# Complex Formation between Polyisobutylene and Cyclodextrins: Inversion of Chain-Length Selectivity between β-Cyclodextrin and γ-Cyclodextrin

**Akira Harada,* Jun Li, Syukuko Suzuki, and Mikiharu Kamachi***

*Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan*

*Received May 17, 1993*
*Revised Manuscript Received July 28, 1993*

Since cyclodextrins (α-CD, β-CD, and γ-CD) were discovered, a large number of inclusion complexes of cyclodextrins with low molecular weight compounds have been prepared and characterized.[1] However, there were no reports on the complex formation between cyclodextrins and polymers when we started our project on the inclusion complexes of cyclodextrins with polymers. Previously, we reported that α-CD formed complexes with poly(ethylene glycol) of various molecular weights to give crystalline complexes in high yields, as the first example of the complex formation between CD and a polymer,[2] although β-CD did not form complexes with poly(ethylene glycol) of any molecular weight. Recently, we have reported that β-CD formed crystalline complexes with poly(propylene glycol)[3] though α-CD did not form a complex with poly(propylene glycol). We have also reported the preparation of a polyrotaxane in which many α-CDs are threaded on a poly(ethylene glycol) chain by capping the end groups with bulky substituents.[4] Wenz *et al.* also reported α-CDs threaded on a polyamine.[5] Now we have found that β-CD and γ-CD formed complexes with polyisobutylene (PIB), a water-insoluble polymer, and that the chain-length selectivities between β-CD and γ-CD are reversed.

When PIBs (Polyscience; MW = 500, 800, 1350, and 2700) (liquid) were added to aqueous solutions of β-CD (0.18 g/10 mL) or γ-CD (0.08 g/mL) and the mixture was sonicated (Branson B1200; 45 kHz, 60 W) at room temperature for 5 min, the mixture became turbid and the complexes were formed as crystalline precipitates. This is the first observation that cyclodextrin formed a complex with water-insoluble polymers in the solid state. α-CD did not form complexes with PIB, although α-CD formed a complex with poly(ethylene glycol) quantitatively. β-CD and γ-CD formed complexes with PIB. Figure 1 shows the yields of the complexes as a function of the molecular weight of PIB. The yields are based on the starting amount of CD and the stoichiometry of CD to PIB as described below. Saturated aqueous solutions of CD and PIBs (liquid; 3 equiv as monomer units to CD) were used. The yields of the complexes of PIB with γ-CD increased with an increase in the molecular weight of PIB. The complexes were obtained almost quantitatively with PIB of molecular weights of 800 and 1350 and γ-CD. In contrast, the yields of the complexes of PIB with β-CD decreased with an increase in the molecular weight of PIB. The chain-length selectivities are reversed between β-CD and γ-CD. γ-CD did not form complexes with the low molecular weight analogs, such as 2,2-dimethylbutane and 2,2,4-trimethylpentane. β-CD formed a complex with 2,2,4-trimethylpentane in high yield and with 2,2-dimethylbutane in moderate yield.

The complex formation of γ-CD with PIB was studied quantitatively. The amount of the complex formed increases with an increase in the amount of PIB added to the aqueous solution of γ-CD. The amount of the complex showed similar values even if excess amounts of PIB were used, indicating stoichiometric complexation. The continuous variation plot for the formation of the complex between γ-CD and PIB showed a maximum at 0.25, indicating 3:1 (isobutylene unit:γ-CD) stoichiometry. This result suggests that three isobutylene units were bound in each γ-CD cavity. The stoichiometry was confirmed by the use of $^1$H NMR spectroscopy. The length of the three isobutylene units corresponds to the depth of the γ-CD cavity (7 Å). Figure 2 shows a proposed structure of the complex between γ-CD and PIB.

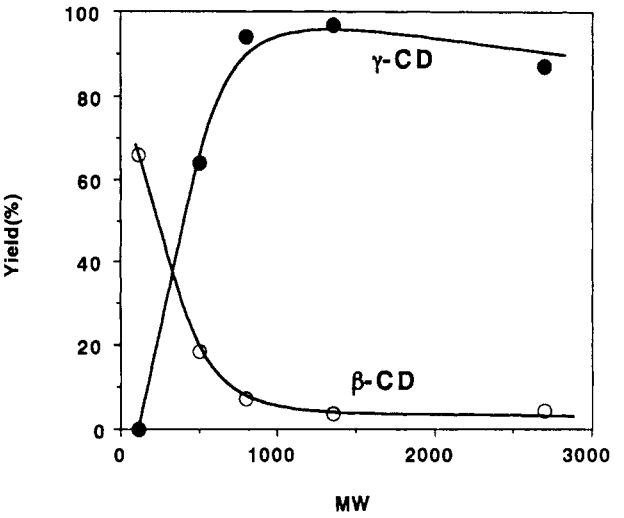


**Figure 1.** Yields of the complexes between PIB and cyclodextrins as a function of the molecular weight of PIB: (●) γ-CD–PIB complex; (○) β-CD–PIB complex.

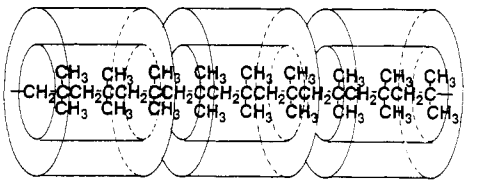

**Figure 2.** Proposed structure of the PIB–γ-CD complex.

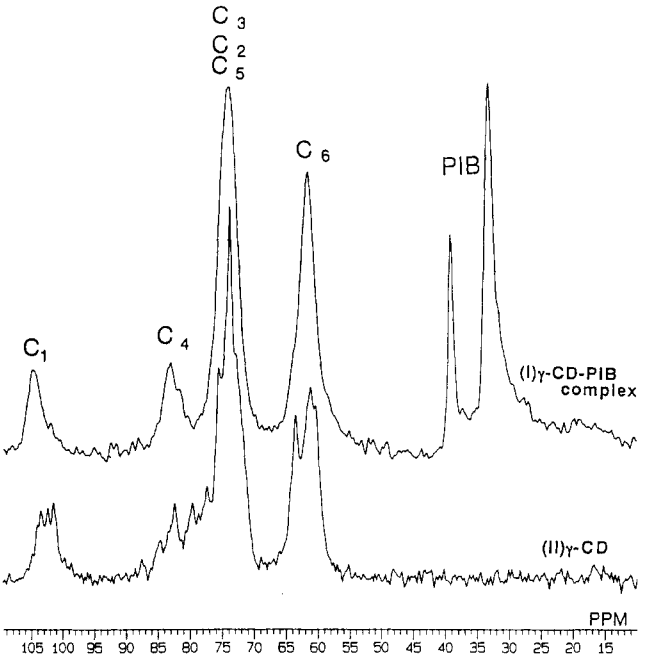


**Figure 3.** $^{13}$C PST/MAS spectrum of the complex between PIB and γ-CD (upper) and that of γ-CD (lower).

0024-9297/93/2226-5267$04.00/0 

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 resulted in solubilization of the complex, indicating that hydrogen bonding between CDs plays an important role in stabilizing the complex. The X-ray diffraction pattern of the complexes between γ-CD and PIB shows that the complexes are crystalline. The pattern of the complex is totally different from that of nonincluded γ-CD. This result suggests that the packing structure of the complex is different from that of free γ-CD.

Molecular model studies show that a PIB chain is able to penetrate the γ-CD cavity, while the PIB chain cannot pass through the α-CD cavity owing to the hindrance of the dimethyl groups on the main chain. The hindrance of the dimethyl groups makes PIB difficult to penetrate β-CD cavities. These views are in accordance with our results that γ-CD formed a complex with PIB but α-CD did not form complexes with PIB. Model studies further indicate that the single cavity accommodates three isobutylene units. The $^{13}C$ PST/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 3).

In conclusion, β-CD and γ-CD form complexes with polyisobutylene, and α-CD did not form complexes with PIB; 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.[6]

## References and Notes

(1) (a) Szeltli, J. *Cyclodextrins and Their Inclusion Complexes*; Akademiai Kiado: Budapest, Hungary, 1982. (b) Bender, M. L.; Komiyama, M. *Cyclodextrin Chemistry*; Springer-Verlag: Berlin, 1978. (c) Saenger, W. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 344.
(2) Harada, A.; Kamachi, M. *Macromolecules* **1990**, *23*, 2821.
(3) Harada, A.; Kamachi, M. *J. Chem. Soc., Chem. Commun.* **1990**, 1321.
(4) Harada, A.; Li, J.; Kamachi, J. *Nature* **1992**, *356*, 325.
(5) Wenz, G.; Keller, B. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 197.
(6) Harada, A.; Li, J.; Kamachi, M. *Chem. Lett.*, in press.