Chapter 1

Polypseudorotaxanes and Polyrotaxanes

1.1. INTRODUCTION

As implied by their names, polypseudorotaxanes/polyrotaxanes[1] are constructed simply by incorporating pseudorotaxane/rotaxane moieties into polymers. According to how the cyclic and linear units are connected, different kinds of polypseudorotaxanes and polyrotaxanes can be made; those that have been studied up to now or are possible are summarized in Figure 1. Depending on the location of the pseudorotaxane/rotaxane unit, polypseudorotaxane/polyrotaxanes can be divided into two types: main chain polypseudorotaxanes (A and B in Figure 1)/polyrotaxanes (E-I in Figure 1), in which the pseudorotaxane/rotaxane unit is a part of the main chain, and side chain polypseudorotaxanes (C and D in Figure 1)/polyrotaxanes (J and K in Figure 1), in which the pseudorotaxane/rotaxane unit is a part of the side chain.

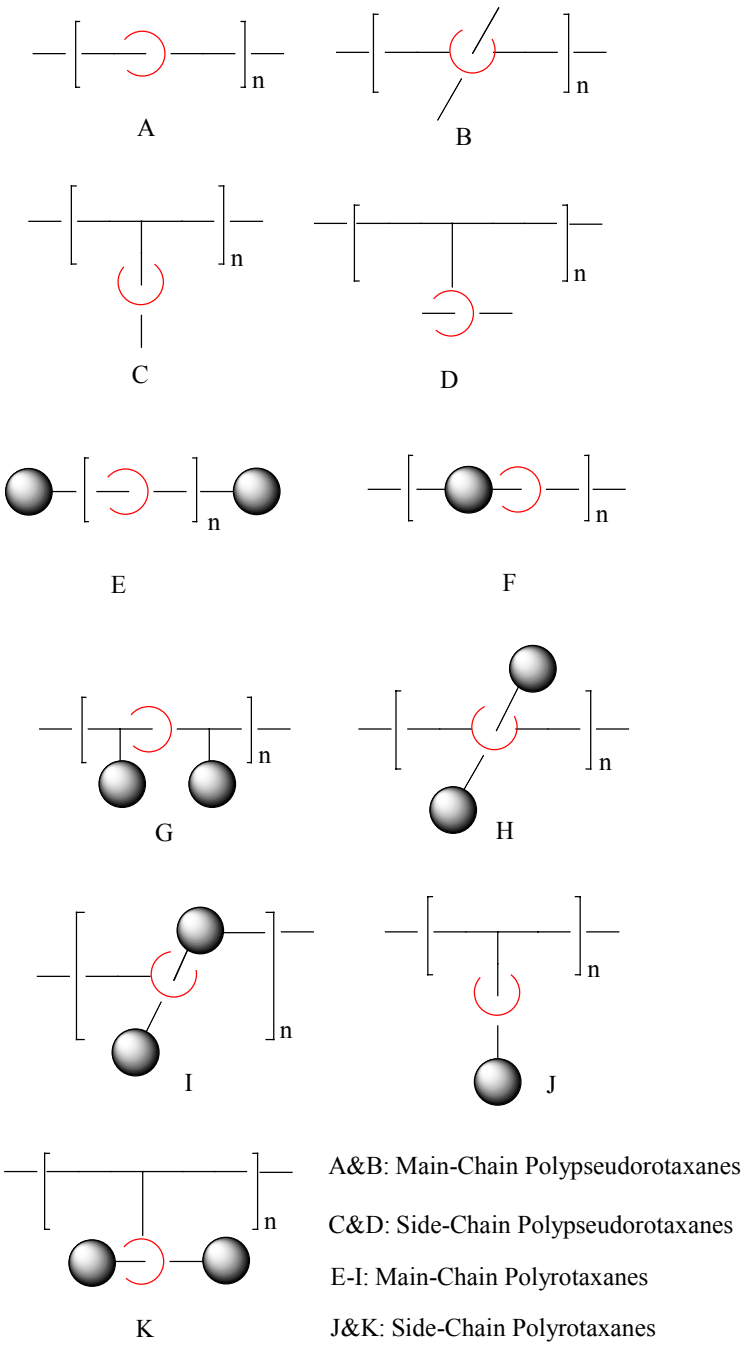


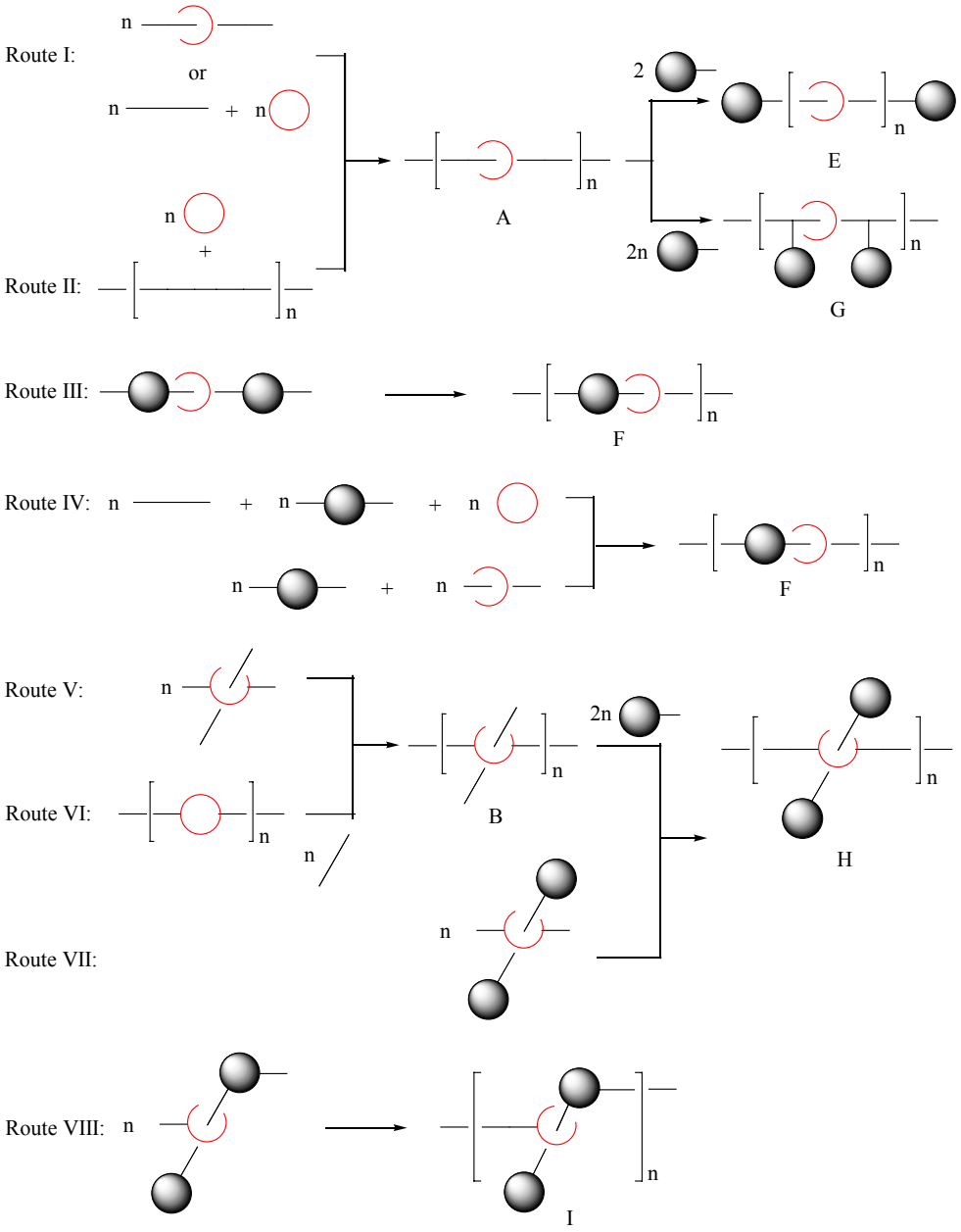
Figure 1. Various types of polypseudorotaxanes and polyrotaxanes.

Polypseudorotaxanes and polyrotaxanes possess mechanically linked subunits, for which the connecting forces are non-covalent interactions, while conventional polymers have covalent linkages only. Because there is no covalent bond between their linear and cyclic components, polypseudorotaxanes and polyrotaxanes can be viewed as composites at a molecular level. This is different from the interlocked structure form in interpenetrating polymer networks, where interlocking takes place on a supramolecular level. Due to their architectural differences from conventional polymers, polypseudorotaxanes and polyrotaxanes have unique properties. Since we published a review on polypseudorotaxanes and polyrotaxanes in 1994,[1a] remarkable progress has been made in the two fields of polypseudorotaxanes and polyrotaxanes in last decade. Here we will review this recent progress in five parts: main chain polypseudorotaxanes and polyrotaxanes incorporating cyclodextrins, main chain polypseudorotaxanes and polyrotaxanes incorporating crown ethers, other polypseudorotaxanes, polyrotaxanes and related structures, and properties and potential applications.

1.2. MAIN-CHAIN POLYPSEUDOROTAXANES AND POLYROTAXANES INCORPORATING CYCLODEXTRINS

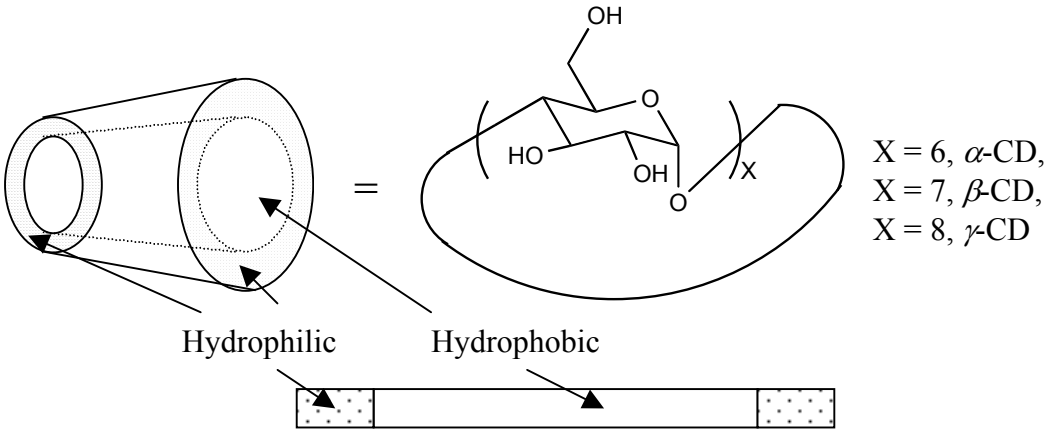
The main routes used or conceived to make main chain polypseudorotaxanes and polyrotaxanes are shown in Scheme 1. Route I involves the polymerization of a pseudorotaxane, while route II involves threading of *n* macrocycles onto an existing polymer. Route III is a polymerization of a rotaxane monomer. In route IV, the copolymerization of a difunctional pseudorotaxane and a difunctional stopper affords a polyrotaxane of type F in Figure 1. Route V also involves the polymerization of a pseudorotaxane. The difference between the two pseudorotaxanes used in route I and route V is that the two functional groups are on the linear component for the former but on the cyclic component for the latter. Linear components in route VI are threaded into the macrocycles incorporated in a preformed polymer to form a polypseudorotaxane of type B in Figure 1. Then stoppers are introduced to produce a polyrotaxane of type H in Figure 1. In route VII the polymerization of a rotaxane provides us with a polyrotaxane but here the two functional groups are on the cyclic component. This is different from the

rotaxane used in route III where two functional groups are on the two stoppers respectively. In route VIII, the polymerization of a difunctional rotaxane prouduces a polyrotaxane of type I in Figure1 but here the cyclic component and the linear component each bear a functional group.



Scheme 1. Synthetic routes for main chain polypseudorotaxanes and polyrotaxanes.

Cyclodextrins (CDs), extensively studied as host molecules in polypseudorotaxanes and polyrotaxanes, are a series of cyclic oligosaccharides of 1,4-linked D(+)-glucose units.[2] The three most commonly used CDs are α-, β-, and γ-CD. They have a cylindrical cavity having a depth of ca. 7.0 Å and an internal diameter of ca. 4.5 Å for α-CD, ca. 7.0 Å for β-CD, and ca. 8.5 Å for γ-CD.[2] These cylindrical cavities possess hydroxyl functionalities on the two rims and hydrocarbon and ether moieties in the interior of the cavity. Therefore CDs have a hydrophobic interior and hydrophilic external faces. The typical linear species used to form inclusion complexes with CDs have two hydrophilic ends and a hydrophobic middle part. When a guest like this and a CD dissolve in water or a polar solvent, the hydrophobic part of the guest species will insert inside of CD while the hydrophilic parts will stay outside to produce an inclusion complex. Therefore, the formation of these inclusion complexes is a result of CDs' geometry and functionality.



Yamaguchi et al.[3] used route I to synthesize a polyrotaxane 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 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. This polyrotaxane contains a blocking group in every structural unit of the main chain, as shown in Figure 2.

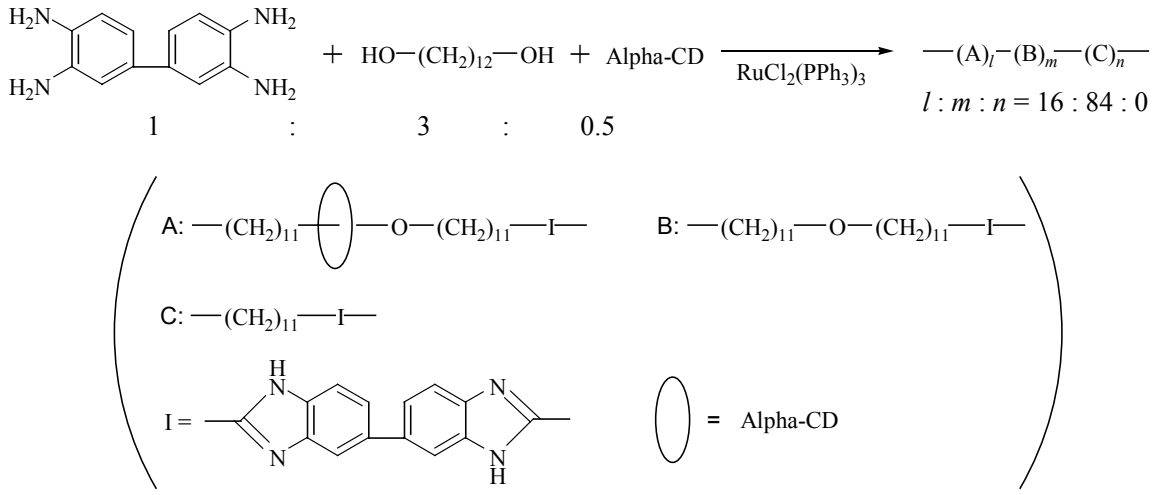


Figure 2. Polyrotaxane containing a blocking group in every structural unit of the polymer chain.

Wenz and Keller[4a,b] empolyed route II to prepare some main chain polyrotaxanes based on α-CD. In these polyrotaxanes, the steric barrier provided by the pyridyl rings traps the α-CD rings mechanically on the linear component. Later they made some other polyrotaxanes based on β- and γ-CD.[4c] The formation of the tetraphenylenecyclobutane blocking groups along the backbone of **4** was achieved by irradiating aqueous solution of **3**, which self-assembles spontaneously from its separate components, **1** and **2**, in the presence of both β- and γ-CD (Figure 3).

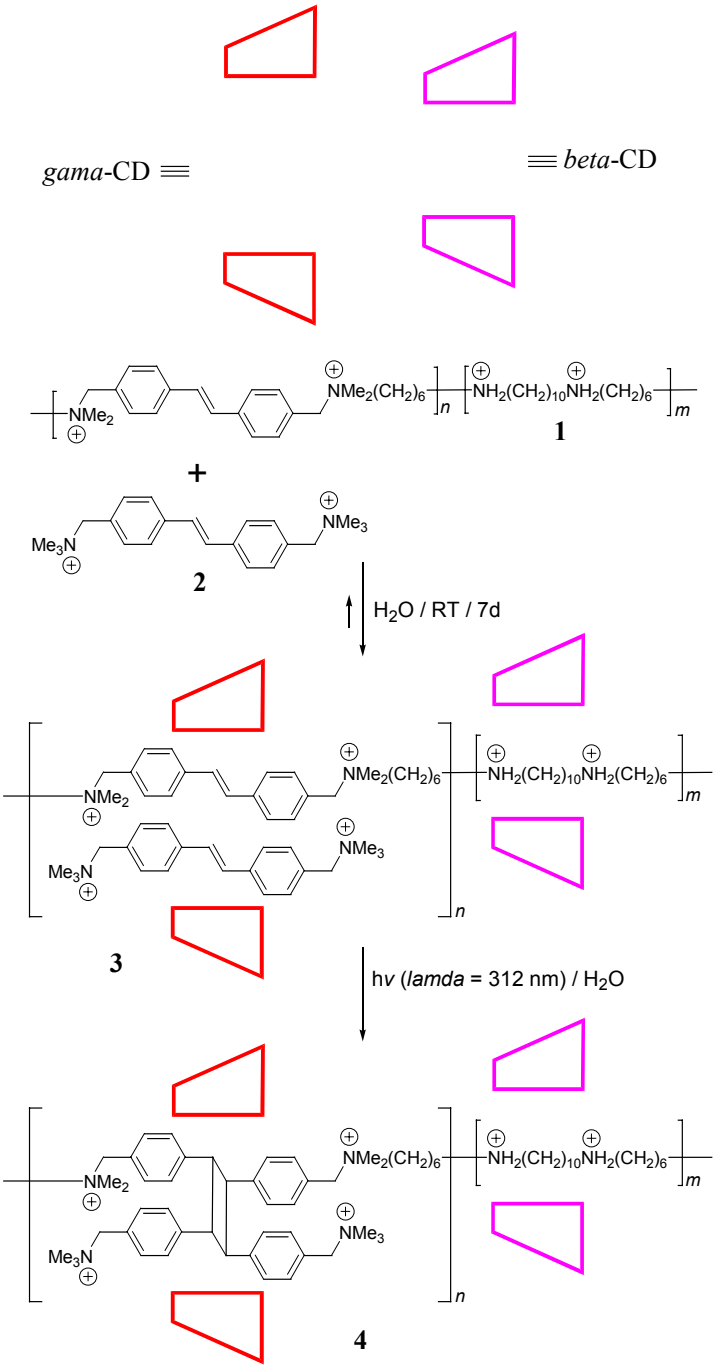


Figure 3. Synthesis of the cyclodextrin-based polyrotaxane **4** incorporating bulky groups along its polymer backbone.

Geckeler and coworkers prepared the first fullerene-terminated soluble poly(azomethine)-based polyrotaxane with β-CD as the macrocylic component in order to improve the solubility of poly(azomethine), a important conducting polymer, in common organic solvents.[5]

Yui's group has been very active in preparing CD-based polypseudorotaxanes and polyrotaxanes.[6-12] The linear polymers used in these polypseudorotaxanes and polyrtoaxanes are mainly poly(ethylene glycol) (PEG) and poly(propylene glycol) (PPG). They used route II to prepare a series of biodegradable polyrotaxanes mainly based on hydrolysis of terminal stoppers.[6-9] This group[10a,b] used route II to make a polyrotaxane, in which many β-CDs are threaded onto a triblock copolymer of PEG and PPG capped with fluorescein-4-isothiocyanate (Figure 4). The majority of the β-CDs moved toward the PPG segment with increasing temperature, although some β-CDs may reside on the PEG segments. This polyrotaxane was applied as a model of stimuli-responsive molecular assemblies for nanoscale devices. They made a new water-soluble main-chain polypseudorotaxane (Figure 5) by simple mixing of two aqueous solutions of poly(ε-lysine) and α-CD.[10c] This polypseudorotaxane has a higher decomposition temperature than both poly(ε-lysine) and α-CD. Recently pH-responsive polypseudorotaxanes of polyethylenimines with various molecular weights threaded through α- or γ-CD were prepared by this group.[10f] In the study of polypseudorotaxanes based on α-CD and biodegradable poly(L-lactide)-poly(ethylene glycol)- poly(L-lactide) triblock copolymer, they found that α-CDs could slide over the flanking bulky poly(L-lactide) blocks to form an inclusion complex with poly(ethylene glycol) blocks while α-CDs form very stick pseudorotaxanes with the end blocks of poly(L-lactide).[10g] Further studies were done on an ABA triblock copolymer, consisting of linear polyethylenimine (PEI) and PEG (PEI-*block*-PEG-*block*-PEI), for pH-dependent polypseudorotaxane formation with α-CDs.[10i] Although no complexation was observed for the mixture of α-CDs and PEI homopolymers, the polypseudorotaxane of PEI-*block*-PEG-*block*-PEI copolymer with α-CDs was prepared. Furhermore, the ratio of repeating units to α-CD could be controlled by adjusting pH. In the preparation of a tripeptide-terminated polyrotaxane,[11] Yui and coworkers found that the formation of the supramolecular structure could enhance the

accessibility of a membrane-bound zinc metalloexopeptidase to the terminal peptide moiety. This finding will provide a new design of polymers with controlled degradation profile for biomedical applications. Some other polyrotaxane-related structures with potential biological applications, such as drug delivery, were prepared by this group.[12]

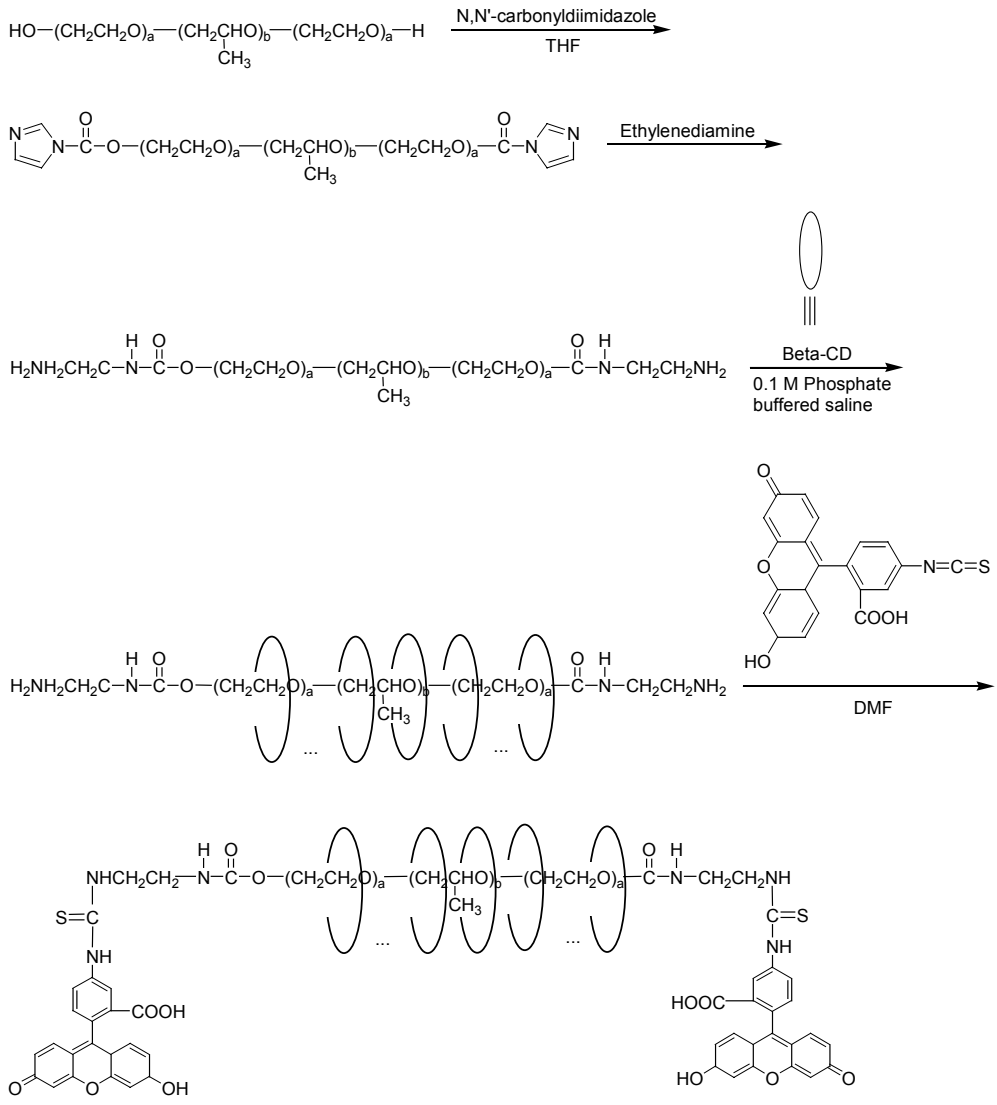


Figure 4. Synthesis of a polyrotaxane consisting of β-CD and poly(ethylene glycol)-poly(propylene glycol) triblock copolymer.

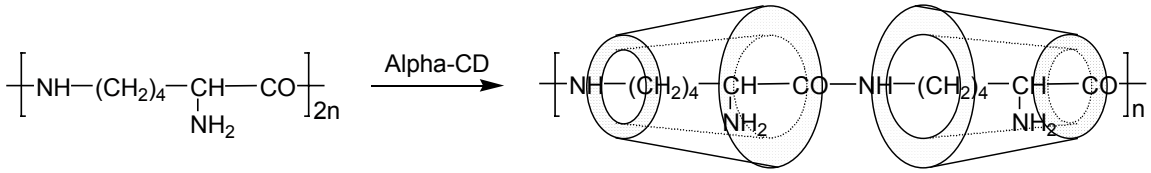


Figure 5. Synthesis of a main-chain polypseudorotaxane based on poly(ε-lysine) and α-CD.

The interaction between the CD-based polyrotaxanes and the surrounding water molecules plays an important role on the mechanical properties and reactivity of polyrotaxanes in aqueous solutions. Sano's group used Raman intensity of the collective band to study the order of the structure of water molecules in order to clarify this type of interaction.[13]

Recently, people have become interested in carbohydrate-displaying pseudopolyrotaxanes and polyrotaxanes of CDs threaded onto linear polymer chains as dynamic multivalent neoglycoconjugates.[14] Yui and coworker studied α-CD-based poly(ethylene glycol) polyrotaxanes displaying variable amounts of maltose residues in a concanavalin A hemagglutination assay.[14a] The Stoddart group prepared α-CD-based pseudopolyrotaxanes displaying lactosides for binding to lectins.[14b,c] All these studies demonstrated that the formation of supramolecular structures, like polypseudorotaxanes and polyrotaxanes, could enhance protein-carbohydrate interactions in a dynamic multivalent way.

Lo Nostro et al. studied the kinetics of the threading of CDs onto linear polymers, α-CD onto PEG[15a] and β- & γ-CD onto PPG.[15b,c] They found that the threading was favored by low temperature and solvents with a strong hydrogen bonding network (D_2O > H_2O > urea). A model was proposed to interpret the temperature and solvent composition effect on the threading process. Furthermore, transition state theory was used to calculate the Gibbs free energy change (ΔG) related to this process and the number of α-CD molecules that participated in the formation of the three polypseudorotaxanes. It was found that ΔG changes little with temperature. An enthalpy/entropy compensation was found in these systems. They studied the effect of

salts on the threading process for a polypropylene glycol derivative with β-CD. Changes in the threading time are strongly dependent on the nature of both cations and anions. They demonstrated that the diversity of salt effects is related to the microscopic frequency dependent dielectric properties of the ion pair, which account for the dispersion potential experienced by the different ions in solution. Recently they found that threaded α-CD rings on PEG polymer chains form wormlike aggregates ("poly-CD") in water solutions.[15d] Tait and Davies[15e] studied the kinetics of polypseudorotaxane formation between the cyclodextrin and poly(ethylene glycol) dimethyl ether (DMPEG) using the lag time approach. They found that the inclusion of poly(ethylene glycol) by α-CD is mainly driven by the precipitation of the polypseudorotaxane. Though α-CD has been found not be able to form polypseudorotaxanes with PPG,[15b,c] it can form polypseudorotaxanes with a PEG-PPG random copolymer[15f] and PPG-PEG-PPG triblock copolymers[15g] as shown by works done by Li and coworkers. The kinetic studies of these inclusion complexes revealed that the threading time is strongly dependent on the PPG block lengths, because the α-CD molecules have to first overcome the energy barrier to slide over the PPG blocks before forming stable complexes with the middle PEG block.[15g]

Harada and coworkers[16] reported the synthesis of the first molecular tube (MT) by crosslinking adjacent hydroxyl groups on α-CDs in a polyrotaxane in 1993. Because of the MT's large and hydrophobic cavity, it can form inclusion complexes with guest molecules containing a long hydrophobic segment. One MT recently made by Yui's group[17] is shown in Figure 6. First α-CDs were threaded onto α,ω-diamino poly(ethylene oxide) to form a polypseudorotaxane, **5**. Then **5** was capped to produce a polyrotaxane **6**. Hydroxyl groups adjacent to the α-CDs on **6** were crosslinked by epichlorohydrin to form **7**. At last the dinitrophenyl groups at the ends of **7** and the linear polymer backbone were removed to form the MT, **8**. This group studied thermodynamics involved in the inclusion complexations of the MT with sodium dodecyl sulfate (SDS)[17a] and sodium alkyl sulfonates (C_nSO_3Na).[17c] They found that the inclusion complex between MT and SDS was more stable than that between α-CD and SDS. Each MT was observed to form the inclusion complex with two guest molecules, SDS or C_nSO_3Na with different alkyl chain lengths. Enthalpy/entropy compensation was also found in the two systems. The

thermodynamic analysis of inclusion complexation between α-CD-based MT and poly(ethylene oxide)-*block*-poly(tetrahydrofuran)-*block*-poly(ethylene oxide) triblock copolymer (PEO-*b*-PTHF-*b*-PEO) demonstrated that the dehydration of the triblock copolymer is a key factor in inclusion complexation between MT and PEO-*b*-PTHF-*b*-PEO.[17d] This group also prepared a supramolecular network through inclusion complexation of an α-cyclodextrin-based molecular tube with grafted PEG.[17b]

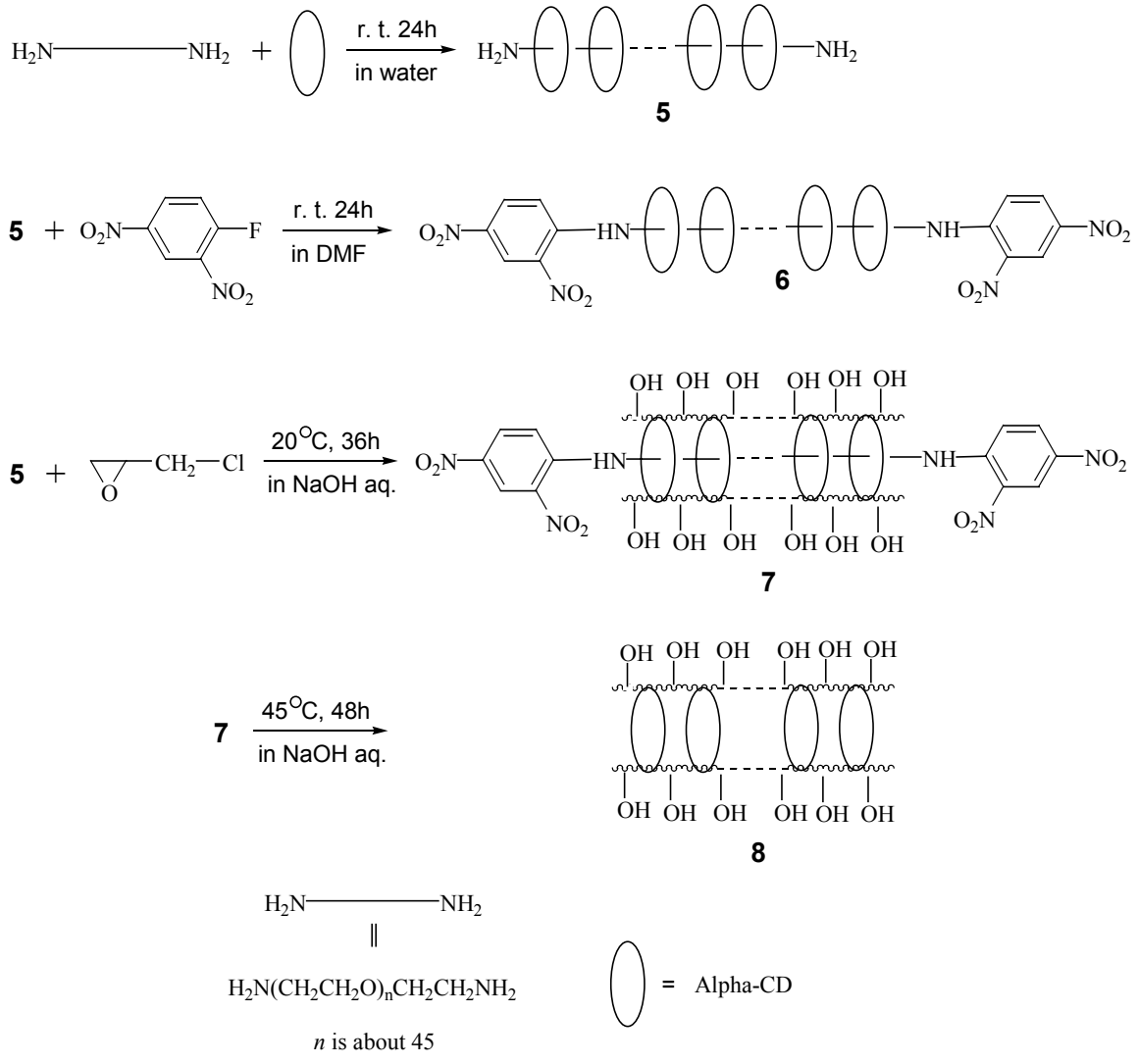


Figure 6. Preparation of α-CD-based molecular tube

Recently much attention has been directed to the manufacture of polypseudorotaxanes and polyrotaxanes containing photoisomerizable azobenzene groups and CDs because of their potential applications in the construction of photoresponsive materials.[18]

Yamamoto's group used γ-CD to make a main-chain polypseudorotaxane composed of an azobenzene polyester.[19b] They found the photoisomerization of the azobenzene polyester was reversible but that of the polypseudorotaxane is irreversible. This phenomenon was ascribed to the stabilization of the *cis*-azobenzene unit of the polypseudorotaxane by hydrogen bonding with γ-CDs. This group made some other main-chain polypseudorotaxanes and polyrotaxanes based on α-CD with polyurethane[19a] or polyurea[19c] as the polymer backbone. DSC measurements indicated that the polyurethane-based polypseudorotaxanes had lower glass transition temperature than the corresponding CD free polymers, while the polyurea-based polyrotaxanes show higher glass transition temperature than that of the corresponding CD free polymers. For the former, the decrease was due to weaker intermolecular hydrogen bonding between the urethane functions than the corresponding polyurethane;[19a] for the latter the increase is a result of the decrease of flexibility of the polymer chain because of the inclusion of rigid α-CDs onto the polyalkylene part.[19c]

A series of conjugated polyrotaxane insulated molecular wires were synthesized by Anderson's group.[20] These polyrotaxanes have conjugated polymer cores, such as poly(*para*-phenylene), polyfluorene, and poly(*para*-phenylenevinylene), threaded through CDs. The presence of CDs has little effect on the absorption spectra of polyrotaxanes, but causes a blue shift in the emission compared with the corresponding unthreaded conjugated polymers. Furthermore the fluorescence efficiencies were increased upon the formation of the polyrotaxane structure.

Udachin and coworkers[21] reported the first single crystal X-ray structural analysis of a polyrotaxane containing PEG and β-CD. Steffen et al.[22] studied the influence of ring size on the behavior of polypseudorotaxanes at mica surfaces. Kamitori and coworkers[23a] studied the crystal structure of polypseudorotaxanes composed of β-CD and poly(trimethylene oxide) and PPG. Harada's group[23b] synthesized new polypseudorotaxanes containing inorganic polymers, poly(dimethylsiloxane) (PDMS).

They found that α-CD did not complex with PDMS, but β- and γ-CD did. Shigekawa and coworkers[23c] demonstrated that the movement of α-CDs in a α-CD/PEG polyrotaxane could be manipulated by the tip of a scanning tunneling microscope.

Recently Harada and coworkers used the photodimerization of terminal anthracene groups to prepare a series of main-chain polyrotaxanes.[24a-c] They prepared a poly(polyrotaxane) from photoreaction of a 9-anthracene-capped polyrotaxane (Figure 7). In this process, first the inclusion complexation between α-CD and PEG with one end capped with 9-anthracene produced a semi-polyrotaxane, which was capped using 9-anthracenecarboxylic acid to give a polyrotaxane. Exposure of this polyrotaxane to visible light afforded a poly(polyrotaxane) by cyclodimerization of the terminal anthryl moieties. This poly(polyrotaxane) can be converted into the starting polyrotaxane by irradiation with UV light or heating. Later they prepared a polyrotaxane by photoreactions of a precursor complex between β-cyclodextrin with PPG having a triphenylmethyl group at one end and a 2-anthryl group at the other end.[24b] A similar method was used in the fabrication of polyrotaxanes based on γ-CD and PPG.[24c]

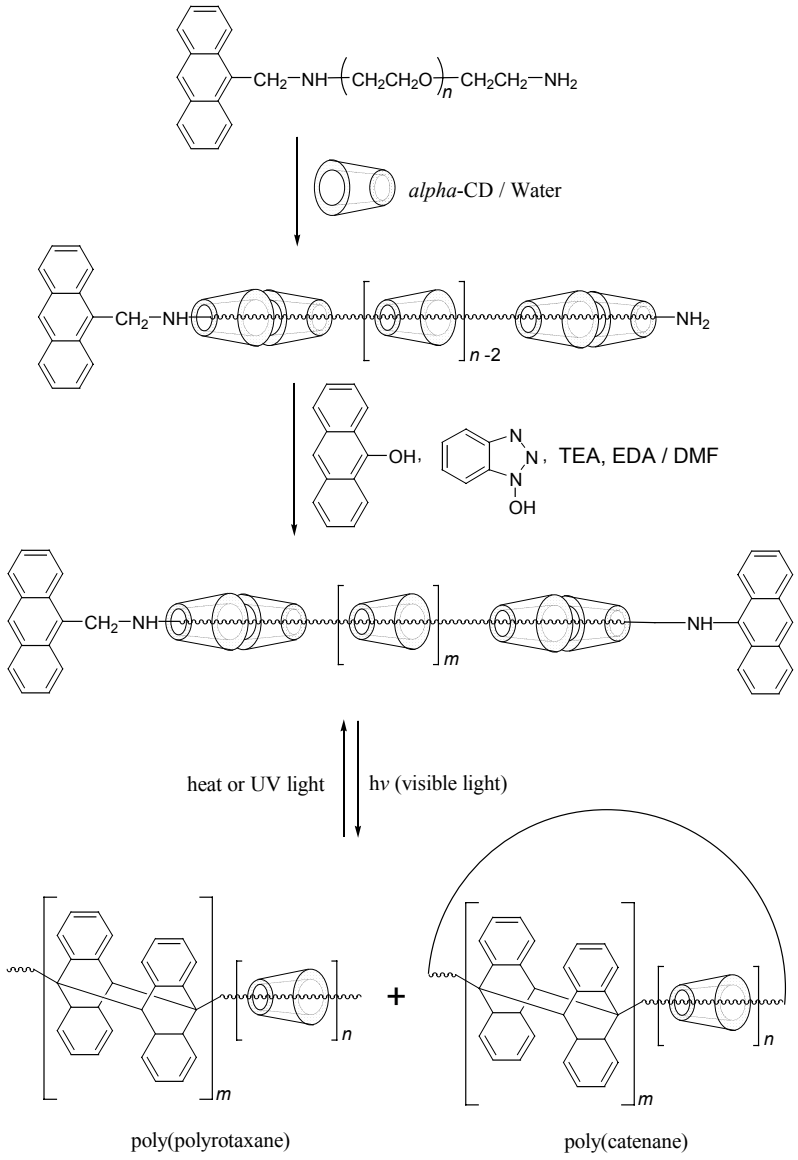


Figure 7. Preparation of a poly(polyrotaxane) by photoreaction.

Molecular dynamics simulations were performed by Pozuelo et al.[25] for polyrotaxanes formed by PEG and α-CD. The number of α-CDs the polymer can capture is limited by its length. The main source of stabilization of these polyrotaxanes is van der Waals interactions. Hydrogen bonding between adjacent α-CDs slightly favor head-to-head, tail-to-tail sequences over head-to-tail sequences (this conclusion agrees with the polyrotaxane made by Yui's group shown in Figure 4). The α-CDs in polyrotaxanes are more symmetric and less distorted than the isolated α-CDs. The PEG in the polyrotaxane

is more extended than an unperturbed chain, because it has a larger population of *trans* states at the internal bonds.

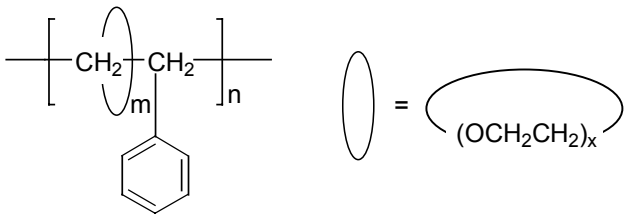
Hwang and coworkers[26] demonstrated that the threading following by recrystallization methodology might be a simple route to prepare a well-defined polymer structure on a micrometer scale by production of hexagonal microfibers from recrystallization of a α-CD/PEG polypseudorotaxane in water.

1.3. MAIN-CHAIN POLYPSEUDOROTAXANES AND POLYROTAXANES INCORPORATING CROWN ETHERS

Crown ethers are macromonocyclic polyethers. They have been widely studied as hosts for organic salts, such as secondary ammonium salts[27] and paraquat derivatives.[28] In the past ten years Gibson's group was active in the preparation of main chain polyrotaxanes incorporating crown ethers.[29-44] They have utilized crown ethers to synthesize a variety of polypseudorotaxanes and polyrotaxanes.[29-40] By carrying out step-growth polymerizations in the presence of unfunctionalized crown ethers, main chain polyester[29,30] and polyurethane[31,32] polypseudorotaxanes of Type A (Scheme 1) were prepared. By use of bulky monomers in step-growth polymerizations in the presence of unsubstituted crown ethers, as exemplified by the preparation of poly(ester rotaxane)s[33,34] and poly(urethane rotaxane)s,[35] polyrotaxanes of Type F resulted. Reaction of poly(methacryloyl chloride) with 5-hydroxymethyl-1,3-phenylene-1',3'-phenylene-32-crown-10 resulted in highly branched or crosslinked polymers of Type H, depending on the solvent and concentrations, as a result of self-association of the crown ether via hydrogen bonding and subsequent self-threading of the crown ether moieties.[33a] Poly(styrene rotaxane)s[36] and poly(acrylonitrile rotaxane)s[37] of Types A and F resulted from chain-growth polymerizations. Main chain poly(acrylate rotaxane)s and poly(methyl methacrylate rotaxane)s of Type A were also prepared using free radical polymerization.[38] Main-chain polypseudorotaxanes of Type B have been investigated by this group.[39]

The statistical threading method (route II in Scheme 4) was employed to prepare polyrotaxanes based on polystyrence.[36a] Here a free radical initiator carrying a bulky

tetraarylmethane-based group was used in order to increase the overall threading efficiency. They observed that the stoppers are required to prevent dethreading during the preparation of polyrotaxanes.[29,33a,33b] In order to improve threading more, hydrogen bonding was introduced into their polyrotaxanes.[31a,31b,43] The influence of the size of the macrocyclic crown ether on the threading efficiency also was considered.[29b] A series of similar poly(styrene/crown ether pseudorotaxane)s (Figure 8) was prepared. It was found that the *m/n* values of these polypseudorotaxanes did not simply increase with the ring size because of different threading and dethreading processes for different sized cyclics.[44] Later this group studied the relationship between feed composition, the ratio between the cyclic and acyclic starting materials, and *m/n* value.[38b]



Crown ether macrocycle	*m*/*n*
30C10, x=10	-
"42C14", x=14	0.021
"48C16", x=16	0.019
"60C20", x=20	0.014

Figure 8. Poly(styrene/crown ether rotaxane)s

In order to have a detailed understanding of the threading process, Gibson's group[33a] introduced difunctional blocking groups to make main chain polyrotaxanes (type H in Scheme 1) by route IV (Figure 9). The introduction of the blocking group increased the *m/n* value to 0.061, about 5 times of that of a polyrotaxane of type A without blocking groups.[45] What is more important is that they found that the *m/n* value increased with decreasing temperature for the first time.

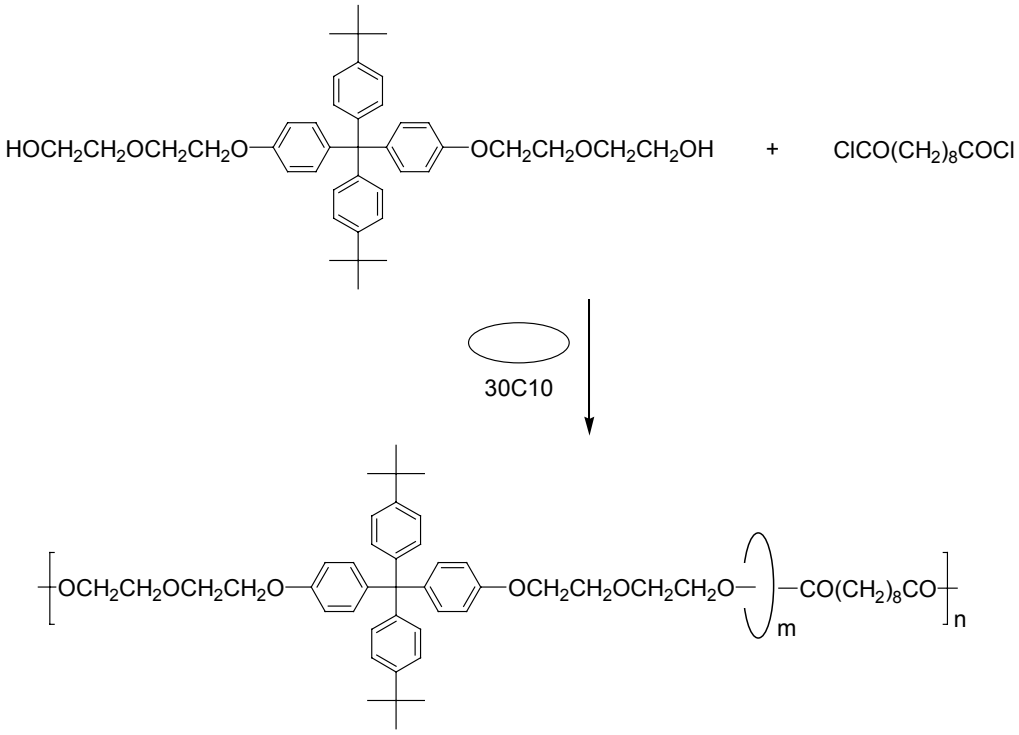


Figure 9. Synthesis of a main-chain polyrotaxane from a difunctional monomer incorporating a blucky group.

In a word, the threading efficiency depends on the introduction of stoppers, the strength of the interactions between the marcocyclic crown ether and the linear component, the size of the crown ether, the ratio between the cyclic and acyclic starting materials, and threading temperature.

Later, this group designed route VI to prepare main chain polypseudorotaxanes of type B. The polyester polypseudorotaxane in Figure 10 was prepared by reacting bis(5-hydroxymethyl-1,3-phenylene)-32-crown-10 with sebacoyl chloride.[38] In this method, first a crown ether was incorporated into a linear polymer chain. Then low molar-mass paraquat units were threaded into the cavities of the cyclic repeat units of the backbone to form polypseudorotaxanes. In their preparation of polyamide based polypseudorotaxanes,[42b] they found that the threading of the crown ether moieties is the key step, leading to polypseudorotaxane, polyrotaxane and polycatenane structures to an extent dependent upon the their cavity size *and* the propensity for cyclization of the polymer backbone.

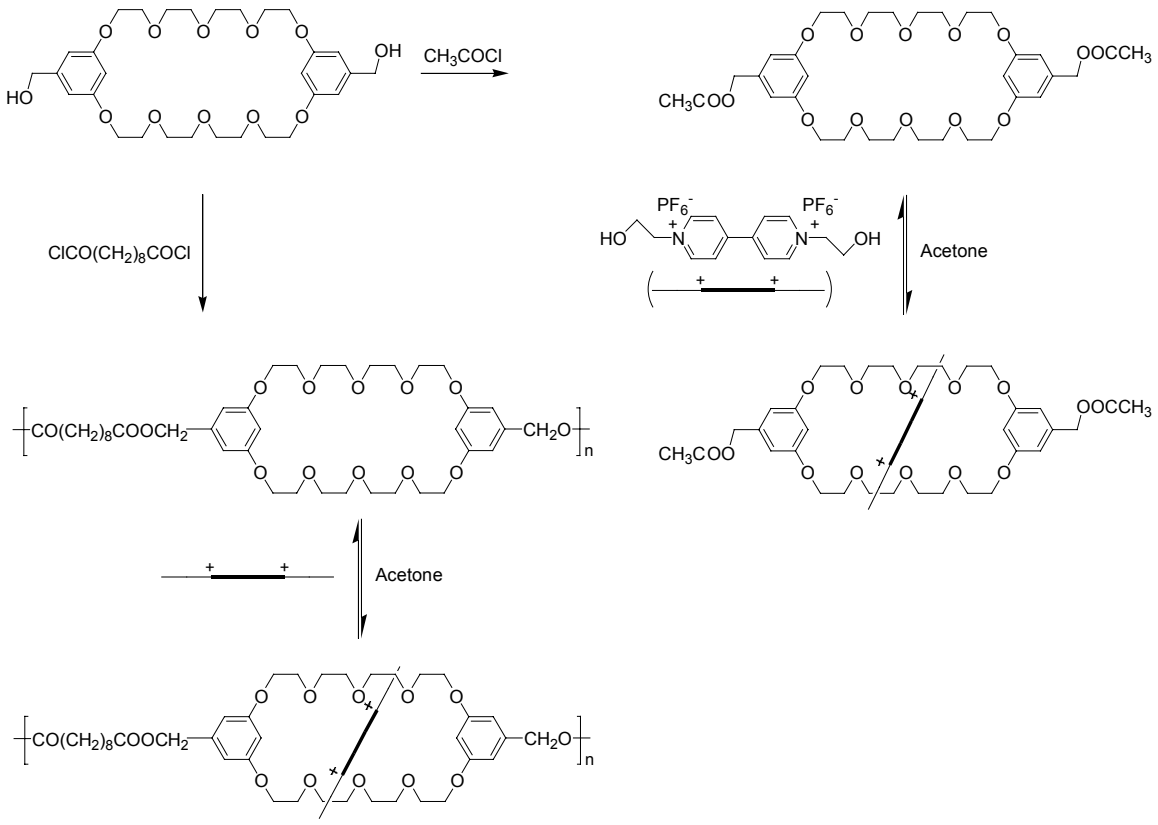


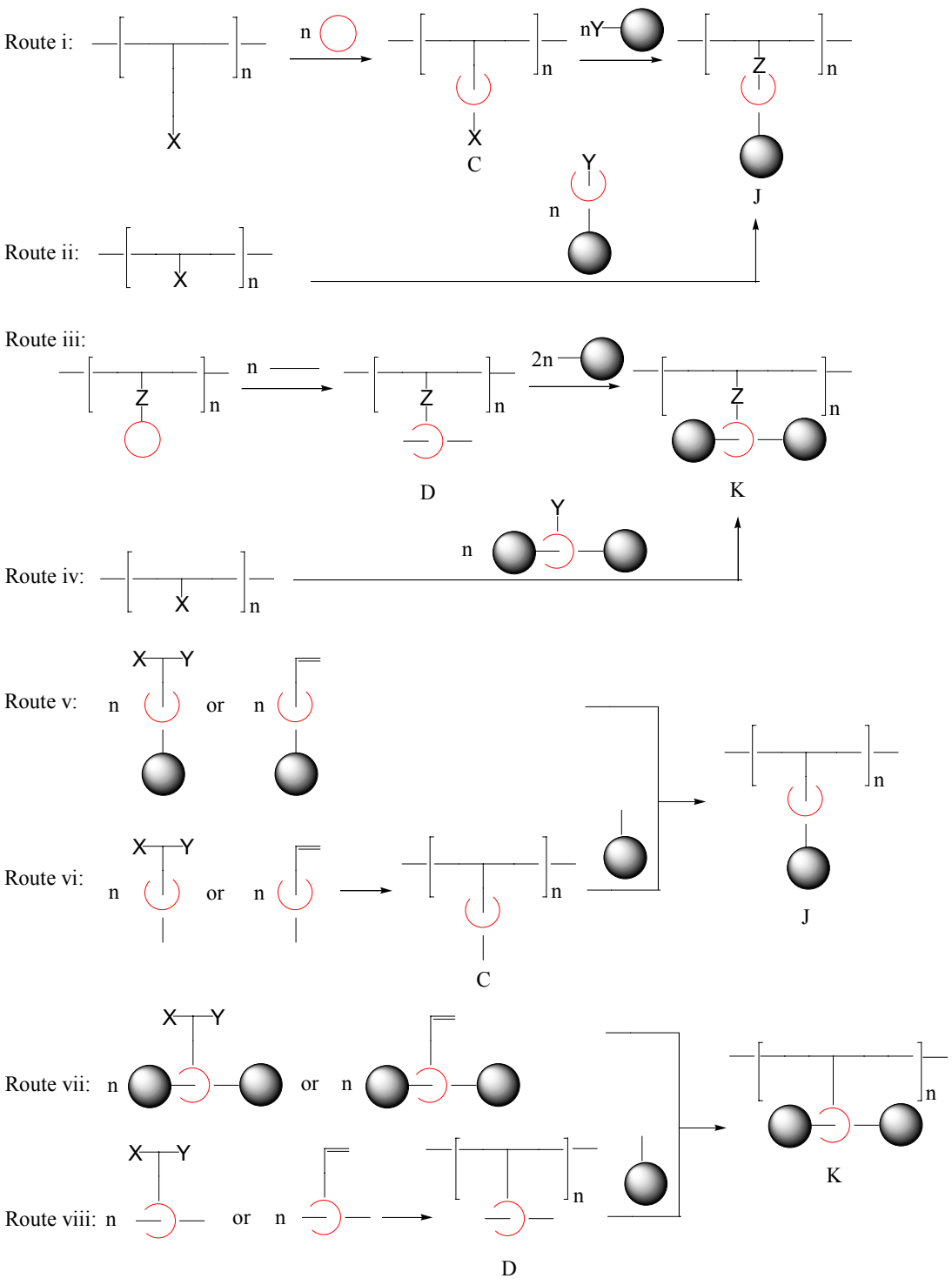
Figure 10. Synthesis of a polyester main chain polypseudorotaxane

Beckham's group prepared some main-chain polyurethane-based polyrotaxanes from hexamethylene diisocyanate and either ethylene glycol or diethylene glycol in crown ether solvents.[46] It was found the threading efficiency increased with increasing crown ether ring size.

1.4. SIDE-CHAIN POLYPSEUDOROTAXANES AND POLYROTAXANES

Side-chain polypseudorotaxanes and polyrotaxanes can be prepared by the routes in Scheme 2. In route i macrocyclic components are threading onto the side chains of an existing polymer to get the polypseudorotaxane. Then stoppers are introduced to obtain polyrotaxanes. Route ii involves the reactions between the functional groups on [n]-pseudorotaxanes and the functional groups on the side chains of the polymer. Linear components in route iii are threaded into the macrocycles on the side chains of a polymer

to produce a polypseudorotaxane of type D and then stoppers are introduced to get a polyrotaxane of type K. In route iv, the functional groups on the rotaxanes react with the functional groups on the side chain to afford a polyrotaxane of type K in Figure 1. In routes v-viii, the homopolymerization of a pseudorotaxane or rotaxane monomer leads to the formation of a polyrotaxane of type J or K in Figure 1.



Scheme 2. Synthetic routes for side chain polypseudorotaxanes and polyrotaxanes.

In addition to being used in the preparation of main chain polypseudorotaxanes and polyrotaxanes, CDs were also successfully employed in the construction of side chain polypseudorotaxanes and polyrotaxanes.

Ritter and coworkers reported side chain polyrotaxanes incorporating CDs for the first time in 1991.[47] Their synthetic procedure (route ii in Scheme 2) is shown in Figure 11. First 2,6-di-O-methyl β-CD was threaded onto a monofunctional compound **9** in water or chloroform to afford a semi-rotaxane **10**. Then **10** was reacted with a preformed copolymer **11** based on poly(methyl methacrylate) in organic solvents to derive side chain polyrotaxane **12**. Later on, poly(ether-sulfone),[48] poly(methacrylate),[49a,b] and poly(acryloylamide)[49c] were also chosen as backbones to prepare new side chain polyrotaxanes incorporating CDs by this group.

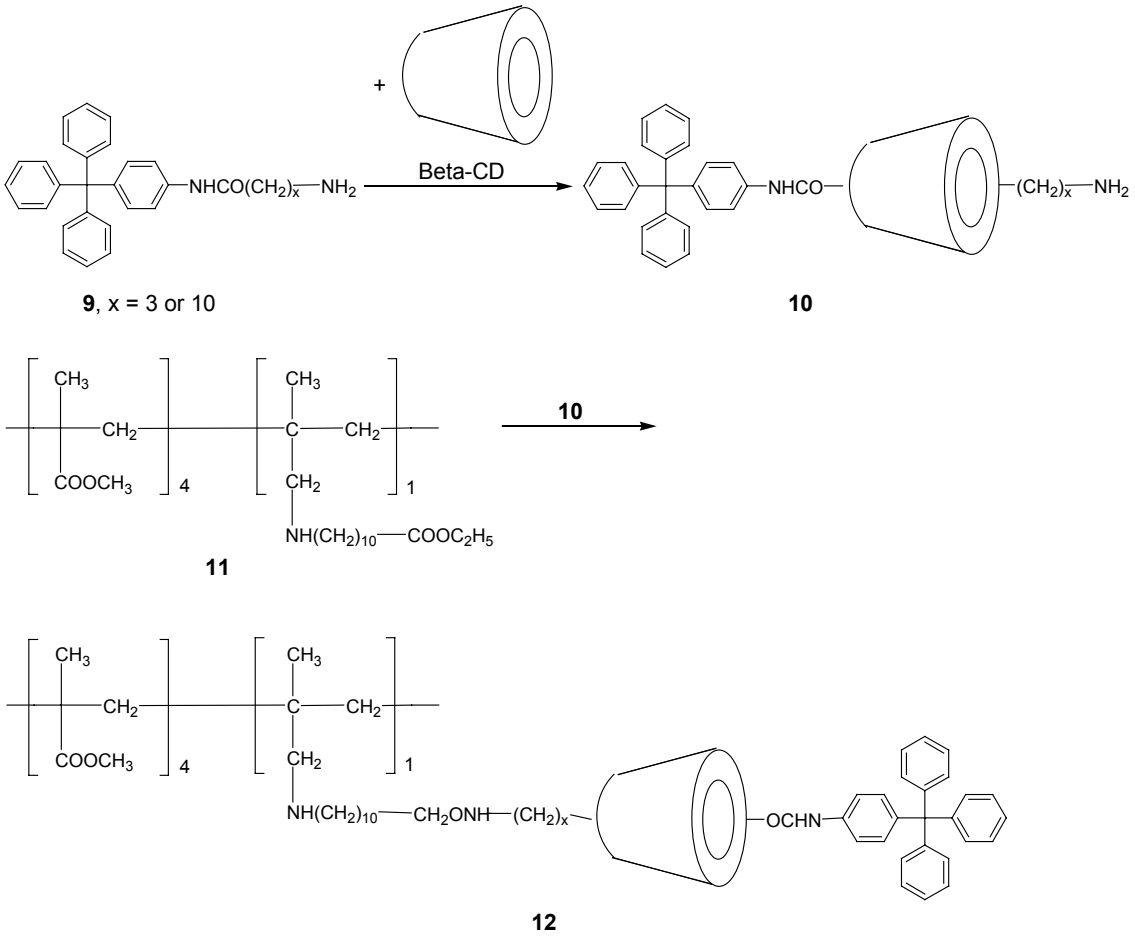


Figure 11. Synthesis of a side-chain polyrotaxanes based on β-CD.

Yamamoto's group[50] prepared poly(*p*-phenylenebenzimidazole)s-based side-chain polyrotaxanes with crown ether-metal complexes as the stoppers in DMF. Treatment of these polyrotaxanes with H_2O causes detachment of the crown ether molecules and dethreading of α-CD from the side chain.

Swager et al.[51] made some new side chain polypseudorotaxanes (Figure 12). These unique polypseudorotaxanes are not included in Figure 1. For these, part of the cyclic component is a part of the polymer backbone.

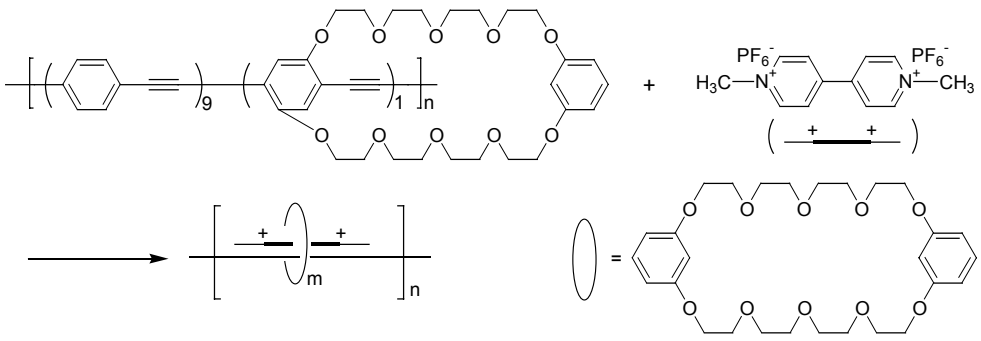


Figure 12. Preparation of a side-chain polypseudorotaxane.

Takata and coworkers[52a] made side-chain polypseudorotaxanes by radical homopolymerization of semirotaxanes consisting of a crown ether wheel and acrylate axle bearing a bulky end-cap and ammonium group (route v in Scheme 2). Gibson's group also prepared side-chain polypseudrotaxanes[52b] of type D in Figure 1 and polyrotaxanes[52c] of type J in Figure 1 with crown ethers as the macrocylic components.

Yamaguchi et al.[53] synthesized a novel side chain polyrotaxane by N-alkylation of poly(benzimidazole)s with the appropriate semirotaxanes composed of a trimethyl-cyclodextrin encircling a linear component bearing a bulky trityl group at one end and a bromide leaving group at the other. These polyrotaxanes have much higher solubility in organic solvents than their parent polymers.

1.5. OTHER POLYPSEUDOROTAXANES, POLYROTAXANES, AND RELATED STRUCTURES

Cucurbituril (Figure 13) is a hexameric macrocyclic compound. Although the size of its cavity is similar to that of α-CD, its highly symmetrical structure with two identical openings distinguishes it from α-CD and the polar carbonyl groups at the portals allow it to bind ions and molecules through charge-dipole and hydrogen-bonding interactions.[54]

Cucurbituril has been applied to construct a variety of polypseudorotaxanes and polyrotaxanes by Kim's group by the combination of self-assembly and coordination chemistry.[55] For these systems, a stable pseudorotaxane was formed first by threading a cucurbituril with a short linear molecule and then metal ions were used as linkers to

organize the resultant pseudorotaxanes into one-dimensional and two-dimensional polypseudorotaxanes and polyrotaxanes. The overall structure of a polypseudorotaxane or a polyrotaxane constructed in this way was determined by the interplay among various factors including the coordination preferences of the metal ion, spatial disposition of the donor atoms with respect to the cucurbitruil beads in the pseudorotaxane, and the size and coordination ability of the counterion. When $Cu(NO_3)_2$ was used, a one-dimensional polyrotaxane (Figure 13) was obtained.[55a] This polyrotaxane is important because it is the first one formed on a coordination polymer, the first one containing a cyclic component on every repeating unit, and the first one to be structurally characterized by single-crystal X-ray crystallography. Though the pseudorotaxane was used, a two-dimensional polycatenated polyrotaxane network was obtained when $AgNO_3$ was used, while a linear one-dimensional coordination polyrotaxane was obtained when AgTos was used.[55b] For the pseudorotaxane in which the number of carbon atoms between the two secondary ammonium sites was five instead of four and the pyridyl groups were connected to the chain at the 3-position instead of the 4-position, a one-dimensional coordination polymer[55c,f] arranged in a helical fashion was generated when $AgNO_3$ or $Ag(NO_3)_2$ was used, while a two-dimensional polyrotaxane[55e] with large cavities and channels was obtained when $Cu(NO_3)_2$ was used. They also prepared a three-dimensional polyrotaxane network[55d] from a pseudorotaxane with cyano terminal groups by using lanthanide metal ions as the linkers and square-wave-shaped one-dimensional main-chain polyrotaxanes[55i] from a preorganized L-shaped pseudorotaxane by using Ni^{2+} and Zn^{2+} ions as the linkers. A polypseudorotaxane was synthesized from polyviologen and cucurbituril in water by simple stirring at room temperature.[55g] The degree of threading (number of cucurbituril beads per repeat unit) can be precisely controlled from 0.1 to 1.0 by controlling the amount of cucurbituril added. The threaded cucurbituril beads are localized at the middle of the decamethylene units of the polymer through hydrophobic and charge-dipole interactions, to afford a well-defined microstructure in aqueous medium. Some side-chain polypseudorotaxanes containing cucurbituril were also prepared by this group.[55h] They exhibit higher conformational rigidity and thermal stability than their parent polymers. Furthermore, for these polypseudorotaxanes, threading and dethreading of the cucurbituril macrocycles can be reversibly controlled by the pH of the solution. Recently

they prepared a double-chained polyrotaxane by threading cucurbituril onto a double-chained one-dimensional coordination polymer.[55j]

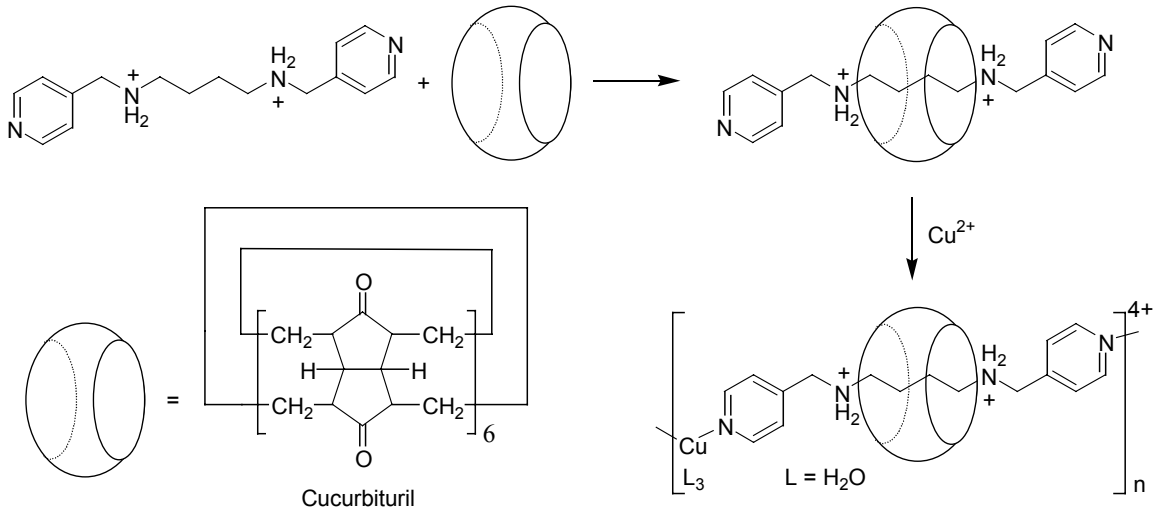


Figure 13. Preparation of a 1 D polyrotaxane based on cucrbituril.

Cucurbituril was also used in preparing polyamide-based main-chain polypseudorotaxanes and polyrotaxanes by interfacial condensation,[56a,b] main-chain polyrotaxanes by catalytic self-threading,[56c,e] and main-chain polypseudorotaxanes by post-threading.[56d]

Chen and coworkers demonstrated the fabrication of a two-dimensional polyrotaxane network[57a] via π-π interactions and a three-dimensional polypseudorotaxane network[57b] based on metal-coordination between silver salts and flexible pyridyl-type ligands in the solid state as shown by X-ray single-crystal analysis.

After the syntheses of some conducting polymers[58a-d] containing metallorotaxanes, Swager and coworkers[58e,f] reported the synthesis of the first conducting polymetallorotaxanes (Figure 14) by electrochemical polymerization of metallorotaxanes. These supra-molecular systems can reversibly bind Zn^{2+}, Cu^{+}, and Cu^{2+}. Furthermore they have conductivity profiles characteristic of localized redox conductors. Later they[58g] used two-step electropolymerization of metallorotaxanes to prepare three-strand conducting ladder polymers, wherein one of the conjugated chains is sandwiched between two other chains. In this structure the internal polymer behaves as a partially

isolated molecular wire when the outer strands are in an insulating state. A similar conjugated polyrotaxane was prepared by Sauvage's group[59a,b] via copper(I)-templated strategy and electropolymerization. The rebinding of Cu^+ is only possible if lithium is present during Cu^+ removal. This is different from the above conjugated polyrotaxane. Sauvage and coworkers[59c,d] also prepared some other conjugated polyrotaxanes using metal-templated strategies and electropolymerization with the aim to ensure better tuning of the electronic coupling between the rotaxane coordinating site and the conjugated wiring backbone. They demonstrated that subtle changes in the coordinating unit could dramatically improve the metalation-demetalation properties of these materials.

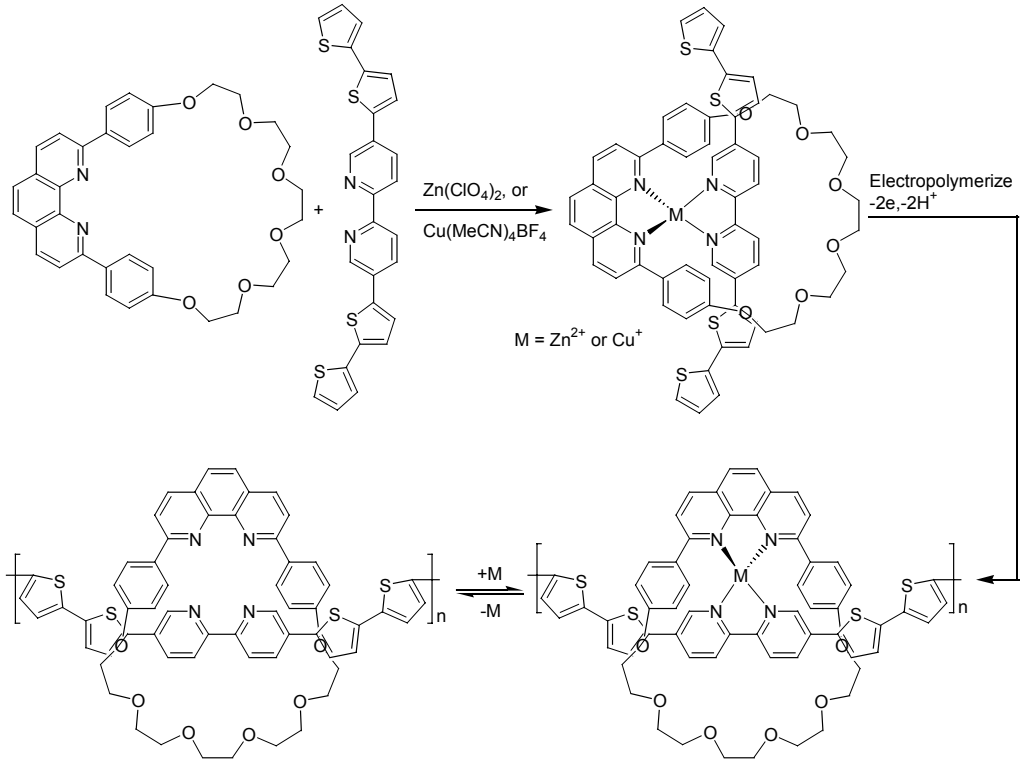


Figure 14. Synthesis of the first conducting polymetallorotaxanes

Most of the polypseudorotaxanes and polyrotaxanes are based on linear polymer backbones. To study new properties and applications of branched and crosslinked polypseudo-rotaxanes and polyrotaxanes will surely be very interesting in terms of topology and potential applications.[1c] Mechanically branched network polyurethanes with

a side chain rotaxane structure (Figure 15) were prepared in Gibson's group for the first time.[39] When the solvent was diglyme, a hydrogen bonding self-complex **13** formed from the monohydroxy crown ether, 5-hydroxymethyl-1,3-phenylene-32-crown-10. Then it was reacted with a preformed poly(methacroyl chloride) via exo esterification to form structure **14** or via endo esterification to form mechanically crosslinked structure **15** in the final product **16**, because both polymer backbone and the crown ether are big enough to prevent dethreading. However, when DMSO was used as the solvent for the esterification, only linear polymer was obtained. The reason is that only the linear structure **14** could form because DMSO is a very strongly competitive solvent for hydrogen bonding and the driving force for rotaxane formation was suppressed. In this way, the topology of polymers can be simply controlled by change of reaction solvent. Furthermore, similar branched and network poly(methacrylate rotaxane)s were also made by this group.[41]

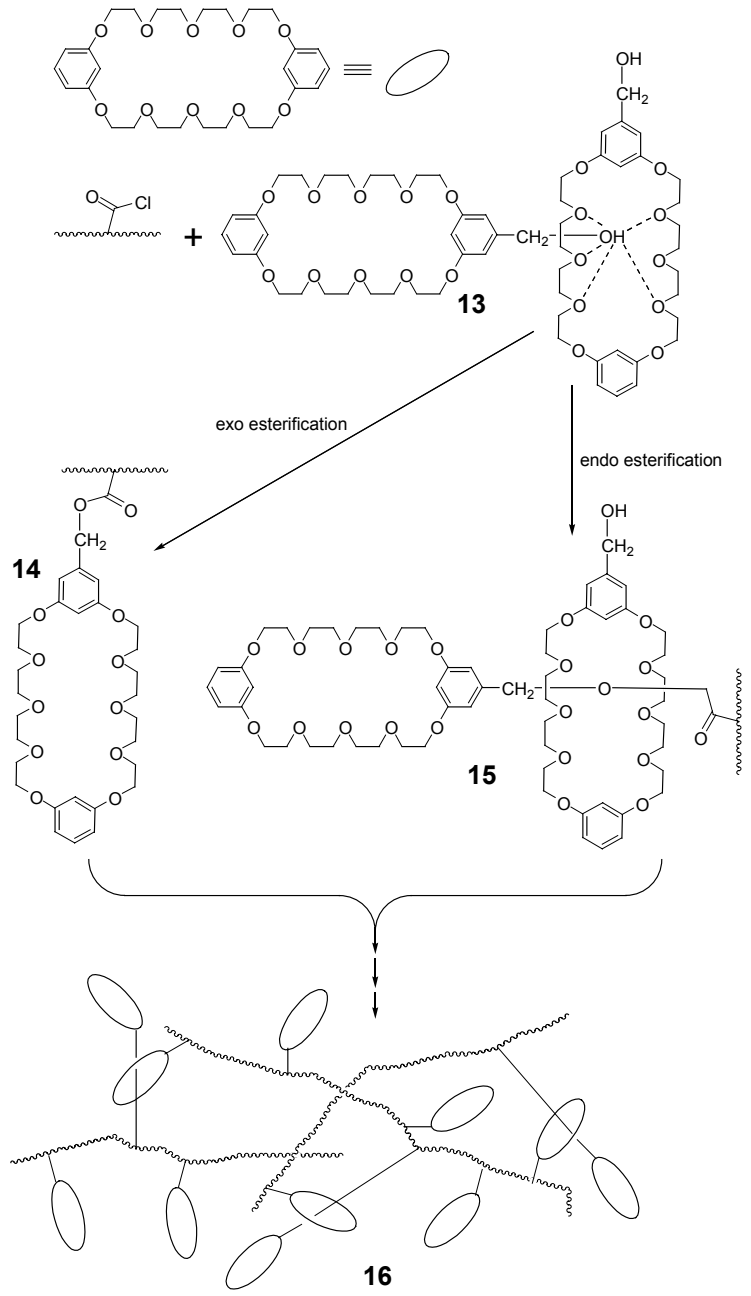


Figure 15. Mechanism for the formation of the mechanically branched and network polymers with a side chain rotaxane structure.

Bis(polypseudorotaxane)s composed of metallobridged bis(*β*-cyclodextrin)s possessing the ligated copper(II) center and PEG chains were synthesized by Liu and

coworkers.[60a] An infinite mechanically linked 2D polyrotaxane network based on 1,4-bis(imidazol-1-yl-methyl)benzene was prepared by Hoskins and coworkers.[60b]

π-π stacking and charge transfer interactions also have been used to construct polypseudorotaxanes. Owen and Hodge[61] synthesized a series of polypseudorotaxanes (Figure 16) by using tetracationic cyclophane cyclobis(paraquat-phenylene) as the cyclic component. This cyclophane was quickly threaded onto some preformed polymers in acetone. High *m/n* values of these polypseudorotaxanes show that π-π stacking and charge transfer interactions are very efficient driving forces for the manufacture of polypseudorotaxane and polyrotaxanes. Mason and coworkers[28,62a,62b,62c] studied similar systems but they focused on studies of the threading process and molecular motion. Based on this tetracationic cyclophane macrocycle, Tamaoki's group prepared a poly[2]rotaxane of type L by route IX in Scheme 1 with low molecular weight.[62d]

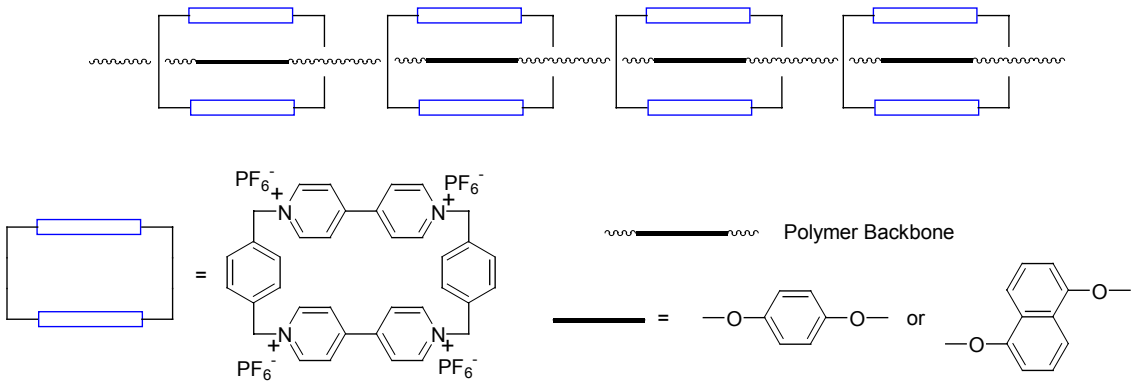


Figure 16. A polypseudorotaxane with cyclobis(paraquat-phenylene) as the cyclic component

Tetracationic cyclophane cyclobis(paraquat-phenylene) also was used in the preparation of polyrotaxanes for mechanical linking by a stepwise approach[63a,c] and polypseudorotaxanes based on conjugated polymers.[63b] For the later, it was found that the efficient charge transfer interaction between the electron-rich units on the conjugated polymer and the electro-poor cyclophane afforded a high conductivity of the polypseudorotaxanes.

Yui's group[64] also prepared a series of PEG-based hydrogels. The study of the hydrolytic erosion behavior of hydrogels cross-linked by a hydrolyzable polyrotaxane revealed that the time to reach complete gel erosion was prolonged by decreasing the polyrotaxane content and increasing the PEG/α-CD ratio.[64a,b] Further study was performed to evaluate their cell adhesion and proliferation.[64d] It was found that the cells recognize the surface heterogeneity due to the polyrotaxane structure and the cell adhesion and proliferation is controllable by the polyrotaxane content in feed. The hydrogels cross-linked by the polyrotaxane can be used as long-term stable, but actually hydrolyzable hydrogels for polymeric scaffolding in tissue engineering.[64a,b]

Ito and coworkers[65b] made a polyrotaxane gel by figure of eight crosslinking. Polyrotaxane gels can be regarded as a third type of gel, separate from the chemical and physical gels because they are topological gels in which the polymer network is interlocked by topological restrictions. This group also made other polyrotaxane-related structures.[65a,c]

Recently *p-tert*-butylcalix[8]arene (Figure 17) was used to construct main chain polyrotaxanes with PEG as the polymer backbone.[66] These polyrotaxanes were prepared by the polycondensation of *p-tert*-butylphenol with paraformaldehyde in the presence of PEG. The polyrotaxane yield and the composition were dependent on the molecular weight of PEG.

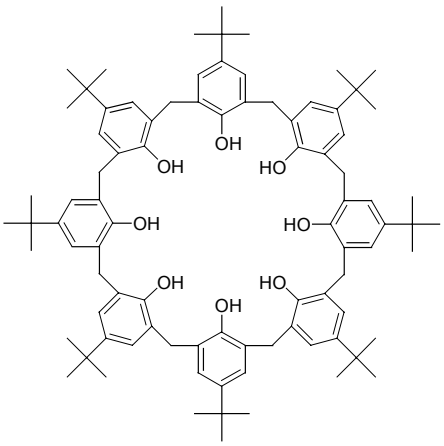
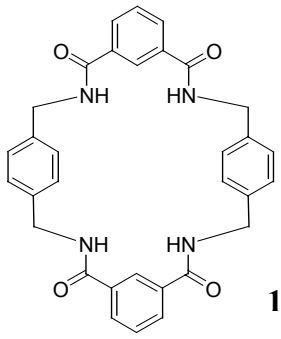


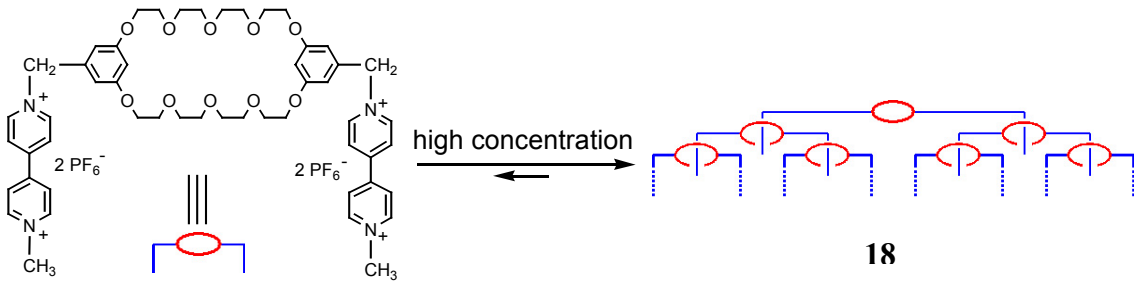
Figure 17. The structure of *p-tert*-butylcalix[8]arene

Tetraamide macrocycle **17** was used in the fabrication of main-chain, side-chain, and cross-linked network polyrotaxane architectures stoppered by bulky isocyanate groups from the polymerization of cheap and readily obtainable rotaxane monomers.[67]



17

Huang and Gibson[68] reported the formation a three-dimensional supramolecular hyperbranched polypseudorotaxane **18** from the self-organization of an AB_2 monomer **19** based on the bis(*m*-phyenylene)-32-crown-10/paraquat recognition motif.



19 **18**

Liu's group reported a water-soluble nanometer-scale metallocapped polyrotaxane from the inclusion complexation of azocalixarenes with metallo-bridged bis(*β*-CD)s.[69] This polyrotaxane has highly selective binding for Ca^{2+}. Recently they prepared supramolecular aggregates from gold nanoparticles and polypseudorotaxanes of L-tryptophan-modified *β*-CD threaded by amino-terminated PPG as captors for fullerenes.[70] The size and sedimentation rate of these aggregates mainly depend on the lengths of the PPG chain.

Kihara and coworkers[71] used the solid state end-capping of α-CD/PEG polypseudorotaxanes possessing hydroxy-terminated axles to prepare polyrotaxanes. This method was extended to the fabrication of a polyrotaxane network from a functionalized polyrotaxane.

Material and chemical recycling of cross-linked polymers is important. Takata's group[72] provided a new concept for recyclable cross-linked polymers by utilizing mechanical linkages in a polyrotaxane network capable of undergoing reversible assembly and disassembly. The polyrotaxane comprises a poly(crown ether) polyurethane and a bisammonium salt disulfide.

A new type of polyrotaxane architecture, comprising two interpenetrating chains of rings, was prepared by Puddephatt's group.[73] The synthesis combines the techniques of organometallic chemistry, coordination chemistry, and self-assembly through hydrogen bonding. Loeb's group reported a polypseudorotaxane based on a protonated version of the 1,2-bis(4,4'-bipyridinium)ethane/24-crown-8 ether motif in the solid state.[74a] Later they prepared linear one-dimensional and square-grid two-dimensional metal-based polyrotaxanes by using metal-ligand self-assembly as shown by X-ray single-crystal crystallography.[74b]

1.6. PROPERTIES AND POTENTIAL APPLICATIONS

The applications of a material are decided by its properties. In polypseudorotaxanes and polyrotaxanes, covalent bonds are supplemented by mechanical links, especially non-covalent bonds such as hydrogen bonding and charge transfer. This unconventional combination of interactions accounts for the great differences in properties between these two types of materials and covalent materials studied by molecular chemistry.[1f]

1.6.1. Solubility

Usually the solubilities of polypseudorotaxanes and polyrotaxanes are very different from their components. Because the hydrophilic properties or high polarity of

the exterior of the CDs, many CD-based polypseudorotaxanes and polyrotaxanes[6-9,10c,10f,47,75] are soluble in water and some polar solvents though their parent polymers are hydrophobic or nonpolar. Especially Yui's group use this property to prepare a series of biodegradable CD-based polyrotaxanes,[6-9,75d] which can potentially be used as drug carriers and tissue scaffolds. The solubility of crown ether-based polypseudorotaxanes and polyrotaxanes in methanol and/or water was improved because of the hydrogen bonding between the crown ethers and solvents[30,45,37a] or the hydrogen bonding between the crown ethers and the polymer backbone.[31b] These studies imply potential applications of the polypseudorotaxane or polyrotaxane concept in coatings, adhesives, and water-borne processing.[1g]

1.6.2. Stability

Obviously polyrotoaxanes are more thermodynamically (not necessarily thermally though) stable than their corresponding polypseudorotaxanes because of the existence of stoppers. It is also obvious that the polypseudorotaxanes/polyrotaxanes with attractive forces, such as hydrogen bonding and charge transfer, between their components are more stable that those without attractive forces between their components. This is the reason that few polypseudorotaxanes and polyrotaxanes were prepared in recent years by statistical threading and chemical conversion.[1g] Though there are strong attractive forces between their components, dethreading still can happen in some polypseudorotaxane, and polyrotaxane systems when a salt or other substance is added or the temperature increases.[1g] Recently Yui and coworkers[10c,f] found the thermal stability of their biodegradable polyrotaxane is better than the thermal stability of the separate components, poly(ε-lysine) and α-cyclodextrin. They thought this was because of the formation of complex. The same results were obtained in the studies of polypseudorotaxanes based on α-CD and PPG-PEG-PPG triblock copolymers[15g] and polypseudorotaxanes of α- and γ- CDs with poly(butylenes carbonate).[76]

1.6.3. Photoelectronic properties

The introduction of photo- and electronic-active elements into the polypseudorotaxane and polyrotaxane structure has led to the studies of the photoelectronic properties of these materials.

A [2]rotaxane[77] was synthesized from a Zn(II)-phthalocyanine with polyether substituents containing π electron rich hydroquinone segments and a cyclobis(paraquat-*p*-phenylene) tetracation containing π electron deficient bipyridinium units. It was found that fluorescence quenching of the Zn(II)-phthalocyanine was enhanced dramatically in MeCN. Swager and coworkers[51] observed the same phenomenon in their polyrotaxane systems. It was believed that this phenomenon was caused by rapid migration of the hole-electron pair to the rotaxane sites followed by rapid combination. They also found that the conductivity of these polyrotaxanes was lower than the parent polymer.

Some conjugated polyrotaxanes containing metals were synthesized by Sauvage's group.[59,78] The deposition of electroactive films with a polyrotaxane organic backbone using a pre-assembling principle was described.[78a] These films can retain their structure and the metal can be reintroduced after demetallation. Later they made some conducting polyrotaxanes.[59,78c] It was found that the Cu(I) binding was reversible only if lithium was present during copper removal.

A series of polyrotaxanes as a light-harvesting antenna model was constructed by Ueno and coworkers.[79] These polyrotaxanes consists of various ratios of α-CD and naphthalene-appended α-CD threaded by a PEG chain bearing anthracene moieties at each end. Here naphthalene and anthracene moieties act as energy donors and energy acceptors, respectively. It was found that antenna effect becomes more marked with increasing number of naphthalene-appended α-CD units in the polyrotaxanes, but energy transfer efficiency decrease with this increase.

1.6.4. Viscosity

The threading of cyclic components onto the polymer backbone has an important influence on the solution viscosity and melt viscosity. Up to now it has been found that

this influence depends on the properties of cyclic components and the polymer backbone, the value of *m/n*, and the types of solvents.

Gibson and coworkers[38b] studied the effect of the threading on the solution viscosity of polypseudorotaxanes. It was found that the higher the degree of threading, m/n, the higher the intrinsic viscosity. Several factors were believed to have attributed to this increase. Upon threading, the solvated volume of the polymer will increase and lead to the higher viscosity. The chain extension resulting from the ionic repulsion between the complexed dicationic paraquat guests can also increase the viscosity. Furthermore, as the degree of threading increases, these repulsive forces will also be more prevalent. This effect can also cause the viscosity to increase.

This group[30,80] also found that poly(ester rotaxane)s have higher intrinsic viscosities than their parent polymers because of the increase of hydrodynamic volume due to the presence of the cyclic components. The types of solvents could also affect the viscosity of polyrotaxanes.[30] When the solvent was changed from THF to a mixture of THF and methanol (10:1), the intrinsic viscosity of polyrotaxane decreased, while the intrinsic viscosities of the parent homopolymer and a copolymer with poly(ethylene oxide) were unaffected by the solvent change. This solvent dependence is due to the differential solvation of the linear and cyclic components.

In the studies of poly(urethane-crown ether rotaxane),[81] it was also found that the polyrotaxane had higher viscosity than the corresponding parent polyurethane because the presence of the cyclic species causes the polyrotaxane adopt an expanded conformation. Wenz and Keller[4a] observed that the viscosity of their CD-based main-chain poly(amine rotaxane) increased with increasing *m/n*. Even for side-chain poly(methacrylate CD rotaxane)s,[47] viscosities were higher than those of the model systems.

Though the solution viscosities of polypseudorotaxanes and polyrotaxane are higher than their parent polymers, the melt viscosity of a poly(ester rotaxane) studied by Gibson's group was lower than that of the corresponding model polymer.[30,80] This is because the cyclic components prevent polymer chain entanglements in the melt state, and therefore the melt viscosity decreases.

1.6.5. Phase behavior-glass transition temperatures and melting points

A glass transition temperature (T_g) is the temperature at which a polymer undergoes a conversion from a glassy amorphous state to a rubbery state. The T_g change resulting from the threading of cyclic species onto the polymer backbone depends on the miscibility of the cyclic species and the polymer backbone. If they are compatible, only one T_g, corresponding to a single phase, will be observed for the polypseudorotaxane or polyrotaxane. If they are immiscible, two T_gs will present. Furthermore, The T_g corresponding to the polymer backbone will be unchanged, while a second T_g for cyclic species maybe will be observed.[1f]

Because polystyrene and crown ether are not compatible, the poly(styrene/crown ether rotaxane)s (Figure 8) described in section 3 have two T_gs for linear and cyclic species. Conversely, the cyclic and linear components of poly(urethane/crown ether rotaxane)s[35,46,81] are miscible because of the hydrogen bonding between them, so only one T_g was observed for these polrotaxanes. This T_g increases when the value of *m/n* decreases or the percentage of blocking groups in the polymer backbone increases.[35] Even for branched poly(urethane/crown ether rotaxane)s[39,41] formed by self-threading interactions, only one glass transition was also observed. For the polyrotaxanes[38] containing cyclic components in their polymer backbone, T_g increases when more linear components, 4,4'-bipyridinium ions, were complexed into the cyclic components.

Usually polypseudorotaxanes and polyrotaxanes[19c,49,75a,75b,75c] incorporating CDs have higher T_gs than their corresponding polymer backbones because of the rigidity of CDs.

A melting point (T_m) is the temperature at which the physical state of a solid changes to the liquid state. Only when the value of *m/n* is high, the cyclic component aggregate along the polymer backbone. If the cyclic component and polymer backbone are immiscible, two T_ms will be observed for a polypseudorotaxane or polyrotaxane.[30,45] Otherwise, only one[36b] or even no[35,81] melting point can be observed for the polypseudorotaxane or polyrotaxane.

1.6.6. Other properties and applications

Han and Antonietti used cyclodextrin-based polypseudorotaxanes as templates for the generation of porous silica materials,[82] whose pore diameter depends on the pH values of silica condensation. The direct replication is just obtained at pH 2.0, whereas larger pores are found at higher pH values. They explained this as the result of aggregation of polypseudorotaxanes via hydrogen bonding toward arrays or bundle structures. Later the same group prepared porous silica materials through nanocasting of stable isolated polypseudorotaxanes from α-CD and polyamines.[83] These silica materials possess quite high porosity and elongated pores.

Yui et al. introduced carboxy ethyl ester groups to all the primary hydroxyl groups in α-CD, which was threaded onto a PEG chain to prepare carboxy ethyl ester-polyrotaxanes as calcium chelating polymers in the field of oral drug delivery.[84]

Beckham et al. used diffusion-ordered 2D NMR spectroscopy (DOSY) to study self-diffusion behavior polyrotaxanes in dilute solution.[85] For a polyrotaxane based on polystyrene and 30-crown-10, it was found that the threaded macrocycles exhibit self-diffusion coefficients similar to those of the polymer, while the diffusion coefficients for the unthreaded macrocycles are much larger.[85a] The DOSY technique is particularly useful for polyrotaxanes in which weakly interacting macrocycle and polymer offer no other detectable spectroscopic signature, because the threading can be proven and the fraction of threaded macrocycles can be determinated. This group also used the formation of polypseudorotaxanes to purify cyclic polymers from linear precursors.[86]

Ogoshi and Chujo used CD-based main-chain and side-chain polypseudorotaxanes to prepare transparent and homogeneous organic-inorganic polymer hybrids. Here CDs played a role as a compatibilizer between organic polymer and inorganic silica gel because of the hydrogen-bonding interaction between hydroxyl moieties of CDs and residual silanol groups of silica gel.[87]

1.7. CONCLUSIONS AND PERSPECTIVE

Because of the introduction of mechanical linking, polypseudorotaxanes and polyrotaxanes have novel topologies and properties compared with conventional small molecules and polymers. These supramolecular materials are studied all over the world now.

Depending on how the cyclic and linear components are connected, polypseudorotaxanes and polyrotaxanes can be divided into main-chain, side chain, and others.

The most commonly used macrocycles for the construction of polypseudorotaxanes and polyrotaxanes are crown ethers and cyclodextrins though other macrocycles, such as cucurbituril and tetracationic bisparaquat cyclophane, are also used.

A lot of tools have been employed to characterize polypseudorotaxanes and polyrotaxanes. However, the most powerful tool is NMR.

Due to their novel topologies, polypseudorotaxanes and polyrotaxanes have different properties, including solubility, stability, photoelectronic properties, viscosity, phase behavior, from conventional polymers. Studies have demonstrated that the degree of to which they differ depends on not only the properties of threaded cyclic and linear components but also the threading efficiency.

From previous analysis, we know that low association constants have limited the preparation of large supramolecular systems. It also has an important influence on the stability of supramolecular systems. The requirement for high association constants makes it necessary to prepare new more powerful hosts and guests. Most of the polypseudorotaxanes and polyrotaxanes obtained up to now are linear. The possibility of making two and three dimensional polypseudorotaxanes and polyrotaxanes, such as hyperbranched, dendritic, and crosslinked ones (Figure 18), is very interesting and important in terms of new topologies and properties. Molecular weight and polydispersity are two important factors determining the ultimate properties of polymers. Using recently developed living polymerization methods,[88] such as SFRP[89] (stable free radical polymerization), and the feature of mechanical linking of pseudorotaxanes and rotaxanes, we can prepare non-covalent (mechanical) reversible block and graft copolymers with

pseudorotaxane structure (Figure 19) with precisely controlled molecular weight and polydispersity. Furthermore, if stoppers are introduced in these copolymers, they will change into non-covalent copolymers with rotaxane-type mechanically interlocked structures. This is one advantage compared with non-covalent copolymers employing the non-threaded structures based on H-bonding or other non-covalent interactions.[90]

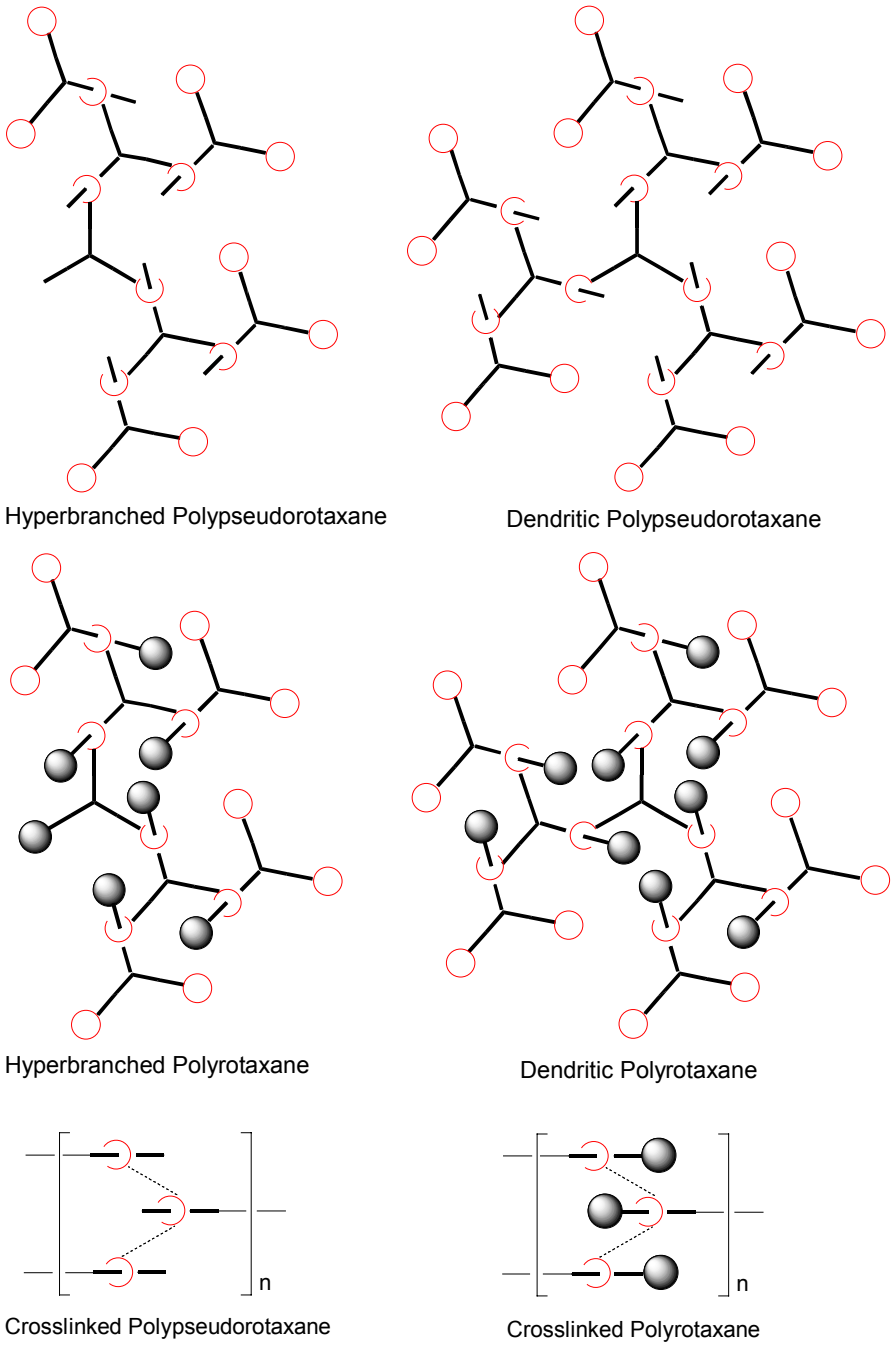


Figure 18. Polypseudorotaxanes and polyrotaxanes with new topologies.

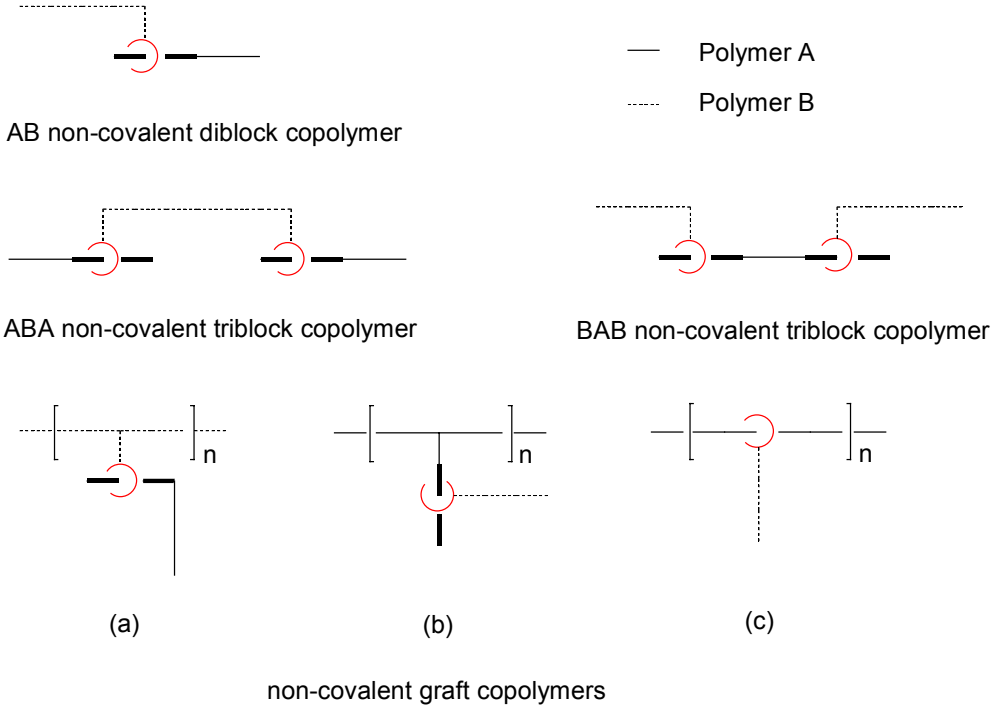


Figure 19. Non-covalent block and graft copolymers with pseudorotaxane structures.

Acknowledgements

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