

STRUCTURE--REACTIVITY RELATIONSHIP OF CATALYSTS FOR RING-  
OPENING POLYMERIZATION OF SOME OXIRANES

Teiji Tsuruta

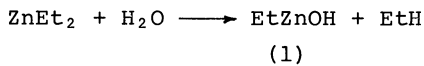
Department of Industrial Chemistry, Faculty of Engineering,  
Science University of Tokyo, Kagurazaka, Shinjuku-ku,  
Tokyo 162, Japan

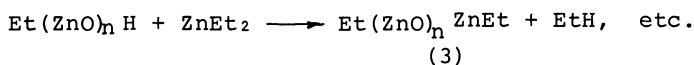
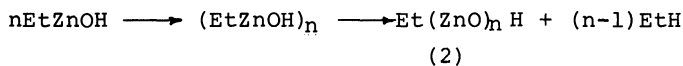
**Abstract** - This paper will review structure--reactivity relationship of organozinc and other organometallic catalysts in the ring-opening polymerizations of some oxiranes. The catalytic behavior of diethylzinc-water system was changeable in response to the ratio of diethylzinc to water. GPC study of a poly(methyloxirane) sample prepared by  $\text{Et}_2\text{Zn}/\text{H}_2\text{O}(1/0.1)$  showed the cationic nature of this catalyst system in contrast with the anionic nature of  $\text{Et}_2\text{Zn}/\text{H}_2\text{O}(1/1)$  system. Any of catalyst systems consisting of  $\text{Et}_2\text{Zn}$  and alcohol did not exhibit cationic nature irrespective of the mole ratio of the two components. Active species operative in the  $\text{Et}_2\text{Zn}/\text{CH}_3\text{OH}$  system was shown to be zinc dimethoxide. The reaction mechanism for the stereospecific polymerization of methyloxirane catalysed by zinc dimethoxide was elucidated in terms of the enantiomorphic catalyst site control model. Results of stereoselective and asymmetric selective (or stereoelective) polymerizations of some thiirane and oxirane with optically active organo-zinc or -cadmium catalyst were discussed in the light of recent studies with our model catalyst having a well-defined structure. Poly(methyloxirane) prepared with N-methyl- $\alpha, \beta, \gamma, \delta$ -tetraphenylporphin/ $\text{ZnEt}_2$  as catalyst was found to have a narrow molecular weight distribution and an unusual percentage of the triad tacticities. Since the porphin catalyst system was able to form a living system, it was possible to prepare block copolymers with 100% efficiency. A novel type of asymmetric selective (or stereoelective) polymerization of epichlorohydrin was found to take place with an optically active salen-type complex as catalyst. The nature of some catalysts for copolymerization of oxirane with carbon dioxide was also discussed in comparison with that for oxirane homopolymerization.

We have long been interested in the reactivity and stereospecificity of organozinc compounds as catalyst for oxirane polymerization (Refs. 1-5). In this paper, the writer will review structure--reactivity relationship of organozinc and other organometallic catalysts in the ring-opening polymerizations of some oxiranes.

1. DIETHYLZINC-WATER AND DIETHYLZINC-ALCOHOL SYSTEM AS CATALYST FOR METHYLOXIRANE POLYMERIZATION

It is widely recognized that  $\text{Et}_2\text{Zn}-\text{H}_2\text{O}$  system is the most active catalyst for the stereospecific oxirane polymerization (Ref. 6). A variety of chemical species operative in the polymerization reaction were previously shown to be formed according to the following equations:





The maximum catalyst activity was obtained when the mole ratio of  $\text{ZnEt}_2$  with  $\text{H}_2\text{O}$  is unity, where the predominant formation of chemical species (2) was realized. Comparison of an X-ray diffraction diagram of (2) with that of zinc oxide showed that the arrangement of zinc and oxygen atoms in (2) was similar to that in zinc oxide in which each atom was surrounded tetrahedrally by four other atoms. However, crystallinity of (2) was shown to be much lower than that of zinc oxide, so that (2) was considered to have disordered wurtzite structures.

Chemical species (3) was formed when less amount of water was used. Contrary to the anionic nature of (2), species (3) exhibited cationic nature. For instance, (3) induced a cationic polymerization of tetrahydrofuran. Recent study (Ref. 7) on GPC of a poly(methyloxirane) sample prepared by  $\text{Et}_2\text{Zn}/\text{H}_2\text{O}$  (1/0.1) showed clearly the cationic nature of this catalyst system (Fig. 1).

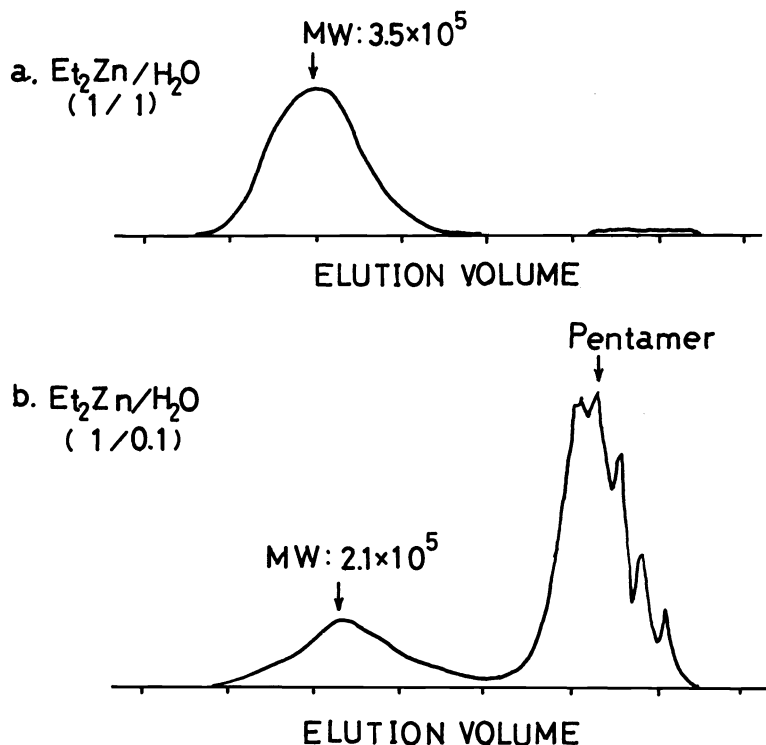


Fig. 1. GPC chromatograms of poly(methyloxirane) produced by  $\text{Et}_2\text{Zn}/\text{H}_2\text{O}$  system as catalyst.  $\text{Et}_2\text{Zn}/\text{H}_2\text{O}=1/1$  (mol/mol) (a),  $\text{Et}_2\text{Zn}/\text{H}_2\text{O}=1/0.1$  (mol/mol) (b).

More than 50 weight percent of the polymer obtained was found to consist of oligomers including pentamer and lower molecular weight compounds, in which head-to-head or tail-to-tail enchainments of the monomeric units are involved to a significant extent. This result is in good agreement with our previous finding (Refs. 8&9) that the optical activity of a polymer prepared from (R)-methyloxirane with  $\text{Et}_2\text{Zn}/\text{H}_2\text{O}(1/0.5)$  catalyst was very much lower than that prepared with  $\text{Et}_2\text{Zn}/\text{H}_2\text{O}(1/1)$  system. The lowered optical activity of the former polymer was ascribed to the inversion reactions which took place under the cleavage of  $\text{MeCH}^*\text{-O}$  bond, instead of  $\text{CH}_2\text{-O}$  bond, in the propagation stage.

The active species of  $\text{ZnEt}_2\text{-CH}_3\text{OH}$  system was proven to be zinc dimethoxide. Catalytic activities of zinc dimethoxide depended strongly on the method of

preparation. Almost no activity was found in crystalline powdery zinc dimethoxide prepared from  $\text{ZnCl}_2$  with  $\text{LiOMe}$  in methanol or  $\text{ZnEt}_2$  with methanol by standing at  $80^\circ\text{C}$ . On the other hand, highly active zinc dimethoxide could be prepared when the reaction between  $\text{ZnEt}_2$  (1 mol) and  $\text{CH}_3\text{OH}$  (2 mol) is carried out under vigorous stirring and refluxing (Ref. 10). The active zinc dimethoxide was shown to have disordered structure in terms of the X-ray diffraction diagram. It is to be noted that no trace of cationic nature is associated with  $\text{ZnEt}_2$ - $\text{CH}_3\text{OH}$  system, irrespective of the mole ratio of  $\text{ZnEt}_2$  with  $\text{CH}_3\text{OH}$ .

The active zinc dimethoxide was an insoluble powdery substance and the polymerization was started with thoroughly heterogeneous catalyst system. As the polymerization proceeded, granular particles of the insoluble zinc dimethoxide were gradually disintegrated to form a colloidal dispersion. As reported previously (Ref. 10), this polymerization system is lacking a termination reaction, so that the colloidal catalyst system, compared with the insoluble catalyst system, should be responsible for the formation of higher molecular weight polymer.

A marked difference in the polymerization behavior in response to  $\text{CdEt}_2$  as initiator was found in methylthiirane and methyloxirane (Ref. 1). Neither  $\text{CdEt}_2$ -ROH nor  $\text{CdEt}_2$ - $\text{H}_2\text{O}$  induced the oxirane polymerization, whereas these organocadmium systems easily polymerized methylthiirane to high-molecular weight polymers. A catalyst system consisting of  $\text{CdEt}_2$  and  $\text{CH}_3\text{COSH}$ , however, could induce the polymerization of methyloxirane (Ref. 11). The favored activity of the catalyst system was discussed in terms of  $d\pi$ - $d\pi$  bonding, on the basis of spectroscopic data.

## 2. STEREOSPECIFICITY OF ORGANOMETALLIC CATALYSTS IN THE OXIRANE AND THIIRANE POLYMERIZATIONS

The reaction mechanism for the stereospecific polymerization of methyloxirane with zinc dimethoxide was satisfactorily explained by the enantiomorphic catalyst sites model, in which a symmetrical distribution of  $d^*$ -sites and  $l^*$ -sites was assumed as the origin of the steric control mechanism (Ref. 5). Matsuzaki and Uryu (Ref. 12) reported previously that the triad tacticity of poly(methyloxirane) prepared with  $\text{Et}_2\text{Zn}$ -methanol catalyst accorded with values calculated on the basis of the enantiomorphic model (Ref. 13 & 14),

$$\begin{aligned} I &= 1 - 3\sigma_2(1 - \sigma_2) & (1) \\ H &= 2\sigma_2(1 - \sigma_2) & (2) \\ S &= \sigma_2(1 - \sigma_2) & (3) \end{aligned}$$

where parameter  $\sigma_2$  is a probability of entering D-monomer at  $d^*$ -catalyst site. The triad tacticity data for the poly(methyloxirane) samples prepared with  $\text{Zn}(\text{OMe})_2$  were also in good agreement with the enantiomorphic model. For instance (Ref. 15), the unfractionated polymer was found to have triad population (%):

$$I(51), H(32), S(17) \text{ and } \sigma_2(0.80)$$

For the acetone insoluble (at  $-30^\circ\text{C}$ - $22^\circ\text{C}$ ) fraction (Ref. 7) (38 wt %):

$$I(83), H(12), S(6) \text{ and } \sigma_2(0.94)$$

And the acetone soluble (at  $-30^\circ\text{C}$ ) fraction (62 wt %) had the tacticities:

$I(33), H(45), S(22)$  and  $\sigma_2(0.68)$ . Acetone is known as an appropriate solvent for fractionation of poly(methyloxirane)s according to their degree of tacticities. Instead of acetone fractionation, GPC technique with chloroform as eluent was applied to fractionate the whole polymer prepared with zinc dimethoxide catalyst (Ref. 7). This experiment revealed that the higher molecular weight poly(methyloxirane) had a lower isotacticity ( $I, 47; H, 35; S, 18$ ) than the lower molecular weight polymer ( $I, 53; H, 32; S, 15$ ). The catalyst surfaces of the insoluble zinc dimethoxide may provide active sites having higher chirality compared with those of the colloidal catalyst. When the catalyst system has an unsymmetrical distribution of  $d^*$ -sites and  $l^*$ -sites, an asymmetric selective (or stereoelective) polymerization takes place. First example was reported by the writer using  $\text{ZnEt}_2$ - $d$ -borneol system as catalyst (Ref. 16).

Extensive studies have been carried out by Spassky, Sigwalt et al. on the stereoselective and stereoelective polymerizations of thiirane and oxirane (Refs. 17-20). They found that  $R(-)3, 3$ -dimethyl-1,2-butanediol- $\text{ZnEt}_2(1:1)$

system had an extremely high stereoelective nature both in oxirane and thirane polymerizations.

Spassky, Sigwalt et al. (Refs. 21&22) revealed also that some cadmium compounds including simple salts are excellent initiators for stereoselective polymerization of methylthiirane. For instance, the isotactic diad percent in the poly(methylthiirane) sample prepared by Cd D-tartrate catalyst was more than 95%, in contrast with 69% that was found in a polymer sample prepared by Zn D-tartrate as catalyst. Surprisingly, Cd DL-tartrate also exhibited the same level of stereoselectivity as Cd D-tartrate. It is to be noted that just the opposite situation was found in the stereoelective ability of the two tartrates. Only very slight optical activity was associated with the poly(methylthiirane) sample prepared by Cd D-tartrate, whereas  $[\alpha]_D^{25} -5.8$  (in benzene) for the polymer sample by Zn D-tartrate.

In the light of recent results of our studies with model catalyst system(Refs. 23-25), it is reasonably assumed that any of zinc or cadmium compounds possess their intrinsic chirality around the metal atoms, even when none of the ligand has chiral structure (see Chapter 3). The intrinsic chirality around the metal atom should be the origin of d\*-site and l\*-site. For some reason, cadmium compounds can afford the catalyst sites having higher chirality compared with zinc compounds.

Catalyst sites of zinc and cadmium D-tartrates should be composed of the following chemical species in terms of chirality:

d\*-Zn D-tartrate and l\*-Zn D-tartrate

d\*-Cd D-tartrate and l\*-Cd D-tartrate

The higher stereoelectivity of Zn D-tartrate compared to Cd D-tartrate may be ascribed to the larger difference between reactivities of the two diastereomeric zinc tartrates toward D- or L-methylthiirane. On the other hand, the stereochemical reactivity of d\*(or l\*)-Cd tartrate may scarcely be influenced by the nature of chirality of tartrate ligands.

### 3. $[\text{EtZnOMe}]_6[\text{MeOZnOMe}]$ AND $[\text{EtZnOCH}_2\text{CH}_2\text{OMe}]_6[\text{Zn}(\text{OCH}_2\text{CH}_2\text{OMe})_2]$ AS MODEL COMPOUNDS FOR ENANTIOMORPHIC CATALYST SITES

It was desirable to elucidate the stereocontrol mechanism in terms of the molecular level considerations. No information, however, has been available concerning the chiral structure of d\*-sites and l\*-sites, because the active zinc dimethoxide is a disordered powdery substance. An organozinc complex,  $[\text{EtZnOMe}]_6[\text{MeOZnOMe}]$ , (4), was isolated by us in a form of single crystal (Ref. 23).

According to the X-ray analysis by N. Kasai et al. (Refs. 24&25), the organozinc complex consists of two enantiomorphous distorted cubes which share a corner. This structure was proven to be retained even in benzene solution in the temperature range from 5 to 80°C.

T. Hagiwara, M. Ishimori and T. Tsuruta (Refs. 5&7) carried out NMR analysis of a reaction system in which  $[\text{EtZnOMe}]_6[\text{MeOZnOMe}]$  and DL-methyloxirane were allowed to react in benzene at 80°C. They found that all of the observed signal in the reaction system can reasonably be explained in terms of the initiation mechanism by one of the inner methoxy groups. The triad tacticities of poly(methyloxirane) prepared with the zinc complex as catalyst were found to be in good agreement with those anticipated from the enantiomorphous catalyst sites model. For instance, an acetone insoluble (at -30°C~0°C) fraction (16 wt%) was found to have triad population(%):

I(68), H(21), S(11) and  $\sigma_2$ (0.88)

Acetone soluble (at -30°C) fraction (84 wt%) had tacticities:

I(40), H(39), S(21) and  $\sigma_2$ (0.74)

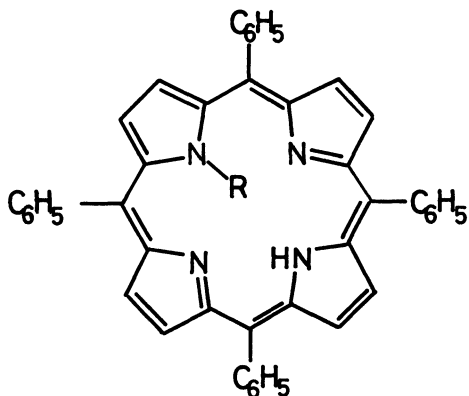
The tacticity data suggest that complex (4) afford more uniform distribution, in terms of chirality, of d\*-sites and l\*-sites compared with  $\text{Zn}(\text{OMe})_2$ , though the latter catalyst involves active sites having superior stereospecificity to the former. According to the recent study by N. Kasai et al. on  $[\text{EtZnOCH}_2\text{CH}_2\text{OMe}]_6[\text{Zn}(\text{OCH}_2\text{CH}_2\text{OMe})_2]$ , (5), this complex has a similar spatial structure to complex (4). The steric control ability of the zinc methoxyethanolate complex, (5), was found to be inferior to that of (4).

#### 4. UNIQUE BEHAVIOR OF CATALYSTS HAVING PORPHYRIN OR SALEN TYPE LIGAND

S. Inoue and N. Takeda (Ref. 26) have recently found that poly(methyloxirane) prepared with N-methyl- $\alpha, \beta, \gamma, \delta$ -tetraphenylporphin(6)/ZnEt<sub>2</sub> as catalyst has a narrow molecular weight distribution ( $M_w/M_n=1.15$ ) and an unusual percentage of the triad tacticities:

I(18), H(40) and S(42).

The observed tacticities did not conform to the enantiomorphous catalyst site control mechanism (Eqs. (1), (2) and (3) in Chapter 2).



(6) : R=CH<sub>3</sub>

(7) : R=H

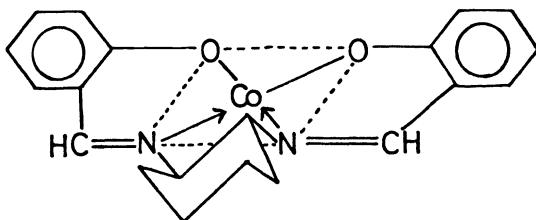
The stereoregulation in this polymerization is presumably operated by chiral structures of growing chain end including some contribution from the penultimate unit.

A catalyst system,  $\alpha, \beta, \gamma, \delta$ -tetraphenylporphin (7)/Et<sub>2</sub>AlCl system, was found to exhibit an extremely high activity in the methyloxirane polymerization. The polymer obtained by (7)/Et<sub>2</sub>AlCl catalyst consisted only of head to tail enchainments, in contrast with polymers prepared with Et<sub>2</sub>AlCl alone, and had a tacticity population:

I(47), H(43) and S(10).

These values conformed to the growing chain end control model without penultimate effect. End group study on an oligomeric product showed that the oligomer carried a chlorine and a hydroxyl group at each terminal. Inoue et al. concluded the polymerization to be initiated by the insertion of the oxirane ring into Cl-Al bond of the catalyst to form an aluminum alkoxide linkage. One of the most significant features of (7)/Et<sub>2</sub>AlCl is its ability to form a "living system": 100% catalyst efficiency, narrow MW distribution and no termination. By using this catalyst system, it was possible to prepare block copolymers with 100% efficiency.

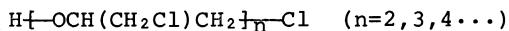
A novel type of asymmetric selective polymerization of epichlorohydrin was found by Y. Tezuka, M. Ishimori and T. Tsuruta (Ref. 27) with the aid of an optically active cobalt (II) salen complex, N,N'-disalicylidene-(1R,2R)-1,2-cyclohexanediaminatocobalt (II), (8), coupled with AlEt<sub>3</sub>, as catalyst.



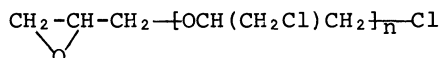
(8)

Most of the reaction products were acetone-soluble. The acetone-soluble part was dissolved in benzene and washed with aq. HCl to remove catalyst residue. After washing with water, the benzene solution was freeze-dried to leave

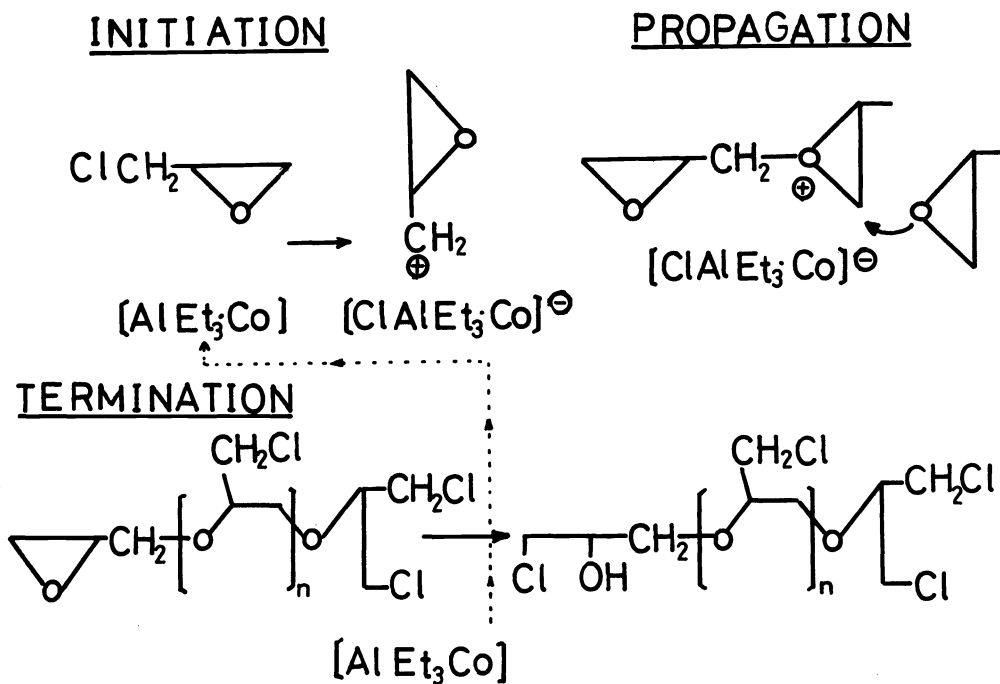
oligomers which showed (-) optical rotation. The optical activity was also observed in the unreacted monomer recovered, indicating that an asymmetric selective (or stereoelective) reaction took place in this polymerization. Though the asymmetric selection of the monomer was conducted by the cobalt complex, the single use of (8) did not induce any reaction with ECH under this reaction condition. The acetone-soluble oligomers were studied by means of GPC. Much simpler GPC patterns were observed for the samples prepared with the (8)/AlEt<sub>3</sub> system, compared to samples with AlEt<sub>3</sub> alone as catalyst. Each oligomer observed as one of a series of GPC peaks was fractionated by preparative GPC technique. The isolated fractions were proven to be a series of oligomers,



by means of <sup>1</sup>H- and <sup>13</sup>C-nmr, IR and mass spectroscopies. When the acetone-soluble par was directly fractionated by GPC without any pretreatment with aq. HCl, the formation of oligomer having an oxirane ring at the terminal was observed:



The circular dichroism(CD) study and gas evolution analysis indicated that (8) and AlEt<sub>3</sub> formed a molecular complex in benzene, no cleavage of Al-Et bond being observed in the binary system. From these results, it was concluded that the ECH polymerization should proceed according to a cationic mechanism:



##### 5. CATALYSTS FOR COPOLYMERIZATION OF OXIRANE WITH CARBON DIOXIDE

An alternating copolymerization between oxirane and CO<sub>2</sub> was previously found possible with the use of the ZnEt<sub>2</sub>-H<sub>2</sub>O system as catalyst (Ref. 28). According to later studies, binary systems involving primary amine, dihydric (or trihydric) phenol, aromatic dicarboxylic acid, aromatic oxycarboxylic and many other related compounds as the partner component with ZnEt<sub>2</sub> formed

the most effective catalyst systems for the copolymerization (Ref. 29). These catalyst systems are characterized by the repetition of ZnO (or ZnN) linkages as seen in (2) or (3). For the copolymerization of oxirane with carbon dioxide, ZnEt<sub>2</sub>/H<sub>2</sub>O (1/1) system exhibited the highest catalytic activity. A study (Ref. 30) of the copolymerization of (R)-methyloxirane with carbon dioxide showed that more than 95% of the ring-opening took place at CH<sub>2</sub>-O bond during the propagation process. These results suggested that the active catalyst operative in this copolymerization should be an anionic species like (2) rather than the cationic species like (3) (see Chapter 1). Zinc dimethoxide has no activity for the copolymerization, though this compound is one of the most excellent catalysts for the homopolymerization of oxirane. The lack of the activity in the copolymerization seems to be correlated with the absence of the repetition of ZnO linkages in the zinc dialkoxide.

$\alpha, \beta, \gamma, \delta$ -Tetraphenylporphinatoaluminum methoxide (9) has recently been reported by S. Inoue et al. (Ref. 26) to effectuate the copolymerization of methyloxirane with carbon dioxide, though the content of oxycarbonyl units was 40 mole %. In the catalyst system, (9), no repetition of AlO linkage seems to be involved. Further study will be required for elucidating the structure-reactivity relationship of catalysts in the oxirane polymerization including the copolymerization with carbon dioxide.

## REFERENCES

1. T. Tsuruta, The Stereochemistry of Macromolecules (Marcel Dekker, Inc., New York), Vol. 2, 177 (1967) and references therein.
2. T. Tsuruta, J. Polymer Science, D6, 179 (1972).
3. T. Tsuruta, Pure and Appl. Chem., 48, 267 (1976).
4. T. Tsuruta, ACS Symposium Series, 59, 178 (1977).
5. T. Tsuruta, J. Polymer Sci., Polymer Chem. Ed. (in press).
6. Y. Ishii, S. Sakai in "Ring Opening Polymerization", Edited by K. C. Frisch and S. L. Reegen, Marcel Dekker, New York, 1969, p. 13 and references therein.
7. T. Hagiwara, M. Ishimori and T. Tsuruta, Makromol. Chem., 181, in press (1980).
8. S. Tsuchiya and T. Tsuruta, Makromol. Chem., 110, 123 (1967).
9. S. Tsuchiya and T. Tsuruta, Kobunshi Kagaku (Chemistry of High Polymers), 25, 717 (1968).
10. M. Ishimori, Ginho Hsiue, and T. Tsuruta, Makromol. Chem., 123, 52 (1969).
11. M. Ishimori, O. Nakasugi, K. Yokobori and T. Tsuruta, Makromol. Chem., 171, 41 (1973).
12. T. Uryu, H. Shimazu and K. Matsuzaki, Polymer Letters Edition, 11, 275 (1973).
13. T. Fueno and J. Furukawa, J. Polymer Sci., A2, 3681 (1964).
14. T. Fueno, R. A. Shelden and J. Furukawa, J. Polymer Sci., A3, 1279 (1965).
15. M. Ishimori, K. Tsukigawa, T. Nakada and T. Tsuruta, J. Macromol. Sci.-Chem., All, 379 (1977).
16. S. Inoue, T. Tsuruta and J. Furukawa, Makromol. Chem., 53, 215 (1962).
17. P. Sigwalt, Pure and Applied Chem., 48, 257 (1976) and references therein.
18. M. Sepulchre, N. Spassky and P. Sigwalt, Israel J. Chem., 15, 33 (1976/77).
19. C. Coulon, N. Spassky and P. Sigwalt, Polymer, 17, 821 (1976).
20. A. Momtaz, N. Spassky and P. Sigwalt, Polymer Bulletin, 1, 267 (1979).
21. K. J. Ivin, E. D. Lillie, P. Sigwalt and N. Spassky, Macromolecules, 4, 345 (1971).
22. M. Marchetti, E. Chiellini, M. Sepulchre and N. Spassky, Makromol. Chem., 180, 1305 (1979).
23. M. Ishimori, T. Tomoshige and T. Tsuruta, Makromol. Chem., 120, 161 (1968).
24. M. Ishimori, T. Hagiwara, T. Tsuruta, Y. Kai, N. Yasuoka and N. Kasai, Bull. Chem. Soc. Japan, 49, 1165 (1976).
25. M. Ishimori, T. Hagiwara and T. Tsuruta, Makromol. Chem., 179, 2337 (1978).
26. N. Takeda and S. Inoue, Makromol. Chem., 179, 1377 (1978).
27. Y. Tezuka, M. Ishimori and T. Tsuruta, ACS Polymer Preprints, 20, 798 (1979).
28. S. Inoue, H. Koinuma and T. Tsuruta, J. Polymer Sci., B7, 287 (1969).
29. S. Inoue, Chemtech, 6, 588 (1976) and references therein.
30. S. Inoue, H. Koinuma and T. Tsuruta, Polymer J., 2, 220 (1971).