatenanes and related materials were published,[2,3,18−30] a lot of progress has been achieved in this field. Here we will review the recent progress from 1995 until June 20th, 2009. Many polycatenane-like structures in the crystalline state based on coordination complexes of inorganic compounds have been reported and studied;[31−38] however, they will not be discussed in this review.

1.2. Classes of Polycatenanes

Polycatenanes have many subclasses. The typical polycatenanes that have been studied up to now or are possible are summarized in Figure 1. Structure **A** represents a series of linear polymers consisting of only mechanically interlocked macrocycles. Polycatenanes of type **A** can be viewed as "optimized " [*n*]catenanes (*n* is a large number). Since polycatenanes of type **A** are constructed solely by the noncovalent interlocking of cyclic components, the effects of the topologically bonded structures on properties will be maximized. Also, aesthetically speaking, these structures are perfect and appealing in terms of the polycatenane concept. Therefore, polycatenanes of type **A** are the dreams of many researchers, but up to now their synthesis is still one of the most difficult synthetic goals and remains elusive.

Polycatenanes of type **B** are derived from [*x*]catenanes (*x* is a small number, e.g., 1 or 2) by incorporating the difunctional [*x*]catenane subunits, in which both rings are functionalized, into linear polymer main chains. Obviously, the cleavage of the physical linkages of the catenane subunits will lead to degradation of the polymer chains. Since bifunctional [2] - or bis[2]catenanes are not overly difficult to synthesize and the essential structural feature of poly[2]catenanes (**B**, **C**, and **D** in Figure 1, when $x = 1$) is the mechanical linkage as in polycatenanes type **A**, most work up to now has been done with type **B** systems.

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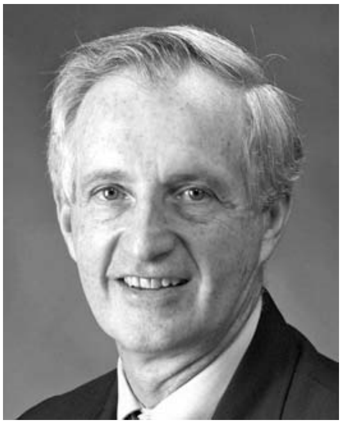
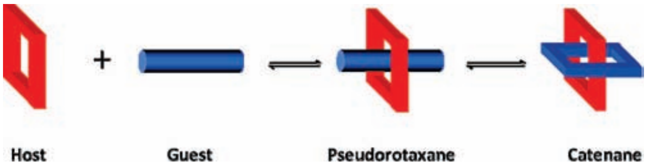


Harry W. Gibson has been Professor of Chemistry at Virginia Tech since 1986. He was raised in the Adirondack mountains of northern New York state. He obtained his B.S. in Chemistry with distinction in 1962 and his Ph.D. in Organic Chemistry in 1965, both at Clarkson University, under the supervision of Prof. Frank D. Popp. After a postdoctoral with Prof. Ernest L. Eliel at the University of Notre Dame, in 1966 he joined Union Carbide Corporation in Tarrytown, NY. In 1969 he moved to Xerox Corporation's Webster, NY, R&D center and rose to Senior Member of the Research Staff. He left in 1984 to join Signal Corporation in Des Plaines, IL, as Senior Research Scientist. During his industrial career he was involved with ethylene oxide chemistry, liquid crystals, xerographic toners, photoconductors, conducting polymers, membranes, and dielectric polymers. He has been a visiting professor at UCLA (with Fraser Stoddart, 1998), Durham (with Jim Feast, 1998), and the University of Florida (with Ken Wagener, 2008). Since 2006 he has been a Guest Professor at Zhejiang University in China. His current research interests include molecular recognition and self-assembly processes of polymers and small molecules, fullerene chemistry and applications, and ionic liquids as solvents for and components of polymers.

Polycatenanes of type **C**, which is an isomer of type **B**, are formed by incorporating [*x*]catenanes bearing two functional groups or a single difunctional moiety (i.e., a vinyl group) on the same ring into polymer chains. As for type **D**, the [*x*]catenane subunits exist as branches on the polymer backbone. However, unlike the cases of type **A** and type **B**, breaking the physical linkage of the catenane subunits in type **C** and type **D** systems will not necessarily result in degradation of the polymer chains. Polycatenanes of type **E** can be viewed as the products of the end-to-end cyclization reaction of polypseudorotaxanes or polyrotaxanes. Type **F** illustrates a series of networks which are formed solely by catenane subunits. In the networks some rings are interlocked with more than two other rings and act as cross-link points. Type **G** represents a series of universal networks compared with **F**; the catenane subunits exist as branches, cross-link points or repeating units in the polymer networks along with other linear linking units.

Thus, depending on the location and connection of the catenane subunits, polycatenanes can be divided into four major classes. (1) In main chain polycatenanes, the catenane subunits are located in the polymer main chains (**A** and **B** in Figure 1). (2) In side-chain polycatenanes (**C** and **D** in Figure 1), the catenane subunits are pendant groups. (3) "Ring around the rosy" polycatenanes are based on cyclic polymers onto which cyclic species are mechanically interlocked (**E** in Figure 1). (4) Polycatenane networks may be entirely or partially composed of catenane subunits (**F** and **G** in Figure 1). For simplicity and clarity, this review is divided into the following four parts: (1) main chain polycatenanes and their properties; (2) side-chain polycatenanes and their properties; (3) catenane structures based on cyclic polymers; and (4) catenane structures in the polymer networks.

Scheme 1. Threading of a Linear Guest through the Cavity of a Cyclic Host Produces a Pseudorotaxane: Subsequent Cyclization of the Linear Component Yields a [2]Catenane



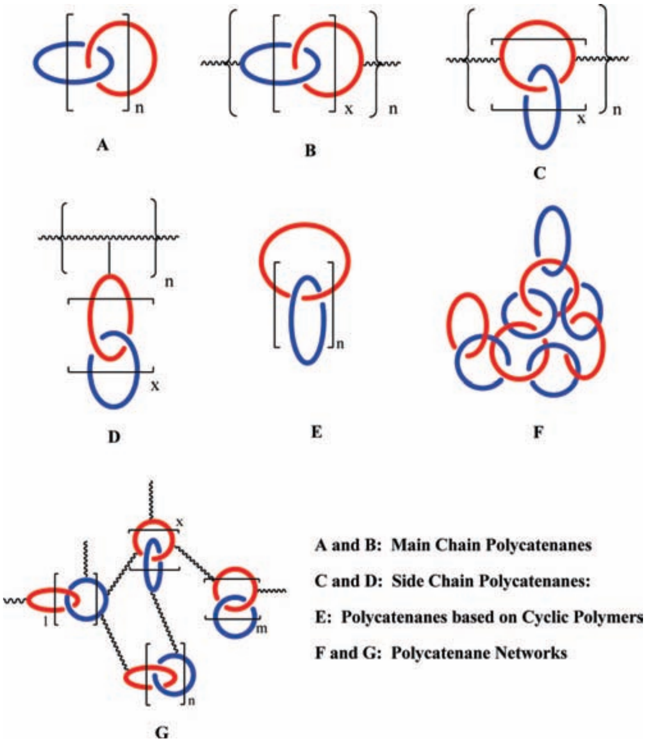
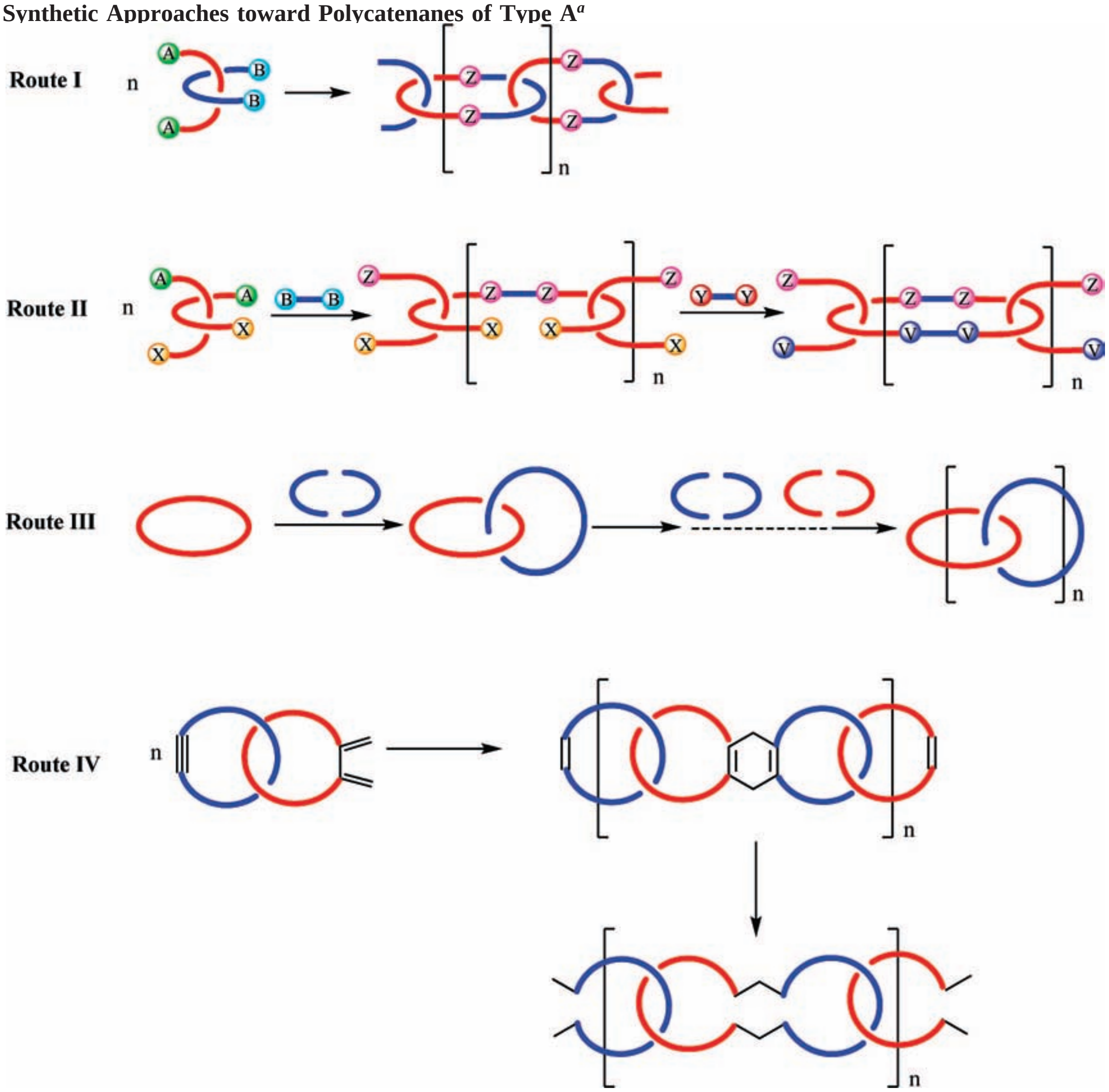


Figure 1. Classes of polycatenanes. Blue ring may be equal to red ring. $n, x, m, l \geq 1$.

Scheme 2. Synthetic Approaches toward Polycatenanes of Type A[a]



[a] Functional group A reacts with B to yield Z linkages. Functional group X reacts with group Y to yield V linkages.

2. Main Chain Polycatenanes and Their Properties

2.1. Linear Polycatenane/[*n*]Catenane Systems

The linear polycatenane of type **A** in Figure 1 is a polymer constructed solely of mechanically interlocked cyclic components. Like simple catenane synthesis, the efficient preparation of polycatenane **A** requires the macrocycle precursors to be preorganized in favor of the cyclization reactions. The preorganization is commonly achieved by utilizing template effects, such as hydrogen bonding,[39−43] $\pi-\pi$ stacking,[44−46] metal coordination,[47−49] and hydrophobic interactions.[43,50,51] Up to now, though some strategies have been proposed, successful preparation of polycatenanes of type **A** has yet to be achieved.

Several strategies are summarized in Scheme 2. The first proposed strategy (route I) relies on the polymerization between template-preorganized AA and BB type monomers.[18,52] Obviously, branching and cross-linking may well occur during the polymerization. If so, the product will be an undefined network containing rotaxane and catenane units instead of the desired linear polycatenane.

As a step forward, Shaffer and Tsay[53] devised another template-directed stepwise polymerization approach (route II in Scheme 2). This approach appears more feasible than route I, since the linear polymer is formed before cyclization of the macrocyclic units in the polymer chains. High dilution techniques[54−56] would be used to favor the cyclization reactions. But the high dilution conditions will lead to slow reactions. Moreover, the branching and cross-linking reactions probably still cannot be completely avoided.

A template-directed stepwise synthetic approach (route III in Scheme 2) theoretically could successfully afford linear polycatenanes of type **A** via stepwise threading and cyclization,[57−60] but the separation after each step will be difficult and tedious and the yield will be very low. Therefore, this approach is not suitable to make high molecular weight polycatenanes on large scales in order to investigate their properties. One-pot reaction strategies are much better than stepwise strategies, but the means to achieve this remain unknown. Several other attempts toward polycatenanes based on interfacial reactions or chemical conversion were made,[61−63] but none of them proved successful.

A promising strategy was proposed by Takata et al.[28,64] Their strategy circumvents the cyclization and threading steps, which are the bottleneck during the previous attempts to prepare polycatenane **A**. As shown by route IV in Scheme 2, a sequence of Diels−Alder polymerization of the [2]catenane and subsequent double-bond cleavage by ozonolysis should afford polycatenanes. Takata et al. already success-

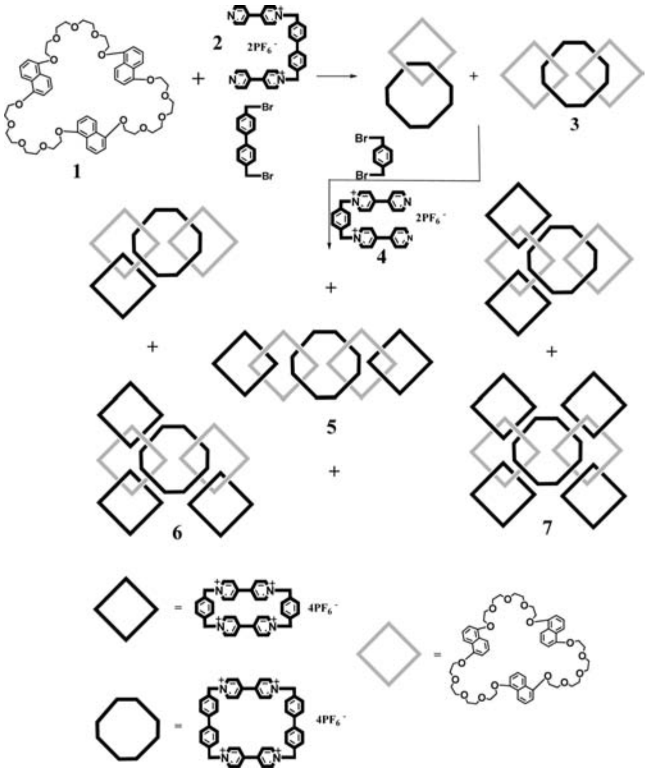


Figure 2. Synthesis of [5]Catenane (Olympiadane, **5**), [6]Catenane (**6**), and [7]Catenane (**7**)

fully used a Diels−Alder reaction and ozonolysis to enlarge one ring of a [2]catenane.[65] Moreover, a similar bridged poly[2]catenane,[66] which will be discussed below, was successfully prepared by Takata et al. Based on these results, this strategy possibly opens a new window for the synthesis of polycatenanes.

Up to now, the most impressive progress toward linear polycatenanes of type **A** was made by Stoddart et al.[57,60] By employing a stepwise synthetic approach (Figure 2), [5]catenane (**5**), which was named “Olympiadane” because its structure resembles the symbol of the Olympic movement, and [6]- and [7]catenane (**6** and **7**) were successfully prepared and fully characterized. The cyclization reaction between dicationic salt **2** complexed by excess crown ether **1** and 4,4′-bis(bromomethyl)biphenyl and following counterion exchange afforded [3]catenane (**3**). **3** was used as substrate for the cyclization reactions between **4** and 1,4-bis(bromomethyl)benzene. After counterion exchange, “Olympiadane” (**5**) was obtained in a relatively low yield (18%). By utilizing ultrahigh pressure conditions, the yield of **5** was increased to 30% and nonlinear [6]- and [7]catenanes (**6** and **7**) also were obtained in relatively good yields (28%, 26%). Although the linear [5]catenane was successfully prepared by the stepwise approach, this approach is not suitable to obtain higher linear polycatenanes due to the reason mentioned above.

2.2. Main-Chain Poly[2]catenanes and Their Properties

As mentioned above, poly[2]catenanes have the essential mechanically linked structure, and these simplest of polycatenanes can be prepared easily compared with polycatenanes of type **A** (Figure 1). Up to now, much effort has been devoted to this, and many poly[2]catenanes have been successfully prepared. The main synthetic routes used to prepare poly[2]catenanes are shown in Scheme 3. In order to make poly[2]catenanes, commonly functional [2]catenane monomers are prepared first and then polymerized. In route 1, difunctional [2]catenanes are formed directly by the cyclization reactions of preorganized precursors. In route 2, difunctional [2]catenanes are prepared by the template-directed coupling reactions of two different kinds of hemicycle precursors with or without functional groups. Route 3 involves stepwise cyclization of the two kinds of hemicycle precursors with and without functional groups. After the first cyclization reaction, one of the hemicycle precursors threads through the macrocycle formed during the first cyclization step. During the second cyclization step, noncovalent bonds are used as templating units. Unlike the case of route 3, in route 4 covalent bonds are used as templating units during

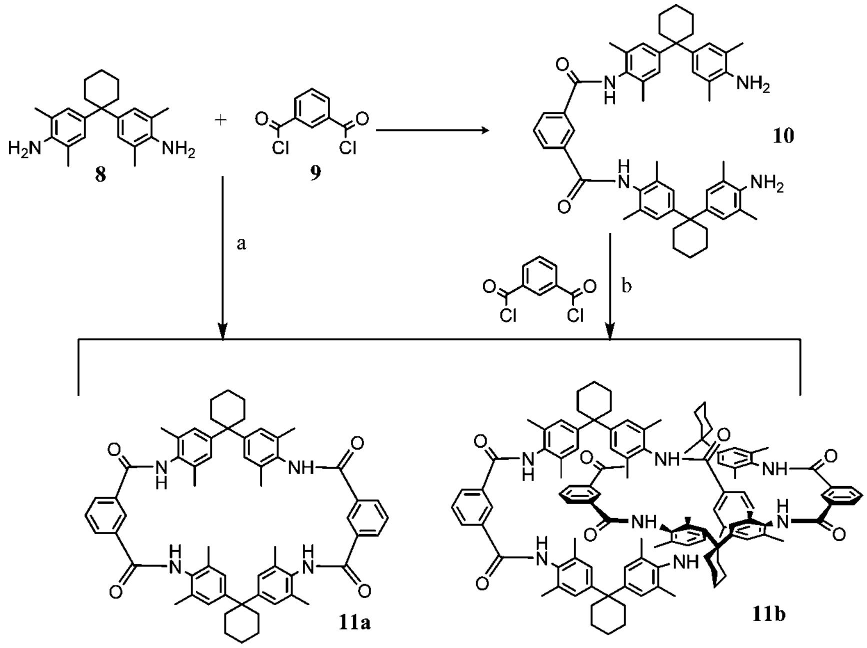
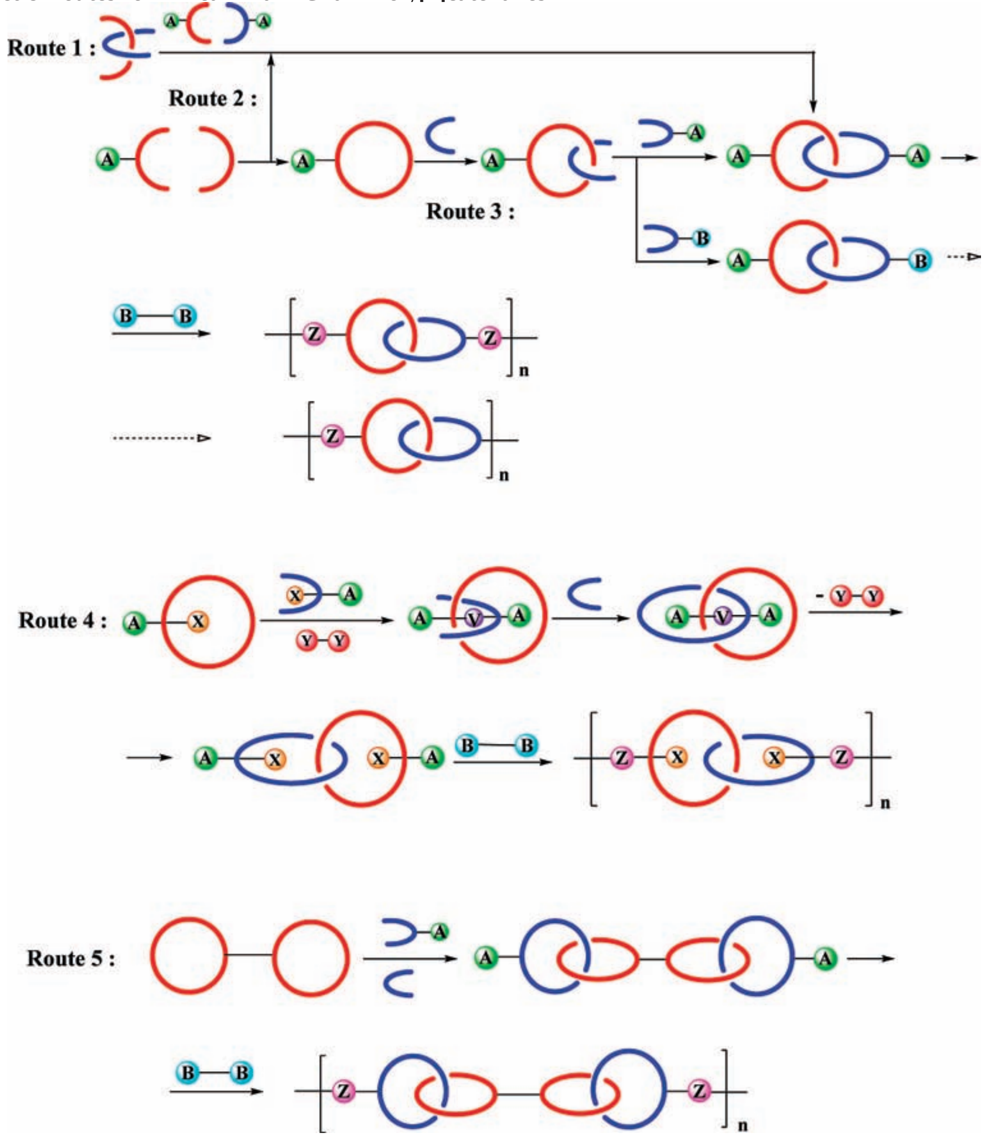


Figure 3. Vögtle’s one-step (a) and Hunter’s two-step (b) synthetic strategies toward amide-based [2]catenanes **11b**.

Scheme 3. Synthetic Routes for Linear Main Chain Poly[2]catenanes[a]



[a] Functional group A reacts with group B to produce Z linkages. The functional group X reacts with the spacer with two Y functional groups to produce V linkages.

the second cyclization step. Route 5 is similar to route 3; the difference is that the macrocycle precursors involved before the second cyclization step are replaced by linked- or bis(macrocycle)s.

2.2.1. Amide-Based Systems

The first amide-based [2]catenane systems (**11b** in Figure 3) were discovered by Hunter[39,67] and Vögtle[40,68] independently. The cyclization reactions were templated by hydrogen bonds and $\pi-\pi$ stacking interactions. Vögtle's synthetic strategy was a one-pot reaction (a in Figure 3). The amide-based [2]catenane **11b** was prepared in 8% yield by the reaction between cyclohexano-substituted diamine **8** and isophthaloyl dichloride (**9**). Also, the simple cyclic dimer **11a** and the analogous cyclic tetramer were produced during this one-pot reaction. Hunter's synthetic strategy involved a two-step approach (b in Figure 4), and the yield of **11b** was much better (34%) than that of the one-pot reaction. Simple one- or two-step syntheses and easy functionalization make this kind of [2]catenane appealing.[41,69,70]

Geerts et al. reported the first successful preparation of amide-based oligo[2]catenanes in 1995 (Figure 4) by using route 2 (Scheme 3).[71] In their work, the Hunter−Vögtle type [2]catenanes were prepared by employing Hunter's two-step method. An aryl bromide substituent was incorporated on each of their two rings via diamine **12** and the bromodiacid chloride. The product may exist as three different isomers: IN-IN **13a**, IN-OUT **13b**, and OUT-OUT **13c**,[72] but only IN-OUT **13a** and OUT-OUT **13b** were obtained, in 5% and 9% yields, respectively. The catenane structures with macrocycles bearing the first substituent "out" or "in" were defined as OUT and IN. The isomeric catenanes were conformationally frozen and could not rotate freely because of the intermolecular hydrogen bonding. Thus, the isomers were stable and could not be interconverted even at high temperatures.[69−71,73] Polymerizations of **13a** with different rigid comonomers **14a−d** were tried via Pd^0 coupling. However, reactions between **13a** and **14a**,**b** did not proceed to give even oligomers according to the gel-permeation chromatographic (GPC) results. On the contrary, the coupling reactions between **13a** and **14c**,**d** afforded oligo[2]catenanes **15a** and **15b** in yields of 84% and 99%, respectively. GPC analyses indicated that the number-average molecular weights (M_n) of **15a** and **15b** were 3.0 and 3.3 kDa, respectively,

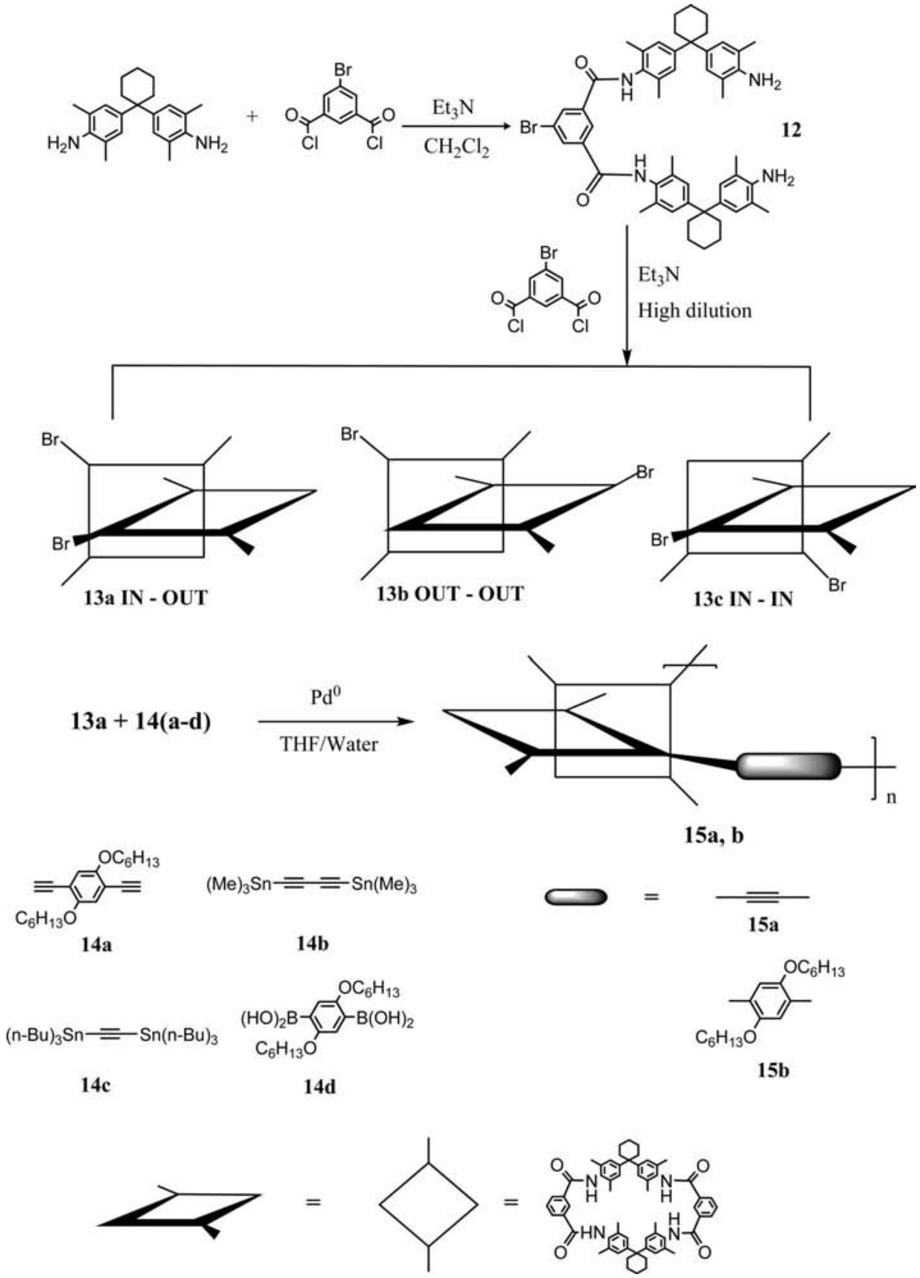


Figure 4. Synthesis of amide-based oligo[2]catenanes **15a** and **15b**.

and that the weight-average molecular weights (M_w) were 3.6 and 5.0 kDa. The degrees of polymerization (DP_n) of **15a** ranged from 1 to 5. Higher oligomers ($DP_n = 6-8$) were observed by fast atom bombardment mass spectrometry (FAB-MS). Although only modest molecular weights were obtained, differential scanning calorimetry (DSC) revealed that the glass transition for **15b** was around 245°.

A more rigid [2]catenane linkage was used by Geerts et al. to prepare poly[2]catenanes **18a** and **18b** (Figure 5).[74] Isomeric dibenzyloxy[2]catenanes (**16a**, IN-OUT and **16b**, OUT-OUT) were synthesized by the reaction between the diamine and 5-benzyloxyisophthaloyl chloride. The inertness of the Hunter-Vögtle type [2]catenanes toward polymerization was attributed to their poor solubility in common organic solvents, because of their compact structure and intermolecular hydrogen bonding. In order to increase the solubility, the isomeric dibenzyloxy[2]catenanes were subjected to N-methylation[40] of the amide functional groups. The subsequent hydrolysis of the benzyloxy groups afforded in 16% and 8% total yields two isomeric bisphenolic [2]catenanes **17a** (IN-OUT) and **17b** (OUT-OUT), which were highly soluble in chlorinated solvents. An interesting phenomenon should be noted here. After the N-methylation reaction, although both of the isomeric dibenzyloxy[2]catenanes have eight amide groups, the major product of the methylation reaction of the IN-OUT isomers was a 7-fold N-methylated [2]catenane **17a** in a yield of 77%. Conversely, the major product of the methylation reaction of OUT-OUT isomers was 8-fold N-methylated [2]catenane **17b** in a yield of 33%. The reactivity difference between the two isomers was ascribed to the steric hindrance of the IN substituent on the OUT macrocycle in the IN-OUT isomer. Therefore, an important conclusion was made − the reactivity of one macrocycle in catenanes is governed by the presence of the other. Also, according to the information about the dynamic properties of **17a** and **17b** from ^1H NMR investigations, no temperature dependence was observed. This observation indicated that the [2]catenane structures used were highly

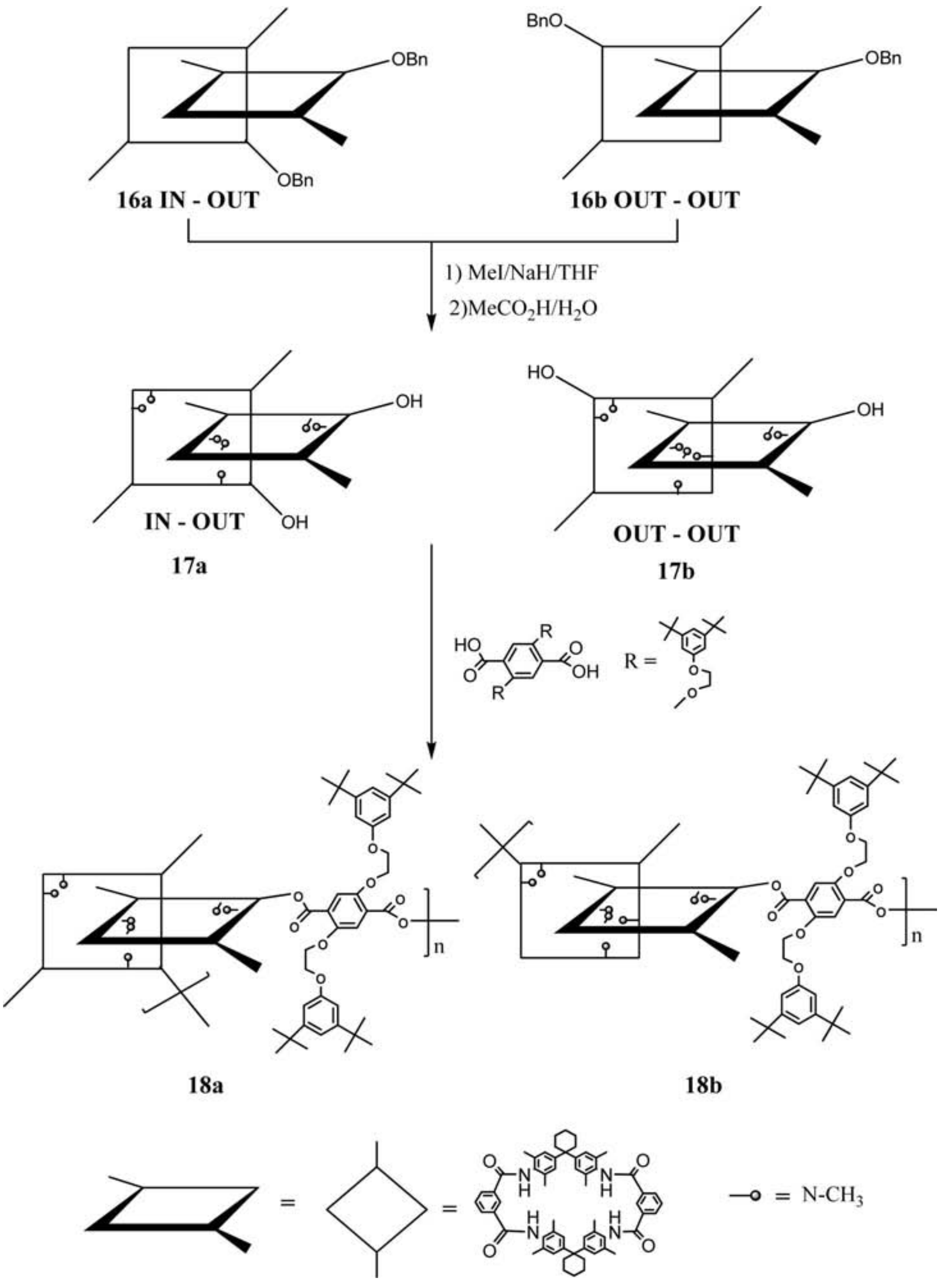


Figure 5. Synthesis of amide-based poly[2]catenanes **18a** and **18b**. BnO means benzyloxy group.

rigid. As a result, the corresponding poly[2]catenanes would possess very poor relative mobility of the macrocycles in the catenane subunits. Polymerization of **17a** and **17b** with the substituted terephthalic acid under mild conditions[75] afforded polyesters **18a** and **18b** in yields ranging from 94% to 97%. The successful preparation of these poly[2]catenanes was proven by proton nuclear magnetic resonance spectrometry (^{1}H NMR) and Fourier transform infrared spectroscopy (FTIR). The molecular weights of **18a** and **18b** were characterized by GPC, viscometry, and matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS). These investigations indicated M_n and M_w values of 34.0 kDa and 59.1 kDa for **18a** and 46.6 kDa and 95.6 kDa for **18b**. The number average degrees of polymerization (DP$_n$) of **18a** and **18b** determined by GPC with universal calibration[76] were 13 and 18, respectively.

It is anticipated that the properties of poly[2]catenanes in solution will reflect the mobility elements contained in the catenane subunits. The Kuhn segment length (l_k) of a polymer chain indicates the equilibrium flexibility in a given solvent.[77−79] The smaller the Kuhn segment length, the more flexible is the polymer chain. Kuhn segment length values of **18a** and **18b** in THF were estimated from GPC and viscometric data. The results indicated that **18a** ($l_k = 27$ Å) forms a more compact coil in solution compared with **18b** ($l_k = 44$ Å). As a conclusion, the catenane geometry, the IN-OUT isomer compared with the OUT-OUT isomer, and intermolecular interactions have important roles in the formation and properties of poly[2]catenanes.

Thermogravimetric analysis (TGA), DSC, and wide-angle X-ray scattering analysis were employed to investigate the solid-state properties. Since both poly[2]catenanes have polyaromatic amide-ester structures, they were expected to have high thermal stability. According to TGA results, the thermal stability of both poly[2]catenanes was pretty high (up to 380°). This result was consistent with the expectation. DSC results revealed both poly[2]catenanes had high T_g values: 277 °C for **18a** and 207 °C for **18b**. The results of

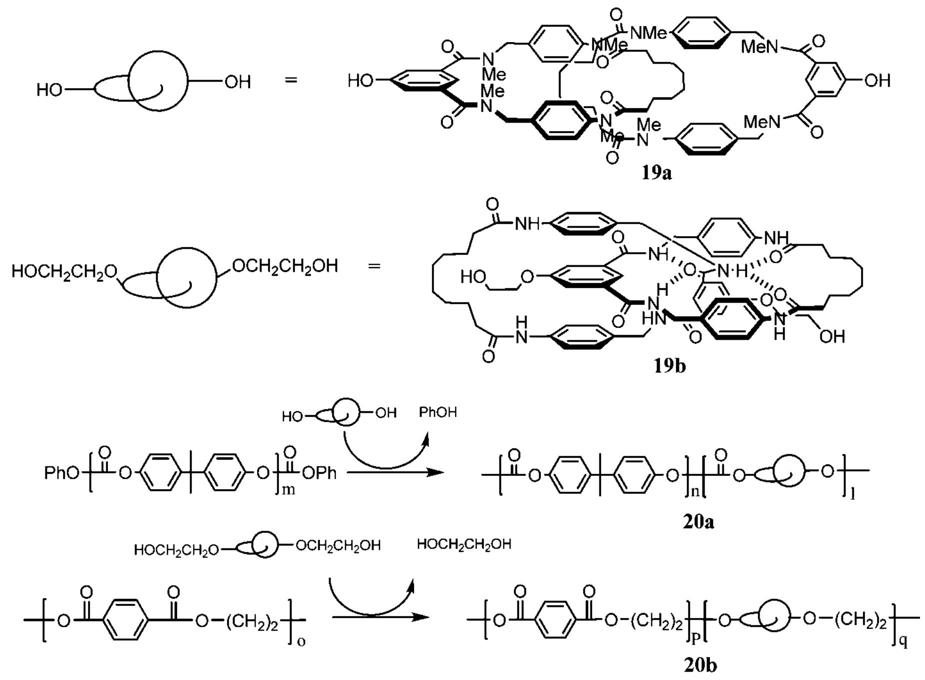


Figure 6. Synthesis of amide-based poly[2]catenanes **20a** and **20b** by copolymerization of [2]catenanes **19a** and **19b** with PC and PET prepolymers, respectively.

wide-angle X-ray scattering analyses indicated that both poly[2]catenanes are amorphous.

Leigh, Bailly, and co-workers reported another similar, but very interesting, approach to amide-based poly[2]catenanes.[80] In their work, amide-based bifunctional [2]catenane[81,82] structures were incorporated into a commercially available polymer—polycarbonate (PC)—by solid-state polymerization (SSP) (Figure 6). Unlike the other poly[2]catenane systems in which [2]catenane structures typically made up 90−95% of the molecular weight of the polymers, only limited amounts of [2]catenanes structures (10−30% w/w) were incorporated into the polymer chains. This approach was a smart way to investigate the role played by the mechanically interlocked structures on the polymer properties by comparison with the corresponding conventional polymers. The octa-*N*-methylbisphenol [2]catenane **19a** was synthesized by using a method similar to that mentioned above. 5-Allyloxyisophathalic acid was coupled with 4-aminobenzylamine and then the product was condensed with sebacoyl chloride. In order to get rid of the inter-ring hydrogen bonding and increase the mobility of the catenane macrocycles, the amide groups were methylated and then **19a** was obtained. One significant point should be noted here: the bifunctional [2]catenane **19a** was synthesized on a multigram scale without using chromatographic purification. This is meaningful to prepare sufficient amounts of polymers for the investigation of their properties. The PC prepolymer (M_w = 2.2 kDa, M_n = 1.3 kDa) had a high abundance of phenyl-type chain ends which could balance the chain end stoichiometry and enable the buildup of the copolymers by release of phenol. Different amounts of **19a** were copolymerized with PC prepolymers by solid-state polymerization,[83−85] and poly[2]catenane **20a** resulted. The successful incorporation of [2]catenanes into the polymer was validated by GPC and high-temperature ^{1}H NMR analyses. According to the GPC results using a polycarbonate-based universal calibration, absolute molecular weights were calculated. M_w = 40.1 kDa, M_n = 15.9 kDa, and PDI = 2.5 for copolymers containing 10% (w/w) catenanes; M_w = 41.4 kDa, M_n = 9.9 kDa, and PDI = 4.2 for copolymers containing 20% (w/w) catenanes; M_w = 38.9 kDa, M_n = 8.1 kDa, and PDI = 4.8 for copolymers containing 30% (w/w) catenanes. DSC, ^{1}H NMR, and intrinsic viscosity measurements indicated that the [2]catenane monomers were homogeneously distributed throughout the molecular weight distribution. But heterogeneity in polymerization kinetics may occur at high catenane content. The solid state properties were determined by DSC and dynamic mechanical analysis (DMA) and compared with pure bisphenol-A PC at the same molecular weight level. Interestingly, the results showed only a small influence of the catenane subunits on the T_g values of the copolymers. The insensitivity was attributed to the high internal mobility/flexibility of the catenane subunits in the copolymer chains as a result of the methylation of the amide group in the catenanes. DMA analysis showed a new peak at −6 °C which was linked to the movements of the catenane units.

Further, the solution and crystallization properties of the copolymers **20a** were determined.[86] According to the intrinsic viscosity analysis, the presence of catenanes strongly influenced the interactions between the copolymer and the solvent—dichloromethane. The unperturbed dimensions of the copolymers decreased with increasing catenane percentage. The interaction between catenane subunits and bisphenol-A carbonate segments, which could lead to the shrinkage of the copolymer coil, was suggested as the reason for the decrease of the unperturbed dimensions. DSC measurements were used to investigate the influence of the catenane subunits on the crystallization properties of the copolymers. The percentage of catenanes in the copolymers only had a small influence on the crystallization properties of the copolymers. This result indicated that the copolymers contained both crystallizable (pure bisphenol-A PC) and uncrystallizable segments (composed mainly of catenane subunits). The catenane subunits in the copolymers accumulated in the uncrystallizable segments upon increasing monomer concentration and did not influence the crystallizable segments.

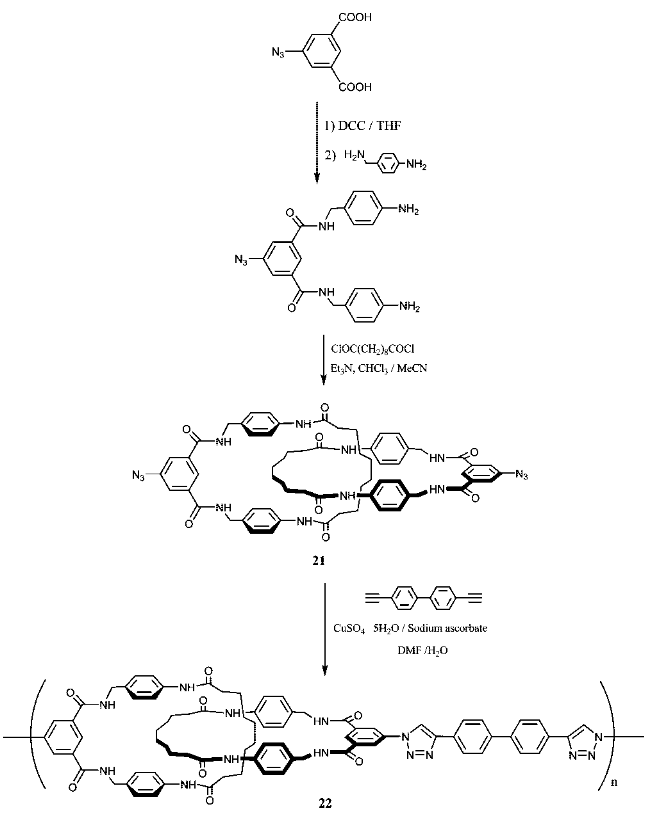


Figure 7. Synthesis of amide-based poly[2]catenane **22** by 1,3-dipolar cycloaddition of diazido[2]catenane **21** and 4,4′-diethynylbiphenyl. DCC means *N*,*N*′-dicyclohexylcarbodiimide.

In another step forward, Leigh, Bailly, and co-workers[87] tried to incorporate [2]catenanes into another commercially available polymer—poly(ethylene terephthalate) (**PET**) (Figure 6). Compared with **PC**, **PET** has enhanced flexibility and a relatively fast crystallization rate.[88,89] By employing a similar method, dihydroxy[2]catenane **19b** was prepared. Unlike **19a**, the amide groups on **19b** were kept in order to compare the influence of intracatenane macrocycle mobility on polymer properties. Copolymer **20b** was obtained by solid-state copolymerization between different amounts of **19b** and PET prepolymer (M_w = 13.0 kDa, M_n = 7.4 kDa). DSC and ^{1}H NMR analyses proved that the catenanes were quantitatively incorporated into the polymer chains. But a small fraction of the catenanes degraded into macrocycles which were incorporated into the PET as branching points or chain ends. The molecular weights were obtained by GPC determination. M_w = 67.0 kDa, M_n = 25.0 kDa, and PDI = 2.7 for copolymers containing 5% (w/w) catenanes. M_w = 61.0 kDa, M_n = 21.0 kDa, and PDI = 2.9 for copolymers containing 10% (w/w) catenanes; M_w = 52.0 kDa, M_n = 17.0 kDa, and PDI = 3.0 for copolymers containing 20% (w/w) catenanes. Interestingly, unlike **20a**, the T_g value of **20b** increased with the catenane percentage in the copolymers. This difference was ascribed to the specific effect of catenane mechanical linkage (inter- and intramolecular hydrogen bonding).[90] Moreover, compared with PET copolymers containing a bulky and rigid comonomer at the same comonomer concentration, the T_g of the catenane-containing copolymers was relatively low. This observation indicated that the catenane structures in the copolymer still possessed some degree of internal mobility. This suggestion also was proven by analysis of the crystalline phases. Similar to the case of **20a**, increasing the catenane percentage had little effect on the crystallization properties. The catenane structures in the copolymers had some degree of mobility and were concentrated in the amorphous phase.

Yamazaki et al. reported a novel amide-based poly[2]catenane by employing “click chemistry”[91−94] (Figure 7).[95] In their work, diazido[2]catenanes **21** were prepared by employing Hunter’s two-step method. 1,3-Dipolar cycloaddition of diazido[2]catenanes **21** and 4,4′-diethynylbiphenyl at room temperature afforded poly[2]catenanes **22** bearing rigid triazole rings in high yield (88%). GPC analysis indicated that the number-average molecular weight (M_n) of the polymer was 15.0 kDa and the M_n/M_w was 2.0. Cyclodimerization occurred during the polymerization, but the lower reaction temperature inhibited the cyclodimerization without lowering the molecular weight of the poly[2]catenane. For polymerization at 0°, M_n = 16.0 kDa, M_n/M_w = 2.0, and yield = 92%.

Another interesting amide-based poly[2]catenane (or oligo[2]catenane) **23b** was developed by Takata et al. by employing route 3 (Scheme 3). First, the desired [2]catenane monomer **23a** was prepared in a pretty high yield by the coupling reaction between the respective diacid chloride and

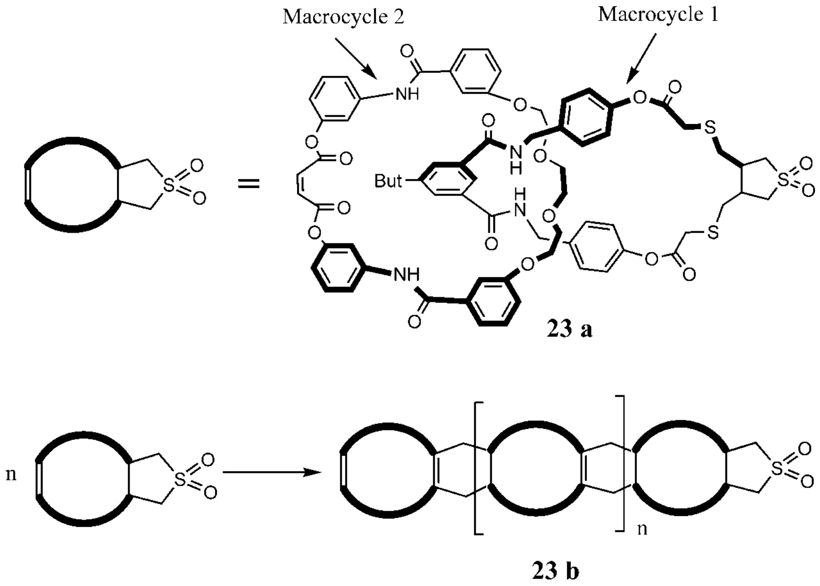


Figure 8. Synthesis of bridged poly[2]catenane **23b** by Diels−Alder polymerization of [2]catenane **23a**.

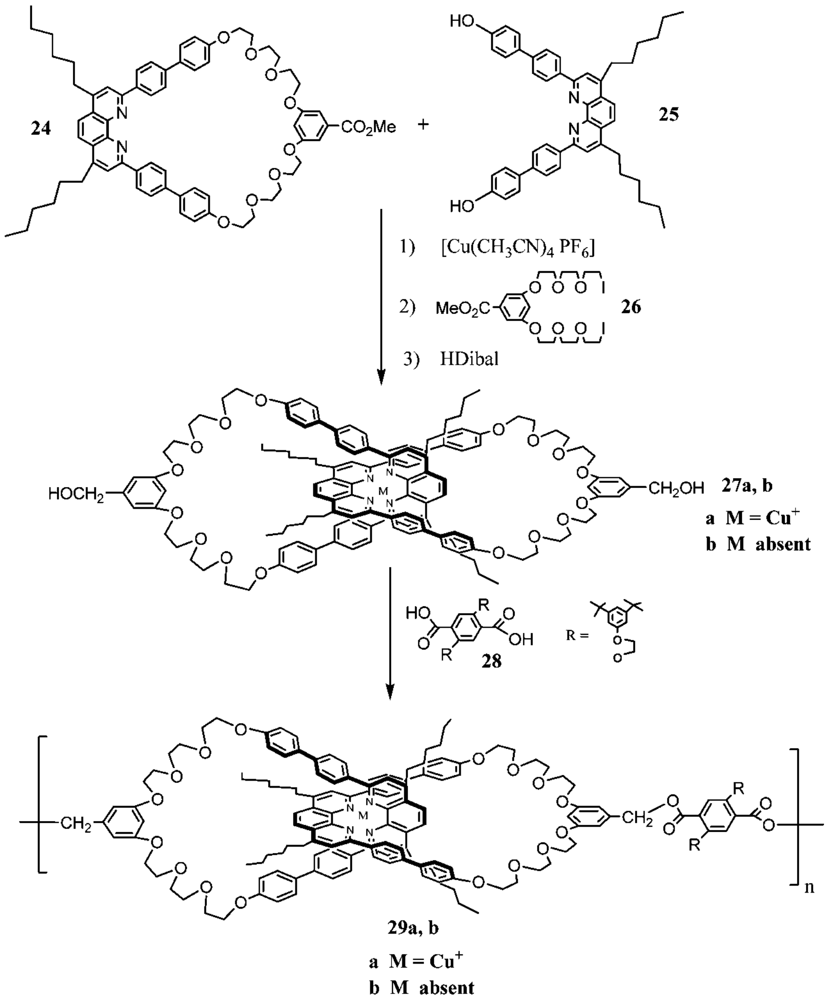


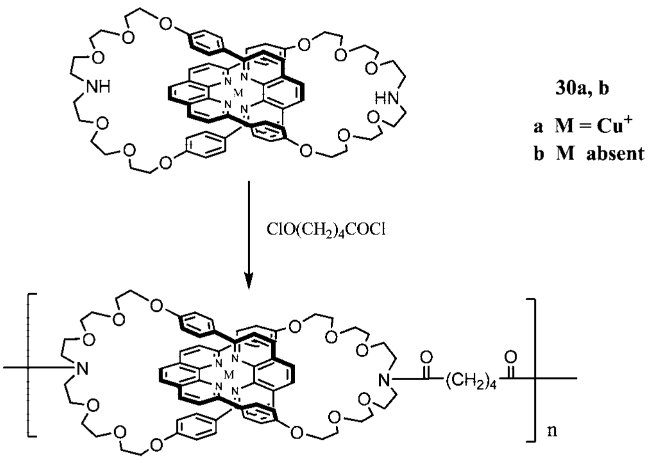
Figure 9. Synthesis of phenanthroline-based poly[2]catenanes **29a**,**b**. HDibal means diisobutylaluminum hydride.

diamine components by using macrocycle-1 (Figure 8) as the template.[66] Macrocycle-1 was proven to be a good precursor for the synthesis of catenanes,[96,97] and the formation of catenane **23a** was driven by intermolecular hydrogen bonding between the two macrocycles. The Diels–Alder polymerization of **23a** was carried out by heating at 140° without solvent for several hours, and poly[2]catenane **23b** was obtained. The polymerization involved two steps: the first step was the decomposition of the sulfolene moiety; the second step was the Diels–Alder reaction of the resulting *exo*-diene with the opposing maleate unit. The successful polymerization was validated by DSC analysis and the aminolysis of **23b**. GPC analysis based on PSt standards gave the molecular weights: $M_n = 3.1$ kDa and PDI = 1.98. Since **23b** was constructed by cyclic components, the molecular weight probably was underestimated. This result was proven by the aminolysis of **23b**. As outlined above, this approach could be extended potentially to the preparation of polycatenanes if conditions for more efficient polymerization can be developed.

2.2.2. Phenanthroline-Based Systems

Sauvage et al. first employed the three-dimensional template effect of transition metals (e.g., copper(I) ions) to make [2]catenanes based on phenanthroline.[48,49,98] In this strategy, the two phenanthroline-type ligands are entwined around a copper(I) center in a tetrahedral geometry that favors the formation of the catenane structures. The preparation of this type of [2]catenane can be achieved via two possible strategies as shown by routes 1 and 3 in Scheme 3. Route 1 is pretty straightforward.[99,100] Route 3, as discussed above, involves stepwise cyclization of the two kinds of hemicyclic precursors. Route 3 is the commonly used method[101−104] due to its better yield and the possibility to make catenanes with two different rings.

The first phenanthroline-type poly[2]catenane was reported by Sauvage and co-workers[105,106] by employing route 3. As shown in Figure 9, first the phenanthroline-containing bisphenol **25** was threaded through the phenanthroline-containing macrocycle **24** using the template effect of copper(I) ions. Then the entwined catenane precursor was coupled with diiodide **26** and the product was reduced to afford [2]catenane monomer **27a**. **27b** was obtained via demetalation with potassium cyanide (KCN). The polymerization reactions were carried out between the bisphenolic [2]catenane monomer **27a** and highly soluble diacid **28**, affording poly[2]catenane **29a**. The structures were validated by ^{1}H NMR, ^{13}C NMR, and MALDI-TOF mass spectrometry. The molecular weight values for **29a** given by GPC analysis were $M_w = 1800.0$ kDa and $M_n = 55.0$ kDa. But the molecular weights are probably overestimated due to the strong dipolar interactions among the oligomer and polymer chains. Poly[2]catenane **29b** was obtained via the demetalation reaction with potassium cyanide (KCN) and not prepared directly from **27b**. The copolymerization between bisphenol **27b** and diacid **28** mainly afforded cyclic



30a, b
a M = Cu$^+$
b M absent

31a, b
a M = Cu$^+$
b M absent

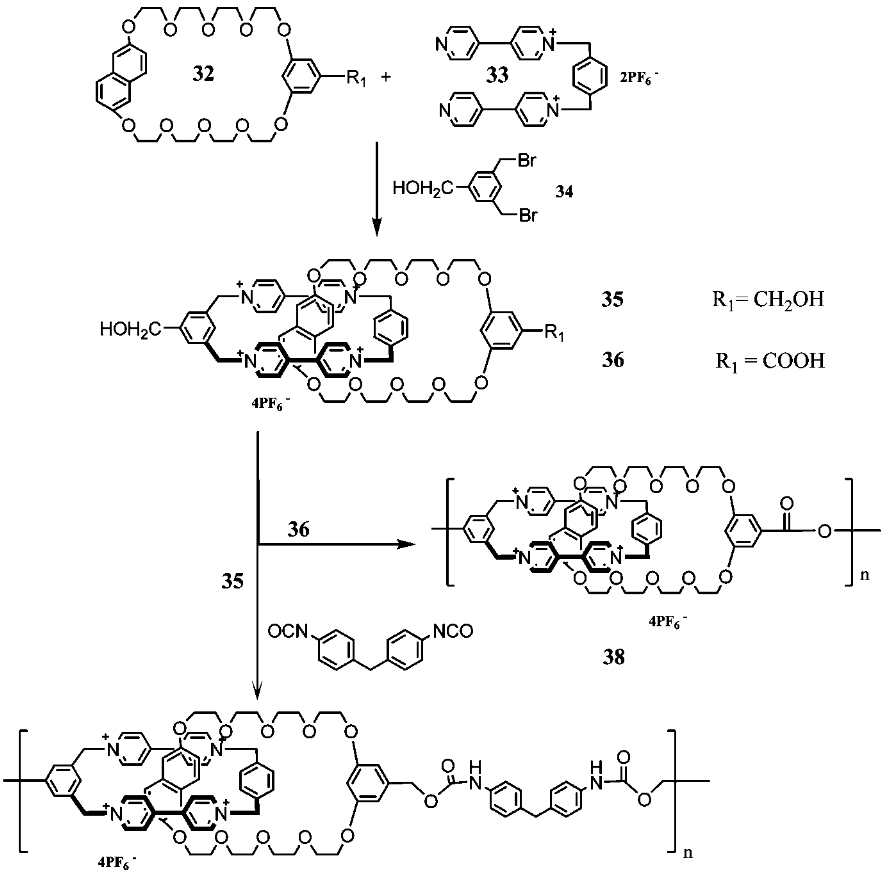
Figure 10. Synthesis of phenanthroline-based poly[2]catenanes **31a**,**b**.

oligo[2]catenanes The high flexibility of the demetallized [2]catenane macrocycles in **27b** was suggested to explain the preferential formation of cyclic oligomers. The GPC analysis with universal calibration[107] gave molecular weight ranges of **29b**: M_w = 42.0−47.0 kDa, M_n = 22.0−25.0 kDa; DP$_n$ = 8−9. A solution investigation gave the upper limit of the Kuhn segment length value (l_k = 27 Å), which was lower than the Kuhn length of the monomer (l_k = 32 Å). Not only the mobility of the [2]catenane subunits but also the flexibility of the ethyleneoxy bridge and the benzyl ester bonds contribute to the low value of the Kuhn segment length. TGA analysis showed reasonable thermal stabilities of **29a** (up to 210 °C) and **29b** (300 °C). DSC analysis revealed that the T_g of the rigid metalated **29a** is slightly higher than the T_g of **29b**.

Shimada and co-workers reported the synthesis of another phenanthroline-type poly[2]catenane[108] (Figure 10). The diamino[2]catenanes **30a**,**b** were prepared in two steps, like the synthesis of **27a**,**b**. Similar to the polymerization of **27b**, the polymerization between **30b** and adipoyl dichloride only afforded intermolecular cyclization "pretzel"-like products.[109] Poly[2]catenane **31a** was obtained via the polymerization between **30a** and adipoyl dichloride, and **31b** was afforded by the subsequent demetalation of **31a**. The successful formation of **31b** was proven by ^{1}H NMR and IR determinations. The molecular weight M_w of **31b** determined by GPC with PS standards was 810.0 kDa. The DP$_n$ calculated was about 609. This result may be significant in view of the lower DPs (DP$_n$ < 20) of the other reported poly[2]catenane systems; however, in view of the results of Sauvage noted above aggregation seems likely, meaning that these values are erroneous.

2.2.3. Tetracationic Cyclophane−Aromatic Crown Ether Based Systems

Another very interesting poly[2]catenane system is a tetracationic cyclophane (namely CBPQT^{4+})-aromatic crown ether-based system. The first synthesis of a tetracationic cyclophane-aromatic crown ether-based [2]catenane, reported



37

Figure 11. Synthesis of tetracationic cyclophane−aromatic crown ether based poly[2]catenanes **37** and **38**.

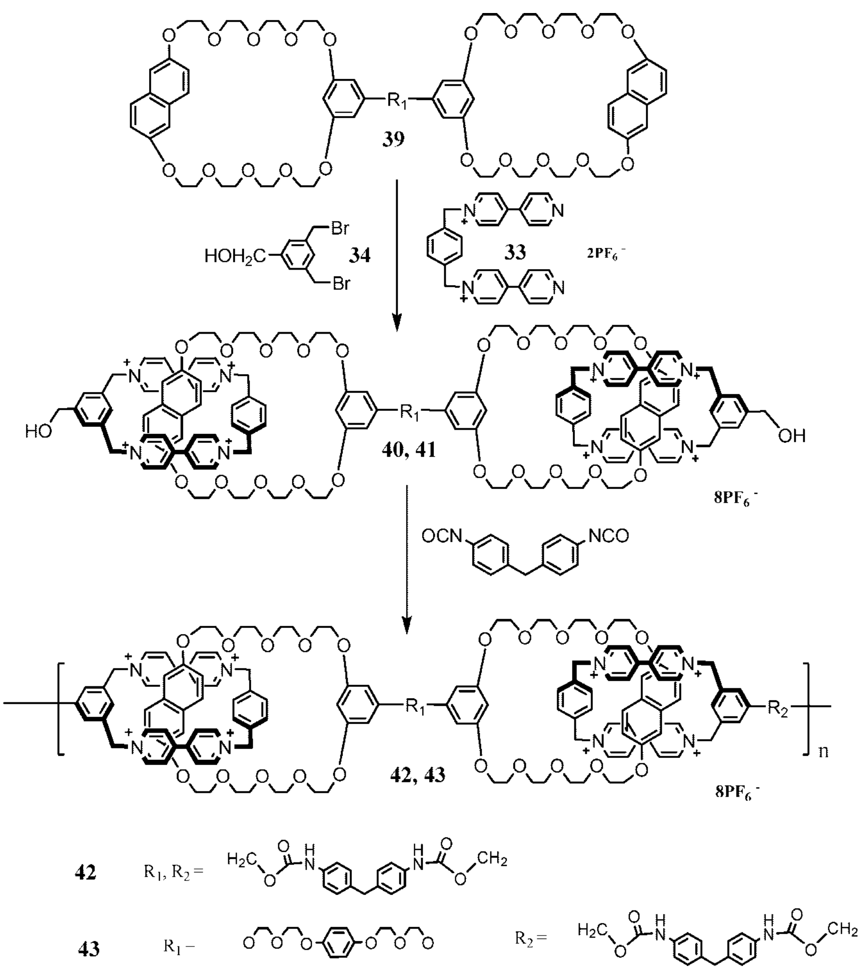


Figure 12. Synthesis of tetracationic cyclophane−aromatic crown ether-based poly(bis[2]catenane)s **42** and **43**.

by Stoddart et al.,[44] utilized the charged π-donor/π-acceptor template methodology, which took advantage of strong binding affinities between a bipyridinium-based cyclophane and a crown ether ring. Like route 3 in Scheme 3, the π-electron-deficient aromatic diparaquat threaded through the π-electron-rich crown ether ring and subsequently coupled with a *m*-xylylene moiety to afford the [2]catenane. The driving forces include several noncovalent interactions, such as π-π stacking, edge-to-face interactions between aromatic rings, and hydrogen bonding.

Stoddart's group has been very active in preparing tetracationic cyclophane-aromatic crown ether based [2]catenanes[110−114] and poly[2]catenanes. The first poly[2]catenane **37**[115,116] synthesized by them is shown in Figure 11. Dicationic salt **33**, dibromide **34**, and functionalized aromatic crown ethers **32** under ultrahigh-pressure[117] followed by counterion exchange afforded difunctionalized [2]catenane monomers **35** and **36**. The polymerization of diol monomer **35** with bis(4-isocyanatophenyl)methane in acetonitrile successfully afforded poly[2]catenane **37**. GPC determination performed on the chloride analogue of polyurethane **37** gave a molecular weight M_n of 26.5 kDa, corresponding to a DP$_n$ of 17. Since the [2]catenane monomers are unsymmetrical, the polymer chains could incorporate three different bridging units along the main chains. The diphenylmethane subunits could connect two identical crown ether rings, two identical cyclophane rings, or one crown ether ring and one cyclophane ring. Therefore, **37** probably was a mixture of different constitutional isomeric types.

It should be noted here that the early attempts to make poly[2]catenanes by polyesterification between [2]catenanes bearing two complementary functional groups—one hydroxyl group and one carboxylic group on each ring—did not afford any polymers or even oligomers. This observation presumably was a result of unfavorable stereoelectronic effects that lower the reactivity of the complementary functional groups. By utilizing a similar synthetic methodology, difunctional [2]catenane **36** was prepared. Not surprisingly, the direct polyesterification of AB monomer **36** was not successful. The CH_2OH groups then were converted into CH_2Br groups and poly[2]catenane **38** was successfully made via the polyesterification reaction with the carboxylate salt and subsequent counterion exchange.[118] GPC analysis of this polyester showed a molecular weight (M_n) of 35.0 kDa, corresponding to a DP$_n$ of 25. Although no cyclic oligomer formation was reported, it is reasonable to presume that some amount of cyclic oligomers was formed during the polyesterification based on Shimada's results.[108]

Going one step further, Stoddart and co-workers prepared two poly(bis[2]catenane)s[118] (Figure 12). The longer bis[2]catenanes have the potential advantage of suppressing intramolecular cyclization during polymerization. **40** and **41** were synthesized by employing the same template-directed coupling reaction between the dicationic bis(bipyridinium) salt **33** and substituted *m*-xylylene dibromide **34** followed by counterion exchange. Poly(bis[2]catenane)s **42** and **43** were obtained by polymerization of diols **40** and **41** with bis(4-isocyanatophenyl)methane. The chloride salts of polyurethanes **42** and **43** were analyzed by GPC. According to GPC results,

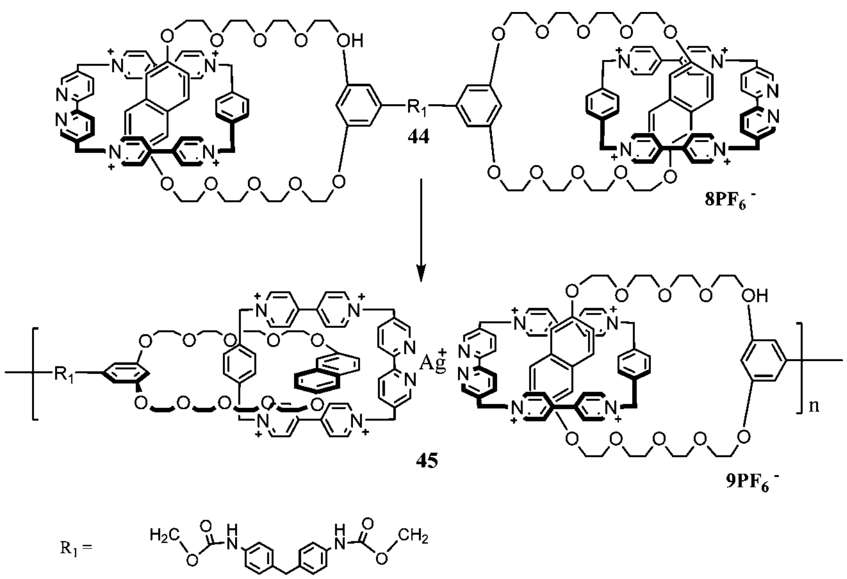


Figure 13. Synthesis of tetracationic cyclophane−aromatic crown-ether based poly(bis[2]catenane) **45**.

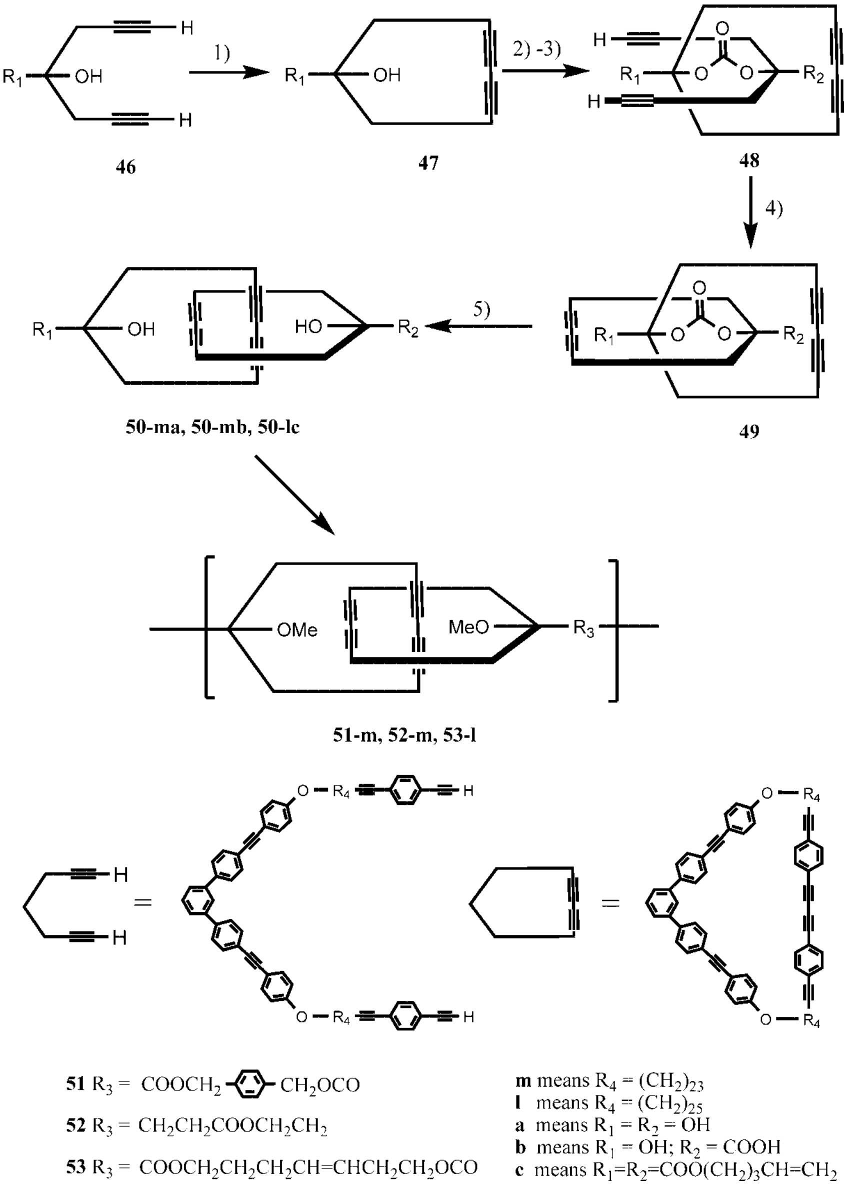
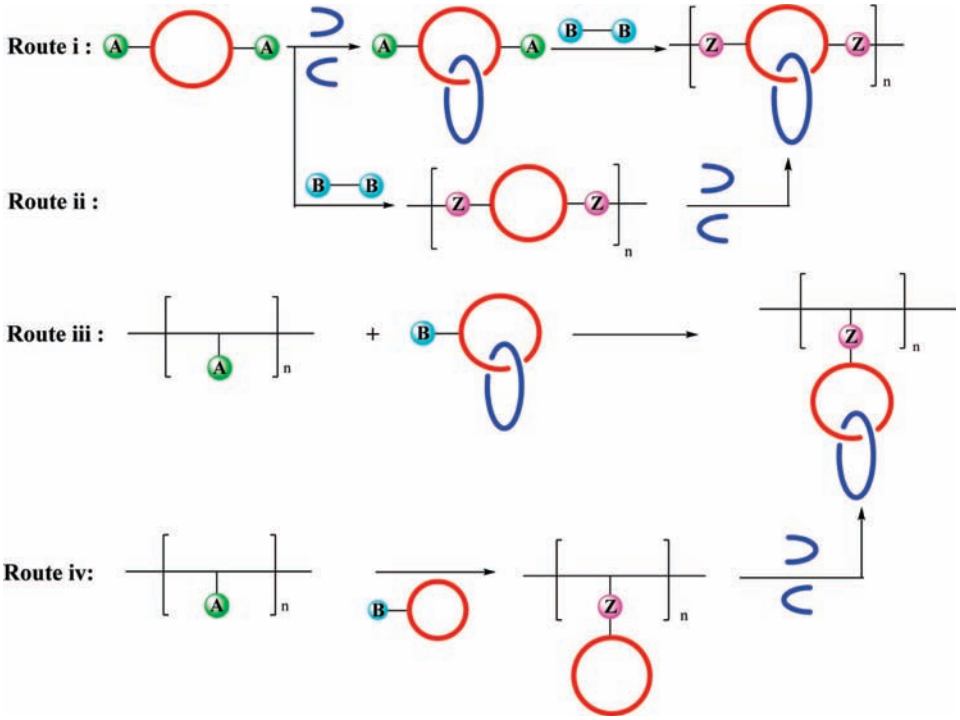


Figure 14. Synthesis of poly[2]catenanes **51-m**, **52-m**, and **53-l** by utilizing a covalent bond as a template.

Scheme 4. Synthetic Routes for Side-Chain Poly[2]catenanes: Functional Group A Reacts with Group B To Produce Group Z

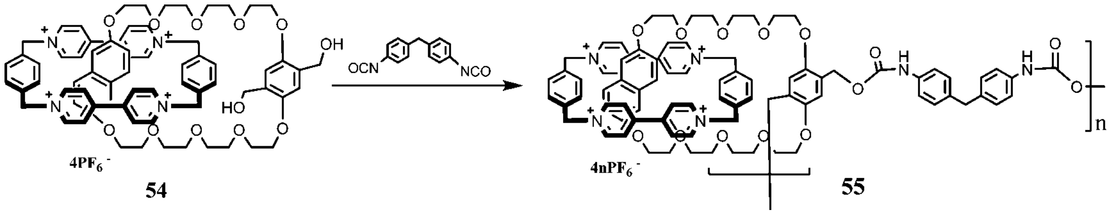


42 and **43** had the same molecular weight (M_n): 45.0 kDa (DP_n = 15).

An interesting poly(bis[2]catenane)[119] based on a transition metal chelation effect was also reported by Stoddart et al. (Figure 13). By utilizing the same synthetic method as for **40**, bis[2]catenane monomer **44**[120] was prepared and combined with CF_3SO_3Ag in acetonitrile at room temperature. After counterion exchange, the poly(bis[2]catenane) **45** was isolated. The molecular weight (M_n) determined by GPC with protein standards was 150 kDa, corresponding to a DP_n of 40 for this 1-dimensional silver complex. This approach provides an alternative method for assembly of the catenane monomers into high molecular weight polymers.

2.2.4. Other Poly[2]catenane Systems

Godt et al. designed and synthesized poly[2]catenanes[121−123] having huge and highly mobile rings via route 4 of Scheme 3. Unlike the systems discussed above, which use noncovalent interactions to template the synthesis of monomeric [2]catenanes, a carbonate group was used as a covalent template or tether and the catenane structures were generated after the second cyclization reaction (Figure 14). Difunctional [2]catenane monomers were prepared via the following steps:[121,123] (1) The macrocycle **47** was obtained by employing the oxidative cyclodimerization of dialkyne **46**[124] under pseudohigh dilution. (2) The phenolic group was converted into a chloroformate group. (3) The sodium salt of **46** was threaded though macrocycle **47**, and subsequent intrapseudorotaxane carbonate formation afforded **48**. (4) The oxidative cyclodimerization of **48** produced **49**. (5) Finally, large ring [2]catenanes (more than 63 membered) **50** were obtained by cleaving the carbonate group. Electron paramagnetic resonance (EPR) analysis revealed that the [2]catenanes adopt all possible coconformations in equal abundances. In other words, the macrocycles of the [2]catenanes were able to rotate freely and have a high degree of lateral movement freedom as well. Three kinds of [2]catenane monomers (**50-ma**, **50-mb**, and **50-lc**) were polymerized. **50-ma**, bearing two carboxylic groups on each ring, was polyesterified with 1,4-bis(bromomethyl)benzene, and poly[2]catenane **51-m** was obtained. GPC analysis revealed a broad mass distribution, and a considerable amount of intramolecular cyclic pretzel-like product was formed. The average molecular weights given by GPC analysis with PS calibration were M_w = 95.2 kDa and M_n = 28.9 kDa, corresponding to DP_n = 10. **52-m** was prepared by the polyesterification of AB monomer **50-mb**. Similarly, a broad mass distribution and a significant amount of cyclic product were indicated. GPC analysis with PS calibration showed the average molecular weights were M_w = 56.4 kDa and M_n = 20.9 kDa, corresponding to DP_n = 7. The very convenient and facile reaction—acyclic diene metathesis (ADMET)[125−127] polymerization—was tried in an attempt to increase the molecular weight of the polymers. Acyclic α,ω-diene **50-lc** was polymerized with a typical Grubbs catalyst to give poly[2]catenane **53-l**.[128,129] The molecular weights provided by GPC analysis with PS



54 **55**

Figure 15. Synthesis of side-chain poly[2]catenane **55**.

calibration were $M_w = 69.3$ kDa and $M_n = 33.0$ kDa, corresponding to $DP_n = 12$. But its ^1H NMR spectrum indicated that the product probably was comprised of cyclic oligomers, since no signals for the terminal olefinic protons were observed. All the poly[2]catenanes synthesized based on this approach have relatively low DPs, and considerable amounts of cyclic side products were obtained during the polymerization. This observation is understandable in light of Shimada's[108] and Sauvage's[105,106] results, considering the high flexibility of the large ring [2]catenanes. In any case, the strategy designed and used here still is meaningful by providing a new methodology for the synthesis of polycatenanes.

3. Side-Chain Polycatenanes and Their Properties

Side-chain polycatenanes (**C** and **D** in Figure 1), as implied by their name, are polymers in which the catenane subunits are part of the pendant groups. Since the catenane structures exist as pendants or branches, different properties are expected compared to the cases of the main chain polycatenanes. Theoretically, an [*n*]catenane structure could be introduced into the polymer as branches. But from the point of the synthetic methodology, there is the same problem as in the preparation of the linear poly[*n*]catenanes. Thus, up to now, only poly[2]catenane-type side-chain polycatenanes have been reported. Here we will mainly discuss the preparation of side-chain poly[2]catenanes. These poly[2]catenanes can be prepared by the routes shown in Scheme 4. In route i, the difunctional [2]catenane monomers bearing both functional groups on the same ring are synthesized first and then incorporated into the polymer to produce side-chain poly[2]catenanes. In route ii, the macrocycles are incorporated into the polymer backbone first and then cyclization reactions of the other macrocycle's precursors via pseudorotaxane formation afford side-chain poly[2]catenanes. In route iii, the monofunctionalized [2]catenane monomer is directly incorporated via grafting reactions. Similar to route ii, in route iv the macrocycles are grafted onto the polymer first and this process is followed by the cyclization reaction between the second macrocycle's precursors via a pseudorotaxane intermediate. Obviously, routes i and iii are more significant than routes ii and iv in terms of synthetic feasibility and the integrity of the resulting poly[2]catenanes.

Stoddart et al. reported the first side-chain poly[2]catenanes[118,130] based on the tetracationic cyclophane-aromatic crown ether via route i (Figure 15). By utilizing the familiar π-donor/π-acceptor template method, difunctional [2]catenane monomer **54** bearing both hydroxyl groups on the same ring was prepared. The polymerization of **54** with bis(4-isocyanatophenyl)methane afforded side-chain poly[2]catenane **55**. The successful formation of polyurethane **55** was proven by GPC and IR analyses. GPC determination performed on the chloride salt of **55** gave a molecular weight M_n of 27.0 kDa, corresponding to a DP_n of 20.

Simone et al. reported another tetracationic cyclophane-aromatic crown ether type side-chain poly[2]catenane via route i (Figure 16).[131] [2]Catenane monomer **57** bearing two 3,4-(ethylenendioxy)thiophene groups on the same ring was prepared via the coupling reaction between the dicationic bis(bipyridinium) salt and *p*-xylylene dibromide in the presence of the templating crown ether **56**, followed by counterion exchange. By electrochemical polymerization of the thiophene units of **57**, side-chain poly[2]catenane **58** was formed, as proven by cyclic voltammetry.[132]

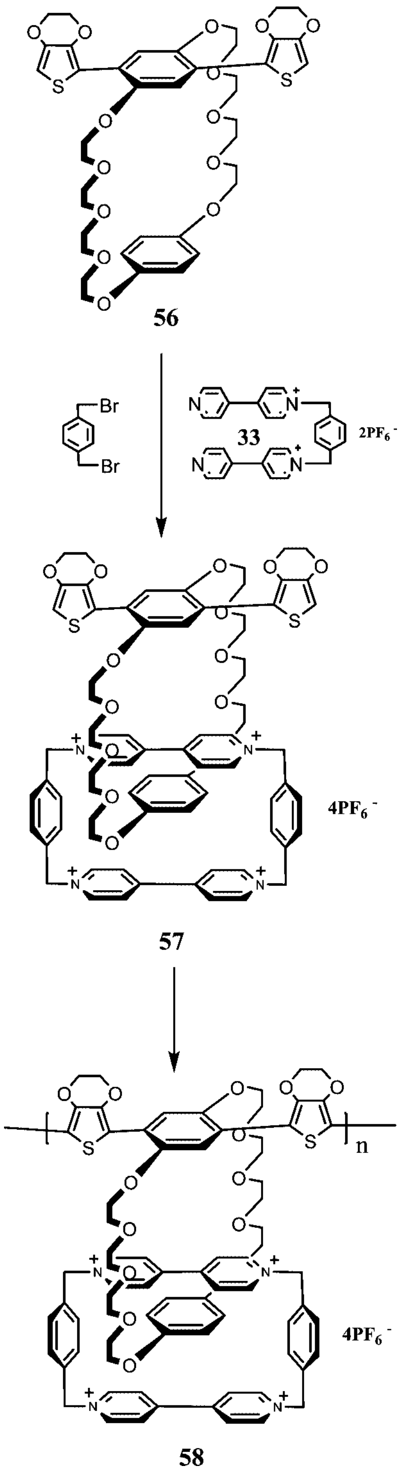


Figure 16. Synthesis of side-chain poly[2]catenane **58**.

Recently, Bria et al. reported a synthesis of a side-chain poly[2]catenane by "click chemistry" (Figure 17).[133] An alkyne group was introduced into the [2]catenane monomer **61** by the template-directed coupling reaction between dicationic bis(bipyridinium) salt **33** and the alkyne-substituted *p*-xylylene dibromide **60** in the presence of dinaphtho crown ether **59**.[134] Polymer **63** was prepared by substitution of the chloro group on styrene-vinylbenzyl chloride copolymer **62** ($M_n = 3.7$ kDa, $M_w = 6.3$ kDa) with sodium azide.[135−138] Several "click chemistry" attempts were performed by using either $CuSO_4$/ascorbic acid or CuI as catalyst;[139−142] the $CuSO_4$/ascorbic acid proved to be the most effective catalyst. The side-chain poly[2]catenane **64** was obtained by subse-

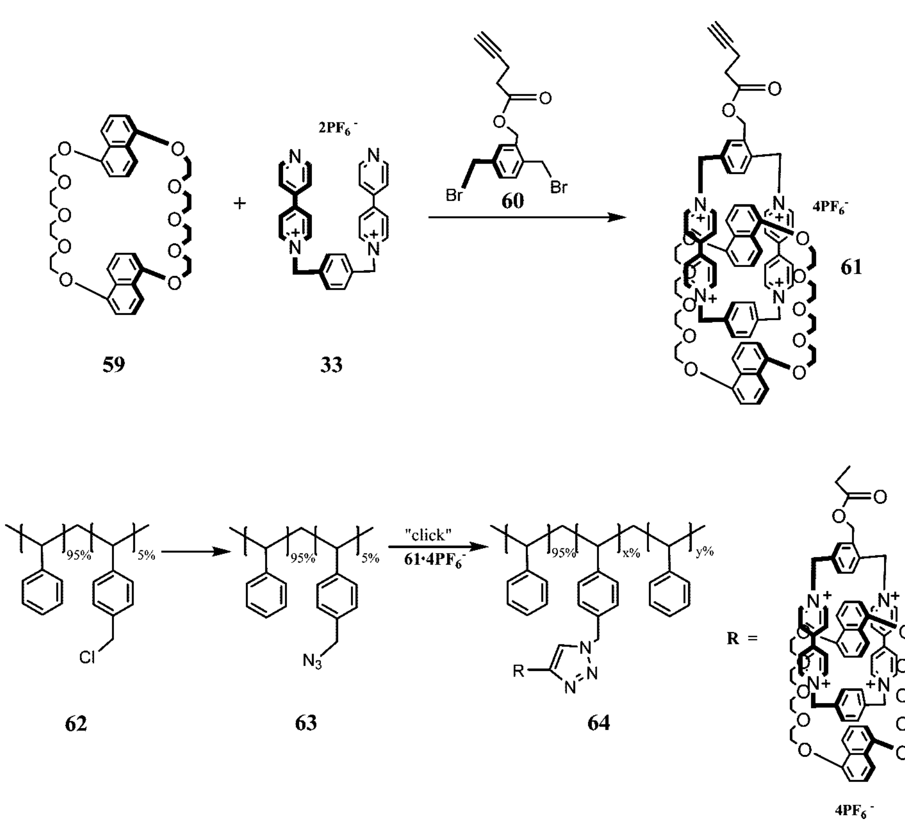


Figure 17. Synthesis of side-chain poly[2]catenane **64**.

quent precipitation, and the polymer structure was proven by FTIR and ^{1}H NMR analyses. Moreover, ^{1}H NMR and FTIR results indicated that the reaction of all of the available azide groups did not occur. The low grafting density was attributed to a combination of Coulombic repulsion of the cyclophane units and steric hindrance brought about by the bulky catenane units.[143] The exact ratio between catenane structures which were "clicked" onto the polymer chains and unreacted azido groups could not be determined due to the broad nature of the ^{1}H NMR signals.

Stoddart's group reported another similar bistable side-chain poly[2]catenane system based on the tetracationic cyclophane-aromatic crown ether motif (Figure 18).[144] By employing the same method described above, bistable [2]catenane monomer **67** bearing a alkyne group was afforded via template-directed coupling reaction between dicationic bis(bipyridinium) salt **33** and alkyne-substituted *p*-xylylene dibromide **66** in the presence of crown ether macrocycle **65**. The bistability of **67** arises from an equilibrium between two switchable isomers in which the ground-state coconformation (GSCC) and the metastable-state coconformation (MSCC) correspond to encirclement within the polyether ring of the tetrathiafulvalene (TTF) and dioxynaphthalene (DNP) units, respectively, by the CBPQT^{4+} ring. At 298 K, the ratio between GSCC and MSCC is about 9:1.[145] Side-chain azide-functionalized polymer **70** (M_w = 55.0 kDa, M_n = 39.0 kDa, PDI = 1.4) was synthesized by the atom transfer radical polymerization (ATRP) of azide-functionalized monomer **69**, which was prepared by the reaction between 2-(2-(2-azidoethoxy)ethoxy)ethanol **68** and methacryloyl chloride. The bistable side-chain poly[2]catenane **71** was obtained via "click chemistry" between polymer **70** and [2]catenane monomer **67**. ^{1}H NMR analysis gave a molecular weight M_n of 128.0 kDa. Size exclusion chromatography coupled with multiangle light scattering (SEC-MALS) indicated M_n = 870.0 ± 61.0 kDa, M_w = 1300.0 ± 70.0 kDa, and PDI = 1.5 ± 0.1, suggesting aggregation. The SEC-MALS, dynamic light scattering (DLS), and scanning electron microscopic (SEM) analyses showed that poly[2]catenane **71** self-assembled in solution into a supramolecular architecture consisting of hollow spherical nanoparticles in solution and their higher aggregates. Variable temperature (VT) ultraviolet–visible spectroscopy (UV/vis) of **71** indicated that low temperature favored the GSCC isomer and high temperature favored the MSCC isomer. Also, the TTF moiety underwent a sequential and reversible two-electron oxidation process (TTF to TTF$^{\bullet+}$ to TTF^{2+}) and this process triggered switching through circumrotation of the polyether ring with respect to the CBPQT^{4+} ring; therefore, the switching behavior of the bistable poly[2]catenane **71** can be induced electrochemically or chemically; this was proven by UV/vis, cyclic voltammetric (CV), and differential pulse voltammetric (DPV) analyses. These observations proved that the bistable poly[2]catenane, which assembles into larger secondary superstructures, still works as a molecular switch under chemical or electrochemical control.

4. Catenane Structures Based on Cyclic Polymers

The subjects discussed above focus on the incorporation of the topological catenane structures into linear polymer chains, as shown by types **A**–**D** in Figure 1. In this section, catenane structures based on cyclic polymers,[23,146–152] as shown by type **E** in Figure 1, will be discussed. The polymeric catenanes of type **E** are composed of at least one cyclic polymer threaded through other cyclic polymers or relatively small rings. Polymeric catenanes, as the unwanted side products formed during the preparation of the cyclic

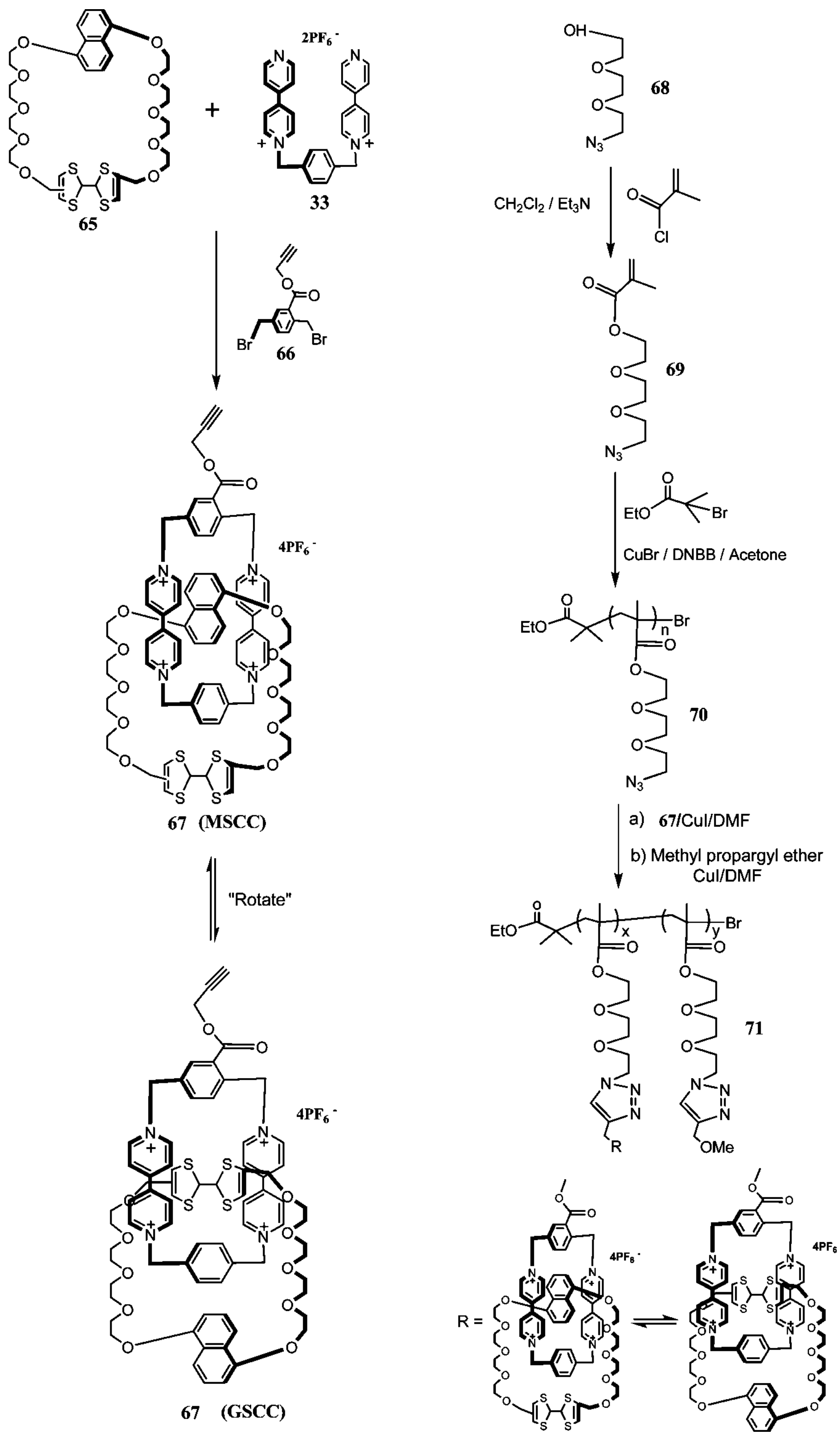
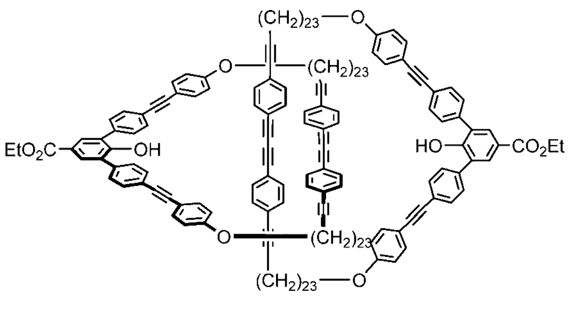


Figure 18. Synthesis of bistable side-chain poly[2]catenane **71**.

polymers, have been well-known for a long time.[23,153,154] But the separation of the polymeric catenanes always is problematic in view of the complexity of the crude product, which is composed of polydisperse catenated, linear, and cyclic species.[155] Commonly proposed or used approaches toward polymeric catenanes all involve threading of a linear polymer through preformed cyclic polymer rings and subsequent cyclization of the threaded linear polymer chains in the resultant pseudorotaxane.[156−158] High-dilution conditions are always required so as to favor the cyclization process vs linear chain extension. But on the other hand, the high dilution conditions statistically limit the extent of threading. In order to solve this problem, Unsal and Godt designed and synthesized polymeric [2]catenane **72**[123,159] (Figure 19) by utilizing a covalent bond—a carbonate group—to favor the threading. This strategy is the same strategy used by Godt et al. to synthesize poly[2]catenanes **51-m**, **52-m**, and **53-l**. Poly[2]catenanes **51-m**, **52-m**, and **53-l** are also good examples in that the cyclic components are quite large.

Hogen-Esch and co-workers reported the successful synthesis, isolation, and characterization of a polystyrene−poly(2-vinylpyridine) (**PS-P2VP**) block copolymeric [2]catenane[160,161] (Figure 20), in which the two macrocycles comprise the two blocks. The synthesis includes two steps. First, the linear



72

Figure 19. Structure of polymeric [2]catenane **72**.

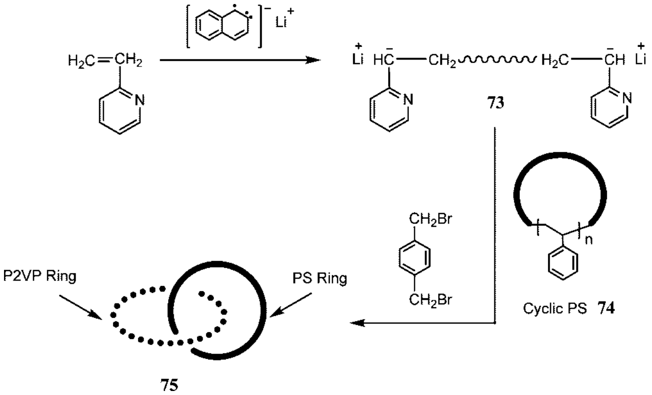


Figure 20. Synthesis of polystyrene−poly(2-vinylpyridine) (**PS-P2 VP**) based copolymeric block [2]catenane **75**.

P2VP dianion **73** was prepared by the polymerization of 2-vinylpyridine initiated by lithium naphthalenide. Then, the cyclization of the **P2VP** dianion with 1,4-bis(bromomethyl)benzene was carried out in the presence of a relatively high concentration of cyclic polystyrene **74**[162] (apparent peak molecular weight: $M_p = 4.5$ kDa) in order to favor catenane formation via the intermediate pseudorotaxane. The crude product was a mixture including polymeric catenane **75**, cyclic polystyrene **74**, and other side products. By taking advantage of the orthogonal solubility[163] between the polymeric catenane and other side products, **75** was isolated by washing the crude product with methanol, which is a good solvent for **P2VP** and a poor solvent for **PS**, and cyclohexane, which is a good solvent for cyclic **PS** and a poor solvent for **P2VP**. Since both methanol and cyclohexane are poor solvents for copolymeric [2]catenane **75**, it was collected as a solid after the washing protocols. Indications for the successful formation of the polymeric catenane were obtained by GPC and NMR analyses. The molecular weight (M_p) given by GPC was about 10.3 kDa, corresponding to the sum of the masses of the two rings. Fluorescence studies showed that the excimer emission of the **PS** block in **75** was significantly lower than those of both the linear and cyclic block copolymers **PS**-b-**P2VPs**, composed of blocks with similar molecular weights to those of the blocks in **75**. This observation was attributed to the unusual topology, which allows close contact of the pyridyl and styryl units in the catenane but not in the other polymers, and provided further evidence for the formation of the copolymeric [2]catenane structure.[164]

Takano et al. recently reported a synthesis of a catenated polystyrene (**PS**)−polyisoprene (**PI**) with high molecular weight[165] (Figure 21). The telechelic poly(isopropenylnaphthalene-*b*-styrene-*b*-isopropenylnaphthalene) **76**[166,167] was

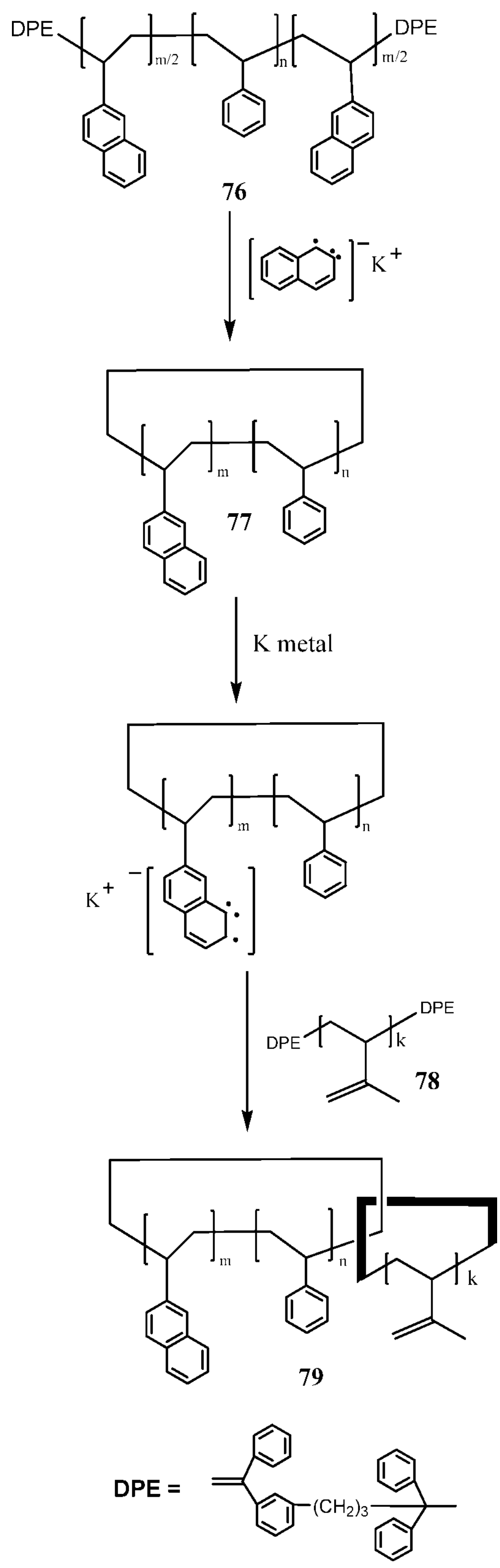


Figure 21. Synthesis of polystyrene (**PS**)−polyisoprene (**PI**) based copolymeric [2]catenane **79**.

prepared via living anionic polymerization followed by a two-step chemical modification of the chain ends. Cyclic polymer **77** ($M_p = 11.3$ kDa) was formed by cyclodimerization of triblock copolymer **76** initiated by potassium naphthalenide under high dilution conditions. Telechelic **PI** **78** was synthesized by the same process. Then cyclic polymer

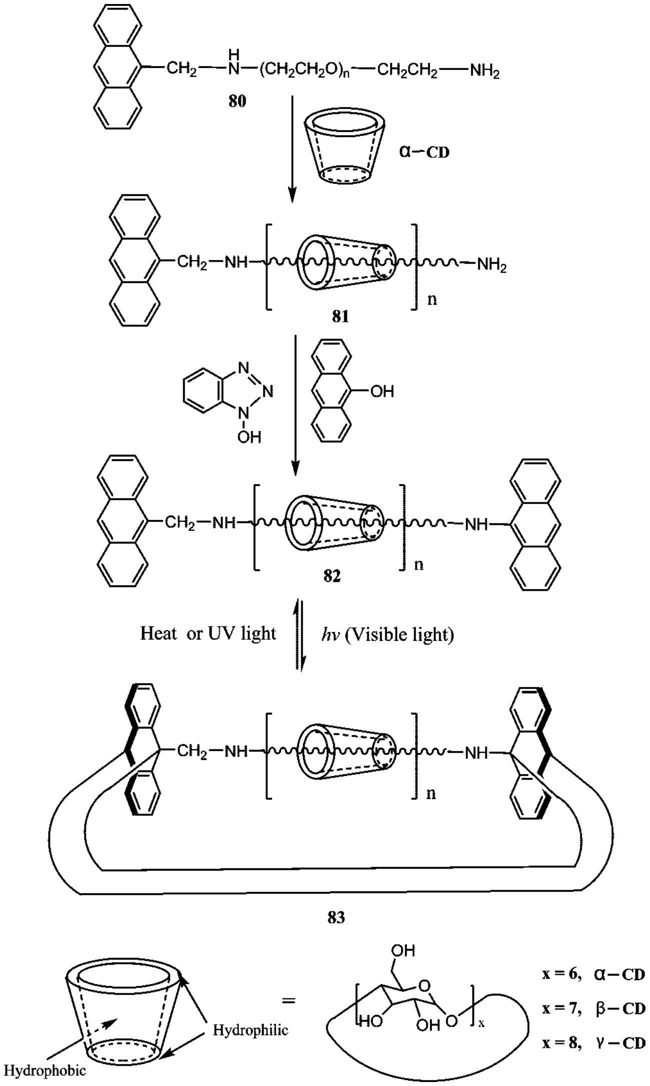


Figure 22. Synthesis of polycatenane **83**.

77 was converted to the radical-anion with potassium metal and telechelic **PI 78** was added into the dilute radical-anion solution of **77**. Cyclodimerization of **78** proceeded by electron transfer under high dilution conditions to yield polymeric [2]catenane **79** (M_n = 36.8 kDa). The separation of the crude product was performed in two steps. In the first step, the crude product was washed with *n*-hexane to remove the remaining **PI 78** and its cyclic derivative. In the second step, GPC was used to remove **77**. Successful formation of the copolymeric [2]catenane structure was confirmed by GPC, NMR, and ozonolysis. Transmission electron microscopic (TEM) investigation revealed that **79** exhibited a nanophase-separated structure in the bulk.

Another subset of polymeric catenanes of type **E** consists of cyclic polymers and other relatively small rings. Harada and co-workers reported a synthesis of this type of polycatenane based on cyclodextrins[168] (Figure 22). Cyclodextrins (CDs),[169−175] as good hosts in supramolecular chemistry, are constructed of 6 or more 1,4-linked D-glucopyranoside units. Three commonly used are α-, *β*-, and *γ*-cyclodextrins (CDs) (Figure 22), containing 6, 7, and 8 glucopyranoside units, respectively. Since the CDs have hydrophilic external faces and hydrophobic interior faces, linear guest molecules with suitable sizes that have two hydrophilic ends and a hydrophobic middle part thread through the cavities of CDs in polar solvents. Thus, the hydrophilic ends of the guest molecules stay outside in the polar solvent and the hydrophobic middle parts will insert into the cavities of CDs, freeing the previously entrapped solvent and resulting in an entropic driving force for complexation. Harada et al. found α-cyclodextrin (α-CD) forms inclusion complexes with poly(ethylene glycol) (**PEG**).[176,177] Therefore, α-CD was selected as a cyclic component and **PEG** was used as the axle. First the **PEG 80** (M_w = 2.0 kDa) with a 9-anthryl group at one end of the polymer chain was prepared; the 9-anthryl group prevents dethreading and forms dimers upon photoirradiation.[178,179] Then the **PEG 80** was treated with α-CD and semipolyrotaxane **81** was obtained. Semipolyrotaxane **81** was capped with another 9-substituted anthracene to afford polyrotaxane **82**, which contained one CD for every two ethyleneoxy units. The exposure of polyrotaxane **82** to visible light in dilute solution (7×10^{-3} mM) afforded polycatenane **83** ($DP_n = 2-10$) and unreacted linear polymer. Several other so-called "molecular necklaces", which were composed of CDs with other nonpolymeric rings, were reported by Harada's group,[180,181] Kim's group,[182−186] and Stoddart's group.[187] Since they are not polymeric, they will not be discussed in detail here.

5. Catenane Structures in the Polymer Networks

Catenane structures are probably formed during the cross-linking of many polymer networks, but the structures are not always recognizable due to the complexity of polymer networks and analytical technique limitations. Typical polymer networks based on catenane structures are illustrated by type **G** and type **H** in Figure 1. Type **F**, named polycatenane networks, represents polymer networks which are formed solely by catenane subunits. In these networks some rings are interlocked with more than two other rings and act as cross-link points. Type **G** represents a more general series of polycatenane networks compared with **F**. The catenane subunits exist as branches, cross-link points, or repeating units in the polymer networks. Although the existence of polycatenane networks of type **F** was proven by the investigation of kinetoplast DNA of *Crithidia fasciulata*,[188,189] in which thousands of DNA minicircles are mechanically interlocked with each other, the synthesis and characterization of polycatenane networks still are problematic on account of their complexity.

Endo et al. reported a synthesis of poly(1,2-dithiane) (**PDT**)[190,191] which was suggested to include polycatenane structures due to the propensity for cyclization in this system (Figure 23). Polymer **86** resulted from the bulk polymerization of 1,2-dithiane **84** above its melting point without initiators. ^{13}C and ^{1}H NMR suggested that **PDT** consisted of a macrocylic structure including disulfide bonds; the cyclic structure was further proven by mass spectroscopy and photodegradation analysis. Moreover, the molten state of the **PDT** showed a rubbery plateau according to dynamic viscoelastic measurements. The T_g of **PDT** decreased with increasing molecular weight. All of these observations are different with respect to linear **PDT** with benzyl mercaptan moieties as terminal groups. These results provided other evidence for the formation of polycatenane networks. Further, they tried the thermal copolymerization[192] between 1,2-dithiane **84** and lipoic acid (**LPA**) **85**, and a copolymer **87** with high molecular weight was obtained. Similar to **86**, **87** contained polycatenane entanglement structures which were confirmed by ^{13}C NMR, ^{1}H NMR, and dynamic viscoelasticity measurements. However, the copolymer **87** was still

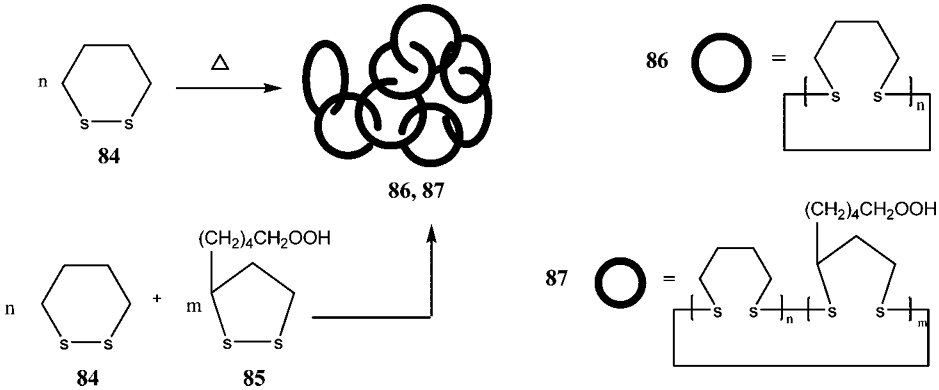


Figure 23. Synthesis of poly(1,2-dithiane)s **86** and **87** with polycatenane entanglement structures.

soluble in organic solvents, such as THF. This behavior was attributed to its lower molecular weight, which was below the gel point. Zinc acetate was used as a cross-linking reagent for **87** and a highly cross-linked metal-ionomeric network[193] resulted. The thermal stability of the ionomeric network was proven to be high, in accordance with the high degree of cross-linking.

Gibson et al. reported preparation of polyamide based polypseudorotaxanes containing polycatenane structures (Figure 24).[194,195] The condensation of bis(5-carboxy-1,3-phenylene)-(3*x*+2)-crown-*x* (**88a**−**d**) with 4,4′-oxidianiline (ODA) and bis[4-(*m*-aminophenoxy)phenyl]phenylphosphine oxide afforded poly(amide crown ether)s **89a**−**d** and **90a**−**b**, respectively. The systems based on the 32-membered crown ethers **89a** ($n = 3$) and **90a** ($n = 3$) were completely insoluble in all solvents, including sulfuric acid, which dissolves Kevlar. The smaller crown ether-based aramides ranged from partly gel−partly soluble (**89b** and **90b**, $n = 2$, 26-membered) to completely soluble (**89c**,**d**, $n = 1, 0$; 20- and 14-membered) systems. GPC revealed that branching decreased as the ring size of the crown ethers decreased. In all cases, ^{1}H NMR was possible for the swollen gels and, of course, the soluble species; no unusual covalent chemistry took place. Mass spectrometry confirmed the formation of cyclic polymers in the polycrown ethers derived from the 32- and 26-membered crown ether diacids, as well as in model aramides from isophthalic acid and ODA, which remain completely soluble. It was, therefore, concluded that branching and network formation takes place first by threading of the crown ether moieties, leading to polypseudorotaxane structures; this coupled with end-to-end cyclization of the linear polyamide leads to catenanes and ultimately catenane networks to an extent dependent upon the cavity size of the crown ether and the propensity for the cyclization of the backbone species.

Later, Garcia et al. observed gel formation during the synthesis of several polyamides containing the benzo-18-crown-6 unit.[196] The gel formation was attributed to the formation of the rotaxane, polyrotaxane, catenane, and/or polycatenane structures. This is not the result of catenane formation via threading of the crown ether moieties, however, because the 18-membered ring is too small to be threaded.

6. Conclusions and Perspective

By incorporation of mechanically interlocked catenane structures, polymers are expected to exhibit novel topologies and properties compared with conventional polymers. For this reason, these polymers have attracted considerable attention and much progress has been made during the past decade.

This review has focused on polymers containing catenane structures. According to the location and connection of the catenane subunits, four major classes were described: main chain polycatenanes, side-chain polycatenanes, catenane structures based on cyclic polymers, and catenane structures in the polymer networks. Up to now, much effort has been devoted to poly[2]catenanes, since they have the essential mechanically linkages associated with the catenane unit and can be prepared easily compared with true polycatenanes of type **A** (Figure 1), which are molecular chains. Many poly[2]catenanes have been successfully prepared. Moreover,

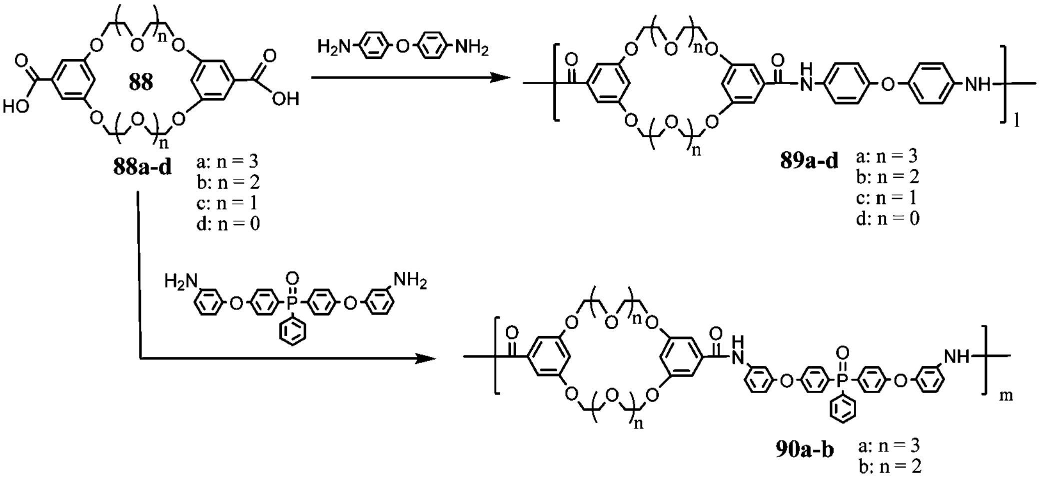


Figure 24. Synthesis of polypseudorotaxanes **89a**−**d** and **90a**−**d** containing polycatenane structures.

Table 1. Properties of Polycatenanes

polycatenane no.		M_n (kDa)	M_w (kDa)	DP_n	PDI	T_g (°C)
5				5	1.00	
7				7	1.00	
15a		$3.0^{a,b}$	$3.6^{a,b}$	1−5	1.2	
15b		$3.3^{a,b}$	$5.0^{a,b}$	2^{r}	1.5	245
18a		$34.0^{a,c}$	$59.1^{a,c}$	13	1.7	277
18b		$46.6^{a,c}$	$95.6^{a,c}$	18	2.1	207
20a	**10% (w/w)**	15.9^{d}	40.1^{d}	11^{r}	2.5	150
	20% (w/w)	9.9^{d}	41.4^{d}	7^{r}	4.2	150
	30% (w/w)	8.1^{d}	38.9^{d}	5^{r}	4.8	149
20b	**5% (w/w)**	$25.0^{b,e}$	$67.0^{b,e}$	19^{r}	2.7	∼75
	10% (w/w)	$21.0^{b,e}$	$61.0^{b,e}$	16^{r}	2.9	∼77
	20% (w/w)	$17.0^{b,e}$	$52.0^{b,e}$	13^{r}	3.0	∼80
22		15.0^{f}	30.0^{f}	11^{r}	2.0^{f}	
		16.0^{g}	32.0^{g}	12^{r}	2.0^{g}	
23b		$3.1^{b,h}$	$6.1^{b,h}$	2	1.9	
29a		$55.0^{b,h}$	$1800.0^{b,h}$		32.7	80
29b		$22.0-25.0^{i,j}$	$42.0-47.0^{i,j}$	8−9	1.7	75
31a						
31b		$810.0^{b,j}$	$3321.0^{b,j}$	609	4.1	
37		$26.5^{k,l}$	$30.0^{k,l}$	17	1.2	
38		$35.0^{k,l}$		25		
42		$45.0^{k,l}$		15		
43		$45.0^{k,l}$		15		
45		$150.0^{k,l}$		40^{r}		
51-m		$28.9^{a,b}$	$95.2^{a,b}$	10	3.3	
52-m		$20.9^{a,b}$	$56.4^{a,b}$	7	2.7	
53-l		$33.0^{a,b}$	$69.3^{a,b}$	12	2.1	
55		$27.0^{k,l}$		20		
58						
64						
71		870.0^{m}	1300.0^{m}		1.5^{m}	
72						
75		$10.3^{a,b}$	$13.39^{a,b}$		1.3	
79		$36.8^{a,b}$	$37.9^{a,b}$		1.0	
82				2−10		
86			$813.0^{a,b}$			
87		$365.0^{a,b,n}$	$726.0^{a,b,n}$		2.0	-43.3^{o}
89	**a**					114
	b	$36.0^{i,p}$	$189.0^{i,p}$	51^{r}	5.2	156
	c	$12.9^{i,p}$	$55.2^{i,p}$	21^{r}	4.2	207
	d	$53.8^{q,j}$	$151.0^{q,j}$	102^{r}	2.8	261
90	**a**					127
	b	$25.6^{i,p}$	$235^{i,p}$	26^{r}	9.1	174

[a] In tetrahydrofuran (THF). [b] Calibration with polystyrene (PSt) standards. [c] MALDI-TOF calibration. [d] In dichloromethane. [e] In chloroform/1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) 98/2. [f] Polymerization temperature was room temperature. [g] Polymerization temperature was 0 °C. [h] In $CHCl_3$. [i] Universal calibration. [j] In dimethylformamide (DMF). [k] Chloride salt of the corresponding polycatenanes with water as solvent. [l] Calibration with protein standards. [m] Determined by SEC-MALS analysis. [n] [LPA] in comonomer (mol %): 50. [o] [LPA] in comonomer (mol %): 58.1. [p] In *N*-methylpyrrolidinone (NMP). [q] Calibration with poly(methyl methacrylate) (PMMA) standards. [r] Calculated value. $DP_n = M_n$/molecular weight of repeating unit.

some progress has been made toward polymeric catenanes and polycatenane networks.

A lot of tools have been employed to characterize these novel polymers, such as NMR spectroscopy, mass spectrometry, GPC, and FTIR. Due to their unique topological nature, polycatenanes are expected to have unique rheological, dynamic, mechanical, and thermal properties. But property investigations have been limited by the low yields and more importantly limited quantities, even with poly[2]catenane systems which are relatively readily prepared. Table 1 summarizes the salient features of the polycatenanes that have been reported and discussed in this review.

Although some progress has been made, the syntheses of high molecular weight polycatenanes of type **A** (Figure 1) have still not been achieved and thus the features of these true “polymer chains” still remain unknown. The expansion of the present systems will be interesting. The development of new strategies or systems with high cyclization efficiencies is required for the preparation of high molecular weight polycatenanes of type **A** and other novel polycatenane systems. Since a lot of effort has already been expended in this field, undoubtedly many new polycatenane systems will be developed and some unique polymeric properties will be revealed in the near future.

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