**Journal of Macromolecular Science, Part A**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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**To cite this Article** Ishimori, Michihiro , Tsukigawa, Kenji , Nakada, Takashige and Tsuruta, Teiji(1977) '$^1$H- and$^{13}$ C-NMR Studies of Polymerization of 2,3-Dideuteromethyloxirane with Zinc Dialkoxide', Journal of Macromolecular Science, Part A, 11: 2, 379 — 390

**To link to this Article: DOI:** 10.1080/00222337708061274

**URL:** http://dx.doi.org/10.1080/00222337708061274

J. MACROMOL. SCI.–CHEM., A11(2), pp. 379-390 (1977)

# $^1$H- and $^{13}$C-NMR Studies of Polymerization of 2,3-Dideuteromethyloxirane with Zinc Dialkoxide*

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## ABSTRACT

The deuterium-decoupled 100 MHz $^1$H-NMR spectra of 2,3-dideuteromethyloxirane and its polymer prepared with a lattice-disordered zinc dialkoxide were analyzed with consideration of the deuterium isotope effects on proton chemical shifts. The results of $^1$H- and $^{13}$C-NMR studies indicated that the initiator for methyloxirane polymerization catalyzed by the diethylzinc–alcohol system was a lattice-disordered zinc dialkoxide, from the aspect of stereoregularity of the polymers obtained.

## INTRODUCTION

It has been reported that the initiator for methyloxirane polymerization catalyzed by diethylzinc-alcohol system is zinc dialkoxide and

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*A part of this study was reported at the Annual Meeting of the Society of Polymer Science, Japan, May 1973.

that the activity of the latter is remarkably dependent upon the mode of arrangement of alkoxy-groups with respect to the zinc atoms [1, 2]. Among organozinc catalysts so far synthesized, an extremely active initiator of the lattice-disordered zinc dialkoxide prepared by reaction of diethylzinc with methanol under reflux in methanol solution, is of particular interest [3].

In this paper we would like to report the features of the polymerization of methyloxirane with the lattice-disordered zinc dialkoxide, a typical coordinate anionic catalyst, where $^1$H-NMR spectra of poly-2,3-dideuteromethyloxirane and $^{13}$C-NMR spectra of polymethyloxirane were investigated from the point of view of stereoregularity of the polymers.

## EXPERIMENTAL

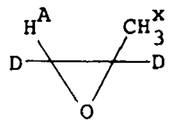
Diethylzinc, methanol, methyloxirane, and solvents were purified as previously described [1-3]. Reagent grades of propyne, deuterium, and 3-chloroperbenzoic acid were used without further purification.

Polymerization technique and isolation of polymers formed were carried out by the methods described previously [2]. The polymerization of the deuterated monomers I-VI was carried out at 35° C for 168 hr under the following conditions: zinc dimethoxide (lattice-disordered)/monomer = 0.2 (mole/mole), monomer/benzene (solvent) = 0.5 (v/v). For the convenience of $^1$H-NMR measurement, preparation of a low-viscosity polymer by using a high concentration of zinc dimethoxide was attempted. The lattice-disordered zinc dimethoxide was prepared by the reaction of diethylzinc with methanol at the temperature of refluxing methanol, and subsequently dried at 120-130° C in vacuo [3]. Polymethyloxirane (LDZn) was obtained at 30° C in 30 min at the ratios, zinc dimethoxide (lattice-disordered)/monomer = 0.05 (mole/mole), and monomer/benzene = 1 (v/v). Polymethyloxirane (ZnM) was prepared at 55° C in 24 hr under the conditions: diethylzinc/methanol = 0.5 (mole/mole), diethylzinc/monomer = 0.05 (mole/mole), monomer/benzene = 1 (v/v).

The deuterium-decoupled 100 MHz $^1$H-NMR spectra of benzene solutions of the deuterated monomer and of its polymers (5-10%, w/v) were recorded on a JEOL PS-100 spectrometer at 23° C. The 25.1 MHz $^{13}$C-NMR spectra of the polymers (10-15%, w/v in chloroform solution) were taken at 70° C with a JEOL PS-100 spectrometer equipped with an IS-100 proton irradiation sweep unit and an SD-HC hetero-spin decoupler.

## RESULTS AND DISCUSSION

2,3-Dideuteromethyloxirane was synthesized by the procedure reported previously [4], that is, 1,2-dideuteropropylene, obtained from reduction of propyne with deuterium using the Lindlar catalyst [5] was epoxidized by 3-chloroperbenzoic acid in dioxane solution to give cis-2,3-dideuteromethyloxirane I as the main product. In addition to I, the methyloxiranes II-VI were certainly formed as side products. The deuterium-decoupled 100 MHz $^1$H-NMR spectrum of these deuterated monomers is shown in Fig. 1.



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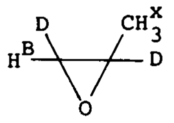

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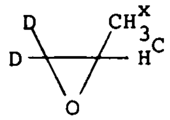

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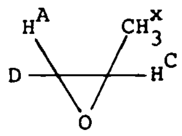

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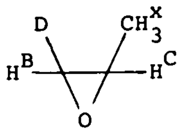

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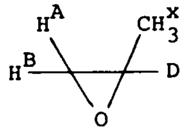

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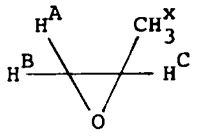

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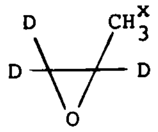

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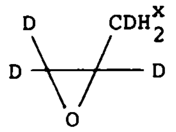

IX

No formation of VII ($ABCX_3$ spin system) was detectable in the spectrum in Fig. 1. Other methyloxiranes, such as VIII and further IX having partially deuterated methyl group might also be formed to some extent; however, they are not discussed here.

In Fig. 1, the signals at $\delta$ 0.86, 1.86 and 2.18 ppm downfield from hexamethyldisiloxane (HMDS) can be assigned to $H^X$ (for I, II, and VI), $H^A$ for I, and $H^B$ for II, respectively, and the broad signal around

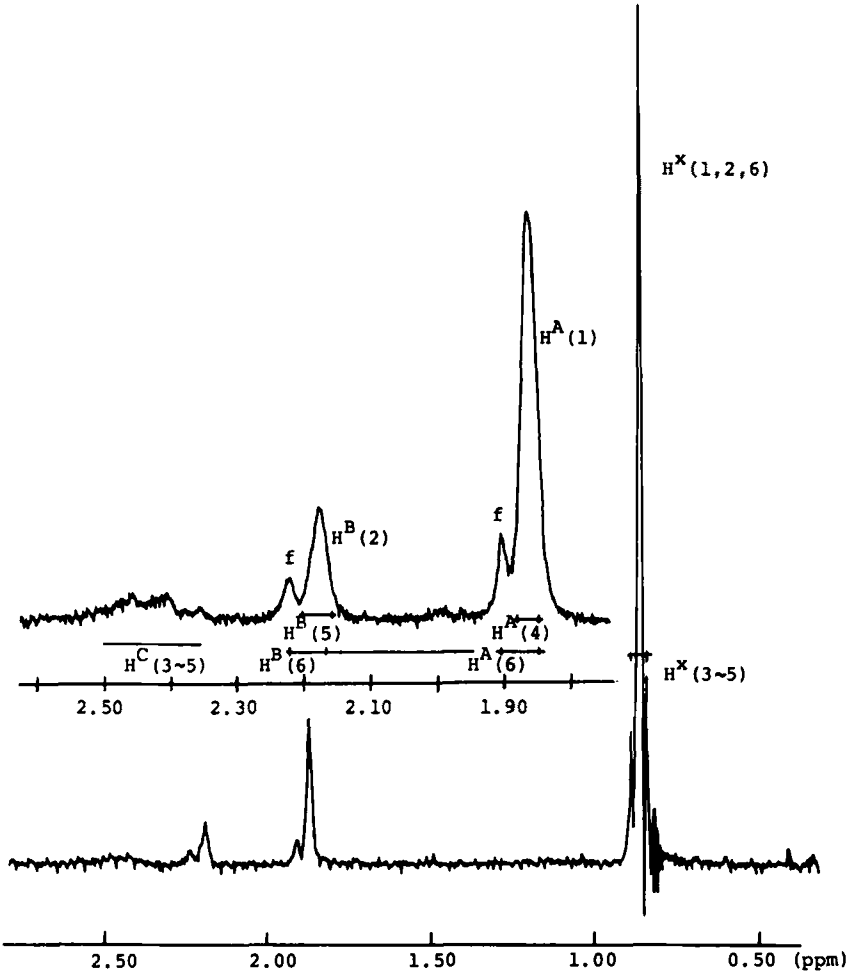

FIG. 1. Deuterium-decoupled 100 MHz $^1$H-NMR spectra of the deuterated monomers I-VI in benzene solution at 23°C with HMDS as internal standard.

2.45 ppm to $H^C$ for III-V [4, 6].* The weak peaks at 0.84 and 0.89 ppm can be assigned to the $H^X$-doublet for III-V, the coupling constant $J_{xc}$ = 5.0 Hz, being coincident with the data given by Musher and Gordon [7].

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*In Fig. 1, $H^A$ for I, $H^B$ for II, etc. are denoted $H^A$(1), $H^B$(2), etc.

The signals as to $CH_3$ groups indicate that the chemical shifts of $H^X$-singlets for $CH_3CD$-type methyloxiranes (I, II, and VI) appear at almost the same position as those of $H^X$-doublets for $CH_3CH$-type methyloxiranes (IV-V), the latter being observed only 0.5 Hz downfield.

On the other hand, the weak peaks $H^A(6)f$ and $H^B(6)f$ were each observed downfield from the positions of $H^A(1)$ and of $H^B(2)$, by 4.3 and 5.0 Hz, respectively. The $H^A(6)f$ and $H^B(6)f$ signals can be ascribed to the fragments of the AB quartet expected for VI as discussed hereafter. The deuterium isotope effects on proton chemical shifts [8] have been established, where the largest effect is caused by the deuterium attached on the same carbon as expected; this is much larger for $C\underline{H}D{-}CH$ ($\approx C\underline{H}D{-}CD$) than for $C\underline{H}H{-}CD$. Thus only small deuterium effects are expected for the $H^A$ and $H^B$ resonances of VI ($CH_2$-type), which were observed downfield to $H^A$ and $H^B$ signals of other methyloxiranes (CHD-type). The other fragments of the doublets paired with $H^A(6)f$ and $H^B(6)f$ are each superimposed on the strong resonances of $H^A(1)$ and of $H^B(2)$ of the dideuterated monomers. Considering the coupling constant $J_{AB} = 5.5 \pm 0.3$ Hz [9], differences in chemical shifts due to deuterium isotope effects on $H^A$ and $H^B$ are calculated approximately as, $|H^A(1) - H^A(6)| = 1.8$ Hz and $|H^B(2) - H^B(6)| = 2.0$ Hz, respectively.

On the other hand, the chemical shift of the $H^A$-doublet for IV ($CH^AD{-}CH$ type) is considered to coincide approximately with that of the $H^A$-singlet for I ($CH^AD{-}CD$ type), and that of the $H^B$-doublet for V with that of the $H^B$-singlet for II, as observed in the case of $CH_3CD$- and $CH_3CH$-type methyloxiranes; as expected from coupling constants $J_{AC} \simeq 4.5$ Hz and $J_{BC} \simeq 2.5$ Hz [9], the doublets $H^A(4)$ and $H^B(5)$ are each superimposed on the $H^A(1)$ and $H^B(2)$ singlets.

The dideuterated monomers are considered to be present roughly at the ratio I : II : III $\simeq$ 1:0.35:0.18, the peak intensity ratio for $H_A$:$H_B$:$H_C$ of the deuterated monomer in Fig. 1. As for the monodeuterated monomers, the ratio can be calculated as IV : V : VI $\simeq 1 \times 0.18$:$0.35 \times 0.18$:$1 \times 0.35$, assuming that protons are present at similar probability to the case of the dideuterated monomers. This rough calculation would also be helpful for assignment of weak signals in

TABLE 1. Chemical Shifts of Methyloxiranes[a]

| | δ (ppm) | | | | | | |
|---|---|---|---|---|---|---|---|
| | $H^A$ | | $H^B$ | | $H^C$, | $H^X$, | Spin |
| Methyloxirane | 1.86 | 1.88 | 2.18 | 2.20 | 2.45 | 0.86 | system |
| I | yes (s) | | – | – | – | yes (s) | $AX_3$ |
| II | – | – | yes (s) | | – | yes (s) | $BX_3$ |
| III | – | – | – | – | yes (m) | yes (d) | $CX_3$ |
| IV | yes (d) | | – | – | yes (m) | yes (d) | $ACX_3$ |
| V | – | – | yes (d) | | yes (m) | yes (d) | $BCX_3$ |
| VI | | yes (d) | | yes (d) | – | yes (s) | $ABX_3$ |

[a] Shifts relative to HMDS in benzene at 23° C; (s) = singlet, (d) = doublet, (m) = multiplet.

the spectra of the deuterated monomers and their polymers. The chemical shifts for the deuterated methyloxiranes I-VI are summarized in Table 1.

The polymerization of the above deuterated monomers I-VI was carried out by using a lattice-disordered zinc dimethoxide as a catalyst. The polymer isolated was fractionated to acetone-insoluble and -soluble parts. The 100 MHz deuterium-decoupled $^1$H-NMR spectra for (A) acetone-insoluble, (B) acetone-soluble, and (C) whole polymers are given in Fig. 2. The chemical shifts of $CH_3$ groups in the above three polymers were observed at $\delta$ 1.06 ppm, the doublets of $H^X$ (P3, 4, and 5) being superimposed on the singlets of $H^X$ (P1, 2, and 6). As to the spectrum of the acetone-insoluble polymer the chemical shift of $H^A$ for P1, the polymer of I is observed at $\delta$ 3.28 ppm and that of $H^B$ for P2, the polymer of II at $\delta$ 3.45 ppm, where the resonance $H^C$ for the polymer, $H^C$(P), is superimposed on that of $H^B$(P), as previously reported [4, 10-12]. The signals of $H^A$ and $H^B$ for the polymer of VI, $H^A$(P6) and $H^B$(P6), were observed downfield to those for $H^A$(P1) and $H^B$(P2) due to lack of a significant deuterium isotope effect, as observed in the case of the monomer. The coupling constant $J_{AB}$ P6, the polymer of VI was measured from the AB quartet as 9.5 Hz. The differences in chemical shifts due to deuterium isotope effects on $H^A$(P) and $H^B$(P) were respectively $|H^A(P1) - H^A(P6)| = 2.2$ Hz and $|H^B(P2) - H^B(P6)| = 2.1$ Hz. A fragment of $H^A$ doublet for P4, the polymer of IV, $H^A$(P4)f, was observed as a shoulder; however, $H^B$(P5) was not detected in the spectrum of Fig. 2A, the coupling constants being reported as, $J_{AC} \approx 5.3$ and $J_{BC} \approx 5.8$ Hz [10-12].

A marked difference was observed between the spectrum of Fig. 2A and that of Fig. 2B. It is well known that the acetone-insoluble polymer is isotactic, having head-to-tail linkages, whereas the acetone-soluble polymer is atactic. Thus the signals at $\delta$ 3.25($H^A$) and 3.41($H^B$) ppm may be reasonably ascribed to the protons in the isotactic diad, and the additional signals in Fig. 2B at $\delta$ 3.22($H^A$) and 3.43($H^B$) ppm to the protons in the syndiotactic diad, in agreement with the assignment for polymers of monodeuterated methyloxiranes

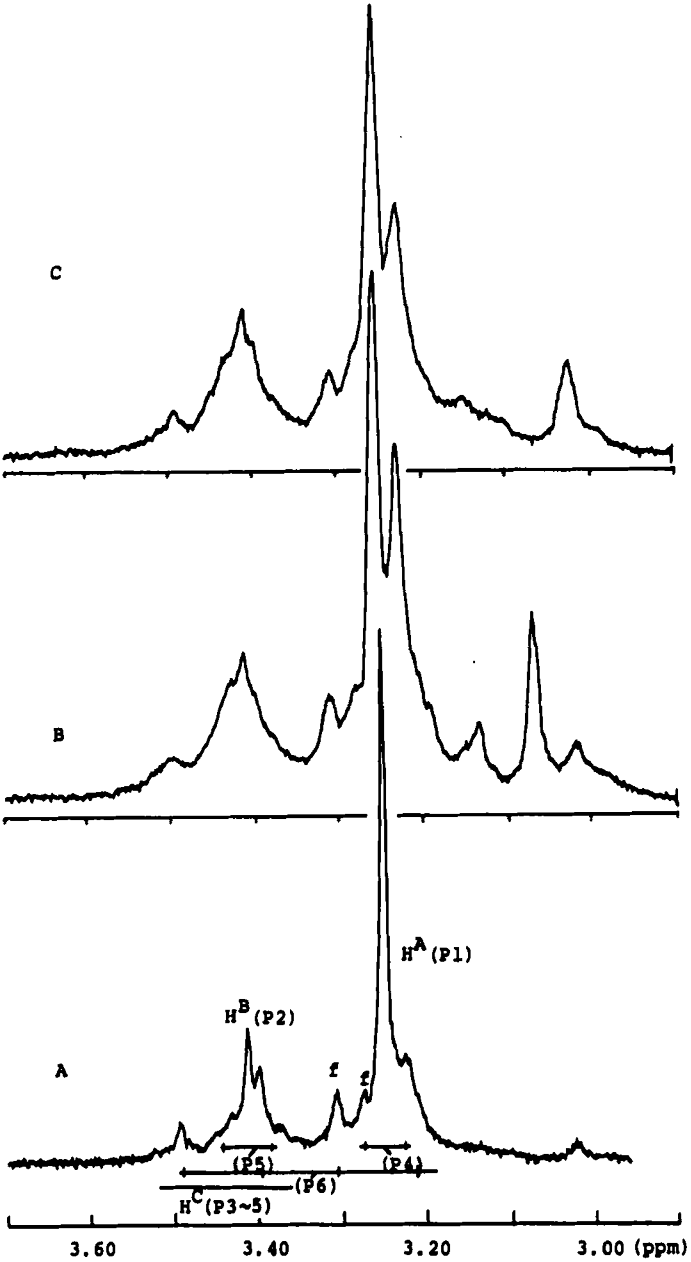

FIG. 2. Deuterium-decoupled 100 MHz $^1$H-NMR spectra of the methylene and methine proton signals of the deuterated polymers of I-VI, P1-P6 (description as in Fig. 1): (A) acetone-insoluble fraction; (B) acetone-soluble fraction; (C) whole polymer.

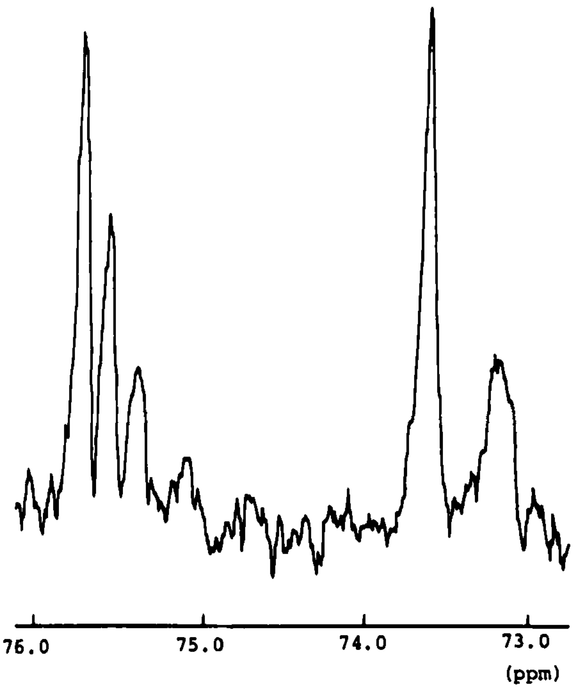

FIG. 3. 25.1 MHz $^{13}$C-NMR spectrum of the main-chain carbons of polymethyloxirane prepared with a lattice-disordered zinc dimethoxide (in chloroform solution at 70° C with TMS as internal standard).

[10-12]. The broad signals around 3.14($H^A$) and 3.38($H^B$) ppm may be assigned to tail-to-tail linkage, and the peaks around 3.10 ppm to OH and $CH_3O$ groups of the polymer chain end (see Experimental).

The most remarkable feature for the NMR spectra of this type of the deuterated polymer is the fairly clear separation of isotactic diad from syndiotactic one in $H^A$(P) signals. Although small amounts of $H^A$(P6) and $H^A$(P4) may disturb the separation to some extent, a reliable tacticity for the whole polymer can be determined using a curve resolver (Du Pont 310), with consideration of $^1$H-NMR spectra of the monomer and isotactic polymer. The area ratio for the $H^A$(P) signals of the whole polymers was given as isotactic diad/syndiotactic diad = 67/33, where P1:P4:P6 = 75 : 8 : 17.

TABLE 2. Polymer Tacticities for Polymethyloxirane Obtained with Organozinc Catalysts

| | Measured | | | | | Calcd[b] | | | |
|---|---|---|---|---|---|---|---|---|---|
| | diad | | triad | | | diad | triad | | |
| Polymethyloxirane[a] | i | s | I | H | S | $\sigma_i$ | $\sigma_I$ | $H_c$ | $S_c$ |
| LDZn | 0.68 | 0.32 | 0.51 | 0.32 | 0.17 | $0.80_0$ | $0.79_5$ | $0.32_6$ | $0.16_3$ |
| ZnM | 0.67 | 0.33 | 0.50 | 0.33 | 0.17 | $0.79_2$ | $0.79_0$ | $0.33_2$ | $0.16_6$ |

[a] LDZn prepared with the lattice-disordered zinc dimethoxide; ZnM prepared with $Zn(C_2H_5)_2/CH_3OH$ (1/2 mole/mole) system.

[b] $\sigma_i$ denotes $\sigma_2$ calculated from measured isotactic diad, $i = \sigma_2{}^2 \quad (1 - \sigma_2)^2$, $s = 2\,\sigma_2(1 - \sigma_2)$. $\sigma_I$, $H_c$, and $S_c$ denote $\sigma_2$, H, and S calculated from measured isotactic triad.

In parallel with the $^1$H-NMR study, the $^{13}$C-NMR spectrum of the nondeuterated polymethyloxirane obtained with the same lattice-disordered zinc dialkoxide catalyst was investigated. The 25.1-MHz $^{13}$C-NMR spectrum of the methylene and methine parts of the whole polymethyloxirane is shown in Fig. 3. The resonance at $\delta$ 17.55 ppm downfield from tetramethylsilane can be assigned to $CH_3$-carbon, that of the doublet 73.61 and 73.20 ppm to isotactic and syndiotactic diads (i and s) due to $CH_2$-carbon, and the triplet at 75.77, 75.60, and 75.42 ppm to isotactic, heterotactic, and syndiotactic triads (I, H, and S) due to CH-carbon, respectively [13, 14]. The area ratios for the diads and triads were measured and are listed in Table 2. The values of isotactic and syndiotactic diads obtained from the $^{13}$C-NMR spectrum are in good agreement with those from the $^1$H-NMR spectrum for poly-2,3-dideuteromethyloxirane.

In comparison with the polymer prepared with the lattice-disordered zinc dialkoxide, the $^{13}$C-NMR spectrum of polymethyloxirane obtained with diethylzinc–methanol (1:2 mole/mole) catalyst system was measured at similar condition. Although the activity of the diethylzinc–methanol catalyst system is much lower than that of the lattice-disordered zinc dimethoxide [3], tacticity data for the polymers obtained with the above two catalysts were found to be approximately the same (see Table 2). The $^{13}$C-NMR data were found to fit the statistics for the enantiomorphic catalyst sites control model [15] as expected: $I = 1 - 3\sigma_2(1 - \sigma_2)$, $S = \sigma_2(1 - \sigma_2)$, and $H = 2\sigma_2(1 - \sigma_2)$, where $\sigma_2$ refers to the probability of D configuration persistence at a D-preferring site and the probability of persistence for L at an L site: $\sigma_2$ were calculated as $0.80 \pm 0.01$ in the above systems. In parallel with the present study, it has recently been determined [16] that a single crystal of zinc dimethoxide complex possesses an enantiomorphic structure, and that polymerization of methyloxirane catalyzed by zinc dialkoxide proceeds with complete inversion of the configuration at the carbon atom attacked by the growing polymer chain end [4]. The results for $^{13}$C-NMR spectra are summarized in Table 2.

It was suggested previously that the initiator for methyloxirane polymerization catalyzed by diethylzinc–alcohol system is a lattice-disordered zinc dialkoxide formed [1]. The results obtained from $^1$H- and $^{13}$C-NMR studies substantiate this mechanism from the aspect of stereoregularity of the polymers obtained, or stereocontrolling factors of active species; much higher activity of the lattice-disordered zinc dialkoxide prepared separately under reflux in methanol solution compared to that of the lattice-disordered one formed in diethylzinc–methanol system can be interpreted from higher extent of the lattice-disorder of zinc dialkoxide and from absence of retardation agents such as ethylzinc alkoxide and alcohol, as previously discussed [3].

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Accepted by editor July 20, 1976
Received for publication July 22, 1976.