SHORT COMMUNICATIONS

**Functional Monomers and Polymers CXXX.[†]
Synthesis of Inclusion Compounds of Dehydrochlorinated
Poly(2-chloroacrylonitrile) in Deoxycholic
and Apocholeic Acid Canals**

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Inclusion polymerization is a unique way to obtain well-designed, tailor-made polymers.^{1,2} Earlier, we found that deoxycholic acid (3 α ,12 α -dihydroxy-5 β -cholan-24-oic acid; DCA) and apocholeic acid (3 α ,12 α -dihydroxy-5 β -chol-8(14)-en-24-oic acid; apoCA) can provide tunnel-like spaces, called canals, which are suitable for one-dimensional polymerization.^{3,4} Our further study was concerned with the asymmetric induction of prochiral diene monomers in such canals during the polymerization to obtain optically active polymers in high optical yield.⁵

On the other hand, electrically conducting polymers, such as polyacetylene, have recently received much attention.^{6,7} Those highly oriented polymers attract much interest, because such chain alignment should improve their physical and chemical properties.⁸⁻¹⁰ It is expected that the incorporation of such polymers into canals will yield a novel type of functional composite materials with unique electrical and optoelectronic properties. The present communication reports the first synthetic example of polymeric inclusion com-

pounds of high unsaturation in DCA and apoCA canals.

RESULTS AND DISCUSSION

The polymerization of 2-chloroacrylonitrile included in DCA and apoCA canals was studied in a way similar to that in the case of butadiene derivatives⁵ (see Figure 1). 2-Chloroacrylonitrile was chosen as the monomer because it could be easily packed into the canals and the fact that its polymerization behavior has been extensively studied.¹¹⁻¹³

DCA- or apoCA-monomer inclusion compounds (2) were prepared, as already described,⁵ by incorporating the monomer molecules into the vacant canals of solvent-free DCA or apoCA crystals (1). Then the monomers present in the canals were polymerized by heating after γ -ray irradiation. During the procedure, the resulting crystalline products were found to keep their original shape and appearance, which was observed by scanning electron microscopy. The melting point of DCA including the polymer (3) (165—166°C;

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Figure 1. Schematic representation of the process of inclusion polymerization and dehydrochlorination using DCA and apoCA as host molecules.

168—170°C for apoCA including the polymer) was found to be lower than that of DCA itself (1) (176—178°C; 172—174°C for apoCA). The methanol-insoluble solids (6), after the extraction of the host molecules with boiling methanol, were found to keep their original crystalline shape of the inclusion compounds by scanning electron microscopy.

In the absence of DCA or apoCA, the polymer yield was low (less than 2 mg from 220 mg of the monomer under the condition used). On the other hand, the inclusion polymerization gave a relatively high yield (50%) of the polymer (110 mg from 1.0 g of DCA, and 55% in case of apoCA, 120 mg from 1.0 g) in the canals, when a 1 : 1 mole ratio of the guest to host molecules was used. The resulting polymers did not melt below 300°C. While the polymers obtained at temperatures lower than 50°C are soluble in acetone, ethyl methyl ketone, dimethyl sulfoxide and dimethylformamide, and insoluble in chloroform, carbon tetrachloride, *o*-dichlorobenzene

and dichloroacetic acid, those obtained at temperatures higher than 80°C are insoluble in all of the above mentioned organic solvents. This suggests a high molecular weight and/or a stereo-regular structure of the polymers formed in the canals.

We further carried out the dehydrochlorination of poly(1-chloro-1-cyanoethylene) [poly(2-chloroacrylonitrile)] included in the DCA or apoCA canals (3), by heating at 140°C without adding an acceptor. The conversion in the DCA canals amounted to 70% after one day, as evaluated by elemental analysis. During the heating procedure, the color of the crystalline substances turned black. However, the included poly(1-cyanovinylene)s (4) kept still their original shape and appearance, as observed by scanning electron microscopy (Figure 2a). The IR spectra showed bands at 2225cm^{-1} due to the cyano groups of the dehydrochlorinated polymers (CN-absorption before the reaction: 2240cm^{-1}). The melting point of the inclusion

Figure 2. Scanning electron microscopic photographs of dehydrochlorinated poly(2-chloroacrylonitrile) included in DCA (4) (a) and of poly(1-cyanovinylene) (7) obtained by dehydrochlorination of poly(2-chloroacrylonitrile) (6) (b).

product (3) in DCA decreased from 165–166°C to 145–147°C after dehydrochlorination to (4), and the product (4) resulting from the inclusion product (3) in apoCA decomposes gradually above 165°C. The black-colored, dehydrochlorinated polymer (5) obtained by separation from the deoxycholic acid canals, also showed the IR absorption band at 2225 cm^{-1} . The polymer did not dissolve in the usual organic solvents, and did not melt below 300°C. A perfect separation of the dehydrochlorinated polymers from the host molecules was not possible by treatment with boiling methanol, probably due to some reactions of the unsaturated polymers with the host molecules in the canals.

The dehydrochlorination of poly(2-chloroacrylonitrile) (6), which was previously separated from the host molecules by treatment with hot methanol, was then carried out at 140–200°C in a way similar to that reported earlier.^{11–13} It is to be noted, in this case, that the resulting polymers kept their layer structure, as can be seen in Figure 2b. From the results, it is suggested that the polymers were dehydrochlorinated in an oriented assembly.

By using the direct current two point method, the electric conductivity of dehydro-

chlorinated poly(2-chloroacrylonitrile) included in DCA canals (4) was measured at room temperature; the value of 10^{-10} to $10^{-11}\ \Omega^{-1}\text{ cm}^{-1}$ in the direction of the canals without doping increased to the value of $10^{-6}\ \Omega^{-1}\text{ cm}^{-1}$ on iodine doping.

Detailed studies on the dehydrochlorination in the canals and the electric properties of the resulting polymers as well as doping studies are now in progress.

EXPERIMENTAL

Commercially available DCA was purified by recrystallization from acetone. ApoCA was prepared by dehydrating cholic acid with zinc chloride in acetone solution and purified by recrystallization from acetone. 2-Chloroacrylonitrile was a commercial reagent of pure grade and purified by distillation before use.

The inclusion compounds (2) were typically prepared as follows: 1.0 g of solvent-free DCA or apoCA and 0.22 g of 2-chloroacrylonitrile (1 : mole ratio of guest to host molecules) were placed in a glass tube 10 mm in diameter, which was sealed in vacuum (10^{-3} mbar) after three freeze-thaw cycles. The sealed tube was allowed to stand at room temperature

for more than 1 h to form the inclusion compounds.

Irradiation of the inclusion compounds (2) in the sealed tube was provided by γ -rays from a ^{60}Co source at 0°C for 1 h with a total dose of 1.0 Mrad. After the irradiation, the tube was warmed at 70°C for 4 days in order to allow the monomer to polymerize in the canal.

The separation of the polymers from the host molecules was performed by pouring the inclusion compounds into excess methanol before or after dehydrochlorination. The methanol-insoluble polymers were washed thoroughly with hot methanol and dried under reduced pressure.

Dehydrochlorination of the inclusion polymers was carried out at 130 – 140°C for one day.

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