Complex Formation between Poly(dimethylsiloxane) and Cyclodextrins: New *Pseudo*-Polyrotaxanes Containing Inorganic Polymers

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Cyclodextrins (α-CD, *β*-CD, and *γ*-CD) form inclusion complexes with various low molecular weight compounds, ranging from nonpolar hydrocarbons to polar acids and amines.[1] We have reported that CDs form inclusion complexes with some organic polymers to give crystalline compounds with high selectivity.[2] For example, α-CD forms complexes with poly(ethylene glycol)[3] and polyethylene (MW < 1000).[4] *β*-CD formed complexes with poly(propylene glycol)[5] and polypropylene (MW < 1000).[6] *γ*-CD formed complexes with poly(methyl vinyl ether)[7] and polyisobutylene.[8] Other groups also reported complex formation between CDs and polyesters.[9] We also prepared a polyrotaxane in which many α-CDs were threaded onto a poly(ethylene glycol) chain.[10] Wenz et al. also reported α-CDs threaded on a polyamine.[11] Both are main chain polyrotaxanes. Now we have found that *β*-CD and *γ*-CD form complexes with poly(dimethylsiloxane) (PDMS), a typical inorganic polymer and that the chain-length selectivities between *β*-CD and *γ*-CD are reversed.

When PDMS (liquid) was added to aqueous solutions of *β*-CD (0.18 g/10 mL) or *γ*-CD (0.23 g/mL) and the mixture was sonicated at room temperature for 10 min, the mixture became turbid, and the complexes were formed as crystalline precipitates. This is the first observation that cyclodextrins formed a complex with inorganic polymers. α-CD did not form complexes with PDMS of any molecular weight. *β*-CD and *γ*-CD formed complexes with PDMS. Figure 1 shows the yields of the complexes as a function of the molecular weight of PDMS. The yields are based on the starting amount of CD and the stoichiometry of CD to PDMS as described below, using saturated solutions of CD and PDMSs (1.5 equiv monomer units to CD). The yields of the complexes of PDMS with *γ*-CD increased with increasing PDMS molecular weight. The complexes were obtained almost quantitatively with PDMS of molecular weights of 750 with *γ*-CD.[12] In contrast, the yields of the complexes of PDMS with *β*-CD decreased with increaseing PDMS molecular weight, although the yield of the complex between *β*-CD and PDMS (MW = 240) is lower than that of PDMS (MW = 400). The chain-length selectivities are reversed between *β*-CD and *γ*-CD. *β*-CD formed a complex with a dimer model compound, hexamethyldisiloxane (HMDS, MW = 162). *β*-CD forms 1:1 complexes with small molecules, which seem to be rather unstable than those with long molecules which give higher order of stoichiometries.

The complex formation of *γ*-CD with PDMS was studied quantitatively. The amount of the complex formed increases with an increase in the amount of

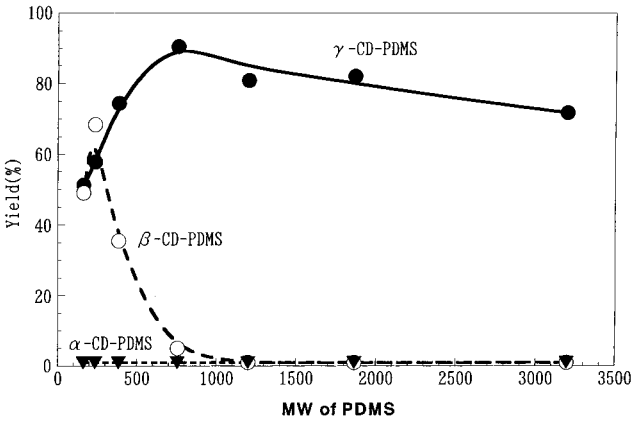

Figure 1. Yields of the complexes between PDMS and cyclodextrins as a function of the molecular weight of PDMS: (●) *γ*-CD-PDMS complex; (○) *β*-CD-PDMS complex; (▼) α-CD-PDMS complex.

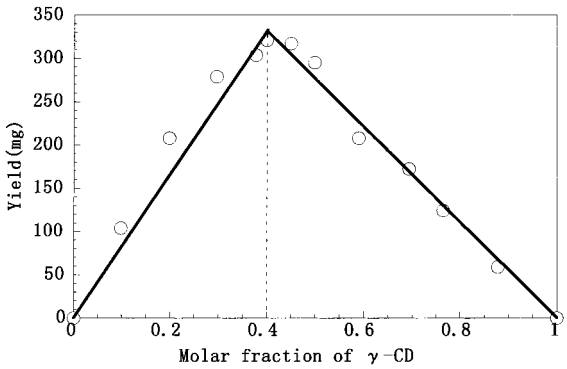

Figure 2. Continuous variation plot for complex formation between *γ*-CD and PDMS (MW 760).

PDMS added to the aqueous solution of *γ*-CD. The amount of the complex showed similar values even if excess amounts of PDMS were used, indicating stoichiometric complexation. The continuous variation plot for the formation of the complex between *γ*-CD and PDMS showed a maximum at 0.40, indicating 2:3 (monomer unit: *γ*-CD) stoichiometry (Figure 2). This result suggests that 1.5 units were bound in each *γ*-CD cavity. The stoichiometry was confirmed by the use of ^{1}H NMR spectroscopy. The length of the 1.5 monomer units corresponds to the depth of *γ*-CD cavity. Figure 3 shows a proposed structure of the complex between *γ*-CD and PDMS.

The complexes were isolated by centrifugation, washed, and dried. The inclusion complexes were thermally stable. The complexes were insoluble in water, and even in boiling water. However, the addition of urea on heating to the suspension of the complex solubilized the complex, indicating that hydrogen bonding between CDs plays an important role in stabilizing the complex. The X-ray diffraction pattern of the complex between *γ*-CD and PDMS shows that the complexes are crystalline. The pattern of the complex is totally different from that of free *γ*-CD.

Molecular model studies show that a PDMS chain is able to penetrate the *γ*-CD cavity, while the PDMS chain cannot pass through the α-CD cavity owing to the hindrance of the dimethyl groups on the main chain.[13]

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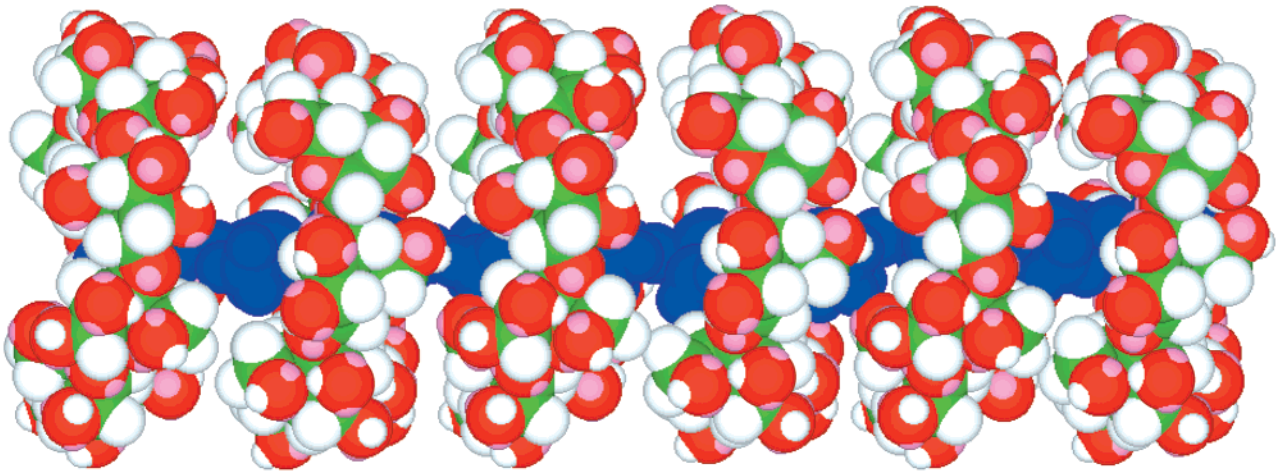

Figure 3. Proposed structure of the PDMS-γ-CD complex.

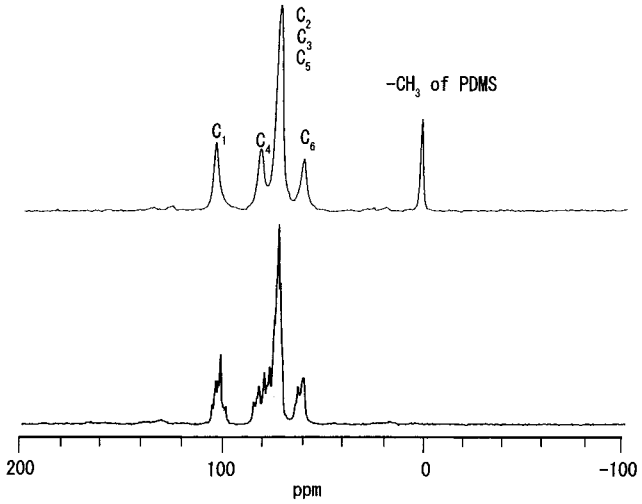

Figure 4. ^{13}C CP/MAS NMR spectrum of the complex between PDMS and γ-CD (upper) and that of γ-CD (lower).

The hindrance of the dimethyl groups makes PDMS difficult to penetrate β-CD cavities. These views are in accordance with our results that γ-CD formed a complex with PDMS but α-CD did not form complexes with PDMS. Model studies further indicate that the single cavity accommodates 1.5 monomer units. The ^{13}C CP/MAS NMR spectrum of the complex shows that each carbon of the glucose can be observed as a single peak, indicating that γ-CD includes the polymer and assumes symmetrical conformation, although that of γ-CD shows a less symmetrical conformation due to the absence of guests in the cavity (Figure 4).

In conclusion, β-CD and γ-CD form complexes with PDMS, and α-CD did not form complexes with PDMS. The chain-length selectivities are totally different between β-CD and γ-CD. Studies of the detailed structures of the complexes are now in progress.

References and Notes

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(12) PDMS (29.2 mg) was put into a tube. Saturated aqueous solution of γ-CD 1.34 mL was added at room temperature. The mixture was supersonically agitated for 15 min and then allowed to stand overnight at room temperature. The precipitated product was collected by centrifugation, and dried under vacuum, washed with THF, and dried under vacuum. The residue was washed with water and dried again under vacuum. Yield: 91%. ^{1}H NMR (pyridine-d_5, 270 MHz): δ 5.71 (d, 8H, C1H of γ-CD), 4.63 (t, 8H, C3H of γ-CD), 4.38 (m 24H, C5H and C6H of γ-CD), 4.27 (m, 8H, C2H of γ-CD), 4.09 (t, 8H, C4H of γ-CD), 0.275, 0.221, 0.202 (m, 66H, methyl H of PDMS), FT-IR (KBr, cm^{-1}): 3390 (ν_s, OH), 2929 (ν_s, CH), 1254 (δ_{as}, Si−C), 1157, 1025 (ν_s, CO), 1025 (ν_{as}, Si−O), 807 (ν_s, Si−C), 526 (ν_s, Si−O).
(13) Molecular model studies were carried out by using MM2 (CS Chem 3D Pro). Internal diameters of α-, β-, and γ-CD are 0.45, 0.7, and 0.85 nm, respectively.[1a]

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