# Inclusion Asymmetric Polymerization of Penta-1,3-dienes in Deoxycholic Acid

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*Summary* γ-Ray irradiation of inclusion compounds of deoxycholic acid with *cis*- and *trans*-penta-1,3-dienes results in asymmetric polymerization leading to polymers with different optical activities.

THE synthesis of optically active polymers by γ-ray irradiation of prochiral monomers included in asymmetric compounds has particular relevance to solid state stereospecific polymerization. As far as we know, there is only one report on inclusion asymmetric polymerization, that is of *trans*-penta-1,3-diene included in perhydrotriphenylene.[1] In order to establish the mechanism and the type of asymmetric induction in this reaction, we used DCA (3α,12α-dihydroxycholanic acid) as the host matrix. This natural optically active acid forms inclusion compounds with numerous hydrocarbon and non-hydrocarbon products.[2]

| Included penta-1,3-dienes | $[\alpha]_D^{26}$[a] | $[\eta]$/dl $g^{-1}$[b] | Polymer structure 1,4-*trans* : 1,4-*cis* : 1,2 |
|---|---|---|---|
| *cis* | −21 | 0·6 | 97 : 3 : 0 |
| *trans* | +0·3 | 0·7 | 91 : 6·5 : 2·5 |
| *cis* + *trans* (30 : 70) | −4 | 0·7 | 92 : 3·5 : 4·5 |
| *cis* + *trans* (70 : 30) | −10 | 0·8 | 91 : 7 : 2 |

[a] For DCA, $[\alpha]_D^{26} = +53°$ (*c* 1, MeOH). For polymers, $[\alpha]_D^{26}$ was measured in $CHCl_3$. [b] Measured in PhMe.

Inclusion compounds between DCA and 2,3-dichlorobutadiene and between DCA and 2,3-dimethylbutadiene have been recently reported.[3] These compounds, after γ-ray irradiation, and removal of DCA with boiling methanol gave the polymer as an insoluble solid. We have found that DCA can form inclusion compounds with pure *cis*- and *trans*-penta-1,3-dienes and also with a mixture of the two. The inclusion compounds were sealed in vials under reduced pressure and irradiated with γ-rays at room temperature with a total dose of 0·5 Mrad in 4 h. After extraction of DCA with boiling methanol, the insoluble residue consisted of optically active polypentadiene. The inclusion compound melted in the range 150—180 °C before irradiation, probably because of decomposition. However, after irradiation, the melting point of the solid was 195 °C (DCA melts at 176 °C).

The polypentadiene obtained was shown by $^1H$ and $^{13}C$ n.m.r. spectroscopy to have predominantly the *trans*-structure. It is interesting to note that polymer obtained from *cis*-penta-1,3-diene shows the highest stereospecificity. In this case optical activity has an opposite sign to that of DCA and it is distinguishable from that of the polymer obtained from the *trans*-isomer. Intermediate values of optical activity were obtained for polypentadienes obtained from a mixture of *cis*- and *trans*-penta-1,3-dienes.

It appears from the initial data (Table) that the polymer obtained from *cis*-penta-1,3-diene is essentially of isotactic type and that this tacticity is not maintained in the polymer derived from the *trans*-isomer.

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