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Inclusion Asymmetric Polymerization in Deoxycholic Acid by "Through-Space" Asymmetric Induction

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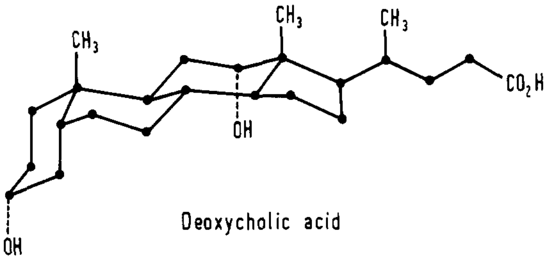
ABSTRACT: *trans*-1,3-Pentadiene (I) and *cis*-1,3-pentadiene (II) can be included in natural asymmetric deoxycholic acid and polymerized in the presence of γ rays. Two polymers with different rotatory powers were obtained: about zero for the polypentadiene from I and $[\alpha]^{25}_{D}$ −21° for the polypentadiene from II. After ozonolysis and recovery of methylsuccinic acid ($[\alpha]^{25}_{D}$ +3.5°), an optical purity of 20% was determined. ^{13}C NMR investigation indicates that the polymer obtained from II has a 1,4-trans stereoregularity higher than that of the polymer obtained from I. From ^{13}C NMR resolution-enhanced spectra of the methyl and methylene groups, the microtacticity of these two polypentadienes was also deduced. Both polymers are atactic with respect to the asymmetric carbon atoms; the polypentadiene from II has a small predominance of isotactic configuration sequences. Some considerations on the microtacticity data suggest that the asymmetric induction in this radical polymerization may occur by van der Waals interactions.

Introduction

Inclusion polymerization is a solid-state reaction that occurs, in the presence of γ rays, in crystalline matrices capable of forming channel-type inclusion compounds with dienic monomers. The best known such matrices are urea, thiourea, and perhydrotriphenylene.[1] This last compound, in particular, is dissymmetric and has been separated into optical antipodes.[2,3]

The first example of inclusion asymmetric polymerization was obtained from an inclusion compound between an antipode of perhydrotriphenylene and a prochiral monomer such as *trans*-1,3-pentadiene.[4]

Deoxycholic acid or 3α,12α-dehydroxycholanic acid



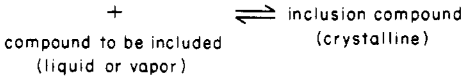
Deoxycholic acid

(DCA), like the three above-mentioned matrices, forms channel-type inclusion adducts with various molecules[5] as well as with 2,3-dichlorobutadiene and 2,3-dimethylbutadiene, which polymerize in the presence of γ radiation.[6] Furthermore, DCA is an asymmetric natural product ($[\alpha]^{25}_{D}$ +54.5°). These facts prompted us to study this particular solid-state polymerization system from two points of view: its general mechanism with particular reference to asymmetric induction during polymerization, and the nature of the polymers obtained.

Inclusion Compounds

DCA is a natural product present in bile; the structure of its channel-type adducts in the crystalline state has been clarified by X-ray diffraction.[7,8] These consist of DCA molecules attached to each other by hydrogen bonds to form planes that approach each other, leaving a channel-shaped space in which guest molecules can be inserted.

As in the case of urea, thiourea, and perhydrotriphenylene (PHTP), the crystal lattice of DCA is unstable too if the guest molecule is missing. In fact an equilibrium exists:[9]



$$\begin{array}{c}\text{matrix (crystalline)}\\ +\\ \text{compound to be included}\\ \text{(liquid or vapor)}\end{array} \rightleftharpoons \begin{array}{c}\text{inclusion compound}\\ \text{(crystalline)}\end{array}$$

Inclusion adducts between DCA and low-boiling compounds may be formed by using the "equilibration" technique already used in the case of PHTP.[10] By this technique, and using the vial shown in Figure 1, inclusion adducts of DCA with *cis*-1,3-pentadiene and of DCA with *trans*-1,3-pentadiene were obtained. These adducts, examined by DTA and by a hot-plate microscope, show a decomposition point between 155 and 160 °C with the formation of a new crystal phase that melts at 176 °C, i.e., the melting point of DCA.

This behavior on heating is general for all low-boiling substances; in fact the inclusion compounds of DCA with acetone and of DCA with methanol (two solvents of this acid) decompose respectively at 130–135 and 145–150 °C. The stoichiometry of the adducts of DCA with pentadiene was calculated by using the vial shown in Figure 1. In the inclusion compounds between DCA and *cis*-1,3-pentadiene, the molar ratio is 2.5 whereas in the inclusion compounds between DCA and *trans*-1,3-pentadiene it is 2.

As already known, these inclusion compounds can be also obtained by precipitation, adding the host compound to a solution of DCA generally in methanol or acetone.[6,11]

Experimental Section

Polymerization. A quantity of DCA (10–50 g) is introduced into part A of the vial shown in Figure 1, which is then sealed under high vacuum. Pentadiene is transferred into part B, which is then also sealed under high vacuum. The dividing sector is broken, and DCA is allowed to "absorb" pentadiene up to a constant level. After equilibrium has been reached, the vial, with or without part B, is subjected to a γ-ray dosage of 0.4 Mrd for 4 h. After irradiation, the inclusion compound between DCA and pentadiene (decomposition point 160 °C) is transformed into the inclusion adduct of DCA–polypentadiene (mp 195 °C). This is extracted continuously with boiling methanol. The DCA is removed completely, and the residue constitutes the polymer. It is possible to obtain 64 mg of polypentadiene per gram of DCA from the inclusion compound against a theoretical yield of 86.6 mg; 54 mg of polypentadiene per gram of DCA can be obtained from the DCA–*cis*-pentadiene adduct against a theoretical yield of 69.3 mg. In both cases the conversion is 80% (yield of methanol-insoluble polymer). From both *cis*- and *trans*-1,3-pentadiene, it is possible to obtain *trans*-1,4-polypentadiene, the physical properties of which are listed in Table I.

The ^{13}C NMR spectra (Figure 2) show that the polypentadiene obtained from *cis*-1,3-pentadiene has a higher structural homogeneity, i.e., has only a small percentage of cis-1,4 arrangement. On the contrary, the polypentadiene obtained from *trans*-1,3 pentadiene shows a greater quantity of cis double bonds as well as a trans-1,2 type arrangement.[12]

Materials and Methods. A commercial deoxycholic acid was further purified by maintaining it under high vacuum at 150 °C

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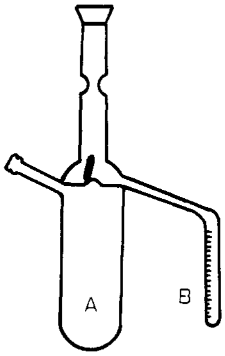

Figure 1. DCA powder is introduced into section A of the vial, and the monomer to be included is placed in section B.

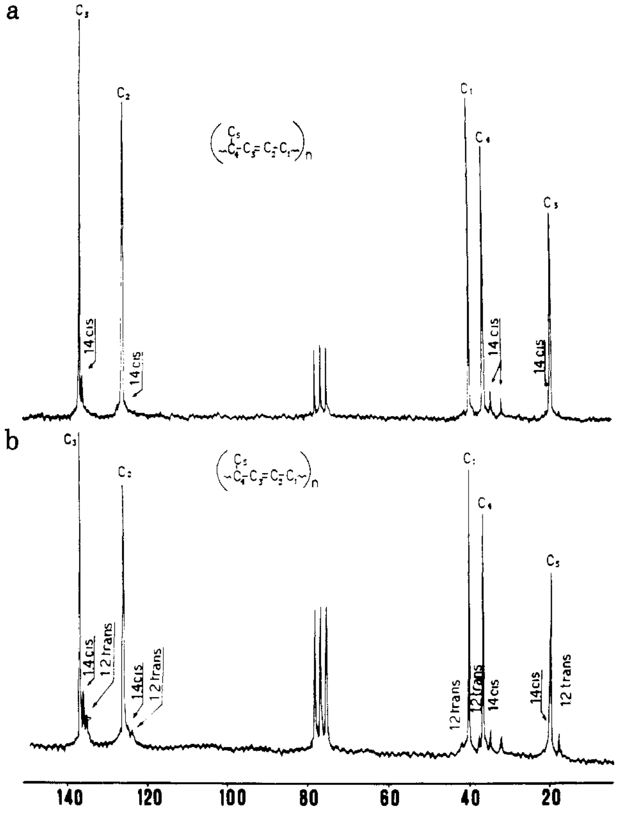

Figure 2. ^{13}C NMR spectra of polypentadiene obtained by DCA inclusion (a) from *cis*-pentadiene and (b) from *trans*-pentadiene. The triplet at 78 ppm comes from $CDCl_3$ solvent.

Table I

			polymer structure		
included 1,3-pentadienes	$[\alpha]^{25}{}_D$,[a] deg	η,[b] dL g^{-1}	trans 1,4, %	cis 1,4, %	1,2, %
cis	−21	0.6	97	3	0
trans	+0.3/−3	0.7	91	6.5	2.5

[a] For DCA, $[\alpha]^{25}{}_D$ +54.5° (*c* 1, MeOH); for polymers, $[\alpha]^{25}{}_D$ was measured in $CHCl_3$. [b] Measured in toluene.

for 24 h. *cis*- and *trans*-1,3-pentadiene and 3-methylpentadiene were pure-grade commercial products. Ozonolysis was carried out as previously described in ref 9. NMR spectra were performed as described in ref 14.

Tacticity of Polypentadiene

As already known, pentadiene consists of prochiral molecules that, in the presence of optically active catalysts[13] or when included in asymmetric matrices, may give rise to optically active polypentadiene.[4]

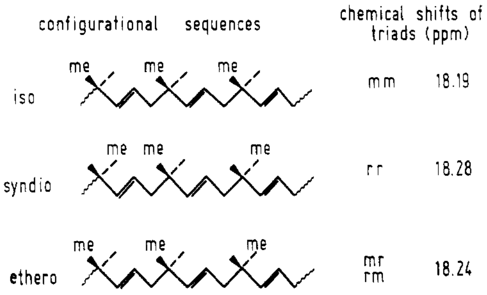

Figure 3. Possible configurational sequences of 1,4-*trans*-polypentadiene chain.

Table II

	area, %	
polymer	$[\alpha]^{25}{}_D$ −21°	$[\alpha]^{25}{}_D$ −3°
mm	52	34
rr	14	19
rm + mr	34	47

DCA is an optically active natural product with $[\alpha]^{25}{}_D$ +54.5°. On γ irradiation the *cis*-1,3-pentadiene included in DCA yields a polypentadiene with $[\alpha]^{25}{}_D$ −21°; the polymer obtained from the trans monomer has optical activity varying between +0.3° and −3°. The difference in rotatory power clearly also points to a difference in the optical purity of the polymers and hence in their microstructure. In fact, by ozonolysis, the polymer with the lower optical activity yields a methylsuccinic acid almost without rotation power, whereas polypentadiene with $[\alpha]^{25}{}_D$ −21°, by ozonolysis, yields a methylsuccinic acid with $[\alpha]^{25}{}_D$ +3.5°. This means that polypentadiene has an optical purity of 20% and a predominant chain configuration of the (−)-(*R*) type.

$$\begin{array}{c} \textit{cis}\text{-1,3-pentadiene included in DCA} \\ (\text{DCA}[\alpha]^{25}{}_D = +54.5^\circ) \\ \downarrow \gamma \text{ rays} \\ \textit{trans}\text{-1,4-polypentadiene, } [\alpha]^{25}{}_D = -21^\circ \\ \downarrow O_3 \\ (+)\text{-}(R)\text{-methylsuccinic acid, } [\alpha]^{25}{}_D = +3.5^\circ \\ \text{optical yield} = 20\% \end{array}$$

The different optical purity of the two polymers indicates a nonidentical tacticity.

The polymers are not crystalline and do not become even partially so on stretching or annealing; therefore no X-ray investigation can be performed. Hence, a general method was developed for the study of the tacticity of polydienes: ^{13}C NMR analysis under particular high-resolution conditions.[14] It has been thus possible to resolve the methyl, methine, and methylene signals (the aliphatic groups) into absorption lines, each corresponding to a different steric situation in the polymer chain (Figure 3). The assignment of each triad and diad was made by comparison with sterically pure polymers and with hydrogenated polydienes.[14,15] The relative intensities of the triads in the multiplets shown in Figure 4 were evaluated by line shape analysis. The experimental pattern was fitted to an envelope of three Lorentzian line shapes, the intensities of which were adjusted to optimal correspondence. The results are shown in Table II. Furthermore, the results of line shape analysis make possible a few observations regarding the microstructure of the polymers and on the polymerization mechanism, in particular, with reference

Table III[a]

polypentadiene	measd tacticity			calcd from Bovey model			calcd from enantiomorphic-site model		
	mm	mr	rr	σ_1	mr	rr	σ_2	mr	rr
$[\alpha]^{25}_{D}$ −21°	0.52	0.34	0.14	0.721	0.40	0.078	0.80	0.32	0.16
$[\alpha]^{25}_{D}$ −3°	0.34	0.47	0.19	0.583	0.48	0.17	0.67	0.44	0.22

[a] The probability parameter σ_1 is calculated by $I = (\text{mm}) = \sigma_1^2$ and used to calculate $H = (\text{mr}) = 2(\sigma_1 - \sigma_1^2)$ and $S = (\text{rr}) = (1 - \sigma_1)^2$. The expressions for calculating σ_2 are $(\text{mm}) = I = 1 - 3(\sigma_2 - \sigma_2^2)$, $(\text{mr}) = H = 2(\sigma_2 - \sigma_2^2)$, and $(\text{rr}) = S = \sigma_2 - \sigma_2^2$.

to optically active polypentadiene.

Two remarks can be made. First, if these triad and diad values (the diad values being obtained from the resolved resonances of the methylene groups) are used in the Coleman–Fox equation

$$\rho = \frac{2(\text{m})(\text{r})}{(\text{mr})} = 1.2$$

the resulting persistence ratio will indicate a Bernoullian statistics in the monomeric unit distribution.[16] The polymer therefore grows according to Bernoullian statistics; i.e., the growing chain does not affect the way in which the monomer is attached to it. In other words, the stereochemistry of the growing chain does not influence the steric control.

Second, this experimental tacticity is consistent with the enantiomorphic model.[17] In fact, the tacticity calculated from the ^{13}C NMR spectra agrees better with the tacticity calculated by the enantiomorphic-site model than with that calculated by the Bovey model.[16] The situation is different for polypentadiene at $[\alpha]^{25}_{D}$ −3°, in which the tacticity seems to agree better with the Bovey model (Table III). In other words, for the optically active polymer, the configuration of the adding monomer is determined primarily by the configuration of the catalyst. In fact the channel, by imposing a well-defined steric situation on the monomer, compels it during polymerization to enter the chain with a definite enantiomeric configuration. That is, we find here a new kind of asymmetric induction: steric control is not transmitted by means of a covalent bond but only through space, that is, through van der Waals interactions.[21] Moreover, from the value of each triad it is possible to deduce the average blockiness of the iso- and syndiotactic diads.

Number-Average Lengths of Blocks

$$[\alpha]^{25}_{D}\ -3°$$

$$\bar{n}_{m} = (\text{mm})/(\text{mr}) + 1 = 2.4$$

$$\bar{n}_{r} = (\text{rr})/(\text{mr}) + 1 = 1.8$$

$$[\alpha]^{25}_{D}\ -21°$$

$$\bar{n}_{m} = (\text{mm})/(\text{mr}) + 1 = 4.0$$

$$\bar{n}_{r} = (\text{rr})/(\text{mr}) + 1 = 1.8$$

For the polymer with $[\alpha]^{25}_{D}$ −21° therefore the average blockiness of the isotactic diad is about 4 and that of the syndiotactic diad is about 2.

The value of the optical purity tells us which of the two configurations prevails over the other and by how much: in this case there is a D/L = 60/40 ratio.

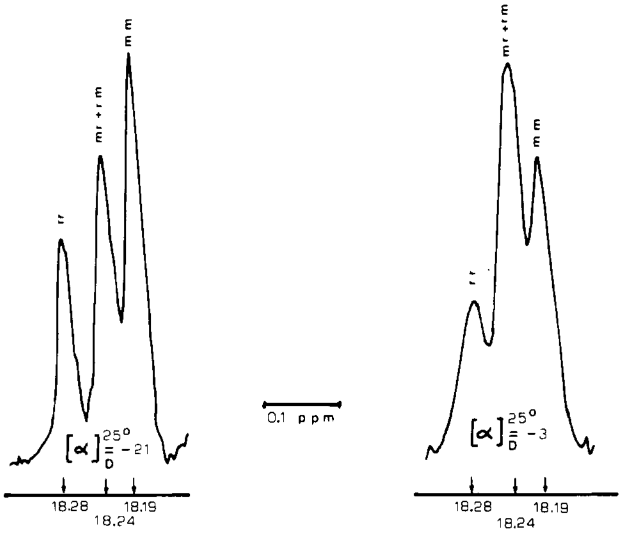

Figure 4. Methyl group ^{13}C NMR expanded spectra of *trans*-1,4-polypentadiene.

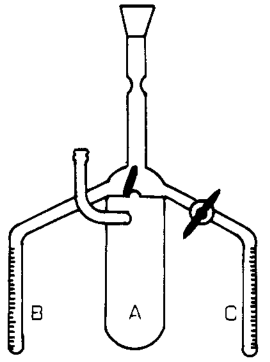

Figure 5. Vial used for including racemic volatile compounds in DCA.

Equilibration in the Presence of Racemic Substances

The hypothesis advanced as to the mechanism of this polymerization system can be confirmed by the equilibrium technique between DCA and low-boiling racemic substances. The vial shown in Figure 5 is filled with DCA (part A) and with *rac*-3-methyl-1-pentene (part B) and sealed under high vacuum. After that the racemic compound vapor is contacted with DCA for a time sufficient for the formation of the inclusion compound. Part B is then removed by flame sealing the neck.

The crystalline powder in A is heated to 120 °C, and the compound, after removal of the inclusion adduct, is collected in C. This 3-methyl-1-pentene has an optical activity of $[\alpha]^{25}_{D}$ −0.6°, equal in absolute value and opposite in sign to the nonincluded 3-methyl-1-pentene residue in part A. Therefore, in the presence of two enantiomers, DCA preferentially includes the enantiomer (−)-(*R*).[18,19] The channel is therefore asymmetric and may establish a diastereomeric relationship with either of the two enantiomers; under the conditions adopted by us, the DCA inclusion compound with (−)-3-methyl-1-pentene is thermodynamically more stable than the DCA inclusion compound with (+)-3-methyl-1-pentene.

Asymmetric Induction

On examining the results obtained from this solid-state polymerization, it would seem reasonable to suppose that, in order to obtain orderly polymerization, there exist

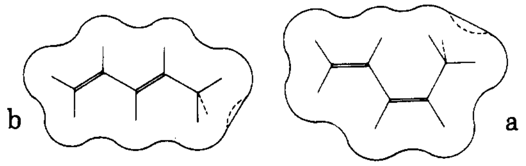

Figure 6. Molecular shape of (a) *cis*-1,3-pentadiene and (b) *trans*-1,3-pentadiene.

certain critical values of the relationship between the form of the included molecules and the form of the channel.

The examination of the polymer structure suggests that the geometric space of the channel maintains its form when the included monomers vary, so that for the monomer with low steric hindrance there is more than one possibility of insertion (at a given thermodynamical stability). In fact, the polymerization of *trans*-1,3-pentadiene yields polymers that are structurally nonhomogeneous and, according to the optical activity values, whose microstructure is not exactly reproducible.

By including *cis*-1,3-pentadiene, a diolefin with a higher steric hindrance, it is possible to obtain a polymer with high structural purity while an increase in the chain isotacticity is obtained. Further confirmation of this trend can be observed in the polymer obtained by inclusion of 2-methypentadiene in DCA.[20]

It is now easy to explain the different behavior of *cis*-pentadiene and *trans*-pentadiene in this inclusion polymerization; Figure 6 shows the differing molecular steric bulkiness of *cis*- and of *trans*-1,3-pentadiene. Clearly, the interactions between *cis*-pentadiene and the channel are greater than between *trans*-pentadiene and the channel; therefore, the steric control of the channel in the *cis*-1,3-pentadiene polymerization is also greater.

The degree of stereospecificity that can be reached with this solid-state DCA polymerization is not noteworthy, particularly if compared with the high stereospecificity obtained with similar systems, such as perhydrotriphenylene and urea. On the other hand, when considering the asymmetric synthesis possible in DCA inclusion compounds, we note that the *trans*-1,4-polypentadiene obtained has the highest optical activity and, which is even more interesting, has a relatively high degree of optical purity. This means that an asymmetric synthesis with a high degree of asymmetric induction occurs in this system.

Registry No. Deoxycholic acid, 83-44-3; *trans*-1,3-pentadiene homopolymer, 25549-62-6; *cis*-1,3-pentadiene homopolymer, 25549-61-5.

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Rate Constants and Activation Energies for Reaction of Benzyl Cation with Ethers in Solution: Initial Step in Carbocationic Polymerization

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ABSTRACT: Rate constants and activation energies for reactions of the benzyl cation with various ethers in solution have been determined by pulse radiolysis. These condensation reactions have activation energies slightly larger (by 0.3–2.0 kcal/mol) than the activation energies calculated for diffusion-limited ion–molecule reactions. Differences in the reactivities of the various ethers with the benzyl cation could be predominantly accounted for by the values of the preexponential factors rather than by the activation energies. Comparison of these rate constants with the relative basicity of the ethers obtained from steady-state systems showed a qualitative agreement.

Introduction

The role of carbocations in the initiation of polymerization reactions has been well established.[1,2] The addition of carbocations to π-, σ-, and n-donor monomers forms the "onium" ion that is the propagating species in polymerization reactions.

Recent interest in oxonium ions is related to the ability of carbocations to initiate the polymerization of cyclic

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