Complex Formation of Poly(ϵ-caprolactone) with Cyclodextrins

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ABSTRACT: Cyclodextrins (CDs) have been found to form inclusion complexes with poly(ϵ-caprolactone) (PEC) to give crystalline compounds. α- and γ-CD formed complexes with these polyesters in high yields, although β-CD gave complexes in moderate yields. The yields of the complexes decreased with increasing molecular weight of the polymer. α-CD−PEC complexes are stoichiometric one-to-one (cyclodextrin: monomer unit) compounds, and γ-CD−PEC complexes are one-to-two compounds when the molecular weights of PEC are low. The complexes were isolated and characterized by ^{1}H NMR, ^{13}C CP/MAS NMR, and X-ray diffraction studies. The inclusion modes are discussed.

Introduction

Much attention has been directed toward the design and construction of nanometer scale ordered structures by supramolecular assembly.[1] One of the most promising approaches to construct nanometer scale structures is the use of specific interactions between polymers and receptors, as exemplified by biological systems. Recently, main-chain and side-chain polyrotaxanes have been prepared and characterized with crown ethers,[2] cyclophanes,[3] cucurbituril,[4] and cyclodextrin (CDs)[5,6] as cyclic components.

CDs are a series of cyclic oligosaccharides consisting of six (α-CD), seven (β-CD), eight (γ-CD), and more glucose units linked by α-1,4 bonds. Their shape is like a hollow truncated cone, and they have no hydroxy groups inside their cavity. Therefore, the hydrophobicity of their cavity gives an ability to include hydrophobic molecules inside their cavity. Since CDs were discovered, a large number of inclusion complexes of CDs with various low molecular weight compounds have been prepared and characterized.[7] However, except for a few examples in which a monomer was polymerized in situ within a CD complex[8,9] and a few reports which suggest interactions between CDs and some polymers in aqueous solution,[10] there were no reports on the inclusion complex formation of CDs with polymers when we started our research on the inclusion complexes of CDs with polymers.[11] We have found that CDs form crystalline complexes with various polymers, such as poly(ethylene glycol) (PEG),[11,12] poly(propylene glycol) (PPG),[13] and poly(methyl vinyl ether) (PMVE).[14] We also found that CDs form complexes with hydrophobic oligomers and polymers, such as oligoethylene (OE)[15] and polyisobutylene (PIB).[16] All these inclusion complexes take *pseudo*-polyrotaxane structures. These polymers are stable and difficult to use as biodegradable polymers, because of C−C or C−O ether bonds in their main chains, which are formed by addition polymerization of vinyl monomers or ring-opening polymerization of epoxides.

Recently, Tonelli et al.[17] reported that poly(ϵ-caprolactone) (PEC) forms clathrate type complexes with urea. Chenite and Brisse et al.[18] reported that aliphatic polyesters, such as poly(trimethylene adipate) (PTA) and poly(trimethylene glutarate) (PTG), form complexes with urea. It is of interest whether biodegradable polymers, such as PEC, poly(hydroxybutyrate), and poly(alkylene adipate)s, are included in a biodegradable framework, like CDs. Except for the examples of the inclusion polymerization of monomer complexes with CDs,[8,9] there have been no reports on the formation of inclusion complexes of CDs with polymers obtained by condensation polymerizations, such as polyesters and polyamides, when we started our research on the inclusion complexes of CDs with polyesters.[19] We found that linear aliphatic polyesters, such as PEC,[19] poly(ethylene adipate) (PEA),[20] PTA,[20] and poly(1,4-butylene adipate) (PBA),[20] form complexes with CDs to give crystalline compounds. After our reports were published, Tonelli et al. reported that α-CDs form crystalline inclusion complexes with PEC[21] and Nylon 6.[22] Wenz et al.[23] reported that α-, β-, and hydroxypropyl-α-CD forms a water-soluble inclusion complex with water-soluble polyester. Tonelli et al. used high molecular weight PEC (M_n = 40 000) and Nylon 6 (M_n = 12 000) and reported on thermal properties of complexes. Wenz et al. used water-soluble polyester (M_n = 11 700 or 14 440) synthesized from dimethyl octane-1,8-dicarboxylate and poly(ethylene glycol) (M_n = 900) and reported about the solubility change of this polymer and the calorimetric analysis on complex formation. In our previous paper, we reported on the stoichiometric complex formation between α-CD and PEC as the first example of the complex formation of CDs with condensation polymers.[19] This paper describes the preparation and characterization of inclusion complexes of CDs with PEC, and the mode of inclusion is discussed in detail.

Results and Discussion

Complex Formation of PEC with CDs. Previously, we reported that α-CD formed complexes with PEG[11,12] and OE[15] of various molecular weights to give crystalline compounds from aqueous solution of α-CD, although β- and γ-CD did not form complexes with PEG and OE under the same conditions. PEG and OE chains fit well into the cavity of α-CDs. The crystal structure of PEC, $[-O-(CH_2)_5-CO-]_n$, showed that the chain conformation is almost planar zigzag; i.e., the CH_2 sequence is planar, but the plane of atoms of the ester group tilts

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slightly from the fiber axis.[24] These data and molecular modeling of PEC suggested that the polymer chains in either all-trans or kink conformations are slim enough to fit in the α-CD cavity.[25]

When an aqueous solution of α-CD was added to PEC above the melting temperature of PEC and agitated by ultrasound for 10 min, the heterogeneous solution became turbid, and complexes were formed as crystalline precipitates (method A). Moreover, when an aqueous solution of α-CD was added to PEC and stirring for 40 h at room temperature, the heterogeneous solution also became turbid, and complexes were formed as crystalline precipitates (method B). These complex formations of PECs with α-CD are similar to those of the complex formation of α-CD with PEG and OE, which have a similar cross-sectional area of the polymer backbone.

The addition of urea, which is thought to affect hydrogen bonds, to the suspension of the α-CD−PEC complex and heating above the melting temperature of PEC resulted in solubilization of the complexes in water. When an aqueous solution of α-CD and urea was added to PEC and treated as method A, the heterogeneous solution did not became turbid. These results indicate that hydrogen bonds play an important role in the formation of the complexes, which is similar to the cases of complex formation of α-CD with PEG.

We also found that α-CDs form complexes not only in aqueous solution but also in *N*,*N*-dimethylformamide (DMF). When a DMF solution of α-CD and PEC was heated at 65 °C for 12 h, the homogeneous solution became turbid, and complexes were formed as crystalline precipitates (method C). Free α-CD and PEC can be removed from the precipitate by washing with water and THF.

Crystal structure[24] and molecular modeling[25] of PEC suggested that the polymer chain in a planar zigzag conformation is too slim to fit snuggly in the *β*-CD and *γ*-CD cavity. When an aqueous solution of *β*-CD or *γ*-CD was added to PEC and treated as method A or method B**,** the heterogeneous solution became turbid and complexes were formed as crystalline precipitates. When a DMF solution of *β*-CD or *γ*-CD was added to PEC and treated as method C**,** precipitates cannot be formed from homogeneous DMF solution.

Figure 1a shows the yields of the complexes of PEC with α-CD as a function of the molecular weight of PEC. The yields are based on the starting amount of α-CD and mole ratio of α-CD to the polymer in the complex, as described in the next section. Molecular weight dependency of the yields of PEC−α-CD complexes by both methods from aqueous solution (methods A and B) is similar. The yields decreased as the molecular weight increased from 530 to 3000. The result suggests that the higher molecular weight PECs are so difficult to disperse in water and that the PEC chains cannot effectively diffuse into the α-CD cavities. This is in contrast to the cases for the complex formation between CDs and hydrophilic polymers, such as PEG,[11,12] and poly(oxytrimethylene) (POx).[26] In these cases, the yield increased with an increase in the molecular weight and then reached saturation (PEG) or decreased with increasing molecular weight (POx).

The yields of PEC−α-CD complexes obtained by method C increased with an increase in the molecular weight and showed a maximum at the molecular weights of 2000; then the yields decrease with an

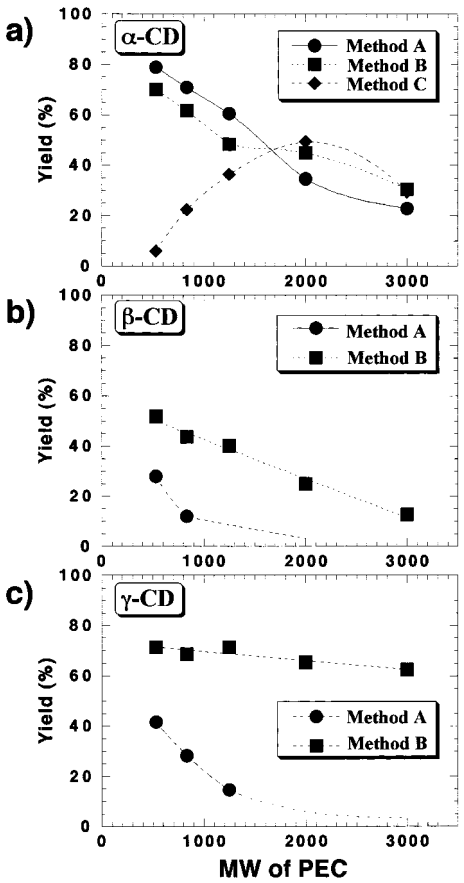

Figure 1. Yields of the complexes of PEC with α-CD (a), *β*-CD (b), and *γ*-CD (c) as a function of the molecular weight of the PEC.

increase in the molecular weight. We have reported the complex formation of OE with α-CD from DMF solution,[15] which showed a similar dependency. (In this case, the yields showed a maximum at a molecular weight of 340.) This stands in sharp contrast to the α-CD−PEC complex formation from aqueous solution (methods A and B). The yields of the complexes with lower molecular weight PECs in DMF solution are lower than those in aqueous solution. These results are due to the fact that the α-CD−PEC complex partly dissolves in DMF.

β-CD formed complexes with PECs in moderate yields from aqueous solution (methods A and B). Figure 1b shows that *β*-CD formed complex more efficiently by method B than by method A. *β*-CD gave complexes with PECs in lower yields than α-CD from aqueous solution, indicating a lower affinity of *β*-CD for PEC than that of α-CD. It is because that twisting of a polymer chain is required to fill the cavity of *β*-CD.

γ-CD formed complexes with PECs in high yields from aqueous solution by method B (Figure 1c). The yields of the complexes of *γ*-CD with PECs of various molecular weights by method B are similar. This is in contrast to the case of the complex formation of PIB with *γ*-CD,[16] where the yields of the complexes increased with increasing molecular weight and reached saturation about the molecular weight of 1000. This result suggests that the inclusion mode of the PEC−*γ*-CD complex is different from that of the PIB−*γ*-CD complex.

Stoichiometries of the Complexes. Figure 2 shows plots of the amount of the complex obtained versus PEC (MW = 530) added. The amounts of the complex formed increase with increase in PEC (MW = 530) added to the

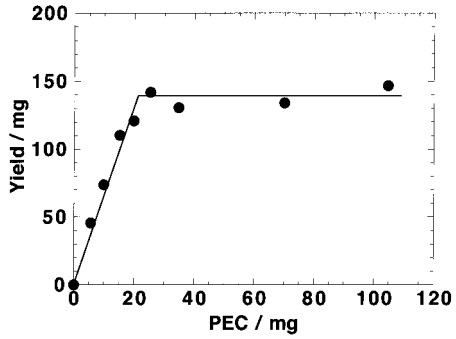

Figure 2. Amount of α-CD−PEC(530) complex as a function of added PEC(530). A saturated aqueous solution of α-CD (1.0 mL, containing 145 mg of α-CD) was used.

α-CD aqueous solution, and a saturation was observed. This saturation shows that the complex formation is stoichiometric. Figure 3a shows a continuous variation plot (Job plot) for the complex formation between PEC (MW = 530) and α-CD. The plots show a maximum at 0.50−0.53 of the α-CD fraction, indicating that α-CD form complexes with PEC with a 1:0.9−1.0 (α-CD:PEC) stoichiometry; i.e., a single cyclodextrin binds to 0.9−1.0 monomer unit of PEC. From the crystal structural data[24] and molecular modeling studies,[25] a length of the monomer unit of PEC is about 8 Å, which corresponds to the depth of α-CD.

We measured ^{1}H NMR spectra of α-CD−PEC complexes obtained by each method and calculated the mole ratio of PEC monomer unit to CD in the complex. Figure 4a shows the mole ratio of PEC to α-CD in the complex as a function of the molecular weight of PEC. The ratios of complexes obtained by method A and method B at low molecular weight region (MW = 530−1250) are nearly 1, which is similar to those obtained from the Job plots (Figure 3a**)**. These results suggest that PECs (MW = 530−1250) form stoichiometric complexes and are wholly included by α-CD. Considering that the ratio increased and the yield of complex was low, PEC at higher molecular weights (MW = 2000−3000) cannot form stoichiometric inclusion complexes with α-CD. It is probably due to the low dispersibility of PEC at higher molecular weight in aqueous solution by methods A and B. The ratios of the complexes obtained by method C are nearly constant. This is because the complex is formed from homogeneous DMF solution by method C.

Figure 3b shows a Job plot for the complex formation between PEC (MW = 530) and β-CD. The plots show a maximum about 0.40 of the β-CD fraction, indicating that β-CD−PEC complexes are formed with about 1:1.5 stoichiometry; i.e., a single cyclodextrin binds 1.5 monomer units of PEC. Figure 4b shows the molecular weight dependency of the mole ratio of PEC to β-CD in the complex, calculated from ^{1}H NMR of complexes. The ratio by methods A and B are larger than those obtained from the Job plot. Considering that the yields of complexes between β-CD and PEC are low, β-CDs include a part of each PEC chain even at low molecular weight. It may be due to the low dispersibility of PEC in aqueous solution and the low affinity of β-CD to PEC.

Figure 3c shows a Job plot for the complex formation between PEC (MW = 530) and γ-CD. It shows a maximum at 0.35−0.37 of the γ-CD fraction; i.e., a single cyclodextrin binds 1.7−1.9 monomer units of PEC. This is just twice the value of α-CD (0.9−1.0). Figure 4c shows the molecular weight dependency of the mole ratio of PEC to γ-CD in complex, calculated from

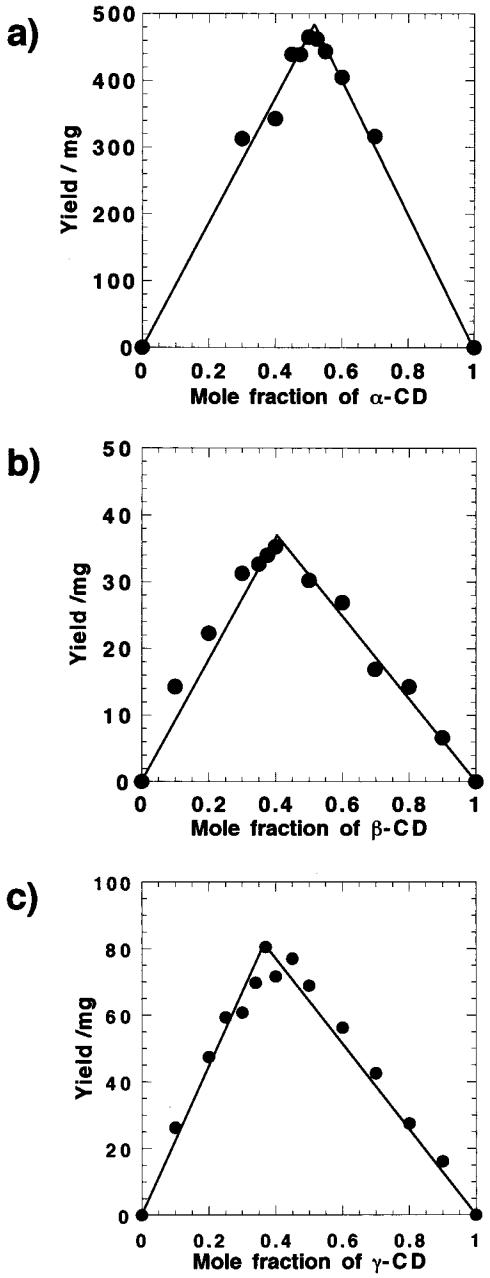

Figure 3. Continuous variation plots for the complex formation of α-CD (a), β-CD (b), and γ-CD (c) with PEC(530): (a) the total amount of α-CD and monomer units of PEC(530) was fixed at 1.0×10^{-3} mol; (b) the total amount of β-CD and monomer units of PEC(530) was fixed at 1.8×10^{-4} mol; (c) the total amount of γ-CD and monomer units of PEC(530) was fixed at 2.2×10^{-4} mol.

^{1}H NMR. The ratio obtained by method A is much higher than the value from the Job plot. It may be due to an inefficient complex formation (Figure 1c). The ratio by method B is 2 at low molecular weight region (MW = 530−2000). At higher molecular weight (MW = 3000), the ratio increases. The diameter of the γ-CD cavity is 8.5−9 Å, which is twice as large as that of α-CD (4.5 Å). But, the height of the cavity of γ-CD is the same as those of α-CD and β-CD (8 Å), which corresponds to the length of the monomer unit. CPK and molecular model studies indicate that the γ-CD cavity is large enough to accommodate two PEC chains, whereas the α-CD cavity is too small to do this.

Binding Mode of the Complexes. The X-ray powder pattern of the α-CD−PEC complex[19] shows that the

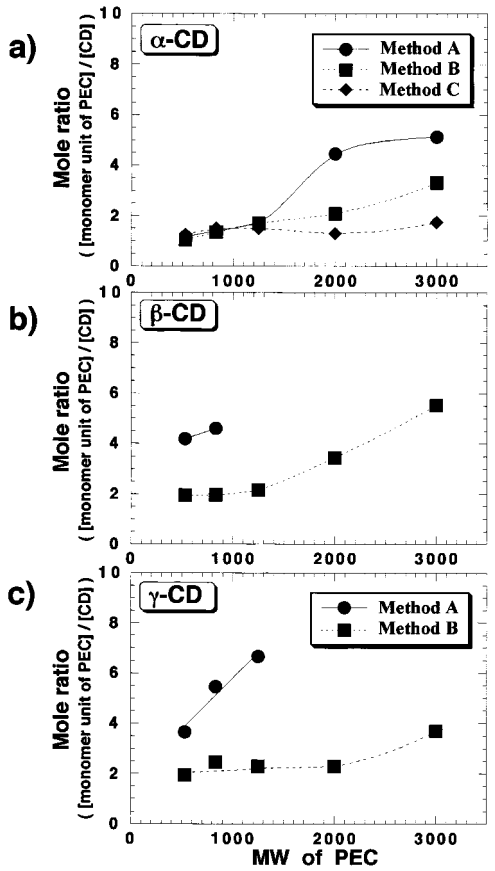

Figure 4. Mole ratio (monomer unit of PEC/CD) at the complexes of PEC with α-CD (a), *β*-CD (b), and *γ*-CD (c) as a function of the molecular weight of the PEC.

complexes are crystalline and is similar to the pattern of the α-CD−PEG complexes,[11,12] which have been reported to have a column structure, and different from that of the α-CD−propionic acid complex, which has been reported to have a cage-type structure. Therefore, the complex of PEC with α-CDs assumes a column structure rather than a cage-type structure.

Figure 5 shows the X-ray powder patterns of *γ*-CD (a), the *γ*-CD−PPG complex (b), and the *γ*-CD−PEC complex (c). The pattern of the *γ*-CD−PEC complex (Figure 5c) is similar to that of the complexes of *γ*-CD with 1-propanol,[27] PMVE,[14b] or PPG (Figure 5b) dried at high temperature under high vacuum, which have been reported to have a column structure, and is different from that of *γ*-CD (Figure 5a),[28] which has been reported to have a cage-type structure. Therefore, the complex of PEC with *γ*-CD also assumes a column structure rather than a cage-type structure.

The ^{13}C CP/MAS NMR spectra of the α-CD−PEC complex[19] and the *γ*-CD−PEC complex (Figure 6) show that CD adopts a symmetrical cyclic conformation in the complex, although CD assumes a less symmetrical conformation in the crystal when it does not include a guest in the cavity. A PEC chain is thought to be included in the cavities of CDs.

CPK and molecular model studies show that a PEC chain is able to penetrate the α-CD cavity and that the length of the polymer chain included in α-CD corresponds to the height of α-CD when molecular weights of PECs are low (<2000). *γ*-CD includes twice as much polymer chain in the cavity than α-CD. Figure 7 shows proposed structures of the complexes of PEC with α-CD and *γ*-CD.

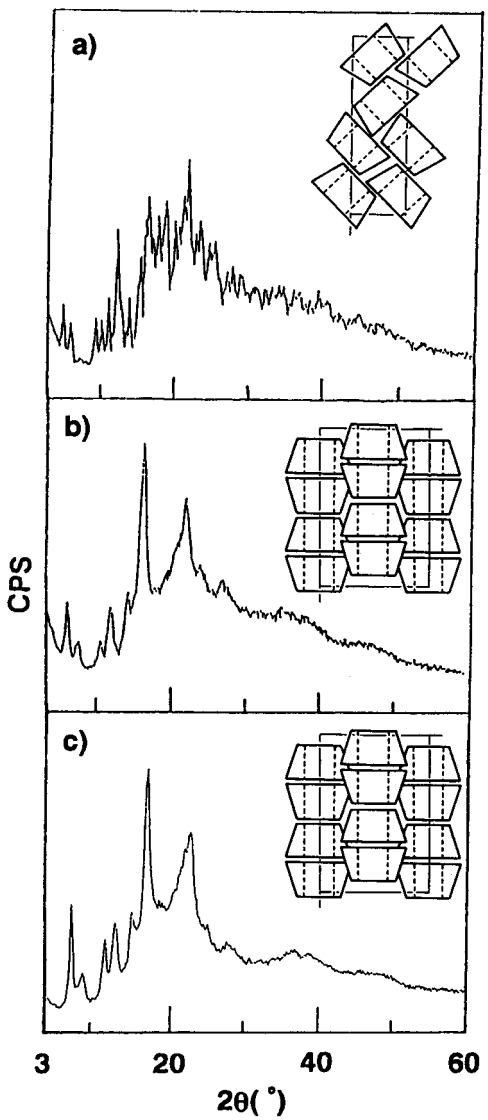

Figure 5. X-ray diffraction patterns for the *γ*-CD (a), the *γ*-CD−PPG complex (b), and *γ*-CD−PEC (MW = 530) complex (c).

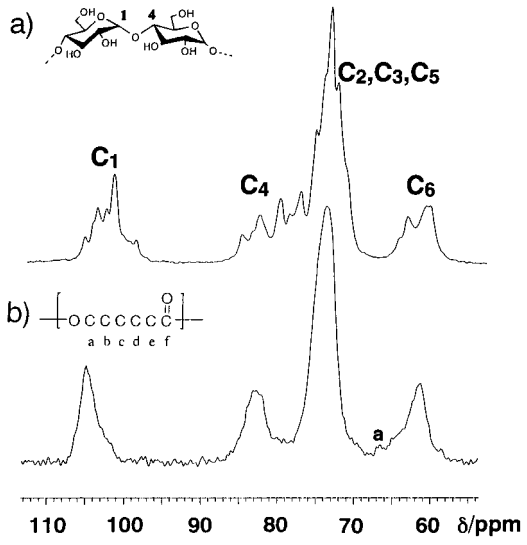

Figure 6. ^{13}C CP/MAS NMR spectra of *γ*-CD (a) and the *γ*-CD−PEC (MW = 530) complex (b).

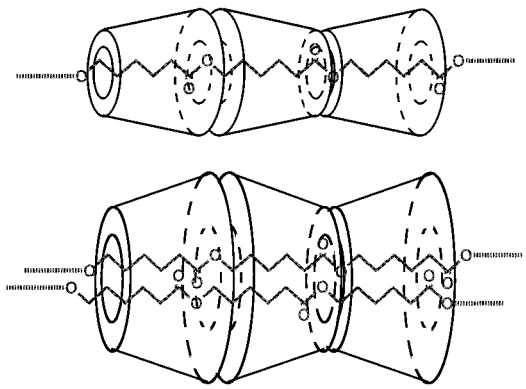

Figure 7. Proposed structure of the α-CD−PEC and γ-CD−PEC complexes.

Now we are studying the complex formation of various polyesters and polyamides with CDs and the detailed structures of the complexes. In addition, we are studying degradation of the polyesters in the complexed form in comparison with their uncomplexed states. The details will be published later.

Experimental Section

Materials. Cyclodextrins (α-, β-, and γ-CD) were kindly supplied by Nihon Shokuhin kako Co., Ltd., and/or obtained from Nacalai Tesque Inc. and Tokyo Kasei Kogyo Co., Ltd. They were used after drying in a vacuum with P_2O_5. Poly(ϵ-caprolactone)s (M_n = 530, 1250, 2000) were purchased from Aldrich Chemical Co., and poly(ϵ-caprolactone)s (M_n = 830, 3000) were obtained from Scientific Polymers Products, Inc. The average molecular weights of the various polymer samples were found by gel permeation chromatography to be within the specification given by the suppliers.

Measurements. Gel permeation chromatography determination was carried out with a Tosoh CCP&8010 system (columns: G3000HXL and G2000HXL). ^{1}H NMR spectra were recorded at 270 MHz in dimethyl sulfoxide (DMSO-d_6) and D_2O at 30 °C on a JEOL JNM EX-270 spectrometer. Chemical shifts were referenced to the solvent values (δ = 2.50 for DMSO-d_6 and δ = 4.70 for HOD). Solid-state ^{13}C CP/MAS (cross-polarization/magic angle spinning) NMR spectra were measured at 100.4 MHz on a JEOL JNM GSX-400 NMR spectrometer with a sample spinning rates of 5.5 kHz at room temperature. Chemical shifts were referenced to the external standard (δ = 17.36 for hexamethylbenzene). FT-IR spectra were observed on a JASCO FT/IR-3 spectrometer. Powder X-ray diffraction patterns were taken by using Cu−Kα radiation with a Rigaku RAD-ROC diffractometer (voltage, 40 kV; current, 100 mA, scanning speed, 3°/min).

Preparation of the Inclusion Compounds. α-CD−PEC Complexes; Method A (Heating and Sonication in Water). PEC (20 mg; monomer unit 1.8×10^{-4} mol) was put into tubes with heating above the melting temperature. A saturated aqueous solution of α-CD (1.2 mL; α-CD 1.8×10^{-4} mol) was added, and the heterogeneous mixtures were ultrasonically agitated for 10 min on heating and then allowed to stand overnight at room temperature. The mixtures became turbid, and the complexes were obtained as white crystalline precipitates. They were collected by centrifugation, dried in a vacuum up to 100 °C, washed with water and dried under vacuum, and then washed with THF and dried under vacuum to give the polymer complex.

α-CD−PEC(530) Complex. Yield: 79%. ^{1}H NMR (DMSO-d_6, 270 MHz): δ 5.50−5.41 (m, 12H, O(2)H and O(3)H of α-CD), 4.80 (d, 6H, C(1)H of α-CD), 4.46 (t, 6H, O(6)H of α-CD), 3.98 (t, 2H, −O−CH_2− of PEC), 3.77−3.56 (m, 24H, C(3)H, C(5)H and C(6)H of α-CD), 3.41−3.30 (m, 12H, C(2)H, and C(4)H of α-CD), 2.27 (t, 2H, −C(=O)−CH_2− of PEC), 1.53 (m, 2H, −O−CH_2−CH_2− of PEC), 1.32−1.29 (m, 4H, −C(=O)−CH_2−CH_2−CH_2− of PEC). IR (KBr, cm^{-1}): 3391 (vs, ν_{OH}), 2927 (vs, ν_{CH}), 1737 (w, $\nu_{C=O}$), 1154, 1078, 1031 (vs, ν_{C-O}). Anal. Calcd for $(C_{36}H_{60}O_{30})_{1.0}(C_6H_{10}O_2)_{1.0}(H_2O)_{3.9}$: C, 43.59; H, 6.78. Found: C, 43.58; H, 6.81.

Method B (Stirring at Room Temperature in Water). PEC (20 mg; monomer unit 1.8×10^{-4} mol) and a saturated aqueous solution of α-CD (1.2 mL; α-CD 1.8×10^{-4} mol) was put into tubes, and the heterogeneous mixtures were stirred for 40 h. The mixtures became turbid, and the complexes were obtained as white crystalline precipitates. The following procedure is the same as method A.

α-CD−PEC(830) Complex. Yield: 62%. ^{1}H NMR (DMSO-d_6, 270 MHz): δ 5.50−5.41 (m, 12H, O(2)H and O(3)H of α-CD), 4.80 (d, 6H, C(1)H of α-CD), 4.45 (t, 6H, O(6)H of α-CD), 3.98 (t, 2.2H, −O−CH_2− of PEC), 3.77−3.56 (m, 24H, C(3)H, C(5)H and C(6)H of α-CD), 3.41−3.30 (m, 12H, C(2)H, and C(4)H of α-CD), 2.27 (t, 2.2H, −C(=O)−CH_2− of PEC), 1.53 (m, 2.2H, −O−CH_2−CH_2− of PEC), 1.32−1.29 (m, 4.4H, −C(=O)−CH_2−CH_2−CH_2− of PEC). IR (KBr, cm^{-1}): 3391 (vs, ν_{OH}), 2927 (vs, ν_{CH}), 1737 (w, $\nu_{C=O}$), 1154, 1078, 1031 (vs, ν_{C-O}). Anal. Calcd for $(C_{36}H_{60}O_{30})_{1.0}(C_6H_{10}O_2)_{1.1}(H_2O)_{4.3}$: C, 43.51; H, 6.82 Found: C, 43.53; H, 6.74.

Method C (Heating and Sonication in DMF). PEC (20 mg; monomer unit 1.8×10^{-4} mol) and a DMF solution of α-CD (2.0 mL; α-CD 1.8×10^{-4} mol) were put into tubes. The homogeneous solutions were ultrasonically agitated for 10 min at room temperature. After standing overnight at room temperature, these solutions heated at 65 °C for 12 h. The mixtures became turbid, and the complexes were obtained as white crystalline precipitates. After cooling, the precipitated products were collected by centrifugation. The following procedure is the same as method A.

α-CD−PEC(2000) Complex. Yield: 50%. ^{1}H NMR (DMSO-d_6, 270 MHz): δ 5.50−5.41 (m, 12H, O(2)H and O(3)H of α-CD), 4.80 (d, 6H, C(1)H of α-CD), 4.45 (t, 6H, O(6)H of α-CD), 3.98 (t, 2.6H, −O−CH_2− of PEC), 3.77−3.56 (m, 24H, C(3)H, C(5)H and C(6)H of α-CD), 3.41−3.30 (m, 12H, C(2)H, and C(4)H of α-CD), 2.27 (t, 2.6H, −C(=O)−CH_2− of PEC), 1.53 (m, 2.6H, −O−CH_2−CH_2− of PEC), 1.32−1.29 (m, 5.2H, −C(=O)−CH_2−CH_2−CH_2− of PEC). IR (KBr, cm^{-1}): 3391 (vs, ν_{OH}), 2927 (vs, ν_{CH}), 1737 (w, $\nu_{C=O}$), 1154, 1078, 1031 (vs, ν_{C-O}). Anal. Calcd for $(C_{36}H_{60}O_{30})_{1.0}(C_6H_{10}O_2)_{1.3}(H_2O)_{1.1}$: C, 45.82; H, 6.67. Found: C, 45.78; H, 6.67.

***β*-CD−PEC Complexes; Methods A and B.** In the cases of β-CD, PEC (20 mg; monomer unit 1.8×10^{-4} mol) and a saturated aqueous solution of β-CD (7.0 mL; β-CD 1.1×10^{-4} mol) were used. The following procedure is the same as the cases of α-CD.

***β*-CD−PEC(530) Complex (Obtained by Method B).** Yield: 52%. ^{1}H NMR (DMSO-d_6, 270 MHz): δ 5.69−5.65 (m, 14H, O(2)H and O(3)H of β-CD), 4.83 (d, 7H, C(1)H of β-CD), 4.42 (t, 7H, O(6)H of β-CD), 3.98 (t, 4H, −O−CH_2− of PEC), 3.66−3.55 (m, 28H, C(3)H, C(5)H and C(6)H of β-CD), 3.38−3.27 (m, 14H, C(2)H, and C(4)H of β-CD), 2.27 (t, 4H, −C(=O)−CH_2− of PEC), 1.54 (m, 4H, −O−CH_2−CH_2− of PEC), 1.32−1.29 (m, 8H, −C(=O)−CH_2−CH_2−CH_2− of PEC). IR (KBr, cm^{-1}): 3409 (vs, ν_{OH}), 2930 (vs, ν_{CH}), 1736 (w, $\nu_{C=O}$), 1156, 1080, 1030 (vs, ν_{C-O}). Anal. Calcd for $(C_{42}H_{70}O_{35})_{1.0}(C_6H_{10}O_2)_{2.0}(H_2O)_{3.1}$: C, 45.70; H, 6.83. Found: C, 45.71; H, 7.11.

***γ*-CD−PEC Complexes; Methods A and B.** In the cases of γ-CD, PEC (20 mg; monomer unit 1.8×10^{-4} mol) and a saturated aqueous solution of γ-CD (0.6 mL; γ-CD 1.1×10^{-4} mol) were used. The following procedure is the same as the cases of α-CD.

***γ*-CD−PEC(530) Complex (Obtained by Method B).** Yield: 71%. ^{1}H NMR (DMSO-d_6, 270 MHz): δ 5.71−5.68 (m, 16H, O(2)H and O(3)H of γ-CD), 4.89 (d, 8H, C(1)H of γ-CD), 4.49 (t, 8H, O(6)H of γ-CD), 3.99 (t, 4H, −O−CH_2− of PEC), 3.64−3.52 (m, 32H, C(3)H, C(5)H and C(6)H of γ-CD), 3.38−3.27 (m, 16H, C(2)H, and C(4)H of γ-CD), 2.27 (t, 4H, −C(=O)−CH_2− of PEC), 1.55 (m, 4H, −O−CH_2−CH_2− of PEC), 1.32−1.29 (m, 8H, −C(=O)−CH_2−CH_2−CH_2− of PEC). IR (KBr, cm^{-1}): 3411 (vs, ν_{OH}), 2932 (vs, ν_{CH}), 1737 (w, $\nu_{C=O}$), 1158, 1080, 1028 (vs, ν_{C-O}). Anal. Calcd for $(C_{48}H_{80}O_{40})_{1.0}(C_6H_{10}O_2)_{2.0}(H_2O)_{3.5}$: C, 45.37; H, 6.79. Found: C, 45.35; H, 6.89.

Influence of the Amount of PEC Added. The saturated aqueous solution of α-CD was held constant at 1.0 mL, while the amounts of PEC added were successively increased. Then, the mixture was treated by method A.

Continuous Variation Method. PECs and saturated aqueous solution of α-CD were put into tubes. The total amount of α-CD (or *β*-, *γ*-CD) and monomer units of PEC was fixed at 1.0×10^{-3} mol (1.8×10^{-4} mol, *β*-CD; 2.2×10^{-4} mol, *γ*-CD), while the molar fractions of monomer units and α-CD (or *β*-, *γ*-CD) were varied from 0 to 1. Then, the mixture was treated by method A.

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