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Functional Monomers and Polymers L.* Post-Irradiative Polymerization of Butadiene in Deoxycholic Acid Canal Complexes

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ABSTRACT

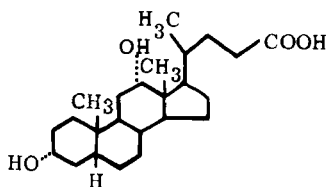
The polymerization of butadiene was studied in deoxycholic acid canal complexes under various reaction conditions. To prepare the starting canal complex containing butadiene, acetone in the deoxycholic acid-acetone canal complex was replaced with butadiene effectively. Post-irradiative polymerization was carried out after irradiation with γ -rays from a Co-60 source. The polymer was found to contain a significant amount of 1,2-units in addition to trans-1,4-units. Various additives had a marked effect on the polymerization behavior, particularly on the polymer yield and the microstructure of the polymer.

*For Part XLIX in this series see M. Akashi, H. Futagawa, Y. Inaki, K. Kondo, and K. Takemoto, Nucleic Acids Research Suppl., No. 3, 7 (1977).

INTRODUCTION

In previous papers of this series [1-5], we reported the inclusion polymerization of various types of monomers using deoxycholic acid ($3\alpha, 12\alpha$ -dihydroxy-5 β -cholan-24-oic acid) (DCA) (I) as the host molecule. In the course of the successive investigation [6], we found that a DCA-2,3-dimethylbutadiene canal complex can be prepared readily by replacing various sorts of "guest" molecules present in the DCA canals with 2,3-dimethylbutadiene monomer, instead of the alternative, direct method for preparing a DCA canal complex based on recrystallization of DCA from methanol in the presence of polymerizable monomers.

The present paper deals with a study on the preparation of DCA-butadiene canal complex by using such a replacement technique, and polymerization of the complex by γ -ray irradiation. Different from the case of 2,3-dimethylbutadiene complex, the structure of the resultant polymers contains a significant amount of 1,2-units in addition to the trans-1,4-unit. The effect of additives on the inclusion polymerization was also studied.



I

EXPERIMENTAL

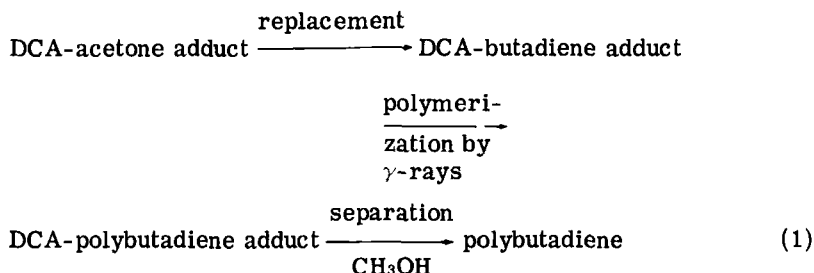
DCA-acetone adduct was first prepared by recrystallizing DCA from acetone. Liquefied butadiene monomer was purified by the freeze-thaw technique and distilled into the tube in vacuo.

Infrared spectra of the DCA adducts and the polymers were obtained by using the KBr disk technique. The content of the microstructural units of the polymer was determined by an infrared spectral measurement carried out in a KRS solution cell of 1.0 mm thickness used for polybutadiene [7, 8]. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were carried out in the same manner as reported earlier [3, 5].

RESULTS AND DISCUSSION

Inclusion Polymerization of Butadiene in DCA Canal

The polymerization of butadiene included in DCA canal was carried out generally in a similar way to that of 2,3-dimethylbutadiene according to Eq. (1):



DCA-Butadiene Adduct. DCA-butadiene adduct was prepared by treating DCA-acetone adduct [6] with an excess of butadiene in a sealed tube for 2 hr at 60°C. The sample was then allowed to stand under ordinary pressure at room temperature to exclude butadiene present outside of the canal complex. It is noteworthy that DCA was scarcely soluble in butadiene, and that the crystals of the canal complexes kept their original shape and appearance even after the treatment. Figure 1 shows DTA diagrams of the samples. The peak at 148°C for DCA-acetone adduct (Fig. 1a) was replaced by a new peak at 158°C (Fig. 1b). The tendency of the DTA diagram change was similar to that of DCA-2,3-dimethylbutadiene adduct, though the boiling points of these monomers were quite different. TGA measurement done at the same time in parallel showed a gradual release of the guest component from the canal in the temperature range between 100 and 150°C, and then a marked release to 165°C. On the other hand, such a gradual release of monomers from the canal in the temperature range of 100-150°C could not be observed in cases of DCA-2,3-dimethylbutadiene [5, 6] and DCA-2,3-dichlorobutadiene adducts [3]. From these results, DCA-butadiene adduct should be concluded as being more unstable than the DCA adducts of 2,3-disubstituted butadienes. Furthermore, butadiene was found to be released from the DCA canal complex when the DCA-butadiene adduct was allowed to stand for a long time at room temperature. The molar ratio of DCA to butadiene in the adduct amounted to nearly 2.

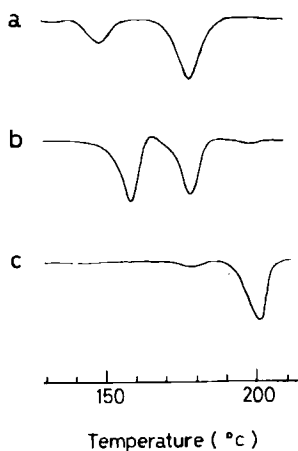


FIG. 1. DTA diagrams for (a) DCA-acetone adduct; (b) DCA-butadiene adduct; (c) DCA-polybutadiene adduct.

DCA-Polybutadiene Adduct. The DCA-butadiene adduct thus prepared was irradiated by γ -rays from a Co-60 source at -196°C to a dose of 0.3 Mrad, and the post-irradiative polymerization was successively done at 0°C for 5 hr. It is noteworthy that the polymerization in question proceeds exclusively in the canal and not outside of it. As can be seen from Fig. 1c, peaks at 158 and 178°C observed for DCA-butadiene adduct were no longer seen for DCA-polybutadiene adduct, and in the latter case, a new peak appeared at 203°C , which is 15°C lower than that of DCA-poly-2,3-dimethylbutadiene adduct [6]. This result suggests that DCA forms more stable adduct with branched molecules such as 2,3-disubstituted polybutadienes than with linear polybutadiene itself. The IR spectrum of the DCA-polybutadiene adduct showed a very weak absorption band at 970 cm^{-1} , which is characteristic for trans-1,4 structure of the polymer.

Polybutadiene. After the polymerization, DCA adducts were poured into excess methanol to separate DCA and the polymers. The polymer was a rubbery solid, soluble in carbon disulfide, toluene, etc. and insoluble in hydrocarbons and alcohols. Its molecular weight amounted to 5×10^4 . The microstructure of the polymer consists of trans-1,4 and 1,2 types in a ratio of 73:27, and cis-1,4 structure was not detectable. This fact is in contrast to the highly trans-1,4 structure of poly-2,3-dimethylbutadiene [5].

It may be recalled that highly trans-1,4 tactic polymers can be obtained by the inclusion polymerization of butadiene using urea

[9, 10] and perhydrotriphenylene [11] as the host molecules. These results suggest the importance of a characteristic spatial control for addition polymerization in the DCA canal complex.

Replacement of Acetone with Butadiene

The conditions for replacing acetone with butadiene in the DCA canal complex were further studied. Figures 2 and 3 show how the replacement of acetone with butadiene in DCA canal depends on the temperature and the time required for the replacement (broken lines). The polymerization was found to proceed very slightly at 0°C in 1 hr; the polymer yield is enhanced with an increase in either the temperature or the time for replacement. The polymer yield tends to reach a limiting value after 2 hr at 60°C.

Further runs were carried out in presence of ethyl acetate as the additive. Like the results obtained in absence of additive, the polymer yield reached saturation after 2 hr at 60°C. In addition, the presence of ethyl acetate was found to cause a decrease in the polymer yield.

Effect of Additives

The inclusion polymerization of butadiene in DCA canal was then studied in the presence of various sorts of additives.

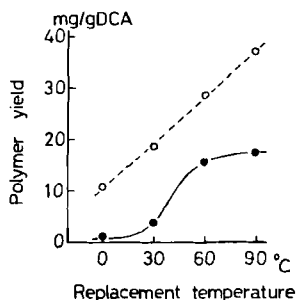


FIG. 2. Yield of the polymer in relation to replacement temperature for post-irradiative polymerization of butadiene in DCA canal complex: DCA-acetone adduct 1.0 g, butadiene 1.0 ml; replacement time 1 hr; irradiation, 0.3 Mrad at -196°C ; post-irradiative polymerization, 0°C for 5 hr: (○) without additive; (●) in the presence of 1.0 ml ethyl acetate.

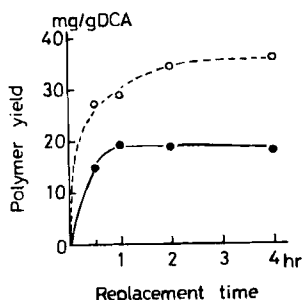


FIG. 3. Yield of the polymer in relation to replacement time for post-irradiative polymerization of butadiene in DCA canal complex: (○) without additive; (●) in the presence of 1.0 ml of ethyl acetate. DCA-acetone adduct 1.0 g, butadiene 1.0 ml; replacement at 60°C; irradiation, 0.3 Mrad at -196°C; post-irradiative polymerization, 0°C for 5 hr.

Effect of Additives on Polymerization. The post-irradiative polymerization was studied in the presence of nine additives. The results are shown in Table 1. It can be seen that addition of various components affected the polymerization yield and the microstructure of the polymers obtained: addition of methanol caused an increase in polymer yield, while it had no effect on the microstructure of the polymer. In contrast to this, addition of acetonitrile, acetone, methyl formate, and ethyl acetate gave polymers composed of more than 90% of trans-1,4 units. Table 1 also shows the decrease in polymer yield on addition of n-hexane and 2,3-dimethylbutane, respectively, which can be regarded as saturated linear and branched butadiene models. Addition of benzene did not cause any structural change of the polymer. Acetic acid was found to inhibit the polymerization of butadiene effectively.

Figure 4 shows infrared spectra of polybutadienes obtained by the inclusion polymerization in the presence of additives. The spectrum of polybutadiene obtained in the presence of ethyl acetate (Fig. 4b) was almost identical to that of the polymer obtained by urea canal polymerization [9], which afforded a highly trans-1,4-tactic polymer. The crystalline-sensitive bands were observed at 1350, 1250, 1060, and 780 cm^{-1} . On the other hand, the spectrum obtained in the presence of methanol indicated a peak at 910 cm^{-1} characteristic of 1,2-addition, and no crystalline-sensitive bands seem to appear (Fig. 4a).

Dependence of the Extent of Polymerization on the Amount of Additives. The inclusion polymerization of butadiene in DCA canal was next carried out, with varying amounts of

TABLE 1. Effect of Type of Additive on the Post-Irradiative Polymerization of Butadiene in DCA Canal Complex^a

Additive	Polymer yield (mg)	Microstructure of polymer trans-1,4:1,2 (%)
None	34	73:27
Methanol	42	73:27
Ethanol	29	76:24
Acetonitrile	18	95:5
Acetone	20	98:2
Methyl formate	17	98:2
Ethyl acetate	20	99:1
n-Hexane	14	97:3
2,3-Dimethylbutane	10	93:7
Benzene	35	72:28

^aDCA-acetone adduct 1.0 g, butadiene 1.0 ml, additives 1.0 ml; replacement, 60°C for 2 hr; irradiation, 0.3 Mrad at -196°C; post-irradiative polymerization, 0°C for 5 hr.

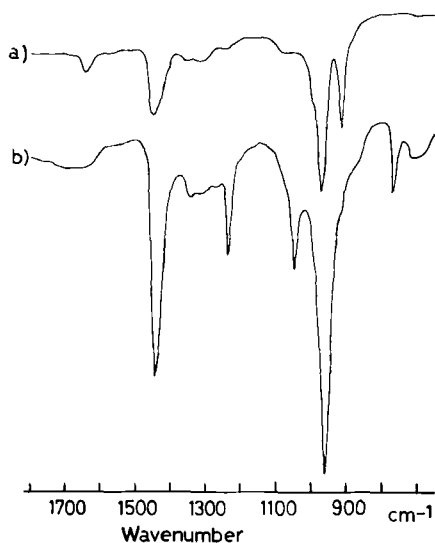


FIG. 4. Infrared spectra of polybutadiene obtained by DCA canal polymerization in the presence of additives: (a) methanol; (b) ethyl acetate.

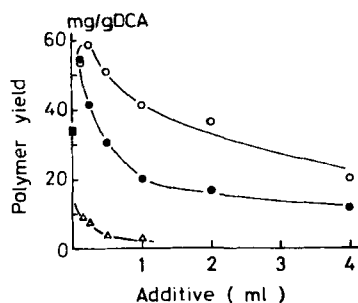


FIG. 5. Relationship between the polymer yield and the amount of additives in the post-irradiative polymerization of butadiene in DCA canal complex: (○) methanol; (●) ethyl acetate; (△) acetic acid. DCA-acetone adduct 1.0 g, butadiene, 1.0 ml; replacement, 60°C for 2 hr; irradiation, 0.3 Mrad at -196°C; post-irradiative polymerization, 0°C for 5 hr.

TABLE 2. Effect of Amount of Additive on the Post-Irradiative Polymerization of Butadiene in DCA Canal Complex^a

Additive (ml)	Microstructure of polymers, trans-1,4:1,2 (%)	
	Methanol	Ethyl acetate
0.12	69:31	72:28
0.25	71:29	85:15
0.50	71:29	98:2
1.00	73:27	99:1
2.00	71:29	99:1

^aDCA-acetone adduct 1.0 g, butadiene 1.0 ml; replacement, 60°C for 2 hr; irradiation, 0.3 Mrad at -196°C; post-irradiative polymerization, 0°C for 5 hr.

methanol, ethyl acetate, and acetic acid as the additives. As shown in Fig. 5, addition of small amounts of methanol and ethyl acetate caused an increase in polymer yield as compared with that in the absence of any additive, and the polymer yield decreased with an increase of amount of additive. No increase in polymer yield was observed on addition of acetic acid.

Table 2 shows the microstructure of the polymers obtained. The microstructure of the polymers obtained in the presence of methanol seems to be identical; however, a polymer with high content of trans-1,4 units (up to 99%) was obtained in the case of adding ethyl acetate.

These results suggest that the polymerization of butadiene in DCA canal can be controlled by the additives competitively.

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