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Preparation of multi-metal cyanide catalysts and ring-opening polymerization of propylene oxide

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Abstract

Polymerizations of propylene oxide have been carried out by using double metal cyanide (DMC) catalyst prepared by reacting $ZnCl_2$ and $K_3[Co(CN)_6]_2$ in the presence of complexing agents and multi-metal cyanide (MMC) catalyst prepared by reacting $ZnCl_2$, $K_3[Co(CN)_6]_2$ and $K_4Fe(CN)_6$) in the presence of complexing agents. The catalysts were characterized by X-ray photoelectron spectroscopy, infrared spectroscopy and X-ray powder diffraction. By controlling the type of complexing agent and metal, and by controlling polymerization parameters, the catalytic activity, initiation time and the unsaturation level of poly(oxy propylene) could be tuned. Both DMC and MMC catalysts showed very high activities, and the MMC catalyst showed high activity in a wide range of temperature (30–130 °C). The POPs obtained by the DMC catalyst and the MMC catalysts were characterized by ultra-low level of unsaturation (0.002–0.01 meq/g) and by polydispersity (MWD = 1.02–1.10). The active sites of DMC-catalyzed polymerization of propylene oxide had both cationic and coordinative characters.

Keywords: Double metal cyanide; Multi-metal cyanide; Polymerization; Propylene oxide

1. Introduction

Double metal cyanide (DMC) complexes, prepared by the reaction of potassium hexacyanocobaltate(III) ($K_3[Co(CN)_6]_2$) and zinc chloride ($ZnCl_2$) in the presence of complexing reagents, are well-known catalysts for the polymerization of epoxides and the synthesis of propylene oxide (PO) based polyether polyols (PPG) which are used in a wide range of polyurethane applications [1]. The DMC complex, originally discovered by General Tire Inc. [2] in the 1960s, was revisited starting in the middle of 1980s, with improvements made by some companies — including ARCO, Shell, and Asahi Glass. Recent improvements have made DMC catalysts much more attractive for commercial manufacture of polyether polyols [3]. Compared to conventional KOH catalysts, DMC catalysts give high-quality PPG products that have low level of unsaturation, narrow molecular weight distribution, and low viscosity. While DMC catalysts offer significant advantages, unlike KOH, DMC catalysts must normally be activated over 2 h before the epoxide can be added continuously to the reactor at high temperature (>100 °C). Usually, a polyol initiator (or starter) and a DMC catalyst are combined and heated under vacuum prior to the addition of a small proportion of monomer [1,3a]. Long initiation time, say several hours, increases cycle time, which undercuts the economic advantage of faster polymerizations. In addition, heating the catalyst for a prolonged period at high temperature above 100 °C can reduce its activity or deactivate it completely [3,4].

In order to solve these problems we have prepared a series of new catalysts employing multi-metals, $K_3[Co(CN)_6]_2$, potassium ferrocyanide(II) ($K_4Fe(CN)_6$) and $ZnCl_2$, and investigated the kinetics of PO polymerization. Effect of the choice of complexing agents and metal of the catalyst and effect of polymerization parameters on the PO polymerization behavior are to be discussed.

2. Experimental

2.1. Material

All materials such as $K_3[Co(CN)_6]_2$, $K_4Fe(CN)_6\cdot 3H_2O$, $ZnCl_2$ and *tertiary*-butyl alcohol (^{t}BuOH) were purchased from Aldrich and used without further purification. Polypropylene glycol (molecular weight = 700; PPG-700) used an initiator was also purchased from Aldrich and used

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as-received. Polymerization grade of propylene oxide and polytetramethylene ether glycol (molecular weight = 1800; PTMEG) were donated by SKC Company (Korea) and BASF Korea Ltd., respectively.

2.2. Preparation of catalysts

Typical DMC catalyst (DMC-1) was prepared by using $K_3[Co(CN)_6]_2$, $ZnCl_2$, and ^{t}BuOH complexing agent according to the literature procedures [3a,4]. The DMC catalyst for polyol with ultra-low unsaturation level (DMC-2) was also prepared by employing the same procedure, except that 3.5 g of PTMEG was used as a co-complexing agent together with a ^{t}BuOH complexing agent.

The MMC catalyst (MMC-1) using ^{t}BuOH as a complexing agent and PTMEG as a co-complexing agent has been prepared according to the following procedures. $K_3[Co(CN)_6]_2$ (1.5 g, 4.5 mmol) and $K_4Fe(CN)_6$ (1.9 g, 4.5 mmol) are dissolved in distilled water (40 mL) in a beaker (solution 1). $ZnCl_2$ (13.63 g, 0.1 mol) dissolved in distilled water (100 mL) and ^{t}BuOH (20 mL) in a second beaker (solution 2). A third beaker contains solution 3: a mixture of distilled water (1 mL), ^{t}BuOH (20 mL) and PTMEG (3.5 g). Solution 2 is added to solution 1 over 60 min at 50 °C with mixing using a mechanical stirrer. Solution 3 is then added and the mixture is stirred for 3 min. The mixture is centrifuged. The resulting catalyst cake is dried at 60 °C under vacuum (30 mmHg) to a constant weight.

2.3. Polymerization of PO and characterization

Polymerization of propylene oxide was carried out by using 1 L autoclave (Parr) at various temperatures. The 70 g of PPG-700 (functionality = 2) was used as an initiator. Detailed polymerization procedures were described elsewhere [4].

X-ray diffraction (XRD) patterns of the catalysts were obtained with a RINT2000 wide angle goniometer 185 using Cu Kα radiation at 40 kV and 30 mA. 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 5° to 70° 2θ with a step size of 0.02° 2θ and a counting time of 3–6 s per step. 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. IR spectra of the catalysts were obtained in transmission mode using a React IR (Asi Applied system). There were 16 scans per experiment at a resolution of 4 cm^{-1}. The hydroxyl value (OHV) is defined as the equivalent amount of KOH corresponding to the hydroxyl groups in 1 g of polymer and analyzed according to ASTM D-4274 D. The total degree of unsaturation of polyols was measured by titration method according to ASTM D2847. Molecular weight distribution (MWD) was measured using a Waters 150 instrument operated at 25 °C, with a set at 10^4, 10^3, and 500 angstroms columns. Polystyrene standard with low polydispersities were used to generate a calibration curve.

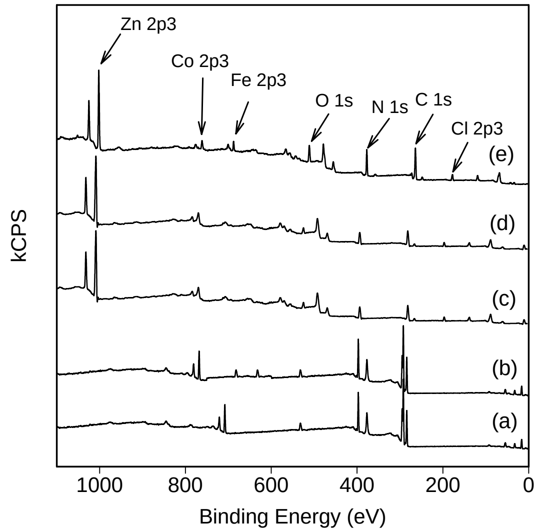

Fig. 1. XPS spectra of: (a) $K_4Fe(CN)_6$, (b) $K_3[Co(CN)_6]_2$, and DMC catalysts: (c) DMC-1, (d) DMC-2, and (e) MMC-1.

3. Results and discussion

3.1. Catalyst characterization

The DMC catalysts prepared by $ZnCl_2$ (excess) and $K_3[Co(CN)_6]_2$ in the presence of complexing agents are expected to have a general formula:

$$Zn_3[Co(CN)_6]_2 \cdot ZnCl_2 \cdot yH_2O \cdot z\text{Complexing agents}$$

The similar general formula is expected for the MMC catalyst prepared by additional introduction of $K_4Fe(CN)_6$:

$$Zn_3[Co(CN)_6]_2 \cdot Zn_2[Fe(CN)_6] \cdot ZnCl_2 \cdot y\text{H2O}$$
$$\cdot z\text{Complexing agents}$$

Atomic identification of these insoluble catalysts is possible using XPS to measure the energy required to create a hole in a core electronic structure. The XPS spectra of the catalysts are shown in Fig. 1 and are summarized in Table 1. The binding energy (1023.7 eV) of zinc atom of $ZnCl_2$ shifts towards lower value by 2.7–3.7 eV after complexation. These chemical shifts results from the coordination of oxygen atom to Zn by reacting $ZnCl_2$ with $K_3[Co(CN)_6]_2$, in the presence of complexing agents. By introducing additional co-complexing agent, PTMEG, together with ^{t}BuOH, the amount of coordinated oxygen is increased from O/Zn = 0.21–0.37. The O/Zn value is further increased to 1.02 for MMC-1 catalyst. The type and the amount of oxygen coordinated to Zn play an important role in the ring-opening polymerization of propylene oxide since oxygen atoms coordinated zinc ion are believed to be a real active center [5]. No

Table 1
Characterization of DMC and MMC catalysts by XPS spectra shown in Fig. 1

Catalyst	Zn $2p^3$		Co $2p^3$		Fe $2p^3$		O 1s		N 1s		C 1s		Cl 2p		O/Zn
	BE (eV)	[AT] (%)	BE (eV)	[AT] (%)	BE (eV)	[AT] (%)	BE (eV)	[AT] (%)	BE (eV)	[AT] (%)	BE (eV)	[AT] (%)	BE (eV)	[AT] (%)	
DMC-1	1020	18.32	780	12.51	–	–	530	3.86	396	22.18	283	40.25	197	2.89	0.21
DMC-2	1021	19.22	778	8.84	–	–	530	7.01	397	20.45	283	42.04	197	2.43	0.37
MMC-1	1021	4.70	779	0.80	706.7	0.69	530	4.90	396	10.02	283	72.96	197	5.92	1.04

activity in the polymerization by using both $K_3[Co(CN)_6]_2$ complex reacted with ^{t}BuOH and $Zn_3[Co(CN)_6]_2 \cdot 12H_2O$ complex prepared in the absence of complexing agents support this fact [4]. Co $2p^3$ of $K_3[Co(CN)_6]_2$ shifts from 781 to 780 eV for DMC-1, to 778 eV for DMC-2 and to 780 eV for MMC-1, respectively, by forming complexes with oxygen coordinated zinc. Fe $2p^3$ of $K_4Fe(CN)_6$ shifts from 707.2 to 706.7 eV for MMC-1 catalyst.

Infrared spectra of $K_3[Co(CN)_6]_2$ and catalysts (Fig. 2) showed a shift of the ν(CN) band from 2133.4 cm^{-1} for $K_3[Co(CN)_6]_2$ to 2198.4, 2195.9 and 2193.1 cm^{-1} for DMC-1, DMC-2, and MMC-1, respectively. The ν(CN) band of 2053.4 cm^{-1} for $K_4Fe(CN)_6$ shifts to 2101.1 cm^{-1} for MMC-1. The ν(CN) of free CN^- is 2080 cm^{-1} [6]. The ν(CN) shift to higher frequencies demonstrates that the CN^- ion acts as not only a σ-donor by donating electrons to the cobalt but also an electron donor by chelating to zinc metal. A slight ν(CN) shift to lower frequencies from DMC-1 catalyst to DMC-2 and MMC-1 catalysts seems to be the effect of electronegativity. Since the electronegativity of Zn is become smaller as the coordinated amount of bulky PTMEG co-complexing agent increases, electron donation from cyanide ligands to Zn becomes decreased, and the ν(CN) is expected to be lower. Thus the coordination strength between Zn and complexing agents in the catalyst is expected to be in the order of DMC-1 > DMC-2 > MMC-1. Evidently the coordination strength is expected to influence PO polymerization behavior (vide infra).

Alteration of the crystal structure can be shown by X-ray diffraction patterns to be dependent on the different surfaces. Fig. 3 shows typical power X-ray diffraction curves of the catalysts of the present study. The X-ray patterns for DMC-1 resemble the pattern for highly crystalline zinc hexacyanocobaltate hydrate [7,8]; however, DMC-2 and especially MMC-1 catalysts, which are synthesized in the presence of ^{t}BuOH complexing agent and PTMEG co-complexing agent, exhibit broad signals at *d*-spacings of 5.75, 5.07, 3.59, 2.54, and 2.28 Å, ascribing to a cubic lattice structure of $Zn_3[Co(CN)_6]_2$ [4,7,8]. This means that DMC-2 and MMC-1 catalysts are substantially amorphous compared with DMC-1 catalyst. The crystallinity of the catalyst may strongly influence the catalytic activity. Highly crystalline $Zn_3[Co(CN)_6]_2 \cdot 12H_2O$ compound, which is prepared in the absence of complexing agent, showed no activity in the propylene oxide polymerization.

3.2. Polymerization of propylene oxide

Semi-batch polymerizations of propylene oxide using DMC-1, DMC-2 and MMC-1 catalysts have been carried out at various temperatures by keeping the pressure of the

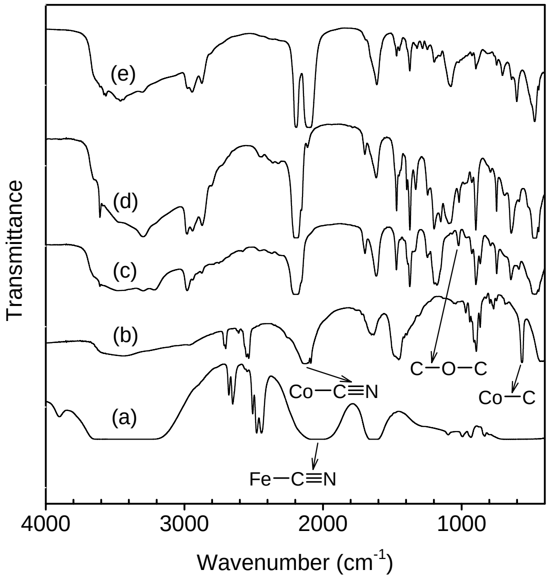

Fig. 2. Infrared spectra of (a) $K_4Fe(CN)_6$, (b) $K_3[Co(CN)_6]_2$, and DMC catalysts: (c) DMC-1, (d) DMC-2, and (e) MMC-1.

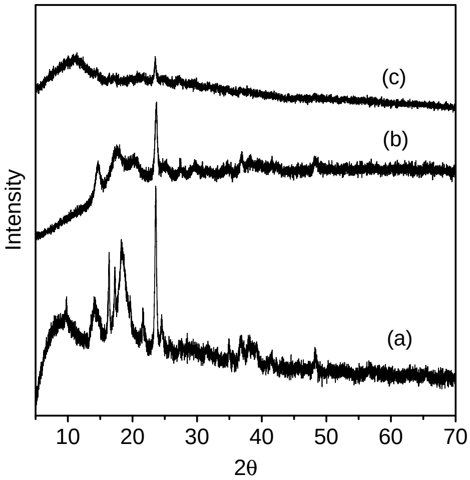

Fig. 3. XRD patterns of DMC and MMC catalysts: (a) DMC-1, (b) DMC-2, and (c) MMC-1.

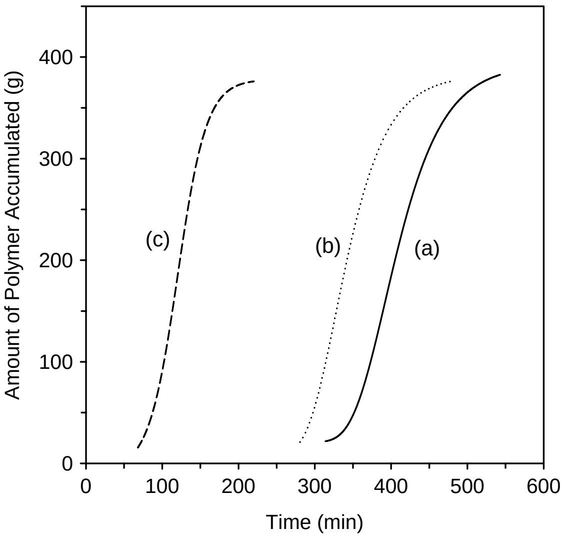

Fig. 4. Amount of polymer accumulated vs. time curves obtained by using DMC and MMC catalysts at $T_p = 115\,^{\circ}C$: (a) DMC-1, (b) DMC-2, and (c) MMC-1. The amount of PPG-700 initiator per batch was 70 g and the amount of catalyst per batch was 0.1 g.

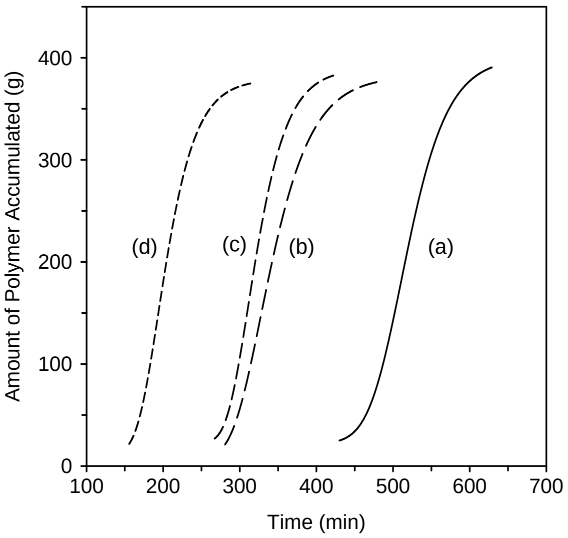

Fig. 5. Amount of polymer accumulated vs. time curves obtained by DMC-2 catalyst at various polymerization temperatures of: (a) 95 °C, (b) 105 °C, (c) 115 °C, and (d) 130 °C. The amount of PPG-700 initiator per batch was 70 g and the amount of catalyst per batch was 0.1 g.

reactor constant at 10 psig. Fig. 4 shows polymerization rate profiles obtained by DMC-1, DMC-2 and MMC-1 catalysts in the presence of PPG-700 as an initiator at 115 °C. All catalysts show very high activity. The maximum polymerization rate ($R_{p,max}$) obtained by differentiating the rate curve was 1720 g POP/g-cat h (POP = poly(oxypropylene) diol) for DMC-1, 1316 g POP/g-cat h for DMC-2 and 2778 g POP/g-cat h for MMC-1. Unlike conventional KOH catalyst, DMC catalysts must normally be activated before the propylene oxide can be added continuously to the reactor. This induction period was longer than 250 min for DMC-1 catalyst and decreased to 190 min and 30 min with DMC-2 and MMC-1 catalysts, respectively. Evidently the induction time decreases by using more weakly coordinating complexing agents such as PTMEG and by using additional metal like $K_4Fe(CN)_6$.

In order to further investigate the detailed rate behavior of the DMC and MMC catalysts, polymerizations were carried out at a polymerization temperature (T_p) range between 30 and 130 °C. Figs. 5 and 6 show an amount of polymer accumulated versus time curves obtained by DMC-2 and MMC-1 catalysts, respectively. The DMC catalysts showed only negligible activity at a low temperature below 90 °C. Polymerization results obtained by DMC-2 catalyst shows

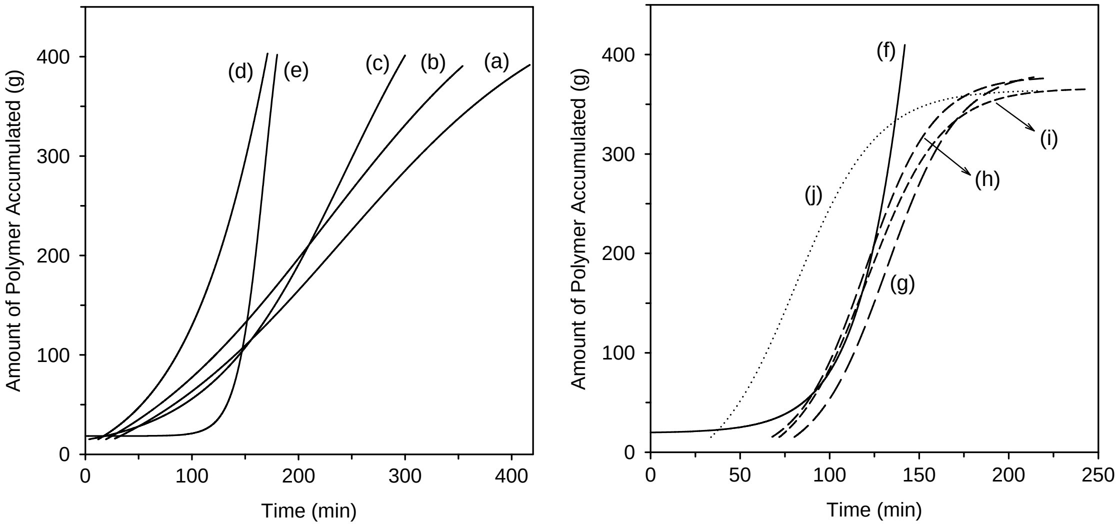

Fig. 6. Amount of polymer accumulated vs. time curves obtained by MMC-1 catalyst at various polymerization temperatures of: (a) 30 °C, (b) 40 °C, (c) 50 °C, (d) 60 °C, (e) 75 °C, (f) 85 °C, (g) 95 °C, (h) 105 °C, (i) 115 °C, and (j) 130 °C. The amount of PPG-700 initiator per batch was 70 g and the amount of catalyst per batch was 0.1 g.

Table 2
Results of ring-opening polymerization of PO catalyzed by DMC and MMC catalysts[a]

Catalyst	Polymer temperature (°C)	Activity, $R_{p,max}$[b]	Unsaturation (meq/g)	OHV		GPC	
				OH value (mg KOH/g)	M_n[c] (g/mol)	M_n (g/mol)	MWD
DMC-1	115	1720	0.017	35.0	3620	3730	1.43
DMC-2	95	1088	0.003	23.8	4710	4830	1.02
	105	1051	0.004	24.1	4650	4840	1.03
	115	1316	0.005	24.2	4640	4880	1.04
	130	1432	0.006	24.3	4610	4810	1.02
MMC-1	30	736	0.002	17.8	6310	6530	1.02
	40	830	0.003	18.6	6010	6140	1.02
	50	1329	0.005	19.4	5780	5880	1.02
	60	3432	0.005	19.7	5690	5810	1.03
	75	6301	0.006	21.2	5290	5450	1.03
	85	9221	0.006	23.5	4780	4940	1.04
	95	2991	0.006	24.5	4570	4740	1.04
	105	3058	0.007	25.6	4380	4390	1.05
	115	2778	0.008	26.0	4310	4370	1.08
	130	2592	0.010	26.3	4270	4350	1.10

[a] The initiator is bi-functional polypropylene glycol.
[b] The unit is g POP/g-cat h.
[c] $M_n = [(f \times 56.1)/\text{OHV}] \times 1000$ (f is the functionality, which is equal to 2).

that there is a big difference in the induction time, which becomes shorten as T_p increases due to a faster formation of polymerization center at high T_p, even if there is not so big difference in the $R_{p,max}$ value according to T_p. The MMC-1 catalyst shows quite different features from DMC catalysts: (1) the MMC-1 catalyst has relatively shorter induction period regardless of T_p, (2) the MMC-1 catalyst shows high polymerization activity at a wide range of T_p and (3) the activity of MMC-1 catalyst is very sensitive to T_p (see $R_{p,max}$ value of MMC catalyst according to T_p in Table 2). These results demonstrate that the activity and thermal stability of polymerization centers deeply depend on the catalyst formulation.

3.3. Characterization of poly(oxypropylene)

Regulating polymerization parameters and controlling the catalyst formulations demonstrate the catalysts of the present study demonstrated to be active enough to allow at a very low concentration, preferably at concentration low enough to overcome any need to remove the catalyst from the POP for further applications. It is well known that base (say KOH) catalyzes not only the addition of propylene oxide to the growing polymer molecule, but also a side reaction in which propylene oxide isomerizes to allyl alcohol [4,9]. Allyl alcohol acts as a monofunctional starter resulting in the production of the propoxylated allyl alcohol, often referred to as monol. The monol is also generated by other types of reaction [4]. Since each monol molecule also contains a terminal double bond, the amount of monol present in the POP can be quantified by measuring the unsaturation level. Table 2 summarizes the properties of polyols together with the polymerization results. DMC-1 catalyst produces POP with reduced level of unsaturation, 0.017 meq/g, relative to conventional KOH catalyzed polyols (typical unsaturations of 0.03–0.10 meq/g). The level of unsaturation was further reduced by using DMC-2 (0.003–0.006 meq/g) and MMC-1 (0.002–0.010 meq/g) catalysts. The monol content increases slightly according to T_p (see DMC-2 and MMC-1 in Table 2); however, all polymers obtained by using DMC-2 and MMC-1 catalysts are characterized by ultra-low level of unsaturation. The ultra-low monol levels shown by DMC-2 and MMC-1 are a result of the proprietary process for polymerizing propylene oxide in which the addition reaction is strongly promoted relative to the isomerization reaction. In this sense the choice of complexing agent and metal plays an important role in suppressing reactions generating the unsaturated chains.

Molecular weight of polymers calculated by using hydroxyl value and those measured by GPC fit well in an acceptable range and decrease as T_p increases as shown in Table 2. It is very interesting to note that all polymers have very narrow polydispersities. The MWD values of polymers obtained by DMC-2 and MMC-1 catalysts are in the range of 1.02–1.10. The very narrow MWD value of polymer can generally be achieved 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. Since we used large excess amount of initiator (0.1 mol) in comparison with catalyst (0.1 g), 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 like 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 narrowing of MWD.

3.4. The nature of the active sites of DMC catalyst

Even though an inherent insoluble nature of DMC and MMC catalysts makes the clarification of polymerization mechanism by using spectroscopic methods, some indirect evidences on the character of active centers could be collected. The DMC and MMC catalysts show cationic characters in that (1) addition of acid to a reactor during polymerization does not kill the active sites completely, (2) $Zn_3[Co(CN)_6]_2$ compound prepared in the absence of complexing agent shows no activity before complexing agents containing oxygen atom are not cationically coordinated, and (3) DMC catalyzed POPs show very narrow polydispersity. On the other hand they show coordinative characters in that (1) the type of metal and complexing agent of the catalysts results in quite different polymerization behaviors, (2) the amount of coordination of the complexing agents deeply influenced polymerization behaviors (see O/Zn ratio in Table 1), and (3) independent polymerizations showed that the rate (as $R_{p,max}$) was proportional to the amount of catalyst. These results show that the PO polymerizations by DMC and MMC catalysts represent both cationic and coordinative characters.

4. Conclusions

A series of DMC catalysts were synthesized by changing the type of complexing agents and metal, and utilized for the polymerizations of propylene oxide. The catalytic activity, initiation time, and the unsaturation level of resulting POP were very sensitive to the type of complexing agents and metal used for the preparation of catalysts. The spectroscopic analyses such as X-ray photoelectron spectroscopy, infrared spectroscopy, and X-ray powder diffraction of the catalysts showed that the complexing and co-complexing agents are coordinated to DMC and MMC catalysts. Both DMC catalysts incorporating PTMEG as a co-complexing agent and MMC catalyst showed highly amorphous structures and very high activities. Especially, MMC catalyst showed high activities at a wide range of T_p between 30 and 130 °C. The resulting POPs were characterized by ultra-low unsaturation level (0.002–0.01 meq/g) and by narrow molecular weight distribution (MWD = 1.02–1.10). Some indirect evidences showed that the active sites of DMC and MMC-catalyzed polymerization of PO had both cationic and coordinative characters.

Acknowledgements

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