

# DMC Catalyzed Epoxide Polymerization: Induction Period, Kinetics, and Mechanism

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**ABSTRACT:** The kinetics of propylene oxide polymerization catalyzed by double metal cyanide complexes was studied by means of pressure measurements. The induction periods were determined as the time as the system pressure began to drop and the reaction rates were considered proportional to the slope of pressure decrease. The induction periods were found to depend on reaction temperature, water content, and the type and amount of catalysts, regulators, and solvents. Elevating reaction temperatures, using dried raw materials, and applying proper regulators favored shortened induction periods. The reaction rates were found to depend on the concentrations of catalyst  $C$ , monomer  $M$ , and regulator  $Tr$  as expressed in the equation

$$R_p = KM^2C/(1 + k Tr),$$

where  $K$  was a rate constant and  $k$  was a transition constant. The rates also depended on reaction temperature. The apparent activation energy was 59.1 kJ/mol according to the Arrhenius equation. A mechanism was proposed for the polymerization which was in good accordance with the experimental results. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1302–1309, 2004

**Key words:** catalysts; ring-opening polymerization; kinetics; polyethers

## INTRODUCTION

Application of double metal cyanide complexes (DMC) in epoxide polymerization has been drawn much attention in the past 2 decades.<sup>1–4</sup> DMC is much more active than conventional acidic or basic catalysts, producing polyethers with much lower unsaturation and much narrower molecular weight distribution. However, kinetics for the synthesis of DMC polyethers is not known in detail as for that of other polyethers. In the presence of DMC catalysts, the epoxide polymerization needs an induction period of minutes or hours.<sup>5</sup> Shortening of this period is expected for improvement of reaction techniques<sup>6</sup> and product qualities. Induction periods were known to depend on the techniques of catalyst preparation and on the contents of water and other impurities.<sup>6,7</sup> For many catalyst systems such as Lewis acids, rare earths, and aluminum porphyrins, the rate of polymerization is known to be first order to concentrations of either monomer or catalyst.<sup>8–10</sup> Yang et al. reported that copolymerization of epoxides with carbon dioxide in the presence of a polymer-supported bimetallic catalyst exhibited special kinetics and mechanism.<sup>11</sup> Similar characteristics have been seen in studies on DMC ether synthesis.

## EXPERIMENTAL

### Materials

Toluene and other solvents, AR, and propylene oxide (PO), industrial grade, were dried with 3A molecular sieves several times to reduce water content to a level below 150 ppm. DMC catalysts were prepared according to reported methods.<sup>12</sup>

### Measurements

<sup>1</sup>H-NMR spectra were recorded in CDCl<sub>3</sub> solution using a Bruker Analytik DRX-400 spectrometer. The <sup>1</sup>H chemical shifts were calibrated with tetramethylsilane. Fourier transform infrared spectra were recorded on a 1725X spectrometer with samples as KBr discs.

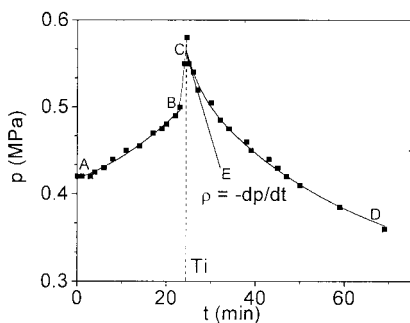
### Determination of water content

Water content in raw materials was determined by the method of Karl Fischer using a KF-1 water analyzer according to the standard GB12008.6–89.

### Determination of induction periods and polymerization rates

The concentration of each material was calculated from its mass and density at the required temperature. Phase equilibrium calculations indicated that this was accurate enough for the attempted work because the majority of the materials remained in the liquid phase

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**Figure 1** Pressure variation during PO polymerization catalyzed by DMC.

under applied conditions. In the polymerization experiments, designed amounts of DMC catalyst and other involatile materials were added to a predried 0.1 L autoclave equipped with a manometer. The autoclave was evacuated, filled with nitrogen, and then put into an oil bath and heated to designated temperatures (105°C unless specified). PO and other volatile materials were quickly injected into the autoclave, which was then sealed. The stirring was turned on and the pressure variation was recorded at intervals as a curve in Figure 1. In the curve, point A corresponded to the moment of material addition (i.e., time 0); the lines AB and BC corresponded to the temperature recovery from cooling using the added materials (the BC line may not be seen depending on the device condition). Once the reaction was initiated, the pressure of the system began to drop. The dropping rate was at its maximum at the very beginning and gradually decreased afterward because of the consumption of the monomer (between points C and D in the curve). Although theoretically point B was the real beginning of the reaction, point C was instead defined as the induction period  $t_0$  for conveniently recording the initiating pressure variation. This would not generate much error because the two points were very close to each other. Using a computer to draw a curve to fit the experimental data between C and D, the absolute slope  $\rho$  (i.e.,  $-dp/dt$ ) of the tangent CE at point C corresponded to the initial (maximum) rate of the reaction.

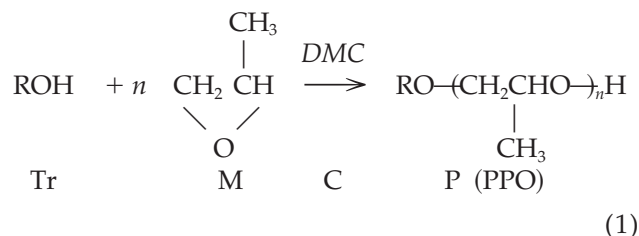
## RESULTS AND DISCUSSION

### Obtaining kinetic data from pressure variation

In general, induction period data can be obtained by recording the monomer conversion during practical whole ether synthesis using complete devices.<sup>5,9,13</sup> Measurements of such data as well as the reaction rates are quite complicated and time consuming. Because propylene oxide has quite a low boiling point and high vapor pressure, it is possible to simplify the

kinetic study by means of pressure observation. The operation process was discussed under Experimental. Parallel measurement was carried out in the absence of catalyst; after the heating stage the pressure was observed to be constant. This implied that the pressure curve drop from point C to D was really due to the reaction.

As eq. (1) shows, synthesis of polypropylene oxide (PPO) was carried out with various amounts of catalyst C (in g/L), initial concentrations of monomer M (in mol PO/L), and regulator Tr (in mol OH group/L). The starting speed of pressure decrease  $\rho$  (i.e.,  $-dp/dt$ ) was recorded for each case.

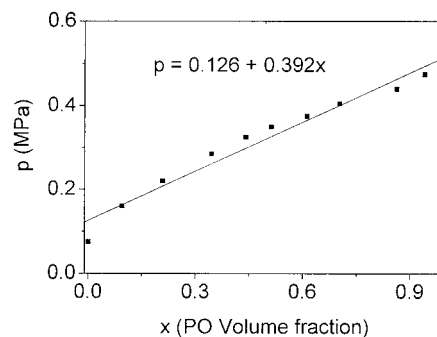


Vapor-liquid equilibrium was evaluated at 105°C for a series of toluene solutions of propylene oxide. The pressure was found to depend on the PO volume fractions  $x$  as showed in Figure 2. Regression resulted in a linear expression [eq. (2)], where the constant  $a = 0.126$  and  $b = 0.392$ . The deviation between the data points and the straight line reflected the difference between real solution and ideal solution.

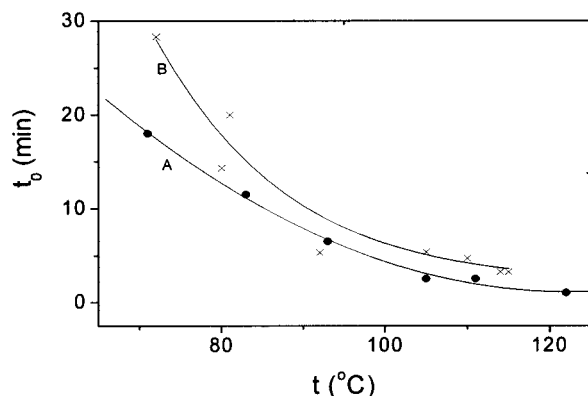
$$p \text{ (MPa)} = a + bx \quad (2)$$

With the formula weight  $F_M = 58.08$  and the density at 105°C  $D_M = 0.709 \text{ g}\cdot\text{mL}^{-1}$ , the monomer concentration  $M$  can be written as in eq. (3) and the polymerization rate  $R_p$  can be expressed as a negative derivative of  $M$ .

$$M \text{ (mol}\cdot\text{L}^{-1}) = \frac{10^3 D_M}{F_M} x \quad (3)$$



**Figure 2** Vapor pressure of PO/PhMe solution at 105°C depending on volume fraction.



**Figure 3** Dependence of induction period on temperature. PO, 9 mL; DMC content based on PO, 0.05 wt%. Curve A, bulk polymerization. Curve B, polymerization in toluene (9 mL).

$$R_p (\text{mol} \cdot \text{L}^{-1} \cdot \text{min}^{-1}) = -\frac{dM}{dt} = -\frac{10^3 D_M}{F_M} \frac{dx}{dt}$$

$$\rho (\text{MPa} \cdot \text{min}^{-1}) = -\frac{dp}{dt} = -b \frac{dx}{dt}$$

$$R_p = K_a \rho \quad (4)$$

$$K_a = \frac{10^3 D_M}{b F_M} = 31.1 \text{ mol} \cdot \text{L}^{-1} \cdot \text{MPa}^{-1}$$

eq. (4) indicates that the polymerization rate is proportional to the rate of pressure dropping. This gives a method for obtaining kinetic data and it is much more convenient than *in situ* NMR, dilatometer, and other methods.

### Factors influencing induction periods

#### Temperatures

Higher temperature favored faster activation and demonstrated correlation as shown in Figure 3. Above 105°C the induction periods were short and tended to remain constant. Therefore, 80~120°C was a suitable range for DMC polyether synthesis.

#### Catalysts

Catalysts with different structure and composition showed different induction periods. In DMC preparation different organic substances may be used to form definite coordination circumstances around zinc. DMC catalysts made of different organic substances brought different induction periods, as shown by the experimental data in Table I. Figure 4 illustrates that different amounts of the same kind of catalyst also affected the induction period. This figure shows that

**TABLE I**  
Induction Periods ( $t_0$ ) of PO Polymerization Using Different Types of DMC<sup>a</sup>

Cat. no.	Chelating agent <sup>b</sup>	$t_0$ (min)
1	PPO + PMPS	8
2	PVAc	4.5
3	PMPS	5
4	PPO	9

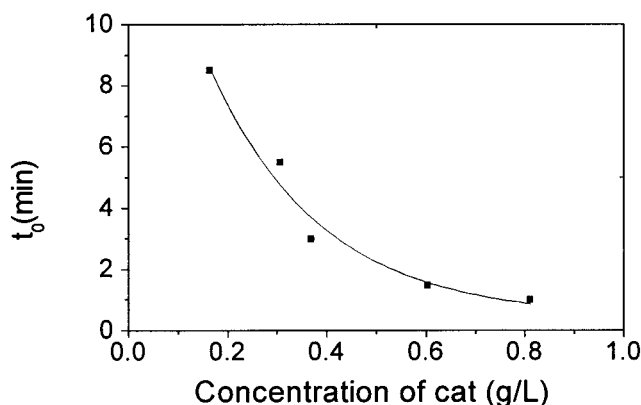
<sup>a</sup>  $M$ , 12.21 mol/L;  $C$ , 0.41 g/L (PO, 9 mL; DMC content based on PO: 0.056 wt %).

<sup>b</sup> PMPS, polymethylphenyl siloxane fluid; PVAc, polyvinyl acetate.

the induction period tended to be constant if enough catalyst was used; otherwise a slightly longer induction period may be observed because the reaction heat was insufficient for the pressure response.

### Regulators and water impurity

Substances containing active hydrogen atoms such as small molecular or macromolecular alcohols are often needed as regulators in polyether synthesis.<sup>14</sup> The lower the molecular weight expected, the more regulator should be applied. However, some substances containing highly active hydrogen atoms such as amines and primary alcohols are known to be unsuitable to be applied as molecular weight regulators.<sup>5,7</sup> This relates to the induction period of polymerization. Table II shows the influence of regulators of different type and with different molecular weights. The results reveal that the more OH groups the regulator contained and the smaller the distance among the OH groups, the longer the induction period. Thus, as regulators offering short induction periods, compounds containing secondary OH groups were better than those containing amine or primary OH groups; PPO resins were better than lower alcohols; diols were



**Figure 4** Dependence of induction period on catalyst contents.  $M$ , 12.21 mol/L (PO, 9 mL;  $\text{H}_2\text{O}$ : 0.0096 wt% based on PO).

**TABLE II**  
The Effect of Different Regulators on Induction Period<sup>a</sup>

Regulator	MW of regulator	Tr <sup>b</sup> (mol/L)	t <sub>0</sub> (min)
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>15</sub> NH <sub>2</sub>	241	0.071	>360
H <sub>2</sub> O	18	0.179	>360
HOCH <sub>2</sub> CHMeOH	76	0.194	>360
HO(C <sub>2</sub> H <sub>4</sub> O) <sub>3</sub> H	150	0.194	40
O(CH <sub>2</sub> CHMeOH) <sub>2</sub>	134	0.182	44
1,4-Cyclohexane diol	116	0.192	10.5
PPO triol	400	0.180	12.5
PPO diol (contg. BF <sub>3</sub> )	500	0.181	9
PPO diol	500	0.213	4

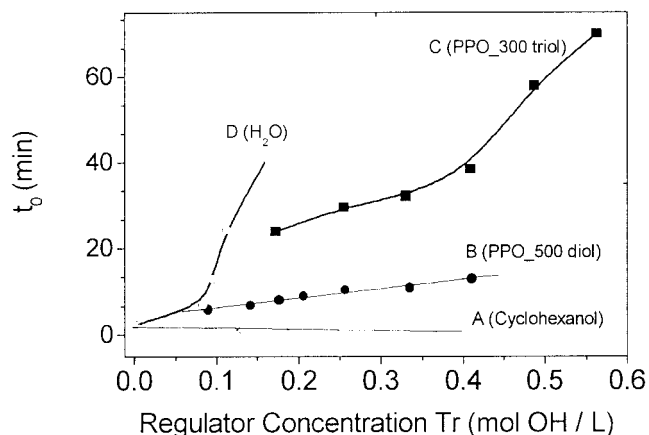
<sup>a</sup> The theoretical molecular weight of polyether product was 8000 g/mol, calculated as  $w_{PO}$ /mol of regulator; cat. content 0.05 wt % based on PO; PO, 9 mL.

<sup>b</sup> Tr represents the concentration of OH or NH groups.

better than triols. This may be because the catalyst cations would be hard to access by monomers in order to initiate the reaction if they were closely surrounded by strong electron donating or chelating regulators. Besides, it was found that the presence of BF<sub>3</sub> or other acidic impurities in the PPO resins as regulators made for long induction periods.

Figure 5 shows variation of the induction periods detected for polymerization experiments with equal amounts of PO and catalyst but different types and concentrations of Tr (calculated as moles of OH groups per liter) regulator. Among them, cyclohexanol was a monofunctional regulator and almost did not influence the induction period. In the presence of PPO diol of molecular weight 500 or PPO triol of molecular weight 300, polymerization would be delayed. If too much trifunctional regulator is used, the reaction may even stop.

Water, as an impurity in the raw materials, can be regarded as a bifunctional alcohol. A small amount of



**Figure 5** Dependence of induction period on regulator concentration. A: Cyclohexanol; B: PPO 500 diol; C: PPO 300 triol; D: H<sub>2</sub>O. A–C: PO 9 mL; DMC 0.05 wt% based on PO. D: PO 9 mL, DMC 0.055 wt% based on PO.

**TABLE III**  
The Effect of Different Solvents on Induction Period

Solvent	t <sub>0</sub> /min		
	Cat. no. 2 <sup>c</sup>	Cat. no. 3 <sup>c</sup>	Cat. no. 4 <sup>c</sup>
None	4.5	5	9
2-butanone	25.0		
Cyclohexane	5.5		
Toluene	5.0 <sup>a</sup> 16 <sup>b</sup>	52 <sup>b</sup>	13 <sup>b</sup>
CH <sub>2</sub> Cl <sub>2</sub>	4.5		
THF	3.0		

<sup>a</sup> Solvent: PO = 1 : 3 (volume).

<sup>b</sup> Solvent: PO = 1 : 1 (volume).

<sup>c</sup> Catalysts are as listed in Table I.

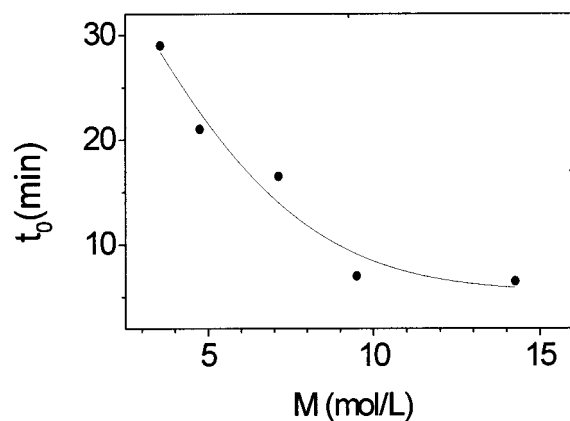
water acted as a regulator.<sup>14</sup> Increasing the water content resulted in a longer induction period; too much water deactivated the catalyst and finally blocked the reaction (curve D in Fig. 5). Therefore, for polyether synthesis, the raw materials should be well dried to keep the OH concentration from water less than 0.08 mol/L; if this concentration exceeded 0.16, the reaction would be prohibited.

#### Solvents

In the DMC catalyzed polymerization, the addition of limited amounts of solvents was found to be helpful in decreasing the system viscosity and making the reaction smoother.<sup>15</sup> However, the addition of large amounts of solvents resulted in dilution of the reacting solution. Table III shows induction periods using different solvents. Application of small amounts of inert solvents such as cyclohexane, toluene, and methylene chloride did not make longer induction periods. Butanone gave a longer induction period and even caused the reaction to stop at a very early stage. The phenomenon may be related to the coordination property of ketones. However, addition of THF gave a short induction period and did not inhibit the reaction any more. In this case, <sup>1</sup>H NMR spectra of the obtained polymer did not show any –OCH<sub>2</sub>CH<sub>2</sub>– signals at 1.5–1.7 ppm as structural units from THF. This indicated that THF did not act as a monomer but just as an excellent solvent for epoxide polymerization.

Table III also shows that using large amounts of solvents resulted in much longer induction periods. Interestingly, the increase of induction periods was found to depend not only on the type and amount of solvents, but also on the type of catalysts used in the polymerization. This may be related to the different composition, different structure, and different response to concentration of each material.

Adding and increasing the amount of solvents decreased the concentrations of the catalyst and the re-



**Figure 6** The effect of monomer concentration on induction period. DMC content, 0.05 wt% based on PO.

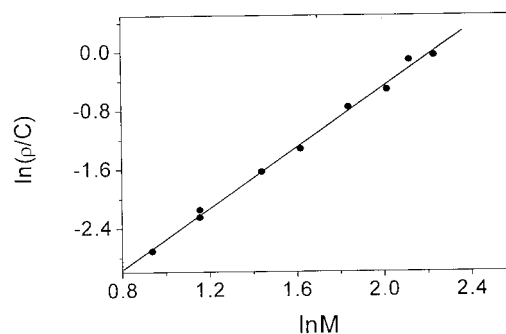
actants; thus, longer induction periods were observed as illustrated in Figure 6.

#### Rates of polymerization in the absence of regulators

The kinetics of DMC catalyzed epoxide polymerization was studied in toluene solutions, because toluene has a comparatively high boiling point, low vapor pressure, and good solubility both for monomer and polymer. Table IV shows the data of catalyst  $C$  (g/L), PO concentration  $M$  (mol/L), and corresponding maximum pressure dropping speed  $\rho$  (MPa/min). Linearly correlating  $\ln\rho$  with  $\ln M$  and  $\ln C$  resulted in the regression equation [eq. (5)], with a regression coefficient of 0.998.

$$\ln \rho = 4.67 + 2.08 \ln M + 0.975 \ln C \quad (5)$$

Equation (5) indicates that the reaction was nearly second order (2.08) to the monomer and nearly first order (0.975) to the catalyst. The effectiveness of the regression can be illustrated by drawing  $\ln(\rho/C) \sim \ln M$  (Fig. 7) and  $\ln(\rho/M_2) \sim \ln C$  (Fig. 8) correlations with the all experimental data in Table IV. It was found that



**Figure 7** Effect of monomer concentration on polymerization rate.  $M$ , mol L<sup>-1</sup>;  $C$ , g L<sup>-1</sup>;  $\rho$  (i.e.,  $-dp/dt$ ), MPa min<sup>-1</sup>. Slope = 2.08, linear regression coefficient (RegCoef), 0.998; relative deviation (RelDev), 2.6%.

they both formed good straight lines with slopes of nearly 2 and 1, respectively. Because the rate of polymerization was proportional to  $\rho$  [Eq. (4)], we had expressions such as eqs. (6) and (7).

$$\rho = 0.00937M^2C \quad (6)$$

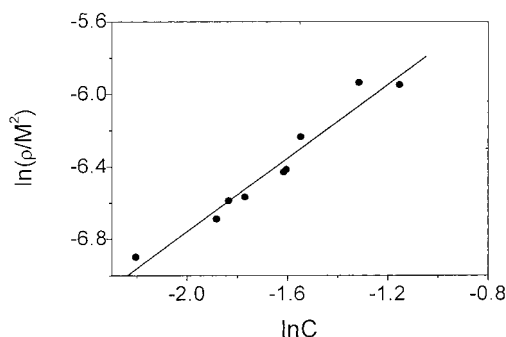
$$R_p = K_a\rho = 0.292M^2C \quad (7)$$

#### Rates of polymerization in the presence of regulators

Addition of active hydrogen containing compounds (regulators) is necessary for regulation of molecular weights in polyether synthesis. The regulators influence the molecular weights by means of chain transition. It was found that along with the addition of regulators, the polymerization rate was decreased to some extent depending on the type and amount of regulators. Regulators with OH functionalities of 1, 2, and 3 were applied to determine the dependence of a function  $M^2C/\rho$  on the OH concentration  $Tr$  (mol OH/L) of the regulators. It was found that they formed straight lines as shown in Figure 9. The three lines crossed each other in a small area of  $Tr = 0$ ; all

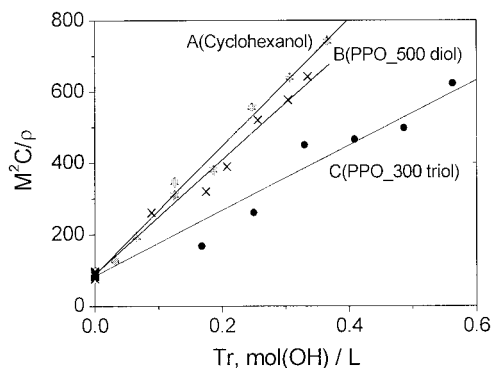
**TABLE IV**  
Maximum Pressure Dropping Speed in PO  
Polymerization in Toluene Solutions

Run	$M$ (mol · L <sup>-1</sup> )	$C$ (g · L <sup>-1</sup> )	$\rho$ (MPa · min <sup>-1</sup> )
1	2.55	0.1990	0.0132
2	3.18	0.1704	0.0179
3	3.18	0.1102	0.0129
4	4.22	0.1597	0.0312
5	5.05	0.1522	0.0406
6	6.29	0.2129	0.1000
7	7.51	0.2010	0.1200
8	8.32	0.2685	0.2400
9	9.32	0.3156	0.3000



**Figure 8** Effect of DMC concentration on polymerization rate. Slope = 1.01, RegCoef = 0.977, RelDev = 8.3%.



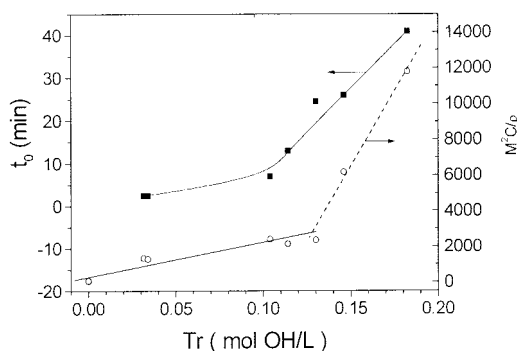


**Figure 9** Regulator effect on rate of polymerization. A. Cyclohexanol, PO 13 mL; DMC 0.0047 g;  $M^2C/\rho = 88.4 + 1795Tr$ , RegCoef = 0.997, RelDev = 2.0%. B. PPO 500 diol, PO 10 mL; DMC 0.0043 g;  $M^2C/\rho = 89.6 + 1597Tr$ , RegCoef = 0.995, RelDev = 2.7%. C. PPO 300 triol, PO 10 mL; DMC 0.0042 g;  $M^2C/\rho = 84.8 + 913Tr$ , RegCoef = 0.986, RelDev = 4.7%

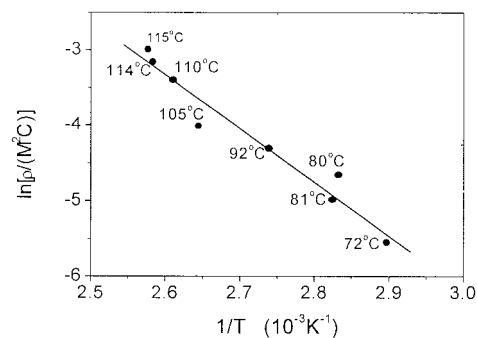
the data points existed in Table IV (or Figs. 7 and 8) also overlapped each other in this area. Regression of the three lines is given in the figure legends.

The effects of water were investigated by the same method as above, giving the results illustrated in Figure 10. The addition of water made a longer induction period and a slower reaction rate as in the case of other regulators. However, if the water amount exceeded certain limits, the induction period increased and the reaction rate decreased much more quickly. This indicated that the catalyst had been deactivated. This was because the water molecule is very small and possesses two hydroxyl groups; thus, water is a much more effective regulator than any other and must just be used in limited amounts.

Applying the above-obtained results, the rate of polymerization at 105°C can be expressed as in Eq. (8), where  $k$  is the chain transition constant and takes the value of 178.8, 16.8, 15.0, and 8.6 L mol<sup>-1</sup>, respectively,



**Figure 10** Effects of water on the polymerization rate and induction period.  $M^2C/\rho = 181.1 + 19,046.8Tr$ ; RegCoef = 0.965, RelDev = 0.965;  $M = 12.21 \text{ mol} \cdot \text{L}^{-1}$ ,  $C = 0.38 \times \text{g} \cdot \text{L}^{-1}$ ;  $k = 178.8 \text{ L} \cdot \text{mol}^{-1}$ .



**Figure 11** Effect of temperature on rate of PO polymerization. PO, 9 mL; toluene: 9 mL; DMC content based on PO: 0.05 wt%. RegCoef = 0.977, RelDev = 8.2%.

for H<sub>2</sub>O, cyclohexanol, PPO diol 500', and PPO triol 300.

$$R_p (\text{mol} \cdot \text{L}^{-1} \cdot \text{min}^{-1}) = K_a \rho = 0.292 M^2 C / (1 + k Tr) \quad (8)$$

### Polymerization at other temperatures

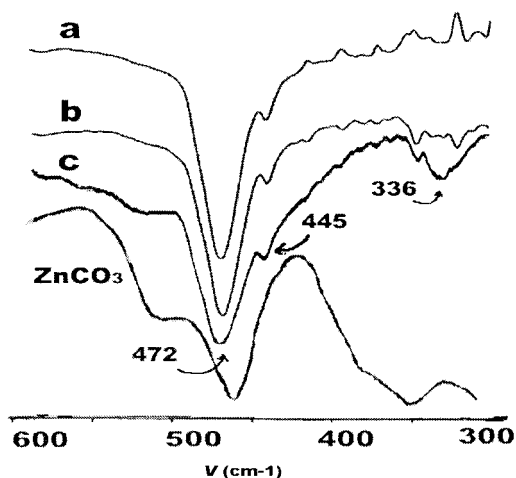
Dependence of reaction rates on temperatures in the range of 70~115°C was evaluated for DMC catalyzed PO polymerization in toluene without using regulators. According to the Arrhenius equation, the logarithm of  $\rho/(M^2C)$  was plotted to the reciprocal of absolute temperature and formed a good straight line (Fig. 11). From the slope ( $7.11 \times 10^3$ ) of the line the active energy  $E$  was determined to be 59.1 kJ/mol. This value may be slightly varied by using different catalysts; it was consistent with that reported for metal porphyrin (50.4 kJ/mol)<sup>16</sup> and rare earth (61.3 kJ/mol)<sup>9</sup> catalytic systems. Further, applying the so-obtained activation energy in eq. (8), the rate at other temperatures can be calculated by eq. (9).

$$R_p (\text{mol} \cdot \text{L}^{-1} \cdot \text{min}^{-1}) = 4.28 \times 10^7 \times e^{-7110/T} \times M^2 C / (1 + k Tr) \quad (9)$$

### Polymerization process and mechanism

It has been revealed that the zinc ion is the center ion in DMC catalysts and the cobalt only acted to improve the activity of the center ion.<sup>17</sup> Further, it has also been revealed that in the bimetallic cyanide catalyzed copolymerization of epoxides with carbon dioxide, the involvement of epoxide molecule is necessary to accomplish the initiation stage.<sup>11</sup> It is reasonable to consider the synthesis of DMC polyethers to consist of similar characteristics at the initiation stage. Actually, DMC catalysts cannot be activated by themselves without interaction with epoxide monomers.

In the literature,<sup>18</sup> the presence of IR signals of Zn-O bonds in the active centers was not observed; thus, the



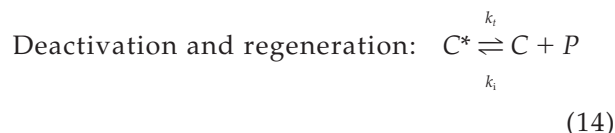
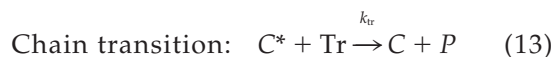
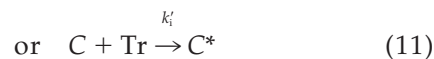
**Figure 12** Infrared spectra of catalyst at different stages of polymerization. (a) Neat catalyst. (b) Catalyst during induction period. (c) Catalyst just after induction period.

monomer insertion into these bonds as common polymerization reactions was suspected. We tried to collect more carefully the catalyst to submit IR characterization, respectively, before reaction and in the cases simulating the initiation and propagation stages (Fig. 12). Besides the signals at 472 and 445  $\text{cm}^{-1}$  for the bimetallic salts, a characteristic peak at 340  $\text{cm}^{-1}$  gradually formed during the reaction. A similar peak at 340  $\text{cm}^{-1}$  can also be seen in the IR spectra of zinc carbonate and zinc acetate. Based on this observation, we do not think it is reasonable to deny the presence of the Zn–O bonds in the active centers and the monomer insertions as common polymerization reactions.

Theoretically, the active center in a propagating chain may be deactivated through decomplexation between the metal and the polymer chain ends. It is also possible to regenerate an active polymer chain via a reversed process of the above. However, the active chain ends were much more easily reacted with the molecular weight regulators if present, forming inert polymer and releasing the original active centers.

Thus, we suggest the scheme in Figure 13 to illustrate the mechanism of DMC catalyzed PO regulated polymerization. The reacting manner between regulator  $R\text{-OH}$  and the active center was based on the experimental fact that most of the regulators after the reaction entered the polymer chains instead of keeping their original state as small molecules.

Elemental reactions for DMC catalyzed epoxide polymerization are written as eqs. (10–14), in which  $C$ ,  $M$ ,  $\text{Tr}$ ,  $C^*$ , and  $P$  are, respectively, the amount of catalyst, molar concentrations of the monomer, regulator (counted in OH groups), active centers, and inactive polymer chains. The letters above the arrows are rate constants of the elemental reactions.



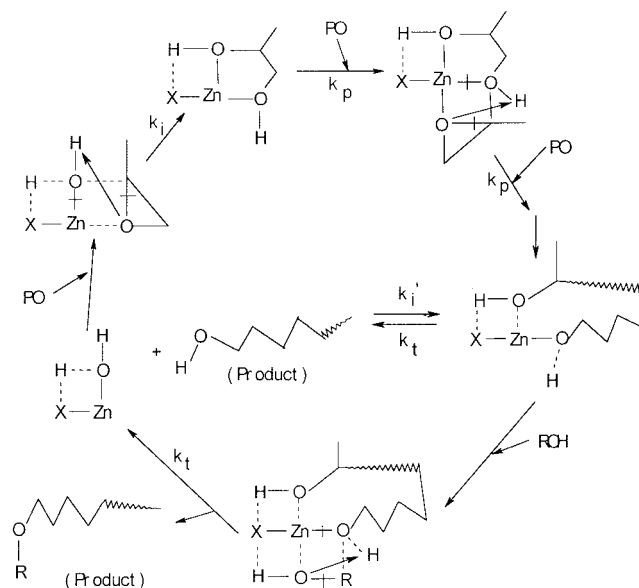
Assuming that the concentration of active centers remains constant at the steady state,

$$dC^*/dt = k_iCM + k_i'C\text{Tr} + k_i'CP - k_{tr}C^*\text{Tr} - k_tC^* = 0.$$

$$C^* = (k_iM + k_i'(\text{Tr} + P))C / (k_t + k_{tr}\text{Tr}) \quad (15)$$

$$R_p = -dM/dt = k_pC^*M$$

Replace  $C^*$  with eq. (15), if  $k_iM \gg k_i'(\text{Tr} + P)$ , the rate of polymerization should be



**Figure 13** Mechanism of PO polymerization catalyzed by DMC. (X, anions in the catalyst).

$$R_p = KM^2C/(1 + k Tr), \quad (16)$$

where  $K = k_p k_i / k_t'$ ,  $k = k_{tr} / k_t$ . Equation (16) expresses the kinetics of DMC catalyzed epoxide polymerization. It is consistent with the experiments and perfectly explained the correlations illustrated by Figures 7–9.

Contrarily, if in eq. (13),  $k_i M \ll k_i'(Tr + P)$ , then the rate would be  $R_p = K' MC / (1 + k^{-1} Tr^{-1})$ , where  $P \approx k'' Tr'$ ,  $k''$  was a constant,  $K' = k_p k_i'(1 + k'') / k_{tr}$ . This implied that the reaction speeded up with the addition of regulators and thus conflict with all the facts. The above investigation revealed that the initiation happened between the catalyst and the monomer [eq. (10)], rather than between the catalyst and the regulator [eq. (11)]. Therefore, the molecular weight regulator is not really necessary for the initiation, and it is not proper to call regulators "starters."

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