Functional Monomers and Polymers. XXXIX. Synthesis of Optically Active Poly(*trans*-2-methylpentadiene) by Asymmetric Inclusion Polymerization in Deoxycholic Acid*

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Inclusion polymerization is one of the unique polymerization techniques used in the solid state to prepare stereoregular polymers, particularly optically active diene polymers. In 1967, Farina, *et al.*,¹ reported on the first asymmetric inclusion polymerization of *trans*-penta-1,3-diene using chiral perhydrotriphenylene as the host molecule. Very recently, Audisio, *et al.*,² studied the inclusion asymmetric polymerization of penta-1,3-dienes in deoxycholic acid (3 α ,12 α -dihydroxy-5 β -cholan-24-oic acid, I). The natural steroidal

acid as the host molecule. It is worth noting that the polymer thus prepared showed a substantially higher optical rotation than the rotations of other usual synthetic vinyl and diene polymers hitherto known.

Commercially available deoxycholic acid was purified by repeated recrystallization from acetone. *trans*-2-Methylpenta-1,3-diene was a commercial reagent of pure grade (Aldrich Co.) and was used without further purification. The monomer—deoxycholic acid inclusion compounds were prepared as follows: 1.0 g of deoxycholic acid, 0.4 ml of *trans*-2-methylpenta-1,3-diene, and 2.5 ml of ethanol were placed in a glass tube of 12-mm diameter, which was then sealed under vacuum (1×10^{-3} mmHg) after three freeze-thaw cycles. The sealed tube was warmed to 70–80°C to give a homogeneous solution and then cooled gradually. Formation of the adducts was indicated by the appearance of small needle-like crystals. The tube was exposed to γ -irradiation from a Co⁶⁰ source at –196°C for 2 hr with a dose rate of 3.0×10^5 rad/hr. After the irradiation, the tube was warmed overnight at 50°C in order to allow the content to postpolymerize, and then cooled again to –196°C and cut off. The content of the tube was immediately poured into excess methanol to separate deoxycholic acid from the polymer formed. The polymers thus

acid in question is a chiral molecule and forms stable inclusion compounds with a variety of organic substances,³ including vinyl and diene monomers;^{4,5} the polymerization of these monomers included in the deoxycholic acid canal was comprehensively studied.^{4–7}

In this communication, we wish to describe the first synthesis of the optically active polymer, poly(*trans*-2-methylpentadiene), from its prochiral monomer, *trans*-2-methylpenta-1,3-diene, by asymmetric inclusion polymerization using deoxycholic

* For Part 38 of this series, see ref 7.

obtained were washed with hot methanol thoroughly and dried under reduced pressure (18-mg yield).

The polymer which resulted melted at 159–164°C and was soluble in *o*-dichlorobenzene and tetralin. Its viscosity number (η_{sp}/c) in *o*-dichlorobenzene at 70°C was 0.26 dl/g ($c=0.20$ g/dl). IR and ^1H —NMR spectra were found to be almost identical with those of poly(2-methylpentadiene) obtained by inclusion polymerization using racemic perhydrotriphenylene as the host molecule.⁸

The polymer was found to show a high optical rotation of the same sign as that of deoxycholic acid itself ($[\alpha]_D=+55^\circ$ in ethanol): $[\alpha]_D=+250^\circ$; $[\alpha]_{577}=+290^\circ$; $[\alpha]_{546}=+350^\circ$; $[\alpha]_{435}=+560^\circ$; $[\alpha]_{365}=+940^\circ$ (measured at 26°C in 0.11×10^{-3} g/ml in *o*-dichlorobenzene solution). It is noteworthy that these specific rotation values are much higher than those of polypentadienes obtained either by inclusion or by coordination polymerization. That is, *cis*-1,4-polypentadiene obtained by inclusion polymerization in deoxycholic acid canal² showed a specific rotation of -21° ($[\alpha]_D$ in toluene), and *trans*-1,4-polypentadiene obtained by the polymerization in chiral perhydrotriphenylene showed one of $+7.5^\circ$ ($[\alpha]_D$).^{1,9} It should also be recalled that the coordination polymerization of these monomers gave polymers having specific rotation values of

$+10^\circ$ to -10^{+10} and -7.95^{+11} .

Thus, we obtained poly(*trans*-2-methylpentadiene) with high optical rotation by a radiation-induced canal polymerization technique, using deoxycholic acid as the host molecule. Studies of the polymerization behavior in detail, as well as of the properties of the polymers obtained, are now in progress.

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