

Inclusion Polymerization of Various Diene Monomers in Apocholic Acid Canals

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ABSTRACT. The inclusion polymerization of diene monomers with different sizes and shapes in apocholic acid canals was studied under γ -ray irradiation. It was found that the sizes and shapes of monomers profoundly influenced the microstructures of the corresponding polymers obtained. Thus, polybutadiene contained a significant amount of 1,2-units like usual radical polymerization in solution. Polyisoprene consisted of a mixture of head-to-tail and head-to-head (tail-to-tail) addition. The introduction of two methyl groups into butadiene led to the synthesis of polymers with almost exclusively head-to-tail, 1,4-trans structure.

1. Introduction

We found that a natural steroidal acid, deoxycholic acid and its derivative, apocholic acid (Figure 1), can serve as effective host components for inclusion polymerization [1-4]. These hosts meet the requirements for the synthesis of stereoregular as well as optically

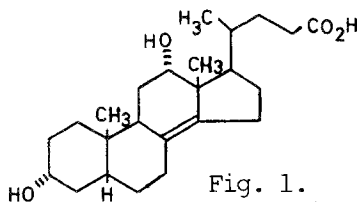


Fig. 1.
Apocholic acid

active polymers by inclusion polymerization in the canals. We so far concentrated on studies of asymmetric inclusion polymerization of prochiral pentadienes and their derivatives [4-6]. The dependence of the asymmetric induction on various polymerization conditions became clear [7]. In case of (E)-2-methylpentadiene in apocholic acid canal complexes the optical yield amounted to 36% at maximum.

By the way, the sizes and shapes of both canals and guest molecules which can be accommodated depend on the mutual positions and on the separation of two adjacent bilayers formed by hydrogen bonds among host molecules [8]. This suggests that monomers with different sizes and shapes can be included into the canals in different ways, which may bring different microstructures of the polymers obtained by inclusion polymerization in the canals.

In order to find a relationship between the sizes and shapes of the monomers and the microstructures of the corresponding polymers obtained,

the present paper is concerned with the inclusion polymerization of various diene monomers with different sizes and shapes in apocholic acid canal complexes.

2. Materials and Methods

Apocholic acid was prepared according to Devor and Marlow [9]. Butadiene, isoprene and pentadiene were commercially available. 2,3-Dimethylpentadiene was prepared by Wittig reaction of 3-methylpent-3-en-2-one with methylenetriphenylphosphorane [10,11]. Other monomers were synthesized according to the literature ; 2,3-dimethylbutadiene [12], 2-methylpentadiene [13], 3-methylpentadiene [14], 4-methylpentadiene [15]. They were purified by fractional distillation, and the mixture of (E)- and (Z)-isomers was separated by preparative gas chromatography using β, β' -oxydipropionitrile as the liquid phase.

The inclusion polymerization of these diene monomers in apocholic acid canals was carried out as previously reported [4,7].

Melting points of canal complexes were determined on a hot-stage polarizing microscope and were uncorrected. Molecular weight was measured by vapor pressure osmometry. Infrared spectra were obtained using KBr disk technique. The content of the microstructural units of the polybutadiene was determined by an infrared spectral measurement carried out in a KRS solution cell of 1.0 mm thickness [16]. $^1\text{H-NMR}$ spectra were measured at 150°C in *o*-dichlorobenzene at 100 MHz on a JNM-RS-100 (JEOL) spectrometer. $^{13}\text{C-NMR}$ spectra were measured in CDCl_3 at 15.00 MHz on a JNM-FX60S (JEOL) spectrometer.

3. Results and Discussion

The inclusion polymerization of various diene monomers in apocholic acid canals was studied in the same way as the case of deoxycholic acid canal complexes [6,7]. The apocholic acid-monomer canal complexes were at first prepared in sealed tubes by absorbing the monomer molecules into vacant canals of solvent-free apocholic acid crystals. Then the monomers present in the canals were post-polymerized by heating after γ -ray irradiation.

The crystals of apocholic acid canal complexes kept their original shapes and appearance during the polymerization just like the case of deoxycholic acid. It was assured that all monomers used polymerize in the canals and not outside of them, because the polymer yield was less than 1.0 mg per 0.50 cm^3 of monomer in the absence of apocholic acid under the condition studied. The methanol-insoluble solid or rubbery polymers after the extraction of apocholic acid with boiling methanol were characterized.

Table I summarizes the result of the inclusion polymerization of various diene monomers in apocholic acid canals.

The polymer yields attained 65-80 mg per 1.0 g of apocholic acid except for (E)-2,3-dimethylpentadiene. The yields reach saturation after a sufficient long polymerization time.

Table I. Properties of polymer-canal complexes and polymers obtained by the inclusion polymerization of various diene monomers in apocholic acid canals^{a)}

Monomer	Mp ^{b)} (°C)	Polymer yield ^{c)} (mg)	Mp of polymer (°C)	M.W. ($\times 10^4$)	Microstructure 1,4-trans:1,4-cis:1,2 (%)
Butadiene	178-184	65	(rubber)	4.0	63 : 8 : 29
Isoprene	184-190	69	(rubber)	1.2	92 : 7 : 1 ^{f)}
(E)-Pentadiene	192-195	76	(rubber)	1.0	91 : 9 : 0
(Z)-Pentadiene	192-195	77	(rubber)	1.0	88 : 12 : 0
2,3-Dimethyl- butadiene	199-205	80	201-207	d)	>99 : 0 : 0
(E)-2-Methyl- pentadiene	185-192	80	132-140	3.5	95 : 5 : 0
(Z)-2-Methyl- pentadiene	179-182	80	133-137	4.0	>99 : 0 : 0
3-Methyl- pentadiene	173-178	80	(rubber)	1.9	>99 : 0 : 0
4-Methyl- pentadiene	184-188	78	(rubber)	1.0	>99 : 0 : 0
2,3-Dimethyl- pentadiene	158-163	30	205-215	e)	e)

a) Apocholic acid 1.0 g ; Monomer 0.5 cm³ ; γ -ray irradiation, 1.0 Mrad ; Post-polymerization, 24 hours at 50°C.

b) Melting points of apocholic acid-polymer canal complexes after inclusion polymerization.

c) Polymer yield per 1.0 g of apocholic acid.

d) η_{sp}/c of the polymer was 0.028 dl/g in *o*-dichlorobenzene in 0.05 g/dl of the solution.

e) The polymer was insoluble, so the microstructure was not determined.

f) Ratio of head-to-tail addition to head-to-head one was 3:2.

Polymer-Canal Complexes :

Most of canal complexes obtained after polymerization melted at higher temperatures than that of apocholic acid itself (176-8°C). The most remarkable increase of the melting point was observed in the case of 2,3-dimethylbutadiene. This is probably because the polymer chains fit in the canals best among the polymers studied due to its suitable size and symmetric shape. On the other hand, polybutadiene does not seem to stabilize the canal complexes due to its small cross section as compared with that of the canal.

Microstructures of Polymers :

The microstructures of the resulting polymers were determined by IR, ¹H-

NMR, ^{13}C -NMR spectroscopies. It was found that the microstructures strongly depended on the sizes and shapes of the monomer molecules used, though the polymers always contained 1,4-trans units preferentially.

Butadiene : The resulting polymer contained 63% 1,4-trans, 8% 1,4-cis, 29% 1,2-units, which was measured by IR spectroscopy [16]. Figure 2(a) shows the ^{13}C -NMR spectrum of the polybutadiene. The strong resonance due to methylene carbon of the 1,4-trans-1,4-trans sequence appeared at 32.8 ppm [17]. The absorption due to methyne and methylene carbons of 1,2-1,4-trans sequence appeared at 30.2, 33.8, 38.2 and 43.5 ppm, while the absorption due to 1,2-1,2 sequence did not appear at 38.7 and 40.9 ppm [18]. This indicates that 1,2 units in the polymer chain are isolated in 1,4-trans sequence.

This microstructure is similar to that of a polymer obtained by free radical polymerization in solution [19], which demonstrates that inclusion polymerization proceeded without the steric control in the apocholic acid canals. So it is assumed that the monomer molecules are loosely trapped into the canals and not oriented in them regularly enough to yield a highly 1,4-trans polymer.

Isoprene : The introduction of one methyl group into butadiene led to a dramatic increase of the content of 1,4-trans units with the decrease of 1,2 units. Furthermore, in case of isoprene, we recognized other arrangements; head-to-tail or head-to-head (tail-to-tail).

Figure 2(b) shows the ^{13}C -NMR spectrum of the polyisoprene obtained. It can be seen that the absorption of methylene carbon was separated into two peaks. The peaks at 26.8 and 39.8 ppm are assigned to head-to-tail addition and ones at 28.3 and 38.6 ppm head-to-head (tail-to-tail) [20]. The ratio of these additions was estimated to be about 3:2.

It is assumed that the orientation of the monomer molecules in the canals are suitable for 1,4 addition, but not for head-to-tail one.

Pentadiene : In the ^{13}C -NMR spectrum shown in Figure 2(c), the absorption peaks due to head-to-tail, 1,4-trans (20.0, 32.2, 35.0 ppm) and 1,4-cis (20.5, 36.9, 40.3 ppm) units are observed, while the ones due to head-to-head (tail-to-tail) addition are hardly observed [21]. It is noteworthy that the polypentadiene has a different microstructure from the polyisoprene in spite of the same one methyl-substituted butadienes. This may be attributed to the different shapes of the monomers, which cause different orientations of the monomers in apocholic acid canals.

As shown in Table 1, the polymer contained a significant amount of 1,4-cis units. The polymer obtained from (E)-isomer had more amount of 1,4-trans units than that from (Z)-isomer. It is considered that (E)-isomer arranges in the canals in a different way from (Z)-isomer because of the different shapes of the monomers, which may lead to the preparation of slight different microstructures of the polymers.

2,3-Dimethylbutadiene : The resulting solid polymers after extracting with boiling methanol had the original appearance of the canal complexes and melted above 200°C. They were practically insoluble in usual organic solvents, such as CCl_4 and CHCl_3 , but soluble in *o*-dichlorobenzene and hexachlorobutadiene above 120°C. Figure 3(a) shows the IR and ^1H -NMR spectra. These spectra were identical to those of polymers obtained by deoxycholic acid inclusion polymerization [3] as well as by the polymerization with a Ziegler-type catalyst [22], which afford

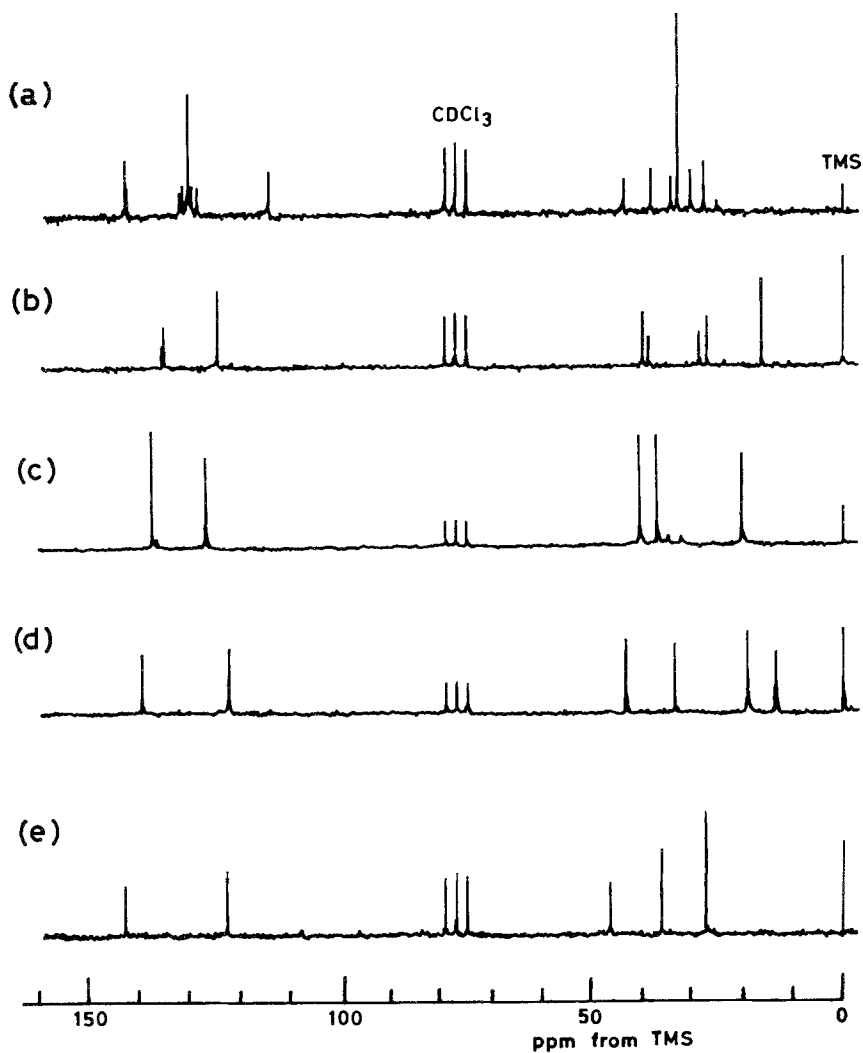


Fig. 2. ^{13}C -NMR spectra of the polymers obtained by inclusion polymerization of diene monomers in apocholic acid canals.

(a): butadiene, (b): isoprene, (c): (E)-pentadiene,
(d): 3-methylpentadiene, (e): 4-methylpentadiene.

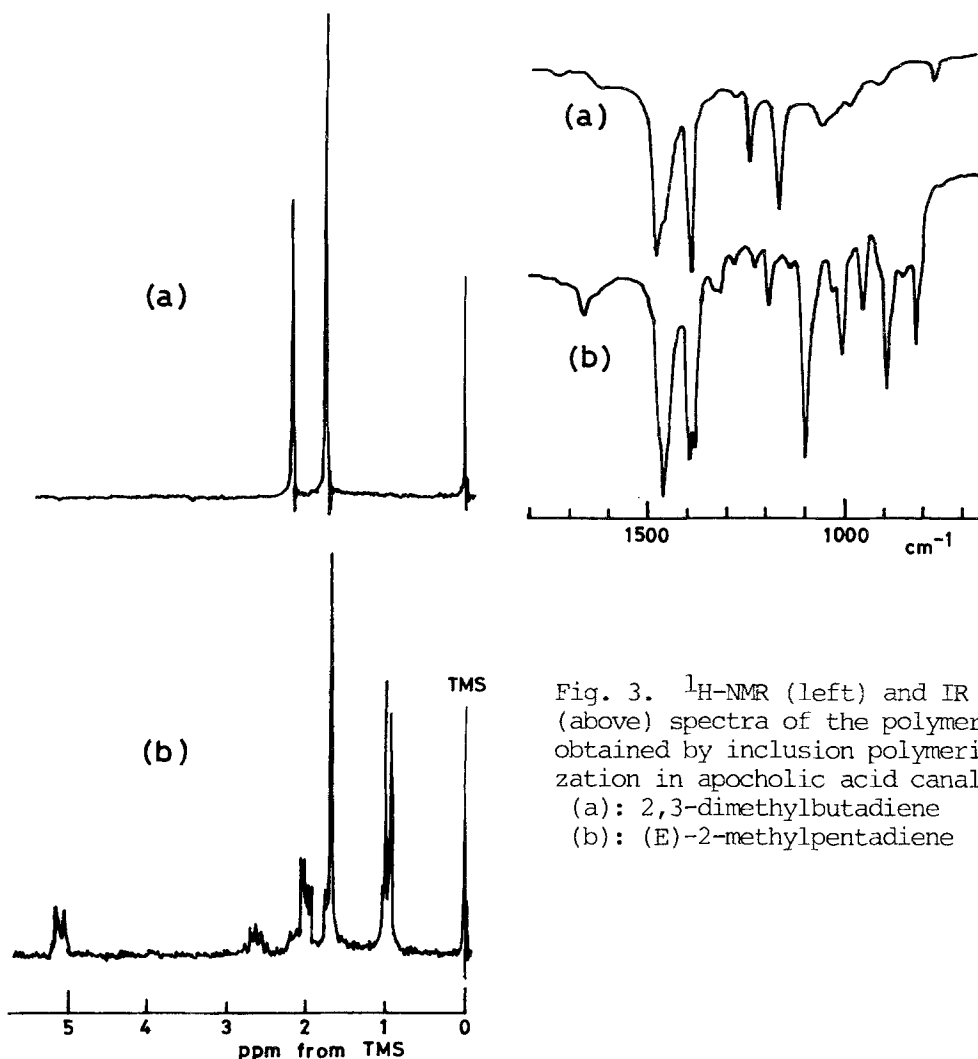


Fig. 3. $^1\text{H-NMR}$ (left) and IR (above) spectra of the polymers obtained by inclusion polymerization in apocholic acid canals.
 (a): 2,3-dimethylbutadiene
 (b): (E)-2-methylpentadiene

almost complete 1,4-trans polymers.

2-Methylpentadiene : The separated solid polymers had the original appearance of the canal complexes just like the case of 2,3-dimethylbutadiene and melted in the range of 132-140°C. In contrast to the latter, the former polymers were soluble in CCl_4 and CHCl_3 .

Figure 3(b) shows the IR spectrum of the polymer from (E)-isomer measured on KBr dispersions. The crystalline-sensitive bands were observed at 805, 880, 940, 990 and 1180 cm^{-1} . These bands disappeared in CCl_4 solution. The spectrum was almost identical to that of the polymer obtained by deoxycholic acid or perhydrotriphenylene inclusion polymerization [23].

Figure 3(b) shows the $^1\text{H-NMR}$ spectrum of the polymer from (E)-isomer

in *o*-dichlorobenzene at 150°C. The small peak at 1.76 ppm is assigned to methyl protons of 1,4-cis units [24], while the peak was hardly observed in case of (Z)-isomer. Although the polymer was not soluble enough to get a high S/N value in the ¹³C-NMR spectrum, six peaks characteristic of 1,4-trans units were observed.

The ozonolysis of the polymer followed by treatment with 2,4-dinitrophenylhydrazine gave only the corresponding hydrazone of α -methyllevulinic acid. This supports the existence of the almost complete head-to-tail structure.

3-Methyl- or 4-Methylpentadiene : The resulting polymers obtained from both monomers are rubbery and soluble in CCl₄, CHCl₃ and so on. Figure 2(d) and 2(e) show the ¹³C-NMR spectra of the polymers. In both spectra strong six absorption peaks are observed, which indicates that the polymers contain more than 99% of head-to-tail, 1,4-trans structure.

As mentioned above, the introduction of two methyl groups into butadiene enabled us to get the polymers with almost complete head-to-tail, 1,4-trans structure. In those cases, it is considered that the monomer molecules orient regularly and fit suitably in the canals so that we can prepare highly stereoregular polymers.

In addition, we tried the inclusion polymerization of three isomers of 2,4-hexadiene ((E)-(E), (E)-(Z) and (Z)-(Z) isomers), but we obtained few polymers. It should be noticed that (E)-(Z) and (Z)-(Z) isomers can be polymerized in perhydrotriphenylene canal complexes [23].

Finally we carried out the inclusion polymerization of three methyl-substituted butadiene, (*E*)-2,3-dimethylpentadiene. The resulting solid polymer had the melting point at 205-215°C but no solubility in usual organic solvents. It dissolved slightly on standing in air for a long time, probably because of its partial decomposition by oxygen. The ¹H-NMR spectrum of the polymer suggests the existence of 1,4-trans units.

Comparison of Hosts :

Apocholic acid is a flexible host which can include a variety of monomers with different sizes and shapes. And the stereochemical control for the polymerization in the canals work effectively in case of two methyl-substituted butadienes, such as 2,3-dimethylbutadiene, 2-methylpentadiene and so on, while not in case of small monomers, such as butadiene and isoprene.

In contrast to apocholic acid, urea and thiourea hosts are highly selective [25], while perhydrotriphenylene host is highly flexible with respect to the sizes and shapes of their guest monomers [23]. The inclusion polymerization in their canals affords the corresponding diene polymers with almost exclusively 1,4-trans structure.

It can be concluded from the comparison of these results that apocholic acid has an intermediate capability between urea, thiourea and perhydrotriphenylene as regards both the selectivity of the guest molecules and the stereochemical control for inclusion polymerization in the canals.

This difference might be explained by the difference of the bonding forces among host molecules. In case of urea and thiourea hosts, the intermolecular forces consist of hydrogen bonds, so the sizes and shapes of the canals are fixed. This causes the strong selective inclusion of

butadiene for urea and 2,3-dimethylbutadiene for thiourea, respectively. On the other hand, perhydrotriphenylene molecules combine each other by van der Waals forces. The weak interaction enables the host to change the size and shape of the canal in accord with the size and shape of the guest monomer. Therefore, the perhydrotriphenylene inclusion polymerization always yields highly stereoregular polymers. However, apocholic acid canal complexes are constructed by both forces; thus, apocholic acid molecules form hydrogen-bonded bilayer sheets, which contact each other by van der Waals forces [26]. The change of the size and shape of the canal should be limited due to the limited change of the bilayer sheets. This may be the reason why the apocholic acid inclusion polymerization gives the highly stereoregular polymers in case of two methyl-substituted butadienes.

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