SHORT COMMUNICATIONS

Relative Size Effect on the Polymerization with Methyl Cholate Inclusion Compounds

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Inclusion polymerization can be recognized as a one-dimensional polymerization in an anisotropic molecular-level space, while conventional ones in solution or in bulk are three-dimensional ones in isotropic macroscopic-level spaces. This generalization is based on our following finding; in the former case, the relative size between a monomer molecule and a channel plays a decisive role in the polymerization behavior, while such a relative size effect can be neglected in the latter case.[1]

We so far studied the effect by use of a pair of host, deoxycholic acid (DCA) and apocholic acid (ACA) (Channel size: ACA > DCA). In order to discuss the effect in further detail, we need another hosts which form channels slightly different from those of DCA and ACA in size. Recently, we found that cholic acid (CA) and its derivatives form channel-type inclusion compounds with a variety of organic substances.[2-4] We now find that methyl cholate (MC) among these hosts can serve as the third host suitable for the one-dimensional inclusion polymerization.
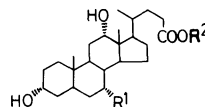
Cholic acid (CA); $R^1 = OH$, $R^2 = H$
Methyl cholate (MC); $R^1 = OH$, $R^2 = CH_3$
Deoxycholic acid (DCA); $R^1 = H$, $R^2 = H$
Methyl deoxycholate; $R^1 = H$, $R^2 = CH_3$
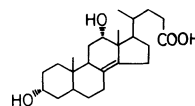
Apocholic acid (ACA)

This communication deals with the relative size effect on the polymerization with MC inclusion compounds, as compared with those in DCA and ACA ones. The effect can be understood through a structural viewpoint that MC channels are larger in size than DCA and ACA ones.

EXPERIMENTAL

Methyl cholate was prepared from commer-

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cially available cholic acid (Sigma Co.) by esterification with methanol containing hydrogen chloride.[5] The crude product was purified by recrystallization from methanol. The solvent-free methyl cholate was obtained by heating at 110°C for 20 hours under vacuum. The inclusion compound of a monomer with methyl cholate was prepared as follows; 1.0 g of methyl cholate and an equimolar amount of a monomer were placed in a glass tube of 10 mm diameter, which was sealed under vacuum (10^{-3} Torr) after three freeze thaw cycles. The tube was allowed to stand at 25°C over 20 hours to form inclusion compounds, and then exposed to γ-irradiation from a ^{60}Co source at 0°C for one hour with a total dose of 1.0 Mrad. After the irradiation the tube was allowed to stand at a definite temperature in order to postpolymerize and then cooled again to -78°C. The contents were immediately poured into an excess amount of methanol to separate the polymer from methyl cholate. The methanol-insoluble fraction was filtered, dried under vacuum, and weighed.

The microstructures of the polymers were determined on the basis of IR, ^{1}H, and ^{13}C NMR spectroscopy. ESR measurements were carried out as described earlier.[11]

RESULTS AND DISCUSSION

We carried out the inclusion polymerization of various diene and vinyl monomers by use of MC and its derivatives. The procedure was similar to that employed for DCA and ACA. MC gave a significant amount of the polymers, while CA and methyl deoxycholate did not. In the absence of the host molecules, we obtained only a trace amount of the polymers under the same conditions.

We studied the inclusion polymerization using MC in detail. And we compared the polymerization behavior with ones in cases of DCA and ACA,[1,6] with respect to the polymerizability of the included monomers, the stability of the included propagating
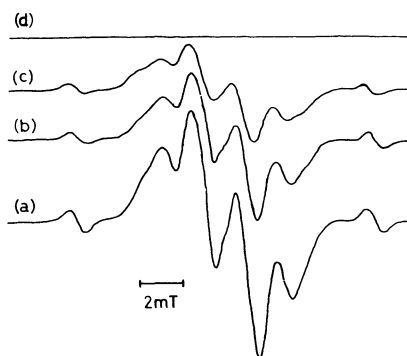

Figure 1. ESR spectra of the propagating radicals derived from methyl 2,4-pentadienoate in methyl cholate inclusion compounds. They were observed at 25°C (a), 50°C (b), 75°C (c), and 100°C (d).

radicals, and the microstructure of the resulting polymers, as described below.

First, conjugated diene monomers, such as 2,3-dimethyl-1,3-butadiene and 1-chloro-1,3-butadiene, polymerized to give rubber-like polymers, while solid polymers in cases of DCA and ACA. The diene monomers with no or one methyl substituent gave the polymers in poor yields, while in significant yields in DCA and ACA channels. In addition, conventional vinyl monomers, such as methyl methacrylate and so on, polymerized to yield atactic polymers, although such vinyl monomers hardly polymerized in channels of DCA and ACA.[7]

Secondly, the propagating radicals were not so stable as those in case of DCA and ACA. We often observed ESR spectra derived from both the propagating radicals and the host radicals at room temperature. Figure 1 shows the ESR spectra of the radicals derived from the inclusion compound of MC with methyl 2,4-pentadienoate. The signals disappeared by increasing temperature up to 100°C, whereas they did not in cases of DCA and ACA.[6]

Thirdly, the stereoregularity of the resulting diene polymers was much lower than those in cases of DCA and ACA. The content of 1,4-*trans* structure was 70 to 90%, while it was almost quantitative in the latter case. For
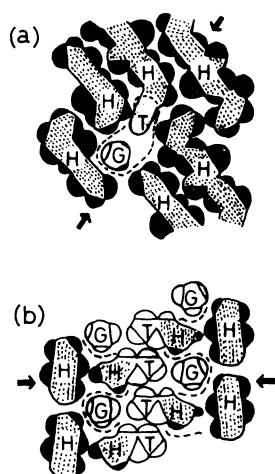
Figure 2. Schematic drawings of cross-sections of the methyl cholate inclusion compounds with 0.2 Å of thickness by means of space-filling models.[9] (a): A horizontal view; two arrows correspond to the cross-section shown in the lower figure (b). (b): A vertical view; two arrows show the position of the section of the upper figure (a). "H", "T", and "G" indicate methyl cholate, its tail part, and methanol, respectively. Dotted lines show the approximate edges of the channel together with side pockets.

example, in case of poly(2,3-dimethyl-1,3-butadiene) obtained by the inclusion polymerization in MC channels, the ^{1}H NMR spectrum showed two large peaks at 1.78 and 2.18 ppm due to 1,4-*trans* structure as well as neighboring small peaks due to 1,4-*cis* structure. The content of 1,4-*trans* structure is higher than that of the polymer obtained in solution, but lower than those obtained quantitatively in DCA and ACA channels.[8]

We observed relative size effects from three viewpoints as mentioned above. All the results are consistent with an idea that the polymerization reaction spaces of MC channels are larger than those of DCA and ACA ones. This is supported by a molecular graphics study[9] of the crystal structure of the inclusion compound of MC with methanol.[3] Figure 2 shows horizontal and vertical views of the assembly. The MC molecules basically form bilayer assembly to leave channels with side

pockets, like the cases of DCA, ACA, and CA.[4] The esteric parts of the steroidal tails and the methanol molecules are located in the channels and the side pockets, respectively. In the absence of methanol, however, we may expect that the monomer molecules could be included into the channels and the side pockets instead of the tails and the methanol molecules. Moreover, we clarified that cholic acid inclusion compounds show guest-responsive structural changes through tail parts of the host molecules.[10] Nonpolar character of the esteric part of the MC may lead to an increase of the flexibility of the assembly. Therefore, it seems reasonable to assume that MC channels can serve as polymerization reaction spaces a little larger than DCA and ACA ones.

In conclusion, the present study demonstrates that MC can provide a new channel suitable for the study on the relative size effect on the inclusion polymerization. Further systematic research for the design of channel-type organic inclusion compounds would be useful for finding various molecular-level spaces for polymerization reactions.

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