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## PROPYLENE OXIDE HOMOPOLYMERIZATION AND COPOLYMERIZATION WITH CARBON DIOXIDE BY $\gamma$ -ALUMINA-SUPPORTED ZINC COORDINATION CATALYSTS

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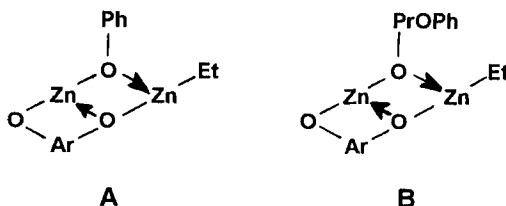
### ABSTRACT

Propylene oxide was homopolymerized and copolymerized with carbon dioxide in the presence of catalysts based on ethylzinc phenoxide or ethylzinc 1-phenoxy-2-propoxide and/or diethylzinc and  $\gamma$ -alumina as a support. The propylene oxide homopolymerization yielded poly(propylene oxide) with an average molecular weight of about  $20 \times 10^3$ , and consisting of the prevailing amorphous fraction and the crystalline fraction. The copolymerization of propylene oxide and carbon dioxide produced poly(propylene carbonate) with an average molecular weight of about  $30 \times 10^3$  and was accompanied by the formation of propylene carbonate. The polymeric products obtained were characterized by means of elemental analysis, IR, UV,  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectroscopy, and molecular weight determinations. On the basis of these studies, especially those concerning the polymer end-groups and the chain microstructure, a possible structure of the active sites in  $\gamma$ -alumina-supported zinc coordination catalysts and a possible mechanism of the initiation and propagation reactions in propylene oxide homopolymerization and copolymerization with carbon dioxide are presented.

## INTRODUCTION

The polymerization of propylene oxide and its copolymerization with carbon dioxide in the presence of supported catalysts based on diethylzinc or other metal alkyls (e.g., diethylcadmium, tributylboron, triethylaluminum) and metal oxides (e.g., alumina, silica, silica-alumina) have been studied [1–4]. The  $\gamma$ -alumina-diethylzinc system appears to exhibit a considerably high activity in homopolymerization, leading to poly(propylene oxide) [1, 2], as well as in copolymerization, leading to poly(propylene carbonate) [3, 4]. It was reported [3] that diethylzinc reacts with the surface hydroxyl groups of  $\gamma$ -alumina to give mainly the Al–O–Zn–Et species.

In the course of our investigations on propylene oxide homopolymerization [5, 6] and copolymerization with carbon dioxide [7–9] in the presence of homogeneous catalysts derived from reactions of diethylzinc with polyhydric phenol [e.g., catechol, 4-*tert*-butylcatechol (Ar(OH)<sub>2</sub>)] and phenol (PhOH) or alcohol (1-phenoxy-2-propanol, PhOPrOH), we postulated that the catalyst's active sites involve structures in which the oxygen atom of the phenoxy or alkoxy group of the OZnO unit is coordinated at the zinc atom of the adjacent EtZnO group (A and B, respectively).



The phenolato-zinc species (A) were found [6, 9] to initiate polymerization via propylene oxide incorporation into the OZn–OPh bond both in homopolymerization and copolymerization systems. But the alcoholato-zinc species (B) appeared to initiate copolymerization via carbon dioxide incorporation into the OZn–OPrOPh bond [9]. Propylene oxide incorporation into this bond was proved [6] in the homopolymerization system. It was shown [10, 11] that diethylzinc–phenol catalysts containing only OZnO units are less active in the copolymerization of propylene oxide and carbon dioxide than those containing both the OZnO and EtZnO units. On the other hand, diethylzinc–polyhydric phenol catalysts with only EtZnO units lacked any catalytic activity in the copolymerization of propylene oxide and carbon dioxide [8].

It is worth noting that the copolymerization of propylene oxide and carbon dioxide in the presence of homogeneous catalysts based on trialkylaluminum (instead of diethylzinc) and multiprotic compound leads to copolymers containing a considerable excess of propylene oxide units with respect to carbon dioxide units incorporated into chains [12, 13].

This work deals with propylene oxide homopolymerization and copolymerization with carbon dioxide in the presence of supported catalysts derived from reactions of ethylzinc compounds like ethylzinc phenoxy or ethylzinc 1-phenoxy-2-

propoxide and/or diethylzinc ( $\text{EtZnX}$ ;  $\text{X} = \text{OPh}$ ,  $\text{OPrOPh}$ ,  $\text{Et}$ ) with  $\gamma$ -alumina. Such catalysts are expected to contain  $\text{OZnO}$  or  $\text{EtZnO}$  units as well as having these units occur together at the surface, depending on the mode of catalyst preparation. Our studies were especially aimed at supplying information concerning the initiation and propagation reactions.

## EXPERIMENTAL

### Materials

Diethylzinc ( $\text{Et}_2\text{Zn}$ ), propylene oxide (PO), phenol (PhOH), and the solvents used were commercially obtained and purified by the usual procedures. Ethylzinc phenoxide ( $\text{EtZnOPh}$ ) and ethylzinc 1-phenoxy-2-propoxide ( $\text{EtZnOPrOPh}$ ) were obtained by the reactions of diethylzinc with equimolar amounts of phenol and 1-phenoxy-2-propanol, respectively [6]. Carbon dioxide was used without further purification.  $\gamma\text{-Al}_2\text{O}_3$  (60–80 mesh powdered alumina with a surface area of  $150 \text{ m}^2/\text{g}$ ) was calcined at  $500^\circ\text{C}$  for 16 hours and then kept under reduced pressure at ambient temperature for 1 hour prior to use. 1-Phenoxy-2-propanol (PhOPrOH) was prepared from phenol and propylene oxide [14]. All the materials were stored under deoxygenated and dried nitrogen.

### Preparation of Supported Catalysts

The amount of surface hydroxyl groups of  $\gamma$ -alumina was determined using sodium naphthalenide according to a known procedure [15].

Catalysts were prepared immediately before use. To a 50-mL glass round vessel containing 10 mL purified toluene and  $\gamma$ -alumina, a measured amount of ethylzinc compound ( $\text{EtZnX}$ ;  $\text{X} = \text{OPh}$ ,  $\text{OPrOPh}$ ,  $\text{Et}$ ) (or an equimolar mixture of ethylzinc compounds) was slowly added under stirring in a nitrogen atmosphere. After the addition was completed the content of the vessel was stirred vigorously until ethane evolution ceased. The volume of ethane evolved was measured in a gas buret. The catalyst obtained was filtered off, washed with a large amount of toluene (under nitrogen), and dried under vacuum at room temperature.

### Polymerization Procedure

Measured amounts of a supported catalyst, eventually *n*-hexane, and monomers were placed in a 60-mL glass ampule or stainless steel autoclave. The amount of ethane evolved during the introduction of PO in the case of the  $\text{Et}_2\text{Zn}$ - $\gamma$ -alumina catalyst was measured in a gas buret. The reaction vessel was then heated to the reaction temperature and kept standing in a thermostated oil bath for the required time. Then the products were worked up and the polymer was isolated according to methods described previously [6, 9]. The propylene carbonate (PC) content formed as a by-product, apart from poly(propylene carbonate) (PPC) in a copolymerization system, was determined in the postreaction mixture by means of IR spectroscopy ( $\nu_{\text{C}=\text{O}} = 1800 \text{ cm}^{-1}$  for PC,  $\nu_{\text{C}=\text{O}} = 1750 \text{ cm}^{-1}$  for PPC).

## Analysis of Polymers

The polymeric products were characterized by means of elemental analysis (Perkin-Elmer 240 microanalyzer) (PPC), IR spectroscopy (Specord 80 Carl-Zeiss Jena),  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectroscopy (Varian VXR 300 MHz spectrometer, in  $\text{CDCl}_3$ ), UV spectroscopy (Philips PU 8740 UV/VIS spectrometer, in THF), and viscosity measurements (Ubbelohde viscometer, in benzene).

## RESULTS AND DISCUSSION

### Catalysts

Determinations of the surface hydroxyl groups of  $\gamma$ -alumina showed them to occur as 0.48 mmol/g support. The amounts of ethane evolved during the reaction of the ethylzinc compound ( $\text{EtZnX}$ ;  $\text{X} = \text{OPh}$ ,  $\text{OPrOPh}$ ,  $\text{Et}$ ) with such  $\gamma$ -alumina were found to correspond to the amount of surface hydroxyl groups of the support. Thus, catalysts obtained by using the ethylzinc compound in an equimolar amount with respect to hydroxyl groups of  $\gamma$ -alumina are characterized by the appearance of the  $\text{Al}-\text{O}-\text{Zn}-\text{X}$  species in which  $\text{X} = \text{OPh}$  for the alumina- $\text{EtZnOPh}$  system (**1**),  $\text{X} = \text{OPh}$  and  $\text{Et}$  (1:1 by mole) for the alumina- $\text{EtZnOPh}/\text{Et}_2\text{Zn}$  (1:1 by mole) system (**2**),  $\text{X} = \text{OPrOPh}$  for the alumina- $\text{EtZnOPrOPh}$  system (**3**),  $\text{X} = \text{OPrOPh}$  and  $\text{Et}$  (1:1 by mole) for the alumina- $\text{EtZnOPrOPh}/\text{Et}_2\text{Zn}$  (1:1 by mole) system (**4**), and  $\text{X} = \text{Et}$  for the alumina- $\text{Et}_2\text{Zn}$  system (**5**).

### Polymerization of Propylene Oxide

Propylene oxide was polymerized in the presence of catalysts **1-5** at  $70^\circ\text{C}$  for 7 days. All these catalysts appeared to yield poly(propylene oxide) with an average molecular weight in the  $9 \times 10^3$  to  $31 \times 10^3$  range (Table 1).

The presence of the catalyst's aromatic moiety as the  $\text{C}_6\text{H}_5\text{O}$ -chain end-group in poly(propylene oxide), obtained using catalysts **1-4**, was detected by means of  $^1\text{H}$ -NMR spectroscopy ( $\delta = 6.9$ - $7.1$  ppm),  $^{13}\text{C}$ -NMR spectroscopy ( $\delta = 114.5$ ,  $129.5$ ,  $159.5$  ppm), and UV spectroscopy ( $\lambda_{\text{max}} = 271.2$ ,  $278.0$  nm). This shows propylene oxide incorporation into the  $\text{OZn}-\text{OPh}$  bond in catalysts **1** and **2** and into the  $\text{OZn}-\text{OPrOPh}$  bond in catalysts **3** and **4**. Such an initiation reaction mode is consistent with that established for propylene oxide polymerization by diethylzinc-polyhydric phenol catalysts [6].

It was observed that propylene oxide polymerization by catalyst **5** is accompanied by relatively fast ethane evolution in the initial period (during monomer addition) and that the amount of ethane evolved corresponds almost quantitatively with the amount of ethyl groups present in the catalyst. Poly(propylene oxide) obtained by this catalyst was found to contain unsaturated  $\text{CH}_3\text{CH}=\text{CHO}-$  and  $\text{CH}_2=\text{C}(\text{CH}_3)\text{O}-$  chain end-groups. This was concluded from the presence of chemical shifts at  $\delta = 18.2$  [ $\underline{\text{C}}\text{H}_3\text{CH}=\text{}$ ],  $114.0$  [ $\text{C}\underline{\text{H}}_3\text{CH}=\text{}$ ], and  $132.2$  [ $=\underline{\text{C}}\text{HO}-$ ] ppm, attributable to the former group, and at  $\delta = 16.1$  [ $=\text{C}(\underline{\text{C}}\text{H}_3)\text{O}-$ ],  $88.1$  [ $\underline{\text{C}}\text{H}_2=\text{}$ ], and  $160.9$  [ $=\underline{\text{C}}(\text{CH}_3)\text{O}-$ ] ppm, attributable to the latter group, apart from chemical shifts at  $\delta = 17.4$  [ $-\text{CH}(\underline{\text{C}}\text{H}_3)\text{O}-$ ],  $72.8$ - $73.3$  [ $-\underline{\text{C}}\text{H}_2-$ ], and  $75.1$ - $75.5$  [ $-\text{CH}(\underline{\text{C}}\text{H}_3)\text{O}-$ ] ppm, characteristic of chain monomeric units, in the  $^{13}\text{C}$ -NMR

TABLE 1. Homopolymerization of Propylene Oxide (PO) by Ethylzinc Compound (EtZnX)- $\gamma$ -Alumina Catalysts<sup>a</sup>

| Run | Catalyst, X =            | Poly(propylene oxide) |              |                               |                                   | Monomer conversion, mol/g-atom Zn |
|-----|--------------------------|-----------------------|--------------|-------------------------------|-----------------------------------|-----------------------------------|
|     |                          | Yield                 |              | Crystallinity, <sup>b</sup> % | $M_v \times 10^{-3}$ <sup>c</sup> |                                   |
|     |                          | %                     | g/g catalyst |                               |                                   |                                   |
| 1   | 1 OPh                    | 77.1                  | 2.90         | 32.0                          | 31                                | 112.5                             |
| 2   | 2 OPh/Et <sup>d</sup>    | 78.0                  | 2.99         | 33.5                          | 16                                | 113.5                             |
| 3   | 3 OPrOPh                 | 77.0                  | 2.83         | 6.3                           | 19                                | 112.5                             |
| 4   | 4 OPrOPh/Et <sup>d</sup> | 78.1                  | 2.95         | 20.0                          | 18                                | 113.5                             |
| 5   | 5 Et                     | 80.1                  | 3.11         | 14.0                          | 9                                 | 116.7                             |

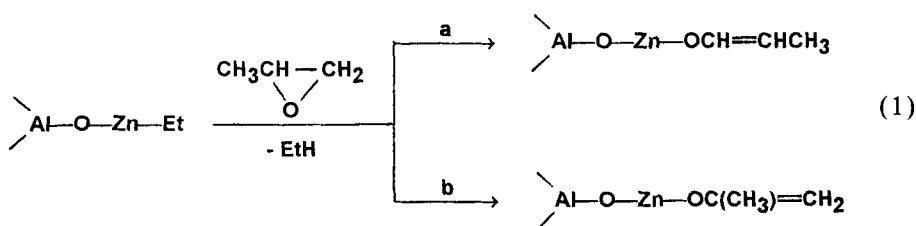
<sup>a</sup>Reaction conditions:  $\gamma$ -alumina = 2 g (amount of surface hydroxyl groups = 0.48 mmol/g support); EtZnX = 0.96 mmol; PO = 140 mmol (10 mL); reaction medium = *n*-hexane (10 mL); 70°C; 7 days.

<sup>b</sup>Crystalline, isotactic fraction, insoluble in methanol at 0°C.

<sup>c</sup>From viscosity measurements (in benzene at 25°C) and the equation  $[\eta] = 1.12 \times 10^{-4}(M_v)^{0.77}$ ; see Reference 16.

<sup>d</sup>In a 1:1 mole ratio.

spectrum of the polymer produced by catalyst 5. The intensities of the respective signals attributed to the chain end-groups in this spectrum indicate the  $\text{CH}_3\text{CH}=\text{CHO}-$  group to be predominant. Thus, the formation of active species in propylene oxide polymerization by catalyst 5 can be explained in terms of ethane elimination according to Eq. (1):



Such a reaction is consistent with previous observations concerning alkane evolution in the reaction of propylene oxide with an organometallic compound [17]. It is obvious that the species formed during ethane elimination from catalyst 5 can initiate polymerization via propylene oxide incorporation into the  $\text{OZn-OCH=CHCH}_3$  and  $\text{OZn-OC(CH}_3\text{)=CH}_2$  bonds.

The poly(propylene oxide) obtained by catalysts 1-5 was found to consist mainly of an amorphous fraction and a minor crystalline fraction (Table 1). <sup>13</sup>C-NMR spectra of both the amorphous and the crystalline fraction of the polymer obtained in propylene oxide polymerization by catalyst 2 (Table 1, Run 2) are presented in Fig. 1.

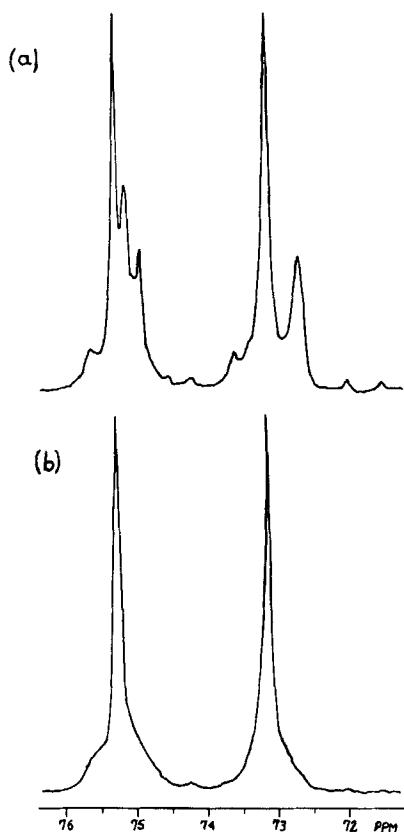


FIG. 1.  $^{13}\text{C}$ -NMR spectra ( $\text{CH}_2$ ,  $\text{CH}$  groups) of PPO obtained with the catalyst  $\gamma$ -alumina-EtZnOph/Et $_2$ Zn (1:1 by mole) (2): (a) amorphous, methanol-soluble fraction; (b) crystalline fraction insoluble in methanol at 0°C; solvent,  $\text{CDCl}_3$ .

The spectrum of the amorphous poly(propylene oxide) fraction (Fig. 1a) exhibits chemical shifts at  $\delta = 73.2$  and  $72.7$  ppm ( $\underline{\text{C}}\text{H}_2$ ) (attributable to isotactic and syndiotactic diads, respectively) and at  $\delta = 75.3$ ,  $75.2$ , and  $74.9$  ppm ( $\underline{\text{C}}\text{H}$ ) (characteristic of isotactic, heterotactic, and syndiotactic triads, respectively) [6]. The mole fraction of isotactic diads in this spectrum is equal to 0.68. Similar values were obtained for amorphous polymers yielded by other catalysts (Table 1, Runs 1 and 3-5). The spectrum of the crystalline poly(propylene oxide) fraction (Fig. 1b) exhibits two nonsplitted signals at  $\delta = 75.3$  ( $\underline{\text{C}}\text{H}$ ) and  $73.2$  ( $\underline{\text{C}}\text{H}_2$ ) ppm, indicating an isotactic enchainment of propylene oxide units. Values of the  $\sigma_2$  parameter calculated (according to literature data [18]) from  $^{13}\text{C}$ -NMR spectroscopic analysis of the diad and triad tacticities for the amorphous fraction of poly(propylene oxide) and for the crude, not fractioned poly(propylene oxide) obtained by catalysts 1-5, are presented in Tables 2 and 3, respectively.

These values correspond to those determined previously by Tsuruta et al. [18, 19] for the polymer formed in propylene oxide polymerization by catalysts of the  $\text{ZnEt}_2$ -ROH type [R = Me,  $\text{MeOCH}_2\text{CH}_2$ ,  $\text{MeOCH}_2\text{CH}(\text{Me})$ ] and thus corroborate the mechanism of enantiomorphic catalyst site control of the polymer chain

TABLE 2. Tacticities of Amorphous Poly(Propylene Oxide) (PPO)

| Catalyst | Diad % <sup>a</sup> |          |                   | Triad % <sup>c</sup> |          |          | $\sigma_2^{(1)d}$ |
|----------|---------------------|----------|-------------------|----------------------|----------|----------|-------------------|
|          | <i>i</i>            | <i>s</i> | $\sigma_2^{(i)b}$ | <i>I</i>             | <i>H</i> | <i>S</i> |                   |
| 1        | 67                  | 33       | 0.79              | 49                   | 27       | 24       | 0.79              |
| 2        | 68                  | 32       | 0.80              | 45                   | 32       | 23       | 0.76              |
| 3        | 68                  | 32       | 0.80              | 48                   | 30       | 22       | 0.78              |
| 4        | 68                  | 32       | 0.80              | 47                   | 32       | 21       | 0.77              |
| 5        | 67                  | 33       | 0.79              | 50                   | 26       | 24       | 0.79              |

<sup>a</sup>Area ratio, calculated from <sup>13</sup>C-NMR spectrum for methylene carbon region of the polymer.

<sup>b</sup> $\sigma_2^{(i)}$  calculated from isotactic diad:  $i = \sigma_2^2 + (1 - \sigma_2)^2$ ; see Reference 18.

<sup>c</sup>Area ratio, calculated from <sup>13</sup>C-NMR spectrum for methine carbon region of the polymer.

<sup>d</sup> $\sigma_2^{(1)}$  calculated from isotactic triad:  $I = 1 - 3\sigma_2(1 - \sigma_2)$ ; see Reference 18.

growth. It is worth mentioning that the values of  $\sigma_2$  obtained for crude, not fractionated poly(propylene oxide) yielded by  $\gamma$ -alumina-supported zinc coordination catalysts (1–5) are somewhat higher than those determined for the polymer yielded by homogeneous catalysts based on diethylzinc, dihydric phenol and phenol, or 1-phenoxy-2-propanol (containing sites A and B, respectively) [6].

### Copolymerization of Propylene Oxide and Carbon Dioxide

Propylene oxide and carbon dioxide were reacted in the presence of catalysts 1–5. The respective copolymers of nearly equimolar composition (evidenced by elemental analysis), poly(propylene carbonate), and the cyclic carbonate, propylene carbonate, were found to be formed in comparable yields (Table 4).

The <sup>1</sup>H-NMR spectrum of poly(propylene carbonate) obtained by catalyst 2 (Table 4, Run 1) exhibits chemical shifts at  $\delta = 1.1$ – $1.2$  [–CH(CH<sub>2</sub>)–], 4.1

TABLE 3. Tacticities of Crude, Not Fractionated Poly(Propylene Oxide) (PPO)

| Catalyst | Diad % <sup>a</sup> |          |                   | Triad % <sup>c</sup> |          |          | $\sigma_2^{(1)d}$ |
|----------|---------------------|----------|-------------------|----------------------|----------|----------|-------------------|
|          | <i>i</i>            | <i>s</i> | $\sigma_2^{(i)b}$ | <i>I</i>             | <i>H</i> | <i>S</i> |                   |
| 1        | 77                  | 23       | 0.86              | 56                   | 30       | 14       | 0.82              |
| 2        | 70                  | 30       | 0.82              | 55                   | 27       | 18       | 0.82              |
| 3        | 69                  | 31       | 0.81              | 47                   | 30       | 23       | 0.78              |
| 4        | 72                  | 28       | 0.83              | 56                   | 26       | 18       | 0.82              |
| 5        | 76                  | 24       | 0.86              | 59                   | 25       | 16       | 0.84              |

<sup>a–d</sup>See the respective footnotes in Table 2.



TABLE 4. Copolymerization of Propylene Oxide (PO) and Carbon Dioxide by Ethylzinc Compound (EtZnX)- $\gamma$ -Alumina Catalysts<sup>a</sup>

| Run            | Catalyst | Poly(propylene carbonate) <sup>b</sup> |         |       |              |                       | Propylene carbonate yield, % | Monomer <sup>d</sup> conversion, mol/g-atom Zn |
|----------------|----------|--|---------|-------|--------------|-----------------------|------------------------------|--|
|                |          | Reaction                               |         | Yield |              | $M_n \times 10^{-3c}$ |                              |  |
|                |          | Temp, °C                               | Time, h | %     | g/g catalyst |                       |                              |  |
| 1 <sup>c</sup> | 2        | 70                                     | 20      | 7.1   | 0.48         | 33                    | 7.4                          | 21.1   |
| 2 <sup>c</sup> | 3        | 70                                     | 20      | 1.6   | 0.10         | —                     | 2.0                          | 5.2  |
| 3 <sup>c</sup> | 4        | 70                                     | 20      | 9.4   | 0.63         | 28                    | 13.5                         | 33.4   |
| 4 <sup>c</sup> | 5        | 70                                     | 20      | 16.8  | 1.15         | 20                    | 12.6                         | 42.9   |
| 5              | 1        | 70                                     | 20      | 5.7   | 0.38         | 24                    | 5.7                          | 16.6   |
| 6              | 2        | 70                                     | 20      | 11.0  | 0.74         | 35                    | 13.4                         | 35.6   |
| 7              | 2        | 100                                    | 6       | 10.2  | 0.69         | 32                    | 10.2                         | 29.7   |
| 8              | 2        | 35                                     | 70      | 7.2   | 0.49         | 38                    | 1.8                          | 13.1   |
| 9              | 3        | 70                                     | 20      | 4.0   | 0.26         | —                     | 4.9                          | 12.9   |
| 10             | 4        | 70                                     | 20      | 17.0  | 1.13         | 22                    | 27.7                         | 65.2   |
| 11             | 5        | 70                                     | 20      | 19.7  | 1.35         | 37                    | 13.1                         | 48.2   |

<sup>a</sup>Reaction conditions:  $\gamma$ -alumina = 2 g (amount of surface hydroxyl groups = 0.48 mmol/g support); EtZnX = 0.96 mmol; PO = 140 mmol (10 mL); CO<sub>2</sub> = ca. 60 atm.

<sup>b</sup>High-molecular-weight fraction, insoluble in methanol; satisfactory results of elemental analysis were obtained.

<sup>c</sup>From viscosity measurements (in benzene at 35°C); calculated from the equation  $[\eta] = 1.11 \times 10(M_n)^{0.8}$ ; see Reference 2.

<sup>d</sup>Resulting in both poly(propylene carbonate) and propylene carbonate formation; calculated for each comonomer.

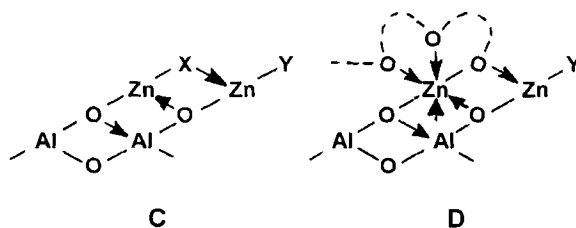
<sup>e</sup>Reaction medium, *n*-hexane (10 mL).

[—CH<sub>2</sub>—], and 4.9 [—CH(CH<sub>3</sub>)—] ppm (similar values were reported previously for poly(propylene carbonate) obtained with diethylzinc–water catalyst [20]), which are characteristic for —CH<sub>2</sub>CH(CH<sub>3</sub>)OC(O)O— units, and at  $\delta = 6.8$ –7.1 ppm, characteristic for the C<sub>6</sub>H<sub>5</sub>O— end-group of the chain. The presence of the C<sub>6</sub>H<sub>5</sub>O group at the chain end was also evidenced by UV spectroscopy ( $\lambda_{\max} = 271.6, 278.3$  nm). Similar <sup>1</sup>H-NMR and UV spectra were recorded for polymers obtained by catalysts 1, 3, and 4. The presence of the catalyst's aromatic moiety as the chain end-group in poly(propylene carbonate), obtained using catalysts 1–4, testifies for propylene oxide incorporation into the OZn—OPh bond in catalysts 1 and 2 and for carbon dioxide incorporation into the OZn—OPrOPh bond in catalysts 3 and 4. Such an initiation reaction mode is consistent with that found for propylene oxide–carbon dioxide copolymerization by diethylzinc–polyhydric phenol–phenol or alcohol catalysts [9]. The initiation reaction in copolymerization in the presence of catalyst 5 involves carbon dioxide incorporation into OZn—OCH=CHCH<sub>3</sub> and OZn—OC(CH<sub>3</sub>)=CH<sub>2</sub> bonds, formed analogously to the propylene oxide homopolymerization system.

Propylene carbonate formation, apart from poly(propylene carbonate), can be explained in terms of copolymer chain depolymerization [8, 9, 21].

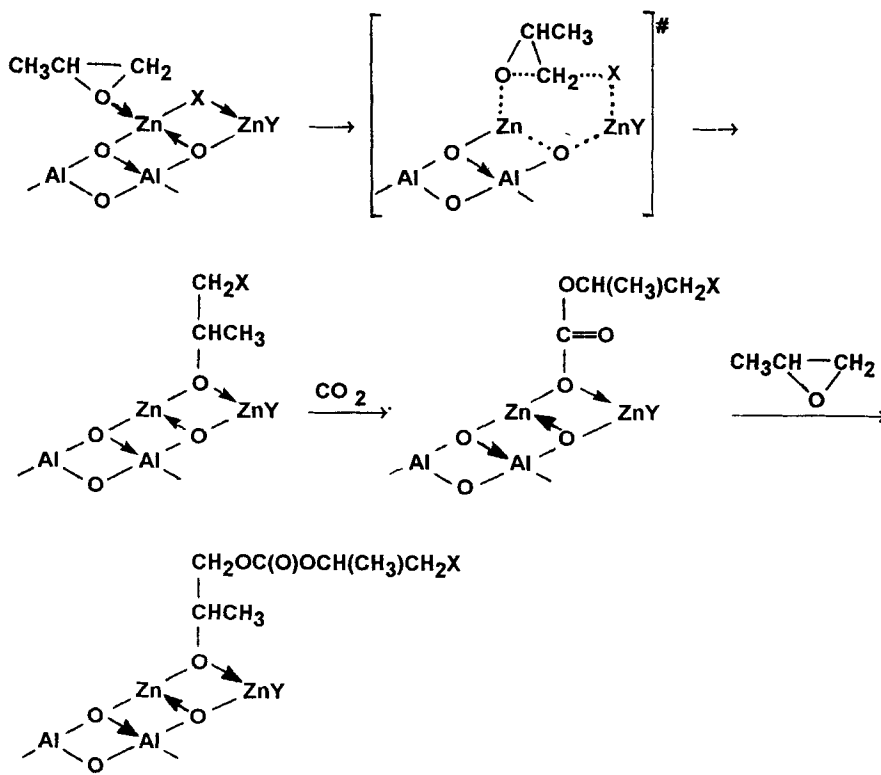
**Active Sites and Polymerization Mechanism**

Considering the results obtained in this study, taking into account data concerning propylene oxide homopolymerization and copolymerization with carbon dioxide in the presence of catalysts based on diethylzinc and polyhydric phenol [5-12], and also using data concerning the structure of the alumina surface [22], the active sites in polymerization by  $\gamma$ -alumina-supported zinc coordination catalysts are proposed to involve structure C.



X = PhO, PhOPrO, CH<sub>3</sub>CH=CHO, CH<sub>2</sub>=C(CH<sub>3</sub>)O; Y = X, Et;  
 ---O-----O-----O- = PPO chain.

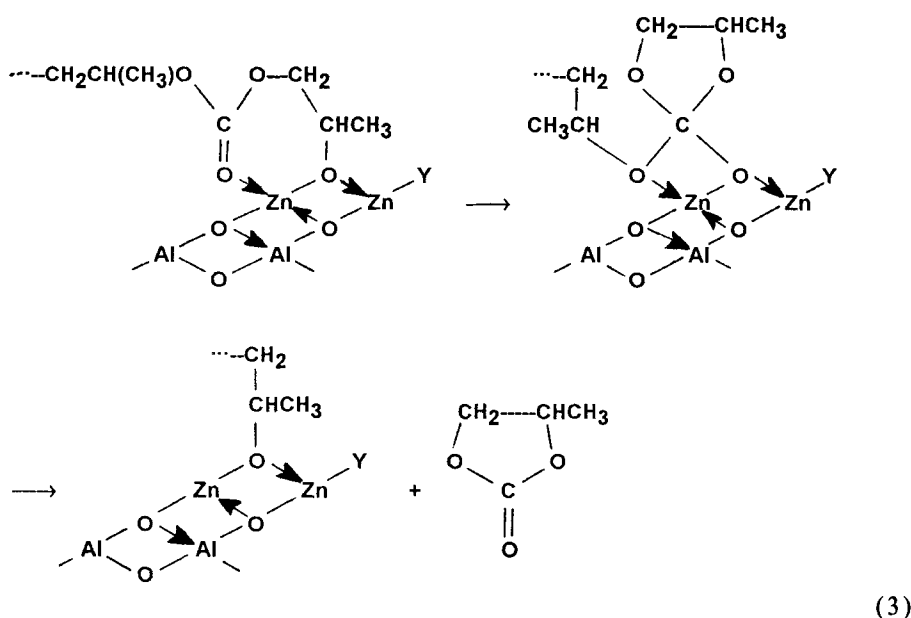
The polymerization involving such active sites most probably occurs by a mechanism analogous to that postulated to operate in the presence of homogeneous catalysts [6, 9]. Thus, the reaction scheme can be proposed as in Eq. (2).



(2)

The catalyst's enantioselectivity, which results in isotactic poly(propylene oxide) formation, appears when the zinc atom of the  $\text{OZnO}$  unit becomes six-coordinated due to its complexation with the oxygen atoms of the growing polymer chain (D), analogous to what was proposed [6] for homogeneous systems.

Complexation of the growing copolymer chain with this zinc atom in the copolymerization reaction results in cyclic carbonate formation (Eq. 3), in a way similar to that postulated for homogeneous systems [9, 21].



## CONCLUSION

Propylene oxide homopolymerization and copolymerization with carbon dioxide in the presence of  $\gamma$ -alumina-supported catalysts containing  $\text{Al-O-Zn-O}$  surface species proceed in both initiation and propagation steps involving the  $\text{AlOZn-O}$  active bond, analogous to the case of their respective reactions carried out in the presence of homogeneous zinc-based coordination catalysts. When  $\gamma$ -alumina-supported catalysts with  $\text{Al-O-Zn-Et}$  surface species are used, the initiation step involves reaction of propylene oxide with the  $\text{AlOZn-Et}$  bond, resulting in formation of the  $\text{AlOZn-O}$  active bond under ethane elimination; this is in contrast to their respective homogeneous zinc-based catalysts containing  $\text{O-Zn-Et}$  bonds in which the  $\text{OZn-Et}$  bond is not susceptible to reaction with propylene oxide.

The behavior of  $\gamma$ -alumina-supported zinc coordination catalysts is similar to that of the respective homogeneous catalysts in propylene oxide homopolymerization in terms of the catalyst's enantioselectivity and to propylene oxide-carbon dioxide copolymerization in terms of cyclic propylene carbonate formation.

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