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SHORT COMMUNICATIONS

Functional Monomers and Polymers CLXVII.† Asymmetric Inclusion Polymerization of 1-Alkyl-1,3-butadienes in Deoxycholic Acid and Apocholic Acid Canals by Long-Lived Propagating Radicals

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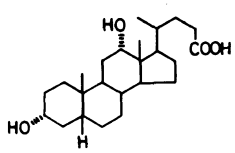
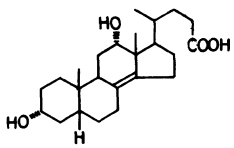
Asymmetric inclusion polymerization is an excellent way for obtaining highly stereoregular and optically active polymers by "through space" asymmetric induction.[1] However, applicable monomers are so far limited to only methyl-substituted 1,3-butadienes (BD), such as 1,3-pentadiene,[2] 2-methyl-1,3-pentadiene,[3] 2,4-hexadiene,[4] and 1,3-cyclodienes.[5] In spite of impressive progress in asymmetric synthesis over the past decade,[6] there seem to be only a few studies on asymmetric polymerization of BD derivatives except for the inclusion method.

In a series of extensive studies on inclusion polymerization using deoxycholic acid (DCA, I) and apocholic acid (ACA, II) as the host molecules, we showed that even butadiene monomers with bulky and/or polar substituent groups can be polymerized in the canals of the hosts.[7,8] The reason for the success lies in the possible prolonged postpolymerization due to thermally stable propagating radicals in the canals. This finding enabled us to challenge the inclusion polymerization of many diene monomers not applicable so far.

We report here the first example of asymmetric inclusion polymerization of five prochiral monomers, that is, l-alkyl-BDs (alkyl: ethyl, propyl, isopropyl, butyl, and *t*-butyl) in DCA and ACA canals by long-lived propagating radicals. ESR observation of the propagating radicals is also described.



(I)



(II)

EXPERIMENTAL

1-Alkyl-BD monomers were prepared by the

† For Part CLXVI of this series, see M. Miyata, M. Shibakami, and K. Takemoto, *J. Chem. Soc., Chem. Commun.*, 655 (1988).

reaction of Grignard reagents of the corresponding alkyl halides with acrolein, followed by hydrolysis and subsequent dehydration of the alcohols.[9] 1-*t*-Butyl-BD was prepared by the reaction of *t*-butylmagnesium bromide with crotonaldehyde.[10] DCA and ACA were purified by recrystallization from acetone. The resulting crystals were dried at 110°C for 20 h under vacuum for removal of acetone molecules present as the guests.

The inclusion polymerization was carried out as follows: 1.0 g of host crystals (2.4 mmol) and a monomer (1.2 mmol in case of DCA or 2.4 mmol in case of ACA) were placed into a 10 mm diameter glass tube, which was sealed under high vacuum (10^{-3} mbar). The host crystals absorbed the monomer to yield the corresponding inclusion compounds, which were irradiated by γ-rays from a ^{60}Co source at 0°C for one h at a total dose of 1.0 Mrad. Postpolymerization was carried out for 7 days at 50°C and 2 or 4 days at 100°C. The resulting polymers were separated from host molecules by pouring the crystals into a large amount of methanol. The methanol-insoluble, viscous residue was purified by reprecipitation to methanol from chloroform solution, dried and weighed.

The microstructures of the polymers were determined on the basis of IR, ^{1}H and ^{13}C NMR spectroscopy. ESR measurements were carried out as described earlier.[11] Specific rotation was measured in chloroform with a JASCO DIP-181 digital polarimeter.

RESULTS AND DISCUSSION

The inclusion polymerization of five 1-alkyl-BDs (alkyl: ethyl, propyl, isopropyl, butyl, and *t*-butyl) was carried out in a similar way to that of various 2-alkyl-BDs.[7] The results are summarized in Table I. The methanol-insoluble polymers were separated by filtration after the extraction of host molecules with boiling methanol. The polymers were rubbery and sticky except for 1-isopropyl-BD in DCA canals and 1-*t*-butyl-BD in both canals. The polymer yield was the highest in case of 1-

Table I. Inclusion polymerization of various 1-alkyl-1,3-butadienes in DCA and ACA canals[a]

Alkyl	Host	Postpolymerization		Polymer yield in %	$\bar{M}_w$[b]	Content of 1,4-*trans*[c] in %	$[\alpha]_D^{30}$[d] in deg
		Temperature in °C	Time in days				
Ethyl	DCA	50	7	34	5300	99	+8.4
	ACA	50	7	23	4500	95	+11.6
Propyl	DCA	100	2	19	4500	95	+7.8
	ACA	100	2	19	7100	90	+9.6
Isopropyl	DCA	100	4	24	2800	95	+1.0
	ACA	100	4	9	3800	65	+3.6
Butyl	DCA	100	2	13	5800	90	+3.3
	ACA	100	2	4	5700	—[e]	+5.1
t-Butyl	DCA	100	4	11	3600	—[e]	0.0
	ACA	100	4	5	5200	—[e]	+3.7

[a] γ-Ray irradiation: dose rate = 1 Mrad h^{-1}, 1 h, 0°C. mole ratio in feed: DCA/monomer = 2/1, ACA/monomer = 1/1.
[b] Measured by gel permeation chromatography in chloroform using standard polystyrenes.
[c] Measured by ^{13}C NMR spectroscopy.
[d] Measured in chloroform.
[e] Not determined due to low solubility of the polymers.

ethyl-BD. The introduction of methyl groups into the monomer led to decrease in the polymer yields.

The resulting polymers had highly 1,4-addition structures, as confirmed by IR, ^{1}H and ^{13}C NMR spectroscopy. The ratio of 1,4-*trans* to 1,4-*cis* structure depended on the sort of both monomer and host. The 1,4-*cis* and 1,2-content was found generally to be a little higher in ACA canals than in DCA canals. This is attributed to the fact that the size of an ACA canal is a little larger than that of a DCA canal. In this regard, we reported recently a decisive role of relative size between a canal and monomer for BD monomers with different numbers of methyl groups.[12] It is reasonable that relatively stereoirregular polymers are obtained when the monomer molecules are loosely included in relatively large canals.

The resulting polymers showed positive optical activity of the same sign as that of DCA ($[\alpha]_D = +55°$ in ethanol) or ACA ($[\alpha]_D = +50°$ in ethanol). Asymmetric polymerization of 1-alkyl-BD is now extended to BDs having long alkyl chains in addition to 1-methyl-BD[2] and 1-*s*-butyl-BD.[13] The values were not so high as those of *cis*-1,3-pentadiene ($[\alpha]_D = -21°$)[2] and *trans*-2-methyl-1,3-pentadiene ($[\alpha]_D = -163°$)[3], indicating the polymers not to have highly isotactic structures.

The slow proceeding of the polymerization suggests the existence of thermally stable intermediates of living-type. Earlier, we indicated from ESR studies using free radical initiators that γ-rays-induced polymerization of methyl-substituted BDs in DCA and ACA canals proceeds via radical mechanism.[11] Also in the case of 1-alkyl-BDs, we observed the ESR spectra of propagating radicals in both canals. Figure 1 shows the ESR spectra of the propagating radicals of 1-ethyl-BD (III) and 1-isopropyl-BD (IV) in DCA canals, as measured during the polymerization in the same way as described earlier.[11] The spectra consist of six or four lines with about 1.4 to 1.8 mT of

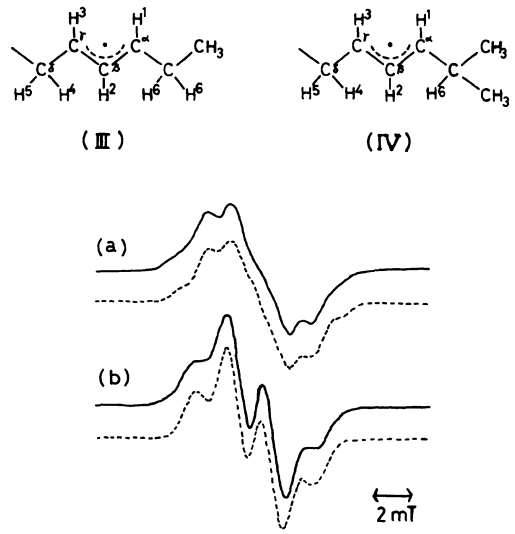


Figure 1. ESR spectra of propagating radicals in deoxycholic acid canals at 50°C. (a) 1-Ethyl-BD. (b) 1-Isopropyl-BD. (——), observed; (------), simulated.

hyperfine splitting constants, and are well assigned to allylic propagating radicals.[14]

The spectrum of (III) (Figure 1(a)) was simulated with a set of hyperfine splitting constants of $A_{H^1} = 1.40$ mT, $A_{H^2} = 0.40$ mT, $A_{H^3} = 1.40$ mT, $A_{H^4} = 1.01$ mT, $A_{H^5} = 0.70$ mT, and $A_{H^6} = 1.40$ mT on the assumption of a Gaussian with 0.95 mT of linewidth. The apparent six line spectrum is considered due to the fact that hyperfine splittings with A_{H^2} and A_{H^5} were smeared out because of the broad linewidth. The spectrum of (IV) (Figure 1(b)) was also simulated with a set of hyperfine splitting constants of $A_{H^1} = 1.50$ mT, $A_{H^2} = 0.40$ mT, $A_{H^3} = 1.50$ mT, $A_{H^4} = 1.71$ mT, $A_{H^5} = 0.23$ mT, and $A_{H^6} = 0.0$ mT on the assumption of a Gaussian with 1.30 mT linewidth. The apparent four line spectrum is considered due to the fact that hyperfine splittings with A_{H^2}, A_{H^5}, and A_{H^6} were smeared out because of the broad linewidth.

The spectra were observed even after one month at room temperature, indicating that the polymerization proceeds by living-like radicals with long lifetimes. The living character can be explained by the fact that the

propagating radicals in the the canals are completely isolated from those present in other neighboring canals by the wall of host molecules, which may lead to a remarkable depression of the termination reaction.

It is known that allylic inhibition occurs in case of radical polymerization of vinyl monomers. However, the inhibition does not occur in the case of 1-alkyl-BDs. This is probably because the reactivity of the diene monomers with free radicals is higher than that of vinyl monomers.[15]

Thus, we succeeded in preparing the optically active polymers of 1-alkyl-BD monomers by long-lived propagating radicals through the inclusion polymerization using DCA and ACA as the chiral hosts. Until now, there are only two reports on asymmetric polymerization of diene monomers via radical mechanism by use of an optically active ester of pentadienoic acid[16] and perhydrotriphenylene inclusion compounds.[17] A more detailed study is now in progress, and the results will be published in the near future.

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