Inclusion Complexes Formation between Cyclodextrins and Poly(1,3-dioxolane)

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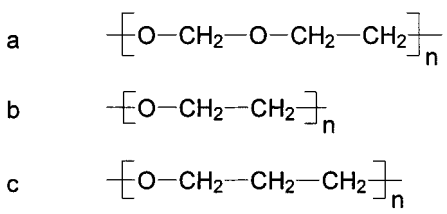
Introduction. Cyclodextrins (CDs) are a series of cyclic oligosaccharides consisting of six to eight glucose units called α-, *β*-, and *γ*-CD, respectively, which can form inclusion complexes with a wide variety of low molecular weight compounds ranging from nonpolar organic molecules to rare gases.[1] The driving forces of complex formation were thought to be the geometric compatibility or fit and intermolecular interaction between hosts and guests.

Several researchers[2,3] have reported that many linear polymeric guests could form inclusion complexes with CDs resulting in main-chain pseudopolyrotaxanes since the past decade. When the polymers were added into the CD solutions and then sonicated, crystalline inclusion complexes precipitated. As the result of X-ray diffraction study, all crystalline inclusion complexes between CDs and polymeric guests are columnar in structure. For example, poly(ethylene glycol) (PEG) can form inclusion complexes with α-CD[2] and *γ*-CD[4] while poly(propylene glycol) (PPG) can only form inclusion complexes with *β*-CD.[5] As Tonelli et al. pointed out, the study of crystalline inclusion complexes provides an approach to investigate the behaviors of single polymer chains in isolated and well-defined environments.[6] Furthermore, it is helpful in understanding the mechanism of molecular recognition between hosts and polymeric guests. This work reports that α-, *β*-, and *γ*-CDs are all able to form crystalline inclusion complexes with poly(1,3-dioxolane) (PDXL). The phenomenon is observed for the first time, though it was reported that PEG can form inclusion complexes with α-CD[2] and poly(oxytrimethylene) (POx) can form inclusion complexes with both α-CD and *β*-CD.[7] Among the three polyethers, PDXL possesses the highest oxygen atom density (see Scheme 1), and it seems the intermolecular interaction can get over the geometric incompatibility when it takes the predominate position. Furthermore, the outcomes of this article are important in probing the driving force in the crystalline inclusion complex formation between cyclodextrins and polymer chains.

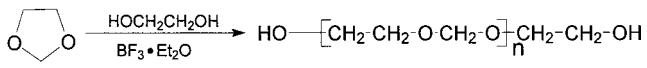
Experimental Section. a. Materials. 1,3-Dioxolane (Shanghai Solvent Co.) was refluxed with CaH_2 for 2 h and then distilled. *β*-CD (Yunan Cyclodextrins Co.) was recrystallized in water. α-CD and *γ*-CD (Cavamax W6 and W8) were kindly supplied by Rohm & Haas Co. and used without further purification. $BF_3{\cdot}Et_2O$ and ethylene glycol were purified under standard methods.

b. Measurements. FT-IR spectra were measured with a Perkin-Elmer Paragon 1000 spectrometer. Molecular weight measurements were performed with a K-7000 (Knauer Co., German) vapor pressure osmometer (VPO). X-ray powder diffraction patterns were taken by a Rigaku III Dmax 2500 using Cu Kα radiation. ^{1}H NMR spectra were recorded in DMSO with a Bruker AVANCE 500 spectrometer operated at 500 MHz.

Scheme 1. Molecular Structures of (a) Poly(1,3-dioxolane), (b) Poly(ethylene glycol), and (c) Poly(oxytrimethylene)



Scheme 2. Synthesis of Poly(1,3-dioxolane)



c. Synthesis of the Polymer. PDXL was prepared by bulk polymerization under nitrogen atmosphere using ethylene glycol as the initiator and $BF_3{\cdot}Et_2O$ as the catalyst.[8] The reaction was terminated by ammonium solution. The products were precipitated in methanol at −5 °C, then washed with cold methanol, and dried under vacuum at 40 °C for 24 h.

PDXL1: FT-IR (KBr): 3501.4 (OH), 2939.9 (v as CH_2), 2881.9 (v s CH_2), 1459.6 (δ CH_2), 1411.7 (m, δ $-CH_2C-$), 1122.2 (s, v as C−O−C), and 1040.3 cm^{-1} (s, v s C−O−C)

PDXL2: FT-IR (KBr): 3501.7 (OH), 2940.7 (v as CH_2), 2882.1 (v s CH_2), 1459.3 (δ CH_2), 1412.3 (m, δ $-CH_2C-$), 1123.3 (s, v as C−O−C), and 1036.2 cm^{-1} (s, v s C−O−C)

M_n: 1555 (PDXL1), 1932 (PDXL2).

d. Preparation of Inclusion Complexes. Weighed α-CD was dissolved in water, and then aqueous PDXL solution was added. The mixture was stirred at 30 °C for 2 h and allowed to stand overnight. The precipitate was filtered and washed with water several times to remove those nonincluded materials. Other products were obtained under the same conditions.

Results and Discussion. When aqueous solutions of PDXL were added to CD solutions at 30 °C, all became gradually turbid. The appearance of precipitate is considered as evidence for the formation of crystalline inclusion complexes between CDs and polymer chains.[2] All CDs (i.e., α-, *β*-, and *γ*-CD) can form crystalline inclusion complexes with PDXL, as observed here for the first time.

The solution of PDXL with α-CD became turbid in just 1 min after being mixed and that of PDXL with *γ*-CD in about 5 min. In comparison, the product of *β*-CD with PDXL appeared after half an hour.

When the precipitate of *γ*-CD with PDXL was added into a large amount of water, it dissolved gradually. Contrarily, the precipitation of α-CD with PDXL is more stable since it does not dissolve in a large amount of water.

Figure 1 shows the X-ray powder diffraction patterns of α-CD and that of the inclusion complex between α-CD and PDXL (M_n = 1932). The diffractogram of α-CD−PDXL complex is similar to those of the inclusion

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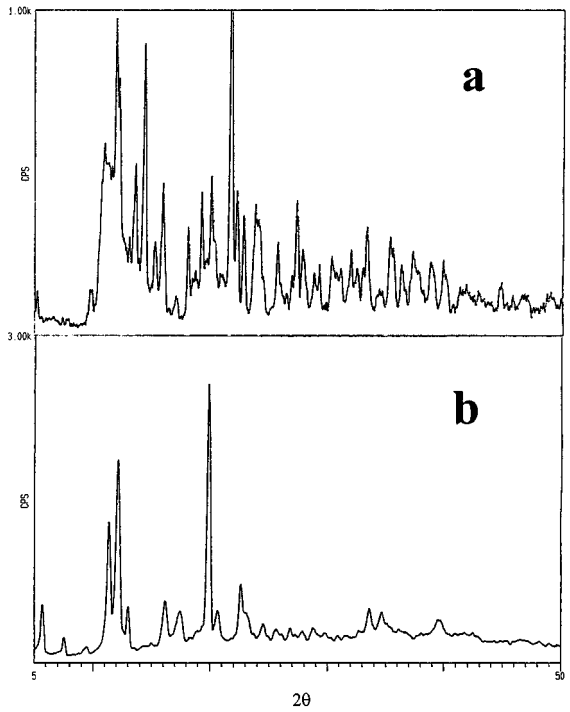

Figure 1. X-ray powder patterns of (a) α-CD and (b) the crystalline inclusion complex between α-CD and PDXL (M_n = 1932).

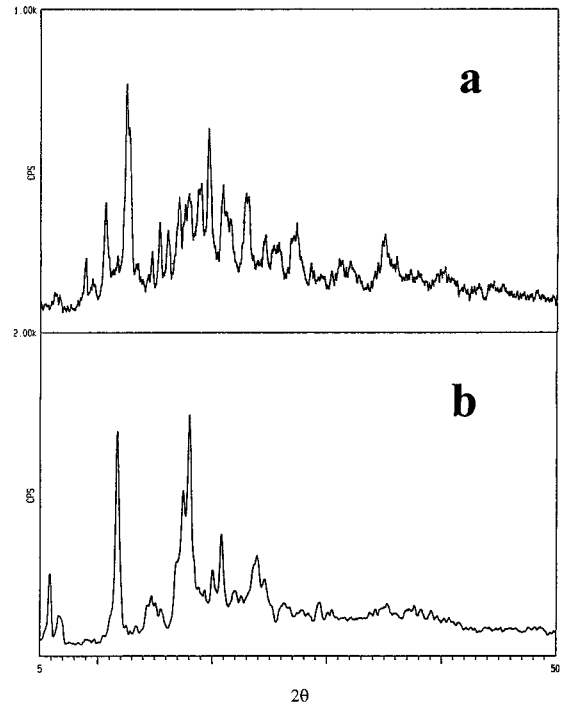

Figure 2. X-ray powder patterns of (a) β-CD and (b) the crystalline inclusion complex between β-CD and PDXL (M_n = 1932).

complexes between α-CD and PEG,[2] POx,[7] poly(ϵ-caprolactone) (PCL),[9] and so on. The characteristic reflection at $2\theta = 20°$ means that the columnar structure has been formed in the complex between α-CD and PDXL, instead of a cage structure.

The X-ray powder patterns of β-CD and that of the inclusion complex between β-CD and PDXL (M_n = 1932) are seen in Figure 2. The pattern of the β-CD−PDXL complex is similar to that of the inclusion complex between β-CD and PPG,[5] which has been reported to have the columnar structure. Therefore, the inclusion complex of PDXL with β-CD also likely assumes a columnar structure.

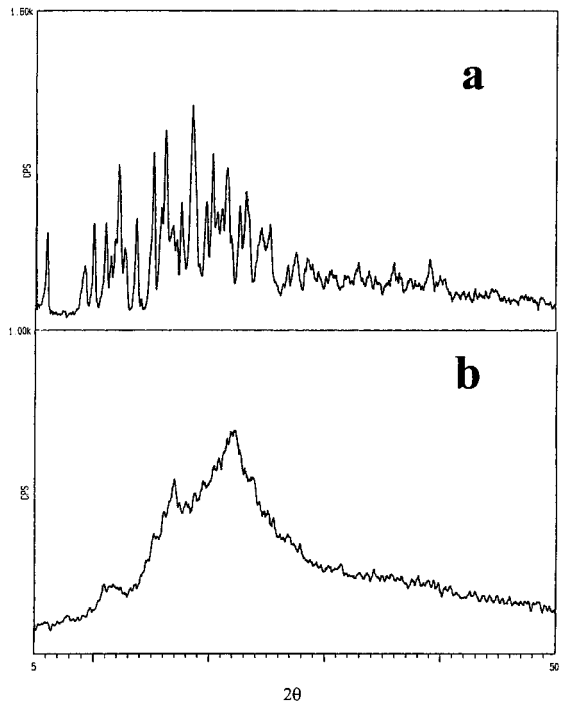

Figure 3. X-ray powder patterns of (a) γ-CD and (b) the crystalline inclusion complex between γ-CD and PDXL (M_n = 1932).

The X-ray powder patterns of γ-CD and that of the inclusion complex between γ-CD and PDXL (M_n = 1932) are displayed in Figure 3. The pattern of the γ-CD−PDXL complex is different from that of pure γ-CD where CDs are arranged in a cage-type packing.[10] However, it is similar to those of the inclusion complexes between γ-CD and poly(alkyl vinyl ether),[11] polyisobutylene (PIB),[12] and poly(alkyl adipate),[13] which have been reported to have a columnar structure. Therefore, the inclusion complex of PDXL with γ-CD assumes a columnar structure rather than a cage-type structure.

In general, PDXL is able to form crystalline inclusion complexes with all three CDs, i.e., α-, β-, and γ-CDs. As reported previously, PEG only forms inclusion complexes with α-CD[2] and γ-CD[4] and PPG only forms an inclusion complex with β-CD.[5] These phenomena were attributed to the geometric compatibility or fit between hosts and polymeric guests. It seems the intermolecular interaction plays an important role due to the high oxygen atom density in PDXL chains. Therefore, PDXL can form crystalline inclusion complexes with all three CDs. The results of X-ray diffraction study indicate that all the crystalline inclusion complexes have columnar structures.

Figure 4 shows the ^{1}H NMR spectra of PDXL and that of the inclusion complex between α-CD and PDXL (M_n = 1932) in DMSO. In the ^{1}H NMR spectrum of the dissolved inclusion complex between α-CD and PDXL, we find hydrogen atom signals belonging to both α-CD and PDXL molecules. If a PDXL chain takes the zigzag configuration, the length of one dioxolane unit is calculated as 0.59 nm. The depth of CD molecules is 0.7 nm. Therefore, one α-CD molecule can contain 1.2 dioxolane monomer units theoretically. However, the experimental ratio of the PDXL (monomer units) to

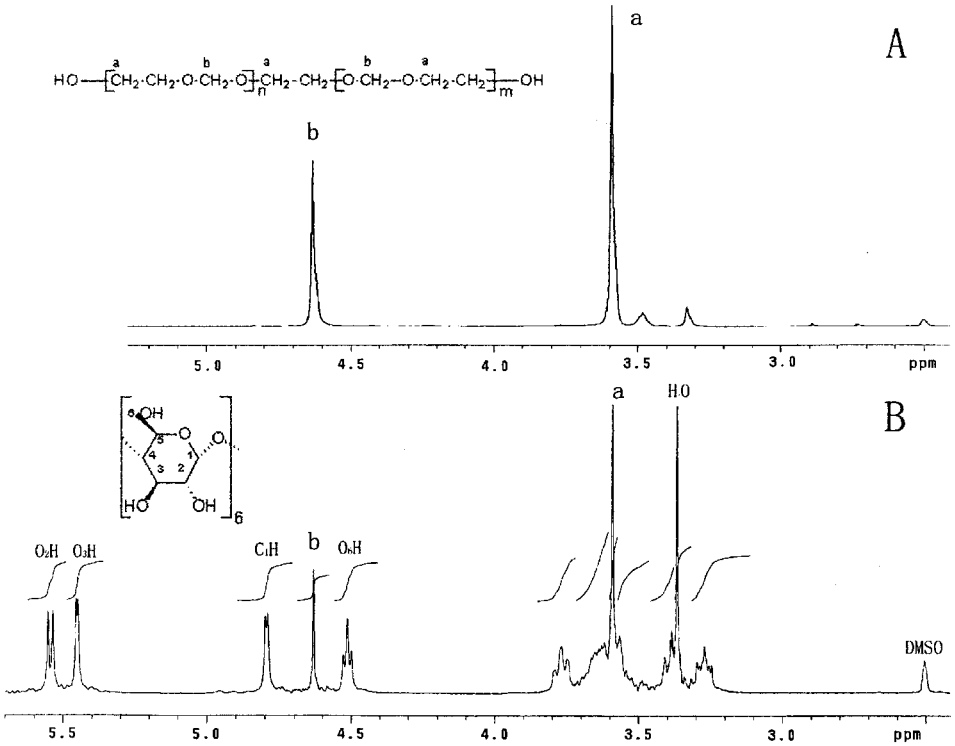

Figure 4. ^{1}H NMR spectra of (A) PDXL and (B) the inclusion complex between α-CD and PDXL (M_n = 1932) in DMSO.

α-CD is about 2.1, which means that the inclusion complex is not perfect in stoichiometry. This may be caused by the reaction conditions. When the mixed solution was sonicated, the ratio decreases, and these results will be published elsewhere. In the case of the complex between γ-CD and PDXL, the ratio is about 3.2 (PDXL monomer units to γ-CD). This means that double PDXL chains were included in γ-CD.

Conclusion. Crystalline inclusion complexes between three kinds of CDs and low molecular weight PDXL were obtained and studied. It is observed for the first time and is important in probing the driving force in the crystalline inclusion complex formation between cyclodextrin and polymer chains. The X-ray powder patterns of the products demonstrated that the resultant inclusion complexes are crystalline and have the columnar structure.

Further studies are in progress.

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References and Notes

(1) Szejtli, J. *Cyclodextrins and Their Inclusion Complexes*; Akademiai Kiado: Bugdapest, 1982.
(2) (a) Harada, A.; Kamachi, M. *Macromolecules* **1990**, *23*, 2821. (b) Harada, A.; Li, J.; Kamachi, M. *Macromolecules* **1993**, *26*, 5698.
(3) (a) Wenz, G.; Keller, B. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 197. (b) Klyamkin, A. A.; Topchieva, I. N.; Zubov, V. P. *Colloid Polym. Sci.* **1995**, *273*, 520. (c) Herrmann, W.; Keller, B.; Wenz, G. *Macromolecules* **1997**, *30*, 4966. (d) Weickenmeier, M.; Wenz, G. *Macromol. Rapid Commun.* **1997**, *18*, 1109. (e) Panova, I. G.; Gerasimov, V. I.; Topchieva, I. N. *Polym. Sci., Ser. B* **1998**, *40*, 336. (f) Yoshida, K.; Shimomura, T.; Ito, K.; Hayakawa, R. *Langmuir* **1999**, *15*, 910.
(4) (a) Harada, A.; Li, J.; Kamachi, M. *Nature* **1994**, *370*, 126. (b) Panova, I. G.; Gerasimov, V. I.; Kalashnikov, F. A.; Topchieva, I. N. *Polym. Sci., Ser. B* **1998**, *40*, 415.
(5) (a) Harada, A.; Kamachi, M. *J. Chem. Soc., Chem. Commun.* **1990**, 1322. (b) Harada, A.; Okada, M.; Li, J.; Kamachi, M. *Macromolecules* **1995**, *28*, 8406.
(6) (a) Vasanthan, N.; Tonelli, A. E.; Nojima, S. *Macromolecules* **1994**, *27*, 7220. (b) Huang, L.; Allen, E.; Tonelli, A. E. *Polymer* **1999**, *40*, 3211. (c) Lu, J.; Shin, I. D.; Nojima, S.; Tonelli, A. E. *Polymer* **2000**, *41*, 5871.
(7) Harada, A.; Okada, M.; Kamachi, M. *Acta Polym.* **1995**, *46*, 453.
(8) Kubisa, P. Cationic Polymerization of Heterocyclics. In Matyjaszewski, K., Ed.; *Cationic Polymerizations: Mechanisms, Synthesis, and Applications*; Mercel Dekker: New York, 1996; pp 437−553.
(9) (a) Harada, A.; Kawaguchi, Y.; Nishiyama, T.; Kamachi, M. *Macromol. Rapid Commun.* **1997**, *18*, 535. (b) Huang, L.; Tonelli, A. E. *Polymer* **1998**, *39*, 4857.
(10) (a) Maclennan, J. M.; Stezowski, J. J. *Biochem. Biophys. Res. Commun.* **1980**, *92*, 926. (b) Harada, K. *Chem. Lett.* **1984**, 641. (c) Harada, K. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 2763.
(11) Harada, A.; Okada, M.; Kamachi, M. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 535.
(12) Harada, A.; Suzuki, S.; Okada, M.; Kamachi, M. *Macromolecules* **1996**, *29*, 5611.
(13) Harada, A.; Nishiyama, T.; Kawaguchi, Y.; Okada, M.; Kamachi, M. *Macromolecules* **1997**, *30*, 7115.

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