Polymeric Rotaxanes

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Contents

1. Introduction

In the past three decades, chemistry has changed from focusing on a single molecule to molecular assemblies. Through the discovery of macrocycles, the chemistry of molecular recognition started by Cram,[1] Pedersen,[2–4] and Lehn[5,6] more than 40 years ago. The chemistry of molecular recognition progressed to that of host−guest chemistry mainly by Cram et al., while Lehn proposed the concept of supramolecular chemistry as "molecules beyond the molecule". In 1987, Pedersen, Cram, and Lehn were awarded the Nobel Prize in Chemistry.[7–9] Since then numerous supramolecular architectures have been constructed and studied as new components for materials as well as entities related to biological structural formation and functions. Nanoscience and nanotechnology appeared about a decade ago. The construction of supramolecular structures has attracted much attention from not only chemists but also biologists and physicist as a bottom-up procedure to construct nanoscale architectures.

During the last two decades, construction of interlocked molecules has received much attention because interlocked molecules such as rotaxanes and catenanes have unique structures and properties. Prior to the host−guest technique,

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Akihito Hashidzume was born in 1970, graduated from the Department of Macromolecular Science, Faculty of Science, Osaka University in 1992, and received his Doctorate of Science from Osaka University in 1997. His doctoral thesis was on polymerization of carbon−nitrogen double bonds. After earning his Ph.D., he began working at the Department of Macromolecular Science, Graduate School of Science, Osaka University, as an assistant professor. His research interests include polymer synthesis, water-soluble polymers, and polymer assemblies. He is a member of the Chemical Society of Japan, the Society of Polymer Science Japan, and the American Chemical Society.

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interlocked molecules were prepared using conventional reactions where interlocked structures are statistically formed in quite low yields. However, molecular recognition has led to high yields of rotaxanes and catenanes without high dilution, and since then, various interlocked molecules have been prepared.

Although the reactions of the complexes of amines with cyclodextrin (CD) and those of carboxylic acids,[10] and formation of polyrotaxanes using cyclic urethanes during polymerization were reported,[11−13] CDs were found to thread onto a polymer chain to give polyrotaxanes for the first time in 1990.[14]

To date, various polyrotaxanes have been investigated as new building blocks to construct nanostructures as well as to realize novel functions. Figure 1 shows the number of papers on rotaxanes and polyrotaxanes published by year. Although the number of published papers has been increasing, since 2000 this increase has been exponential.

This review covers mainly peer-reviewed papers on polymeric rotaxanes since 1990. Many types of cyclic compounds have been extensively used to construct rotaxanes and catenanes, and the cyclic component for polyrotaxanes includes crown ethers,[15−18] cyclophanes,[19,20] calix[n]arenes,[21−23] CDs,[24−28] cucurbiturils,[29] and cyclobis(paraquat-p-phenylene).[30] To date, different types of polyrotaxanes, including main chain polyrotaxanes and side chain polyrotaxanes (Figure 2), have been prepared. Herein the sections are classified according to the polyrotaxane structure: main chain polyrotaxanes and side chain polyrotaxanes. In the next sections, various polyrotaxanes are discussed according to their structures and components.
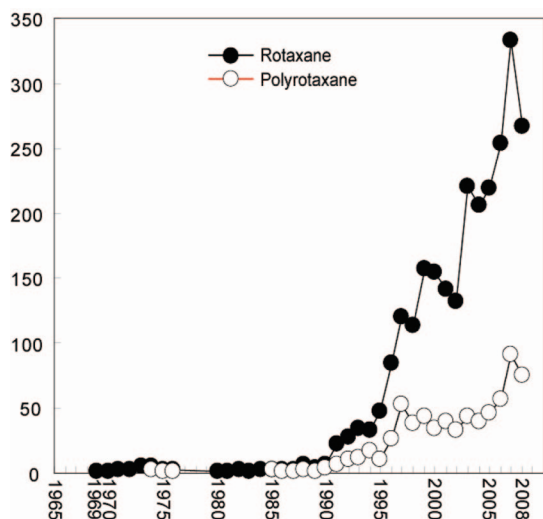
Figure 1. Number of the reports concerning polyrotaxanes chemistry from 1965 to 2008.
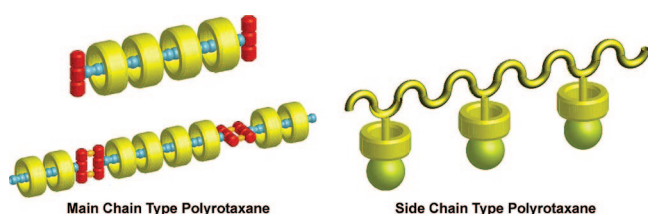

Figure 2. Typical strucutres of polyrotaxanes.

Since the 1970s, our group has strived to prepare polyrotaxanes. Although rotaxanes have been synthesized since the 1970s, the early results are summarized in the book *Molecular Catenanes, Rotaxanes and Knots*.[31] Harrison et al. synthesized [2]rotaxane by reacting the linear axel and a ring molecule attached to a solid support.[32] However, the yield for a single reaction was limited to 0.08%, and repeating the reaction over 70 times only increased the yield to 6%. Since then different types of rotaxanes have been prepared. Except for rotaxanes with cyclic polymethylenes, crown ethers[33] and CDs have been extensively used as the cyclic component to construct rotaxanes.

The review is focused mainly on CD-based systems. However, polymeric rotaxanes containing other cyclic compounds are also introduced.

2. Main Chain Polyrotaxanes

Different methods produce main chain polyrotaxanes. One is the polymerization of rotaxanes. In this method, inclusion compounds of diamines are treated with inclusion compounds of dicarboxylic acids, and then a condensation reaction of diamines and diacids gives poly*pseudo*rotaxanes. Another is threading cyclic molecules onto axis molecules to form a polymer of poly*pseudo*rotaxanes. This method has yielded a variety of polyrotaxanes, but the ends of the polymer chain are blocked by bulky substituents.

This section covers both the synthesis and properties of poly*pseudo*rotaxanes and polyrotaxanes, depending on the type of cyclic compound. There have been numerous overviews about the interlocked structures of rings, such as rotaxane and catenanes.[15,16,18,34−51] This section focuses on poly*pseudo*rotaxanes and polyrotaxanes with polymers as axis molecules.

Table 1. Chemical Structure and Properties of Cyclodextrins (CDs)

	α-CD	β-CD	γ-CD
Molecular Weight	972	1135	1297
No. of Glucose Units	6	7	8
Cavity Diameter (nm)	0.47	0.60	0.75
Height of Torus (nm)	0.79	0.79	0.79

2.1. Main Chain Polyrotaxane with Cyclodextrin (CD)

CDs are a family of macrocyclic oligosaccharides, the most common of which are composed of 6 (α), 7 (β), or 8 (γ) α-1,4-linked D-glucopyranose units.[24,25,27,28,52] Table 1 lists the physical properties of CDs. Construction of polyrotaxanes using CDs can be categorized in three types: the "threading" approach, "slipping" approach, and "inclusion polymerization" approach, which are depicted in parts a−c, respectively, of Figure 3. The "clipping" approach is physically impossible for the self-assembly of CD and an axis molecule. Poly*pseudo*rotaxanes have been prepared by the threading approach in aqueous media. The major driving forces for forming CD inclusion complexes are hydrophobic and van der Waals interactions between the inner surface of the CD ring and the hydrophobic sites of the guests. Tables 2−11 identify reported poly*pseudo*rotaxanes, which incorporate CDs using an axis polymer, such as polyethers, cationic polymers, polyamines, polyesters, π-conjugated polymers, polyolefins, polyamides, polyurethanes, and inorganic polymers.

2.1.1. Polyethers

In 1990, we successfully prepared inclusion complexes of CDs with polyethers. α-CD forms inclusion complexes with poly(ethylene glycol) (PEG)[14,53−56] to give poly*pseudo*rotaxanes in high yield. Although β-CD does not yield inclusion complexes with PEG, β-CD produces complexes with poly(propylene glycol) (PPG)[56−58] to give poly*pseudo*rotaxanes. α-CD does
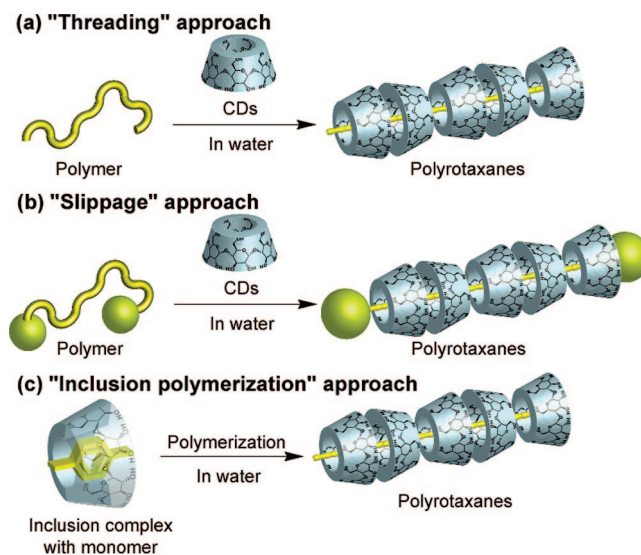

Figure 3. Schematic illustration of construction of poly*pseudo*rotaxanes incorpating CDs.

Table 2. Complex Formation between CDs and Polyethers

Polymer	Structure	$\overline{M_w}/10^3$	Yield (%)			Ref.
			α–CD	β–CD	γ–CD	
PEG	—(CH₂ CH₂ O)ₙ	1.0	92	0	trace	14,53-56
PTMO	—((CH₂)₂ CH₂ O)ₙ	1.0	94	47	trace	56,59,61-63
PTHF	—((CH₂)₃ CH₂ O)ₙ	1.0	86	trace	99	62
PPG	—(CH₂ CH O)ₙ CH₃	1.0	0	96	80	56-58
PMVE	—(CH₂ CH)ₙ OCH₃	1.0	0	0	80	59,60
PEVE	—(CH₂ CH)ₙ OEt	1.2	0	0	71	59
PnPVE	—(CH₂ CH)ₙ OnPr	1.2	0	0	4	59

not form complexes with PPG, but γ-CD forms inclusion complexes with poly(methyl vinyl ether) (PMVE)[59,60] to give poly*pseudo*rotaxanes. The cross-sectional area and the size of the CDs are correlated. Harada's group discovered an efficient formation of poly*pseudo*rotaxanes with other water-soluble polyethers, such as poly(tetramethylene oxide) (PTHF),[56] poly-(ethyl vinyl ether) (PEVE),[59] and poly(*n*-propyl vinyl ether) (PnPVE)[59] (Table 2).

2.1.1.1. Poly(ethylene glycol)s (PEG). Inclusion complexes of oligo(ethylene glycol) with α-CD have been studied in detail. Although ethylene glycol, di(ethylene glycol), and tri(ethylene glycol) do not form inclusion complexes with α-CD, tetra(ethylene glycol) and longer ethylene glycol polymers form complexes with α-CD. The yield of the complex increases as the polymer molecular weight increases, and complexes are obtained almost quantitatively with PEG when the degree of the polymerization is greater than 10.[14,53−56,61] In contrast, cyclic oligo(ethylene glycol)s show the opposite trend. Although dioxane forms a 1:1 complex with α-CD, 24-crown-6 gives a two to one (CD: crown ether) complex with α-CD.[57]

PEG was the first polymer found to form inclusion complexes with α-CD in the solid state (Figure 4). The yields of the complexes increase as the molecular weight of PEG increases, and the complexes are obtained in nearly quantitative yield using PEG with a molecular weight above 1000. Regardless of the molecular weight, α-CD does not form complexes with PPG.[56−58,61] These supramolecular structures are supported by the X-ray diffraction pattern and ^{13}C CP/ MAS NMR spectra. The formation of poly*pseudo*rotaxanes depends on the cavity size of CDs. Two ethylene glycol units are included in a single CD cavity.

Similar changes in the X-ray powder pattern have been observed for α-CD and poly(oxytrimethylene) (PTMO)[56,59,61−63] or poly(tetrahydrofuran) (poly(THF)).[62] When PEG and α-CD are mixed, the X-ray powder pattern changes from cage type to channel type (Figure 4). Although PEG forms complexes with α-CD only by mixing, PEGs containing large groups, such as 2,4-dinitrophenyl and 3,5-dinitrobenzoyl groups, do not produce changes in the X-ray powder pattern of α-CD even after two months, indicating that PEG enters the α-CD cavity from its small end groups.[64] Takata and Harada et al.[65,66] have prepared polyrotaxanes from complexes of α-CD with

poly(THF) in a similar manner. Tonelli et al.[67] have also reported complex formation of α-CD with PEG without a solvent.

We have prepared single crystals of inclusion complexes of α-CD with hexa(ethylene glycol) and tetra(ethylene glycol) dibromide, which are consistent with single X-ray crystal structure analysis. Figure 5 shows the results of X-ray crystallographic studies on the inclusion complexes of PEG with α-CD. α-CDs form columnar structures in a head-to-head and tail-to-tail fashion with an ethylene glycol chain inside the tunnel formed by α-CDs.[68]

Moreover, inclusion compounds comprised of PEGs with high molecular weights (above 100,000) have yielded physical hydrogels where the crystalline parts are formed by the PEG complexes as the cross-linking parts. Heating the hydrogels results in homogeneous solutions, and this process is reversible.[55]
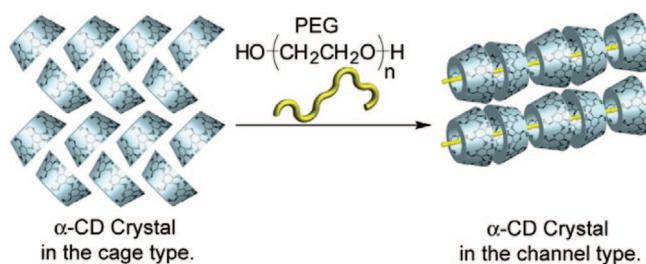

Figure 4. Schematic illustration of the formation of poly*pseudo*rotaxane between α-CD and PEG in the solid state.
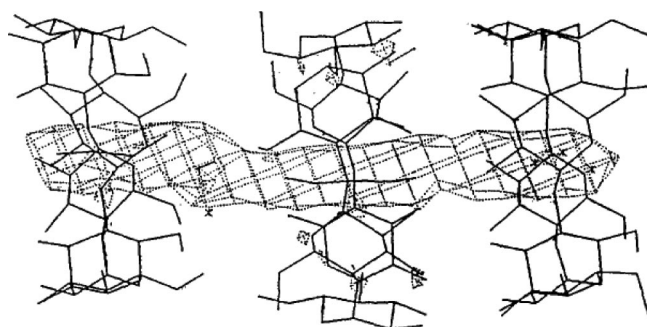

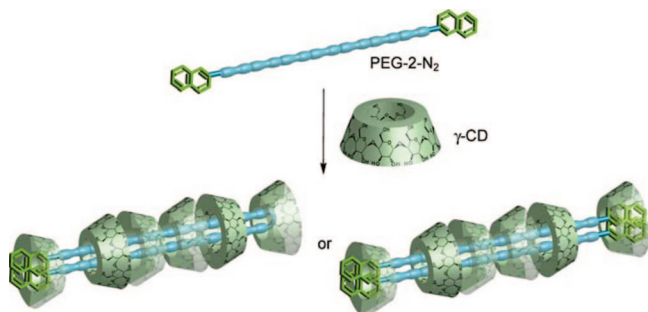**Figure 5.** Electron density of hexa(ethylene glycol) in complex with *a*-CD.

Figure 6. Double strand complex incorporating γ-CD and PEG-2-N$_2$.
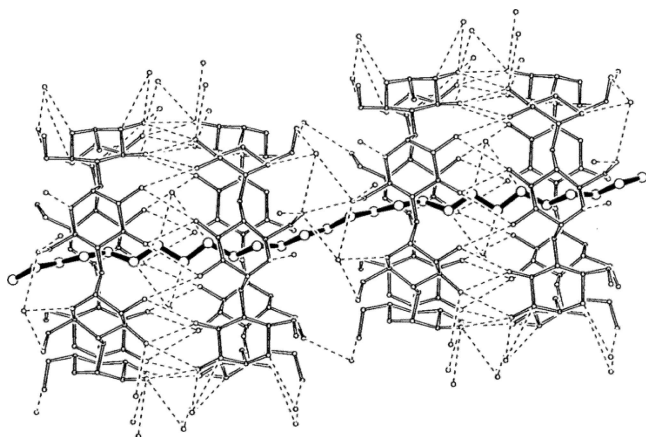

Figure 7. Crystal structure of the β-CD−PEG inclusion complex. The crystal packing structure is head-to-head. Reprinted with permission from ref 70. Copyright 2000 American Chemical Society.

Negligible complexation occurs between γ-CD and PEG, and the amount is too small to characterize. However, bis(3,5-dinitrobenzoyl)-PEG and bis(2,4-dinitrobenzoyl)-PEG form crystalline complexes with γ-CD in high yields, but α-CD does not form inclusion complexes with these PEG derivatives because the end groups are too large to thread into the cavities of α-CD. The authors have found that two ethylene glycol chains are included in the γ-CD cavity.[69] PEG with fluorescent probes at the ends of the polymer chain and bis(1-naphthylacetyl)-PEG (PEG-1-N$_2$) and bis(2-naphthylacetyl)-PEG (PEG-2-N$_2$) complexes show a large contribution from excimers, which are collective excitations arising from the interactions between two nearby naphthyl groups, and they confirm only a monomer emission in the absence of γ-CD. These complexes are composed of double chains of PEG, which penetrate the cavity of γ-CDs (Figure 6).

Although PEG does not form inclusion complexes with β-CD by mixing aqueous solutions, poly*pseudo*rotaxanes have been obtained by crystallizing a one-to-one mixture of PEG and β-CD at 70 °C for several months. X-ray crystallographic studies show that a PEG chain is threaded through hydrogen-bonded head-to-head dimers, which include three monomeric units in every one β-CD (Figure 7),[70] and the polymer chain is highly disordered about the axis of the channel passing through a stack of CD dimers.

2.1.1.2. Poly(propylene glycol) (PPG). β-CD forms inclusion complexes with PPG, but α-CD does not yield crystalline inclusion complexes with PPG,[56−58,61] and α-CD and β-CD form complexes with poly(oxytrimethylene) to give poly*pseudo*rotaxanes. The cross section of the polymers is correlated with the CD cavity size.[56,59,61,62] Figure 8 shows the crystal structures of the complexes of β-CD with polymers,
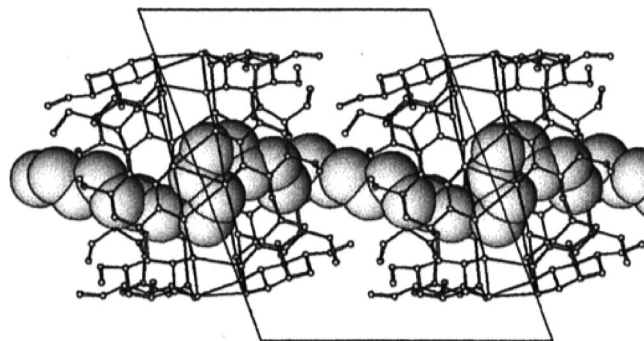

Figure 8. Columnar structure composed of four symmetry related β-CDs and PTMO, viewed from the *b*-axis (for clarity, molecules are rotated by 10° along the vertical axis). Reprinted with permission from ref 71. Copyright 2000 American Chemical Society.

Table 3. Complex Formation between CDs and Polyamines

Polymer structure	CDs	Ref.
$\left[NH {-} (CH_2)_2 \right]_n$	α−CD, γ−CD	74
$\left[NH {-} (CH_2)_{11} \right]_n$	α−CD	72
$\left[NH {-} (CH_2)_{10} {-} NH {-} (CH_2)_3 \right]_n$	α−CD	73
$\left[NH {-} (CH_2)_4 {-} \underset{NH_2}{CH} {-} CO \right]_n$	α−CD	75,76

PTMO (average $M_w = 1.4 \times 10^3$), and PPG (average $M_w = 425$) determined by X-ray crystallographic analysis. PTMO and PPG penetrate 97 and 22 Å (14 and three β-CDs), respectively, and all have a *trans* conformation.[71]

2.1.1.3. Poly(vinyl ether)s. Only γ-CD forms inclusion complexes with poly(methyl vinyl ether) (PMVE).[56,59−61] Although the molecular composition of PMVE is the same as that of PPG and POM, the complexes are stoichiometric in the crystalline state. The only difference is the position of the oxygen atom in the polymer chain. In the formation of inclusion complexes, the cross section of the polymer is correlated with the CD cavity size. γ-CD also forms inclusion compounds with poly(ethyl vinyl ether) (PEVE)[59] and poly(*n*-propyl vinyl ether) (PnPVE),[59] whereas α- and β-CD do not form complexes with these polymers. The order of the maximum yield of the complexes is PnPVE > PEVE > PMVE.

2.1.2. Polyamines

Poly(iminoundecamethylene),[72] poly(iminotrimethyleneiminodecamethylene),[73] polyethylenimine,[74] and poly(ε-lysine)[75,76] have been reported to form poly*pseudo*rotaxane (Table 3).

The formation of poly*pseudo*rotaxanes with polyethylenimines depends heavily on the pH of the aqueous medium. Although the maximum yield of poly*pseudo*rotaxane with α-CD and γ-CD has been observed at pH 11.0, complexation does not occur in the pH range below 8.0 due to protonation of the secondary amine groups in polyethylenimines. Polyethyleneimine forms a 2:1 inclusion complex with α-CD ([EI]:[α-CD] = 2:1) and a 4:1 complex with γ-CD ([EI]:

Table 4. Complex Formation between CDs and Cationic Polymers

Polymer structure	CDs	Ref.
$\left[\begin{array}{c}\text{Me}\\\text{N}^+(\text{CH}_2)_{10}\\\text{Me}\end{array}\right]_n$ n Br$^-$	α–CD, γ–CD	82,83
$\left[\begin{array}{c}\text{H}\\\text{N}^+(\text{CH}_2)_{11}\\\text{H}\end{array}\right]_n$ n Br$^-$	α–CD	82,83
$\left[\begin{array}{c}\text{H}\\\text{N}^+(\text{CH}_2)_6\text{N}^+(\text{CH}_2)_{10}\\\text{H}\quad\text{H}\end{array}\right]_n$ 2n Br$^-$	α–CD	82,83
$\left[\begin{array}{c}\text{H}\\\text{N}^+(\text{CH}_2)_6\text{N}^+(\text{CH}_2)_{12}\\\text{H}\quad\text{H}\end{array}\right]_n$ 2n Br$^-$	α–CD	82,83
$\left[\begin{array}{c}\text{H}\\\text{N}^+(\text{CH}_2)_3\text{N}^+(\text{CH}_2)_{10}\\\text{H}\quad\text{H}\end{array}\right]_n$ 2n Br$^-$	α–CD	82,83
$\left[{}^+\text{N}\bigcirc\bigcirc\text{N}^+(\text{CH}_2)_{10}\right]_n$ n Br$^-$	α–CD	84-86

[γ-CD] = 4:1), which agree with the poly(ethylene glycol)-based poly*pseudo*rotaxane system.[74]

Poly(iminoundecamethylene)[72] and poly(iminotrimethylene-iminodecamethylene)[73] contain a long hydrophobic alkyl chain, which must be included in the α-CD cavity.

2.1.3. Cationic Polymers

Axis molecules with pyridinium and pyridylpyridinium terminal groups have been used to form [2]rotaxane capped with metal−organic stoppers.[77,78] Charged centers are necessary at both ends of the aliphatic chains to achieve dynamic stability.[79,80] CDs form inclusion compounds with certain ionic polymers.[81] For example, α-CD and β-CD form inclusion complexes with viologen polymers to give complexes soluble in water. The ^{1}H NMR spectrum of the polymer does not change upon the addition of γ-CD in D$_2$O solution. In contrast, the ^{1}H NMR spectrum changes significantly upon adding α-CD or β-CD. The spectrum of the polymer in the presence of α-CD shows that each peak splits into two, indicating that α-CD forms stable complexes with the cationic polymer. The spectrum of the polymer in the presence of β-CD shows that all the peaks are broadened, indicating dynamic complexation.

Other poly(bolaamphiphile)s,[82,83] which have long hydrophobic parts and hydrophilic groups (cationic groups), and poly(viologen),[84,85] allow threading of CD rings under homogeneous conditions in aqueous solutions (Table 4). Poly*pseudo*rotaxanes between the polyelectrolyte and α-CD are stabilized by steric hindrance and the hydrophilicity of the cationic groups.[86]

2.1.4. Hydrophobic Polymers

While we were preparing inclusion complexes of CDs with hydrophilic polymers, we discovered that CDs even form inclusion complexes with hydrophobic polymers, such as polyethylene and polypropylene, with molecular weights less than 10,000.[53,61]

γ-CD selectively forms inclusion complexes with poly-(isobutylene).[87] The MW selectivity of this polymer is reversed between β-CD and γ-CD; although β-CD forms complexes with low molecular weight compounds and the yields of the complexes decrease as the molecular weight increases, γ-CD gives complexes with this polymer and the yields increase with molecular weight. In addition, CDs form inclusion complexes with some polyesters, including poly-(alkylene adipates)[88] and poly(ε-caprolactone).[89−91]

In these cases, the polymer sample is heated with aqueous solutions of CD with vigorous stirring or agitation by sonication. The polymer sample is partly solubilized in aqueous solutions, and the complexes form as a solid state.
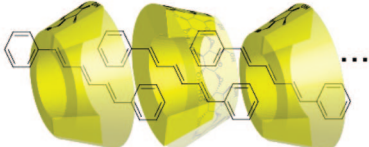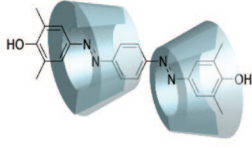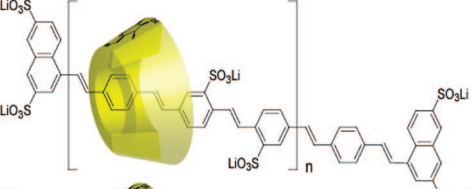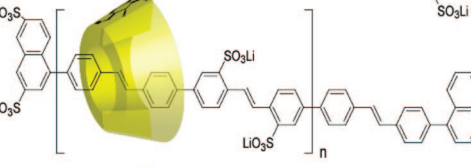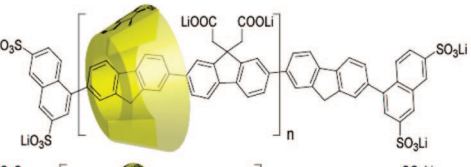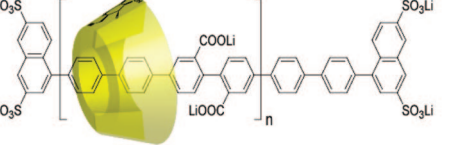
2.1.4.1. Polyesters. Research in recent years has focused on renewable polymers to protect the environment and to efficiently utilize natural resources. Biodegradable polymers, polyesters, and polyamides are important not only as renewable polymers but also due to their potential in pharmaceutical and biomedical applications.

Formation and characterization of poly*pseudo*rotaxanes with polyesters, such as poly(trimethylene adipate) (PTA), poly(1,4-butylene adipate) (PBA), poly(ethylene adipate) (PEA),[88] poly(ε-caprolactone) (P(ε-CL),[89−91] poly(L-lactide) (PLLA),[92] atactic poly((R,S)-3-hydroxybutyrate) (a-PHB),[93] poly-((R)-3-hydroxybutyrate) (i-PHB),[94] P(ε-CL)-PEO-P(ε-CL),[95] P(ε-CL)-b-PLLA,[96] and P(ε-CL)-PPG-P(ε-CL),[97] are summarized in Table 5. α- and γ-CDs form complexes with these polyesters in high yields, while β-CD forms complexes in moderate yields. Although the complexation yields of α-CD with PTA and PBA decrease as the molecular weight increases, α-CD forms complexes with PEA in high yields

Table 5. Complex Formation between CDs and Polyesters

Polymer structure		CDs	Ref.
$\left[\text{O}(\text{CH}_2)_2\text{O}\overset{\text{O}}{\underset{}{\text{C}}}(\text{CH}_2)_4\overset{\text{O}}{\underset{}{\text{C}}}\right]_n$	PEA	α-CD, γ-CD	88
$\left[\text{O}(\text{CH}_2)_3\text{O}\overset{\text{O}}{\underset{}{\text{C}}}(\text{CH}_2)_4\overset{\text{O}}{\underset{}{\text{C}}}\right]_n$	PTA	α-CD	88
$\left[\text{O}(\text{CH}_2)_4\text{O}\overset{\text{O}}{\underset{}{\text{C}}}(\text{CH}_2)_4\overset{\text{O}}{\underset{}{\text{C}}}\right]_n$	PBA	α-CD	88
$\left[\text{O}(\text{CH}_2)_5\overset{\text{O}}{\underset{}{\text{C}}}\right]_n$	P(ε-CL)	α-CD, γ-CD	89-91
PLLA	α-CD	92
a-PHB	γ-CD	93
i-PHB	α-CD	94
P(ε-CL)-PEO-P(ε-CL)		α-CD, γ-CD	95
P(ε-CL)-b-PLLA		α-CD	96
P(ε-CL)-PPG-P(ε-CL)		α-CD, γ-CD	97

Table 6. Complex Formation between CDs and π-Conjugated Molecules

Chemical Structures	CDs	Ref.
	β-CD, γ-CD	118
	α-CD	119
	β-CD	123,124
	α-CD, β-CD	122
	β-CD	122
	β-CD	120-122

Figure 9. Crystal structure of the DM-β-CD-bithiophene inclusion complex. Carbon and oxygen of β-CD are shown in gray and red, respectively. Carbon and sulfur of bithiophene are shown in gray and yellow, respectively.

even at higher molecular weights. α-CD-P(ε-CL) complexes are stoichiometric one-to-one (CD:monomer unit) compounds, whereas γ-CD-P(ε-CL) complexes are one-to-two compounds when the molecular weights of P(ε-CL) are low. A mixture of γ-CD and a-PHB produces poly*pseudo*rotaxanes in high yield.[93] Only α-CD forms a poly*pseudo*rotaxane with i-PHB. i-PHB and a-PHB selectively form crystalline inclusion complexes with different CDs. The formation of poly*pseudo*rotaxanes is controlled by the chemical structure and stereochemistry.[94] When the poly*pseudo*rotaxane of P(ε-CL)-PPG-P(ε-CL) is prepared by α-CD, only P(ε-CL) blocks are incorporated in the α-CD cavity, whereas both P(ε-CL) and PPG blocks are included in the poly*pseudo*rotaxane of P(ε-CL)-PPG- P(ε-CL) and γ-CD.[97]

2.1.4.2. π-Conjugated Polymers. π-Conjugated polymers have attracted much interest due to their high charge-mobility along individual polymer chains.[98−100] Recently, π-conjugated polymers have been used in practical applications, including light-emitting diodes,[101−104] thin-film field effect transistors,[105,106] photovoltaic cells,[107,108] and sensors.[109,110] However, realization of nanomolecular devices has been precluded by the difficulties in the development of nanosized molecular electronics in insulating π-conjugated polymers and wiring molecules between nanoelectrodes. The formation of an insulated π-conjugated polymer, which is called an

"insulated molecular wire",[61,111−117] is expected to prevent cross-talk and short-circuits. Preparing insulated molecular wires with CDs, which self-organize in aqueous solutions, makes it easy to wrap π-conjugated polymers such as poly*pseudo*rotaxanes and polyrotaxanes. Tables 6 and 7 summarize previous reports about poly*pseudo*rotaxanes and polyrotaxanes with π-conjugated polymers (oligomers), such as *all-trans*-1,6-diphenyl-1,3,5-hexatriene,[118] azo-dyes,[119] poly(paraphenylene) (PPP),[120−122] poly(fluorene) (PF),[122] poly(4,4′-diphenylenevinylene) (PDV),[122] poly(phenylenevinylene) (PPV),[123,124] polythiophene (PT),[125−131] polyaniline (PANI),[132−139] and poly(azomethine) (PAM).[140−144]

all-trans-1,6-Diphenyl-1,3,5-hexatriene forms nanotube aggregates by incorporating as many as 20 β-CD and 20−35 γ-CD rings in aqueous solution or the solid state. The tubular arrangement of CDs is likely due to the side-by-side self-assembling of the rodlike guest, which is included within the CD cavities. Diphenylhexatriene molecules are staggered with respect to each other along the axes of the nanotubes.[118] Anderson and his co-workers have used a Suzuki coupling reaction[145] to prepare polyrotaxanes based on PPP, PF, PDV, and PPV in aqueous solutions.[120−124] These polyrotaxanes have conjugated polymer threaded through 0.9 ± 1.6 CDs per repeat unit. Bulky naphthalene-3,6-disulfonate end groups prevent the macrocycles from slipping off the conjugated polymer chains. The fluorescence spectra of these polyrotaxanes indicate that the presence of the threaded CD reduces the flexibility of the conjugated polymer. Both the solution and the solid-state photoluminescence quantum yields are enhanced upon threading the conjugated polyaromatic cores through α- or β-CDs, and the emission spectra of the polyrotaxanes are blue-shifted compared to those of the corresponding unthreaded polymers.[122]

Some researchers have employed polythiophenes, which are an important representative class of π-conjugated polymers due to their thermal stability, as molecular wires. Polythiophenes can be prepared via coupling reactions, such as Yamamoto coupling and Suzuki coupling, and electrochemical polymerization techniques.[125−131] Although bithiophene (2T) forms 1:1 inclusion complexes with 2,6-dimethyl-β-CD (DM-β-CD)[127] (Figure 9) and hydroxypropyl β-CD
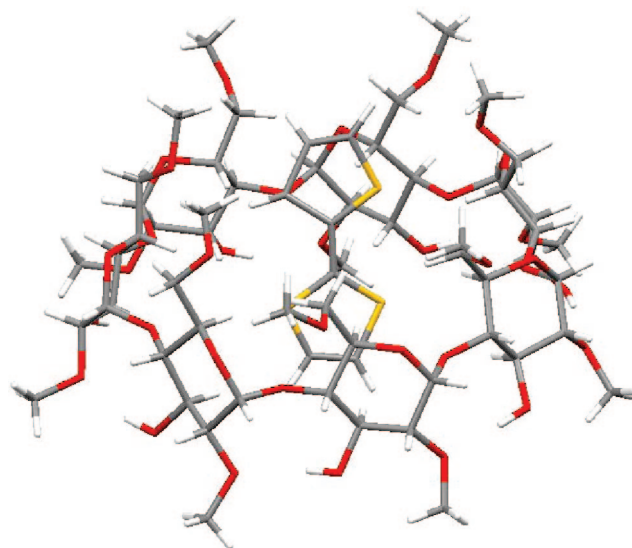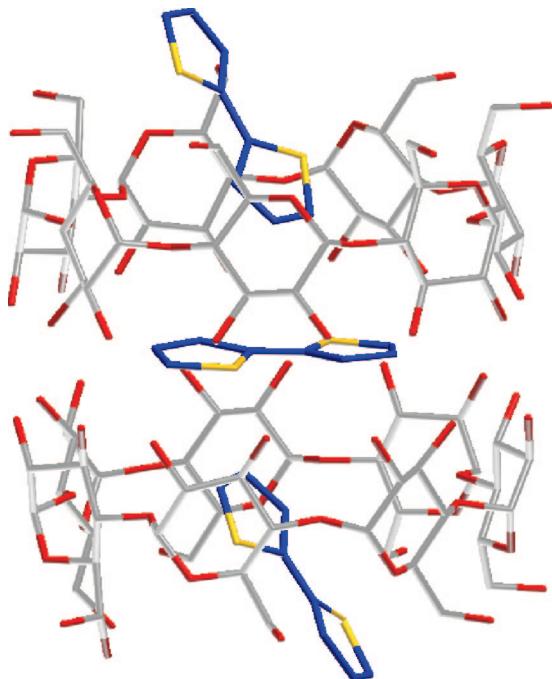
Figure 10. Crystal structure of the β-CD-bithiophene inclusion complex. Carbon and oxygen of β-CD are shown in gray and red, respectively. Carbon and sulfur of bithiophene are shown in blue and yellow, respectively. Reprinted with permission from ref 126. Copyright 2004 American Chemical Society.

(HP-β-CD),[128] β-CD forms a 3:2 inclusion complex with bithiophene (Figure 10).[126]

The inclusion complex between HP-β-CD and 2T gives a poly*pseudo*rotaxane with polythiophene, which can be prepared by electropolymerization in aqueous solutions.[128] The inclusion complexes, 2T⊂β-CD and 2T⊂DM-β-CD, are polymerized by aqueous oxidative reaction to obtain poly*pseudo*rotaxanes.[126,127] ^{13}C CP/MAS NMR indicates that the DM-β-CD molecule in the inclusion complex with polythiophene has a symmetrical cyclic conformation, but DM-β-CD assumes an asymmetrical conformation in the crystal when not hosting a guest in the cavity. A polythiophene chain is included in the cavities of DM-β-CD. The number-average molecular weight of poly(2T) is up to 5×10^3. Although there are a few reports on the polymerization of thiophenes with CDs in water, the resulting poly(ethylenedioxy thiophene) does not contain CD molecules,[129] indicating that the CD molecules dissociate from poly(ethylenedioxy thiophene) during the polymerization and a rotaxane type structure is not formed.

Water-soluble β-CD-poly*pseudo*rotaxanes containing poly-(thiophene-2,5-diyl) or poly(3-methylthiophene-2,5-diyl)s as an axle have also been prepared by the threading method. Stirring the reaction mixture for a prolonged period causes further threading of β-CD onto the water-soluble poly*pseudo*rotaxanes to give the water-insoluble poly*pseudo*rotaxanes. UV−vis measurements reveal that the inclusion of poly(3-methylthiophene-2,5-diyl)s by β-CD depends on the flexibility of the main chain and the molecular weight.[130]

Hadziioannou and co-workers have prepared polythiophene rotaxanes with anthracene stoppers catalyzed by nickel-catalyzed Yamamoto coupling in DMF.[125] Although polyrotaxanes containing π-conjugated polymer have been reported, uses of polydisperse polyrotaxanes have yet to be discussed. Monodispersed polyrotaxanes, bithiophene-[2]rotaxane (2T-[2]rotaxane), and terthiophene-[2]rotaxane (3T-[2]rotaxane) have been prepared by the Suzuki coupling reaction of 6-*O*-(4-iodophenyl)-β-CD with di-(1,3,2-dioxaborolan-2-yl)oligothiophene (oligothiophene diboric ethylene glycol esters) in an aqueous solution of DM-β-CD (Scheme 1 and Table 7). According to MALDI-TOF mass spectroscopy, the crude product contains dumbbell-shaped molecules, [2]rotaxanes, [3]rotaxanes, 4T-[3]rotaxane, and 6T-[3]rotaxane. These rotaxanes and dumbbell-shaped molecules can be purified by preparative reverse phase chromatography.[131]

2.1.4.3. Polyolefins. The yields of complexes of α-CD with oligoethylene (OE) are higher than those of β- and γ-CDs under the same conditions.[146] β-CD forms complexes with squarane, whereas α-CD does not.[61,147] The solid state structures of both polyethylene and *trans*-polyacetylene included in α-CD can be calculated by molecular mechanics.[148]
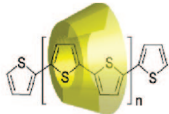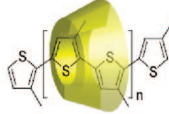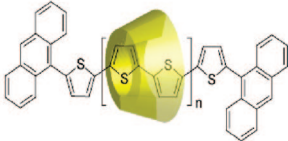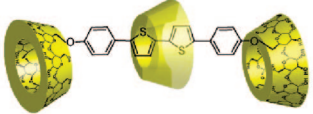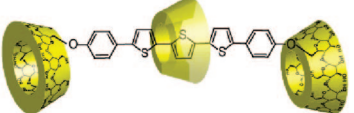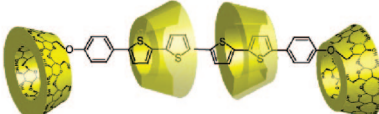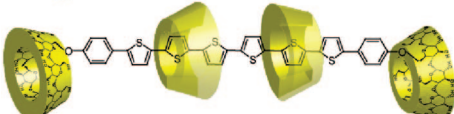
Polybutadienes (PBs)[149] and polyisoprenes (PIPs)[150] form inclusion complexes with CDs with a high selectivity for crystalline compounds. β-CD forms complexes only with low molecular weight PIP, whereas γ-CD forms complexes with higher molecular weight PIP. Regardless of molecular weight, α-CD does not form complexes with PIP. The yields of γ-CD complexes increase as the molecular weights of PIP increase until a maximum is reached at ca. 7×10^3, and then they decrease. α- and β-CDs form complexes only with low molecular weight PB and a high 1,4-addition content, whereas γ-CD forms complexes with PB with a high 1,2-

Scheme 1. Preparation of DM-β-CD-oligothiophene Based Rotaxanes with the End Stopper of β-CDs[a]
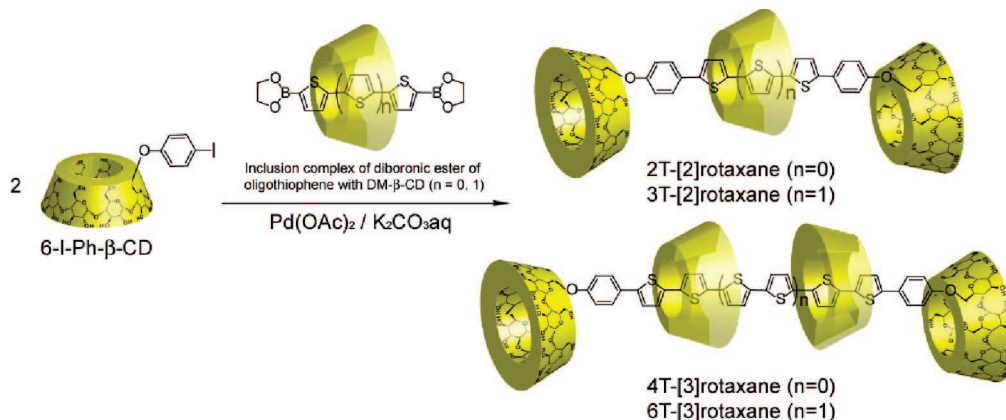
[a] Reprinted with permission from ref 131. Copyright 2007 American Chemical Society.

Table 7. Complex Formation between CDs and Poly(thiophene)s

Polymer structures	CDs	Ref.
	β-CD HP-β-CD DM-β-CD	126-128
	α-CD β-CD	130
	β-CD	125
	DM-β-CD	131
	DM-β-CD	131
	DM-β-CD	131
	DM-β-CD	131

Table 8. Complex Formation between CDs and Polyolefins

Polymer structure		$\overline{M_w}/10^3$	Yield (%)			Ref.
			α–CD	β–CD	γ–CD	
$-(CH_2\text{-}CH)_n$ $\qquad OH$	PVA	22	0	0	0	146
$-(CH_2\text{-}CH)_n$ $\qquad CONH_2$	PAAm	10	0	0	0	146
$-(CH_2\text{-}CH_2)_n$	OE(20)	0.56	63	0	0	146
$-(CH_2\text{-}CH)_n$ $\qquad CH_3$	PP	ca. 0.8	0	40	7	53,61
CH_3 $-(C\text{-}CH_2)_n$ CH_3	PIB	ca. 0.8	0	8	90	87
$-(CH_2\text{-}CH\text{-}CH_2\text{-}CH_2)_n$ $\qquad CH_3$	Squarane	0.43	0	62	24	61,147
$-(CH_2CH=CHCH_2\text{-}X\text{-}CH_2CH)_n$ $\qquad\qquad\qquad\quad CH=CH_2$	PB	2.0	1.3	31	24	149, 151, 152
$-(CH_2CH=CCH_2\text{-}X\text{-}CH_2CH)-$ $\qquad\quad CH_3 \qquad\quad C=CH_2$ $\qquad\qquad\qquad\qquad\quad CH_3$	PIP	0.62	0	3.0	6.3	150

content in low yields. The yields of the γ-CD complexes decrease as the molecular weight of PB increases.

PBs form inclusion complexes with CDs stereoselectively to give crystalline compounds in bulk.[151] Although α-CD does not form inclusion complexes with PB in aqueous solution, α-CD forms inclusion complexes with PBs with 1,4-*cis*- and 1,4-*trans*-butadiene units in bulk upon heating at 100 °C. On the other hand, PB with 79% of the 1,2-structure does not form inclusion complexes with α-CD. The yield of the inclusion complexes increases as the content of the 1,4-*cis*-structure of PB increases and as the molecular weights of PBs decrease.

γ-CD forms inclusion compounds with two different high molecular weight isotactic polyolefins, i.e., polypropylene (i-PP) and poly(butene-1) (i-PB) (Table 8). Both coalesced i-PP and i-PB are obtained after removing the host γ-CD and display different characteristics compared to those of the as-received or corresponding control samples.[152]

2.1.4.4. Polyamides and Polyurethanes. Nylon-11 has been prepared by inclusion polymerization of *pseudo*rotaxanes, which incorporates aminoundecanoic acid and α-CD at high temperatures (150−250 °C) (Table 9).[153,154] The X-ray powder diffractograms of the inclusion complexes support channel-type packing. Inclusion compounds between α-CD and β-CD and nylon-6 have been formed by a solution heating technique (M_n = 12 kg mol^{-1}).[155−157]

Polyurethane-CD poly*pseudo*rotaxanes have been prepared by mixing isocyanate and a dihydroxyl monomer in the presence of permethylated α-CD or permethylated β-CD in DMF at 120 °C. According to ^{1}H NMR and elemental

analysis, the molar ratio of CD to the repeating unit is low (0.08−0.25). Polyurethane-CD poly*pseudo*rotaxanes with a lower T_g correspond to the inhibition of intermolecular hydrogen bonding of the urethane groups.[158]

Poly*pseudo*rotaxanes incorporating β-CDs and polyamides can be prepared from a mixture of diamines and diacid dichlorides.[10]

2.1.4.5. Inorganic Polymers. β- and γ-CDs form inclusion complexes with poly(dimethylsiloxane)s (PDMS)[159,160] and poly(dimethylsilane)s (PSi)[161,162] of various molecular weights to yield crystalline material (Table 10). However, α-CD does not form complexes with PDMS and PSi regardless of molecular weight. The yields of β-CD-PDMS and β-CD-PSi inclusion complexes decrease as the polymer molecular weight increases. In contrast, the yields of γ-CD-PDMS and γ-CD-PSi inclusion complexes increase as the molecular weight increases until reaching a maximum around 760, and then they gradually decrease. β-CD and γ-CD show opposite trends for chain-length selectivity. The β-CD-PDMS inclusion complexes are stoichiometric 1:1 compounds when the molecular weights of PDMS are low. The γ-CD-PDMS inclusion complexes are 2:3 (CD:monomer unit of PDMS) compounds, whereas the γ-CD-PSi inclusion complexes are 1:3 (γ-CD:monomer unit of PSi). The PSi main chain in the cavities of γ-CD takes an *all-trans* conformation. The formation of poly*pseudo*rotaxanes with PSi has been confirmed by the circular dichroism induced by the CD rings.[163] Other measurements of the circular dichroism spectra have confirmed that the PSi chain has a helical form.[164]

2.1.5. Block Copolymers

Site-selective complexation plays an important role in constructing supramolecular structures in biological systems and in chemical processes, and it should play a crucial role in constructing artificial supramolecular structures in polymeric systems. CDs form inclusion complexes with Triton X-405 in a site-selective manner. α-CD specifically binds an ethylene glycol, and β-CD binds the hydrophobic end group (an iso-octylphenyl group and a phenyl group) (Figure 11).[165]

Table 9. Complex Formation between CDs and Polymers

Polymer structure	CDs	Ref.
(Nylon 11)	α–CD	153,154
	α–CD	153,154
	α–CD	153,154
	α–CD	153,154
(Nylon 6)	α–CD β–CD	155-157
	PM-α–CD PM-β–CD	158
	α–CD	10
	α–CD	10
	α–CD	10
	α–CD	10

Table 10. Complex Formation between CDs and Inorganic Polymers

Polymer structure	$\overline{M}_w/10^3$	yield (%)			Ref
		α–CD	β–CD	γ–CD	
PDMS	3.2	0	0	72	159, 160
PSi	0.8	0	0	57	161, 162

Pluronic PEO-PPO-PEO triblock copolymers where thinner PEO blocks flank the middle PPO block form site-selective poly*pseudo*rotaxanes. β-CD can selectively thread the middle PPO block to form poly*pseudo*rotaxanes,[166] while α-CD selectively includes the flanking PEO blocks (Table 11).[167] PPO-PEO-PPO triblock copolymers form poly*pseudo*rotaxanes with α-CD in high yields. The flanking bulky PPO blocks should thread through the α-CD cavity to regioselectively form a stable poly*pseudo*rotaxane with the middle PEO block.[168,169]

2.1.6. α-CD Polyrotaxanes

Polyrotaxanes where numerous α-CDs are threaded on a PEG chain have been prepared by reacting complexes
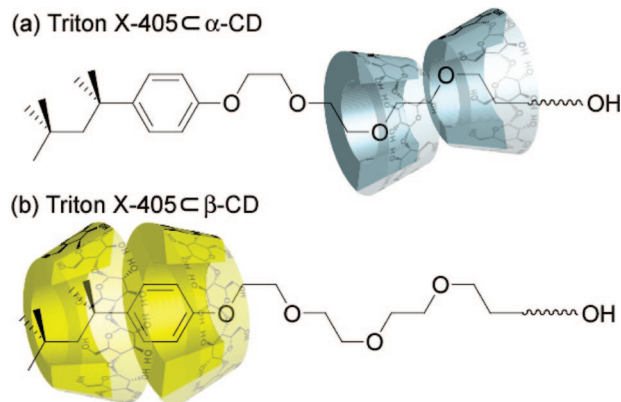
Figure 11. Proposed strucutres of Triton X-405 with α-CD and β-CD, respectively.

Table 11. Complex Formation between CDs and Triblock Copolymers

Polymer structures	CDs	Ref.
PEO-PPO-PEO	α-CD	167
PEO-PPO-PEO	β-CD	166
PPO-PEO-PPO	α-CD	168,169

between α-CDs and PEG bisamines with 2,4-dinitrofluorobenzene, which is sufficiently bulky to prevent dethreading (Figure 12).[170−172] Beginning from PEG, various molecular weights of polyrotaxanes have been prepared. Fifteen to 100 α-CD molecules are captured in each polyrotaxane. Fractionation of the product prepared from PEG of average molecular weight 1.0×10^4 using GPC has yielded a
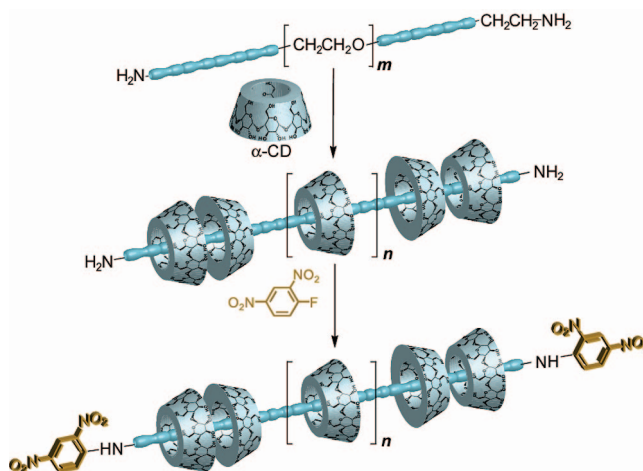
Figure 12. Schematic illustration of the preparation of polyrotaxane incorporating PEG and α-CD.
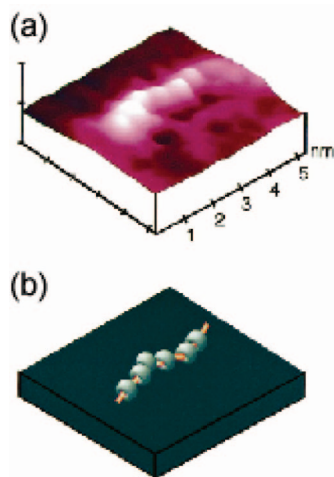
Figure 13. STM image of the molecular necklace (a) and its schematic structure (b).
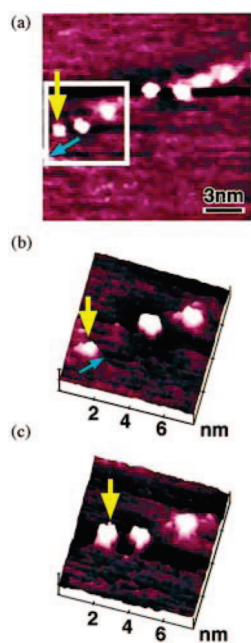
Figure 14. STM images of the simple-shuttling. Reprinted with permission from ref 175. Copyright 2000 American Chemical Society.

polyrotaxane with over 130 α-CD molecules. This is the first example of a polyrotaxane (not a *pseudo*rotaxane), which can be classified as a "molecular necklace".

In polyrotaxanes, the wheel components can shuttle along the axis component. The shuttling of CDs in polyrotaxanes has been observed by scanning tunneling microscopy (STM).[173] Figure 13 shows a typical STM image of a molecular necklace on a MoS$_2$ substrate, which is regularly aligned with the α-CD. The linear movement of α-CD on PEG can be manipulated by the Pt/Ir tip in STM like a "molecular abacus".[174] Figure 14 shows images acquired before and after each manipulation. The CDs are arranged mainly in head-to-head and tail-to-tail conformations; about 20% form in a head-to-tail conformation.[175]

2.1.7. CD Molecular Tubes

The authors have prepared a "molecular tube" by cross-linking adjacent α-CD units in a polyrotaxane (molecular
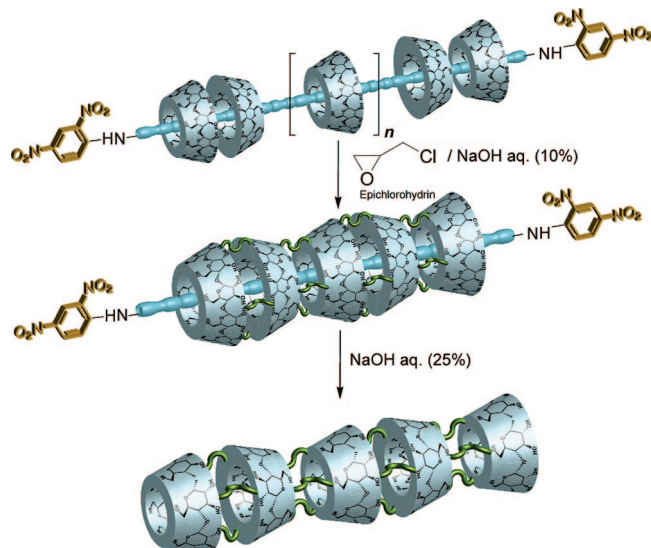
Figure 15. Schematic illustration of the preparation of molecular tubes incorporating α-CD.
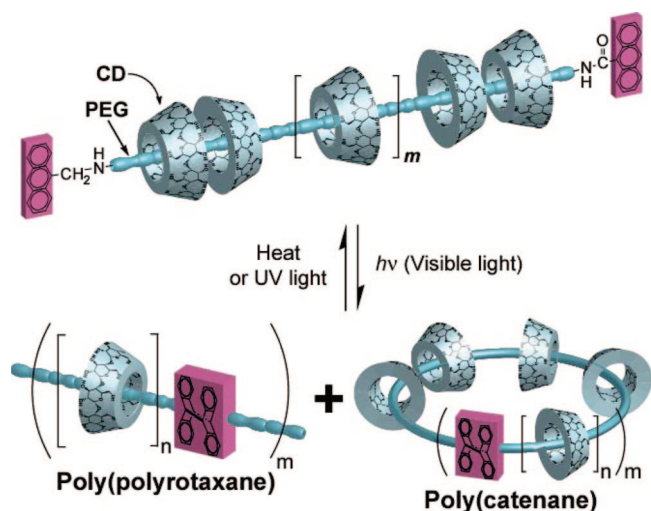
Figure 16. Preparation of an α-CD-based polyrotaxane using photoreactions. Reprinted with permission from ref 178. Copyright 2003 American Chemical Society.

necklace) (Figure 15).[63,176,177] Epichlorohydrin is added to the molecular necklace dissolved in 10% NaOH. Epichlorohydrin reacts with the hydroxyl groups of the threaded α-CD, which links each α-CD. The 2,4-dinitrofluorobenzene moieties, which are bulky stoppers at both ends, are removed by treating with a strong base (25% NaOH). The yield of the molecular tube is 92%, and the average molecular weight is estimated to be ca. 2×10^4 by GPC. The molecular tube can accommodate I$_3^-$ ions in an aqueous solution of KI−I$_2$ efficiently, whereas α-CD does not.

2.1.8. Preparation of Polyrotaxanes by Photoirradiation

Anthracene groups are large enough to prevent dethreading of α-CD and β-CD from an axle, and photoirradiating produces dimers. Poly(polyrotaxane)s and poly(catenane)s can be obtained by photoirradiating polyrotaxanes with anthracene groups as stoppers. The authors have prepared poly(α-CD-polyrotaxanes) by photoirradiating polyrotaxanes with 9-anthracene (Figure 16).[178] The ^{1}H NMR spectrum of the product shows broad resonance bands due to α-CD and PEG, and the absence of absorption bands due to monomeric
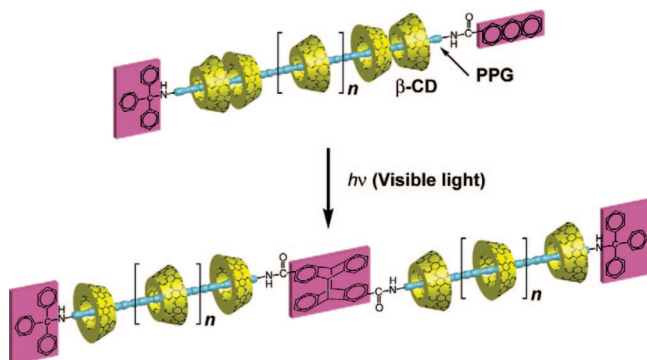
Figure 17. Preparation of a β-CD-based polyrotaxane using photoreactions. Reprinted with permission from ref 179. Copyright 2004 American Chemical Society.
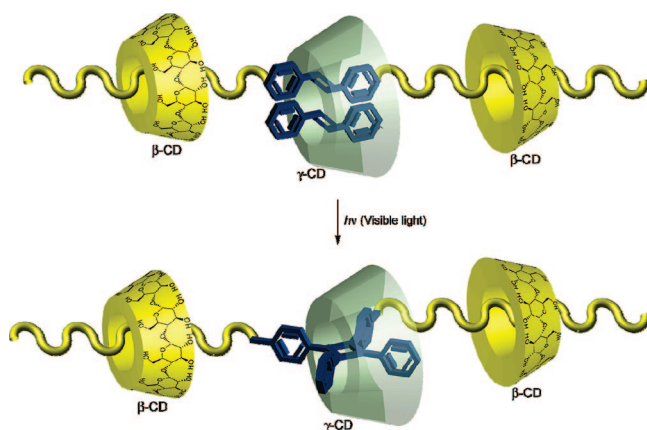
Figure 18. Stoppering of a poly*pseudo*rotaxane by photochemical [2 + 2] cycloaddition.

9-anthracene. Characteristic absorption and emission bands due to monomeric 9-anthracene have completely disappeared.

A polyrotaxane with numerous β-CD molecules has been prepared by photoreactions of a precursor complex between β-CD and PPG with a triphenylmethyl group at one end and a 2-anthryl group at the other end (Figure 17).[179] By irradiating the precursor complex with visible light ($\lambda \geq 340$ nm), photodimerization of the 2-anthryl groups forms a polyrotaxane. GPC data indicates that the elution volume of the β-CD polyrotaxane is smaller than that of the starting material, indicating that the hydrodynamic size of the β-CD polyrotaxane is larger than that of the starting material.

Some macrocyclic molecules currently inserted into rotaxanes have a cavity of ca. 6 Å in diameter, including crown ethers, a cucurbituril (CB[6]), and α- and β-CDs, making interlocked molecules relatively easy to prepare. However, preparing rotaxanes or polyrotaxanes containing larger macrocyclic molecules with a cavity of larger than 7.0 Å diameter by the threading method is difficult. γ-CD has a cavity of 7.5–8.3 Å in diameter. Triphenylmethyl blocking groups along the polymer main chain in the presence of both β- and γ-CDs have been formed by irradiating with UV light in aqueous solutions. These blockings self-assemble spontaneously by γ-CD in the polyrotaxane and are composed mainly of β-CD polyrotaxane (Figure 18).[180] The 9-anthryl group is large enough to prevent α- and β-CDs from dethreading, but it is small enough for γ-CD to thread onto the polymer chain. However, the photocyclodimerization products of 9-anthracene groups are large enough to prevent γ-CD from dethreading.[181–185] Polyrotaxanes containing
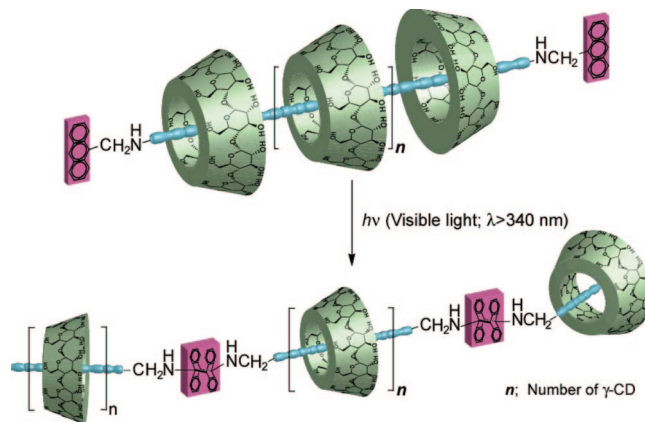
Figure 19. Preparation of γ-CD polyrotaxane. Reprinted with permission from ref 186. Copyright 2004 American Chemical Society.

Scheme 2. Synthesis of Polyrotaxanes Containing CE and Polyurethane
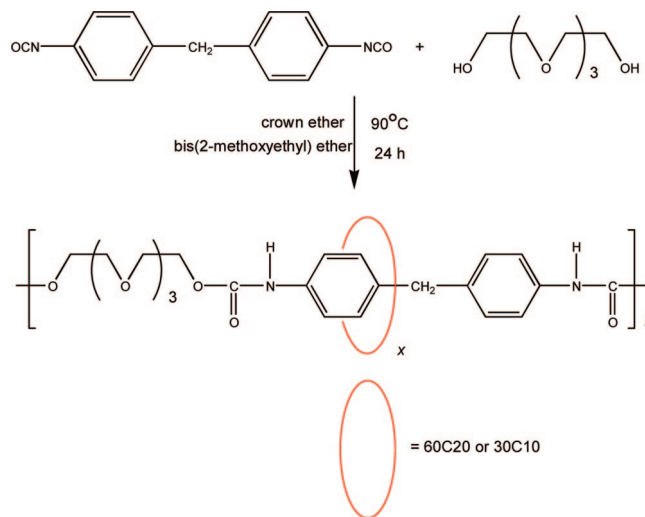
γ-CDs have been prepared by photocyclodimerization reactions of 9-anthryl groups at the ends of a polymer chain in the presence of γ-CDs (Figure 19).[186] GPC data indicates that the molecular weight of the γ-CD polyrotaxane is higher than that of the starting materials. The ^{1}H NMR spectrum of the γ-CD polyrotaxane shows that the resonance bands due to the 9-anthryl group are absent, but a new signal at 8 ppm, which is assigned to the cyclic dimer of the 9-anthryl groups, appears.

2.2. Main Chain Polyrotaxane with Crown Ethers (CEs)

Crown ethers (CEs) are monomacrocyclic polyethers,[17,33,187–195] which have been widely studied as hosts for organic salts, such as secondary ammonium salts and paraquat derivatives. Gibson's group has utilized CEs to synthesize a variety of poly*pseudo*rotaxanes and polyrotaxanes. Main-chain polyurethanes and polyesters were prepared by step-growth polymerizations in the presence of unfunctionalized aliphatic CEs.

Gibson and co-workers synthesized polyurethane rotaxanes based on 60-crown-20 or 36-crown-12 (Scheme 2).[196–200] They found that the larger the crown, the higher the threading efficiency. The stoppers also greatly increased the threading efficiency. Beckham et al. prepared some main chain

Scheme 3. Preparation of Poly(sebacate CE)s and Poly*pseudo*rotaxanes

Scheme 4. Preparation of Polyrotaxanes Using Difunctional Blocking Groups

Scheme 5. Synthesis of Polyrotaxane-like Assembly
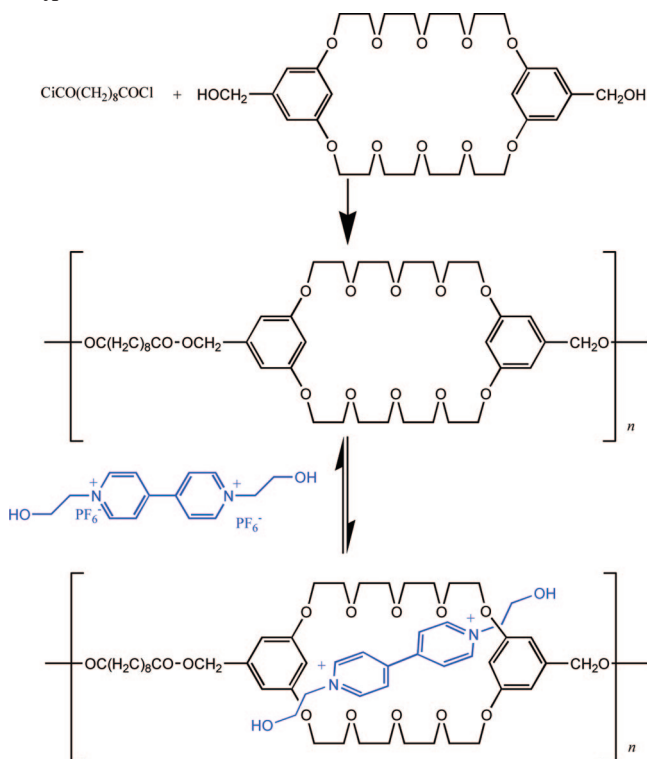
polyurethane-based polyrotaxanes from hexamethylene diisocyanate and either ethylene glycol or di(ethylene glycol).[201] They also found the threading efficiency increased with increasing CE ring size. The polyrotaxanes have significantly lower glass transition temperatures than the model polyurethane. Crystallization occurs in the polyrotaxanes without dethreading of the macrocycle. This phenomenon provides evidence that improved processability and ordering may be possible simultaneously with well-designed polyrotaxanes. A series of poly*pseudo*rotaxanes containing polysebacate backbones and ethylene oxide-based CEs such as 30-crown-10, 42-crown-14, 60-crown-20, and bis(*p*-phenylene)-34-crown-10 were synthesized via step growth polymerizations using diacid chloride-diol and transesterification reactions.[202−204] Several poly(ester crown ether)s containing 20-, 26-, and 32-membered rings in the main chain were also synthesized to explore the effect of the cavity size, structure of the comonomers, and polymerization process on *in situ* rotaxane formation (Scheme 3).[205−208] A strategy to completely eliminate dethreading of captured cyclics during the preparation of polyrotaxanes was developed by using difunctional blocking groups (Scheme 4).[209,210] They synthesized hydrocarbon-based macrocycles, 40- and 44-membered macrocycles, for the ultimate syntheses of polyrotaxanes.[211]

Polyrotaxanes of 60-crown-20 with polyacrylonitrile were also prepared.[212,213] Main-chain poly(methyl methacrylate rotaxane)s were also prepared using free radical polymerization.[214] The threading efficiency depends on the introduction of stoppers, the strength of the interactions between the macrocyclic CE and the linear component, the size of the CE, the ratio between the cyclic and acyclic starting materials, and threading temperature. They designed and synthesized azo-type radical initiators which can afford end-blocked polyrotaxanes *via* free radical polymerizations of styrene monomers in the presence of cyclic species.[215,216]
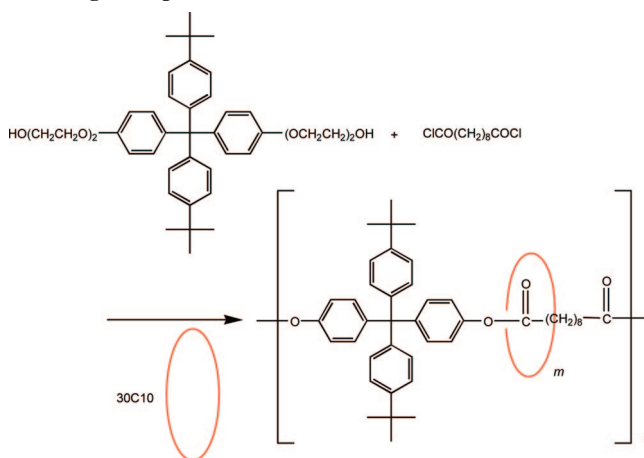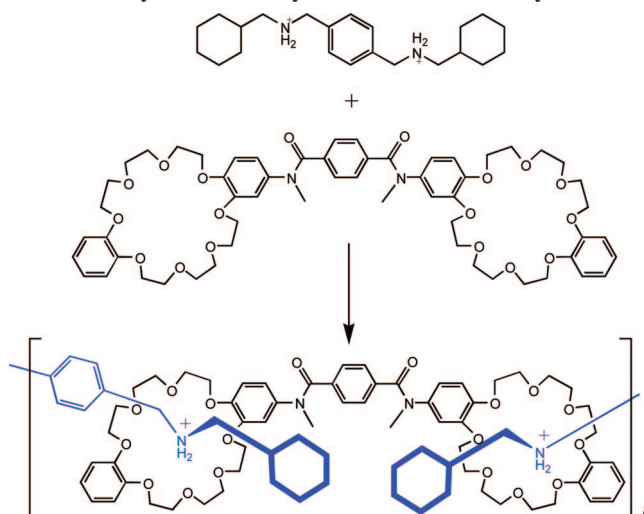
Takata et al. demonstrated that the multiple slipping of dumbbell components into macrocyclic ones having the appropriate size complementarity, of bis-ammonium salt and CE dimer (bis-CE) in acetone or acetonitrile, yielded polyrotaxane-like assembly (Scheme 5). The polyrotaxane-like assembly was easily converted to the monomers and bis-CE in a polar solvent such as DMSO.[217] They succeeded in synthesizing polyrotaxane networks by using the reversible thiol-disulfide interchange reaction based on dynamic covalent chemistry (Scheme 6).[218−222] They reported the synthesis of head-to-tail poly[2]rotaxane by the self-polycondensation of the [2]rotaxane monomer via the Sonogashira coupling reaction.[223]

Loeb et al. also synthesized *pseudo*[2]rotaxanes from protonated 1,2-bis(4,4′-bipyridinium)ethane axles and DB24C8 wheels, which associate in the solid state to form poly*pseudo*rotaxanes by hydrogen bonding or π-stacking.[224] The *pseudo*[2]rotaxanes can be involved in metal−ligand self-assembly reactions and be extended to polymeric systems and linear 1D and square-grid 2D or 3D metal-based polyrotaxanes.[225,226] Stoddart and co-workers prepared large macrocyclic compounds with the topologies of catenanes and molecular nacklaces during the synthesis of polyrotaxanes by Wittig step-growth polymerization between a dibenzylic bis(triphenylphosphonium)-stopped [2]rotaxane, with an

Scheme 6. Polyrotaxane Network Synthesized from polyCE and Bisammonium Salt

Scheme 7. Template-Directed Synthesis of [2]Rotaxane and [n]Rotaxanes
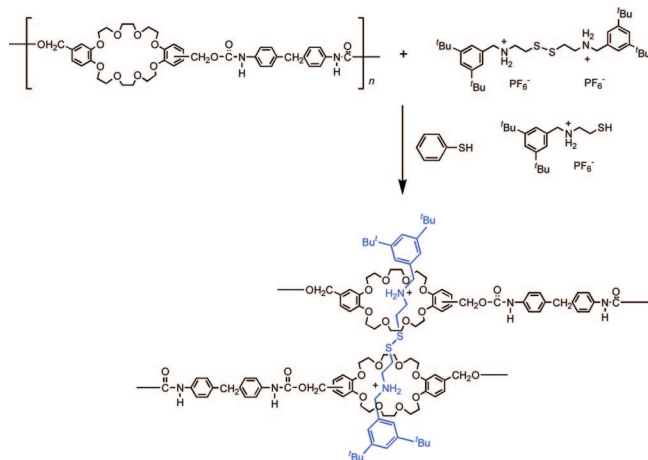
ammonium recognition site encircled by a DB24C8 ring, and appropriate derivatives of terephthaldehyde carrying bulky groups.[226]

A general synthetic method for making rotaxanes, the "threading-followed-by-stoppering" approach, involves several macrocycles. Although this approach is relatively simple, it does not provide complete control over the number of threaded macrocycles; that is, the rings or beads are often not threaded onto all of the available recognition sites on the axles. Alternatively, a template-directed "clipping" approach in which the macrocycles are formed from acyclic precursors in the presence of templating recognition sites on the dumbbells has provided a versatile means for the construction of some lower-order rotaxanes. Recently, dynamic covalent chemistry, exemplified by reversible imine formation, metal−ligand exchange, and olefin metathesis, has been demonstrated to be an effective tool for the preparation of various exotic mechanically interlocked molecular compounds. It has been found that, in the presence of an appropriate template, one of the possible compounds in the dynamic library, after mixing the different components, can be amplified to give the thermodynamically most stable product. Stoddart et al. have reported an example of such a template-directed synthesis of linear and branched [n]rotaxanes by employing dynamic covalent chemistry in the form of reversible imine formation (Scheme 7).[227−232] In the presence of the dumbbell-shaped compound containing an axial-recognition site, the condensation of 2,6-pyridinedicarboxaldehyde and tetra[ethyleneglycol bis(2-aminophenyl)ether] forms selectively and near quantitatively a [24]crown-8 ring that becomes clipped onto the dumbbell. Such thermodynamically controlled, template-directed amplification is driven by a series of noncovalent bonding interactions that include hydrogen bonds and aromatic $\pi−\pi$ interactions between the dumbbell and the ring. The thermodynamic product, a [2]rotaxane, was converted into a stable *pseudo*[2]rotaxane by fixing of the two imine bonds. Moreover, such a template-directed, thermodynamic clipping approach has proven to be effective and efficient in the synthesis of sterically bulky, mechanically interlocked dendrimers.
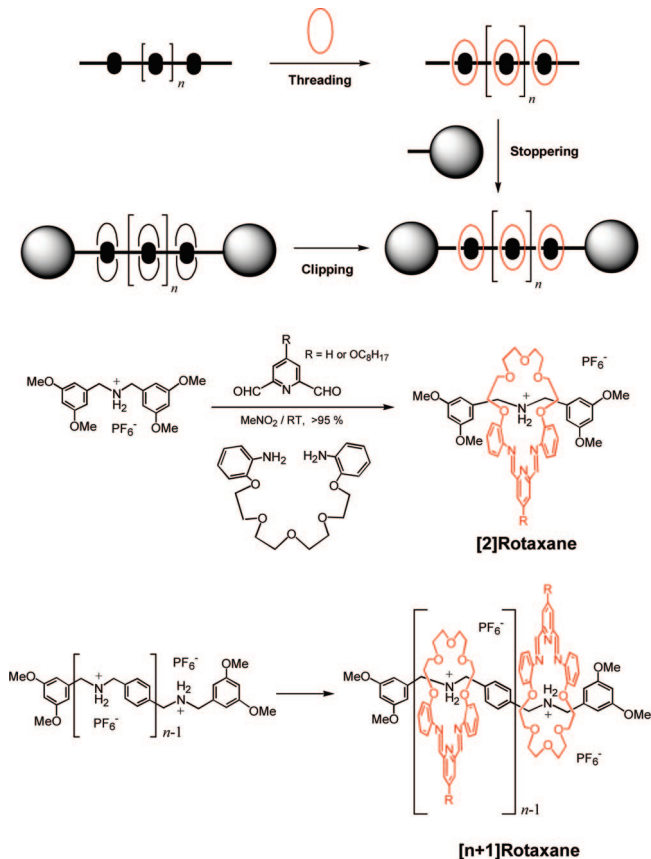
2.3. Main Chain Polyrotaxanes with Other Wheel Compounds

2.3.1. Cucurbit[n]uril-Based System

The cucurbit[n]urils (CB[n], $n = 5−10$) are a family of pumpkin-shaped macrocycles derived from glycol-uril and formaldehyde. CBs are often regarded as CD analogues, and the cavity sizes of CB[6], CB[7], and CB[8] roughly correspond to those of α-, β-, and γ-CD, respectively, although their guest affinities are different. The binding behavior of CB[6] has been explored by Mock and co-workers since the 1980s.[233] The central cavity of a CB is hydrophobic, like that of a CD, but the rims of a CB are lined with convergent carbonyl groups, which lead to strong charge−dipole interactions with cationic guests, as well as hydrogen-bonding interactions with organic ammonium ions. Thus, CBs generally bind cationic and neutral guests but not anions. CB[5] accommodates small molecules such as N_2; CB[6] binds protonated α,ω-diaminoalkanes $^+NH_3(CH_2)_nNH_3^+$ ($n = 4−7$, $K = 10^5$ to 10^6 M^{-1} in aqueous formic acid) as well as neutral species such as THF; CB[7] forms 1:1 complexes with larger cations, such as methyl viologen (MV^{2+}, $K = 2 \times 10^5$ M^{-1} in aqueous buffer) and neutral molecules such as ferrocene; CB[8] has such a large cavity that it is able to simultaneously accommodate two aromatic guests with the size of (E)-diaminostilbene. The poor solubilities of CBs can be a critical factor limiting their use. Most binding studies are performed in aqueous acid, as CBs are insoluble in most organic solvents. Several routes to functionalized CBs have been pursued to overcome this problem, particularly with CB[5] and CB[6], but efficient routes to soluble derivatives of CB[7] and CB[8] have yet

Scheme 8. Polyrotaxane Containing CB Molecules
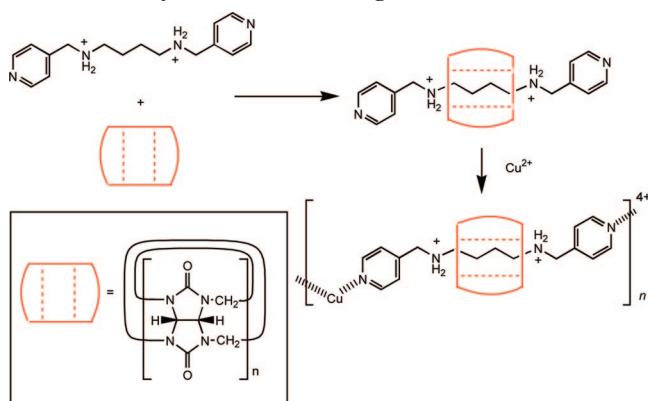
Scheme 9. Helical Polyrotaxane: CB "Beads" Threaded onto a Helical One-Dimensional Coordination Polymer

Scheme 10. Synthetic Strategy to One- and Two-Dimensional Polyrotaxanes
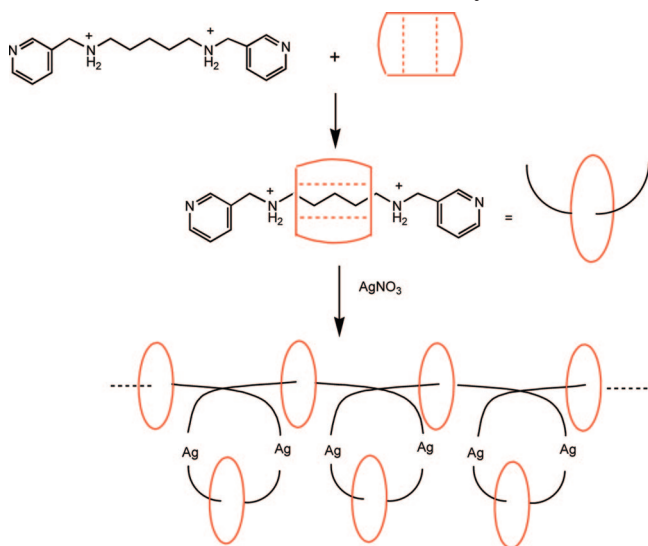
to be developed. Many cationic dyes form stable 1:1 inclusion complexes with CB[7] in aqueous solution (association constants $K > 10^5$ M^{-1}). Complexation generally enhances the photostability of the dye, as with CD complexes. The remarkably low polarizability inside the CB cavity extends the fluorescence lifetimes of the encapsulated dyes. Many CB-based rotaxanes, polyrotaxanes, and poly-*pseudo*rotaxanes have been reported.

Kim and co-workers have developed a simple way to construct a rotaxane containing CB as a "bead" and spermine as a thread by taking advantage of the strong tendency of CB to form inclusion complexes with aliphatic diammonium ions (Scheme 8). They reported the self-assembly and X-ray crystal structure of a polyrotaxane containing CB molecules threaded on a 1D coordination polymer in the solid state.[234] This polyrotaxane was unique in several aspects, being (1) the first formed on a coordination polymer, (2) the first containing a cyclic component in every repeating unit, and (3) the first to be structurally characterized by single-crystal X-ray crystallography. They also prepared a helical 1D polyrotaxane in which cyclic "beads" are threaded onto a helical coordination polymer (Scheme 9).[235] Extending this approach, they constructed an unprecedented polyrotaxane containing cyclic beads threaded on 2D coordination polymer networks. Moreover, the 2D and 3D polyrotaxane networks are fully interlocked (Scheme 10).[236–242]

Buschmann et al. used the complex of CB with the 1,6-hexanediammonium ion as a preorganized structure for the

synthesis of mono- and polyamide rotaxanes by condensation reactions with acids or diacid chlorides.[243,244] They also showed that both CB[6] and α-CD are able to include poly(ethylene glycol) with molecular weight 2000 to give a poly*pseudo*rotaxane.[245]

Steinke et al. prepared a main chain polyrotaxane in which polymerization and rotaxane formation occur simultaneously, due to the presence of the catalytically active self-threading macrocycle CB. They used catalytic 1,3-dipolar cycloadditions to give a polyrotaxane (Scheme 11).[246,247]

2.3.2. Cyclobisparquat/Cyclophane-Based Systems

Charge transfer or $\pi-\pi$ interactions have been used to prepare poly*pseudo*rotaxanes. A series of poly*pseudo*rotaxanes was synthesized by using the tetracationic cyclophane cyclobis(paraquat-phenylene) as the cyclic component. This cyclophane was quickly threaded onto some polymers. High ratios between the cyclic and acyclic starting materials of these poly*pseudo*rotaxanes show that hydrogen bonding, $\pi-\pi$ stacking, and charge transfer interactions are efficient driving forces for the construction of poly*pseudo*rotaxanes and polyrotaxanes. Parsons and Mason et al.[248–250] studied the threading process and molecular motion of the ring component along the polymer chain (Scheme 12). The NMR signals of cyclobis(paraquat-phenylene) bound onto the polymer chain by threading can be distinguished from those moving freely in solution. Chujo and co-workers also used this ring compound to prepare poly*pseudo*rotaxanes (Scheme 13).[251] The mixing of 2-benzylidene-4-phenyl-1,3-dithiole and cyclobis(paraquat-phenylene) in DMSO produced a green-brown solution, which showed a charge-transfer (CT) absorption band. The ^{1}H NMR spectrum of the dithiole, after

Scheme 11. Main Chain Polyrotaxane Synthesized by Catalytic 1,3-Dipolar Cycloaddition in the Presence of CB[6][a]
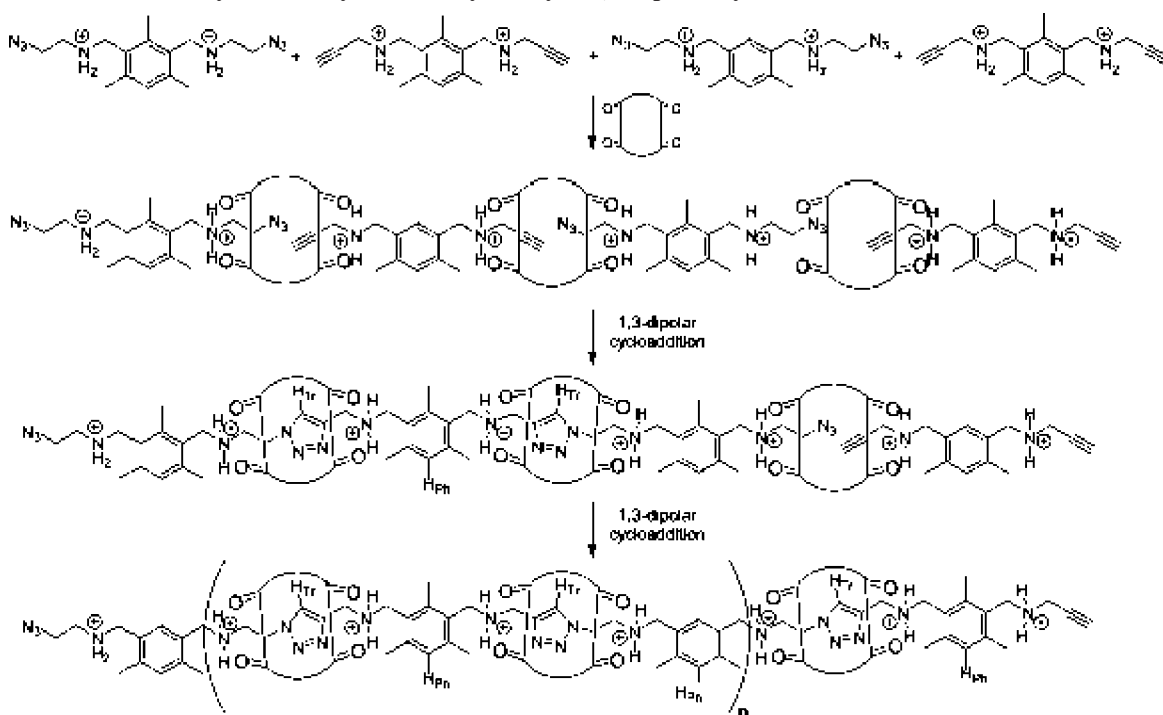
[a] Reprinted with permission from ref 247. Copyright 2004 American Chemical Society.

Scheme 12. Formation of the Poly*pseudo*rotaxane from Cyclobis(paraquat-phenylene) and a Polyether Derivative
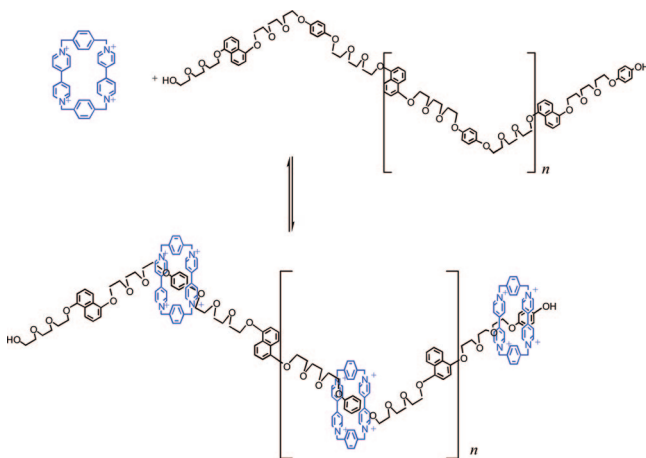
Scheme 13. Self-assembly of Cyclobis(paraquat-phenylene) and Dithiafulvene Polymer in DMSO
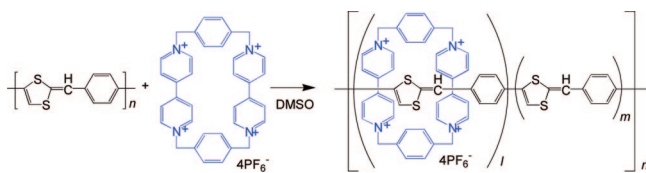
adding the cyclic acceptor in DMSO-d_6, showed upfield shifts of the peaks for the dithiafulvene moiety, indicating that an insertion of the dithiole into the cyclic acceptor by a CT interaction led to the formation of a *pseudo*rotaxane. The self-assembly of the π-conjugated dithiafulvene polymer and the cyclic acceptor by a CT interaction gave poly*pseudo*ro-taxanes in DMSO. The UV–vis and ^{1}H NMR spectra of the poly*pseudo*rotaxanes suggested that the incorporation ratio of the cyclic acceptors into the polymers depends on the molecular weights of the polymers. In addition, the

effective CT interaction between the dithiafulvene unit and the cyclic acceptor was found to afford a high conductivity of the poly*pseudo*rotaxane.

Cyclobis(paraquat-phenylene) was also used in the preparation of polyrotaxanes.[251] The monomeric rotaxane, bearing two protected functional groups, was used to obtain a dimer, following a new approach of sequential deprotection–coupling steps which can lead to mechanically linked polyrotaxanes (Scheme 14).[252,253]

The "click chemistry" approach is highly efficient and functional group tolerant and proceeds under mild reaction conditions, making it appropriate for the template-directed synthesis of mechanically interlocked molecules. Employing this new approach, a series of [*n*]rotaxanes have been prepared in a convergent and efficient manner.[254] Recently, Stoddart and co-workers have synthesized polymers that contain π electron-donating 1,5-dioxynaphthalene units encircled by cyclobis(paraquat-*p*-phenylene) by using the copper(I)-catalyzed azide–alkyne cycloaddition to give a polyrotaxane (Scheme 15).[255] Cooke and co-workers extended this methodology to synthesize not only polyrotaxanes but also polycatenanes.[256]

A dicationic cyclophane, which was synthesized for the first time by Diederich in 1991,[257] can be used as a ring component to construct poly*pseudo*rotaxanes and polyrotaxanes (Scheme 16).[258,259] Anderson et al. presented the crystal structure of a rotaxane between the cyclophane and an anionic azo dye, which shows that the cyclophane embraces the center of the dye; sodium coordinates to both the dye and the cyclophane, as well as DMSO solvent molecules, resulting in an infinite polyrotaxane network.[260]

2.3.3. Metal Coordination Systems

Metal ions play an important role to expand the rotaxane structures into the higher-ordered polyrotaxane frameworks, as shown in CE or CB systems. Metal coordination chemistry

Scheme 14. Schematic Representation of the Stepwise Polymerization Procedure To Give a Mechanically Linked Polyrotaxane[a]
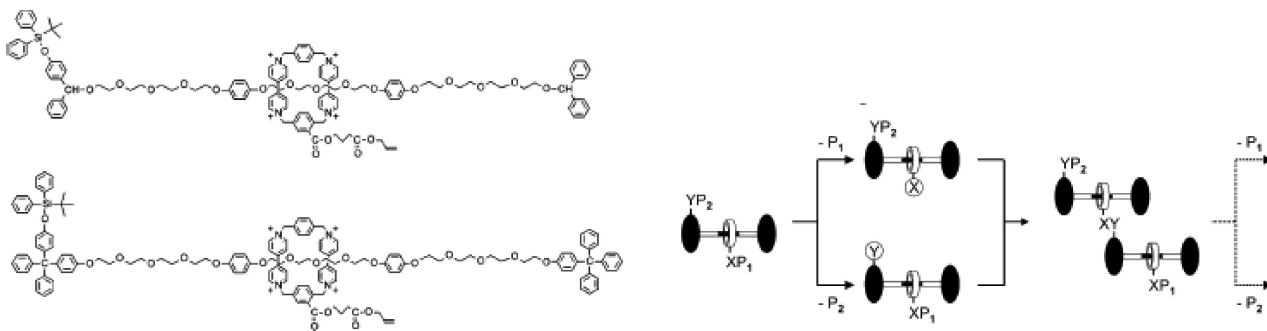
[a] Reprinted with permission from ref 253. Copyright 2003 American Chemical Society.

Scheme 15. Synthesis of a Polyrotaxane Using "Click" Chemistry[a]
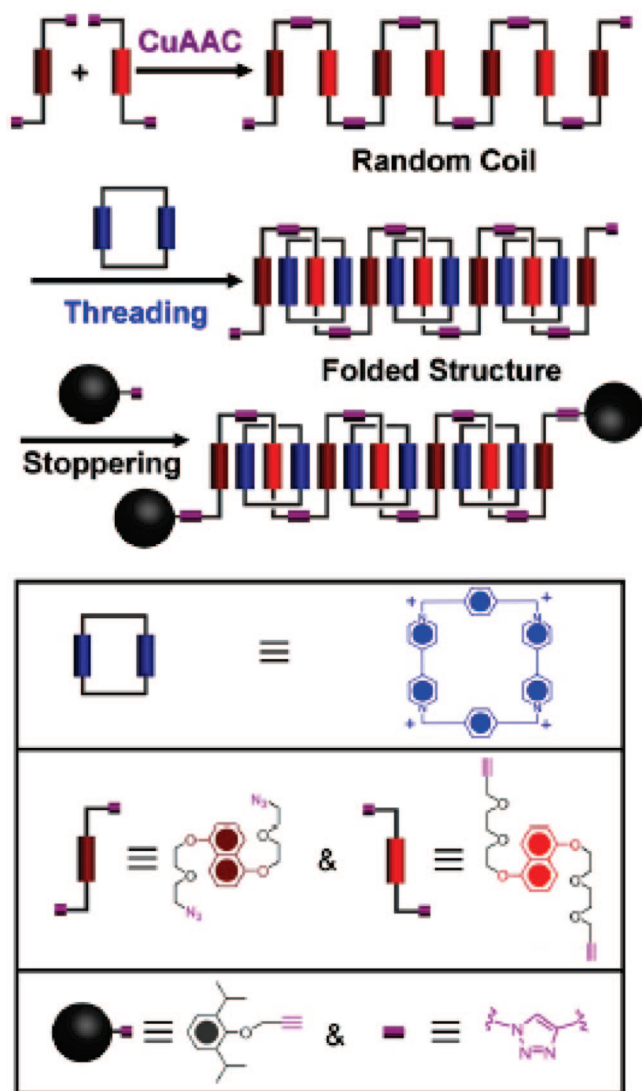
[a] Reprinted with permission from ref 255. Copyright 2008 The National Academy of Sciences of the USA.

can also be applied to immobilize the wheel components to the axial molecules. Sauvage and co-workers showed that the use of transition metals as templating agents allowed strict control of the molecular assembly of the rotaxane precursors (Scheme 17).[261−265] They also showed that subtle substituent effects allow control of the electronic and complexation/decomplexation behavior of the conjugated polyrotaxanes.[266]

Swager et al. synthesized conjugated poly*pseudo*rotaxanes by the electropolymerization of thiophene-terminated monomers with copper(I) and zinc(II) ions as templates.[267,268] Polymetallorotaxanes can exhibit remarkably high conductivities when the redox potential of the metal matches the oxidation potential of the π system, thus leading to potential applications in chemoresistive sensors (Scheme 18).[269] Metal-directed self-assembly was also used to synthesize a conducting three-strand conducting ladder polymer.[270] This conjugated poly*pseudo*rotaxane binds reversibly to Zn^{2+} and Cu^{2+} ions, which alters its conductivity and suggests potential applications in sensors. Lehn and co-workers applied a metal-directed strategy to the synthesis of a *pseudo*[4]rotaxane.[271−273]

Robson et al. synthesized two-dimensional polyrotaxanes by using $Zn(1,4\text{-bis(imidazol-1-ylmethyl)benzene})_2(NO_3)_2$ (Figure 20) or $Ag(1,4\text{-bis(imidazol-1-ylmethyl)benzene})_3$-$(NO_3)_2$.[274−276] A polyrotaxane architecture, comprising two interpenetrating chains of rings, was prepared by the combination of organometallic chemistry, coordination chemistry, and self-assembly through hydrogen bonding.[277] Now, there are many studies on the construction of higher-ordered poly*pseudo*rotaxane and polyrotaxane architectures using metal coordination chemistry.[278−285]

2.3.4. Calixarene-Based System

There are many reports on supramolecular formation between calixarenes and small molecules. However, only a few examples were reported on calixarene-based polyrotaxanes. A water-soluble nanometer-scale metallocapped polyrotaxane was prepared by the inclusion complexation of azocalixarenes with metallo-bridged CD dimers, displaying highly selective binding for Ca^{2+} (Scheme 19).[286] A polyrotaxane formed by the polycondensation of *p-tert*-butylphenol with paraformaldehyde in the presence of poly(ethylene glycol)s was reported.[287]

2.4. Applications of Main Chain Polyrotaxanes

2.4.1. Biodegradable Polyrotaxanes and Hydrogels

Recently, CD-based polyrotaxanes and poly*pseudo*rotaxanes have led to interesting developments of supramolecular biomaterials such as biodegradable polyrotaxanes and hydrogels.[288−293] Due to their controllable size, low cytotoxicity, and unique architecture, CD-based supramolecules have potential for a broad range of medical applications. Supramolecular hydrogels based on the self-assembly of the inclusion complexes between CDs with biodegradable block copolymers could be used as promising injectable drug delivery systems for sustained con-

Scheme 16. Synthesis of [*n*]Rotaxanes Bearing Dicationic Cyclophanes[*a*]
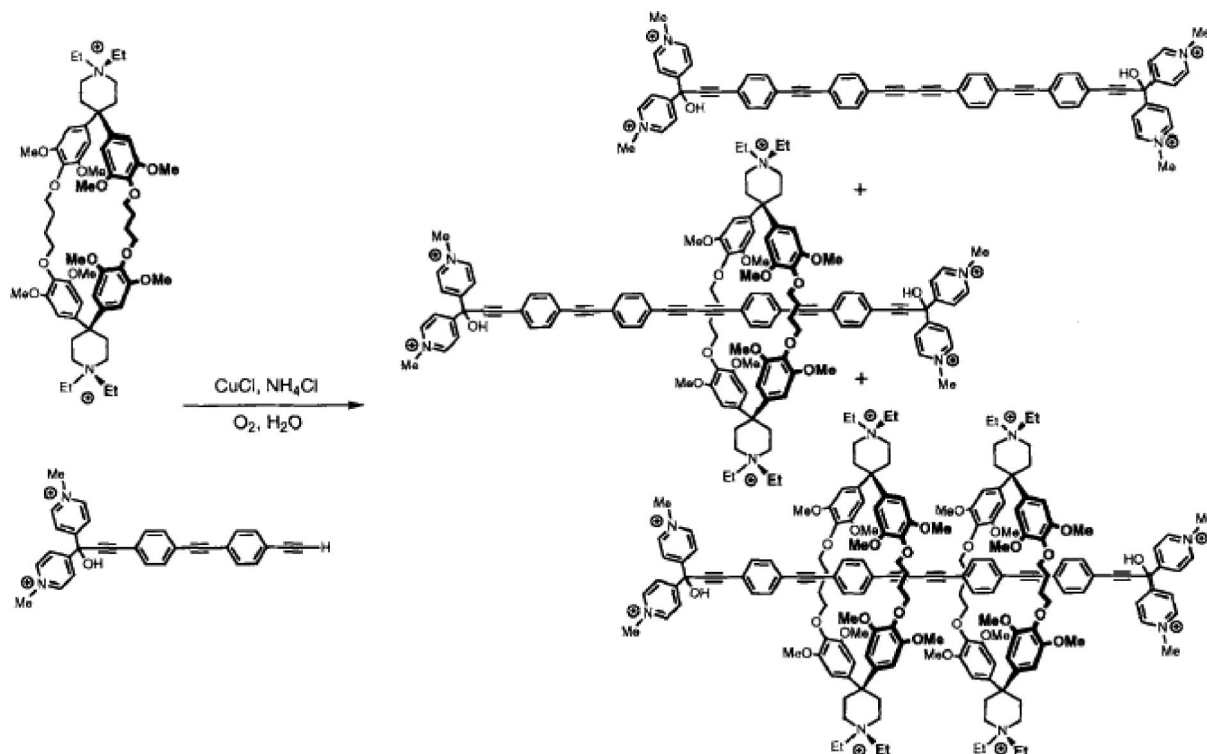
[*a*] Reprinted with permission from ref 258. Copyright 1996 Wiley VCH.

Scheme 17. Threading of a 2,9-Diphenyl-1,10-phenanthroline Moiety Bearing Two Electropolymerizable Pyrrole Groups through the Coordinating Macrocycle Using the Templating Ability of Co^{2+}[*a*]
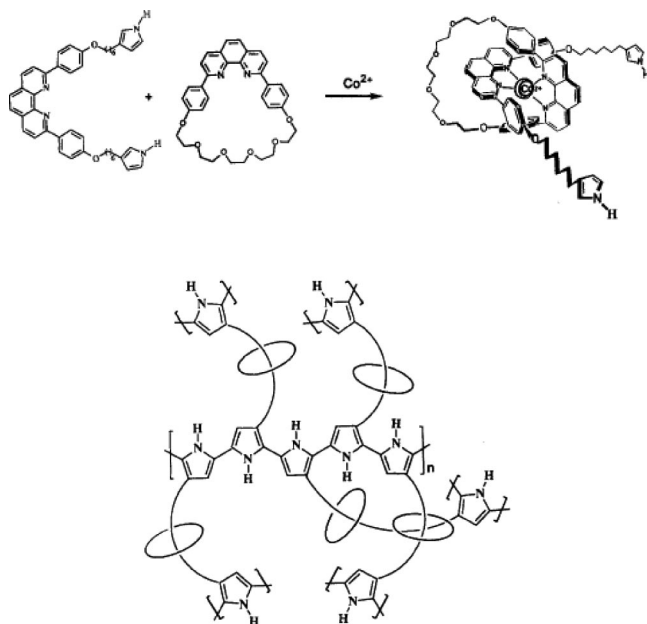
[*a*] Reprinted with permission from ref 261. Copyright 1996 Wiley VCH.

trolled release of macromolecular drugs. Biodegradable polyrotaxanes with drug-conjugated CDs threaded on a polymer chain with degradable end caps could be interesting supramolecular prodrugs for controlled and targeted delivery of drugs (Figure 21).

Scheme 18. Polymetallorotaxane with Reversible Metal Ion Binding Rotaxane Structure
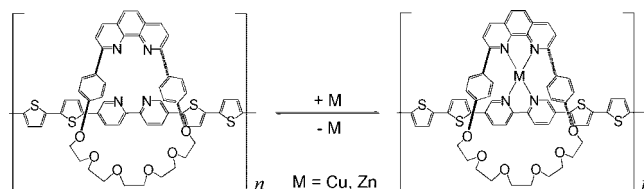
Hydrolyzable polyrotaxanes, in which many α-CDs are threaded onto a poly(ethylene glycol) (PEG) chain capped with L-phenylalanine via ester linkages, were synthesized by Yui and co-workers (Scheme 20).[294,295] A β-CD-based biodegradable polyrotaxane was prepared by capping both terminals of a poly*pseudo*rotaxane consisting of hydrazide-terminated PEG-block-PPG-block-PEG and β-CD-succinates with monoaldehyde α-CDs. By decreasing the pH of the solution including poly*pseudo*rotaxane and sodium 2-(*p*-toluidino)naphthalene-6-sulfonate (TNS), the fluorescence intensity of TNS increased with time, indicating cleavage of the terminal hydrazone bonds followed by β-CD-succi-

1,4-bis(imidazol-1-ylmethyl)benzene
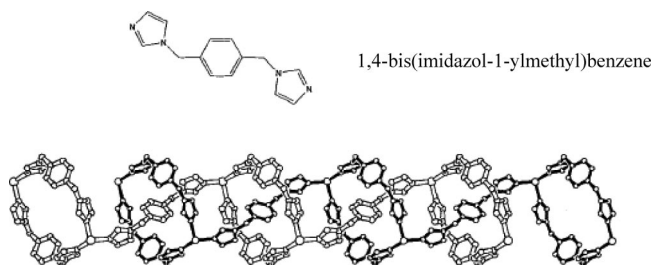
Figure 20. A polyrotaxane column of a {Zn(1,4-bis(imidazol-1-ylmethyl)benzene)$_2$$^{2+}$}$_n$ framework. Reprinted with permission from ref 274. Copyright 1997 Wiley VCH.

Scheme 19. Metallo-Capped Polyrotaxane Constructed by CD Dimer and Azo-Calixarene
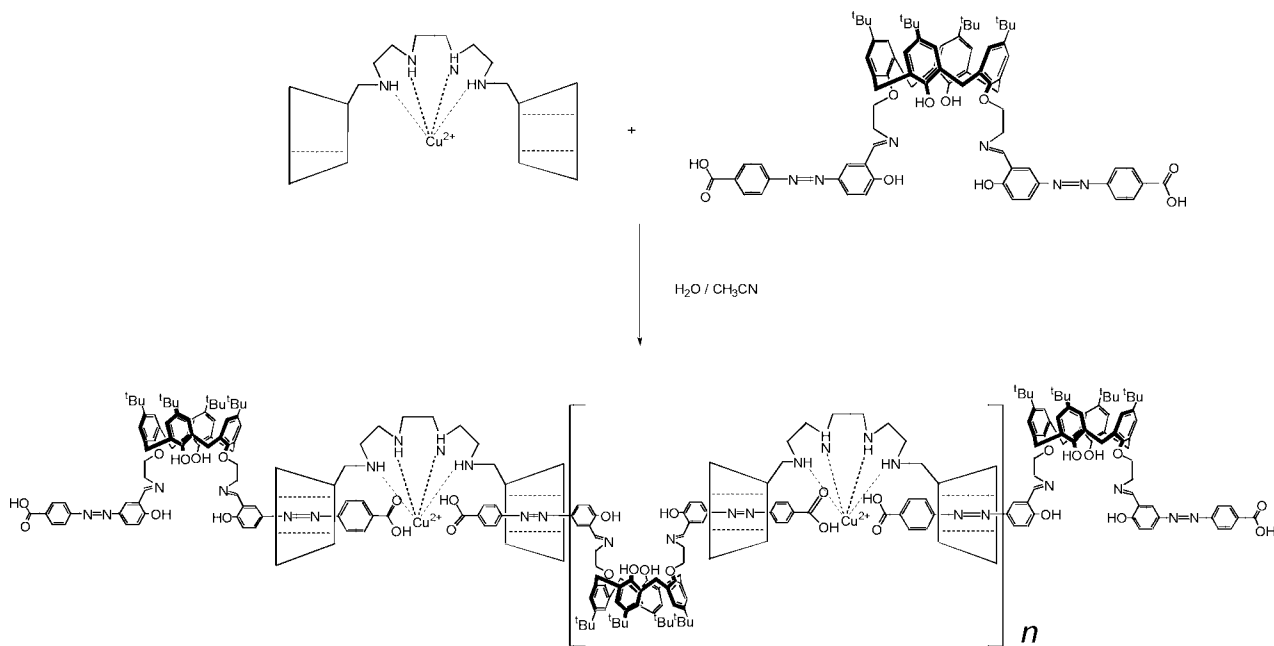
Scheme 20. Hydrogels Cross-Linked with Hydrolyzable Polyrotaxane[a]
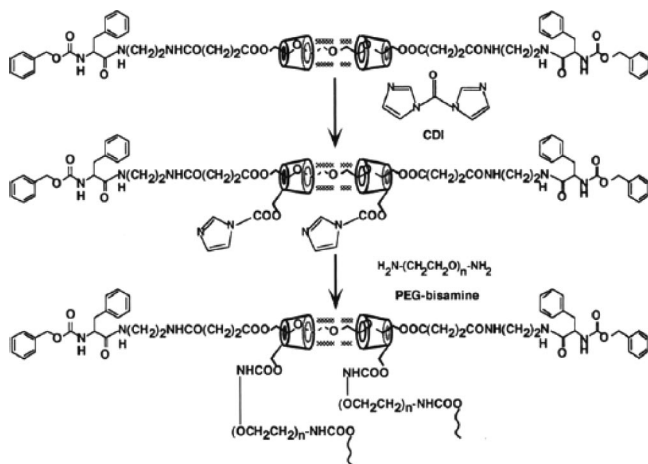
[a] Reprinted with permission from ref 294. Copyright 2000 The Japanese Society for Artificial Organs.

nate release. The terminal α-CD moieties of the polyrotaxane were found to be useful for self-assembled formation with some guest molecules.[296] The polyrotaxane also showed unique thermoresistant properties due to the supramolecular structure. The supramolecular structure was completely dissociated by terminal ester hydrolysis. PEG hydrogels cross-linked with the polyrotaxane were prepared as candi-
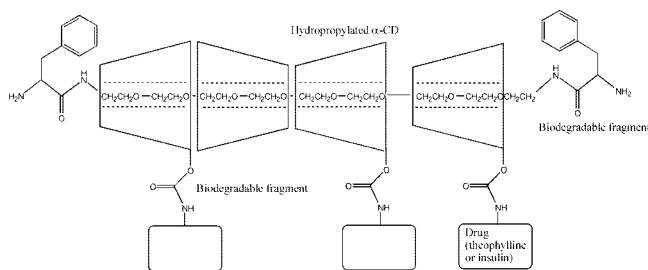
Figure 21. Drug−polyrotaxane complex prepared by using poly(ethylene oxide), L-phenylalanine, and hydropropylated α-CD.

Scheme 21. Polyion Complex Formation of the Polyrotaxane with Plasmid DNA and its DNA Release by Supramolecular Dissociation
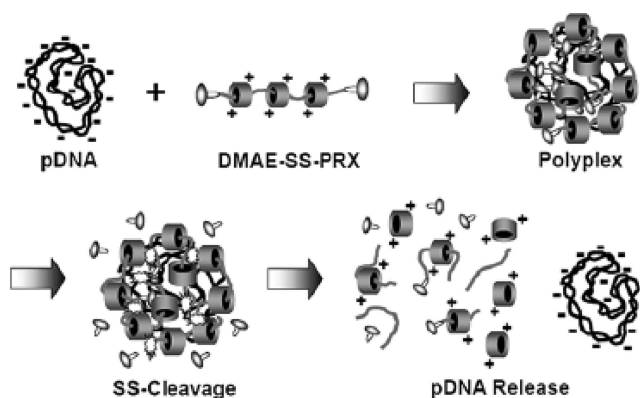
date implantable materials for tissue engineering. It was suggested that controlling the rate of terminal ester hydrolysis and the following supramolecular dissociation may dominate the disappearance of the hydrogel.[297]

A gene delivery system was also devised by using biocleavable polyrotaxanes, in which dimethylaminoethyl-modified CDs are threaded onto a PEG chain capped with benzyloxycarbonyl-L-tyrosine via disulfide linkages. This involves the formation of a stable polyion complex against a counter polyanion and the intracellular plasmid DNA release from the polyion complex accompanied by the dissociation of polyrotaxanes (Scheme 21).[298]

Supramolecular hydrogels have been synthesized via enzymatic oxidative coupling of polypseudorotaxanes derived from the self-assembly of α-CD with 3-arm p-hydroxyphe-nylpropionate terminated PEG as a macromer by using a horseradish peroxidase (HRP)/H_2O_2 catalytic system. These hydrogels exhibited a decreasing trend in dynamical mechanical properties with increasing amount of α-CD in regard to the blank hydrogel made without α-CD (Figure 22).[299] Polyrotaxane-based stationary phases for capillary electrochromatography were prepared by cross-linking polymers of CD-polyrotaxanes.[300,301] A topological network architec-
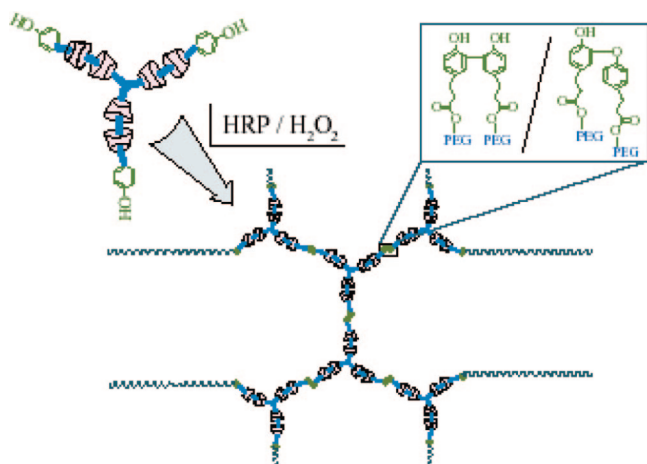
Figure 22. Schematic representation of the 3D cross-linked supramolecular hydrogel network structure. Reprinted with permission from ref 299. Copyright 2007 Higher Education Press and Springer-Verlag.

ture was constructed by Okumura and Ito (Figure 23).[302] They utilized an intermolecular cross-linking reaction of ring components among polyrotaxanes to lead to sliding cross-link points. This allows a sliding motion of the network polymer chains through the figure-of-eight junction. The swelling as well as the viscoelastic properties were found to be solvent dependent, reflecting the structural changes of the network.[303,304]

2.4.2. Molecular Tubes Prepared from Polyrotaxanes

Since Harada et al. reported the synthesis of a molecular tube by cross-linking the adjacent α-CDs in a single
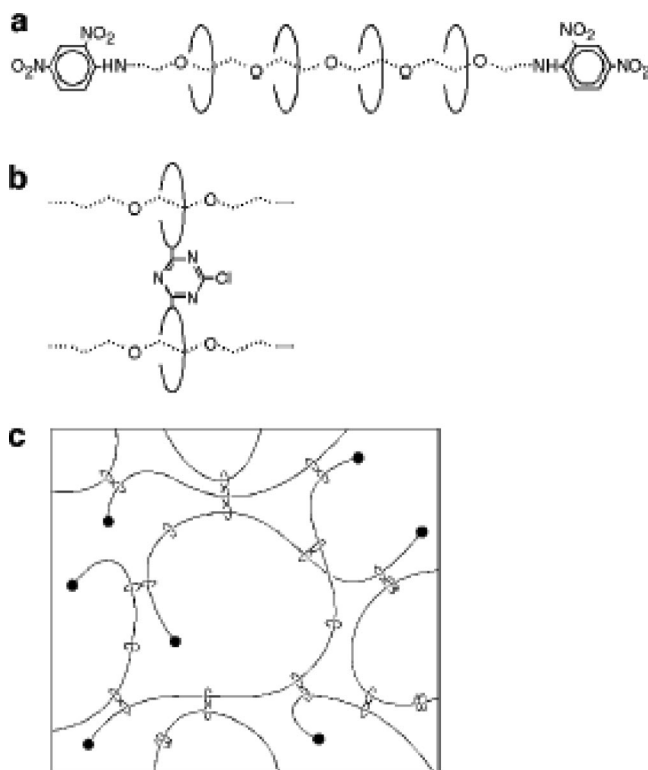
Figure 23. Polyrotaxane prepared by mixing α-CD and PEG with an end cap (a). The figure-of-eight cross-link was formed by covalently cross-linking CDs (b). The schematic representation of polyrotaxane gel (c). Reprinted with permission from ref 302. Copyright 2001 Wiley-VCH.

polyrotaxane and subsequent dissociation of the included PEG after hydrolysis, studies of complex formation between a molecular tube and various small molecules or linear polymers have begun.[305−307] A supramolecular assembly, bis(molecular tube)s composed of complexes of ligand-bridged β-CDs and platinum(IV) ion or nickel(II) ion, has been fabricated via the *pseudo*rotaxane with poly(propylene glycol) (Scheme 22).[308,309]

Yazdanparast et al. reported that the CD-based molecular tube could improve the refolding yields of two different enzymes: carbonic anhydrase and alkaline phosphatase.[310] The denatured carbonic anhydrase and alkaline phosphatase were refolded with yields of 51 and 61% using 15 and 5 mg/mL of the molecular tube, respectively, under the optimal developed refolding environments. Regardless of lower refolding yields compared with a liquid-phase artificial chaperone assisted approach, this solid-phase artificial chaperone system was thought to have a benefit from easier and faster separation of the refolded product from the refolding environment and recycling of the stripping agent.

2.4.3. Supramolecular Light-Harvesting Antenna

Supramolecular light-harvesting antenna systems were constructed by using polyrotaxanes, in which α-CD and naphthalene-appended α-CD molecules are threaded by a poly(ethylene glycol) chain with anthracene units at both ends (Scheme 23). Ueno et al. examined the effects of the component ratio of the polyrotaxanes on the efficiencies of energy migration and energy transfer by fluorescence emission and excitation spectra and by fluorescence decay measurements.[311] Upon irradiation, photons captured by the naphthalene rings were transferred to the terminal anthracene end cap.

2.4.4. Insulated Polymers

A series of insulated molecular wires has been synthesized by using rotaxanes and polyrotaxanes, in which the conjugated π-system is encapsulated by threading through macrocycles.[117] Anderson et al. used Suzuki coupling to synthesize conjugated polyrotaxanes from a diboronic acid and a water-soluble diiodide with a bulky monoiodide stopper in the presence of β-CD (Figure 24).[121−123] The average degree of polymerization was determined by NMR and mass spectra. They succeeded in imaging the structure of individual polyrotaxane molecules by tapping mode AFM, while it was not possible to image individual unthreaded polymer molecules.[124] An anthracene-terminated β-CD-polyfluorene polyrotaxane was also synthesized by Yamamoto coupling.[125] Some other insulated polymers were synthesized by using CDs with polythiophenes,[126,128,130,312−314] polyazomethine,[132,140,143] polyanilines,[135] and polysilanes,[161,162] respectively. Ito and co-workers examined complex formation between polyanilines and cross-linked CD nanotubes.[136,144]

2.4.5. Stimuli-Responsive Molecular Shuttles Using Polyrotaxanes or Polypseudorotaxanes

The construction of stimuli-responsive molecular devices and molecular machines[50,241,315−352] by using supramolecular materials is a great challenge. Recently, attention has been focused on the construction of molecular shuttles[198,353−391] in which a ring moves back and forth like a shuttle between two or more "stations" in response to external stimuli. Some molecular muscles[392−397] and molecular motors[375,398−410] have

Scheme 22. Bis(molecular tube)s Composed of Complexes of Organoselenium-Bridged β-CDs and Platinum(IV) Ion (A) or Nickel(II) Ion (B)[a]
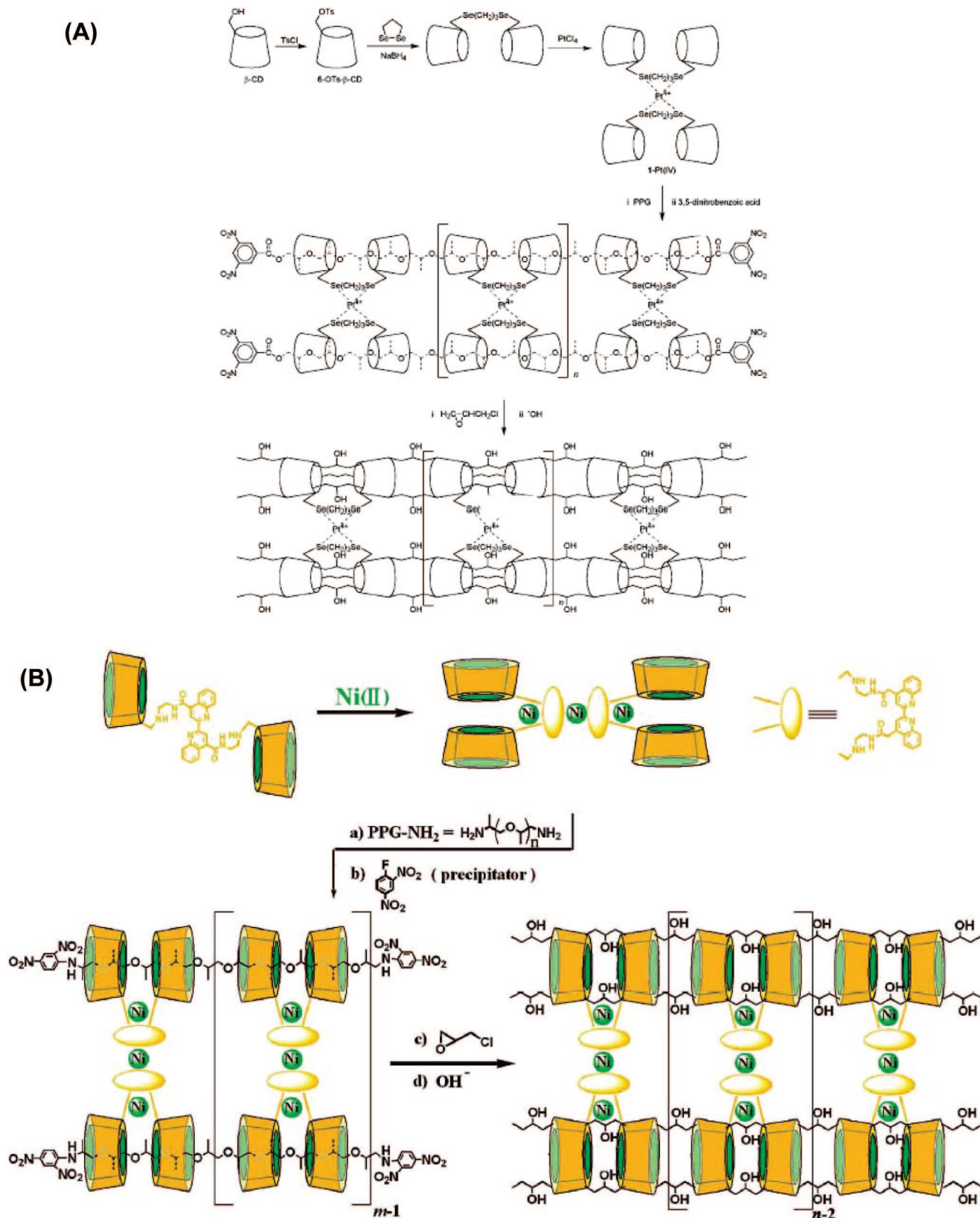
been synthesized on the concept of rotaxanes. Among the growing collection of molecular systems under consideration for nanoscale device applications, mechanically interlocked compounds derived from stimuli-responsive [n]rota-xanes[337,361,364,369,378,382,384,388,408,411−436] show great promise. These systems demonstrate dynamic, relative movements between their components, such as shuttling, enabling them to serve as stimuli-responsive switches operated via revers-

Scheme 23. Poly*pseudo*rotaxane Prepared by Adding α,ω-Diaminopolyethylene Glycol into Aqueous Solutions Containing Different Ratios of Naphthalene-Modified α-CD (NpCD) and Native α-CD
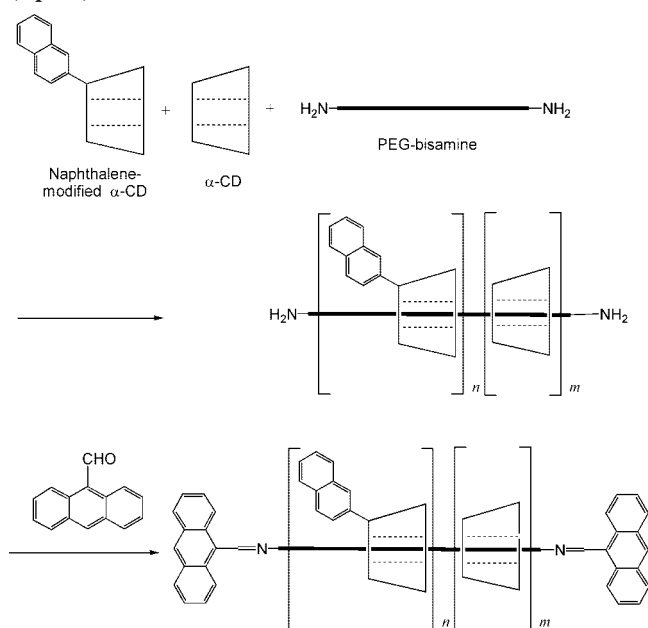
ible, electrochemical oxidation—reduction, the addition of chemical reagents, the changes of pH and temperature, and the photoirradiation. Recently, novel stimuli-responsive molecular shuttles have been prepared by using poly*pseudo*rotaxanes or polyrotaxanes.[74,166,198,415,432,433,437−456]

A series of pH-dependent poly*pseudo*rotaxanes have been synthesized by Yui and co-workers. They used linear polyethylenimines (PEIs) with various molecular weights and α- or γ-CD. The maximum yield of the recovered poly*pseudo*rotaxane precipitates was observed at pH 11.0, whereas no complexation was observed in the pH range below 8.0 due to the protonation of secondary amine groups in PEI backbones.[74] Yui's group succeeded in synthesizing a lot of pH-responsive polyrotaxanes consisting of CDs and linear triblock copolymers such as PEI-PEG-PEI (Figure 25) or poly(ε-lysine)-grafted dextrans.[439−442] The pH-sensitive supramolecular micelles based on CD polyrotaxanes and mesoporous silica-supported CD poly*pseudo*rotaxanes (Scheme 24) were also prepared by the other groups.[443,444] Some thermally responsive polyrotaxanes[166,445−450] based on CDs were also reported by Yui et al. A polyrotaxane consisting of many β-CDs and a triblock copolymer of PEG and poly(propylene glycol) (PPG) capped with bulky end groups was synthesized as a model of stimuli-responsive supramolecules for nanoscale devices (Scheme 25). The polyrotaxane was reversibly soluble or insoluble in water in response to temperature. This was achieved through the assembled and dispersed states of β-CDs along the block copolymer. Intermolecular hydrogen bondings of β-CDs as well as the PEG segment length of the copolymer were found
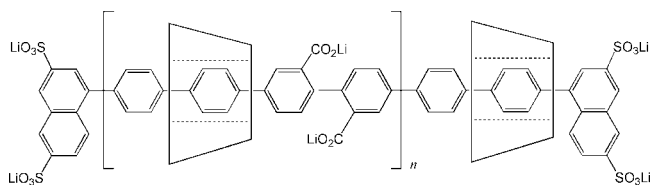
to be predominant factors for regulating such thermally switchable behavior of the polyrotaxane.[166] Endo and co-workers reported a thermoresponsive system, which is simply prepared by mixing β-CD with a PEG having amino groups in the both terminals. The thermoresponsive behavior of this system was confirmed by the repeatable and keen response of its viscosity and transmittance of visible light to repeated heating-and-cooling cycles (Scheme 26).[449] Takeoka and co-workers have synthesized physically and mechanically optimized polymer gels by using CD-based polyrotaxanes with a close-packed colloidal crystal as a template, in which the polymer chains with bulky end groups are not covalently cross-linked like chemical gels nor do they interact attractively like physical gels, but are topologically interlocked by figure-of-eight cross-links (Scheme 27). The slide-ring gel has freely movable cross-links, which have a pulley effect on tensile deformation. Their gel exhibited solvatochromic behavior based on the change in structural color.[450] Stoddart and co-workers have utilized the poly*pseudo*rotaxanes consisting of CDs and polyviologens for a protein assay (Figure 26).[451,452]

Kim and Yui synthesized a poly*pseudo*rotaxane consisting of CB[7][453] and 2,6-*O*-dimethyl-β-CD as ring components and *N*,*N*′-3-phenylenebis(methylene)dipropargylamine and bisazidopropylene glycol in the main chain (Scheme 28). The poly*pseudo*rotaxane structure was maintained in aqueous solution over a wide range of pH values with the 2,6-*O*-dimethyl-β-CD units contributing to increased solubilization of the poly*pseudo*rotaxane without dethreading. The pH-responsive movement of the CB[7] units in the poly*pseudo*rotaxane was observed.[454] A pH-responsive poly*pseudo*rotaxane has also been synthesized via CB[6]-catalyzed 1,3-dipolar cycloaddition using diazide and dialkyne monomers, which contain a long aliphatic spacer (Scheme 29). When amine groups are protonated at an appropriate pH, CB[6]s are located on the triazole rings due to ion−dipole interaction, whereas at high pH they move onto the hydrophobic aliphatic spacer rather than slipping off the poly*pseudo*rotaxane.[433]

Bis(*m*-phenylene)-32-crown-10-functionalized poly(propyleneimine) dendrimers of the first and third generations have been synthesized by Gibson and co-workers. The interaction between the host moiety and paraquat diol has been investigated. Upon protonation of the tertiary amines in the dendritic interior, binding became statistical, and the average apparent association constant increased by 5-fold. This effect was attributed to rigidification of the dendrimer, which makes its binding sites more accessible and less crowded.[432] Swager et al. reported a polythiophene-based conducting poly*pseudo*polyrotaxane that exhibits both a reversible attenuation in conductivity and an anodic shift in redox potential in the presence of a π-deficient 4,4′-bipyridyl guest (Scheme 30).[455] Electrochemical studies of polymetallorotaxane films were also reported by Divisia-Blohorn et al.[456]

3. Side Chain Polyrotaxanes and Polypseudorotaxanes

3.1. Background of Side Chain Polyrotaxanes and Polypseudorotaxanes

Biomacromolecules, such as proteins and nucleic acids, interact selectively with low molecular weight or macromolecular species by noncovalent bonds (i.e., hydrogen bonding,

Figure 24. Polyrotaxane prepared from β-CD and poly(*p*-phenylene).
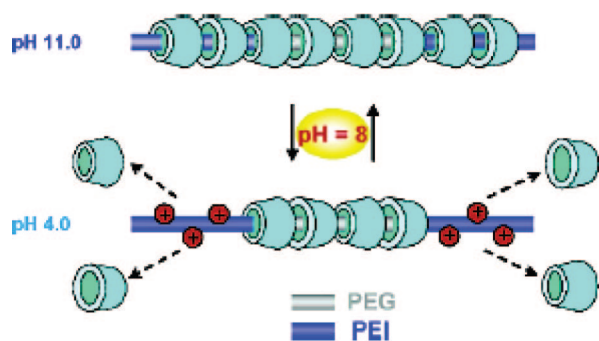
Figure 25. Schematic representation of the block-selective poly*pseudo*rotaxane formation via pH variation (a) and pH-dependent changes in stoichiometry between [EI + EG] and [α-CD]. Reprinted with permission from ref 439. Copyright 2004 American Chemical Society.
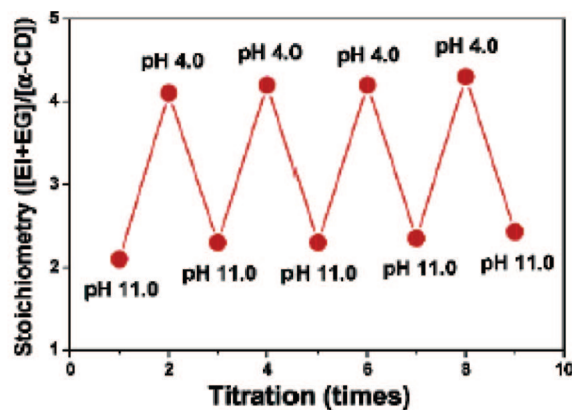
Scheme 24. pH-Responsive Release of Guest Molecules from a Mesoporous Silica Particle*[a]*
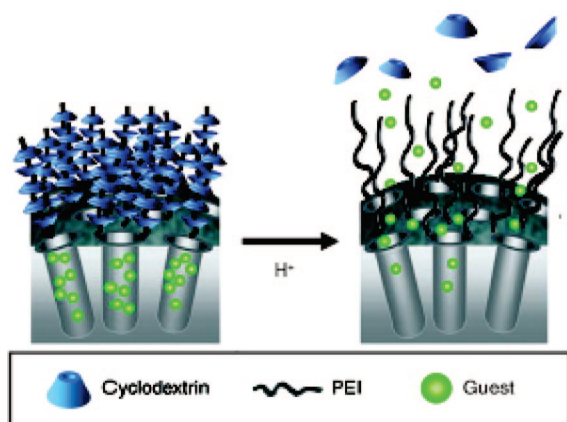
[a] Reprinted with permission from ref 444. Copyright 2007 Wiley-VCH.

electrostatic interaction, hydrophobic interaction, and van der Waals interaction) of their side chains arranged appropriately by the main chain, leading to the formation of well-controlled supramolecular complexes which express various functions necessary for living activities.[457−459]

One class of polymeric rotaxanes consists of side chain polyrotaxanes and poly*pseudo*rotaxanes. Since side chain polyrotaxanes and poly*pseudo*rotaxanes are formed by host−guest interactions of polymer side chains with low molecular weight species or with other polymer side chains, these polyrotaxanes and poly*pseudo*rotaxanes can be considered as model systems for supramolecular complexes of biomacromolecules. Thus, side chain polyrotaxanes and poly*pseudo*rotaxanes are an important class of supramolecular complexes.

Polyrotaxanes are composed of axes and rotors, in which the rotors are interlocked on the axes by bulky stoppers at both ends of the axes, whereas poly*pseudo*rotaxanes are also composed of axes and rotors, in which the rotors are not interlocked, and thus poly*pseudo*rotaxanes are in equilibrium. Obviously, polyrotaxanes are more stable than poly*pseudo*rotaxanes, and synthesis of polyrotaxanes requires more steps of reactions than does synthesis of poly*pseudo*rotaxanes. Since poly*pseudo*rotaxanes are in equilibrium, poly*pseudo*rotaxanes are responsive to external stimuli, sometimes leading to considerable changes in solution properties. Therefore, side chain poly*pseudo*rotaxanes can be regarded as better models of supramo-

Scheme 25. Thermally Induced Localization of Cyclodextrins in a Polyrotaxane Consisting of β-CDs and PEG-PPG Triblock Copolymer*[a]*
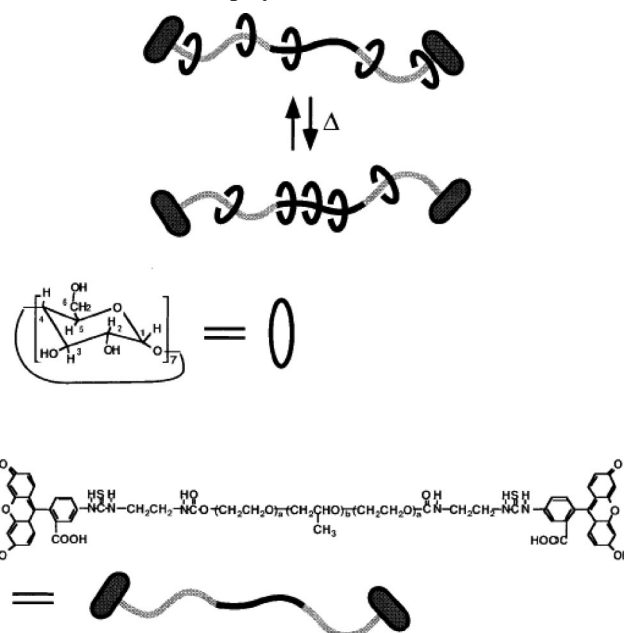
[a] Reprinted with permission from ref 447. Copyright 1999 Wiley-VCH.

Scheme 26. Reversible Thermoswitching Behavior between Fluid and Gel-like States in a Bulk Mixture System of β-CD and Amine-Terminated Polyether*[a]*
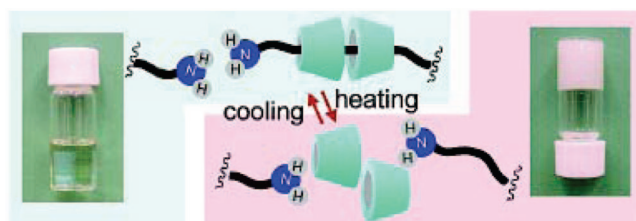
[a] Reprinted with permission from ref 449. Copyright 2006 American Chemical Society.

lecular complexes of biomacromolecules. There have been only a few pieces of research that deal with side chain poly*pseudo*rotaxanes as model systems for supramolecular complexes of biomacromolecules apart from research by our research group. However, utilizing characteristic properties of polymer chains, such as rheological and

Scheme 27. Schematic Procedure of the Preparation of a Porous Slide-Ring Gel Using a Close-Packed Colloidal Crystal as a Template[a]
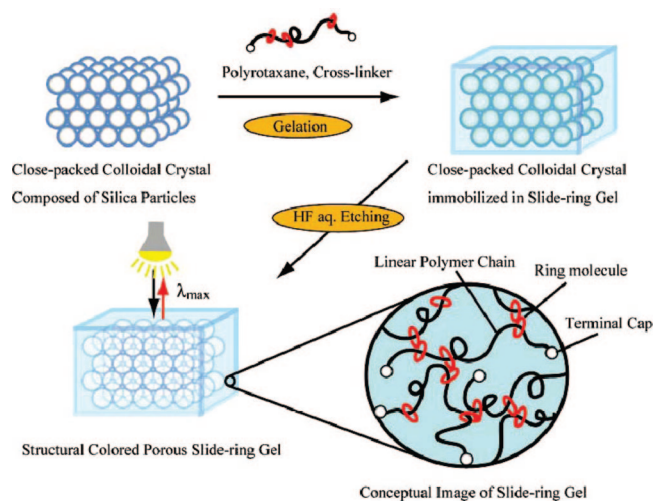
[a] Reprinted with permission from ref 450. Copyright 2008 American Chemical Society.
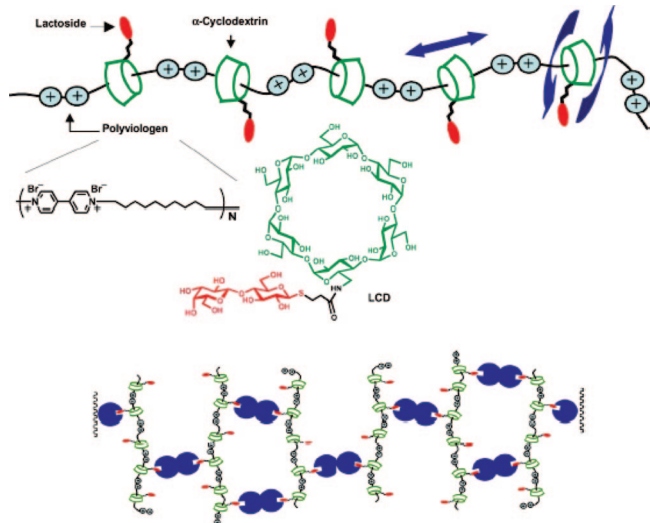
Figure 26. (A) Schematic representation of poly*pseudo*rotaxanes composed of lactoside-displaying CD (LCD) rings and polyviologen threads and (B) the idealized model of precipitate obtained as a result of the binding of a bivalent galactoside-binding protein-1 (Gal-1) with poly*pseudo*rotaxanes. Reprinted with permission from ref 452. Copyright 2007 Elsevier.

colloidal properties, side chain polyrotaxanes and poly*pseudo*rotaxanes have been used in various applications, including gel formation, catalysis, drug release, and separation. Because of the ease of synthesis and wide ranges of applications, there have been a larger number of publications on side chain poly*pseudo*rotaxanes.

This section reviews a variety of side chain polyrotaxanes and poly*pseudo*rotaxanes. In this section, planar and spherical guest molecules are included as axis molecules in a broad sense.

3.2. Categories of Side Chain Polyrotaxanes and Polypseudorotaxanes

In this section, side chain polyrotaxanes and poly*pseudo*rotaxanes are categorized into the following three

Scheme 28. Proposed Location of CB[7] and 2,6-*O*-Dimethyl-*β*-CD at pH 2 and 11
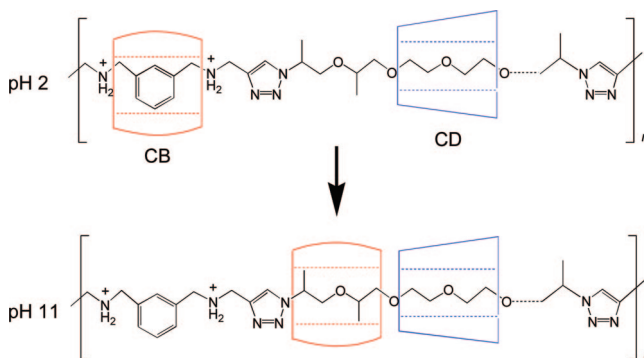
Scheme 29. A pH-Responsive Poly*pseudo*rotaxane Bearing CB[6]s
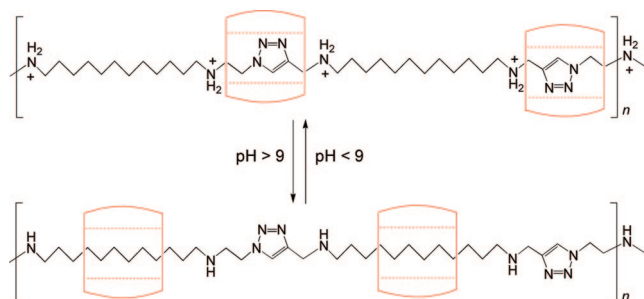
Scheme 30. Conducting Poly*pseudo*rotaxane with a Chemoresistive Responsibility
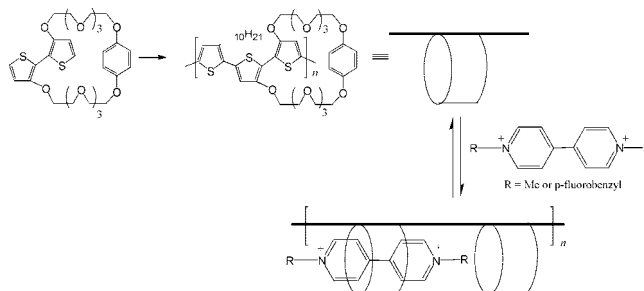
systems (Scheme 31): (i) rotor/polyaxis systems, (ii) polyrotor/axis systems, and (iii) polyrotor/polyaxis systems. As rotors, several macrocyclic compounds, including CDs, crown ethers (CEs), cyclophanes (CPs), and cucurbiturils (CB[*n*]s), have been employed. Among them, CDs are of increasing interest recently because water borne systems have attracted much interest from the ecological viewpoint. Therefore, a larger part of side chain polyrotaxanes and poly*pseudo*rotaxanes have utilized CDs as rotors.

3.3. Rotor/Polyaxis Systems (See Scheme 31a and b)

3.3.1. CD-Based Systems

3.3.1.1. Polyrotaxanes. The formation of CD-based side chain polyrotaxanes has been extensively studied by Ritter and his colleagues (Tables 12 and 13).[460−470] Their first CD-based side chain polyrotaxanes were synthesized by coupling of 4′-triphenylmethyl-4-aminobutananilide or 4′-triphenyl-methyl-11-aminoundecananilide with mixed anhydrides, derived from a copolymer of methyl methacrylate and 11-methacryloyl aminoundecanoic acid by treatment with ethyl chloroformate, in the presence of 2,6-dimethyl-*β*-CD.[460] Side

Scheme 31. Schematic Representation of Side Chain Polyrotaxanes (a, c, and e) and Poly*pseudo*rotaxanes (b, d, and f) of Rotor/Polyaxis (a and b), Polyrotor/Axis (c and d), and Polyrotor/Polyaxis (e and f) Systems
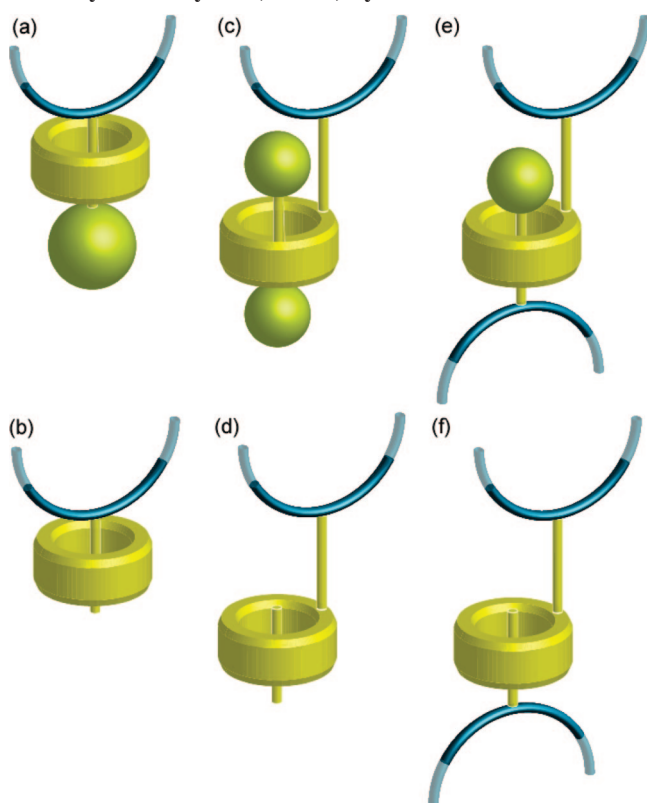
Table 12. Side Chain Type Polyrotaxanes Incorporating 2,6-*O*-Dimethyl-β-CD

Polymer structures
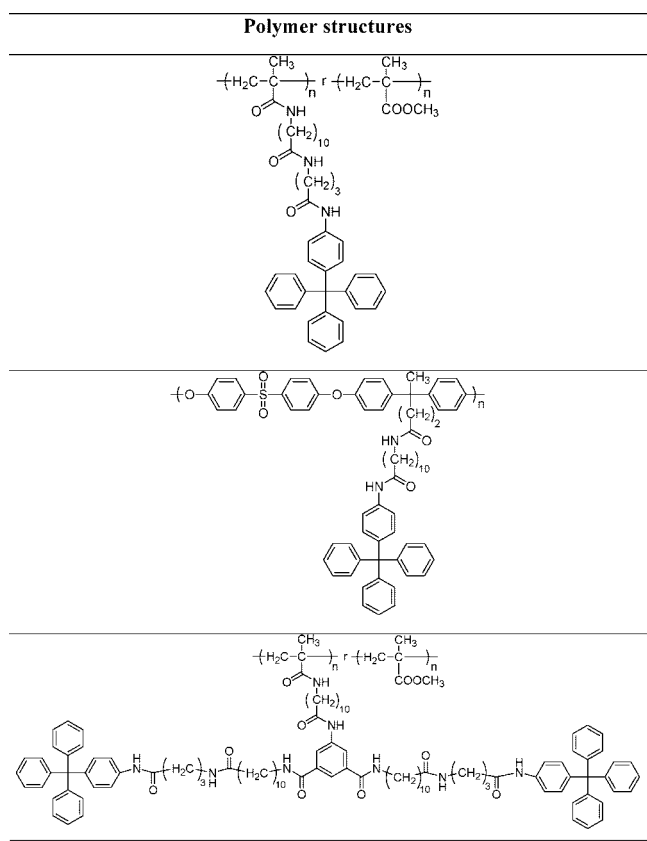
Table 13. Side Chain Type Polyrotaxanes Incorporating 2,6-*O*-Dimethyl-β-CD

Polymer structures
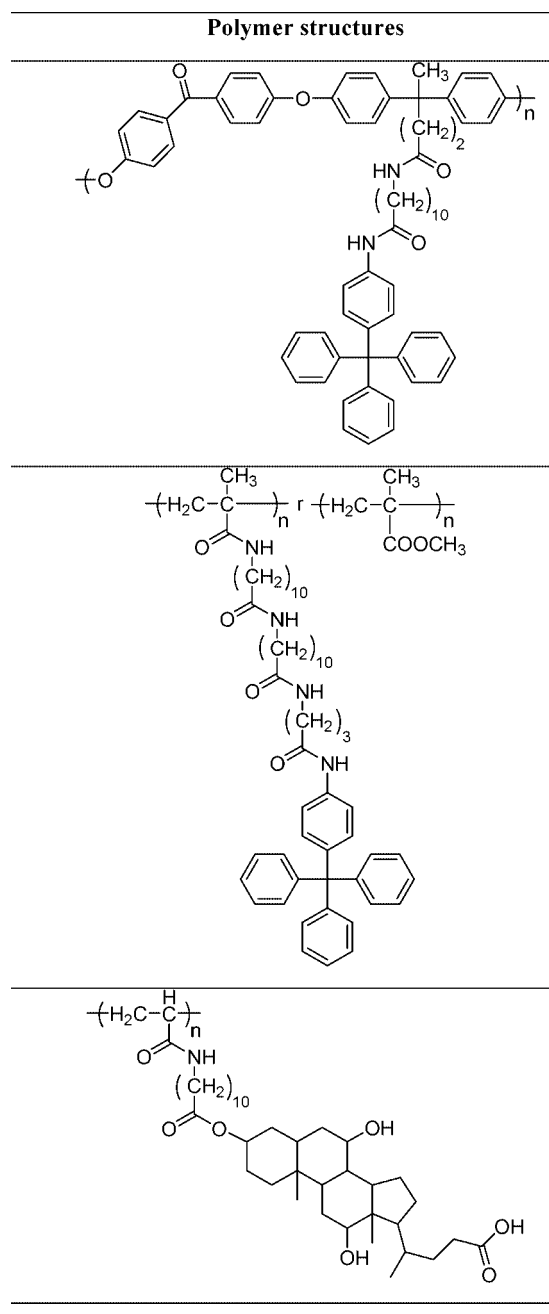
chain polyrotaxanes were also synthesized from aromatic polysulfone and poly(ether ether ketone) with 2,6-dimethyl-β-CD by amide coupling of semirotaxane by Born et al.[463,465] Some characteristics of the side chain polyrotaxane were compared with those of the corresponding guest model compound: the polyrotaxane exhibited a higher glass transition temperature, a higher solubility in organic solvents, upfield shifted signals in ^{1}H NMR, and a larger hydrodynamic volume because of the rotaxane structures in their side chains. From copolymers of 5-[(11-methacryloylamino)]isophthaloylbis(12-azadodecanoic acid) and methyl methacrylate, side chain polyrotaxanes were synthesized by coupling with a semirotaxane of 4-amino-*N*-[4-(triphenylmethyl)phenyl]butanamide and 2,6-dimethyl-β-CD.[464] NMR confirmed the formation of the side chain polyrotaxanes. From poly(ether sulfone), side chain polyrotaxanes were also synthesized, and their topological arrangements were characterized, in which

ca. 80% of the side chains were included by peracetylated CD molecules.[467] Compared with characterization data for the model graft polymer, it was likely that the CD molecules were homogeneously distributed on their side chains with unidirectional inclusion, whereas the CD molecule somehow included the aromatic anilide residue of the stopper group from the secondary rim. The glass transition temperature for the side chain polyrotaxane was considerably higher ($\gg$143 °C) than that for the model graft polymer (111 °C). A "poly(tandem-rotaxane)", a side chain polyrotaxane bearing branched side chains, in which both the branches were included by methylated β-CD, was reported by Born and Ritter.[466] As the degree of methylation in the CD was increased, the glass transition temperature decreased, indicating that the mobility of the CD moieties increased with the degree of methylation. Side chain polyrotaxanes were synthesized using a lipase from Candida antarctica.[468] Macromonomers were first prepared from 11-methacryloylaminoundecanoic acid by oligomerization of 12-hydroxydodecanoic acid using a lipase from Candida antarctica. The macromonomers were copolymerized with methyl methacrylate to form comblike polymers bearing free carboxyl groups at the end of the oligoester grafts. These free carboxyl groups were then coupled with semirotaxane of *N*-(4-aminobutanoyl)-4-triphenylmethylaniline and 2,6-dimethyl-β-CD to form side chain polyrotaxanes bearing statistically more than one 2,6-dimethyl-β-CD molecule per side chain. A water-soluble semirotaxane monomer formed from 3-*O*-(11-acryloylaminoundecanoyl)cholic acid and 2,6-dimethyl-β-CD was polymerized by a redox initiating system to obtain a side chain polyrotaxane.[469] The polymeric product was fractionated into fractions insoluble and slightly soluble in water, both of which were side chain polyrotaxanes. The water-insoluble fraction was a side chain polyrotaxane of a higher degree of polymerization, of which more than 40 mol % side chains were included by 2,6-dimethyl-β-CD, whereas the water-soluble fraction was a side chain polyrotaxane of a lower degree of polymerization, of which nearly 100 mol % side chains were included by 2,6-dimethyl-β-CD. Another type of side chain polyrotaxanes were synthesized by polymerization of inclusion complexes of α-CD or methylated β-CD with difunctional monomers, diacrylates, and dimethacrylates of butane-1,4-diol and hexane-1,6-diol, initiated by a redox initiator system in aqueous media.[470] On the basis of glass transition temperatures and IR spectra for the polymers obtained, the authors concluded that a polyrotaxane architecture was formed.

Poly(benzimidazole)s, which were composed of 5,5′-dibenzimidazole-2,2′-diyl moieties linked by phenylene, octamethylene, and bis(undecamethylene) ether linkers, were coupled with triphenylmethyl-capped bromododecyl groups at nitrogen atoms in the benzimidazole using sodium hydroxide in the presence of 2,3,6-trimethyl-β-CD to form side chain polyrotaxanes (Table 14).[471] The content of 2,3,6-trimethyl-β-CD increased from 21 to 100 mol % with increasing length of the linker between benzimidazole residues in the main chain. The side chain polyrotaxanes exhibited increased solubilities in organic solvents, compared with those for the parent polymers. The same research group also reported side chain polyrotaxanes bearing α-CD molecules interlocked by complexes of sodium ion and 15-crown-5.[472] Poly(*p*-phenylenebenzimidazole) was first modified with 12-bromododecan-1-ol using sodium hydroxide to form an *N*-alkylated polymer bearing -ONa at the end of

Table 14. Side Chain Type Polyrotaxanes Incorporating Poly(benzimidazole)s
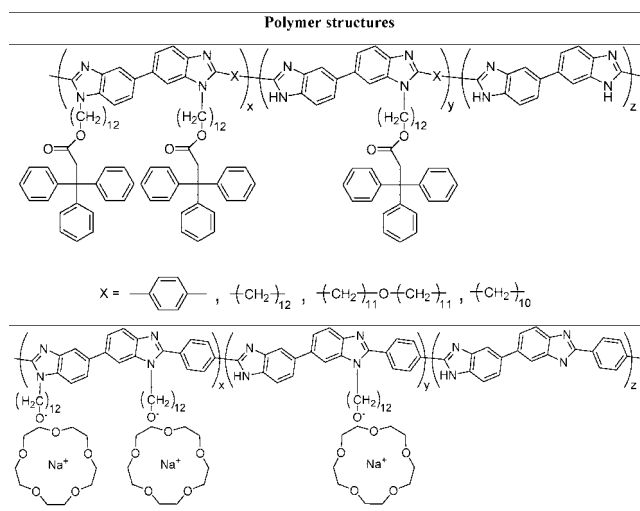
Scheme 32. Chemical Structure of p(AAm)-Based Guest Polymers Carrying Alkyl Groups

R = -CH$_2$CH$_2$CH$_2$CH$_3$
   $x = 11$, p(AAm/*n*-C$_4$(11))

   -CH$_2$CH(CH$_3$)$_2$
   $x = 11$, p(AAm/*i*-C$_4$(11))

   -C(CH$_3$)$_3$
   $x = 9$, p(AAm/*t*-C$_4$(9))

   -CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$
   $x = 9$, p(AAm/C$_6$(9))

   -CH$_2$CH(C$_2$H$_5$)CH$_2$CH$_2$CH$_2$CH$_3$
   $x = 2$, p(AAm/*i*-C$_8$(2))

   -CH$_2$(CH$_2$)$_{10}$CH$_3$
   $x = 1$, p(AAm/C$_{12}$(1))
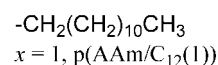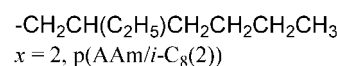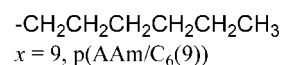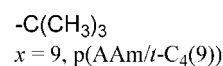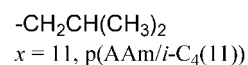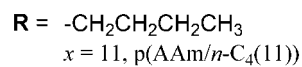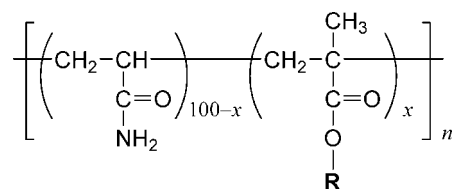
the side chain. The *N*-alkylated polymer was mixed with α-CD in DMF to form a poly*pseudo*rotaxane, in which α-CD molecules included the dodecamethylene side chains. The poly*pseudo*rotaxane was converted to a side chain polyrotaxane by adding 15-crown-5 as a stopper, which formed complexes with -ONa groups. The ^{1}H NMR spectrum for the side chain polyrotaxane indicated that 57% of the side chains formed inclusion complexes with α-CD and that all the -ONa groups formed complexes with 15-crown-5. The complexes of -ONa with 15-crown-5 were decomposed by addition of water, resulting in dethreading of α-CD from the side chains.

A side chain polyrotaxane with unidirectional inclusion was synthesized by using photoisomerization of the azobenzene moiety at the terminal of the side chain (Scheme 32 and Table 15).[473] Based on the previous paper by Harada et al.,[474] side chain poly*pseudo*rotaxanes were formed from hexyl- or dodecyl-modified poly(acrylic acid)s and α-CD. NOESY data confirmed unidirectional inclusion of α-CD.

Table 15. Chemical Structure of p(AAm)-Based Guest Polymers Carrying Alkyl Groups and Azobenzene Groups

Polymer structures

Table 16

Polymer structures	CD
	α-CD
	α-CD
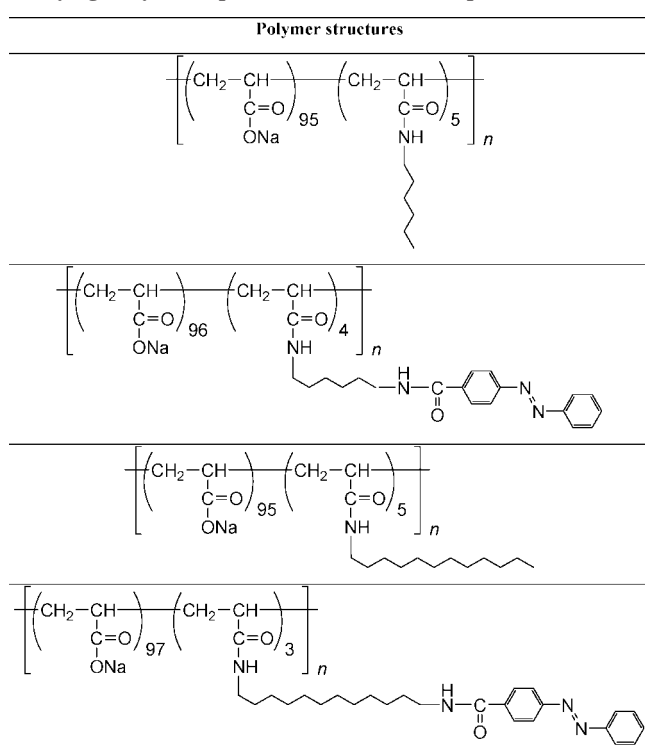
Furthermore, the interaction of α-CD with poly(acrylic acid)s modified with azobenzene moieties through hexamethylene and dodecamethylene linkers was investigated. NOESY data were indicative of the formation of side chain poly*pseudo*rotaxanes for both polymers. The azobenzene moieties were photoisomerized by UV irradiation. In the case of the polymer with the hexamethylene linker, the photoisomerization caused dissociation of the side chain poly*pseudo*rotaxane, presumably because of the short hexamethylene linker. In the case of the polymer of the dodecamethylene linker, on the other hand, the photoisomerization formed a side chain polyrotaxane with unidirectional inclusion.

Polyrotaxanes attached to Au colloidal particles were synthesized by Liu et al.[475] Au colloidal particles were reacted with semirotaxanes of α-CD and aliphatic thiols bearing forrocene as a bulky stopper (Figure 27).

3.3.1.2. Polypseudorotaxanes. The diffusion behavior for α- or β-CD in aqueous solutions of several polyanions (i.e.,
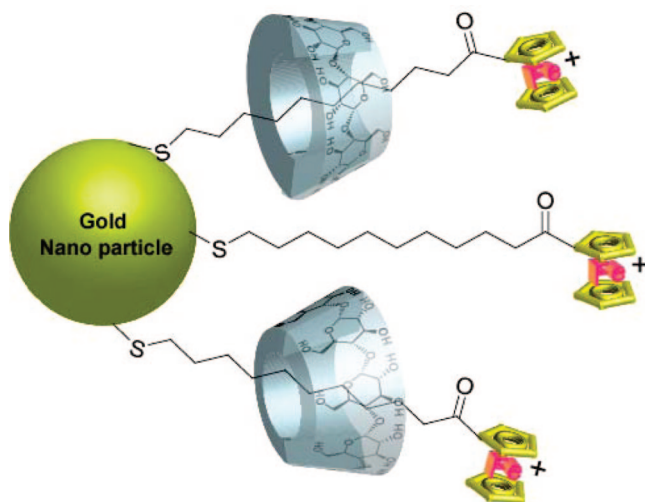
Figure 27. Trapping of α-CD on the gold colloidal particles.

poly(sodium methacrylate) and statistical copolymers of styrene with sodium styrenesulfonate, sodium methacrylate, and sodium acrylate) was investigated by Iijima et al.[476] The diffusion coefficients determined for α- or β-CD depended on the polymer concentration and the degree of neutralization for all the polymers examined and on the styrene content for the styrene based copolymers. The structure of poly-*pseudo*rotaxanes was not characterized in detail. The complexation behavior of α- or β-CD with some polyions (i.e., poly(sodium methacrylate), poly(sodium styrenesulfornate), and copolymers of diallylbenzylmethylammonium chloride and SO₂) was also studied by diffusion coefficient measurements of the CD.[477,478] The integral diffusion coefficient of the CD decreased with increasing polymer concentration, indicative of the complexation of CD with residues in the polymers examined. Applying the theory of McGhee and von Hippel[479] to the diffusion equation, the number of consecutive residues covered by a bound CD, the intrinsic binding constant, and the cooperative parameter for these systems were estimated.

A main chain poly*pseudo*rotaxane formed from poly(ethylene oxide) and α-CD was utilized to synthesize side chain poly*pseudo*rotaxanes.[480] Comblike polymers bearing a number of poly(ethylene oxide) grafts were prepared by atom transfer radical polymerization of a methacrylate monomer bearing a poly(ethylene oxide) chain (M_n = 300, 475, or 1100). The formation of side chain polyrotaxanes of the graft polymers with α-CD was investigated (Table 16). The graft polymers bearing poly(ethylene oxide) grafts of M_n = 475 and 1100 formed inclusion complexes with α-CD whereas the other did not. The formation of side chain poly*pseudo*rotaxanes was confirmed by powder X-ray diffraction, differential scanning calorimetry, and solid-state ^{13}C CP/MAS NMR. The same research group also prepared side chain poly*pseudo*rotaxanes from α-CD and block copolymers of 2-(2-bromoisobutyryloxy)ethyl methacrylate and the methacrylate monomers bearing a poly(ethylene glycol) chain.[481] The formation of side chain poly*pseudo*rotaxanes was confirmed by powder X-ray diffraction, ^{1}H NMR, electron diffraction, scanning electron microscopy, differential scanning calorimetry, and thermogravimetric analyses. It is noteworthy that the poly*pseudo*rotaxane of block copolymers bearing poly(ethylene oxide) grafts of M_n = 475 formed hydrogels through the interaction of channel-type crystalline inclusion complexes. The hydrogels exhibited a thermoresponsive sol−gel transition. The block copolymers bearing poly(ethylene oxide) grafts of M_n = 300 formed crystalline complexes with α-CD in a low yield.

Scheme 33. Chemical Structure of p(AAm)-Based Guest Polymers Carrying Naphthyl Groups

chains, the longer axis of the 2-naphthyl group was rather parallel to the rotation axis of β-CD, which was supported by X-ray crystallographic analysis of the inclusion complex of β-CD with 2-naphthylmethanol.

It has also been reported that the lower critical solution temperature of thermally responsive polymer systems is controlled by the formation of side chain poly*pseudo*rotaxanes. The phase separation behavior of poly(*N*-isopropyl-acrylamide)s bearing adamantyl or cyclohexyl side chains was investigated in the absence and presence of methylated β-CD by Ritter et al.[496,497] The lower critical solution temperature was strongly dependent on the concentration of methylated β-CD added, indicative of the formation of side chain poly*pseudo*rotaxanes. The lower critical solution temperature of the mixtures of the polymers and methylated β-CD was also perturbed by adding potassium 1-adaman-tanecarboxylate, indicating dissociation of the side chain poly*pseudo*rotaxanes. The side chain poly*pseudo*rotaxanes of polymers of acrylamides bearing adamantyl side chains with randomly methylated β-CD were also reported.[498] Aqueous solutions of the side chain poly*pseudo*rotaxanes exhibited phase separation at higher temperatures. In the phase separated state, the side chain poly*pseudo*rotaxanes were dissociated. The rate of the phase separation, i.e., dissociation, strongly depended on the length of linker between the adamantyl side chains and the polymer main chain. Koopmans and Ritter[499] developed a thermally responsive color change system. They prepared a copolymer of acrylamide bearing a Reichardt's dye moiety and *N*-isopropylacrylamide. The copolymer obtained underwent a reversible red-orange color change upon the phase transition at the lower critical solution temperature and upon the formation of the side chain poly*pseudo*rotaxane with CD.

An ionic liquid monomer, 1-butyl-3-vinylimidazolium bis(trifluoromethylsulfonyl)imide, was solubilized in water by complexation with β-CD.[500] Conductivity measurements, NMR, and isothermal titration calorimetry confirmed the formation of inclusion complexes of 1-butyl-3-vinylimida-zolium bis(trifluoromethylsulfonyl)imide with β-CD. In the presence of an enough added salt, which screened electrostatic repulsion, the complexed monomer was polymerized by a radical mechanism to form side chain poly*pseudo*ro-taxanes. The lower critical solution temperature type phase transition behavior of the side chain poly*pseudo*rotaxane formed from poly[1-butyl-3-vinylimidazolium bis(trifluoromethylsul-fonyl)imide] and CDs was further investigated.[501] Isothermal titration calorimetry, dynamic light scattering, and enzymatic decomposition of CD indicated that the side chain poly*pseudo*rotaxane was dissociated with increasing temperature.

Photoregulated thermoresponsive sol—gel transition of mixtures of hydroxypropyl methylcellulose bearing azoben-zene side chains and α-CD was reported on the basis of the lower critical solution temperature of the polymer.[502–504] FT-IR, FT-Raman, ^{1}H NMR, and isothermal titration calorimetry data confirmed the formation of side chain poly*pseudo*ro-taxanes. The photoregulated thermoresponsive sol—gel transition was investigated by rheological measurements at varying temperatures. In the absence of α-CD, the gelation temperature increased after *trans*-to-*cis* photoisomerization of azobenzene side chains by UV irradiation because the *cis* isomer is more hydrophilic than the *trans* isomer and the polymer exhibited a higher gelation temperature (i.e., lower critical solution temperature) after the *trans*-to-*cis* photoi-

Hydrophobically modified water-soluble polymers form various types of aggregates by hydrophobic interaction of their hydrophobic side chains, depending on their architecture.[482] The aggregation behavior is perturbed by adding CDs because CD includes their hydrophobic side chains to form side chain poly*pseudo*rotaxanes. The self-aggregation behavior of pullulan modified with cholesterol moieties was extensively studied by Akiyoshi et al.[483–488] These pullulan samples form nanogels by intermolecular association of cholesterol moieties. The nanogel of cholesterol modified pullulan was dissociated by adding β-CD because β-CD included cholesterol side chains to form a side chain poly*pseudo*rotaxane.[489] Interestingly, reformation of a nanogel of cholesterol modified pullulan was realized by adding 1-adamantanecarboxylic acid, because β-CD forms inclusion complexes, preferably with the adamantane derivative than with cholesterol side chains. Jenkins et al.[490] studied extensively hydrophobically modified alkali soluble (or swellable) emulsions (HASE) (i.e., methyl acrylate/ethyl acrylic acid copolymers modified with nonionic surfactant moieties) as associative thickeners. Since HASE polymers exhibit a strong tendency for intermolecular association, it was difficult to characterize molecularly dispersed HASE polymers. The formation of side chain poly*pseudo*rotaxanes was utilized to determine the weight average molecular weight, the hydrodynamic radius, and the radius of gyration for a molecularly dispersed HASE polymer in the presence of excess β-CD.[491] The self-aggregation and gel formation properties of copolymers of 2-[[*N*-ethyl-*N*-perfluo-rooctylsulfonyl]amino]ethyl acrylate with acrylamide or with *N,N*-diethylacrylamide were studied by Tomczak and Hogen-Esch.[492–494] When β-CD was added to viscous or gel-like aqueous solutions of the copolymers, the solution viscosity decreased. This is because β-CD included fluorinated side chains to form side chain poly*pseudo*rotaxanes. In addition, when sodium 1-adamantanecar-boxylate was added to the side chain poly*pseudo*rotaxanes, the solution viscosity recovered. This is because β-CD formed inclusion complexes preferentially with the adamantane derivative, causing dissociation of poly*pseudo*rotaxanes.

The interaction of CDs with polyacrylamide modified with aromatic groups (i.e., 1- and 2-naphthyl) was investigated by several techniques, including steady-state fluorescence and circular dichroism (Scheme 33).[495] Fluorescence spectra indicated that the intensity increased with increasing β-CD concentration for both 1- and 2-naphthyl side chains, indicative of the formation of side chain poly*pseudo*rotaxanes. Circular dichroism spectroscopy indicated that β-CD included 1-naph-thyl side chains shallowly, whereas it included 2-naphthyl side chains deeply. In the complexes of β-CD and 2-naphthyl side

Figure 28. Photographs for the ternary mixture of 5.0 g/L p(AA/C$_{12}$(5)), 10.0 g/L α-CD, and 2.0 g/L ADA under photoirradiation with visible (a) and UV light (b). Reprinted with permission from ref 505. Copyright 2005 American Chemical Society.

Figure 29. Conceptual illustration for the photoresponsive hydrogel system.

Figure 30. Photographs for the ternary mixture of 5.0 g/L p(AA/C$_{12}$(5)), 12.0 g/L β-CD, and 2.0 g/L FCA before (a) and after (b) oxidation. Reprinted with permission from ref 506. Copyright 2006 Wiley-VCH Verlag GmbH & Co. KGaA.

Figure 31. Conceptual illustration for the redox-responsive hydrogel system. Reprinted with permission from ref 506. Copyright 2006 Wiley-VCH Verlag GmbH & Co. KGaA.

somerization. In the presence of α-CD, on the other hand, the gelation temperature decreased after the *trans*-to-*cis* photoisomerization. In the case of the *trans* isomer (before UV irradiation), the polymer bearing azobenzene side chains formed side chain poly*pseudo*rotaxanes and the hydrophobic azobenzene side chains were fully masked by α-CD. In the case of the *cis* isomer, the side chain poly*pseudo*rotaxanes were dissociated because of the weak interaction of α-CD with *cis*-azobenzene, and then weak hydrophobic association between *cis*-azobenzene side chains caused a decrease in the gelation temperature.

Tomatsu et al.[505,506] composed stimuli-responsive hydrogel systems utilizing side chain poly*pseudo*rotaxanes (Figures 28 and 29). A gel-to-sol transition using the formation of side chain poly*pseudo*rotaxanes from poly(acrylic acid) bearing dodecyl side chains with α-CD was reported.[507] ^{1}H NMR data confirmed the formation of side chain poly*pseudo*rotaxanes. Rheological experiments indicated that addition of α-CD to the hydrogel of dodecyl modified poly(acrylic acid) caused a drastic decrease in the viscosity. This gel-to-sol transition system was extended to photoresponsive systems by adding a photoresponsive competitive guest, 4,4′-azodibenzoic acid.[505] Photoresponsive gel-to-sol and sol-to-gel transitions were realized using the ternary mixture of poly(acrylic acid) bearing dodecyl side chains, α-CD, and 4,4′-azodibenzoic acid. When the ternary gel mixture was irradiated with UV light, 4,4′-azodibenzoic acid was isomerized from *trans* to *cis*, and the mixture underwent a gel-to-sol transition because α-CD formed inclusion complexes more favorably with dodecyl side chains than with *cis*-4,4′-azodibenzoic acid. When the ternary sol mixture was irradiated with visible light, 4,4′-azodibenzoic acid was isomerized from *cis* to *trans* and the mixture underwent a sol-to-gel transition. Furthermore, these gel-to-sol and sol-to-gel transitions occurred repeatedly by repetitive irradiations of UV and visible light. A redox-responsive hydrogel system was also constructed by combination of β-CD,
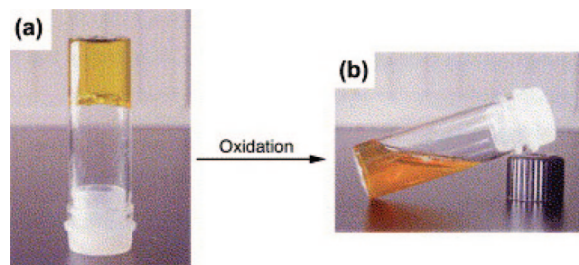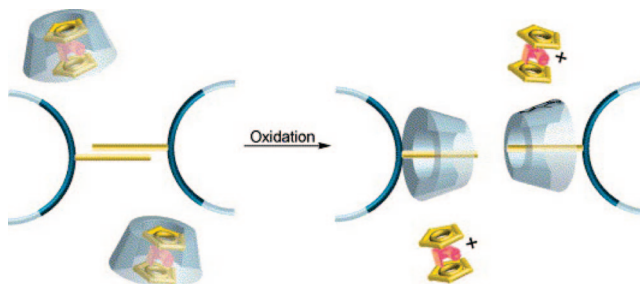
dodecyl-modified poly(acrylic acid), and a redox-responsive guest, ferrocenecarboxylic acid (Figures 30 and 31).[506] In the reduced state of ferrocenecarboxylic acid, the ternary mixture exhibited a gel-like behavior, whereas, in its oxidized state, the mixture exhibited a sol behavior.

Polymerization of 4-(*N*-adamantylamino)-2,3,5,6-tetrafluorostyrene and 2,3,4,5,6-pentafluorostyrene was carried out in aqueous solution in the presence of randomly methylated β-CD by Cinar et al.[508] NMR data were indicative of the formation of inclusion complexes of the fluorinated monomers with randomly methylated β-CD. Kinetic studies of homopolymerization and copolymerization with styrene indicated high polymerizability of the complexed fluorinated monomers in aqueous media. Using a semibatch polymerization technique, polymerization of 2,3,4,5,6-pentafluorostyrene in the presence of randomly methylated β-CD yielded stable latex particles, but in the absence of randomly methylated β-CD, stable latex particles were not formed. This observation implies that the formation of side chain poly*pseudo*rotaxanes is important for the stable latex particle formation.

The formation of side chain poly*pseudo*rotaxanes of poly[(maleic anhydride)-*alt*-(isobutene)] bearing 4-*tert*-butylanilide side chains and β-CD was studied by isothermal titration calorimetry as a model system.[509] The interaction of β-CD with poly(isobutene-*alt*-maleic acid)s bearing *p-tert*-butylphenyl or adamantyl side chains was further investigated by capillary electrophoresis.[510] From the electrophoretic mobilities determined at varying β-CD concentrations, the binding constants were determined to be $(2.8-3.9) \times 10^4$ and $(2.2-3.5) \times 10^3$ M^{-1} for *p-tert*-butylphenyl and adamantyl side chains, respectively. These binding constants agreed well with those determined by isothermal titration calorimetry. They explained the change in electrophoretic mobility upon complexation as a conformational change of the polymers: in the absence of β-CD, polymer chains form rather compact globules, whereas, in the presence of β-CD,

polymer chains take extended conformations because of the formation of side chain poly*pseudo*rotaxanes.

Harada and his colleagues[474,511−513] have been investigating extensively the interaction of CDs with side chains of water-soluble polymers, focusing on the selectivity. The interaction of CDs with polyacrylamide modified with several alkyl groups (i.e., butyl, *sec*-butyl, *tert*-butyl, hexyl, *iso*-octyl, and dodecyl) was first studied by ^{1}H NMR.[474] ^{1}H NMR spectra exhibited downfield shifts for signals of the alkyl side chains, indicative of the formation of side chain poly*pseudo*rotaxanes. Using the peak shift as a function of CD concentration, binding constants were determined for all the pairs of CDs and alkyl side chains. Among the alkyl side chains examined, the dodecyl group exhibited the largest binding constants for all the CDs. Linear alkyl side chains indicated larger binding constants for α-CD, whereas branched alkyl side chains indicated larger binding constants for β-CD: α-CD interacted with the butyl side chain and not with the *tert*-butyl side chain, whereas β-CD interacted with the *tert*-butyl side chain and not with the butyl side chain. On the other hand, α-CD interacts with both model compounds (i.e., butanol and *tert*-butanol). These observations indicated that the selectivity of CD was enhanced because of the steric effect of the polymer backbone. The interaction of CDs with poly(*N*-methacryloyltryptophan) and with poly(*N*-methacryloylphenylalanine) was investigated as a simple model system of macromolecular recognition of proteins.[511] The binding constants for the model compounds, sodium salts of tryptophan and phenylalanine, were not so different (i.e., 43 and 16 M^{-1} for α-CD, 59 and 69 M^{-1} for β-CD, and 12 and 3 M^{-1} for γ-CD, respectively). On the other hand, there was a significant difference in the apparent binding constants for poly(*N*-methacryloyltryptophan) and poly(*N*-methacryloylphenylalanine) (i.e., the binding constants for poly(*N*-methacryloylphenylalanine) were considerably smaller than ca. 10 M^{-1}, whereas those for poly(*N*-methacryloyltryptophan) were 30, 83, and 11 M^{-1} for α-, β-, and γ-CDs, respectively). These observations indicate that a subtle difference in polymer side chains can be critical in macromolecular recognition. The interaction of CDs with micelles formed from a series of alternating copolymers of sodium maleate and dodecyl vinyl ether in aqueous media was investigated to elucidate the effect of polymer molecular weight.[512,513] Here the interaction of CDs with dodecyl side chains competed with self-association of dodecyl side chains. ^{1}H NMR and two-dimensional nuclear Overhauser effect spectroscopy data demonstrated that α-CD interacted significantly with dodecyl side chains to form side chain poly*pseudo*rotaxanes, but β- or γ-CD did not, indicating that the competition with association of dodecyl side chains enhanced the selectivity toward α-CD. ^{1}H NMR measured for the mixtures of the copolymers and α-CD at varying α-CD concentrations exhibited separate signals ascribable to free and complexed dodecyl side chains, indicating that the competitions retarded association and dissociation in the equilibrium. Using the NMR data, the concentrations of free and complexed α-CD were calculated and binding isotherms were prepared. The binding isotherms exhibited sigmoidal curves for all the polymers examined, indicative of cooperative complexation. The binding isotherms also indicated that the complexation was more cooperative for a copolymer of a higher molecular weight. Analysis of the binding isotherms using a model proposed based on the one-dimensional lattice theory indi-cated that the molecular weight dependency of the coopera-tive complexation was due to molecular weight dependent attractive interactions between free dodecyl groups and between complexed α-CD molecules.

Side chain poly*pseudo*rotaxanes of CDs with proteins or with oligopeptides have been reported in a number of papers.[514,515] It is known that CDs interact considerably with aromatic amino acid residues, phenylalanine, tyrosine, and tryptophan,[516−518] and that CDs interact weakly with hydrophobic amino acid residues, valine, leucine, and isoleucine.[519] CDs include these amino acid residues in proteins or in oligopeptides to form side chain poly*pseudo*rotaxanes, resulting in perturbation of their properties: inhibition of aggregation[520−524] and promotion of unfolding (denaturation)[521,524,525] and refolding (renatur-ation).[521]

3.3.2. Crown Ether-Based Systems

Takata et al.[526,527] synthesized CE-based side chain poly-rotaxanes. Semirotaxane monomers, composed of secondary ammonium salts bearing a (meth)acryl group at one end and a bulky bis(*tert*-butyl)phenyl stopper at the other end and dibenzo-24-crown-8, were synthesized. The binding constant for the formation of a semirotaxane acrylate monomer was determined to be 18 M^{-1} by ^{1}H NMR in CDCl$_3$ at 25 °C. The semirotaxane monomer (an equimolar mixture of the (meth)acrylate monomer and dibenzo-24-crown-8) was po-lymerized in benzene at 60 °C initiated by AIBN to form side chain polyrotaxane in 66% yield, in which 42 mol % of monomer units carried the rotor component. The content of the rotaxane unit increased with decreasing polymerization temperature and with decreasing dielectric constant of the solvent used. The effect of the molar ratio of dibenzo-24-crown-8 and the acrylate monomer was not straightforward because of the higher polarity of dibenzo-24-crown-8. Copolymerization of the semirotaxane methacrylate monomer and styrene also yielded the side chain polyrotaxanes. The resulting polyrotaxanes were neutralized by acylation to obtain nonionic polyrotaxanes.

As described in the former subsection, Yamaguchi et al.[472] synthesized side chain polyrotaxane from α-CD and an *N*-alkylated poly(*p*-phenylenebenzimidazole) bearing com-plexes of -ONa and 15-crown-5 at the end of the side chain as stopper. The 15-crown-5 in this side chain polyrotaxane can also be considered as a rotor. Since this side chain polyrotaxane did not have any stopper for 15-crown-5, it is considered as a poly*pseudo*rotaxane.

3.3.3. Cucurbituril-Based Systems

There are only a few examples of CB-based side chain polyrotaxanes and poly*pseudo*rotaxanes. CB[6] was mixed with polyacrylamide or polystyrene bearing ammonium moieties in their side chains to form side chain poly-*pseudo*rotaxanes.[528] The formation of side chain poly*pseu-do*rotaxanes was confirmed by ^{1}H NMR. Relaxation times of ^{1}H NMR measured at 25 and 40 °C indicated an increased rigidity of the poly*pseudo*rotaxanes. TGA measurements indicated an increased thermal stability of the poly*pseudo*ro-taxanes. These side chain poly*pseudo*rotaxanes were dis-sociated at neutral and basic pH and reformed at acidic pH.

3.4. Polyrotor/Axis Systems (See Scheme 31c and d)

3.4.1. CD-Based Systems

3.4.1.1. Synthesis of CD-Based Polyrotor (CD Polymers). Polymers bearing CD moieties are of importance not only for synthesis of side chain polyrotaxanes but also for a variety of applications. Several types of polymers bearing CD moieties have been reported so far: cross-linking of CD, polymerization of CD monomers; and modification of polymers with CD moieties.

Among them, most used CD polymers are polymeric compounds of CD cross-linked by epichlorohydrin, which were first synthesized by Wiedenhof et al.[529,530] as resins for packing chromatographic columns. The polymeric compounds prepared from CDs with epichlorohydrin under basic conditions have complicated branched structures and are usually insoluble in many solvents. However, water-soluble high molecular weight polymers of CD cross-linked by epichlorohydrin ($M_w > 10^4$) were synthesized by optimizing carefully the reaction conditions.[531,532]

Other than CD/epichlorohydrin polymers, several vinyl polymers bearing CD moieties have been reported. Several acrylate monomers bearing CD, i.e., α-CD acrylate, β-CD acrylate, α-CD 6-acrylamidohexanoate, and β-CD 6-acrylamidohexanoate, were synthesized from the corresponding acrylates and *m*-nitrophenyl esters of CDs.[533] Radical polymerizations of β-CD acrylate, α-CD 6-acrylamidohexanoate, and β-CD 6-acrylamidohexanoate yielded water-soluble polymers in high yields, and all the CD monomers were copolymerized with water-soluble monomers (acrylic acid, acrylamide, and *N*-vinylpyrrolidone) to obtain water-soluble copolymers.[533] A β-CD-carrying vinyl monomer was synthesized by reaction of β-CD with maleic anhydride in DMF at 80 °C.[534,535] The β-CD monomer was copolymerized with *N*-isopropylacrylamide using a radical initiator in aqueous solution to obtain a hydrogel copolymer, responsive to pH and temperature.[534,535] Recently, a β-CD polymer was prepared by radical polymerization of mono(1H-1,2,3-triazol-4-yl)(methyl)-2-methylacryl-β-CD, prepared from propargyl methacrylate and 6-azido-6-deoxy-β-CD by click chemistry.[536]

Linear weak polyelectrolytes bearing β-CD moieties as side chains were synthesized by chemical modification of poly(1-vinylimidazole) with a β-CD derivative.[537] A series of β-CD polymers of varying β-CD contents were prepared by modification of poly(vinylamine) with monotosylated β-CD.[538] The polymers obtained under various conditions were fully characterized by 2D ^{1}H−^{1}H correlation spectroscopy (COSY-TOCSY) and 2D ^{1}H−^{13}C heteronuclear correlation (HMQC), and water-soluble poly(vinylamine) with β-CD grafted via only one OH group was prepared under conditions carefully optimized.[539] Poly(allylamine)-based β- or γ-CD polymers were synthesized by chemical modification of poly(allylamine) with monotosylated β-CD[540] or with monotosylated or monocarbomethylated γ-CD.[541] The γ-CD polymer obtained was less soluble in water than the parent polyallylamine, presumably because of hydrogen bonding between NH₂ groups in the polymer and OH groups in the γ-CD moieties, and thus acetylation of unreacted amines yielded very water-soluble polymers.[541] Water-soluble β-CD polymers of varying β-CD contents were prepared by esterification of poly[(methyl vinyl ether)-*alt*-(maleic anhydride)] with the monolithium-alkoxide of β-CD.[542] Recently,

click chemistry was also utilized to prepare a β-CD polymer from poly(propargyl methacrylate) and 6-azido-6-deoxy-β-CD.[536]

3.4.1.2. Synthesis of Side Chain Polypseudorotaxanes. CD-based side chain polyrotors, i.e., polymers bearing CD moieties as side chains, interact with guest molecules to form side chain polyrotaxanes and poly*pseudo*rotaxanes.

The interaction of poly(acryloyl-β-CD) with potassium 2-*p*-toluidinyl-6-naphthalenesulfonate was investigated by fluorescence spectroscopy.[543] As the concentration of poly-(acryloyl-β-CD) increased, the fluorescence intensity of potassium 2-*p*-toluidinyl-6-naphthalenesulfonate increased, indicative of the formation of a complex, which can be considered as side chain poly*pseudo*rotaxane. The increase in the fluorescence intensity was much larger for the β-CD polymer than for low molecular weight model compounds (i.e., β-CD, acryloyl β-CD, and *N*-acryloyl-6-aminocaproyl-β-CD). From the fluorescence data at varying concentrations of β-CD units added, dissociation constants and stoichiometries were determined. Poly(acryloyl-β-CD) formed only a 2:1 complex with potassium 2-*p*-toluidinyl-6-naphthalene-sulfonate, whereas β-CD formed a 1:1 complex at lower concentrations and a 2:1 complex at higher concentrations. This observation indicates positive cooperativity for complexation of potassium 2-*p*-toluidinyl-6-naphthalenesulfonate with polymer-carrying β-CD moieties. The fluorescence intensities of potassium 2-*p*-toluidinyl-6-naphthalenesulfonate in the presence of the poly(acryloyl-β-CD) and poly(*N*-acryloyl-6-aminocaproyl-β-CD) were higher than those in the presence of copolymers of acryloyl-β-CD with acrylamide and with acrylic acid. The larger increase in the fluorescence intensity may be attributed to the restriction of intramolecular rotation of the fluorophore in the rigid environment and to the exclusion of solvent relaxation.

The interactions of epichlorohydrin-cross-linked β-CD polymers with pyrene and with *p*-substituted phenols were investigated and compared with those of β-CD with these chromophores.[544] Potentiometric titration exhibited a larger pK_a for the *p*-substituted phenols in the presence of the β-CD polymer, indicative of the formation of poly*pseudo*rotaxanes. The pK_a shift for the β-CD polymer was smaller than that for β-CD, indicating a more open site for complexes of the *p*-substituted phenols with the β-CD polymer than for complexes with β-CD.

The complexation of pyrene with β-CD side chains in polyallylamine-based β-CD polymers in aqueous media was studied by fluorescence spectroscopy.[545] As the polymer concentration increased, the intensity of pyrene fluorescence increased, indicative of complexation, i.e., the formation of side chain poly*pseudo*rotaxane. The complexation behavior was dependent on the degree of substitution of the polyallylamine-based β-CD polymer used. At higher degrees of substitution (5−23%), only 2:1 complex formation was observed, indicating that pyrene formed inclusion complexes with two β-CD moieties on the same polymer chain because of the higher local concentration of β-CD moieties. Whereas, at lower degrees of substitution (<5%), 1:1 complexes were formed at lower polymer concentrations and 2:1 complexes were formed at higher polymer concentrations, indicating that 2:1 complexes were composed of two β-CD moieties on different polymer chains. The overall binding constant was larger for the β-CD polymer of higher DS and practically constant independent of the polymer molecular weight. The binding constant depended on pH, the ionic strength, and

the concentration of urea added because the conformation and flexibility of the polyallylamine backbone depended on these parameters.

The interaction of adamantane derivatives (i.e., adamantanamine and 1-adamantanecarboxylic acid) with poly[(*N*-vinyl-2-pyrrolidinone)-*co*-(maleic acid)] modified with β-CD moieties through an ester bond was investigated by Weickenmeier and Wenz.[546] Isothermal titration calorimetry confirmed the formation of complexes, i.e., side chain poly*pseudo*rotaxanes. All β-CD moieties in the polymer were accessible by the guest, but binding constants were slightly lower than those for native β-CD presumably because of electrostatic repulsion between the bound molecules of admantane derivatives.

The interaction of water-soluble linear β-CD polymer cross-linked with epichlorohydrin with a cationic surfactant (dodecyltrimethylammonium chloride surfactant (DTAC)) was reported.[547] Viscometry, surface tension, and conductance measurements confirmed the formation of inclusion complexes (side chain poly*pseudo*rotaxanes). Using fluorescence, surface tension, and conductance data, the binding constants were determined. The binding constants were larger at higher salt concentrations because of screened electrostatic repulsion between the bound surfactant molecules. Viscometric data were indicative of a polyelectrolyte behavior of the binary complexes.

3.4.1.3. Catalytic Systems Utilizing Side Chain Polypseudorotaxanes.
Polyrotor/axis systems of side chain poly*pseudo*rotaxanes have also been utilized as catalytic systems.

Catalytic hydrolysis of *p*-nitrophenyl esters by poly(acryloyl-β-CD) was investigated, and it was demonstrated that the β-CD polymer exhibited a higher catalytic activity than did β-CD.[548] Kinetic analysis indicated that the hydrolysis by the β-CD polymer followed Michaelis–Menten kinetics, indicating that the formation of side chain poly*pseudo*rotaxane promoted the hydrolysis. On the basis of the kinetic analysis and spectroscopic data, it is likely that larger substances were included cooperatively by two neighboring β-CD moieties in the polymer.

Catalytic deacylation of aryl esters by a poly(ethylenimine)-based β-CD polymer, prepared from poly(ethylenimine) and tosylated β-CD, was studied by Suh et al.[549] Kinetic data indicated that the substance was included by the β-CD side chain in the polymer (the formation of side chain poly*pseudo*rotaxane) and subsequently attacked by the amine in the polymer close to the binding site. The poly(ethylenimine)-based β-CD polymers were modified with 2,6-diacetylpyridineketoxime moieties and utilized for catalytic hydrolysis of 4-(4′-acetoxyphenylazo)benzenesulfonate.[550] The modified polymers were prepared in site-directed and random manners. In the site-directed modification, inclusion complexes of a precursor of 2,6-diacetylpyridineketoxime, a *tert*-butylphenyl ester of a carboxylic acid, with the β-CD polymer were formed, and then the 2,6-diacetylpyridineketoxime moieties were coupled to amino groups located in the proximity of the binding site. In the random modification, acylation was carried out using the phenyl ester in DMSO. Ni(II) or Zn(II) complexes of both the modified β-CD polymers exhibited catalytic activities for hydrolysis of 4-(4′-acetoxyphenylazo)benzenesulfonate. Kinetic data at varying pH indicated that the k_{cat} value for the β-CD polymer modified in the site-directed manner was three to six times greater than that for the randomly modified polymer.

However, the site directed modified polymer was not productive for deacylation of 4-(4′-acetoxyphenylazo)benzenesulfonate included by the CD moieties presumably because of steric hindrance of the 2,6-diacetylpyridineketoxime moiety.

Catalytic hydrolysis of *p*-nitrophenyl acetate was studied by the poly(vinylamine)-based β-CD polymer.[551] This hydrolysis by the β-CD polymer exhibited Michaelis–Menten type kinetics, indicative of the formation of side chain poly*pseudo*rotaxane. Kinetic data indicated that amine functions in the polymer acted cooperatively with β-CD residues by a nucleophilic attack on the included substrate. The polymers bearing the largest excess of amino groups were most active for the hydrolysis.

Catalytic oxidation of phenol derivatives by iron-5,10,15,20-tetrakis(sulfophenyl)-21H,23H-porphine (FeTPPS$_4$) complexed with cross-linked β-CD polymer was reported as a model system of peroxidase by Zhu et al.[552] Among the 21 phenol derivatives tested, *p*-chlorophenic acid was the optimal substrate for the FeTPPS$_4$/cross-linked β-CD system.

3.4.1.4. Separation Systems Utilizing Side Chain Polypseudorotaxanes.
The relative stabilities of side chain poly*pseudo*rotaxanes have been utilized for separation of a variety of compounds.

Racemic separation of mandelic acid and its derivatives was investigated by chromatography using cross-linked α-CD and β-CD gels.[553] The β-CD gel bound L-(+)-isomers preferentially over D-(−)-isomers and resolved DL-HOCH-PhCO$_2$CH$_3$ to give optically pure D-(−)-isomer in the first fraction. The β-CD gel resolved DL-R^{1}OCHPhCO$_2$R^2 (R^1 = H, R^2 = H, C$_2$H$_5$; R^1 = Me, R^2 = H) with 65–83% purity. The α-CD gel I bound D-(−)-isomers more strongly than L-(+)-isomers but exhibited a smaller resolution than did the β-CD gel. Complexes of Cu(II) ions with β-CD polymer cross-linked with epichlorohydrin were prepared as an HPLC support for nucleosides.[554] The retention data indicated that adenosine and cytidine were retained on the column because of their strong interaction with Cu(II) ions whereas 2′-deoxyadenosine was retained on the column because of the inclusion by β-CD cavities. The interaction of poly(ethylene glycol)s (PEGs) bearing hydrophobic ends (naphthyl and phenyladamantyl) with β-CD/epichlorohydrin polymers immobilized on silica particles was investigated by HPLC.[555] As the content of organic solvent in the eluent increased, the retention volume decreased, while, as the added salt concentration increased, the retention volume increased. These observations are indicative of the formation of inclusion complexes driven by hydrophobic interactions. The reverse retention behavior was observed in the presence of a competitor (hydroxypropyl-β-CD). Utilizing a theoretical model, binding constants for the 1:1 complex formation of hydrophobically modified PEGs with β-CD in the cross-linked polymer were estimated. The binding constant was dependent on the type of hydrophobe on PEGs. Silica beads coated with the polyallylamine-based β-CD polymer were used as an HPLC support to study the retention behavior of some substituted phenol isomers and aromatic compounds on the support.[556] The data obtained were indicative of two retention mechanisms, inclusion complex formation and acid–base interaction.

CDs have been utilized as binding sites for molecularly imprinted polymers. Komiyama et al.[557–559] utilized β-CD polymers cross-linked with toluene 2,4-diisocyanate for molecular imprinting of steroids. They cross-linked β-CD

by toluene 2,4-diisocyanate in the presence of various steroids in DMSO, and they removed the template steroids after polymer formation. The β-CD polymer molecularly imprinted with cholesterol or stigmasterol efficiently and reversibly bound the template steroid in a water/THF mixed solvent. It is likely that the mutual orientation of two or more β-CD moieties in the cross-linked polymer was somehow regulated by complex formation with the steroid template because the steroids used are larger compared with the cavity of a β-CD moiety. The molecularly imprinted β-CD polymer cross-linked with toluene 2,4-diisocyanate was successfully developed for stationary phases of HPLC for steroids.[560] Polymers molecularly imprinted with dipeptides or antibiotics were also prepared from acryloyl-β-CD and N,N'-methylenebisacrylamide.[561,562] Binding studies indicated that the molecularly imprinted polymers bound the template more preferably than did the corresponding nonimprinted polymers. The effective imprinting was obtained using rigid templates bearing more than two hydrophobic residues. Binding constants estimated for the molecularly imprinted polymers by Langmuir analysis were greater than those for nonimprinted polymers. Acryloyl-β-CD, N,N'-methylenebisacrylamide, and vinylated silica gel particles were copolymerized in the presence of a template in aqueous media to obtain a thin layer of molecularly imprinted CD polymer immobilized on the silica gel particles.[563] The silica gel conjugates molecularly imprinted with dipeptides (L-Phe-L-Phe and D-Phe-D-Phe) retained more strongly the templates used, respectively. This technique was also successful for selective separation of amino acid derivatives, antibiotics, and steroids.[563−565] Molecularly imprinted β-CD polymers cross-linked with epichlorohydrin were utilized for an artificial receptor for creatinine.[566] After careful optimization of the preparation conditions, the molecularly imprinted β-CD polymer exhibited selectivity toward creatinine (the template) even when multicomponent solutions containing creatinine, N-hydroxysuccinimide, and 2-pyrrolinidone and binary solutions containing creatinine and creatine were used for adsorption experiments. Adsorption experiments for the molecularly imprinted β-CD polymer of hydroxy groups capped with trimethylsilyl groups indicated that hydrogen bonding interactions were important for the recognition.

3.4.1.5. Controlled Release Systems Utilizing Side Chain Polypseudorotaxanes.
Side chain poly*pseudo*rotaxanes have also been utilized for controlled release of axis molecules.

Water-soluble cationic polymers of β-CD, epichlorohydrin, and choline chloride were synthesized to investigate their interaction with drug.[567] NMR and FT-IR spectroscopy confirmed the formation of inclusion complexes of the cationic β-CD polymer with naproxen (side chain poly*pseudo*rotaxanes). The cationic β-CD polymers exhibited higher hemolytic activities than did parent β-CD and the β-CD polymer cross-linked with epichlorohydrin. The morphological study of erythrocytes was indicative of a cell membrane invagination induced by the cationic groups in the β-CD polymer. It was also found that the cationic β-CD polymers of a high molecular weight or a low charge density exhibited better abilities of drug inclusion and dissolution.

The controlled drug release behavior of three types of hydrogels formed from poly(N-isopropylacrylamide) bearing β-CD moieties was investigated.[568] An anticancer drug (chlorambucil) was loaded into hydrogels via a swelling method. DSC data indicated that the glass transition temperature decreased with increasing amount of chlorambucil

loaded into these polymers, indicative of the interactions of the chlorambucil molecules and the hydrogels (the formation of side chain poly*pseudo*rotaxanes). The controlled release experiments exhibited that the presence of β-CD markedly enhanced release of chlorambucil from shrunken poly(N-isopropylacrylamide) hydrogels and increased the ratio of chlorambucil released in total drug loading content. Drug loading and releasing of poly[N-isopropylacrylamide-co-(acryloyl β-CD)] and poly(N-isopropylacrylamide) hydrogels were also investigated.[569,570] To load model drugs (hydrophobic ibuprofen and hydrophilic tegafur), dried gels were immersed in solutions of the model drugs in alcohol until they were equilibrated. Drug release studies in water at 25 °C revealed the increased loading and the prolonged release of the hydrophobic drug, ibuprofen, from the hydrogels bearing β-CD moieties presumably because of the formation of inclusion complexes of β-CD moieties in hydrogels with ibuprofen (side chain poly*pseudo*rotaxanes). However, β-CD moieties exhibited no or a little effect on the loading or releasing of hydrophilic drug, tegafur.

The interaction of a poly(ε-lysine) bearing α-CD side chains with 3-(trimethylsilyl)propionic acid was studied to indicate that complexation (the formation of side chain poly*pseudo*rotaxane) caused phase separation.[571] The interaction of the poly(ε-lysine) bearing α- or β-CD moieties with a model guest, 3-trimethylsilylpropionic acid, was investigated by Choi et al.[572,573] The formation of inclusion complexes (side chain poly*pseudo*rotaxanes) was confirmed by electrospray ionization mass spectroscopy and X-ray diffraction. The 3-trimethylsilylpropionic acid molecules included in CD moieties acted as a physical cross-linker by hydrophobic and electrostatic interactions. This inclusion complex exhibited a pH responsive viscosity change and a thermoresponsive phase transition. The interaction of poly(ε-lysine)s bearing CD moieties with 6-(p-toluidino)-2-naphthalenesulfonate was further studied by Choi et al.[574] Fluorescence data confirmed the formation of inclusion complexes of the poly(ε-lysine)s bearing CD moieties with 6-(p-toluidino)-2-naphthalenesulfonate (side chain poly*pseudo*rotaxanes). The inclusion complexes for the CD polymers were more stable than those for the corresponding CDs because of cooperativity, although the stability of the inclusion complexes was dependent on the chemical composition of the CD polymers, such as the size and the content of the CD moieties. The inclusion behavior of the CD polymers was modulated by environmental stimuli, i.e., temperature, pH, and ionic strength.

3.4.1.6. Molecular Sensing System Utilizing Side Chain Polypseudorotaxanes.
Side chain poly*pseudo*rotaxanes were utilized for applications of molecular sensing.

Water-soluble poly(phenylene ethynylene) bearing β-CD moieties was synthesized to study its complex formation with some guests.[575] The formation of inclusion complexes (side chain poly*pseudo*rotaxanes) was monitored by a shift of the fluorescence signal or fluorescence quenching (Figure 32).

A series of phenylacetylenes bearing α-, β-, and γ-CD moieties and permethylated β-CD moieties were synthesized and polymerized with a rhodium catalyst to obtain polyphenylacetylenes of high cis-transoid contents.[576,577] The polymers exhibited an induced circular dichroism in the UV−visible region of the polymer backbones because of one-handed helical conformations. The Cotton effect signs were inverted in response not only to temperature and solvent but also to the formation of inclusion complexes (side chain
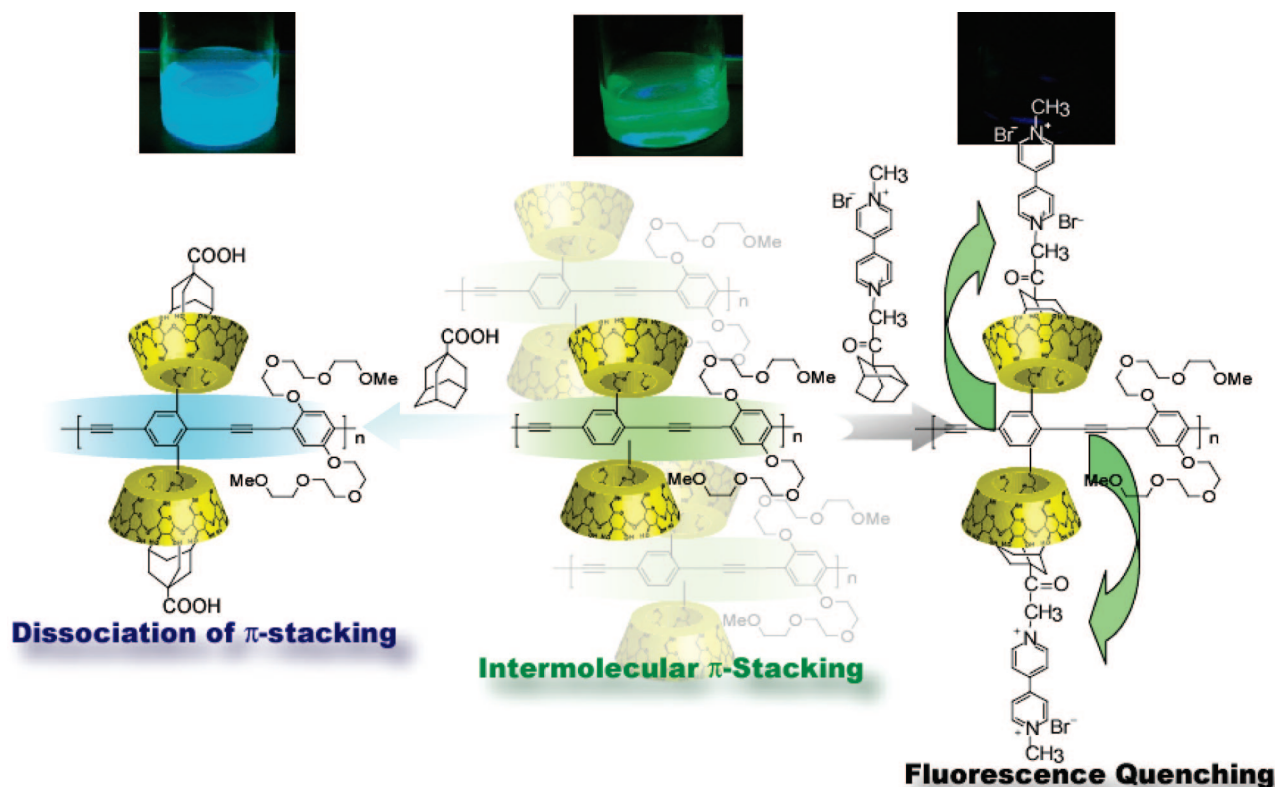
Figure 32. Changes in fluorescence induced by using CD-grafted poly(phenylene ethynylene). Reprinted with permission from ref 575. Copyright 2006 Royal Society of Chemistry.
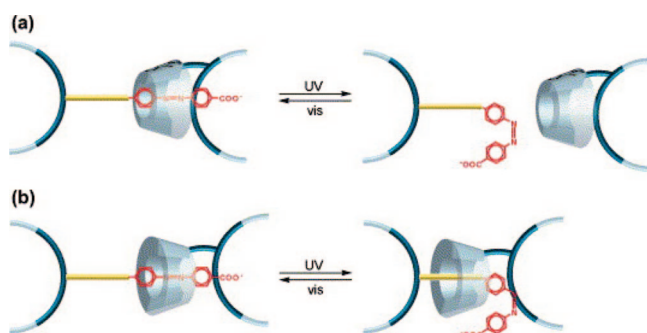
Figure 33. Conceptual illustration for the contrasting viscosity changes for the p(AA/3αCD(2))−p(AA/C$_{12}$Azo(3)) (a) and p(AA/6αCD(2))−p(AA/C$_{12}$Azo(3)) systems (b). Reprinted with permission from ref 586. Copyright 2006 American Chemical Society.

poly*pseudo*rotaxanes) with chiral and achiral cyclic alcohols and with a chiral amine. The inversion of the Cotton effect signs was caused by inversion of the helicity of the polymer backbone, in which the polymer backbone underwent a conformational change, i.e., a change in twist angles of the conjugated double bonds. Thus, the inversion was visible with the naked eye.

Water-soluble multiwalled carbon nanotubes (MWCNTs) bearing β-CD moieties were synthesized by amide coupling between carboxylic acid chloride groups on the surface of MWCNTs and aminoethyleneamino-deoxy-β-CD.[578] The photoinduced electron transfer process from tetrakis(4-carboxyphenyl)porphyrin to the MWCNTs bearing β-CD moieties was investigated by fluorescence, fluorescence decay, transient absorption spectroscopy, and cyclic voltammetry. The photoinduced electron transfer was monitored as fluorescence quenching of tetrakis(4-carboxyphenyl)por-

phyrin. The fluorescence of tetrakis(4-carboxyphenyl)porphyrin was recovered by adding 1-adamantane acetic acid to the mixture of the porphyrin and the β-CD-carrying MWCNTs bearing β-CD moieties. This observation indicated that the formation of inclusion complexes (side chain poly*pseudo*rotaxanes) of the β-CD-carrying MWCNTs with 1-adamantane acetic acid retarded the interaction of the porphyrin with the β-CD-carrying MWCNTs.

The interaction of copolymers of methacryloyl β-CD and *N*-isopropylacrylamide with anions of ionic liquids was investigated by Amajjahe et al.[579] The solubility of the β-CD polymer was switched by the formation of inclusion complexes (side chain poly*pseudo*rotaxanes). Turbidity and dynamic light scattering data indicated that the polymer chains in the inclusion complexes took an expanded or compact conformation depending on the anion. This observation was indicative of polyelectrolyte properties.

3.4.2. Crown Ether- and Cyclophane-Based Systems

Gibson et al.[580−582] synthesized mechanically cross-linked polyrotaxane networks, in which CE side chains include the polymer backbone. Methacrylate esters of 5-(hydroxymethyl)-1,3-phenylene-1′,3′-phenylene-32-crown-10 and 5-(hydroxymethyl)-1,3-phenylene-16-crown-5 were synthesized and polymerized by a radical mechanism.[580,581] The polymer obtained from the methacrylate ester of 5-(hydroxymethyl)-1,3-phenylene-1′,3′-phenylene-32-crown-10 contained polyrotaxane structures, whereas the polymer obtained from the methacrylate ester of 5-(hydroxymethyl)-1,3-phenylene-16-crown-5 did not. This is because the 5-(hydroxymethyl)-1,3-phenylene-1′,3′-phenylene-32-crown-10 is large enough for threading, while 5-(hydroxymethyl)-1,3-phenylene-16-crown-5 is too small. Copolymers of methacrylates bearing dibenzo-

24-crown-8 moieties were prepared and modified noncovalently with dibenzylammonium hexafluorophosphate to form side chain poly*pseudo*rotaxanes.[582] The formation of side chain poly*pseudo*rotaxanes, primarily driven by hydrogen bonding and π-stacking interactions, was investigated by ^{1}H NMR spectroscopy. Analysis using Scatchard and Hill plots indicated that the complexation was anticooperative, with a Hill coefficient ~0.45. Films of the side chain poly*pseudo*rotaxanes showed an increased glass transition temperature compared to the parent polymers.

Swager et al.[455,583−585] utilized the formation of side chain poly*pseudo*rotaxanes of CP-carrying conjugated polymers as molecular sensors. Synthesis and electrochemical properties of a polythiophene bearing CP moieties were reported.[455] The CP-carrying polythiophene interacted with π-deficient molecules, i.e., paraquat and 1,1′-bis(4-fluorobenzyl)-2,2′-bipyridyl, to form inclusion complexes (side chain poly*pseudo*rotaxanes), resulting in both an anodic shift in the oxidation potential of the polymer and a significant decrease in the maximum conductivity of the polymer (ca. 52% at 45 mM guest). A CP-free polythiophene did not exhibit these changes upon addition of the π-deficient molecules. Such a chemoresistor approach is an attractive route into conducting polymer-based sensors wherein resistivity is attenuated by perturbations arising from host−guest interactions. Poly-(bithiophene)s bearing CP moieties were also synthesized and utilized for detection of paraquat.[583] The formation of inclusion complexes of the poly(bithiophene) bearing CP with paraquat (side chain poly*pseudo*rotaxanes) caused a decrease in the carrier mobility, i.e., the conductivity. On the basis of these results, they developed polymer-based devices which demonstrated a real time chemoresistive response to paraquat. Conjugated polymers, poly(*p*-phenyleneethynylene)s, bearing CP moieties were synthesized for the application as chemosensors.[584] The polymers interacted with paraquat to form side chain poly*pseudo*rotaxanes, in which the fluorescence of the conjugated polymers was quenched by electron transfer from the exited state of the conjugated polymers to paraquat. From the Stern−Volmer plots, the static quenching constants were determined. The fluorescence quenching properties of poly(phenyleneethynylene)s and poly(thiophene)s bearing CP-moieties by complexation with paraquat were also compared from the viewpoint of fluorescent chemosensory systems.[585] Fluorescence quenching was enhanced for the CP-carrying polymers because of energy migration. Comparing poly(phenyleneethynylene) structures, the all-para system exhibited more efficient energy migration than did the more electronically localized analogue that contained meta linkages. However, more delocalized poly(thiophene)s exhibited less effective energy migration than did the all-para poly(phenyleneethynylene)s, indicating that delocalization alone is not sufficient for facile energy migration.

3.5. Polyrotor/Polyaxis Systems (See Scheme 31e and f)

3.5.1. CD-Based Systems

Recently, CD-based side chain polyrotaxanes of polyrotor/polyaxis system were reported utilizing a photoresponsive azobenzene stopper.[586] Polymer−polymer interactions for mixtures of a poly(acrylic acid) bearing azobenzene through a dodecamethylene linker and two kinds of poly(acrylic acid) carrying α-CD, in which CDs are attached to the main chain

through the 3- and 6-positions in α-CD, were investigated by viscometry and NMR measurements. These mixtures formed side chain poly*pseudo*rotaxanes. Viscosity data exhibited contrasting changes upon UV irradiation: thinning for the mixture of the 3-position modified α-CD polymer and thickening for the mixture of the 6-position modified α-CD polymer. NOESY spectra confirmed that the viscosity changes were ascribable to differences in how CD moieties interacted with the polymer bearing azobenzene moieties after photoisomerization of azobenzene moieties from *trans* to *cis*: dissociation of inclusion complexes for the mixture of the 3-position modified α-CD polymer and formation of interlocked complexes (side chain polyrotaxane) for the mixture of the 6-position modified α-CD polymer (Figure 32).

The interaction of poly[(maleic acid)-*alt*-(isobutene)]s bearing β-CD and 4-*tert*-butylanilide side groups, respectively, was investigated by Wenz et al.[509,587] Isothermal titration calorimetry data indicated the formation of inclusion complexes of both the polymers with the corresponding model compounds. The formation of side chain poly*pseudo*rotaxanes was confirmed by a large viscosity increase for the mixed solutions. The interaction of the water-soluble epichlorohydrin β-CD polymers with *N,N*-dimethylacrylamide/hydroxyethyl methacrylate copolymers bearing ca. 2 mol % of adamantyl groups was studied by Gosselet et al.[588] At polymer concentrations higher than a certain level, the mixture underwent liquid−liquid phase separation because of the formation of side chain poly*pseudo*rotaxanes, yielding a lower dense phase and an upper liquid phase.

The interaction of α-, β-, or γ-CD-modified poly(acrylic acid) with poly(acrylic acid) bearing octadecyl or adamantyl side chains was investigated by viscometry.[589−591] These mixtures also exhibited a viscosity increase with maxima at approximately a stoichiometric ratio of CD to hydrophobe, indicative of side chain poly*pseudo*rotaxanes. The formation of a side chain poly*pseudo*rotaxane from a dodecyl modified poly(acrylic acid) and an α-CD oligomer cross-linked by epichlorohydrin was utilized to prepare a system which underwent a sol-to-gel transition.[507]

Photoregulated gelation of binary mixtures of an azobenzene-modified polyacrylamide and a polyallylamine-based β-CD polymer was reported by Takashima et al. (Figure 34)[592] In the case of *trans*-azobenzene (before UV irradiation), the mixture formed a supramolecular gel (side chain poly*pseudo*rotaxane). In the case of *cis*-azobenzene (after UV irradition), on the other hand, the mixture was sol.

The formation of thermoresponsive side chain poly*pseudo*rotaxanes was investigated using poly(*N*-isopropylacrylamide)s modified with dodecyl and admantyl groups and β-CD polymers cross-linked with epichlorohydrin.[593,594] Wintgens and Amiel[593] used the surface plasmon resonance technique to explore the association and dissociation kinetics. On the basis of these data, the binding constants were estimated to be higher than 10^4 M^{-1}. Wintgens et al.[594] studied the interaction of the modified poly(*N*-isopropylacrylamide)s and the β-CD polymers by cloud point and visosity measurements. The lower critical solution temperature was shifted upon the formation of side chain poly*pseudo*rotaxanes, depending on the degree of substitution of the modified poly(*N*-isopropylacrylamide)s: the lower critical solution temperature was increased at the degree of substitution of ca. 1 mol % and decreased at the degree of substitution of ca. 4 mol %. Thermoresponsive hydrogel formation through
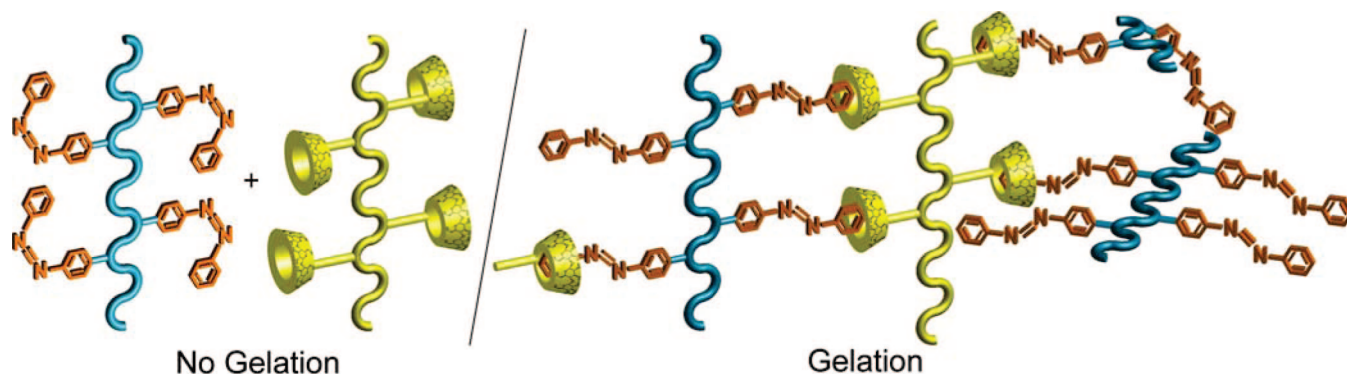
Figure 34. Complex formation and gelation between copolymers containing pendant azobenzene groups and CD polymers.
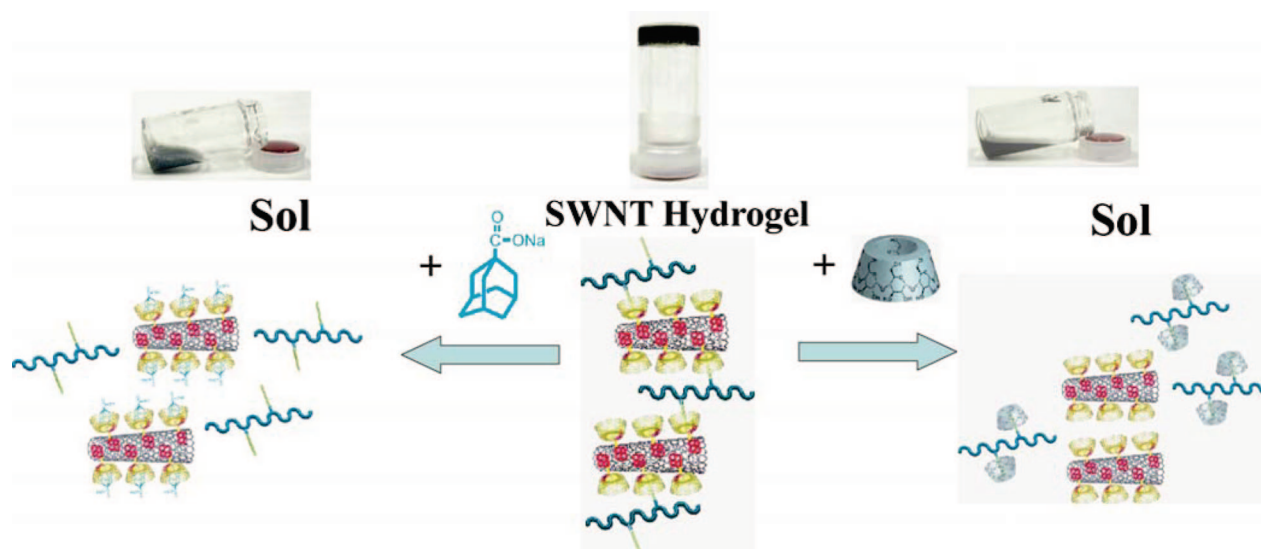
Figure 35. Sol−gel transition of a supramolecular SWNT hydrogel made by using SWNTs with pyrene modified CD and p(AA/C$_{12}$(5)). Reprinted with permission from ref 599. Copyright 2007 American Chemical Society.

a side chain poly*pseudo*rotaxane was also investigated by Kretschmann et al.[497] CD dimers, noncovalent cross-linkers, were mixed with poly(*N*-isopropylacrylamide) bearing adamantyl side chains. As the concentration of the CD dimer increased, the solution viscosity increased, exhibited a maximum, and then decreased. The mixture exhibited a lower cloud point than did the copolymers.

The phase behavior of ternary mixtures of linear β-CD polymers cross-linked with epichlorohydrin, a cationic surfactant (i.e., dodecyltrimethylammonium chloride (DTAC)), and polyanions (sodium dextran sulfates of $M_w = 10000$ and 40000 and poly(sodium sulfate) of $M_w = 70000$) was investigated in aqueous media by Galant et al.[595,596] For a soluble mixture, small-angle neutron scattering and viscometry data demonstrated the formation of ternary complexes (side chain "supramolecular" poly*pseudo*rotaxanes, which are considered as complexes of β-CD polymer and supramolecular polyanions bearing dodecyl side chains). At fixed concentrations of the two polymers, the structure of the complexes depended strongly on the concentration of the surfactant. At surfactant concentrations lower than a certain level, the ternary complexes were of low density and diffuse. As the surfactant concentration increased beyond the level, the ternary complexes became compact, leading to precipitation. The solubility of the ternary complexes decreased in the order poly(sodium sulfonate) > sodium dextran sulfate of lower molecular weight > sodium dextran sulfate of higher molecular weight. Neutron scattering data indicated that the

inner structure of the ternary complexes was inhomogeneous (aggregates of elementary particles with a core−shell structure) at surfactant concentrations lower than the certain level for all the polyanions. At higher surfactant concentrations, the low molecular weight sodium dextran sulfate formed complexes with compact and entangled inner structures, whereas the poly(sodium sulfonate) and the high molecular weight sodium dextran sulfate formed complexes with core−shell inner structures. Analysis at larger length scales revealed that the flexible poly(styrene sulfonate) chains were able to maximize the electrostatic interactions by wrapping up the elementary particles formed from β-CD polymer and the surfactant, whereas the rigid sodium dextran sulfate involved an aggregation mechanism between the same particles. The ternary systems have been extended to systems containing DNA aiming at gene therapy.[597,598]

Single-walled carbon nanotubes (SWNTs) were solubilized with pyrene modified β-CD through the π−π interaction between SWNTs and pyrene moieties (Figure 35).[599] These complexes are considered supramolecular polymers bearing a number of β-CD side chains. Mixing of the complexes with dodecyl modified poly(acrylic acid) afforded gel mixtures, i.e., side chain poly*pseudo*rotaxanes.

The interaction between β-CD polymers cross-linked with epichlorohydrin and hydrophobically modified poly(ethylene oxide) was studied by Amiel et al.[600−602] The hydrophobically modified poly(ethylene oxide)s of different architectures (linear or multiarm branched) and the β-CD polymers

exhibited increased miscibility because of the formation of inclusion complexes between the hydrophobic moieties (naphthalene or adamantane) and β-CD moieties. The binding constants were determined by fluorescence and dialysis measurements. The mixtures exhibited viscoelastic properties, indicative of the formation of polymer aggregates of network structures. Phase diagram studies indicated that the strength of the interactions between the two polymers strongly depended on the number of hydrophobic moieties per poly(ethylene oxide) molecule. Mixtures of unmodified poly(ethylene oxide) and β-CD polymers exhibited segregative phase separation, whereas mixtures of hydrophobically modified poly(ethylene oxide)s and β-CD polymers underwent associative phase separation.

The interaction between hydrophobically modified dextrans and β-CD polymers cross-linked with epichlorohydrin was studied by various techniques including viscometry, phase diagram measurements, surface tension measurements, NMR, and transmission electron microscopy.[603–607] These mixtures formed side chain poly*pseudo*rotaxanes, which were hydrogels, nanoparticles, or phase separated mixtures, depending on the mixing ratio and the molecular parameters (e.g., the type of hydrophobe, the degree of substitution, and the molecular weight of the β-CD polymer). Since some of the β-CD moieties in the poly*pseudo*rotaxanes were unoccupied, these complexes were also investigated as carriers for hydrophobic drugs.[604,605,607]

The formation of particles from poly(ethylenimine)-based β-CD polymers of different architectures (linear and branched) and adamantane modified poly(ethylene glycol) (side chain poly*pseudo*rotaxanes) was reported by Pun et al.[608] The particles obtained were stable at physiological salt concentrations. The particles obtained from the linear β-CD polymer and modified poly(ethylene glycol) exhibited in vitro gene expression equal to or greater than that of linear poly(ethylenimine). Tail vein injections of 120 μg of plasmid DNA formulated with mixtures of the linear β-CD polymer and modified poly(ethylene glycol) into mice did not reveal observable toxicities, and both nucleic acid accumulation and expression were observed in liver.

Ueno et al.[609–612] synthesized polypeptides carrying both CD and fluorescent guest moieties as side chains, which formed supramolecular polymers through the formation of *pseudo*rotaxanes of the side chains. They utilized these polymers as molecular sensors by fluorescence change upon addition of competitive guests.

The formation of hydrogels (side chain poly*pseudo*rotaxanes) from a series of polyacrylamides bearing adamantly side chains and β-CD polymers was reported by Koopmans and Ritter.[613] The viscosity of the resulting hydrogel was dependent on several parameters, i.e., the polymer concentrations, the length of spacer between the adamantyl group and the polymer backbone, the solution pH, and the conformation of the β-CD polymers. Moreover, the hydrogels were stable in solutions of starch hydrolyzing enzyme taka-diastase from *Aspergillus oryzae*.

Komiyama et al.[614,615] utilized molecularly imprinted polymers bearing CD side chains for separation of oligopeptides on the basis of the formation of side chain poly*pseudo*rotaxanes. Two vinyl monomers of β-CD, mono-3-(*N*-acrylamido)-3-deoxyaltro-β-CD and mono-6-(*N*-acrylamido)-6-deoxy-β-CD, were prepared and applied to the molecular imprinting method using amino acid derivatives and oligopeptides as template.[614] The molecu-
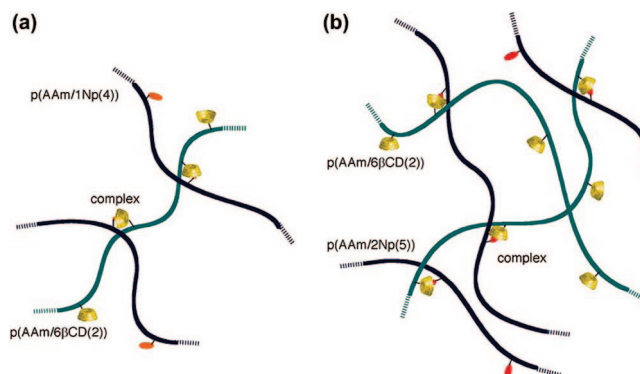
Figure 36. Conceptual illustration for interpolymer aggregates of p(AAm/6βCD(2)) and guest polymers: p(AAm/1Np(4)) (a) and p(AAm/2Np(5)) (b).

larly imprinted polymer from mono-3-(*N*-acrylamido)-3-deoxy-*altro*-β-CD exhibited a considerable enantioselectivity toward protected amino acids, such as *N*-benzyloxycarbonyltyrosine, whereas the molecularly imprinted polymer from mono-6-(*N*-acrylamido)-6-deoxy-β-CD did not. On the other hand, the molecularly imprinted polymers from both the β-CD monomers effectively recognized sequences of tetrapeptides composed of two glycines and two phenylalanines, although the selectivity itself was not remarkable. Using mono-6-(*N*-acrylamido)-6-deoxy-β-CD, silica gel composites coated with polymers molecularly imprinted with peptide hormones were prepared as an HPLC stationary phase.[615] Four samples of angiotensins were used as target peptide hormone: angiotensin I (Asp-Arg-Val-Tyr-Ile-His-Pro-Phe-His-Leu), angiotensin II (Asp-Arg-Val-Tyr-Ile-His-Pro-Phe), [Val^5]-angiotensin I (Asp-Arg-Val-Tyr-Val-His-Pro-Phe-His-Leu), and [Val^5]-angiotensin II (Asp-Arg-Val-Tyr-Val-His-Pro-Phe). HPLC analyses indicated that the retention behavior was strongly dependent on the angiotensin used as template, suggesting that the molecularly imprinted polymers recognized the higher order structures of angiotensins in solution.

To demonstrate enhanced selectivity by multisite interaction, the interaction of a polymer bearing β-CD moieties with poly(acrylamide)s bearing 1- and 2-naphthylmethyl side chains was investigated by viscometry.[616] The formation of inclusion complexes at multisites caused a large difference in the size of interpolymer aggregates, even though the difference in binding constants for complexation of native β-CD with guest moieties was not large (Figure 36).[495]

4. Supramolecular Oligomers and Polymers Bearing Rotaxanes

The supramolecular polymer is a polymer based on the association of monomers through noncovalent interactions and spontaneously forms by aggregation in a solution or in the solid. One characteristic of the supramolecular polymer is the reversibility of the connecting events and annealing or self-healing of the defects. The supramolecular polymer is originally from bifunctional molecules. These systems based on specific hydrogen-bonding as well as on other types of noncovalent interactions have been actively reported by some researchers.[617–640] On the other hand, there are few reports on the formation of supramolecular polymers consisting of rotaxanes.[641] This section focuses on mechanically interwoven polyrotaxanes.

4.1. Structures of Poly[2]rotaxane

X-ray crystallography has been a major source of information about the three-dimensional structures of the host−guest complexes. The structure of interwoven polyrotaxanes was reported by Tabushi in 1982.[642] There are numerous reports on crystal structures of CDs and their inclusion complexes.[643−649] Crystal structures of CDs and their inclusion complexes were classified into cage-, channel-, and layer-type strucutures. These classes depend on the combination of CDs and included guest molecules. When a guest group is attached to a host molecule, the conjugate might form intramolecular complexes[650−659] or intermolecular complexes[50,637,660−677] to give a supramolecular polymer (poly-*pseudo*[2]rotaxane) depending on the flexibility and the length of the guest part. This section focuses on a daisy chain constructed by monosubstituted CD derivatives in crystal structures.

4.1.1. Crystal Structures of β-CD Aliphatic Tethers

The crystal structure of 6-*O*-(*tert*-butylthio)-β-CD showed that 6-*O*-(*tert*-butylthio)-β-CD molecules are arranged along a 2-fold axis and the *tert*-butylmercaptan group was inserted into the next β-CD cavity to form an extended polymeric structure.[642] This is the first example of determination of the crystal structure of monosubstituted CD derivatives and the first evidence concerning the supramolecular polymer of the inclusion complex of a monosubstituted CD (Figure 37).

Tabushi and Higuchi et al. also reported the X-ray crystallographic study of 6-*O*-phenylthio-β-CD and 6-*O*-phenylsulphinyl-β-CD.[678] In the case of 6-*O*-phenylsulphinyl-β-CD, the guest phenylsulphinyl group is more deeply included in the host CD cavity than that of 6-*O*-phenylthio-β-CD. In the packing structures, the molecules are arranged around the screw axis to give a unique polymeric inclusion column structure formed from a single species. The macro-cycles in helical columns are related by a 4-fold screw axis for 6-*O*-phenylthio-β-CD and by a 2-fold screw axis for 6-*O*-phenylsulphinyl-β-CD (Figure 38).

Later, crystal structures of 6-monosubstituted β-CDs, such as 6-*O*-[(*R*)-2-hydroxypropyl]-β-CD, 6-*O*-[(*S*)-2-hydroxypropyl]-β-CD,[679] 6-*O*-(6-cyclo(L-histidyl-L-leucyl))-β-CD,[680] 6-*O*-azido-α-CD, 6-*O*-allyl-α-CD,[681] 6-*O*-[(6-aminohexyl)amino]-β-CD,[682] 6-*O*-(1-propyl)amino-β-CD, and 6-*O*-[(*R*)-1-cyclo-hexylethyl]amino-β-CD,[683] were reported.

4.1.2. Crystal Structures of β-CDs Aromatic Tethers

Harata et al. reported crystal structures of 6-*O*-[(*R*)-1-phenylethyl]amino-β-CD and 6-*O*-[(1*R*,2*S*)-2-hydroxyindan-1-yl]amino-β-CD.[683] They discussed the relationship between crystal packing and the inclusion of the substituent group. In each crystal, the substituent groups were inserted into the adjacent β-CD cavity from the secondary hydroxyl side. This host−guest type self-association through intermolecular inclusion generates a one-dimensional polymeric chain. Later, the crystal structures of 6-*O*-anilino-β-CD,[684] 6-*O*-(4-formylphenyl)-β-CD,[685] 6-*O*-phenylselenyl-β-CD, 6-*O*-(4-bromophenyl)-β-CD,[686] 6-*O*-(4-nitrophenyl)-β-CD,[686] 6-*O*-(4-formylphenyl)-β-CD,[686] and 6-*O*-(*p*-carboxyphenylamino)-β-CD[687] were reported.
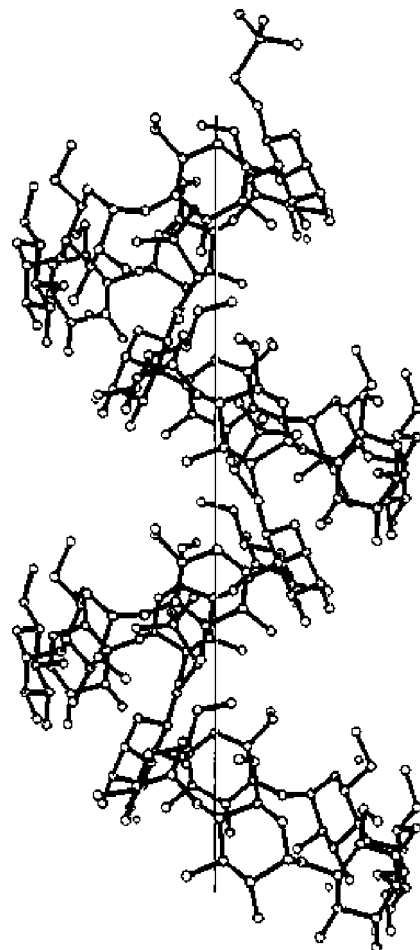
Figure 37. Crystal structures of 6-*O*-(*tert*-butylthio)-β-CD drawing the helical polymer related by the 2_1 screw axis. Reprinted with permission from ref 642. Copyright 1982 American Chemical Society.

4.1.3. Crystal Structures of Cyclic Dimers

6-*O*-(4-Hydroxybenzoyl)-β-CD[686] and 6-aminocinnamoyl-β-CD[688] (Figure 39) formed double threaded dimers (cyclic dimers). These 6-monosubstituted-β-CDs formed a dimeric structure, and the substituent group is inserted into the adjacent β-CD cavity from the primary hydroxyl group to form a columnar channel structure.

Later, the structure of 3-*trans*-stilbene-α-CD was determined by X-ray crystallographic analysis. 3-*trans*-Stilbene-α-CD showed the formation of a tilted double threaded dimer (Figure 40).[689]

4.2. Daisy Chain Oligomers

Many modified CDs have been prepared and characterized as their supramolecular structures in aqueous solutions. Most of them formed intramolecular complexes. Although chro-mophor modified CDs act as chemosensors by the location change of the substitution part from inside to outside of the CD cavities with inclusion of other guest molecules (Figure 41),[650−652] benzoyl modified β-CD did not form supramolecular polymers.[662] This result suggests that some spacer groups are required for efficient formation of intermolecular complexes.
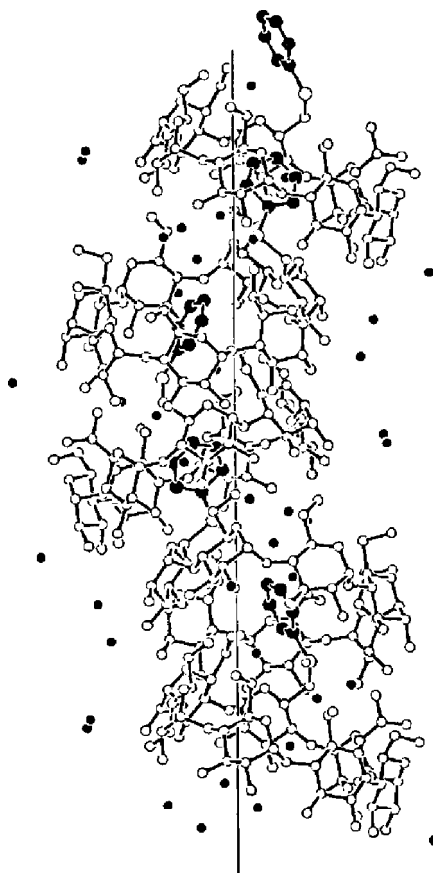
Figure 38. Crystal structures of 6-*O*-phenylthio-β-CD drawing the helical polymer penentrated by the 4_1 screw axis. Reprinted with permission from ref 678. Copyright 1987 Royal Society of Chemistry.
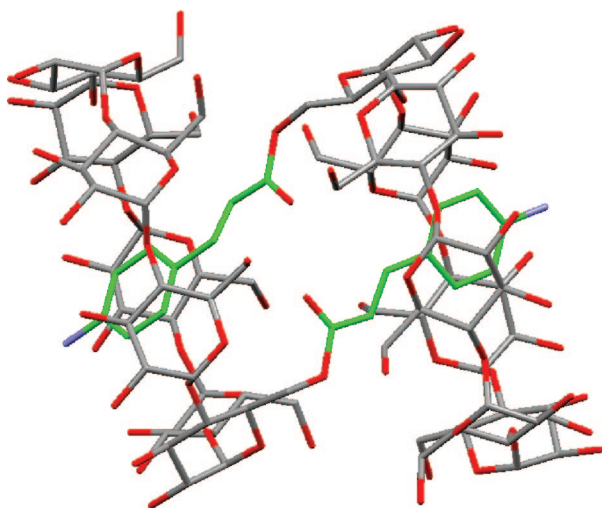
Figure 39. Crystal structure of 6-aminoCiO-β-CD drawing a dimeric columnar structure by a dimeric columnar structure. Reprinted with permission from ref 688. Copyright 2005 American Chemical Society.

4.2.1. Formation of Intramolecular and Intermolecular Complexes by Hydrocinnamoyl-CDs

When CDs are introduced to the hydroxycinnamoyl group at the C6 position, there are differences between the supramolecular structures of 6-hydroxycinnamoyl-α-CD (6-HyCiO-α-CD) and of 6-hydroxycinnamoyl-β-CD (6-HyCiO-
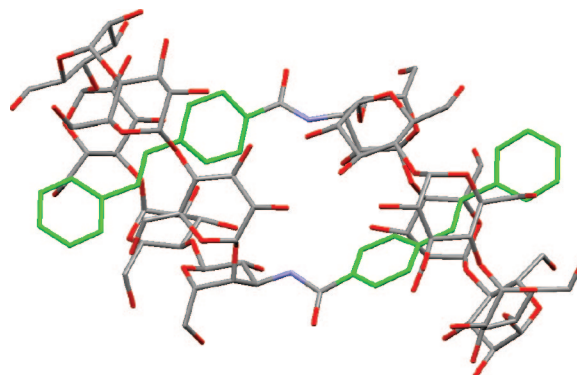
Figure 40. Crystal structure of a double threaded dimer consisting of 3-*trans*-Sti-α-CD. Carbon and oxygen of α-CD are shown in gray and red, respectively. Carbon and oxygen of stilbene amide groups are shown in light green. Reprinted with permission from ref 689. Copyright 2008 American Chemical Society.
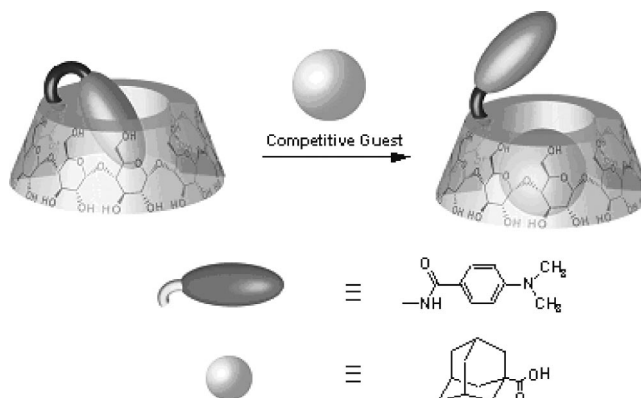
Figure 41. Schematic representation of a fluorescent chemosensor by intramolecular complexes having a chromophor.
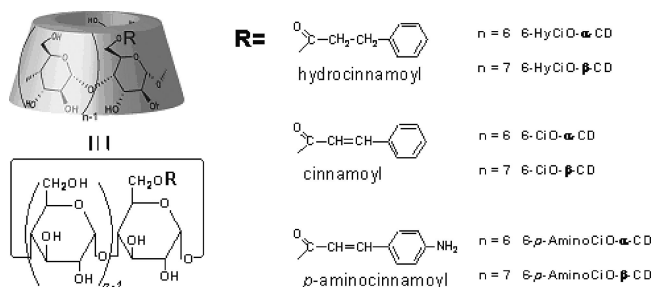
Figure 42. Structures of hydrocinnamoyl and cinnamoyl modified CDs.

β-CD) (Figure 42). The ^{1}H NMR spectra of 6-hydroxycinnamoyl-β-CD (6-HyCiO-β-CD) and 6-HyCiO-α-CD in D$_2$O showed that the peaks of the phenyl protons of the hydrocinnamoyl group shifted toward the same way as those of ethyl hydrocinnamate on addition of CDs, indicating that the phenyl ring was included in the CD cavities. Although the peak shifts of 6-HyCiO-β-CD are independent of the concentrations, the shifts of 6-HyCiO-α-CD are slightly dependent on the concentrations in D$_2$O. The ^{1}H NMR spectra and ROESY spectra of 6-HyCiO-CDs showed correlation peaks between phenyl signals and CD signals, indicating that the phenyl ring is included in its own CD cavity. These results indicate that 6-HyCiO-β-CD forms intramolecular complexes in D$_2$O; however, 6-HyCiO-α-CD forms weak intermolecular complexes in D$_2$O.[672] Proposed structures of 6-HyCiO-CDs in water are depicted in Figure 43.
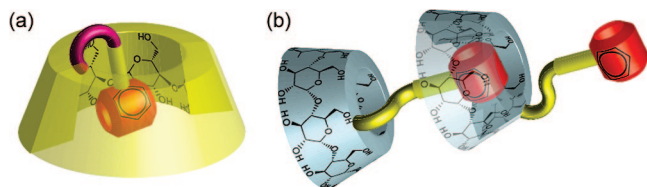
Figure 43. Proposed structures of 6-HyCiO-β-CD (a) and 6-Hy-CiO-α-CD (b).
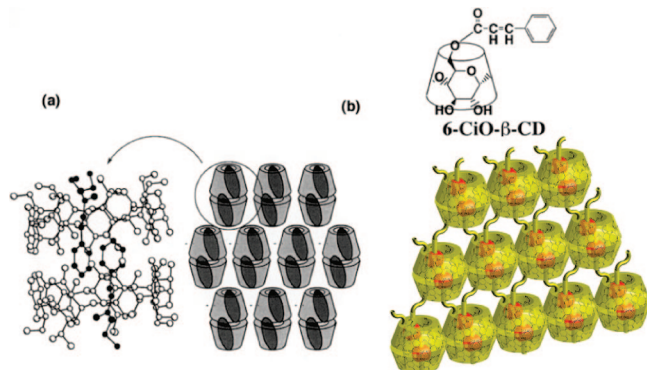
Figure 44. Crystal structure of the β-CD-ethyl cinnamate complex (a) and a proposed structure of 6-CiO-β-CD in the solid state.

4.2.2. Formation of Supramolecular Oligomer Incorporating 6-Cinnamoyl-CDs

6-Cinnamoyl-β-CD (6-CiO-β-CD) is sparingly soluble in water, although most 6-substituted β-CDs are soluble. However, 6-CiO-β-CD was solubilized in water on the addition of adamantane carboxylic acid or p-iodoaniline, which could be included in a β-CD cavity. These results suggest that 6-CiO-β-CD formed supramolecular complexes in the solid state, as shown in the proposed structure in Figure 44. The X-ray powder pattern of 6-CiO-β-CD is similar to that of the complex between β-CD and ethyl cinnamate, in which β-CDs form a layer structure. The crystal structure of 6-aminocinnamoyl-β-CD (6-aminoCiO-β-CD) is shown in Figure 39.

The ^{1}H NMR spectra of 6-cinnamoyl-α-CD (6-CiO-α-CD) showed that the phenyl protons shifted toward the same way as those of methylcinnamate on addition of α-CD, indicating that the phenyl ring is included in a CD cavity. The shifts are dependent on the concentrations in D$_2$O, although they are independent of their concentrations in DMSO-d_6, indicating that 6-CiO-α-CD forms intermolecular complexes in D$_2$O. The ROESY spectrum of that 6-CiO-α-CD shows cross peaks between phenyl signals and CD signals, indicating that the phenyl ring is included in the other CD cavity. The molecular weight of 6-CiO-α-CD measured by vapor pressure osmometry (VPO) at various concentrations in water increased with an increase in the concentrations, and the molecular weight reached saturation at about 3 × 10^3. This result suggests that 6-CiO-α-CD forms an oligomer.[673]

4.3. Cyclic Daisy Chains

Cyclic tri[2]rotaxanes (daisy chain necklace) containing CDs have been obtained by closing a tri[2]rotaxane containing α-CD and 6-(4-aminocinnamate) with 2,4,6-trinitrobenzene sulfonic acid sodium salt.[50,674] (Figure 45). If the molecule changes its conformation (or coconformation), the ring may expand or shrink by external conditions (temperature, solvents, photochemically, electrochemically). These
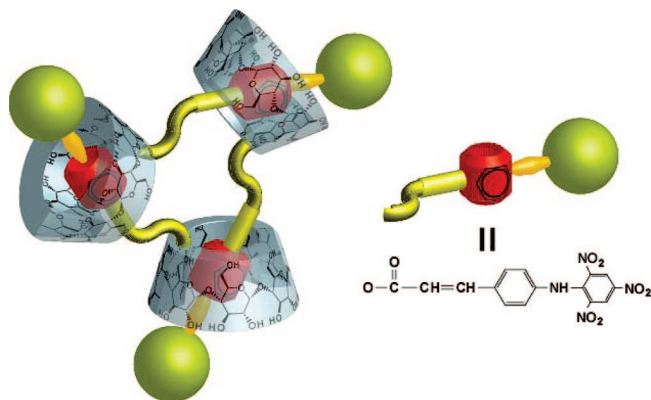
Figure 45. Harada's daisy chain necklace: cyclic tri[2]rotaxane containing α-CD.
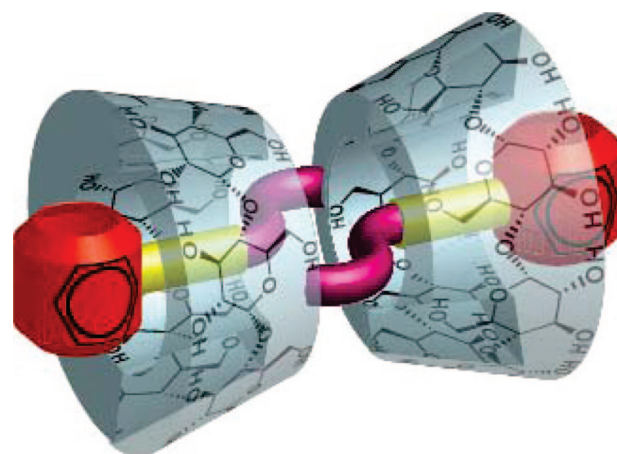
Figure 46. Structure of supramolecular dimers constructed by 6-CiNH-α-CD in an aqueous solution.

compounds are important because the cycle can be used as a chemical valve, as can be seen in ion channels in biological membranes.

4.4. Daisy Chain Dimer Incorporating Cinnamamide-α-CD

The ^{1}H NMR spectra of 6-cinnamamide-α-CD (6-CiNH-α-CD) change with its concentrations in D$_2$O solutions, although the spectra do not change in DMSO-d_6. These results indicate that 6-CiNH-α-CD formed intermolecular complexes in D$_2$O. The ROESY NMR spectra of 6-CiNH-α-CD showed that the phenyl ring is deeply included into the CD cavity. The molecular weight measured by VPO showed the saturation to be about 2 × 10^3, twice as large as that of the monomer unit. Therefore, 6-CiNH-α-CD formed a rigid supramolecular dimer shown in Figure 46.

The fact that 6-CiNH-α-CD formed a supramolecular dimer in which cinnamoyl groups are included from the primary hydroxyl groups led us to use 3-cinnamamide-α-CD (3-CiNH-α-CD) and 3-p-aminoCiNH-α-CD as a building unit (Figure 47), because the phenyl group can be included in α-CD from the primary hydroxyl side successively to form supramolecular polymers. Actually, 3-CiNH-α-CD and 3-p-aminoCiNH-α-CD were found to form long supramolecular polymers with molecular weight higher than 1.6 × 10^4.[675,676] Poly[2]rotaxanes (daisy chain) were formed by 3-p-aminoCiNH-α-CD stabilized by bulky stoppers (trinitrobenzyl sulfonate and adamantanamide) at each end of the guest groups
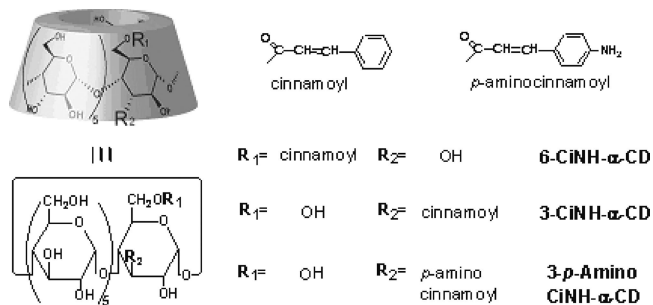
Figure 47. Structures of cinnamamide modified CDs.
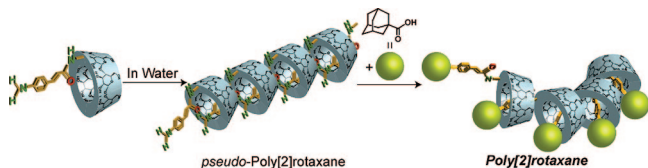
Figure 48. Schematic representation of supramolecular oligomers constructed by 3-CiNH-α-CD in aqueous solution. Reprinted with permission from ref 677. Copyright 2008 Royal Society of Chemistry.
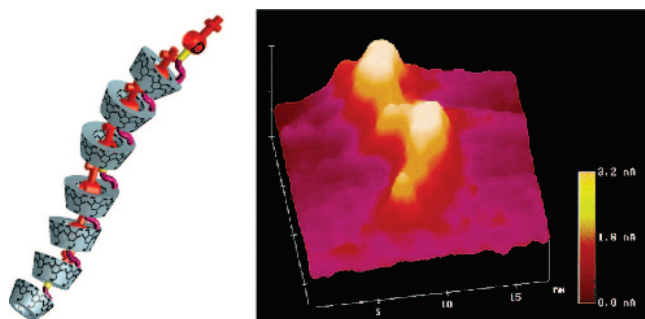
Helical Supramolecular Polymer

Figure 49. Proposed structure of a supramolecular polymer formed by 3-*p*-ʹBocCiNH-α-CD in aqueous solution. Reprinted with permission from ref 690. Copyright 2005 American Chemical Society.

(Figure 48). The poly[2]rotaxane was found to be about 13 units, as measured by MALDI-TOF mass spectra.[676,677]

4.5. Formation of Helical Supramolecular Polymer by *tert*-Boc-Aminocinnam-α-CD

α-CD with a 3-*p*-*tert*-Boc-cinnammoylamino group forms a supramolecular polymer.[690] The existence of substitution/substitution interactions among the adjacent monomers of supramolecular polymer has been proved by the observation of positive and negative Cotton bands in the circular dichroism spectra. The supramolecular polymer was found to form a left handed helical conformation (Figure 49). The formation of helical supramolecular polymer with some cooperativity is shown by the CD spectra.

4.6. Supramolecular Oligomers with Alternating α- and β-Cyclodetrin Units

6-*p*-*tert*-BocCiNH-β-CD formed intramolecular complexes. When adamantane carboxylic acid is added in the solution of 6-*p*-*tert*-BocCiNH-β-CD, the adamantane group is included in the β-CD cavity and the cinnamoyl group is kicked out of the cavity.[691] When adamantane carboxylic acid was attached to α-CD at the 3-position (3-AdHexNH-α-CD)
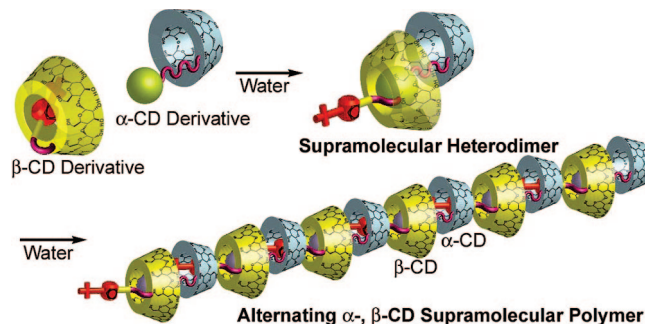
Figure 50. Proposed structures of supramolecular oligomer incorporating 3-AdHexNH-α-CD and 6-*p*-ʹBocCiNH-β-CD. Reprinted with permission from ref 691. Copyright 2004 American Chemical Society.

and the 3-AdHexNH-α-CD was mixed with 6-*p*-*tert*-Boc-CiNH-β-CD in D$_2$O in a one-to-one ratio, they formed a heterodimer, which lines up end-to-end in longitudinal rows to form supramolecular oligomers in an alternating manner (Figure 50).

4.7. Supramolecular Oligomers and Polymers Incorporating Ditopic Host Dimer

CD-based supramolecular polymers have been prepared using a β-CD dimer and ditopic guest dimers having adamantyl groups.[692,693] The ditopic guest dimers with varying flexibility and adamantyl moieties were prepared to investigate the conformation of the supramolecular complexes. The ROESY spectra of the β-CD dimer with the ditopic adamantane guest dimers showed an NOE between the protons of adamantyl substituents and the inner protons of CD. The β-CD dimer forms supramolecular polymers with stiff guest molecules to give high molecular weight supramolecular polymers, and the β-CD dimer gives cyclic supramolecular oligomers with flexible ditopic guest dimers (Figure 51). A 1:1 mixture of the β-CD-PEG dimer and the adamantane-PEG dimer forms of the self-organized intermolecular supramolecular polymers (Figure 52).

The conformation of the stilbene bis(β-CD) dimer in aqueous solution could be photochemically controlled. The ROESY spectra of the β-CD dimer with the adamantyl dimer showed an NOE between the protons of adamantyl moieties and the inner protons of the CD. When the host CD dimer is in the *trans* conformation, supramolecular dimers or small assemblies are formed in solution, whereas in its *cis* conformation supramolecular linear polymers with high molecular weight were observed. Thus, the structure of the supramolecular polymers could be controlled by an external stimulus (Figure 53).[694]

5. Conclusion

A lot of papers on both main-chain polyrotaxanes and side-chain polyrotaxanes have been published since the first reports on the polyrotaxanes. A variety of architectures have been designed and achieved in the construction of polyrotaxanes. Much effort has been directed to achieve new functions using polyrotaxane structures. Dynamic aspects of the polyrotaxanes are investigated for the development of molecular machines and molecular devices. These unique structures of polyrotxanes should be used as a new component of such working molecules and molecular assemblies in the real world in the near future.

β-CD dimer–Guest Dimer **C0**

$$\overline{DP} > 30, \; \overline{M_n} > 9.0 \times 10^4$$
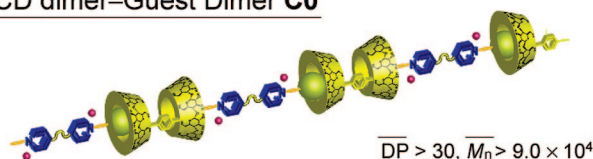
β-CD dimer–Guest Dimer **C2**
&
β-CD dimer–Guest Dimer **C3**
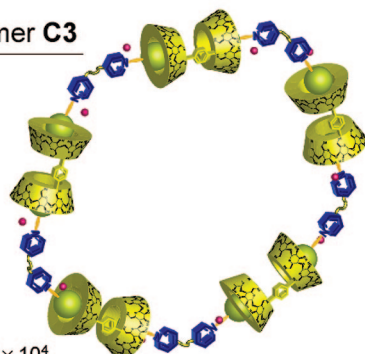
$$\overline{DP} = 3\sim5, \; \overline{M_n} = 1.0 \times 10^4 \sim 1.5 \times 10^4$$

Figure 51. Proposed structures of supramolecular oligomer incorporating β-CD dimer and adamanane dimer. Reprinted with permission from ref 692. Copyright 2005 American Chemical Society.
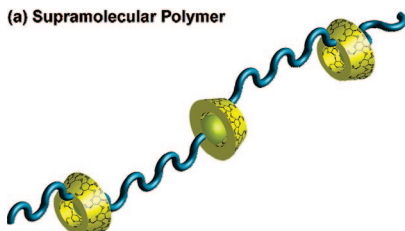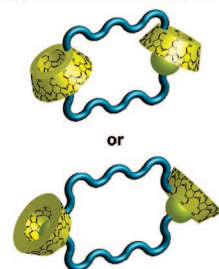
Figure 52. Proposed structures of supramolecular polymer incorporating β-CD-PEG dimer and adamanane-PEG dimer. Reprinted with permission from ref 693. Copyright 2005 American Chemical Society.
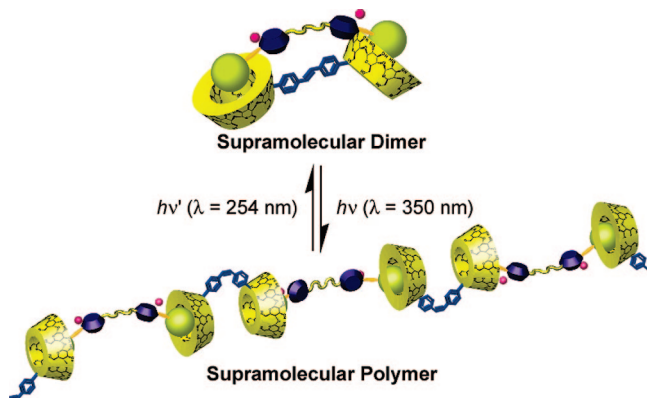
Figure 53. Proposed mechanism of external stimulus-responsive supramolecular polymers constructed by a stilbene CD dimer. Reprinted with permission from ref 694. Copyright 2007 American Chemical Society.

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