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Preparation and structures of supramolecules between cyclodextrins and polymers

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Contents

Abstract

Cyclodextrins (CDs) form inclusion complexes with various polymers with high selectivities to give crystalline compounds. α-CD formed complexes with poly(ethylene glycol) (PEG) and oligoethylene in high yields, although β-CD did not form complexes with PEG. However, β-CD formed complexes with poly(propylene glycol) (PPG). Although α-CD did not form complexes with polyisobutylene (PIB) and poly(methyl vinyl ether) (PMVE), γ-CD formed complexes with PIB and PMVE. There is a good correlation between the sectional areas of the polymers and the sizes of the CDs. The stoichiometries, properties, and structures of the

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complexes are discussed. The yield of the complexes increased with increasing molecular weight. Polyrotaxanes, in which many cyclodextrins are threaded on a poly(ethylene glycol) chain, were prepared by capping the chain ends of the polymers in the complexes with bulky groups.

Keywords: Supramolecules; Cyclodextrins; Polymers

1. Introduction

In recent years, much attention has been focused on molecular recognition of low molecular weight compounds [1]. Crown ethers [2], cryptands [3], cyclophanes [4], and calixarenes [5] have been extensively used as host molecules. However, the guests recognized by these host molecules have been limited to small molecules and simple ions, such as lithium, sodium, potassium, chloroform, and benzene. Host molecules which can recognize and respond sensitively to larger and more complicated compounds and even polymers are required.

In biological systems such as enzymes–substrates, antigen–antibodies, DNA, RNA, and cell adhesion systems, however, macromolecular recognition, that is, recognition of macromolecules by macromolecules, plays an important role in constructing supramolecular structures and maintaining their lives [6]. However, there have been no approaches toward macromolecular recognition by artificial host–guest systems.

Since cyclodextrins were discovered, a great number of reports (more than 10000 papers) have been published on cyclodextrins. However, studies on the inclusion properties of cyclodextrins were limited to those with low molecular weight compounds [7–9]. Cyclodextrins are cyclic molecules consisting of six to eight glucose units linking through α-1-4-glycosidic linkages. They are called α-, β-, and γ-cyclodextrin (CD), respectively. They are known to form inclusion complexes with a wide variety of low molecular weight compounds, ranging from nonpolar hydrocarbons to polar carboxylic acids and amines. There have been no reports on the complex formation of cyclodextrins with polymers when we started our work in early 1980s. Therefore, we have started our project on complex formation between polymers and cyclodextrins.

There have been some examples in which a monomer was polymerized in situ within a cyclodextrin complex. Ogata et al. prepared hexamethylene diamine complexes of β-CD [10]. Polyamides were obtained by condensation of dibasic acid chlorides and the inclusion complexes of the diamine. Maciejewski reported the polymerization and copolymerization of vinylidene chlorides as adducts with β-CD [11]. There are some reports which suggest interactions between cyclodextrins and some polymers in aqueous solutions. Kitano et al. reported that cyclodextrins show some effects on the critical micelle concentrations of some micelle-forming surfactants [12]. Iijima et al. studied diffusion of cyclodextrin in the presence of poly(styrenesulfonate) in aqueous solutions and reported that there are some interactions between cyclodextrin and the polymer [13].

There have recently been reports by Gibson et al. describing the formation of supramolecular complexes bewteen crown ethers and oligomers [14].

Table 1
Complex formation of CDs with hydrophilic polymers

Polymer	Structure	MW	Yield (%)		
			α-CD	β-CD	γ-CD
PVA	$-(CH_2CH(OH))-$	22000	0	0	0
PAAm	$-(CH_2CH(CONH_2))-$	10000	0	0	0
PEG	$-(CH_2CH_2O)-$	1000	92	0	trace
PPG	$-(CH_2CH(CH_3)O)-$	1000	0	96	80
PMVE	$-(CH_2CH(OCH_3))-$	20000	0	0	80

2. Complex formation between cyclodextrins and hydrophilic polymers [15]

We tested whether cyclodextrins would form complexes with some water-soluble nonionic polymers. Table 1 shows the results of the formation of complexes of cyclodextrins with some nonionic polymers. We found that cyclodextrins did not form complexes with some nonionic water-soluble polymers (such as poly(vinyl alcohol) (PVA) and polyacrylamide (PAAm)) by the same procedure as that for low molecular weight compounds. However, we found that α-CD forms crystalline complexes with poly(ethylene glycol) (PEG) in high yield.

2.1. Complex formation of α-cyclodextrin with poly(ethylene glycol) [16]

When aqueous solutions of PEG were added to a saturated aqueous solution of α-CD at room temperature the solution became turbid and the complexes were formed as precipitates when the average molecular weight of PEG was more than 200. [17]

2.1.1. Rates of complex formation

While preparing the complexes of α-CD with PEG we found that the rate of complex formation depends on the molecular weight of PEG. Fig. 1 shows the effects of molecular weights on the rate of turbidity development after mixing the saturated α-CD solution and PEG solution. The figure clearly shows that PEG of molecular weight 1000 forms complexes most rapidly. This may be partly due to the fact that the number of end groups decreases as the molecular weight increases. Addition of the PEG solution to a saturated aqueous solution of β-CD did not cause any change in solution.

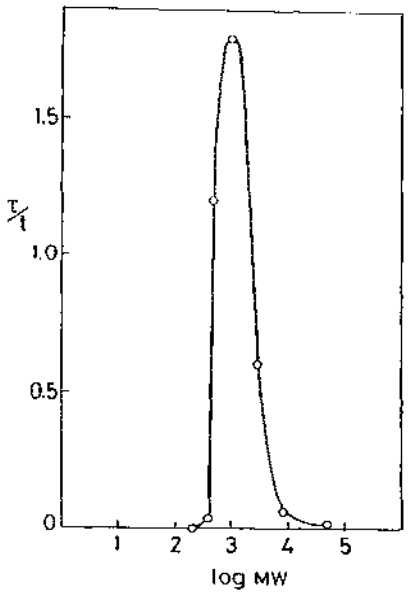


Fig. 1. Effects of molecular weight on the rate of turbidity development after mixing the saturated α-CD and PEG solutions.

2.1.2. Effects of the molecular weight of polymers on the yields of the complexes [18]

The complexes were isolated by filtration or centrifugation. Fig. 2 shows the yields of the complexes of α-CD with PEG of various molecular weights. The yields are calculated on the basis of 2 : 1 (ethylene glycol unit : α-CD) stoichiometry, as discussed in the following section. α-CD did not form complexes with the low molecular weight analogs ethylene glycol, diethylene glycol, and triethylene glycol. α-CD formed complexes with PEG of molecular weight >200. The yields were found to increase with

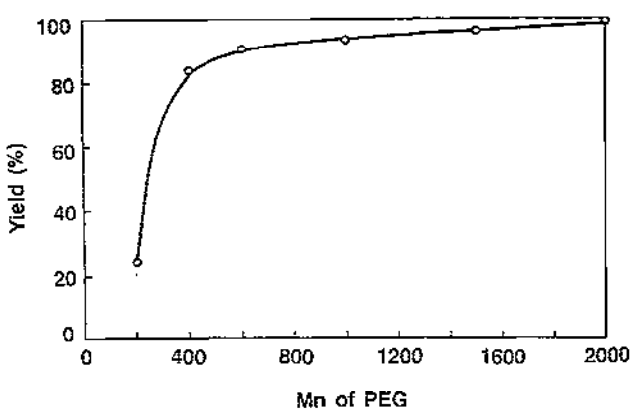


Fig. 2. Yields of the complexes of α-CD with PEG as a function of the molecular weight of PEG.

increasing molecular weight. The complexes were obtained almost quantitatively with PEG of molecular weight > 1000. β-CD did not form complexes with PEG of any molecular weight. Although PEG of molecular weight > 1000 formed complexes with α-CD slowly, they gave high yields after several hours.

This observation that a minimum PEG length is required for the formation of stable cyclodextrin complexes shows the importance of cooperativity in complexation and is similar to the formation of PEG complexes with hydrogen-donor polymers such as poly(acrylic acid).

2.1.3. *Stoichiometries of the complexes*

The complex formation of α-CD with PEG was studied quantitatively. Fig. 3 shows the yields of the complexes of α-CD with PEG of average molecular weight 600 as a function of added PEG. The yields increased linearly when the amount of PEG added was small and leveled off at a molar ratio of 2:1 (ethylene glycol unit:CD). These results indicate that the complex formation is stoichiometric. The saturation values show that more than 90% of the α-CD was consumed by the complex formation with PEG. The continuous variation plots for the complexation between α-CD and PEG also suggest that the stoichiometries of the complexes are all 2:1. The stoichiometries were confirmed by the ^{1}H NMR spectrum. Fig. 4 shows the ^{1}H NMR spectrum of the complex of PEG-600 with α-CD. It should be noted that the stoichiometries of the complexes are always 2:1 even if α-CD and PEG are mixed in any ratio. The length of two ethylene glycol units corresponds to the depth of the cavity of α-CD.

Carbohydrate polymers such as dextran and pullulan did not form insoluble complexes with PEG. Amylose and dextrin also did not form insoluble complexes with PEG. Glucose, methyl glycoside, maltose, and maltotriose did not form

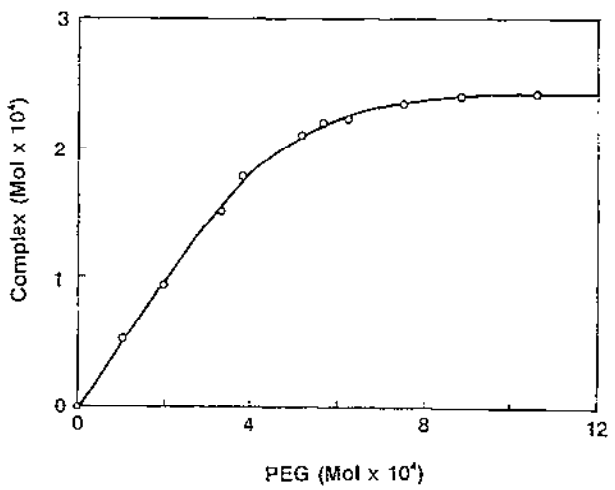


Fig. 3. Amount of α-CD-PEG complexes as a function of added PEG (MW = 600). A total amount of 2 ml of saturated aqueous solution of α-CD was used.

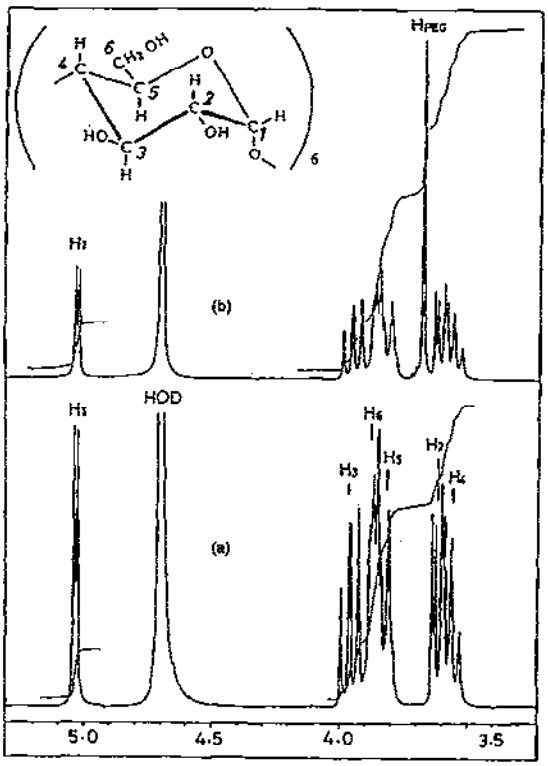


Fig. 4. ^1H NMR spectra of the complexes of PEG with (a) α-CD and (b) α-CD in D_2O.

complexes with PEG. Cyclodextrin derivatives, such as glucosyl-α-CD and maltosyl-α-CD, and soluble polymers of α-CD, did not form insoluble complexes with PEG.

2.1.4. Properties of the complexes

The complexes of α-CD with PEG of low molecular weight (1000) are soluble in water. The complexes of PEG of higher molecular weight can be dissolved in water by heating. The addition of an excess amount of a low molecular weight guest, such as benzoic acid, propionic acid, and propanol, to the suspension of the complex resulted in solubilization of the complex when the molecular weight of PEG was low (1000). The formation of the complex is reversible. In solution, complexes are in equilibrium between the complex and its component. The addition of salts such as NaCl and KCl did not cause any change in the solubility of the complexes. This result indicates that there are no ionic interactions between α-CD and the polymer. The addition of urea, which is thought to affect hydrogen bonds, results in solubilization of the complexes, indicating that hydrogen bonding plays an important role in forming the complexes between PEG and α-CD.

The decomposition points of the complexes are a little higher than that of the cyclodextrin. The complex of α-CD with PEG-1000 decomposes above 300°C,

whereas α-CD melts and decomposes below 300°C. Thus, poly(ethylene glycol) stabilizes α-CD.

2.1.5. Inclusion modes

Fig. 5 shows the X-ray powder patterns of the complex of α-CD with PEG and those with other low molecular weight compounds. Saenger et al. reported that the structures of the inclusion complexes of CDs with low molecular weight compounds can be classified into two groups: 'cage-type' and 'channel-type' [9]. The X-ray powder pattern of the α-CD-PEG complex shows that the complexes are crystalline. The patterns are very similar to those of the complex of α-CD with valeric acid or octanol, which have been reported to have an extended column structure, and totally different from those of the complexes with small molecules such as acetic acid, propionic acid, and propanol, which have a cage-type structure. These results indicate that the complexes of α-CD and PEG are isomorphous with those of channel-type rather than cage-type structure.

Molecular models show that PEG chains are able to penetrate α-CD cavities, while the poly(propylene glycol) chain cannot pass through the α-CD cavity. These views are in accordance with our observation that α-CD forms complexes with PEG but not with poly(propylene glycol). β-CD did not form complexes with PEG. A PEG chain is too slim to fit in the β-CD cavity. However, β-CD forms complexes with poly(propylene glycol). Model studies indicate further that the single cavity (depth 6.7 Å) accommodates two ethylene glycol units (6.6 Å) when ethylene glycol chain assumes a planar zigzag conformation.

Fig. 6 shows the ^{13}C CP/MAS NMR spectra of α-CD and the α-CD-PEG complex. α-CD assumes a less symmetrical conformation in the crystal when it does not include a guest in the cavity. In this case, the spectrum shows resolved C-1 and C-4 resonances from each of the six α-1,4-linked glucose residues. In particular, C-1 and C-4 adjacent to a conformationally strained glycosidic linkage are observed at 80 and 98 ppm, respectively. In the spectrum of the α-CD-PEG complex, however, the peaks at 80 and 98 ppm disappeared. Each carbon of glucose can be observed in a single peak. These results indicate that α-CD adopts a symmetrical conformation and each glucose unit of CD is in a similar environment. The X-ray studies of single crystals showed that α-CD assumes a less symmetrical conformation when it does not include guests in the cavity and α-CD adopts a symmetrical conformation when it includes guests in the cavities. CP/MAS NMR spectra of complexed and uncomplexed CDs are consistent with the X-ray results. So a PEG chain is thought to be included in the cavities.

2.1.6. Complex formation between cyclodextrin and poly(ethylene glycol) derivatives

Table 2 shows results of complex formation between α-CD and PEG with various end groups. First, PEGs with small end groups such as methyl, dimethyl, and amino groups, form complexes. The yields are somewhat higher than with unmodified PEG. This result indicates that interactions (hydrogen bonds) between the OH groups of OEG and those of α-CD are not the driving force for complex formation.

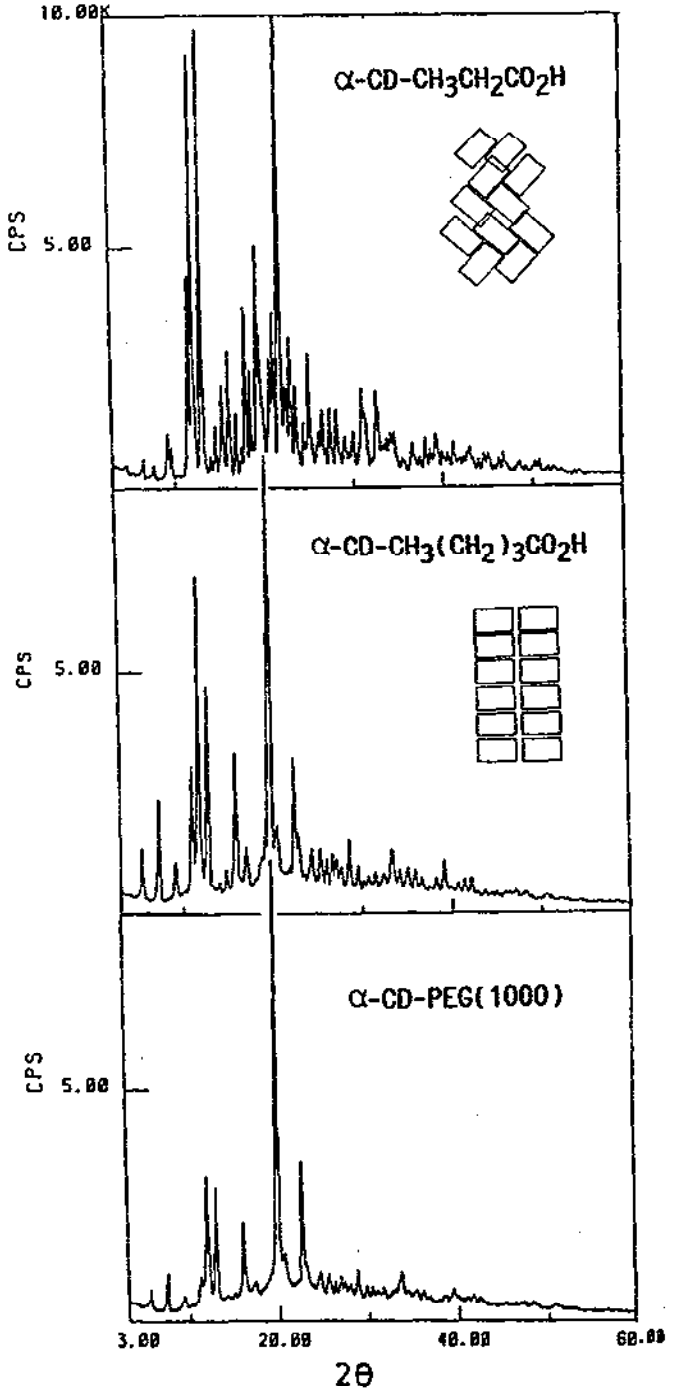


Fig. 5. X-Ray diffraction patterns for α-CD complexes: (a) α-CD-propionic acid; (b) α-CD-valeric acid; and (c) α-CD-PEG (MW = 1000).

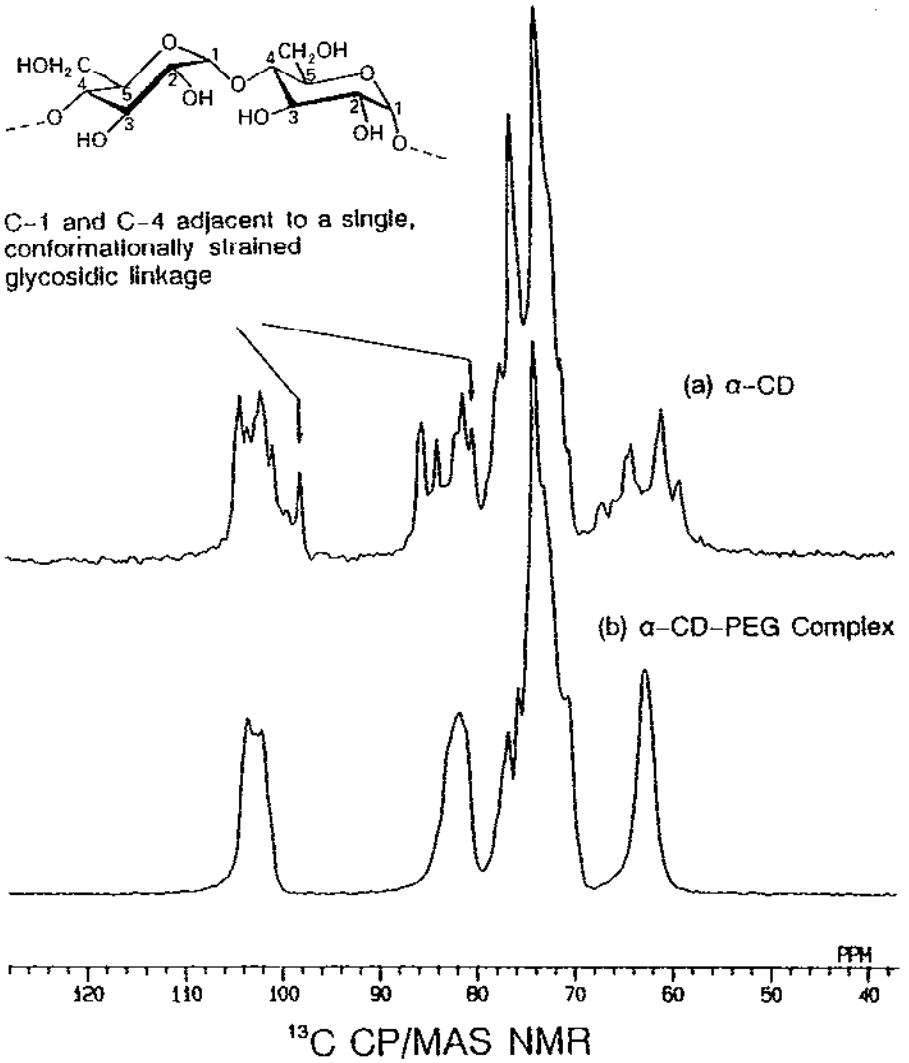
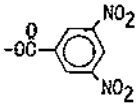
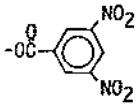
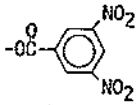
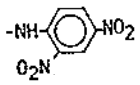
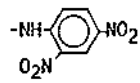


Fig. 6. ^{13}C CP/MAS NMR spectra of (a) α-CD and (b) the α-CD-PEG complex.

PEG carrying bulky substituents at either end of the PEG which do not fit or pass through the α-CD cavity, such as 3,5-dinitrobenzoyl and 2,4-dinitrophenyl groups, did not form any complexes with α-CD.

Fig. 7 shows a proposed structure of the complex of poly(ethylene glycol) with α-CD. The inclusion complex formation of PEG in the α-CD channel is entropically unfavorable, However, formation of the complexes is thought to be promoted by hydrogen bond formation between neighboring cyclodextrins. Therefore, head-to-head and tail-to-tail arrangements are thought to be the most probable structures.

Table 2
Complex formation between CD and PEG with various end groups

$R(CH_2CH_2O)_nCH_2CH_2R'$			Yield (%)	
R	R′	MW	α-CD	β-CD
–OH	–OH	1000	90	0
$-NH_2$	$-NH_2$	1450	90	0
$-OCH_3$	$-OCH_3$	1000	93	0
		900	0	0
	$-OCH_3$	900	77	10
		3700	0	0

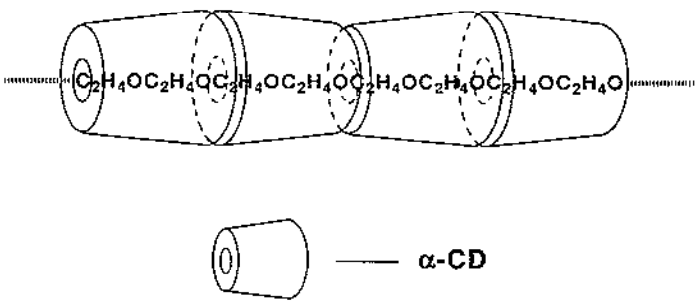


Fig. 7. Proposed structure of the α-CD-PEG complex.

2.1.7. Synthesis of molecular necklace (polyrotaxanes) [19–21]

Recently, much attention has been focused on supramolecular science, science of noncovalent assembly, because of the recognition of the importance of specific noncovalent interactions in biological systems and in chemical processes [22]. Rotaxanes are one of the classical classes of molecules consisting of noncovalent entities, with a 'rotor' and an 'axle' in a single molecule [23]. They were synthesized in a statistical way, but yields were very low [24]. More recently, rotaxanes have attracted renewed interest in the field of supramolecular chemistry because of their unique structures and properties. Rotaxanes can be prepared by closing the end groups of 'axle' using large groups within the ordered environments of the noncovalent templating forces in such a way as to retain the order originally imposed by the weak interactions [25]. By this method complexes containing methylated β-CD and

threads [26–27] have been synthesized. Both symmetric [28–29] and asymmetric [30] ionic rotaxanes containing α-CD have been reported (Fig. 8).

We have succeeded in preparing compounds in which many cyclodextrins are threaded on a single PEG chain. They are trapped by capping the chain ends with bulky groups, as shown in Scheme 1. This is the first example in which many rotors are imprisoned in a single molecule. We named this molecule 'molecular necklace'. Wenz and Keller also reported a rotaxane with many α-CDs [31].

The inclusion complexes of α-CD with PEG bisamine (PEG-BA) were prepared by adding an aqueous solution of PEG-BA to a saturated aqueous solution of α-CD at room temperature, using a method similar to that used to prepare complexes of α-CD and PEG. The resulting complex was allowed to react with an excess of 2,4-dinitrofluorobenzene, which is bulky enough to prevent unthreading. The product was purified by column chromatography on Sephadex G-50 using dimethylsulfoxide (DMSO) as solvent.

The products are insoluble in water and dimethylformamide, but are soluble in DMSO and in 0.1 N NaOH. The products were characterized by UV–vis, X-ray diffraction, ^{1}H NMR, ^{13}C NMR ^{13}C CP/MAS NMR and 2D NOESY NMR spectroscopies. The ^{1}H NMR spectra of the product shows that it is composed of α-CD,

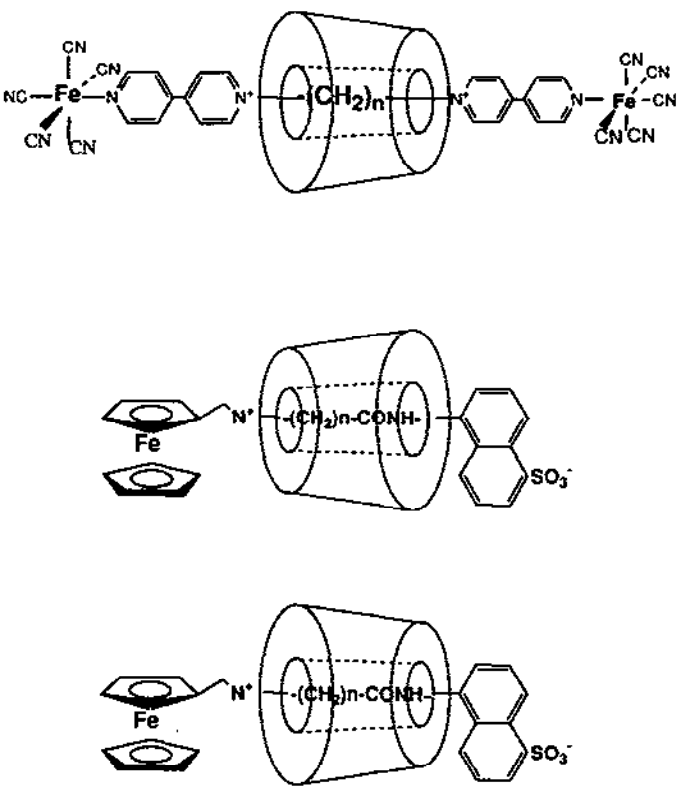
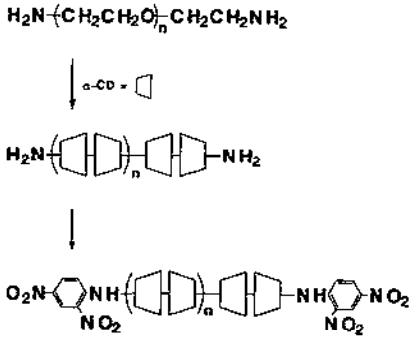


Fig. 8. Symmetric and asymmetric [2]-rotaxanes.



Scheme 1.

PEG-BA, and dinitrophenyl groups and the peaks of CD, PEG, and dinitrophenyl groups are broadened, suggesting that α-CDs move with difficulty on a PEG chain. 2D NOESY NMR spectra show that the signals of H-3 and H-5 protons of α-CD, which are directed toward the inside of the cavity, correlate with the resonance of the CH_2 of PEG, but the H-1, H-2, and H-4 protons, which are located outside the cavity, do not correlate with PEG. These results indicate that a PEG chain is included in the α-CD cavities.

Table 3 shows the results of the preparation of polyrotaxanes of various molecular weights. The number of CDs increases with increasing molecular weight. MN-3350, which was prepared from PEG (MW = 3350), has 20–23 CDs on a PEG chain. This corresponds to a molar ratio of ethylene glycol units to α-CDs of 3.9. More than half of the polymer chain is covered with α-CDs. MN-1450 has 15 α-CDs on a PEG chain. The molar ratio of ethylene glycol units to α-CD is 2.3. This ratio indicates that the complex is almost stoichiometric, i.e. the CDs are packed from end to end of the polymer chain to almost the closest possible extent.

2.3. Complex formation of α-cyclodextrin with monodisperse oligo(ethylene glycol)s [32]

We have used so far commercially available PEGs which are polydisperse. Therefore, the complexes obtained were polydisperse and heterogeneous. We also

Table 3
Molecular weight and composition of polyrotaxanes

Polyrotaxane	MW	No. of ethylene glycol unit	No. of α-CD included	Molar ratio between ethylene glycol units and α-CD
MN-3350	23 500	77	20	3.9
MN-2000	20 000	45	18	2.5
MN*-2001[a]	19 000	45	17	2.6
MN-1450	16 500	35	15	2.3

[a] Prepared from JED-2001.

found that α-CD did not form complexes with low molecular weight analogs, such as ethylene glycol and bis(ethylene glycol). In order to make clear the chain-length selectivity and to obtain pure monodisperse complexes we prepared monodisperse oligo(ethylene glycol)s (OEG) and studied the interactions between α-CD and the pure oligo(ethylene glycol)s.

Oligo(ethylene glycol)s HO(–CH_2CH_2O)n–OH (n=8, 12, 28, 20, 28, 36, 44) were prepared by stepwise reactions starting from α,ω-tetrakis(ethylene glycol) ditosylate and the monosodium tosylate using Bomer's method. The products were purified repeatedly by preparative size-exclusion chromatography (SEC).

Fig. 9 shows the yields of the complexes of α-CD with OEG as a function of the degree of polymerization of OEG. The yields are calculated on the basis of 2:1 stoichiometry. α-CD did not form complexes with ethylene glycol, bis(ethylene glycol), and tris(ethylene glycol). α-CD formed complexes with tetrakis(ethylene glycol) (TEG) and larger OEG. The yields increase sharply with increasing degree of polymerization from 5 to 12. The complexes were obtained almost quantitatively with eicosakis(ethylene glycol) and larger OEG. β-CD did not form complexes with any OEG. The stoichiometries of the complexes are all 2:1 (two ethylene glycol units and one α-CD) when the degree of polymerization is >6. The stoichiometries of the complexes of α-CD with TEG and pentakis(ethylene glycol) (PEG) are 2:1 (CD:OEG).

Table 4 shows the results of complex formation between α-CD and cyclic oligomers of ethylene glycol together with those of linear OEG for comparison. It is interesting that the yields of the complexes of α-CD with cyclic OEG decreased as the size of the guest increased, and those of the complexes of α-CD with linear OEG increased with increasing chain length. Cyclic oligomers of ethylene glycol (crown ethers, 15-crown-5 and 18-crown-6) did not form complexes with α-CD, except for

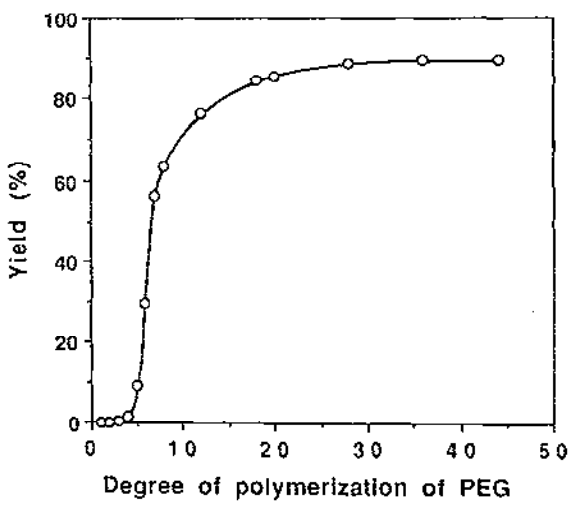


Fig. 9. Yields of the complexes of α-CD with oligo(ethylene glycol) as a function of the degree of polymerization.

Table 4
Yields (%) or complex formation of linear and cyclic oligo(ethylene glycol) with α-CD[a]

	Number of $-CH_2\ CH_2O-$							
	2	3	4	5	6	7	8	12
Linear	0	0	2	9	30	56	64	76
Cyclic	21	—	9	0	0	—	—	—

[a] Complexes formed at 25°C.

12-crown-4 which gave complexes with α-CD in low yield. These crown ethers are too large to fit in the CD cavity and α-CDs are not able to penetrate the chain owing to the absence of the chain ends. These results indicate that end groups are required for complex formation.

2.4. Synthesis of a polyrotaxane containing monodisperse oligo(ethylene glycol) [33]

In Section 2.2 the preparation of polyrotaxanes containing many α-CDs was described. However, in this case the polymers used are polydisperse and the number of CDs in a polymer chain is also polydisperse. The rotaxanes obtained by this method are highly heterogeneous. Moreover, in both rotaxanes only part of the polymer chain is covered with cyclodextrins. In order to obtain homogeneous polyrotaxanes we have prepared monodisperse PEGs (28mer, MW = 1248) because PEGs of molecular weight 1000–1500 were found to be most favorable for complex formation. We have succeeded in preparing complexes between α-CDs and monodisperse diamino-PEG and imprisoning twelve α-CDs on monodisperse diamino-PEG by capping PEG chain ends with bulky substituents. It is an important step toward the 'molecular abacus'.

The ^{13}C NMR spectrum of the polyrotaxane shows that the C-4 and C-6 peaks are doublets; a broad peak at a higher magnetic field and a sharper peak at a lower field, respectively. The broad peaks can be assigned to C-6 and C-4 in the rotaxane, which move with difficulty due to hydrogen bonds between CDs. The sharp peaks at lower magnetic field can be assigned to C-6 and C-4 of the cyclodextrins at both ends because they are not involved in hydrogen bonds and are more flexible than the others and they are susceptible to the effects of the dinitrophenyl groups at the ends of the rotaxane.

The bulky end groups (dinitrophenyl groups) were removed by cleaving the C–N bond with strong base, and the CDs were recovered. The number of cyclodextrins in the polyrotaxane can be estimated from the ^1H NMR spectra, optical rotation, and UV–vis spectra. Twelve α-CDs were found to be included in the polyrotaxane.

2.5. Complex formation of β- and γ-cyclodextrins with poly(propylene glycol) [34]

β-CD does not form complexes with PEG. However, β-CD was found to form complexes with poly(propylene glycol) (PPG), which has methyl groups on a PEG

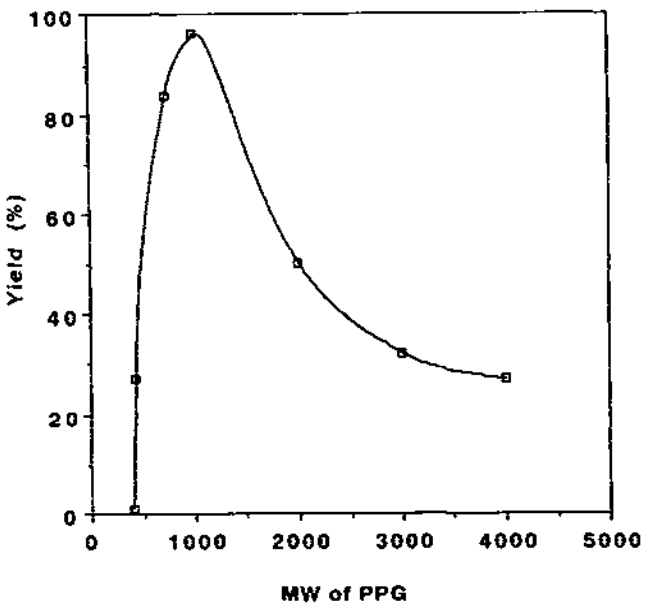


Fig. 10. Yields of the complexes of β-CD with PPG as a function of the molecular weight of PPG.

chain, to give crystalline compounds. α-CD does not form complexes with PPG of any molecular weight. There is a good correlation between the sectional area of polymers and the sizes of CD cavities. Fig. 10 shows the yields of the complexes of β-CD with PPG molecules of various molecular weights. β-CD does not form complexes with the dimer and trimer, but forms complexes with PPG of molecular weight >400. The yields increase with increasing molecular weight of PPG. The complexes were obtained almost quantitatively with PPG of molecular weight about 1000. However, the yields decrease with increasing molecular weight of PPG. γ-CD also forms complexes with PPG in high yields even when the molecular weight of PPG is low (400–725). The stoichiometries are again 2:1 (two propylene units per CD). Molecular model studies show that PPG chains are able to penetrate β-CD cavities, while the PPG chain cannot pass through the α-CD cavity owing to the hindrance of the methyl group on the main chain. These views are in accordance with our results that β-CD forms complexes with PPG but α-CD does not form complexes with PPG. Model studies indicate further that the single cavity accommodates two propylene glycol units.

2.6. *Complex formation between γ-cyclodextrin and poly(methyl vinyl ether) [35]*

Poly(methyl vinyl ether), which has the same composition as that of PPG but with methoxy groups as side chains, did not form complexes with α- and β-CDs. However, it formed complexes with γ-CD, which has the largest cavity in the series of CDs. In this case the stoichiometry is 3:1 (monomer units:CD). The number of

atoms in the main chain included in a single CD is six, which is the same as for α-CD-PEG and β-CD-PPG complexes.

3. Complex formation of cyclodextrins with hydrophobic polymers

We found that cyclodextrins form complexes not only with hydrophilic polymers but also with hydrophobic polymers such as oligoethylene and polyisobutylene. Table 5 shows the yields of the complexes formed by cyclodextrins and some hydrophobic polymers. α-CD forms complexes with oligoethylenes, although β- and γ-CD did not form complexes with oligoethylenes under the same conditions. However, β- and γ-CD formed complexes with polyisobutylene (PIB), although α-CD did not.

3.1. Complex formation of oligoethylene with α-cyclodextrin [36]

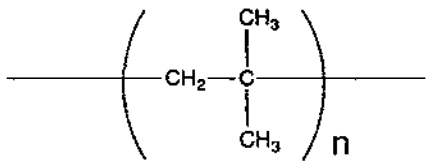
Oligoethylene (OE) was found to form inclusion complexes with α-CD not only from aqueous solutions of α-CD but also from DMF solutions of α-CD to give stoichiometric crystalline compounds in high yield. The yields depend on the degree of oligomerization of OE when DMF was used as solvent. OE with $n<6$ did not form complexes with α-CD in DMF solution. The complexes have stoichiometries of 3:1 (ethylene unit:α-CD). X-Ray diffraction studies and ^{13}C CP/MAS and PST/MAS NMR spectra suggest that the OE chain is included in the channel formed by α-CDs and the OE backbone in the complexes is more flexible than that in uncomplexed state.

3.2. Complex formation of polyisobutylene with γ-cyclodextrin [37]

Fig. 11 shows the yields of the complexes of PIB with β-CD and γ-CD as a function of the molecular weight of PIB. α-CD did not form complexes with PIB of

Table 5
Formation of solid-state complexes between cyclodextrins and hydrophobic polymers/oligomers with various chain sectional areas

Polymer/oligomer	Structure	MW	Yield (%)		
			α-CD	β-CD	γ-CD
OE(20)	$-CH_2CH_2-$	563	63	0	0
squalane	$-CH_2CH(CH_3)CH_2CH_2-$	423	0	62	24
PIB	$-CH_2C(CH_3)_2-$	~800	0	8	90



Polyisobutylene(PIB)

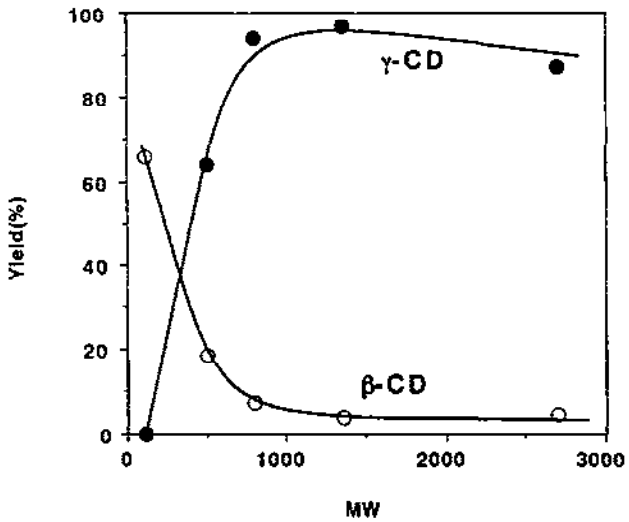


Fig. 11. Yields of the complexes of CDs with PIB as a function of the molecular weight of PIB.

any molecular weight. The yields of the complexes with β-CD decreased with increasing molecular weight of PIB. In contrast, the yields of the complexes with γ-CD increased with increasing molecular weight and the complexes were obtained almost quantitatively with PIB of molecular weight of 1000. The chain length selectivity is totally reversed between β-CD and γ-CD. In particular, β-CD formed complexes with the low molecular weight analogs, monomer and dimer; γ-CD did not form complexes with these low molecular weight compounds.

4. Conclusions

Cyclodextrin were found to form inclusion complexes not only with low molecular weight compounds but also with hydrophilic polymers and hydrophobic polymers to give stoichiometric compounds in high yield. The selectivities shown by cyclodextrins toward polymers are much higher than for low molecular weight compounds. This is due to the fact that the guest polymers have a lot of recognition sites and

the recognition processes are repeated. This is one of the reasons why the living systems are composed of many kinds of macromolecules. This kind of complex formation can be utilized to create new supramolecular architectures and functions [38-41].

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