Ring-Opening Polymerizations of Propylene Oxide by Double Metal Cyanide Catalysts Prepared with ZnX$_2$ (X = F, Cl, Br, or I)

IL KIM, SEUNG HOON BYUN, CHANG-SIK HA

Department of Polymer Science and Engineering, Pusan National University, Jangjeon-dong, Geumjeong-gu, Busan 609-735, Korea

ABSTRACT: Polymerizations of propylene oxide were carried out with double metal cyanide (DMC) catalysts based on Zn$_3$[Co(CN)$_6$]$_2$. Through the control of the type and amount of ZnX$_2$ (X = F, Cl, Br, or I) during the preparation of the catalyst, the catalytic activity, induction period, and unsaturation level in the polyether polyols could be tuned. The DMC catalysts were characterized by X-ray photoelectron spectroscopy, infrared spectroscopy, and X-ray powder diffraction. In general, ZnBr$_2$ was the most effective zinc halide with respect to the properties of the resulting polymers as well as the activity and induction period. The average rates of polymerizations of DMC catalysts prepared with ZnCl$_2$, ZnBr$_2$, and ZnI$_2$ were 889, 1667, and 784 g of polyoxypropylene/g of catalyst h, respectively, with induction periods of about 53, 5, and 60 min, respectively, at 115 °C. The DMC catalysts produced polyoxypropylenes with an ultralow unsaturation level (0.0025–0.0057 mequiv/g) and a narrow molecular weight distribution (1.07–1.42) without high-molecular-weight tails; this resulted in a low viscosity (962–3950 cP). According to the results collected from catalyst characterizations and polymerizations, the active sites of DMC-catalyzed polymerization had mainly coordinative characters. The presence of free anions accelerated the ring-opening procedure and thus enhanced the propagation rate and shortened the induction period. © 2005 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 43: 4393–4404, 2005
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INTRODUCTION

Double metal cyanide (DMC) compounds are well-known catalysts for epoxide polymerization, that is, for polymerizing alkylene oxides such as propylene oxide (PO) and ethylene oxide to yield poly(alkylene oxide) polymers, which are also called polyether polyols.[1,2] In conventional base-catalyzed oxyalkylation reactions, PO and certain other alkylene oxides are subject to a competing internal rearrangement that generates unsaturated alcohols. The resulting product will contain allyl alcohol initiated, monofunctional impurities. As the molecular weight of the polyol increases, the isomerization reaction becomes more prevalent. The monofunctional impurities tend to reduce the average functionality and broaden the polydispersity of the polyol.

Unlike base catalysts such as KOH and CsOH, DMC catalysts do not significantly promote the isomerization of PO. As a result, DMC catalysts can be used to prepare polyols that have low unsaturation values and relatively high molecular weights. DMC catalysts can be

used to produce polyether, polyester, and poly(ether ester) polyols, which are useful in applications such as polyurethane coatings, elastomers, sealants, foams and adhesives.[2] In general, DMC catalysts are prepared by the combination of a metal salt, a metal cyanide salt, and an organic complexing ligand.[1,2]

One drawback of DMC catalyst systems is that DMC catalyst residues are often difficult to remove completely from the polyols after polymerization, and common catalyst removal techniques usually deactivate DMC catalysts.[3] DMC catalysts usually have good activity for epoxide polymerizations. However, because DMC catalysts are relatively expensive catalysts, even more improved activity is desirable to reduce catalyst levels contained in resulting polymers, and this may omit the catalyst removal step. Finally, DMC catalysts normally require an induction period. In contrast to basic catalysts, DMC catalysts ordinarily will not begin polymerizing epoxides immediately upon the exposure of the epoxide and starter polyol to the catalyst. Instead, the catalyst needs to be activated with a small proportion of the epoxide before it becomes safe to begin continuously adding the remaining epoxide. Induction periods of an hour or more are typical yet costly in terms of increased cycle time in a polyol production facility. The reduction or elimination of the induction period is desirable.

To develop DMC catalysts having higher activity and shorter induction periods in epoxide polymerizations, the study of the role of each catalyst component is first needed. However, scientific studies of DMC catalysts are scarce with respect to the commercial importance of DMC catalysts.[3–8] In this study, we prepared a series of DMC catalysts by changing the metal salt, ZnX_2 (X = F, Cl, Br, or I), which is the most important component of the DMC catalyst, and we investigated the effect of the change of the metal salt on the ring-opening polymerization of PO.

EXPERIMENTAL

Materials

All materials, including potassium hexacyanocobaltate(III) [$K_3Co(CN)_6$], zinc fluoride (ZnF_2), zinc chloride ($ZnCl_2$), zinc bromide ($ZnBr_2$), zinc iodide (ZnI_2), and tertiary butyl alcohol (^tBuOH), were purchased from Aldrich and used without further purification. Poly(propylene glycol) (PPG; molecular weight = 700) was also purchased from Aldrich and used as received after drying. Polymerization-grade PO and poly(tetramethylene ether glycol) (PTMEG; molecular weight = 1800) were donated by SKC (Korea) and BASF Korea, Ltd., respectively.

Preparation of the Catalysts

A series of DMC catalysts were prepared with ZnF_2, $ZnCl_2$, $ZnBr_2$, and ZnI_2 as metal salts and $K_3Co(CN)_6$ as a metal cyanide salt in the presence of ^tBuOH as a complexing agent and PTMEG as a cocomplexing agent. As an example, the DMC catalyst with $ZnCl_2$ as a metal salt was prepared according to the following procedure. $K_3Co(CN)_6$ (3.32 g, 0.01 mol) was dissolved in distilled water (20 mL) in a beaker (solution 1). $ZnCl_2$ (6.82 g, 0.05 mol) was dissolved in distilled water (50 mL) and ^tBuOH (10 mL) in a second beaker (solution 2). A third beaker contained solution 3: a mixture of distilled water (0.5 mL), ^tBuOH (10 mL), and PTMEG (2.0 g). Solution 2 was added to solution 1 over 60 min at 50 °C with vigorous mixing with a mechanical stirrer. Solution 3 was then added, and the mixture was stirred for 3 min. The mixture was centrifuged. The resulting catalyst cake was dried at 60 °C *in vacuo* to a constant weight. The other DMC catalysts with ZnF_2, $ZnBr_2$, and ZnI_2 instead of $ZnCl_2$ were prepared with the same procedure; the composition of each compound was kept the same.

Polymerization Procedures

Polymerizations of PO were carried out with a 1-L autoclave (Parr) at various temperatures. PPG (70 g, functionality = 2) was used as an initiator (or starter). The reactor was charged with the initiator and the DMC catalyst (0.1 g) and then purged several times with nitrogen. The mixture was heated to 90 °C and evacuated for over 2 h during stirring to remove traces of water contained in the initiator. Then, 10 g of the PO monomer was introduced into the reactor at a desired polymerization temperature. Additional monomer was added gradually when an initial pressure drop, indicating activation of the catalyst, occurred in the reactor. The polymerization was stopped when the total amount of the added monomer reached 400 g for the effectiveness of stirring. A clear, liquid product was obtained after the removal of the unreacted monomer *in vacuo*. This semibatch polymerization rate was continuously recorded through the

measurement of the weight of the monomer introduced into the reactor with a personal computer connected to an electronic balance through an AD converter. The gauge pressure of the reactor was kept constant at 1.7 bar throughout the polymerization. To determine the reaction rate, a plot of the PO consumption (g) versus the reaction time (min) was prepared.

Measurements

X-ray photoelectron spectroscopy (XPS) analysis of the catalysts was performed on an Escalab 250 induced electron emission spectrometer with Al Kα (1486.6 eV, 12 mA, 20 kV) X-ray sources. Infrared (IR) spectra were recorded on a Shimadzu IR Prestige-21 spectrophotometer with 32 scans per experiment at a resolution of 1 cm^{-1}. X-ray diffraction (XRD) patterns of the catalysts were obtained with a RINT2000 185 wide-angle goniometer with Cu Kα radiation at 40 kV and 30 mA. The slit sizes were 1 (for the divergence slit), 0.05 (for the monochromator slit), and 0.15° (for the detector slit). The data were collected from $2\theta = 5°$ to $2\theta = 70°$ with a step size of $2\theta = 0.02°$ and a counting time of 3–6 s per step. The hydroxyl value was defined as the equivalent amount of KOH corresponding to the hydroxyl groups in 1 g of polymer and was analyzed according to ASTM D 4274 D. The total degree of unsaturation of polyols was measured by a titration method according to ASTM D 2847. The molecular weight distribution (MWD) was measured with a Waters 150 instrument operated at 25 °C, with a set of 10^4-, 10^3-, and 500-Å columns in tetrahydrofuran as a solvent. Polystyrene standards with low polydispersities were used to generate a calibration curve. The viscosity of the polymer was measured at 30 °C. A Brookfield model DV III viscometer (Brookfield Instruments), with a small-scale sample adapter and spindle no. 21, was used to measure the viscosity of the polymer samples. The accuracy of the viscosity measurement was ±15 cP. A thermostated water bath was used to maintain the temperature of the sample through a water jacket fitted to the small sample adapter. The bath temperature was maintained with an accuracy of ±1 °C. Before the experiments were performed, the samples were deaerated. The viscosity measurements were repeated three times each, and the averages of the readings were taken for the analysis of the data.

RESULTS AND DISCUSSION

Characterization of the DMC Catalysts

The reaction of an aqueous solution of a zinc halide and potassium hexacyanocobaltate in the presence of a complexing agent results in insoluble DMC salts of the following general formula:[3]

$$Zn_3[Co(CN)_6]_2 \cdot xZnX_2 \cdot yH_2O \cdot zComplexing\ agents$$

Because of the insolubility of this complex, the difficulty in characterizing the different structural forms of the DMC catalysts was earlier recognized with catalysts containing glyme as a complexing agent.[3] For instance, Livigni etal.[3(d)] described DMC/glyme catalysts as largely amorphous. On the other hand, Kuyper and Boxhoon[4] described the same catalysts as crystalline by giving fairly simple line patterns. In addition, the structure of the catalyst becomes complicated, depending on the preparative conditions and the type of catalyst components chosen. In this sense, the surface analysis of the catalyst is a useful way of investigating the characteristics of the catalyst. The qualitative and quantitative surface formulations of the catalyst were investigated by XPS. The XPS spectra of DMC catalysts prepared with various zinc halides, such as ZnF_2 (DMC-F), $ZnCl_2$ (DMC-Cl), $ZnBr_2$ (DMC-Br), and ZnI_2 (DMC-I), are shown in Figure 1.
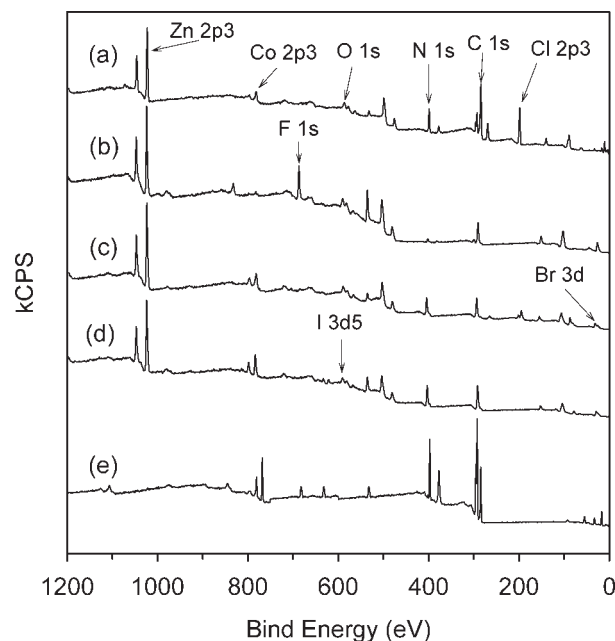

Figure 1. XPS spectra of (a) catalyst DMC-Cl, (b) catalyst DMC-F, (c) catalyst DMC-Br, (d) catalyst DMC-I, and (e) $K_3Co(CN)_6$.

The formation of zinc hexacyanocobaltate(III) led the binding energy (1023.7 eV) of the zinc atom in $ZnCl_2$ to shift toward lower values. The reaction of $ZnCl_2$ with $K_3Co(CN)_6$ ([Zn]/[Co] = 5.0) in the presence of complexing agents led to the shift of the binding energy of the zinc atom to 1021.3 eV. Similar shifts were observed for the DMC catalysts prepared with $ZnBr_2$ (1023.7 to 1020.8 eV) and ZnI_2 (1023.7 to 1021.1 eV) as metal salts. However, no shift was observed for ZnF_2, and a clear F 1s peak appeared at 684.8 eV; this demonstrates that the zinc hexacyanocobaltate(III) complex is not formed with ZnF_2. There exist considerable amounts of free zinc halides (see Cl $2p^3$, Br 3d, and I $3d^5$ in Fig. 1) in the catalyst. The peak assigned to Co $2P^3$ of $K_3Co(CN)_6$ [Fig. 1(e)] shifts from 781 to 780.4 eV for the DMC-Cl catalyst, to 779.9 eV for the DMC-Br catalyst, and to 779.4 eV for the DMC-I catalyst. Only a negligible amount of Co atoms and no shift of the Co $2P^3$ peak observed for the DMC-F catalyst indicate again that the DMC catalyst is not formed with ZnF_2 as a staring zinc halide.

The presence of free $ZnCl_2$ has been reported to be an important factor for achieving high catalytic activity, even if the exact mechanism remains uncertain.[3] To investigate the effect of the amount of zinc halide on the catalytic behavior, we also prepared a series of DMC catalysts by changing
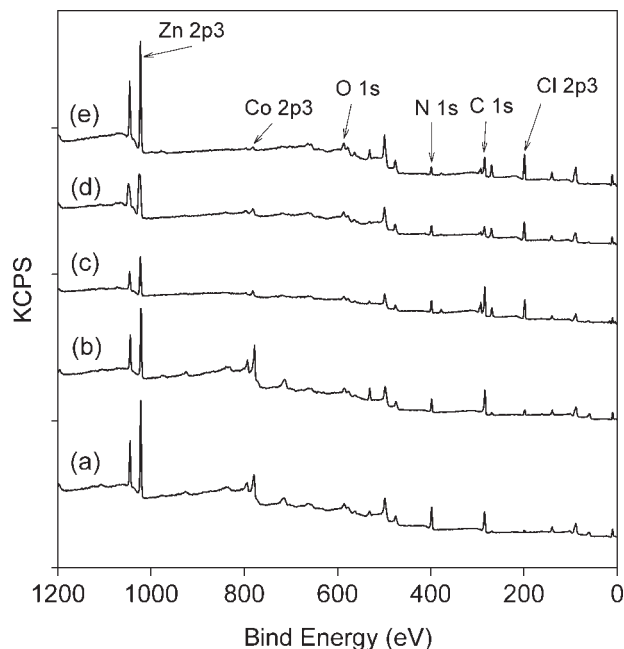

Figure 2. XPS spectra of various DMC catalysts prepared with different [Zn]/[Co] ratios: (a) 0.5, (b) 1.0, (c) 2.0, (d) 5.0, and (e) 10.0.
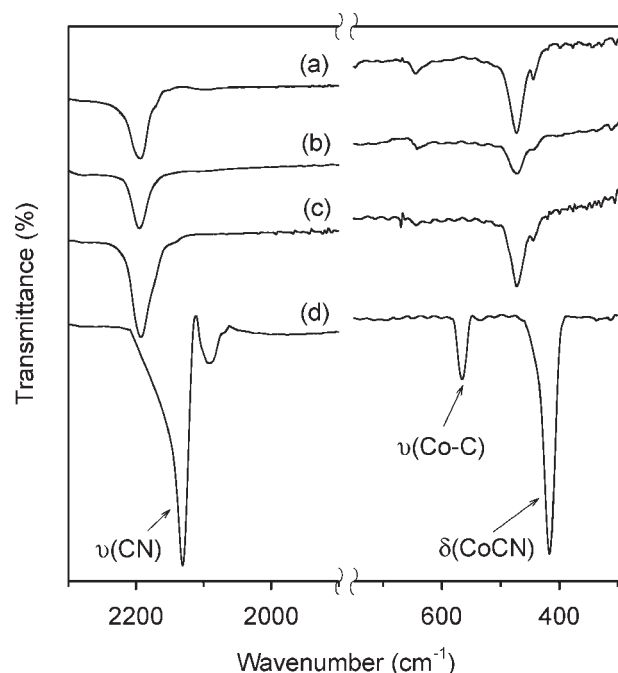

Figure 3. IR spectra of (a) catalyst DMC-Cl, (b) catalyst DMC-Br, (c) catalyst DMC-I, and (d) $K_3Co(CN)_6$.

the [Zn]/[Co] ratio from 0.5 to 10 with $ZnCl_2$. Figure 2 illustrates XPS spectra of the DMC catalysts. As the [Zn]/[Co] ratio increases, the peak assigned to Cl $2p^3$ increases. The catalysts bearing a negligible amount of free $ZnCl_2$ led the binding energy (1023.7 eV) of the zinc atom in $ZnCl_2$ to shift toward lower values: 1020.8 eV for [Zn]/[Co] = 0.5 and 1020.9 eV for [Zn]/[Co] = 1.0. The effect of the existence of the free $ZnCl_2$ on the polymerization behaviors will be discussed later.

Cyano complexes can be identified easily because they exhibit sharp $v(CN)$ at 2200–2000 cm^{-1}. $v(CN)$ of free CN^- is 2080 cm^{-1} (aqueous solution).[9] Upon coordination to a metal, $v(CN)$ shifts to higher frequencies according to the electronegativity, the oxidation state, and the coordination number of the metal. Thus, the $v(CN)$ band of $K_3Co(CN)_6$ can be observed at 2131.3 cm^{-1}, as shown in Figure 3. The formation of the $Zn_3[Co(CN)_6]$ complex by the reaction of $K_3Co(CN)_6$ with ZnX_2 (X = Cl, Br, or I) in the presence of a complexing agent makes the $v(CN)$ band shift further to 2131.3 cm^{-1}. The $v(CN)$ band shift is the same for all catalysts, regardless of the type of zinc halide, because the $Zn_3[Co(CN)_6]$ complex is formed as a main catalyst formulation in all cases. The $v(CN)$ shift to higher frequencies demonstrates that the CN^- ion acts not only as a σ-donor by donating electrons to the cobalt but also as an electron donor by chelating to zinc
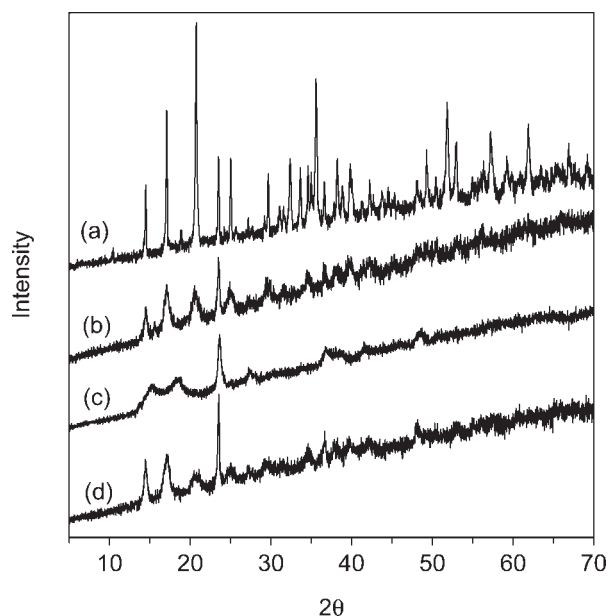
Figure 4. XRD patterns of (a) compound Zn_3 $[Co(CN)_6]_2 \cdot 12H_2O$, (b) catalyst DMC-Cl, (c) catalyst DMC-Br, and (d) catalyst DMC-I.

metal. Electron donation tends to raise $\nu(CN)$ because electrons are removed from the 5σ orbital, which is weakly antibonding, whereas π-back-bonding tends to decrease $\nu(CN)$ because the electrons enter the antibonding $2p\pi^*$ orbital. In general, CN^{-1} is a good s-donor and a poorer p-acceptor. The type of zinc halide made no difference in the shift of the $\nu(CN)$ band because the same double metal salt, $Zn_3[Co(CN)_6]$, was formed, regardless of the type of halogen atom.

In addition to $\nu(CN)$, the cyano complexes exhibit $\nu(MC)$ and $\delta(MCN)$ bands in the low-frequency region. Figure 3 shows the IR spectra of DMC-Cl, DMC-Br, and DMC-I catalysts together with that of $K_3Co(CN)_6$. The $\nu(MC)$ band of $K_3Co(CN)_6$ shifts from 585.1 to 642.3 cm^{-1} for all catalysts, and the $\delta(MCN)$ band of $K_3Co(CN)_6$ shifts from 412.7 to 470.6 cm^{-1} for all catalysts. These results can be interpreted as follows: the M—C π-bonding of $K_3Co(CN)_6$ is increased by the formation of the $Zn_3[Co(CN)_6]$ complex because the degree of M—C π-bonding may be proportional to the number of d-electrons in the F_{2g} electronic level.

The alteration of the crystal structure can be shown by XRD patterns to be dependent on the different surfaces. Figure 4 shows typical powder XRD curves of the DMC-Cl, DMC-Br, and DMC-I catalysts. For the comparison, the X-ray pattern for a DMC catalyst prepared in the absence of

complexing agents is also shown. The pattern of this DMC catalyst resembles the pattern of highly crystalline zinc hexacyanocobaltate hydrate.[10,11] The DMC-Cl and DMC-I catalysts, which are synthesized in the presence of a complexing agent and a cocomplexing agent (PTMEG), are characterized by a sharp peak at $2\theta = 23.6°$ ($d = 3.7$ Å), a broad peak with a maximum at about $2\theta = 20.1°$ ($d = 4.4$ Å), a broad peak with a maximum at about $2\theta = 17.1°$ ($d = 5.2$ Å), and a broad peak with a maximum at about $2\theta = 14.5°$ ($d = 6.1$ Å). The DMC-Br catalyst contains the sharp peak ($2\theta = 23.6°$) plus broad, poorly resolved features between 2θ values of 13.5 and 22.5°, demonstrating a more poorly crystalline structure. The difficulty in characterizing the different structural forms of DMC catalysts was earlier recognized with catalysts containing glyme as the complexing agent. For instance, Herold and coworkers[3] described the DMC/glyme catalyst as largely amorphous. On the other hand, Kuyper and Boxhoon[4] described similar catalysts as crystalline by giving fairly simple line patterns. Unfortunately, no assignment of cell parameters was found. Both of these references failed to provide XRD data. For the amorphous structures of the DMC catalysts of this study to exist, the atomic structure would need to exhibit either no periodicity or no long-range order. Even though the DMC-Cl, DMC-Br, and DMC-I catalysts have broad peaks between 2θ values of 13.5 and 22.5°, these broad peaks are associated with relatively sharp peaks at about $2\theta = 23.6°$. Because an amorphous DMC catalyst would have very broad peaks not associated with any sharp peaks, the DMC catalysts of this study may be poorly crystalline, but they are not amorphous. The crystallinity of the catalyst may strongly influence the catalytic activity. Indeed, the highly crystalline $Zn_3[Co(CN)_6]_2 \cdot 12H_2O$ compound [Fig. 4(a)] prepared in the absence of a complexing agent showed no activity in the PO polymerization.

Polymerization of PO

To investigate the effect of the concentration of zinc halide on the polymerization of PO, semibatch polymerizations of PO were carried out at 115 °C with changes in the concentration of the zinc halide used for the preparation of the catalyst. In Figure 2, we have already shown the XPS spectra of the DMC catalysts prepared with changes in the concentration of $ZnCl_2$ from $[ZnCl_2]/[K_3Co(CN)_6] = 0.5$ to $[ZnCl_2]/[K_3Co(CN)_6] = 10$

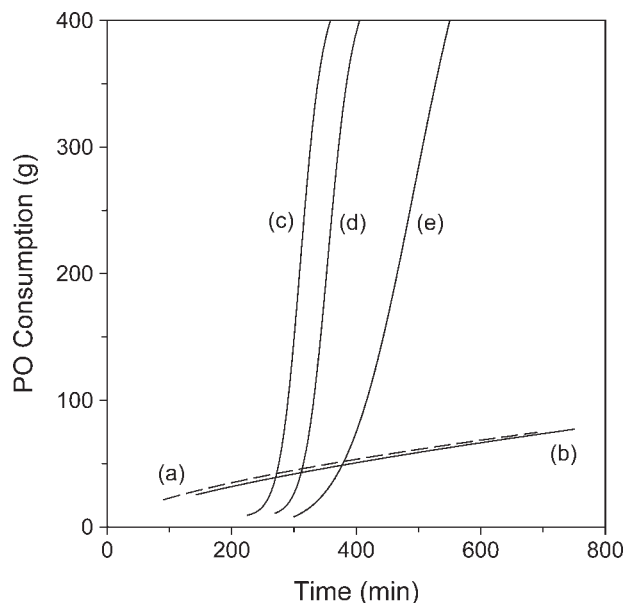**Figure 5.** Polymerization rate curves obtained with various DMC catalysts prepared with different $[ZnCl_2]/[K_3Co(CN)_6]$ ratios: (a) 0.5, (b) 1.0, (c) 2.0, (d) 5.0, and (e) 10.0. The amount of the PPG-700 initiator added was 70 g, the catalyst amount used per batch was 0.1 g, and the polymerization temperature was 115 °C.

during the catalyst preparation step. Figure 5 shows polymerization rate curves obtained by the catalysts containing different amounts of free $ZnCl_2$. As shown in Figure 5(a,b), the absence of free $ZnCl_2$ results in very low catalytic activity; however, the activity increases sharply in the presence of free $ZnCl_2$ [Fig. 5(c,d)]. The excess amount of free $ZnCl_2$ makes the induction period longer. These results demonstrate that (1) some amount of free $ZnCl_2$ is necessary to achieve high activity and (2) there is an optimum concentration of free $ZnCl_2$ to get the shortest induction period.

The DMC complexes prepared with different zinc salts and complexing agents are characterized by great differences in morphology, which can be correlated with the preparation route as well as the kinds of zinc salts employed.[8(c)] This change makes a detailed mechanistic investigation of the DMC-catalyzed polymerization difficult. However, because zinc halides, the main components of the DMC catalyst generating active species, are molecular solids that are soluble in polar solvents such as cyclic ethers, it was interesting to examine their ability in the absence of any ligands to catalyze the polymerization of PO. Relevant to this process, it was well established that $ZnX_2/(n\text{-}Bu_4N)X$ salts catalyze the coupling of monosubstituted oxiranes to cyclic carbonates.[12]

In our study, free $ZnCl_2$ was observed not to polymerize PO. This result raises the important question of what type of zinc species is responsible for the observed change in the polymerization activity in the presence of free zinc halides. Most likely, zinc halides in the presence of an electron-donor ligand (EDL), such as a complexing agent, PPG starter, impurity (e.g., moisture), or PO monomer, may lead to a variety of complexes involving zinc centers that contain quite different ligand sets, such as $ZnX_2(EDL)_2$ or $[Zn(EDL)_4][Zn_2X_6]$, depending on the nature of the coordinating ligand. The formation of these types of zinc complexes has been demonstrated by many authors using zinc halides and various compounds containing nitrogen and oxygen donors.[13] Furthermore, the isolation of zinc salts such as $[Zn(EDL)_4][Zn_2X_6]$ may give a good clue whether the $Zn(EDL)_4^{2+}$ or $Zn_2X_6^{2-}$ species is responsible for the observed activity. Attempts to answer to this question were carried out through the preparation of $Zn(EDL)_4^{2+}$ cation while a different anion was used. The complex $Zn(2,6\text{-dimethoxypyridine})_4(BF_4)_2$, prepared according to a reported procedure,[13(h)] was used in the polymerization of PO in this case to afford no polymer. This indicates to an approximation that the $Zn(EDL)_4^{2+}$ species is not responsible for the catalytic activity observed. The cationic nature of this species is not conductive to promoting further addition of PO.

Under the rigorous polymerization conditions of catalysis, it is possible that the zinc species in solution generates quite complicated intermediate species. As examples of the plausible precursor complexes derived from zinc halides and various oxygen-donor compounds existing in the reaction medium, potential intermediates in the polymerization reactions are complexes **A**, **B**, **C**, **D**, and **E**, as indicated in Scheme 1. These zinc species are derived from $ZnX_2(EDL)_2$ and $[Zn(EDL)_4][Zn_2X_6]$. Except for species **A**, the process affording the intermediate species would be expected to vary significantly with the nature of the halide counterion. In particular, the free halide ion in **C** and **E** may enhance the polymerization rates according to the proposed mechanism shown in Scheme 2. Two basic steps define the mechanism. First, there is the initial binding, along with the activation, of the PO substrate to the metal center. Second, the bound and activated PO is ring-opened and concertedly inserted into the Zn—O bond. We believe that PO is ring-opened at the less substituted C—O bond, and in this step, the synergistic effect of the DMC catalyst is assumed
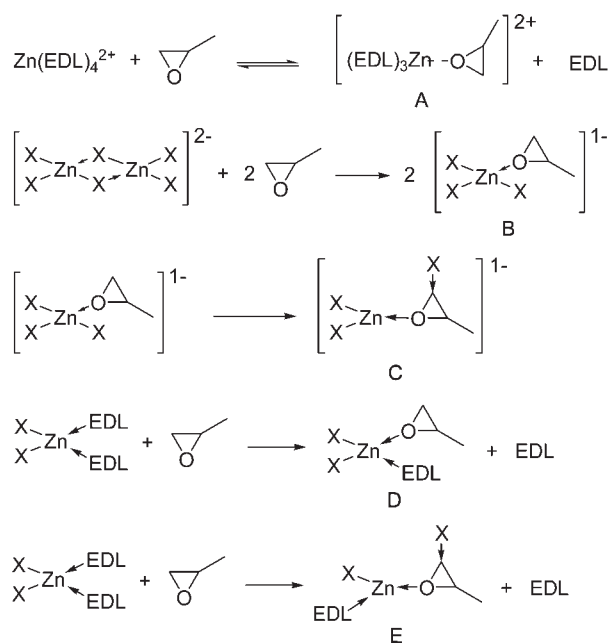
EDL = complexing agents, PPG starter, impurity, and/or monomer
X = halides
cyano fragments are`not shown for the convenience

Scheme 1. Formation of potential intermediates through the reaction of zinc halides and various electron-donor compounds during the polymerization reactions.

because of the nucleophilicity of the free halide ions and the electrophilic interaction of the zinc atom of the DMC catalyst with PO.

In the case of heterogeneous catalytic polymerization using an initiator, the polymerization centers are expected to form in two stages: (1) the formation of active sites S* from a dormant site S in the catalyst surface by the initiator, followed by (2) the formation of a polymerization center C* from an active site and a PO monomer unit. Once the polymerization center forms, the monomer is inserted to give high-molecular-weight polymers (Scheme 2). An active intermo-

lecular transfer reaction between growing polymer chains and hydroxyl group containing compounds results in low-molecular-weight polymer chains. The induction period depends on the exchange equilibrium between the dormant site and active sites during the initial period of polymerization. Strong coordination of complexing species to the dormant sites hinders a fast exchange reaction with the initiator molecule, resulting in the delay of the formation of polymerization centers (C*). Free halide ions should influence all steps of the reaction and thus change the induction period.

To check the coordinative nature of the DMC-catalyzed polymerization of PO, we carried out a series of polymerizations, changing the catalyst concentration from 50 to 320 ppm based on the catalyst concentration in the final polymer products. The resulting polymerization rate curves are shown in Figure 6. As the catalyst concentration increases, the polymerization rate increases monotonously. The maximum rates ($R_{p,max}$) are proportional to the zinc concentration, as shown in Figure 7. Therefore, $R_{p,max} \propto [Zn]$. This demonstrates that the addition of the incoming monomer occurs between the zinc atom and growing polymer bonds as follows:

$$\text{Zn} - P_n + \text{propylene oxide} \overset{k_P}{\to} \text{Zn} - P_{n+1} \quad (1)$$
$$\text{active site}$$
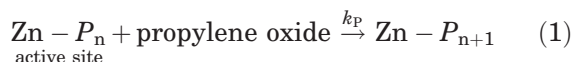
where P_n is the growing polymer chain and k_p is the rate constant of propagation. This type of propagation is a typical step that can be found in the metal-catalyzed coordination polymerizations.

Because the free zinc halide plays important roles in controlling the catalytic activity and induction period (see Schemes 1 and 2), the type of zinc halide might influence the polymerization reactions as well. To check this fact, polymerizations of PO with DMC-Cl, DMC-Br, and DMC-I catalysts were carried out between 50 and 115 °C
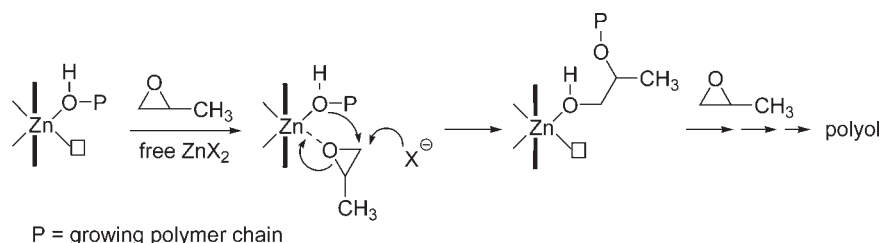
P = growing polymer chain

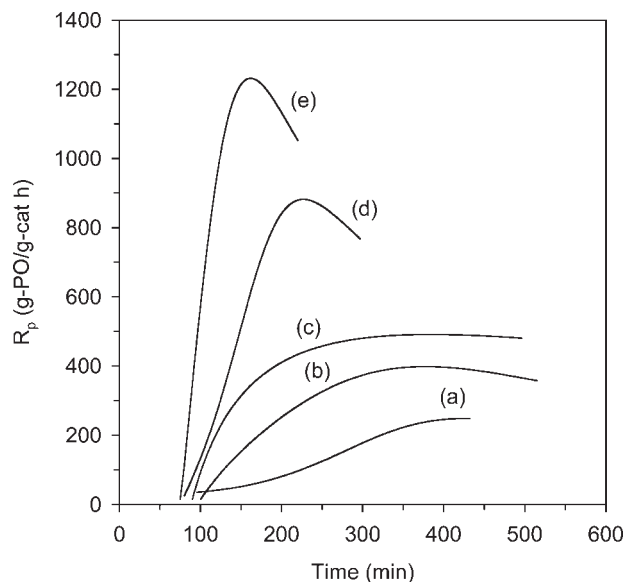**Scheme 2.** Proposed mechanism of polymerization.

Figure 6. Effect of the catalyst concentration on the PO polymerization rate (R_p) obtained by the DMC-Cl catalyst with different amounts of the catalyst based on the catalyst amounts contained in the final polymer products: (a) 50, (b) 100, (c) 150, (d) 250, and (e) 320 ppm. The amount of the PPG-700 initiator added was 70 g, and the polymerization temperature was 115 °C.

with the pressure of the reactor kept constant at 10 psig. As already mentioned, the ZnF$_2$-based DMC-F catalyst showed no activity because no effective catalytic formulation was formed by the reaction of ZnF$_2$ with K$_3$Co(CN)$_6$ in the presence of complexing agents. Figure 8 shows polymerization rate profiles obtained by the DMC-Cl catalyst in the presence of PPG-700 (70 g) as an initiator at various temperatures. The very steep slopes of all the curves demonstrate that the DMC-Cl catalyst shows very high activity once it is activated at 75, 95, and 115 °C. The induction period was about 115 min at a polymerization temperature of 75 °C, and the time decreased to 40 min at 95 °C, a very high activity being sustained; however, it increased to 50 min at 115 °C. In addition, the catalytic activity decreased during the later period of polymerization at 115 °C, most likely because of a decomposition of the catalytic active species. For a polymerization at a low temperature, such as 50 °C, the DMC-Cl catalyst showed only negligible activity.

A series of polymerizations between 50 and 115 °C were also carried out with the DMC-Br and DMC-I catalysts, and the results are shown in Figures 9 and 10, respectively. Both catalysts are characterized by the following features: (1) the activity increases as the temperature

increases, (2) the induction periods of the DMC-Br and DMC-I catalysts are shorter than that of the DMC-Cl catalyst under the same polymerization conditions and become shorter at higher temperatures in general, and (3) the catalytic active species become destabilized during a later period of the polymerizations at a high polymerization temperature (115 °C). Most interestingly the induction periods of the polymerizations by the DMC-Br catalyst above 75 °C and by the DMC-Br catalyst at 75 and 95 °C are shorter than 20 min, which is the shortest induction period reported so far.[2]

Taking a look at the polymerization results shown in Figures 8–10, we can summarize the activity (A) and induction period (IP) as follows.

- At 115 °C, A: DMC-Br $\gg$ DMC-Cl > DMC-I; IP: DMC-Br $\ll$ DMC-Cl < DMC-I.
- At 95 °C, A: DMC-I > DMC-Br > DMC-Cl; IP: DMC-I $\approx$ DMC-Br < DMC-Cl.
- At 75 °C, A: DMC-I $\gg$ DMC-Br > DMC-Cl; IP: DMC-I $\approx$ DMC-Br < DMC-Cl.
- At 50 °C, A: DMC-Br > DMC-I $\gg$ DMC-Cl; IP: DMC-I < DMC-Br $\ll$ DMC-Cl.

As demonstrated by IR and XRD analyses, all catalysts were characterized by similarities of their main catalyst formulation, Zn$_3$[Co(CN)$_6$]$_2$, except for the presence of excess ZnX$_2$. The free zinc halide alone did not show any polymerization activity at all, and the reaction of the zinc
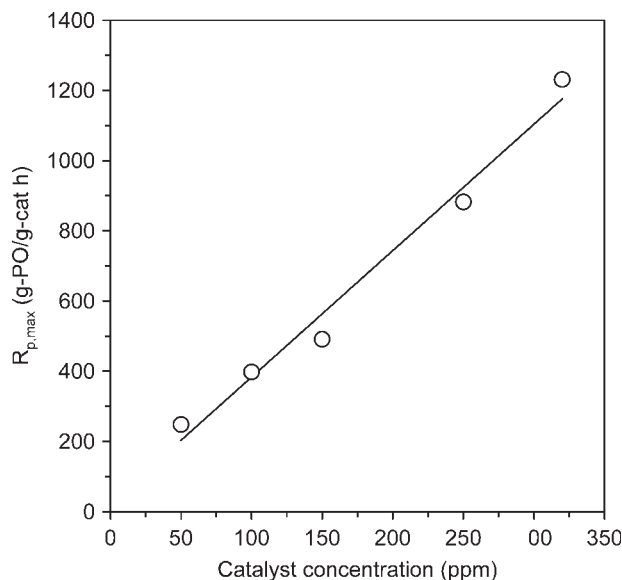

Figure 7. $R_{p,max}$ versus the catalyst concentration obtained from Figure 6.
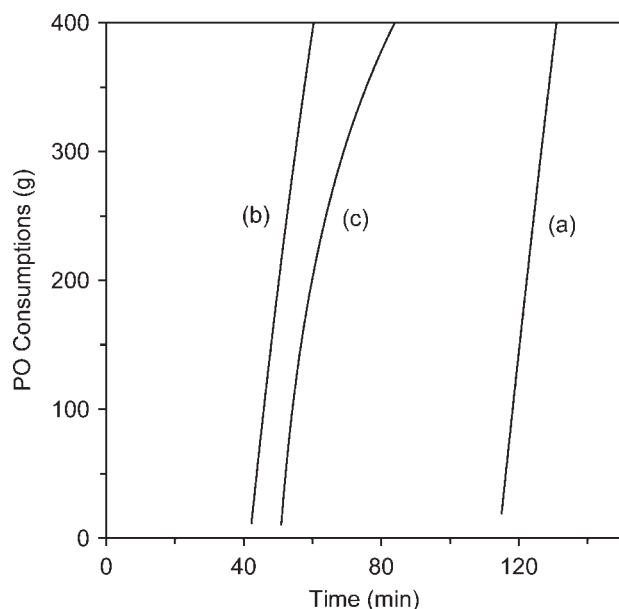
Figure 8. Polymerization rate curves obtained by the DMC-Cl catalyst at various polymerization temperatures: (a) 75, (b) 95, and (c) 115 °C. The amount of the PPG-700 initiator added was 70 g, and the catalyst amount used per batch was 0.1 g.

halide with a complexing agent such as ^{t}BuOH did not form any complex between them. However, the presence of the free zinc halides together with DMC catalysts influenced the catalyst activity quite a lot, as previously shown (Figs. 8–10). Even though more detailed mechanistic studies are needed to explain the effects of the free halide ions, it is postulated that the synergistic effect of the DMC catalyst is assumed because of the nucleophilicity of the free halide ions and the electrophilic interaction of the zinc atom of the DMC catalyst with PO, as shown in Scheme 2. In this sense, the dissociation rate of the free zinc salt, ZnX_2, and the nucleophilicity of the dissociated free halide ions influence the polymerization behaviors. To clarify this postulation, we are investigating a polymerization system introducing various anions with different nucleophilicities during polymerization.

Characterization of Polyoxypropylene (POP)

The catalysts of this study are active enough to allow a very low concentration, preferably a concentration low enough to overcome any need to remove the catalyst from POP for further applications. It is well known that a base (e.g., KOH)

catalyzes not only the addition of PO to the growing polymer molecule but also a side reaction in which PO isomerizes to allyl alcohol.[14] Allyl alcohol acts as a monofunctional starter, resulting in the production of propoxylated allyl alcohol, which is often called monol. Because each monol molecule also contains a terminal double bond, the amount of monol present in POP can be quantified by the measurement of the unsaturation level. Table 1 shows the properties of polyols together with the polymerization results. All catalysts produce POP with a very low level of unsaturation under 0.0057 mequiv/g, with respect to conventional KOH-catalyzed polyols (typical unsaturations of 0.03–0.10 mequiv/g). The level of unsaturation decreases as the polymerization temperature increases for all catalysts. The DMC-Br catalyst produces POP with the lowest unsaturation value (0.0025 mequiv/g) at 50 °C.

The ultralow monol levels of polyols obtained by the catalysts of this study are a result of the proprietary process for polymerizing PO in which the addition reaction is strongly promoted with respect to the isomerization reaction. The choice of the complexing agent as well as the type of metal component should play an important role in suppressing reactions to form the unsaturated chains. However, it still remains uncertain what type of complexing agent and

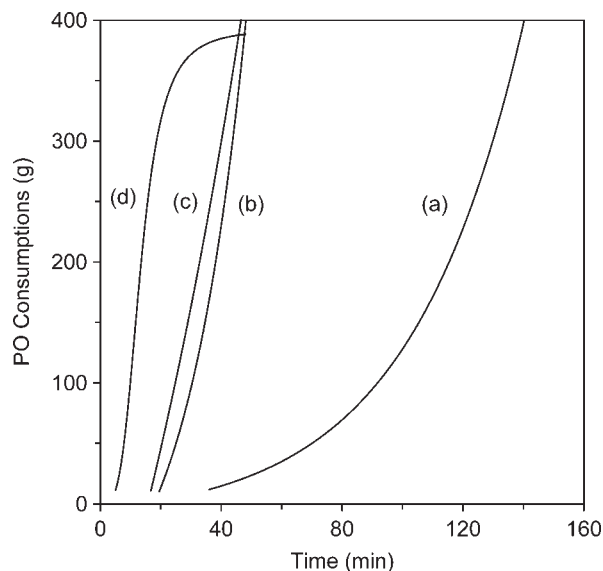**Figure 9.** Polymerization rate curves obtained by the DMC-Br catalyst at various polymerization temperatures: (a) 50, (b) 75, (c) 95, and (d) 115 °C. The amount of the PPG-700 initiator added was 70 g, and the catalyst amount used per batch was 0.1 g.

Figure 10. Polymerization rate curves obtained by the DMC-I catalyst at various polymerization temperatures: (a) 50, (b) 75, (c) 95, and (d) 115 °C. The amount of the PPG-700 initiator added was 70 g, and the catalyst amount used per batch was 0.1 g.
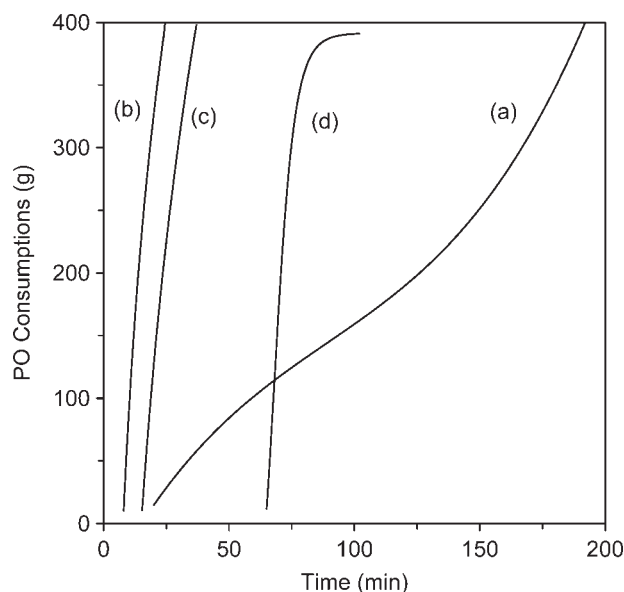
what kind of interaction between the complexing agent and catalyst surface lead to such a low level of unsaturation.

Suppressed isomerization and chain-transfer reactions during the polymerization with DMC catalysts led to POP of a very narrow MWD, as shown in Table 1. The lowest recorded MWD value was 1.07 for the polymerization by the

DMC-Cl catalyst at 95 °C, and the highest was 1.42 by the DMC-I catalyst at 115 °C. For all the catalysts, the molecular weight [number-average molecular weight (M_n) by gel permeation chromatography] of the polymers decreased slightly as the polymerization temperature increased. For example, the M_n value of the polymer obtained by DMC-Br at 50 °C was 4570, and that of the polymer by the same catalyst at 115 °C was 3500.

The very narrow MWD value of a polymer can be obtained by controlled ionic polymerization in a living mode. In this sense, it is interesting to note a mechanistic pathway of DMC catalysis resulting in such a narrow MWD. Because we used a large excess amount of the initiator (0.1 mol) in comparison with the catalyst (0.1 g), an initiator-to-catalyst molar ratio as high as 10^3 or more was reached. Accordingly, it is impossible to assume that all chains grow in a living mode such as controlled anionic polymerization. It is therefore reasonable to assume that a rapid exchange between the dormant and active sites accounts for the control of the molecular weight and the narrowing of the MWD. As a result of the exchange reaction, the dormant sites and transient dead-polymer chains (P_n—OH), which can be reactivated, are generated. If the exchange reaction is faster than the propagation reaction, the number of growing polymer chains remains constant, depending on the initial amount of the initiator; this results in polymers of narrow MWDs. A slow exchange

Table 1. Results of the Ring-Opening Polymerization of PO Catalyzed by DMC Catalysts Prepared with ZnX$_2$ (X = F, CI, Br, or I)[a]

| Catalyst | Polymerization Temperature (°C) | Activity | | Unsaturation (mequiv/g) | GPC | | Viscosity (cP) |
		$R_{p,avg}$[b]	$R_{p,max}$[b]		M_n (g/mol)	MWD	
DMC-CI	115	889	5,733	0.0050	3,290	1.31	1,790
	95	1,290	9,600	0.0050	3,600	1.07	1,260
	75	601	8,200	0.0029	3,970	1.14	975
DMC-Br	115	1,667	8,400	0.0057	3,500	1.38	962
	95	1,539	7,400	0.0046	3,770	1.27	1,280
	75	1,600	6,600	0.0029	4,340	1.09	1,070
	50	567	1,600	0.0025	4,570	1.08	1,910
DMC-I	115	784	9,200	0.0054	3,300	1.42	1,360
	95	2,162	12,800	0.0046	3,660	1.09	2,530
	75	3,333	15,400	0.0030	4,430	1.15	2,420
	50	417	1,320	0.0026	4,560	1.13	3,950

[a] Polymerization conditions: initiator = bifunctional PPG (70 g); amount of the catalyst = 0.1 g.
[b] Average rate ($R_{p,avg}$) and maximum rate ($R_{p,max}$) of polymerization (g of POP/g of catalyst h).

reaction should result in the generation of polymer chains with different chain lengths. This result indicates that the polymerizations proceed in a coordinative way.

The experimental viscosity of the polymer was measured with a Brookfield model DV III viscometer. In general, all DMC catalysts of this study yielded polyols with very low viscosities (962–3950 cP), which demonstrated low contents of high-molecular-weight polyol tails. High contents of high-molecular-weight tails make the MWD of a polyol broader and thus result in an unacceptably high viscosity and reactor fouling. The low viscosity of polyols produced by DMC catalysts must be a favorable condition for processing for polyurethane applications as well as handling.

CONCLUSIONS

A series of DMC catalysts were prepared by the reaction of aqueous solutions of ZnX_2 (X = F, Cl, Br, or I) and potassium hexacyanocobaltate in the presence of a complexing agent; this resulted in insoluble DMC salts. The catalytic activity and the induction time were sensitive to the type of zinc halide used during the preparation of the DMC catalysts. Spectroscopic analyses such as XPS, IR spectroscopy, and X-ray powder diffraction of the catalysts showed that the complexing and cocomplexing agents were coordinated to the DMC catalysts and that free zinc halide was contained in the catalyst matrix. The low polymerization activity in the absence of the free zinc halides demonstrated that they had an influence on the polymerization behavior, most likely as free halide anions formed under the harsh polymerization conditions. As a result, the type of zinc halide used in the catalyst preparation step was one of the important parameters for achieving a highly active catalyst with a short induction period. In general, $ZnBr_2$ was the most effective zinc halide with respect to the properties of the resulting polymers as well as the activity and induction period. The average rates of polymerization with the DMC-Cl, DMC-Br, and DMC-I catalysts at 115 °C were 889, 1667, and 784 g of POP/g of catalyst h, respectively, with induction periods of about 53, 5, and 60 min, respectively.

All the catalysts produced polyols with an ultralow level of unsaturation (0.0025–0.0057 mequiv/g) with narrow polydispersity (1.07–1.42) without high-molecular-weight tails, resulting in a

low viscosity (962–3950 cP). The low level of unsaturation and low viscosity of the polyols should be very important factors for producing high-performance polyurethanes. According to some indirect evidence, the active sites of DMC-catalyzed polymerization had mainly coordinative characters; however, the presence of anions accelerated the ring-opening procedure and thus enhanced the propagation rate and shortened the induction period.

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