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Asymmetric Inclusion Polymerization in Apocholic Acid Canals

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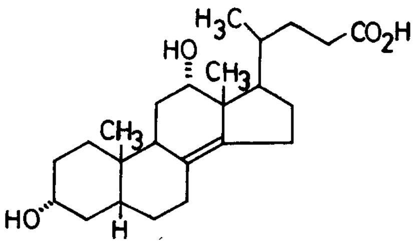
Summary

Asymmetric inclusion polymerization of four prochiral diene monomers was studied in apocholic acid canal complexes. All the polymers obtained were found to show specific rotations of (-) sign,different from the cases of polymerization in deoxycholic acid canals.

Introduction

Asymmetric inclusion polymerization is a novel method for obtaining optically active, stereoregular polymers, which proceeds under the topochemically controlled condition in chiral crystals (GREEN et al. 1979). Recently, two groups have performed the asymmetric inclusion polymerization in question using deoxycholic acid as the host molecule (AUDISIO et al. 1976; MIYATA and TAKEMOTO 1977). In the preceding paper, we reported thus the synthesis of optically active polymers from trans-2-methyl-1,3-pentadiene (MIYATA and TAKEMOTO 1977).

On the other hand, it has been known that apocholic acid forms also stable inclusion complexes with a variety of organic compounds (HERNDON 1967). Recently, the crystal structure of the apocholic acid-acetone inclusion complex has been investigated (LAHAV et al. 1978). In this communication we report the radiation-induced asymmetric polymerization of four prochiral monomers (trans- or cis-1,3-pentadiene and trans- or cis-2-methyl-1,3-pentadiene) in apocholic acid inclusion complexes as the host molecule.



Apocholic acid

Experimental

Materials: All monomers used were prepared according to the literatures (CRAIG 1943; FRANK et al.1947; FREY and ELLIS 1965; CUZIN et al.1967), which were purified by fractional distillation or preparative gas chromatography using β,β'-oxydipropionitrile as the liquid phase, and confirmed to be of more than 99 % purity by gas chromatography. Apocholic acid was prepared by dehydrating cholic acid with zinc chloride in acetone solution (DEVOR and MARLOW 1946), and purified by recrystallizing from acetone. The solvent-free apocholic acid was then obtained by heating at 100°C for 6 hr under vacuum (3 Torr); $[\alpha]_D^{20} = +50°$ (in ethanol).

Procedure of forming apocholic acid-monomer inclusion complexes and their polymerizations: 1.0 g of the solvent-free apocholic acid and 0.50 cm^3 of diene monomer were placed in a glass tube of 10 mm diameter, which was then sealed under vacuum (10^{-3} Torr) after three freeze-thaw cycles. The sealed tubes were stood at 25°C for more than 20 hr to form the inclusion complexes. Irradiation was provided by γ-rays from a ^{60}Co source at 0°C for 2 hr with a total dose of 1.0 Mrad. After the irradiation, the tubes were warmed at 50°C for 48 hr in order to allow the contents to postpolymerize. The contents were then poured into excess methanol to separate apocholic acid from the polymers formed. The polymers thus obtained were washed thoroughly with hot methanol and dried under reduced pressure. The polymers were found to be free from apocholic acid, which was confirmed by IR, ^1H and ^{13}C NMR spectroscopies. It was also found that apocholic acid was stable enough under the irradiation condition used.

Results and Discussion

The procedure for polymerizing the monomers in apocholic acid inclusion complexes was followed in the similar manner to that in deoxycholic acid inclusion complexes. It was found that all monomers used form inclusion complexes with apocholic acid, and polymerize exclusively in the canals and not outside of them under the condition studied. The crystals of apocholic acid inclusion complexes kept their original shapes and appearance during the polymerization. The apocholic acid-polymer inclusion complexes melted at higher temperatures than that of apocholic acid itself. After extraction of apocholic acid with hot methanol, the insoluble residue remained was found to consist of optically active polymers. The polymer yield attained about 80 mg per 1.0 g of apocholic acid.

Table 1 summarizes the properties of the polymers thus obtained. The polymers were found to have pre-

TABLE 1

Properties of Polymers Obtained by Asymmetric Inclusion Polymerization in Apocholic Acid Canal Complexes

Monomer[a]	M.W.[b] (x10^{-4})	Micro-structure(%)[c] 1,4-trans	1,4-cis	$[\alpha]_D^{20}$[d]	Ref.[e] $[\alpha]_D$
trans-1,3-PD	1.0	90	10	-6.5°	+7.5° (PHTP[f]) +0.3° (DCA[g])
cis-1,3-PD	1.0	90	10	-3.7°	-21° (DCA[g])
trans-2-Me-1,3-PD	3.5	95	5	-106°	+90° (DCA[h])
cis-2-Me-1,3-PD	4.0	100	0	-66°	+320° (DCA[i])

a) PD = pentadiene, Me = methyl b) molecular weight measured by vapor pressure osmometry c) measured by ^{13}C NMR spectroscopy d) in CCl4 e) PHTP = perhydrotriphenylene, DCA = deoxycholic acid f) lit. (FARINA et al. 1967; FARINA 1975) g) lit. (AUDISIO et al. 1976) h) lit. (MIYATA and TAKEMOTO 1977) i) lit. (MIYATA et al. in contribution).

dominantly 1,4-trans tactic structure, which was confirmed by IR, ^{1}H and ^{13}C NMR spectroscopies: Poly(1,3-pentadiene) contains a small amount of 1,4-cis structure, while poly(2-methyl-1,3-pentadiene) consists almost exclusively of 1,4-trans structure.

It can be seen from Table 1 that the polymers obtained from prochiral monomers show in general high optical rotation. Furthermore, the optical activity of the polymers shows an opposite sign to that of apocholic acid itself. The results support the asymmetric synthesis by the polymerization in apocholic acid canal complexes.

The table also shows that the sign of the optical rotation of four polymers is (-), and that the polymers obtained from trans prochiral monomers have higher rotation value as compared with those from cis monomers. It is interesting to note that the polymers of 2-methyl-1,3-pentadiene obtained by the inclusion polymerization in deoxycholic acid canals have specific rotation values of (+) sign, while the values obtained by the inclusion polymerization in apocholic acid canals are of (-) sign. The problem how the polymers having the optical rotation values of arbitrary sign can be prepared by choosing appropriate combination of host and guest molecules should be clarified in future. Studies of the polymerization behavior in detail, as well as the properties of the polymers are now in progress.

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