Headline Articles

Preparation and Characterization of Inclusion Complexes of Poly(alkyl vinyl ether) with Cyclodextrins

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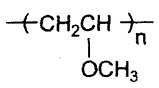
γ-Cyclodextrin (γ-CD) has been found to form inclusion complexes with poly(methyl vinyl ether) (PMVE), poly(ethyl vinyl ether) (PEVE), and poly(*n*-propyl vinyl ether) (PnPVE) of various molecular weights to give stoichiometric compounds in crystalline states. α-Cyclodextrin (α-CD) and β-cyclodextrin (β-CD) did not form complexes with poly(alkyl vinyl ether)s of any molecular weight. γ-CD did not form complexes with the low molecular weight analogs, such as diethyl ether and trimethylene glycol dimethyl ether. The yields of the complexes of γ-CD with PMVE increased with increasing molecular weight (MW) of PMVE and reached saturation at about MW 2000. The yields of the complexes of γ-CD with PEVE and PnPVE increased with increase in MW, reached a maximum at a MW of about 1000 for PEVE and about 250 for PnPVE, and decreased with a further increase in the MW. Complexes were isolated and found to have a 3 : 1 (monomer unit : CD) ratio. The complexes were characterized by IR, ^{1}H NMR, ^{13}C NMR, and X-ray (powder), thermal and elemental analyses. The structures of the complexes are discussed.

Cyclodextrins (CDs) are a series of cyclic oligosaccharides consisting of six to eight glucose units linked by α-1, 4 linkages. They are called α-, β-, and γ-CD, respectively. Cyclodextrins are known to form inclusion complexes with a wide variety of low molecular weight compounds.[1,2] Previously we reported that α-cyclodextrin (α-CD) formed complexes with poly(ethylene glycol) (PEG) of various molecular weights to give crystalline compounds in high yields,[3,4] although β-CD did not form complexes with PEG of any molecular weight. However, β-CD and γ-CD formed complexes with poly(propylene glycol) (PPG) to give crystalline complexes in high yields,[5,6] although α-CD did not form complexes with PPG of any molecular weight. There is a good correlation between cross sectional areas of polymers and sizes of CDs.[7—9] Moreover, we found that γ-CD formed a complex with poly(methyl vinyl ether) (PMVE),[10] which has the same composition ($(C_3H_6O)_n$) as PPG, although α-CD and β-CD did not form complexes with PMVE at all. It is interesting to see if CDs form complexes with poly(alkyl vinyl ether)s and to study their structures and properties (Scheme 1). Now we have studied the complex formation of γ-CD with some poly(alkyl vinyl ether)s in detail. The complex formation is chain-length dependent and stoichiometric. This paper describes formation of inclusion complexes of cyclodextrins with some poly(alkyl vinyl ether)s in detail.

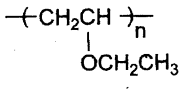
Results and Discussion

Selectivity of Complex Formation. Previously we reported that α-CD formed complexes with poly(ethylene glycol) of various molecular weights to give crystalline compounds, although β-CD did not form complexes with PEG. A poly(ethylene glycol) fits well in a tunnel formed by α-CDs. α-CD also formed complexes with poly(oxytrimethylene) (POT).[11] However, α-CD did not form complexes with poly(propylene glycol) (PPG) of any molecular weight. Instead, β-CD formed complexes with PPG to give crystalline compounds. Interestingly, γ-CD formed complexes with poly(methyl vinyl ether) (PMVE), although α-CD and β-CD did not form complexes with PMVE.

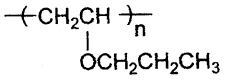
Table 1 shows the complex formation of cyclodextrins with three hydrophilic polymers which have the same composition ($(C_3H_6O)_n$). POT, which has the smallest cross-sectional area, forms a complex with α-CD (diameter of the cavity: 4.5 Å) in high yield, while PPG, which has the larger cross-sectional area, selectively forms complexes with β-CD (diameter of the cavity : 7.0 Å) and γ-CD (diameter of the cavity: 8.5 Å) in high yield. It is of interest that PMVE, which has the same composition as that of POT and PPG but carries a methoxy group as a side chain, does not form complexes with β-CD but forms complexes with γ-CD.[5,6] These results indicate that the relative sizes of the cavities of cyclodextrins to the cross-sectional area of the polymers



Poly(methyl vinyl ether) (PMVE)



Poly(ethyl vinyl ether) (PEVE)



Poly(*n*-propyl vinyl ether) (PnPVE)

Scheme 1. Poly(alkyl vinyl ether)s.

Table 1. Complex Formation of CDs with Hydrophilic Polymers

Polymer		MW	Yield (%)		
			α-CD[a]	β-CD[b]	γ-CD[c]
POT	$(CH_2CH_2CH_2O)_n$	1000	94	47	0
PPG	$(CH_2CHO)_n$ (CH$_3$)	1000	0	96	80
PMVE	$(CH_2CH)_n$ (OCH$_3$)	1000	0	0	80

a) α-CD saturated aqueous solution, 1.5 ml; polymer, 15 mg.
b) β-CD saturated aqueous solution, 7.0 ml; polymer, 15 mg.
c) γ-CD saturated aqueous solution, 2.0 ml; polymer, 15 mg.

are important in the complex formation of polymers with cyclodextrins.

Effects of Molecular Weight of Polymers on the Complex Formation. Figure 1 shows results of the complex formation of γ-CD with PMVE of various molecular weights. γ-CD did not form complexes with the low molecular weight analogs such as diethyl ether and trimethylene glycol dimethyl ether. We have obtained complexes of γ-CD with PMVE of molecular weights higher than 1000. Yields of complexes did not decrease with increasing the molecular weight. In contrast, the yields of the complexes of γ-CD with PEVE are highly dependent on the molecular weight. The yields of the complexes increased with increasing the molecular weight, reached a maximum at about MW 1000, and then decreased (Fig. 2). This may be due to the fact that PEVE is more hydrophobic than PMVE. CDs are difficult to diffuse into the polymer chain. This trend is more evident for complex formation of γ-CD with PnPVE (Fig. 3). Since PnPVE is much more hydrophobic and bulkier than PMVE and PEVE, CDs are difficult to move into the chain. nPVE, which is the monomer of PnPVE, did form complexes with γ-CD. The order of the maximum yield of the complexes is as follows:

PnPVE > PEVE > PMVE.

This result also indicates the importance of the size fitness between γ-CD and a polymer chain. A PMVE is loosely included in a γ-CD cavity, so CDs can move into the polymer chain easily. This result is different from the complex formation between β-CD and PPG. The yields of the complex of β-CD with PPG increase with increase in the molecular weight and reach a maximum and then decreased.[5,6] β-CD did not form complexes with PMVE, PEVE, and PnPVE of any molecular weight.

Figures 1, 2, and 3 show that a minimum chain length of PMVE is required for the formation of crystalline complexes with γ-CD. The same phenomenon was observed in the formation of crystalline complexes of PEG with α-CD. This

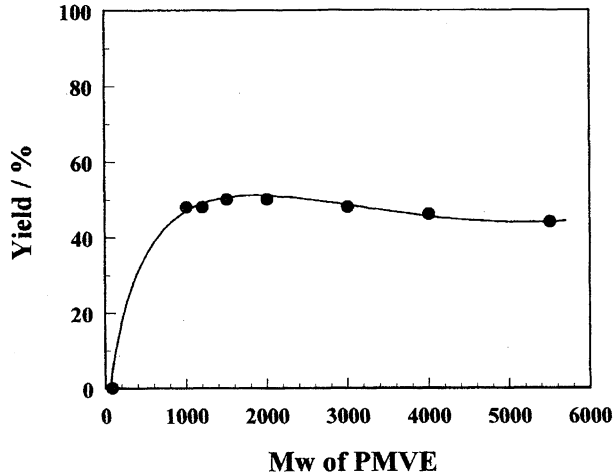


Fig. 1. Yields of the complexes of γ-CD with PMVE as a function of the molecular weight of PMVE.

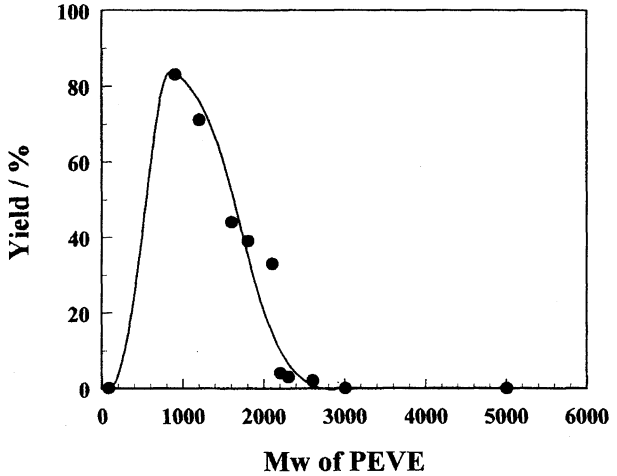


Fig. 2. Yields of the complexes of γ-CD with PEVE as a function of the molecular weight of PEVE.

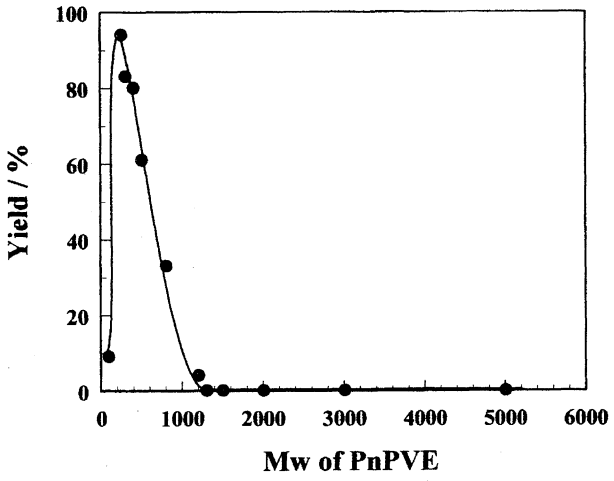


Fig. 3. Yields of the complexes of γ-CD with PnPVE as a function of the molecular weight of PnPVE.

is thought to be the characteristic of the crystalline complex formation between hydrophilic polymers and cyclodextrins. This result shows the importance of cooperative effects in the complex formation. The cooperation is thought to result from the fact that a single polymer chain interacts with many cyclodextrin molecules, that is, a single polymer chain has many binding sites which are recognized by cyclodextrin molecules. The neighboring cyclodextrin molecules bound on a polymer chain interact with each other by forming hydrogen bonds.

Stoichiometry of the Complexes. The amount of the complexes formed increased with an increase in the amount of PMVE added to the aqueous solution of γ-CD. In the complex formation between γ-CD and PMVE, saturation of the formation of the complexes was observed. The results indicate that the complex formation is stoichiometric. Figures 4, 5, and 6 show the continuous variation plots for the formation of complexes of γ-CD with PMVE, PEVE, and nPVE, respectively. The three plots show the maximum

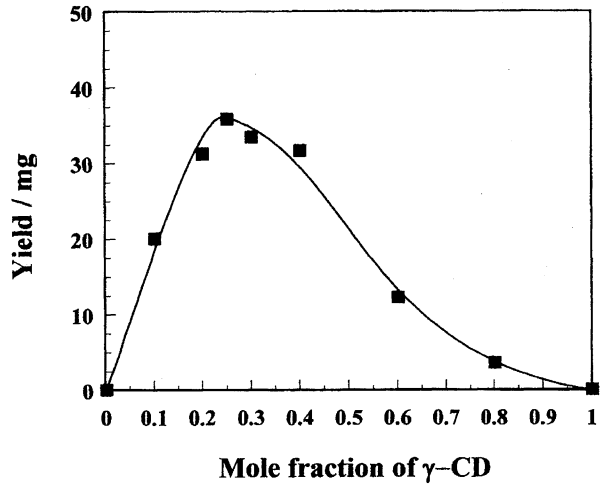


Fig. 4. Continuous variation plots for the complex formation between γ-CD and PMVE (MW = 1200). The total amount of γ-CD and MVE units of PMVE was fixed at 1.72×10^{-4} mol.

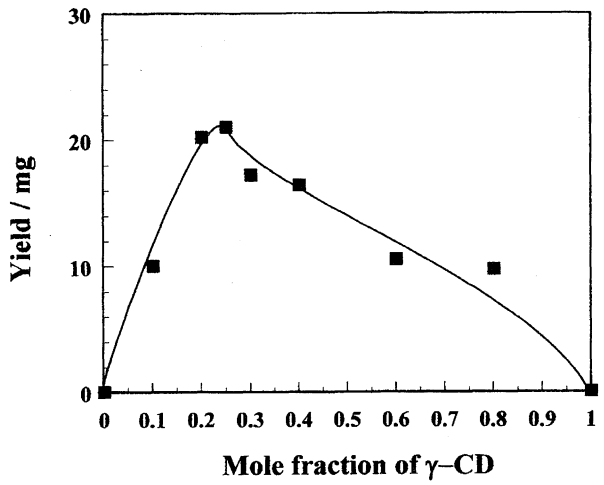


Fig. 5. Continuous variation plots for the complex formation between γ-CD and PEVE (MW = 1400). The total amount of γ-CD and EVE units of PEVE was fixed at 1.67×10^{-4} mol.

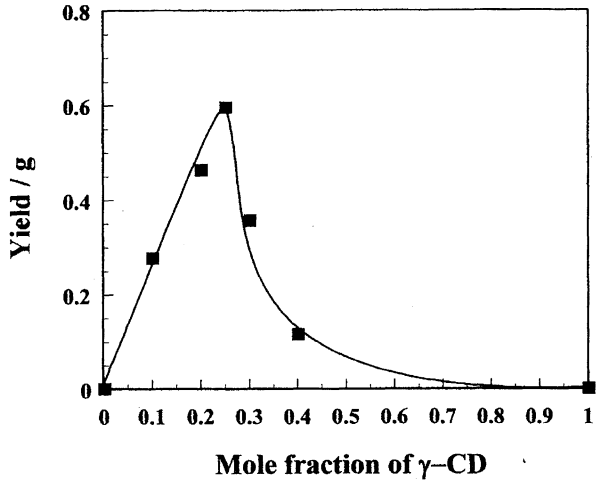


Fig. 6. Continuous variation plots for the complex formation between γ-CD and nPVE. The total amount of γ-CD and nPVE was fixed at 2.97×10^{3} mol.

at the γ-CD molar fraction of 0.25. These results suggest that the stoichiometries of γ-CD–PMVE, PEVE, and nPVE complexes are 3 : 1 (monomer unit : cyclodextrin).

The complexes were isolated by centrifugation and filtration and washed with water to remove uncomplexed CD, dried, and then washed with tetrahydrofuran to remove non-included polymers. Figure 7 shows the ^{1}H NMR spectra of the complex between γ-CD and PMVE of molecular weight 1200. By the comparison of the integral of the peak of CD(1H) and that of methyl group on PMVE, three monomer units were found to bind to a single γ-CD molecule. It should be noted that the stoichiometries are always 3 : 1 (monomer unit : CD) even if the CD and PMVE were mixed in any ratio. Figure 8 shows the ^{1}H NMR spectra of the complex between γ-CD and PEVE of molecular weight of 1200. The spectrum shows that the stoichiometry is 3 : 1 again.

Properties. The complexes of γ-CD with PMVE of any molecular weights are soluble in water. This is in contrast

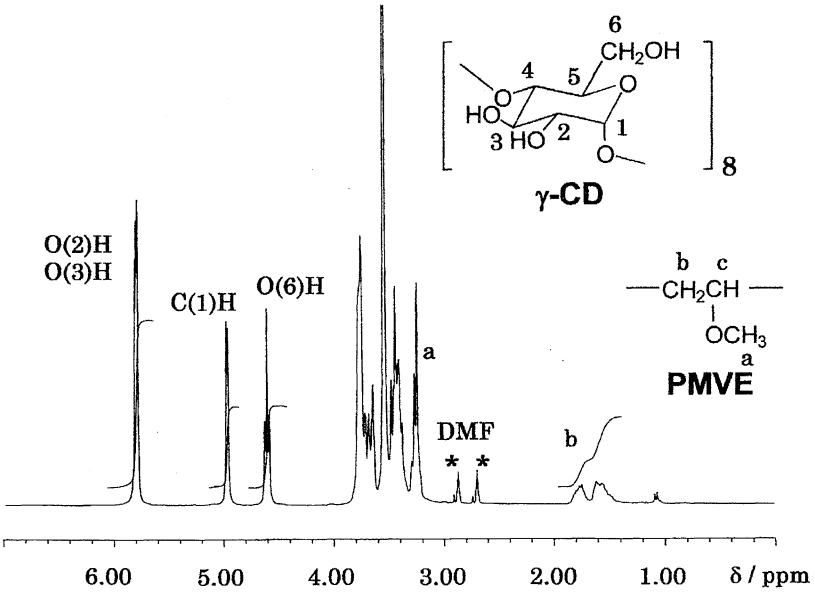


Fig. 7. 270 MHz ^{1}H NMR spectra of the complexes of PMVE (MW = 1200) with γ-CD in DMF-d_7.

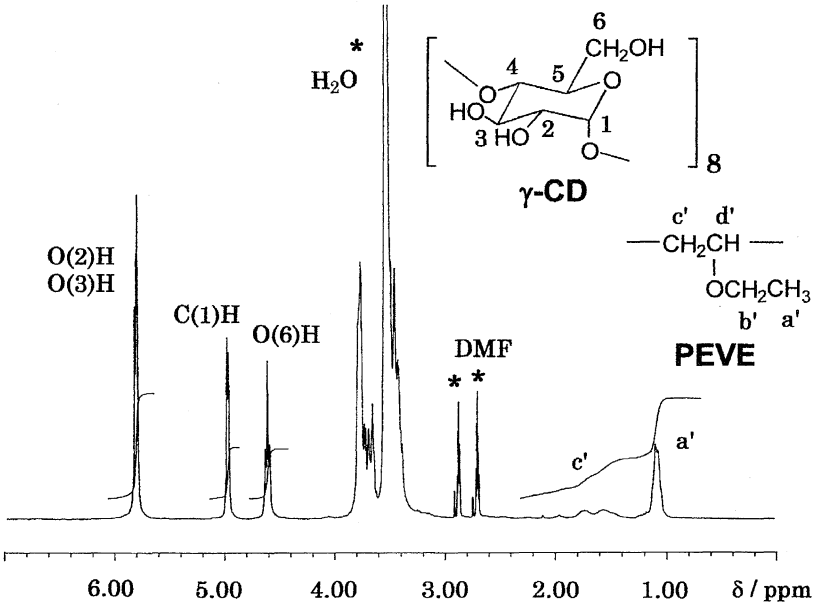


Fig. 8. 270 MHz ^{1}H NMR spectra of the complexes of PEVE (MW = 1200) with γ-CD in DMF-d_7.

to the complexes of PIB with γ-CD, which are insoluble in water even by heating.[12,13] This is owing to the fact that PMVE is more hydrophilic than PIB. The complexes are soluble in dimethyl sulfoxide and *N*,*N*-dimethylformamide. The X-ray diffraction studies (powder) show that all the complexes are crystalline.

The complexes are thermally stabilized. Thermogravimetric analysis shows that the complex begins to decompose at 310 °C, which is a little higher than the decomposition temperature for each component, indicating that a guest PMVE stabilizes γ-CD.

Binding Modes of the Complexes. Figure 9 shows the powder X-ray patterns of γ-CD (a), the complexes of γ-CD with 1-propanol (b) and those of γ-CD with PMVE (MW = 1200) (c). Saenger reported that the structures of the inclusion complexes of CDs with low molecular weight compounds can be classified by two groups. One is "cage type" and the other is "channel type".[14] γ-CD molecules are arranged in a cage-type packing.[15—17] The γ-CD molecules in hydrated γ-CD–1-propanol complexes are stacked to form channel-type cavities.[18,19] Figure 9 shows that all the complexes are crystalline and the pattern of the PMVE complex is different from that of non-included γ-CD, but similar to that of the complex with 1-propanol, which has been proved to have a column structure by the X-ray study of a single crystal of the complex.[9] Takeo and his co-worker[19] found that the crystal structure of γ-CD–1-propanol complex changed by dehydration. The change is due to the transition of the packing arrangement of γ-CD cylinders, from tetrahedral unit cell to hexagonal one. So we measured the powder X-ray

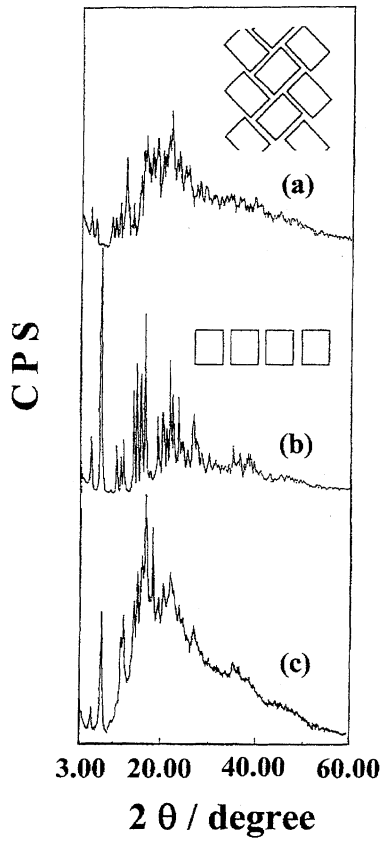


Fig. 9. X-Ray diffraction patterns for γ-CD (a), γ-CD–1-propanol complex (b), and γ-CD–PMVE (MW = 1200) complex (c).

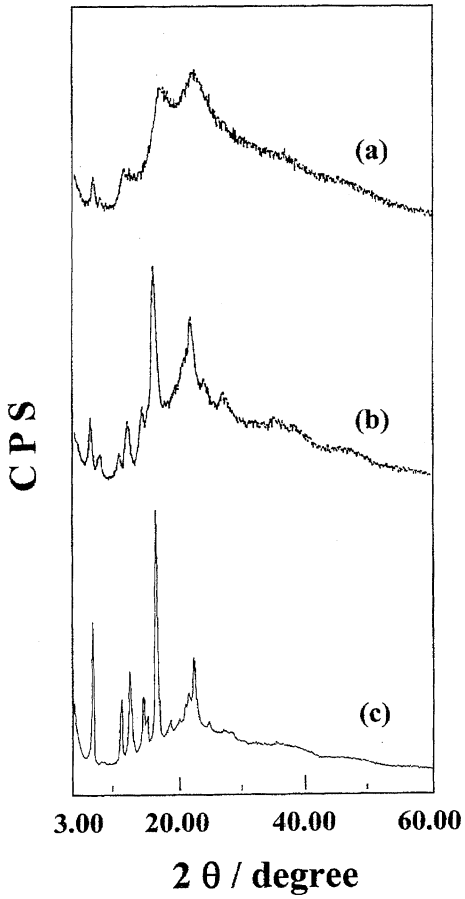


Fig. 10. X-Ray diffraction patterns for γ-CD–1-propanol complex (a), γ-CD–PMVE (MW = 1200) complex (b), and γ-CD–PEVE (MW = 1200) complex (c).

patterns of anhydrous γ-CD–1-propanol and γ-CD–PMVE complexes (Fig. 10 (a), and (b)). When these complexes are dried at 100 °C under high-vacuum, X-ray diffraction diagrams gave similar patterns. We found that the transition of the unit cell of γ-CD–PMVE complex takes place with extent of hydration. The pattern of the complex of γ-CD with PEVE (Fig. 10 (c)) is similar to that of the anhydrous PMVE complex (Fig. 10 (b)).

Figure 11 (a) shows the ^{13}C CP/MAS NMR spectrum of the γ-CD and Fig. 11 (b) shows that of a complex of γ-CD with PMVE (MW = 1000). CP/MAS spectroscopy gives information about macrocyclic conformation of CDs. The ^{13}C shifts of the C-1 and C-4 resonance of γ-CD reflect the dihedral angles around the α-1,4-glycosidic linkage. The ^{13}C shifts of C-6 resonance are related to the conformation about the C-5–C-6 bond. γ-CD assumes a less symmetrical conformation in the crystal when it does not include a guest in the cavity. In this case, the spectrum of γ-CD shows resolved peaks. On the other hand, each C-1, C-4, and C-6 resonance can be observed in a single peak, in the spectrum of the γ-CD–PMVE complex. These results indicate that γ-CD adopts a symmetrical conformation and each glucose unit of γ-CD is in a similar environment. The X-ray studies of single crystals showed that γ-CD adopts a symmetrical conformation when it includes guests in the cavities.[18,19] The CP/MAS NMR spectra of complexes and uncomplexed cyclodextrins are consistent with the results of X-ray studies. Therefore, a PMVE chain is thought to be included in the cavities of cyclodextrins. Figure 12 shows the ^{13}C PST/MAS NMR spectra of γ-CD (a) and γ-CD–PMVE complex (b). ^{13}C PST/MAS is a solid state NMR method which gives stronger signals of relatively flexible carbons of the sample than ^{13}C CP/MAS NMR. The relative intensities of the peaks of PMVE to those of γ-CD are stronger than those in Fig. 11, indicating that the PMVE chain is not so rigid as γ-CD in the complex. These results are consistent with the views that γ-CD molecules from a channel, which constructs the crystal frame of the complexes. The PMVE chain is included in the channel.

Molecular model studies show that PMVE, PEVE, and Pn-PVE chains are able to penetrate γ-CD cavities. Model studies further indicate that the single cavity accommodates three monomer units. The inclusion complex formation of polymers with cyclodextrins is entropically unfavorable. However, formation of the complexes is thought to be promoted by hydrogen bond formation between cyclodextrins. Therefore, the head-to-head and tail-to-tail arrangement, which results in a more effective formation of hydrogen bonds between cyclodextrins, is thought to be the most probable structure. This structure was proved by X-ray studies on a single

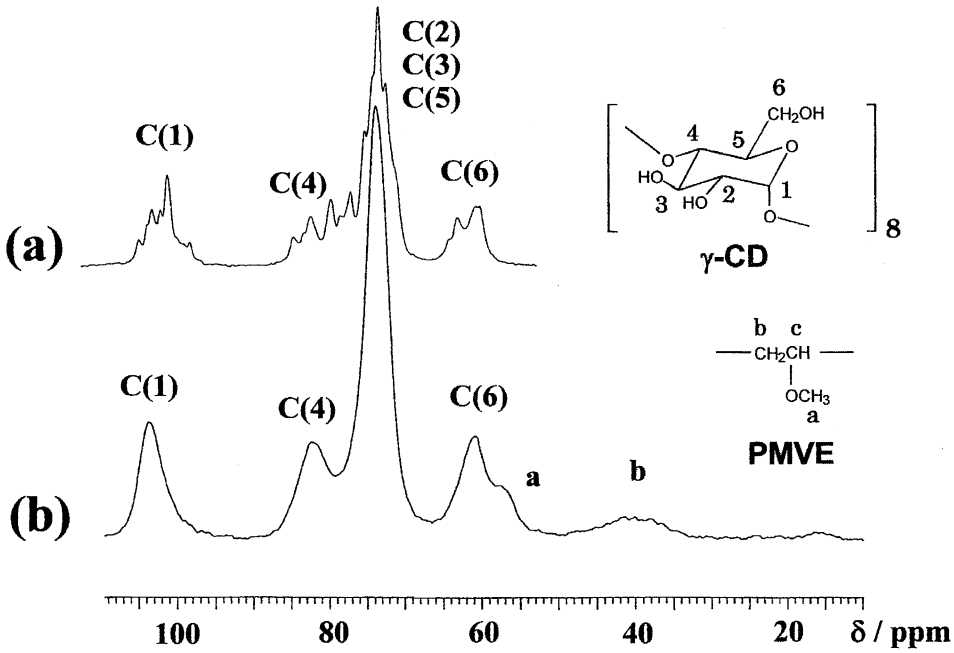


Fig. 11. ^{13}C CP/MAS NMR spectra of γ-CD (a) and the γ-CD–PMVE complex (b).

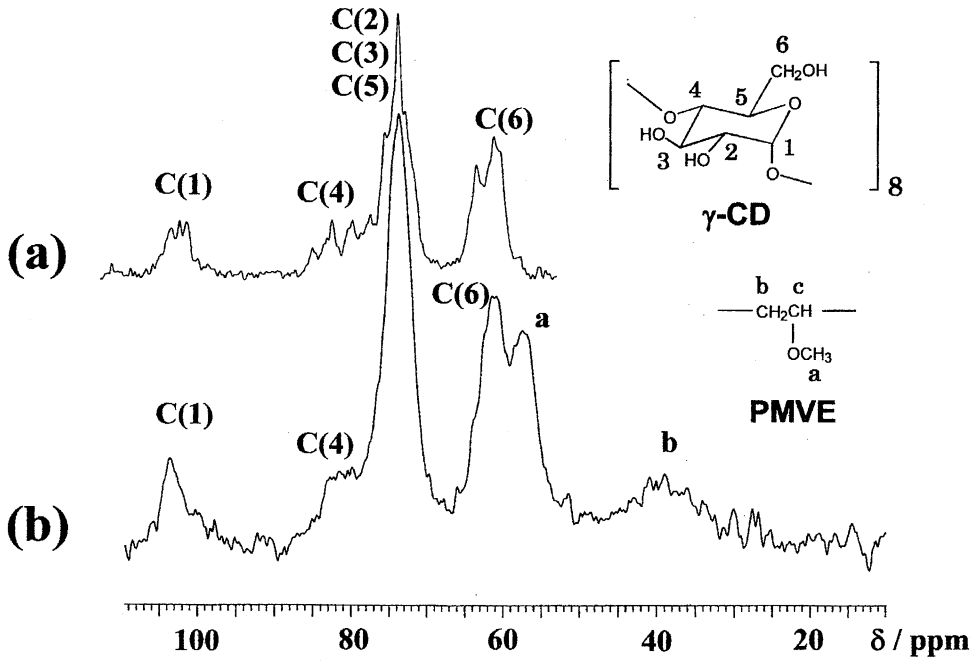


Fig. 12. ^{13}C PST/MAS NMR spectra of γ-CD (a) and the γ-CD–PMVE complex (b).

crystal of the complex between γ-CD and 1-propanol. Figure 13 shows a proposed structure of the complex between γ-CD and PMVE.

In conclusion, γ-CD formed complexes with poly(alkyl vinyl ether)s, such as poly(methyl vinyl ether), poly(ethyl vinyl ether), and poly(*n*-propyl vinyl ether) selectivity and stoichiometrically. This kind of complex formation is of importance in connection with the construction of supramolecular structures in nature and in the artificial world.

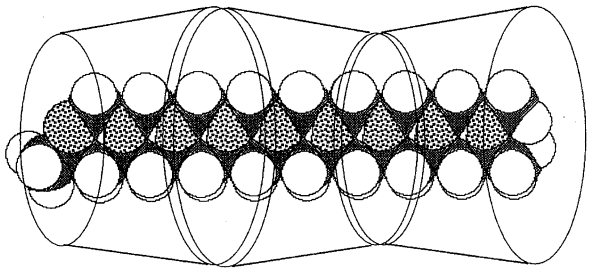


Fig. 13. Proposed structure of the complex between γ-CD and PMVE.

Experimental

Materials. Methyl vinyl ether and diethyl ether–boron trifluoride (1/1) were obtained from Tokyo Kasei Kogyo Co., Ltd. *n*-Propyl vinyl ether was obtained from Fluka. Poly(ethyl vinyl ether) was obtained from Aldrich. α-, β-, and γ-CD were obtained from Nacalai Tesque Ltd.

Measurements. GPC determination was carried out with a Tosoh CCP&8010 system (column; G3000HXL and G2000HXL). ^{1}H and ^{13}C NMR spectra were recorded at 270 MHz for ^{1}H and 67.9 MHz for ^{13}C on a JEOL EX-270 NMR spectrometer in DMF-d_7 at 30 °C. Chemical shift were referenced to the solvent value (δ = 2.70 ppm for ^{1}H and 30.10 for ^{13}C). Powder X-ray diffraction patterns were taken by Cu $K\alpha$ radiation with Rigaku RAD-ROC X-ray diffractometer (voltage, 40 kV; current, 100 mA; scanning speed, 3 ° min^{-1}). ^{13}C-CP/MAS and PST/MAS spectra were measured at 100.5 MHz on a JEOL GSX-400 spectrometer at room temperature. Chemical shifts were referenced to external standard TMS. FT-IR spectra were measured at JASCO FT/IR-3 spectrometer.

Polymerization of Alkyl Vinyl Ether.[20,21] Poly(alkyl vinyl ether)s (PAVEs) were prepared by polymerization of alkyl vinyl ethers with diethyl ether–boron trifluoride (1/1) as an initiator. Polymer samples were fractionated by Sephadex LH-20 column chromatography using methanol as solvent. The molecular weight of PAVE was estimated by a GPC method in THF from the calibration curve derived from standard polystyrenes.

Preparation of γ-CD–PAVE Complexes. To PAVE (10.0 mg) an aqueous solution (2.00 mL) containing 116 mg γ-CD was added at room temperature. The mixture was ultrasonically agitated for 10 min, and then allowed to stand overnight at room temperature. The products precipitated were collected by centrifugation, dried under vacuum, washed with dry THF, and dried under vacuum to give the γ-CD–PAVE complexes.

γ-CD–PMVE4000. Yield: 46%. ^{1}H NMR (270 MHz, DMF-d_7) δ = 5.77—5.75 (m, 16H, O(2)H and O(3)H of γ-CD), 4.97 (d, 8H, C(1)H of γ-CD), 4.55 (t, 8H, O(6)H of γ-CD), 3.76—3.65 (m, 24H, C(3)H, C(5)H and C(6)H of γ-CD), 3.48—3.22 (m, C(2)-H and C(4)H of γ-CD, and methine H and methyl H of PMVE), 1.90—1.40 (m, 6H, methylene H of PMVE). ^{13}C NMR (67.9 MHz, DMF-d_7) δ = 103.04 (C(1) of γ-CD), 82.21 (C(4) of γ-CD), 75.76 (methine C of PMVE), 74.20 (C(2) of γ-CD), 74.11 (C(3) of γ-CD), 73.37 (C(5) of γ-CD), 61.35 (C(6) of γ-CD), 55.94 (methyl C of PMVE). IR (KBr) 3400 (OH), 2925 (CH), 1157, 1080, 1027 (CO) cm^{-1}. Calcd for $(C_{48}H_{80}O_{40})_{1.0}(C_3H_6O)_{3.0}(H_2O)_{5.2}$: C, 43.74; H, 6.98%. Found: C, 43.74; H, 7.21%.

γ-CD–PMVE3000. Yield: 48%. ^{1}H NMR (270 MHz, DMF-d_7) δ = 5.77—5.75 (m, 16H, O(2)H and O(3)H of γ-CD), 4.97 (d, 8H, C(1)H of γ-CD), 4.55 (t, 8H, O(6)H of γ-CD), 3.76—3.65 (m, 24H, C(3)H, C(5)H, and C(6)H of γ-CD), 3.48—3.22 (m, C(2)-H and C(4)H of γ-CD, and methine H and methyl H of PMVE), 1.90—1.40 (m, 6H, methylene H of PMVE). ^{13}C NMR (67.9 MHz, DMF-d_7) δ = 103.04 (C(1) of γ-CD), 82.21 (C(4) of γ-CD), 75.76 (methine C of PMVE), 74.20 (C(2) of γ-CD), 74.11 (C(3) of γ-CD), 73.37 (C(5) of γ-CD), 61.35 (C(6) of γ-CD), 55.94 (methyl C of PMVE). IR (KBr) 3400 (OH), 2925 (CH), 1157, 1080, 1027 cm^{-1} (CO). Calcd for $(C_{48}H_{80}O_{40})_{1.0}(C_3H_6O)_{3.0}(H_2O)_{10}$: C, 41.45; H, 7.20%. Found: C, 41.42; 6.79%.

γ-CD–PMVE2000. Yield: 50%. ^{1}H NMR (270 MHz, DMF-d_7) δ = 5.77—5.75 (m, 16H, O(2)H and O(3)H of γ-CD), 4.97 (d, 8H, C(1)H of γ-CD), 4.55 (t, 8H, O(6)H of γ-CD), 3.76—3.65 (m, 24H, C(3)H, C(5)H, and C(6)H of γ-CD), 3.49—3.26 (m, C(2)-H and C(4)H of γ-CD, and methine H and methyl H of PMVE), 1.85—1.20 (m, 6H, methylene H of PMVE). ^{13}C NMR (67.9 MHz, DMF-d_7) δ = 102.97 (C(1) of γ-CD), 82.16 (C(4) of γ-CD), 75.69 (methine C of PMVE), 74.11 (C(2) of γ-CD), 73.98 (C(3) of γ-CD), 73.26 (C(5) of γ-CD), 61.26 (C(6) of γ-CD), 55.89 (methyl C of PMVE). IR (KBr) 3403 (OH), 2925 (CH), 1157, 1080, 1027 cm^{-1} (CO). Calcd for $(C_{48}H_{80}O_{40})_{1.0}(C_3H_6O)_{3.0}(H_2O)_{6.2}$: C, 43.25; H, 7.03%. Found: C, 43.23; H, 6.83%.

γ-CD–PMVE1200. Yield: 48%. ^{1}H NMR (270 MHz, DMF-d_7) δ = 5.81—5.79 (m, 16H, O(2)H and O(3)H of γ-CD), 4.97 (d, 8H, C(1)H of γ-CD), 4.60 (t, 8H, O(6)H of γ-CD), 3.75—3.64 (m, 24H, C(3)H, C(5)H, and C(6)H of γ-CD), 3.54—3.21 (m, C(2)H and C(4)H of γ-CD, and methine H and methyl H of PMVE), 1.90—1.40 (m, 6H, methylene H of PMVE). ^{13}C NMMR (67.9 MHz, DMF-d_7) δ = 102.98 (C(1) of γ-CD), 82.16 (C(4) of γ-CD), 75.69 (methine C of PMVE), 74.11 (C(2) of γ-CD), 73.98 (C(3) of γ-CD), 73.26 (C(5) of γ-CD), 61.26 (C(6) of γ-CD), 55.89 (methyl C of PMVE). IR (KBr) 3410 (OH), 2935 (CH), 1157, 1080, 1027 cm^{-1} (CO). Calcd for $(C_{48}H_{80}O_{40})_{1.0}(C_3H_6O)_{3.0}(H_2O)_{3.3}$: C, 44.72; H, 6.89%. Found: C, 44.73; H, 7.05%.

γ-CD–PMVE1000. Yield: 48%. ^{1}H NMR (270 MHz, DMF-d_7) δ = 5.79—5.77 (m, 16H, O(2)H and O(3)H of γ-CD), 4.97 (d, 8H, C(1)H of γ-CD), 4.55 (t, 8H, O(6)H of γ-CD), 3.75—3.65 (m, 24H, C(3)H, C(5)H, and C(6)H of γ-CD), 3.54—3.22 (m, C(2)-H and C(4)H of γ-CD, and methine H and methyl H of PMVE), 1.90—1.40 (m, 6H, methylene H of PMVE). ^{13}C NMR (67.9 MHz, DMF-d_7) δ = 103.06 (C(1) of γ-CD), 82.23 (C(4) of γ-CD), 75.78 (methine C of PMVE), 74.21 (C(2) of γ-CD), 74.14 (C(3) of γ-CD), 73.39 (C(5) of γ-CD), 61.37 (C(6) of γ-CD), 55.96 (methyl C of PMVE). IR (KBr) 3410 (OH), 2935 (CH), 1157, 1080, 1027 cm^{-1} (CO). Calcd for $(C_{48}H_{80}O_{40})_{1.0}(C_3H_6O)_{3.0}(H_2O)_{7.8}$: C, 42.47; H, 7.10%. Found: C, 42.47; H, 7.02%.

γ-CD–PEVE2100. Yield: 33%. ^{1}H NMR (270 MHz, DMF-d_7) δ = 5.81—5.78 (m, 16H, O(2)H and O(3)H of γ-CD), 4.97 (d, 8H, C(1)H of γ-CD), 4.60 (t, 8H, O(6)H of γ-CD), 3.78—3.65 (m, 24H, C(3)H, C(5)H, and C(6)H of γ-CD), 3.50—3.25 (m, C(2)H and C(4)H of γ-CD, and O-methine H and O-methylene H of PEVE), 1.80—1.00 (m, 25H, C-methylene H and methyl H of PEVE). ^{13}C NMR (67.9 MHz, DMF-d_7) δ = 103.00 (C(1) of γ-CD), 82.18 (C(4) of γ-CD), 74.12 (C(2) of γ-CD), 74.02 (C(3) of γ-CD), 73.29 (C(5) of γ-CD), 63.99 (O-methylene C of PEVE), 61.27 (C(6) of γ-CD), 15.92 (methyl C of PEVE). IR (KBr) 3401 (OH), 2929 (CH), 1158, 1080, 1029 cm^{-1} (CO). Calcd for $(C_{48}H_{80}O_{40})_{1.0}(C_4H_8O)_{5.0}(H_2O)_{7.9}$: C, 45.37; H, 7.60%. Found: C, 45.37; H, 7.25%.

γ-CD–PEVE1200. Yield: 71%. ^{1}H NMR (270 MHz, DMF-d_7) δ = 5.81—5.79 (m, 16H, O(2)H and O(3)H of γ-CD), 4.97 (d, 8H, C(1)H of γ-CD), 4.61 (t, 8H, O(6)H of γ-CD), 3.76—3.65 (m, 24H, C(3)H, C(5)H, and C(6)H of γ-CD), 3.50—3.38 (m, C(2)H and C(4)H of γ-CD, and O-methine H and O-methylene H of PEVE), 1.80—1.00 (m, 15H, C-methylene H and methyl H of PEVE). ^{13}C NMR (67 MHz, DMF-d_7) δ = 103.02 (C(1) of γ-CD), 82.19 (C(4) of δ-CD), 74.14 (C(2) of δ-CD), 74.04 (C(3) of γ-CD), 73.32 (C(5) of γ-CD), 61.29 (C(6) of γ-CD), 15.89 (methyl C of PEVE). IR (KBr) 3407 (OH), 2928 (CH), 1157, 1080, 1027 cm^{-1} (CO). Calcd for $(C_{48}H_{80}O_{40})_{1.0}(C_4H_8O)_{3.0}(H_2O)_{4.6}$: C, 45.14; H, 7.15%. Found: C, 45.16; H, 7.16%.

γ-CD–PEVE900. Yield: 83%. ^{1}H NMR (270 MHz, DMF-d_7) δ = 5.81—5.78 (m, 16H, O(2)H and O(3)H of γ-CD), (d, 8H, C(1)H of δ-CD), 4.60 (t, 8H, O(6)H of γ-CD), 3.78—3.65 (m, 24H, C(3)-H, C(5)H, and C(6)H of γ-CD), 3.50—3.25 (m, C(2)H and C(4)H of γ-CD, and O-methine H and O-methylene H of PEVE), 1.80—

1.00 (m, 15H, C-methylene H and methyl H of PEVE). ^{13}C NMR (67.9 MHz, DMF-d_7) δ = 103.00 (C(1) of γ-CD), 82.18 (C(4) of γ-CD), 74.12 (C(2) of γ-CD), 74.02 (C(3) of γ-CD), 73.30 (C(5) of γ-CD), 61.28 (C(6) of γ-CD), 15.85 (methyl C of PEVE). IR (KBr) 3402 (OH), 2927 (CH), 1157, 1080, 1028 cm^{-1} (CO). Calcd for $(C_{48}H_{80}O_{40})_{1.0}(C_4H_8O)_{3.0}(H_2O)_{8.8}$: C, 43.10; H, 7.33%. Found: C, 43.10; H, 6.90%.

γ-CD–PnPVE1200. Yield: 4%. ^{1}H NMR (270 MHz, DMF-d_7) δ = 5.81—5.78 (m, 16H, O(2)H and O(3)H of γ-CD), 4.97 (d, 8H, C(1)H of γ-CD), 4.60 (t, 8H, O(6)H of γ-CD), 3.78—3.65 (m, 24H, C(3)H, C(5)H, and C(6)H of γ-CD), 3.49—3.23 (m, C(2)H and C(4)H of γ-CD, and O-methine H and O-methylene H of PnPVE), 1.85—0.80 (m, 56H, C-methylene H and methyl H of PnPVE). ^{13}C NMR (67.9 MHz, DMF-d_7) δ = 103.02 (C(1) of γ-CD), 82.19 (C(4) of γ-CD), 74.14 (C(2) of γ-CD), 74.04 (C(3) of γ-CD), 73.32 (C(5) of γ-CD), 61.29 (C(6) of γ-CD), 23.92 (C-methylene C of PnPVE), 11.13 (methyl C of PnPVE). IR (KBr) 3403 (OH), 2928 (CH), 1157, 1080, 1028 cm^{-1} (CO). Calcd for $(C_{48}H_{80}O_{40})_{1.0}(C_5H_{10}O)_{8.0}(H_2O)_{3.2}$: C, 51.71; H, 8.20%. Found: C, 51.74; H, 8.34%.

γ-CD–PnPVE800. Yield: 33%. ^{1}H NMR (270 MHz, DMF-d_7) δ = 5.81—5.79 (m, 16H, O(2)H and O(3)H of γ-CD), 4.97 (d, 8H, C(1)H of γ-CD), 4.61 (t, 8H, O(6)H of γ-CD), 3.76—3.64 (m, 24H, C(3)H, C(5)H, and C(6)H of γ-CD), 3.51—3.24 (m, C(2)H and C(4)H of γ-CD, and O-methine H and O-methylene H of PnPVE), 1.80—0.80 (m, 17H, C-methylene H and methyl H of PnPVE). ^{13}C NMR (67.9 MHz, DMF-d_7) δ = 103.02 (C(1) of γ-CD), 82.19 (C(4) of γ-CD), 74.14 (C(2) of γ-CD), 74.04 (C(3) of γ-CD), 73.32 (C(5) of γ-CD), 61.29 (C(6) of γ-CD), 23.88 (C-methylene C of PnPVE), 11.11 (methyl C of PnPVE). IR (KBr) 3405 (OH, 2930 (CH), 1156, 1079, 1029 cm^{-1} (CO). Calcd for $(C_{48}H_{80}O_{40})_{1.0}(C_5H_{10}O)_{2.5}(H_2O)_{7.9}$: C, 43.91; H, 7.35%. Found: C, 43.97; H, 6.99%.

γ-CD–PnPVE500. Yield: 61%. ^{1}H NMR (270 MHz, DMF-d_7) δ = 5.77—5.75 (m, 16H, O(2)H and O(3)H of γ-CD), 4.97 (d, 8H, C(1)H of γ-CD), 4.55 (t, 8H, O(6)H of γ-CD), 3.79—3.65 (m, 24H, C(3)H, C(5)H and C(6)H of γ-CD), 3.49—3.22 (m, C(2)H and C(4)H of γ-CD, and O-methine H and O-methylene H of PnPVE), 1.80—0.80 (m, 14H, C-methylene H and methyl H of PnPVE). ^{13}C NMR (67.9 MHz, DMF-d_7) δ = 103.00 (C(1) of γ-CD), 82.18 (C(4) of γ-CD), 74.12 (C(2) of γ-CD), 74.02 (C(3) of γ-CD), 73.30 (C(5) of γ-CD), 61.28 (C(6) of γ-CD), 23.83 (C-methylene C of PnPVE), 10.98 (methyl C of PnPVE). IR (KBr) 3401 (OH), 2933 (CH), 1157, 1079, 1029 cm^{-1} (CO). Calcd for $(C_{48}H_{80}O_{40})_{1.0}(C_5H_{10}O)_{2.0}(H_2O)_{6.5}$: C, 43.91; H, 7.18%. Found: C, 43.89; H, 6.95%.

γ-CD–PnPVE300. Yield: 83%. ^{1}H NMR(270 MHz, DMF-d_7) δ = 5.81—5.79 (m, 16H, O(2)H and O(3)H of γ-CD), 4.97 (d, 8H, C(1)H of γ-CD), 4.61 (t, 8H, O(6)H of γ-CD), 3.76—3.65 (m, 24H, C(3)H, C(5)H, and C(6)H of γ-CD), 3.51—3.24 (m, C(2)H and C(4)H of γ-CD, and O-methine H and O-methylene H of PnPVE), 1.80—0.80 (m, 14H, C-methylene H and methyl H of PnPVE).^{13}C NMR (67.9 MHz, DMF-d_7) δ = 103.02 (C(1) of γ-CD), 82.19 (C(4) of γ-CD), 74.14 (C(2) of γ-CD), 74.04 (C(3) of γ-CD), 73.32 (C(5) of γ-CD), 61.29 (C(6) of γ-CD), 23.88 (C-methylene C of PnPVE), 11.11 (methyl C of PnPVE). IR (KBr) 3395 (OH), 2932 (CH), 1156, 1080, 1029 cm^{-1} (CO). Calcd for $(C_{48}H_{80}O_{40})_{1.0}(C_5H_{10}O)_{2.0}(H_2O)_{7.3}$: C, 43.51; H, 7.22%. Found: C, 43.53; H, 6.97%.

γ-CD–nPVE. Yield: 9%. ^{1}H NMR (270 MHz, DMF-d_7) δ = 6.44 (m, C = methine H of nPVE), 5.77—5.75 (m, 16H, O(2)H and O(3)H of γ-CD), 4.96 (d, 8H, C(1)H of γ-CD), 4.56 (t, 8H, O(6)H of δ-CD), 3.76—3.65 (m, 24H, C(3)H, C(5)H, and C(6)H of γ-CD), 3.51—3.24 (m, C(2)H and C(4)H of γ-CD), 1.57 (m, C-methylene H of nPVE), 0.88 (m, methyl H of nPVE).

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