Formation of Self-assembled Tubular Structures by Mixing Cyclodextrin and Polymers without Solvents

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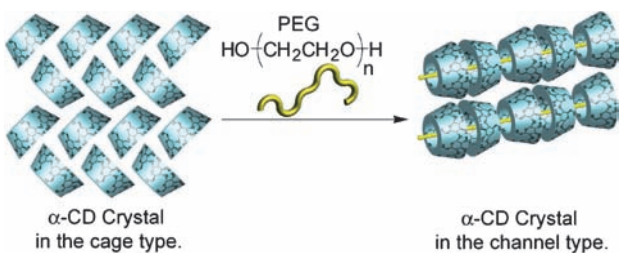
Cyclodextrin has been found to form inclusion complexes with some polymers, such as poly(ethylene glycol) with high selectivity only by mixing powdered crystals of cyclodextrins and polymer samples without any solvents under ambient conditions.

Much attention has been focused recently on the design and construction of nano- to micro-scale structures by supramolecular assembly.[1,2] Most of the supramolecular assemblies have been constructed from the solutions of each component. If the supramolecular structures can be made only by mixing each component without solvents, supramolecules can be considered and used as new materials. Now we have found that supramolecular assemblies are formed only by mixing each component without solvents. Previously, we found that cyclodextrins (CDs) form inclusion complexes with some hydrophilic polymers, such as poly(ethylene glycol) and poly(methyl vinyl ether), to give crystalline compounds with high selectivities, when aqueous solutions of CDs were mixed with aqueous solutions of nonionic polymers.[3,4] We and others prepared polyrotaxanes in which many CDs are entrapped on a polymer chain.[5–7] Later, we found that CDs form complexes not only with hydrophilic polymers but also with hydrophobic polymers, such as oligoethylene, polyisobutylene, and polyesters, when aqueous solutions of CDs were added onto a polymer sample with heating and sonicating.[8] We also found that α-CD forms inclusion complexes with some polymers from their dimethylformamide (DMF) solutions. These results suggest that solvents are not necessarily required for the complex formation. Now we found that CD forms inclusion complexes with some polymers with high selectivity only by mixing CD crystals and polymer samples without any solvents. (Scheme 1).

Crystalline CD was powdered by stirrer and dried at 70 °C in a vacuum. PEG was mixed with CD powder in a ratio of 2:1 (monomer unit of polymer:CD) for 1 h, and the mixture was allowed to stand at room temperature. When α-CD is crystallized from water, they give crystals with cage-type-structure, in which CDs stack each other in such a way that each cavity is capped by other CDs. In this case, the cage-type structure gives a complicated X-ray powder pattern. (Figure 1a) When crystals of α-CD and PEG ($M_W = 400$) were mixed without solvent (α-CD:ethylene glycol unit = 1:2), the X-ray powder patterns changed (Figure 1c); a peak at $2\theta = 22°$ characteristic for the cage type decreased, and a peak at $2\theta = 20°$ characteristic for the channel type appeared and increased. Crystalline solids obtained by mixing an aqueous solution of α-CD and that of PEG ($M_W = 1000$) gave a characteristic channel-type pattern shown in Figure 1b. In this case, an ethylene glycol chain is included in the tunnel formed by CDs as shown by X-ray studies of single crystal of the complex between α-CD and hexa(ethylene glycol).[9]



Scheme 1.

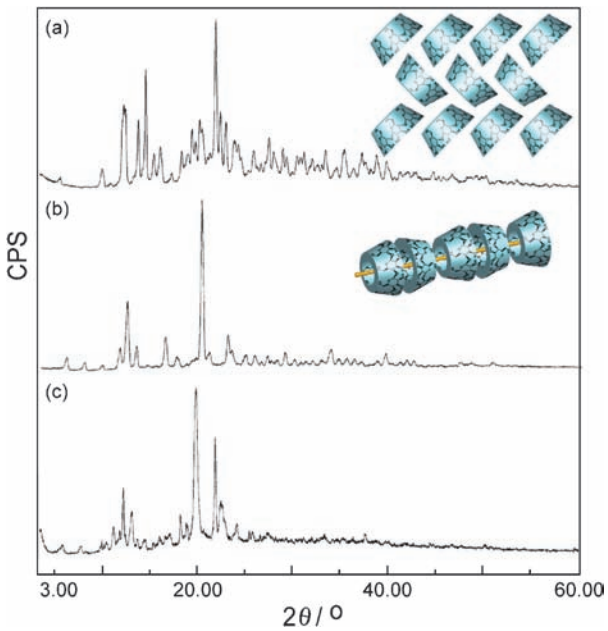


Figure 1. X-ray powder pattern of α-CD crystallized from water (a), that of a complex of α-CD with PEG 400 (M_W = 400) prepared by mixing their aqueous solutions (b), and that of a complex prepared by mixing α-CD and PEG without solvent (c) for 1 year at room temperature.

Ethylene glycol, di(ethylene glycol), and tri(ethylene glycol) did not form channel type structures with α-CD. But tetra(ethylene glycol) and longer poly(ethylene glycol) gave a tunnel structure with α-CDs. The rate of complex formation increased with increase in the chain length up to the molecular weight about 600, and it decreased with further increase in the molecular weight. When the temperature was raised, the rate of the complex formation was accelerated.

Figure 2 shows the time dependence of the complex formation of α-CD with PEG400 and PEG1000. The initial change is rather fast followed by a slow change. The conversion of α-CD–PEG1000 increased slowly and reached saturation after 40 days.

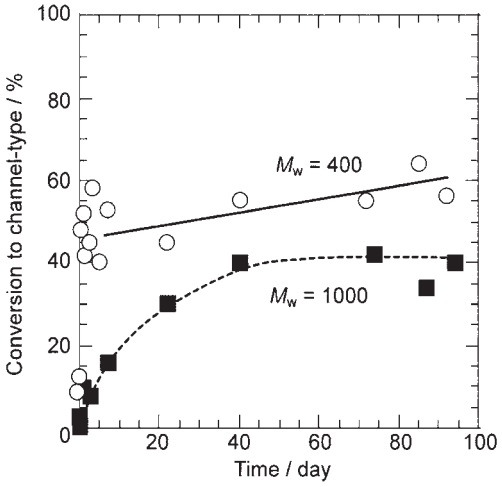


Figure 2. Time dependence of the complex formation of α-CD with PEG 400 and PEG1000 followed by the X-ray powder pattern at room temperature.

When the mixture of α-CD and PEG400 was left more than 1 year, we found that the powder pattern showed that the structure has changed from a cage type to a channel type. A similar tendency was observed in the case of PEG1000. To compare the ring strain of cyclodextrin, α-CD, a complex formed from aqueous solutions of α-CD and PEG 400, and a mixture of α-CD and PEG 400 were evaluated by ^{13}C CP/MAS NMR measurement. α-CD assumes less symmetrical conformation and one of the glucosidic linkages is distorted. In this case, the spectrum of "free" cyclodextrin shows that resolved C1, C4, and C6 resonances from each of glucose unit, because each glucose unit is in a different environment. In contrast, the spectrum of the complex showed that each carbon of glucose could be observed in a single peak, indicating that each glucose unit is in a similar environment. A poly(ethylene glycol) chain is included in a tunnel formed by CDs. Although the peaks of CDs are clearly visible, that of PEG is not clear in the ^{13}C CP/MAS NMR due to the flexibility of the polymer chain in the CD tunnel. However, the PEG peak can be seen in the PST/MAS NMR, which emphasizes the mobile parts. These results are consistent with those of X-ray studies of single crystals of the complexes of α-CD with hexa(ethylene glycol).[9] In the crystal, the structures of α-CDs have been definitely determined. However, the positions of ethylene glycol chains have not been determined accurately in the tubular structure due to the vibrational change of the included guest molecules. These results indicate that a polymer chain can move in the tunnel formed by α-CDs.

Similar results were observed in the cases of α-CD and poly(oxytrimethylene) or poly(tetrahydrofuran). Interestingly, when poly(propylene glycol), which has methyl groups on an ethylene glycol chain and has larger cross-sectional area, was used instead of PEG, the X-ray powder patterns did not change for a prolonged time (more than 2 years). These results indicate that a PPG chain did not form complexes with α-CD. When crystals of β-CD and PEG ($M_W = 1000$) were mixed at room temperature, the X-ray powder patterns did not change for a prolonged time (more than a month). This result indicates that a β-CD ring is too large to fit a PEG chain. γ-CD did not show any changes in the X-ray powder patterns when it was mixed with PEG. PEG carrying large groups such as 2,4-dinitrophenyl groups and 3,5-dinitrobenzoyl groups did not give any changes in the X-ray pattern of α-CD even after 2 months, indicating that PEG comes into α-CD cavity from its small end groups.

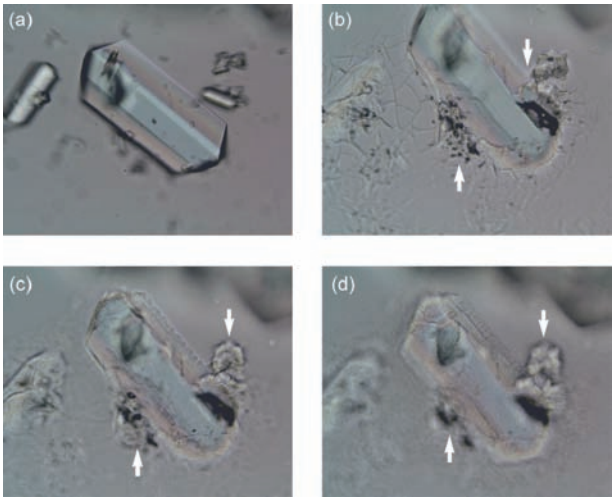


Figure 3. Optical microscope images of α-CD single crystal (a) and α-CD–PEG400 mixture (b)–(d) at hourly intervals. PEG400 was added dropwise to α-CD crystals, and then the mixture was allowed to stand at room temperature.

Figure 3 shows optical microscopic images of an α-CD crystal on addition of PEG400. The surface of the crystal changed on addition of PEG to give new fine crystals. It is noticeable that α-CD does not form a homogeneous phase with PEG. The complex formation takes place at the interface between α-CD and PEG.

In conclusion, a polymer chain can penetrate CD cavities to give polyrotaxane structure without any solvents. This kind of construction of supramolecular structures only by mixing may provide a new method to create a new nanoscale to microscale architectures.

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