CHEMISTRY LETTERS, pp. 237-240, 1993.

Complex Formation between Poly(methyl vinyl ether) and γ–Cyclodextrin

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γ–Cyclodextrin forms an inclusion complex with poly(methyl vinyl ether) in a definite stoichiometry in high yield, although α-cyclodextrin and β–cyclodextrin did not form complexes with poly(methyl vinyl ether). The inclusion complex is a thermally stable crystalline compound.

Cyclodextrins(α-CD, β-CD, and γ-CD) form inclusion complexes with a wide variety of low molecular weight compounds ranging from non-polar organic molecules to rare gases.1) However, the guest molecules have been limited to small molecules, which can fit in the cavity or be accommodated by two cyclodextrin molecules. Recently, we reported that α–CD formed a complex with poly(ethylene glycol) in a crystalline state, as the first example of the complex formation between CD and a polymer,2) although β-CD did not form a complex with poly(ethylene glycol). More recently, we have reported that β–CD formed a crystalline complex with poly(propylene glycol)3) though α-CD did not form a complex with poly(propylene glycol). We have also reported the synthesis 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 γ-CD formed a complex with poly(methyl vinyl ether)(PMeVE) in a definite stoichiometry in high yield although α-CD and β-CD did not form complexes with PMeVE at all.

When aqueous solution of PMeVE (30%, v/v, Tokyo Kasei, $\overline{MW}$=20 000) was added to a saturated aqueous solution of γ-CD (0.23 g/ml) at room temperature, the solution became turbid and the complex was formed as precipitates. This is the first observation that γ-CD selectively formed a complex with a polymer in the solid state. α–CD and β–CD did not form complexes with PMeVE, although α-CD formed a complex with poly(ethylene glycol) quantitatively, and β-CD formed a complex with poly(propylene glycol) almost quantitatively. Although γ-CD formed a complex with PMeVE in 80% yield, it did not form complexes with the low molecular weight analogues, such as diethyl ether and trimethylene glycol dimethyl ether. The complex formation of γ-CD with PMeVE was studied quantitatively. The amount of the complex formed increases with an increase in the amount of PMeVE added to the aqueous solution of γ-CD. The saturation was observed, indicating stoichiometric complexation. The continuous variation plot for the formation of the complex between γ-CD and PMeVE showed a maximum at 0.25, indicating 3:1 (MeVE unit : γ-CD) stoichiometry. This result suggests that three MeVE units were bound in each γ-CD cavity. The stoichiometry was further confirmed by the use of ^{1}H NMR spectroscopy. Figure 1 shows the ^{1}H NMR spectrum of the complex. The spectrum shows that the methyl protons of PMeVE (3H x 3) and C1-H proton of γ-CD (8H) or C2-H and C-4H protons (8 x 2H) in 9 : 8 or 9 : 16 ratio, respectively. The

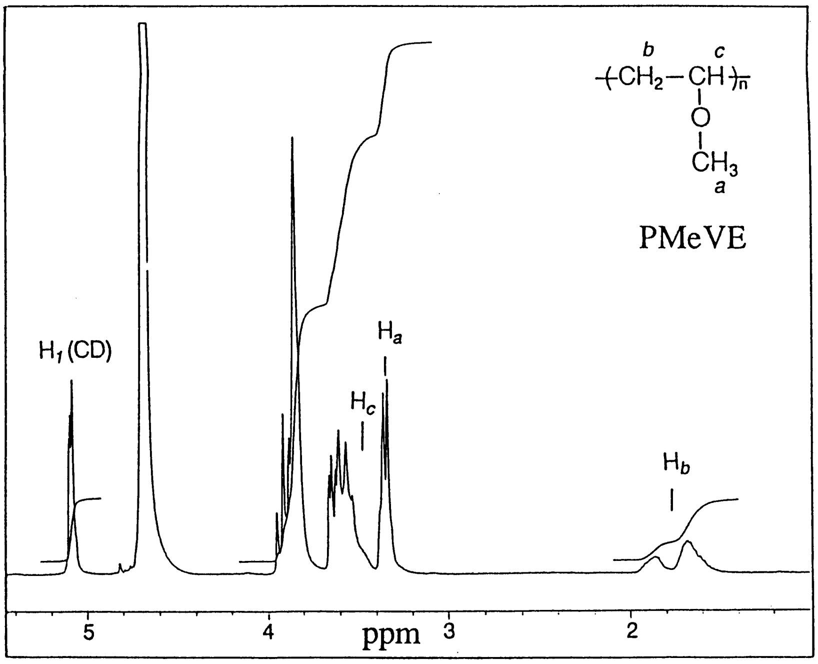

Fig. 1. ^{1}H NMR spectrum of the complex between γ-CD and PMeVE.

length of the three MeVE units corresponds to the depth of the γ-CD cavity (7A). Figure 2 shows a suggested structure of the complex between γ-CD and PMeVE.

The complex was isolated by filtration or centrifugation, washed, and dried. The complex was found to be dissolved in hot water or in a large amount of water. The addition of an excess amount of benzoic acid, which is thought to be a competitive inhibitor, to the suspension of the complex resulted in solubilization of the complex. Thus the formation of the complex seems to be reversible. γ-CD did not form complexes at all with structurally similar polymers, e.g., poly(butyl vinyl ether) and poly(methyl vinyl ketone). They are too large to thread into the cavities. The inclusion complex with PMeVE is thermally stable. Thermogravimetric analysis shows that the complex begins to decompose at 310 °C which is little higher than the decompositon temperature for each component. PMeVE stabilizes γ-CD. The X-ray diffraction pattern shows that the complex is crystalline.

Molecular model studies show that PMeVE chains are able to penetrate γ-CD cavity, while the PMeVE chain cannot pass through the α-CD or β-CD cavity owing to the hindrance of the methoxy group on the main chain. These views are in accordance with our results that γ-CD formed a complex with PMeVE but α-CD and β–CD did not form complexes with PMeVE. Model studies further indicate that the single cavity accommodates three methyl vinyl ether units. The ^{13}C CP/MAS NMR spectrum of the

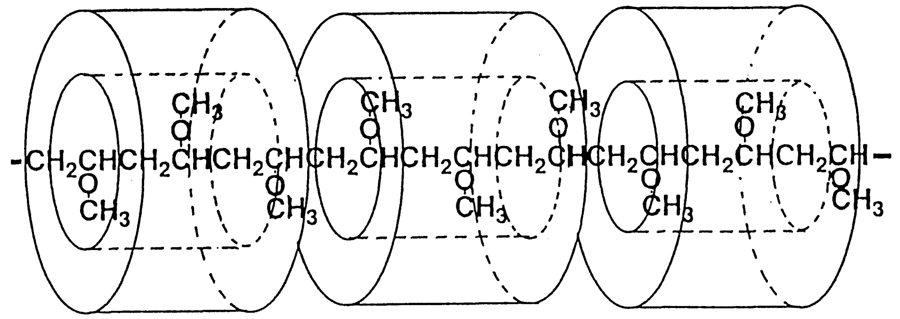

Fig. 2. Proposed structure of the complex between γ-CD and PMeVE.

complex shows that each carbon of the glucose can be observed in a single peak, indicating that γ-CD includes the polymer and assumes symmetrical conformation, although that of γ-CD shows less symmetrical conformation due to the absence of guests in the cavity.

In conclusion, γ-CD specifically forms a complex with poly(methyl vinyl ether) in a definite stoichiometry in high yields, although α-CD and β-CD did not form complexes with PMeVE. Studies of the detailed structure of the complex are now in progress.

References

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(Received October 12, 1992)