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Polymerization of propylene oxide by using double metal cyanide catalysts and the application to polyurethane elastomer

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Dedicated to Professor Won-Jei Cho on the occasion of his retirement

Abstract

Polymerizations of propylene oxide have been carried out by using double metal cyanide (DMC) catalysts based on $Zn_3[Co(CN)_6]_2$. By controlling the type and the amount of complexing agent during preparation of catalyst the catalytic activity, initiation time, and the unsaturation level in polyether polyols could be tuned. Various catalysts prepared by changing the complexing and co-complexing agents were characterized by x-ray photoelectron spectroscopy, infrared spectroscopy, and X-ray powder diffraction. Highly active catalyst prepared by choosing a polytetramethylene ether glycol as a co-complexing agent resulted in polyoxypropylenes (POP) with low very low unsaturation level (0.003–0.006 meq/g) and with narrow molecular weight distribution (MWD = 1.02–1.04). The active sites of DMC-catalyzed polymerization of propylene oxide have both cationic and coordinative characters. ^{13}C NMR analysis showed that the polyols have a random distribution of the configurational sequences and head-to-tail regiosequence, even if the amount of [*rr*] triad of polyol produced by DMC catalyst was larger than that of polyol by conventional KOH catalyst. The distortionless enhancement by polarization transfer analysis showed that there exist regioirregular sequences as well. The stress–strain curves of methylene diisocyanate/1,4-butanediol cured POP-based polyurethane elastomers showed that the unsaturation content contained in POP showed a dramatic effect on the mechanical properties.

Keywords: Propylene oxide polymerization; Double metal cyanide catalyst; Polyurethane

1. Introduction

Double metal cyanide (DMC) complexes are well-known catalyst for the polymerization of epoxides and the synthesis of propylene oxide based polyether polyols (PPG) which are used in a wide range of polyurethane applications [1]. The catalyst was originally discovered by General Tire Inc. [2] in the 1960s. DMC catalyst was revisited starting in the middle of 1980s, with improvements made by some companies—including ARCO [3], Shell [4], and Asahi Glass [6]. Recent improvements have made DMC catalysts much more attractive for commercial manufacture of polyether polyols [3(g)]. Compared with conventional KOH catalysts, DMC catalysts give high-quality PPG products that have low level of unsaturation, narrow molecular weight distribution, and low viscosity [4]. While DMC catalysts offer significant advantages, unlike KOH, DMC catalysts must normally be activated before the epoxide can be added continuously to the reactor. 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 [5]. Long initiation time, say several hour, 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(g)–(i)].

Even though the kinetics of polymerization of propylene oxide (PO) and the properties of resulting polyol are greatly dependent upon the catalyst structure, there have been few reports discussing on the effect of DMC catalyst structure on the polymerization behavior of propylene oxide [7–9]. Insoluble nature of the catalyst makes the investigation of the structure of the catalyst difficult. In this paper kinetics of polymerization of PO using DMC catalysts prepared by

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modifying the composition and the structure has been discussed. The properties of DMC-catalyzed PPG and polyurethane elastomer produced by using resulting PPG are investigated and compared to those of conventional PPG produced by KOH catalyst.

2. Experimental section

2.1. Material

All materials such as potassium hexacyanocobatate(III) ($K_3[Co(CN)_6]_2$), zinc chloride($ZnCl_2$), tertiary butyl alcohol (^{t}BuOH), and 4,4′-methylene diisocyanate (MDI) were purchased from Aldrich and used without further purification. 1.4-Buthanediol (Aldrich) was distilled and stored over Linde type 4A molecular sieves. Dimethylformamide (DMF) purchased from Aldrich was dried by stirring with $MgSO_4$, followed by distillation under reduced pressure. Glycerol propoxylate (molecular weight = 725) and polypropylene glycol (molecular weight = 700; PPG-700) were also purchased from Aldrich and used as received. Polymerization grade of propylene oxide (PO) 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**) with complexing agent (^{t}BuOH) has been prepared according to the literature procedures [3(g)]. The DMC catalyst (**DMC-2**) catalyst using PPG-700 as a co-complexing agent has been prepared according to the following procedures. $K_3[Co(CN)_6]_2$ (3.32 g, 0.01 mol) is 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 PPG-700 (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 inHg) to a constant weight. Catalyst for polyol with ultra-low unsaturation level (**DMC-3**) has been prepared by employing the same procedure, except that 3.5 g of PTMEG is used instead of PPG-700. One more catalyst for polyol with ultra-low unsaturation level (**DMC-4**) was also prepared by the same procedures by increasing the amount of PTMEG from 3.5 to 7.0 g.

2.3. Polymerization of propylene oxide

Polymerization of propylene oxide was carried out by using 1 l autoclave (Parr) at various temperatures. 70 g of PPG-700 (functionality = 2) or glycerol propoxylate (functionality = 3) was used as an initiator. The reactor was charged with initiator and catalyst (0.1 g), and then purged with several time with nitrogen. The mixture was heated to 90 °C and evacuated for over 2 h during stirring in order to remove traces of water contained in the initiator. Then 10 g of propylene oxide monomer was introduced into the reactor at a desired polymerization temperature (T_p). Additional monomer was started to add gradually when an accelerated pressure drop, indicating activation of the catalyst, occurred in the reactor. The polymerization was stopped when the total amount of added monomer reached 400 g. A clear liquid product was obtained. This semi-batch polymerization rate was continuously recorded by measuring the weight of the monomer introduced into the reactor by using personal computer connected with electronic balance through AD converter. The pressure of the reactor kept constant at 10 psig through the polymerization.

2.4. Synthesis of PU elastomer

The PU elastomer of its functionality of 2 was prepared according to a conventional method [3,4]. The amount of the hard segment in the polyurethanes was fixed to 29 wt%. Isocyanate prepolymer were prepared in glass reaction vessels in a laboratory fume hood. The reaction vessel (500 ml round-bottom flask) was equipped with an addition funnel, a mechanical stirrer, and a temperature controller. The reaction was carried out under a dry nitrogen atmosphere to minimize exposure to atmospheric moisture and polyol oxidation. Excess MDI was added to polyoxypropylene diol and reacted at 80 °C until all hydroxyl groups reacted. Typical reaction time for prepolymers was 8 h. After preparing the prepolymer, the next step was that of chain extension with a 1,4-butanediol to make the final PU elastomer. 1.4-Buthanediol dissolved in DMF added dropwise to the mixture at 80 °C for 1 h. DMF and unreacted compounds were removed under vacuum at 30 °C. The resulting mixture was blended uniformly and poured into the molds ($100 \times 10 \times 1$ mm^3) and cured at 100 °C for 24 h in a dry oven.

2.5. Characterization

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 monochrometer 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}. To determine

reaction rate, a plot of PO consumption (g) versus reaction time (min) was prepared and the slope of the curve at its steepest point was measured to find the reaction rate.

^{1}H, ^{13}C NMR and distortionless enhancement by polarization transfer (DEPT) spectra of the polyols were performed on a Varian Gemini 2000 and HP5P with $CDCl_3$ as a solvent. 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-4274D. 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 Å columns. Polystyrene standard with low polydispersities were used to generate a calibration curve.

The tensile strength tests of PU elastomers ($100 \times 10 \times 1$ mm^3 in size) were carried on an Instron 4466 according to the specification of ASTM D882. The crosshead speed was set at 500 mm/min. For each data point, three samples were tested and the average value was taken and reported. Thermal property of PU elastomers were assessed by DSC with a Seiko model 220 differential scanning calorimeter (DSC). In all cases, samples were cooled to about −100 °C and heated to 100 °C at a rate of 10 °C/min, cooled again to −100 °C, and heated again to 100 °C at a rate of 10 °C/min, employing a nitrogen purge. Result of the second heating run were normalized on a weight basis.

3. Results and discussion

3.1. Catalyst characterization

In the present study of catalyst preparation aqueous solution of zinc chloride ($ZnCl_2$) and potassium hexacyanocobaltate ($K_3[Co(CN)_6]_2$) were combined. The resulting precipitate of zinc hexacyanocobaltate ($Zn_3[Co(CN)_6]_2$) was combined with ^{t}BuOH as a major complexing agent. PPG or PTMEG was also utilized as a co-complexing compound. The resulting catalyst is expected to have the general formula:

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

Even if the insolubility of this complex makes the analysis difficult, the surface formulation of the catalyst could be investigated by XPS. Atomic identification in an insoluble solid 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 ^{t}BuOH as a complexing reagent. By introducing additional co-complexing agent, PPG, together with ^{t}BuOH, the amount of coordinated oxygen is increased from O/Zn = 0.21–0.50. When PTMEG is used as a co-complexing agent the O/Zn value increases from 0.21 to 0.37 and the value increases from 0.37 to 0.57 by increasing the amount of PTMEG by two-fold. From these results and reported results [10,11] the structure of the DMC catalyst can be postulated as shown in Fig. 2. 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 [9]. No 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. Part or all of the coordinated ^{t}BuOH (see Fig. 2) should be replaced by other coordinative groups by the addition of co-complexing agent. Co 2P^3 of $K_3[Co(CN)_6]_2$ shifts from 781 eV to 780 for **DMC-1**, to 777 for **DMC-2**, to 778 for **DMC-3** and to 777 eV for **DMC-4**, respectively, by forming complexes with oxygen coordinated zinc. The degree of shift is changed according to the amount of oxygen present in the catalyst surface.

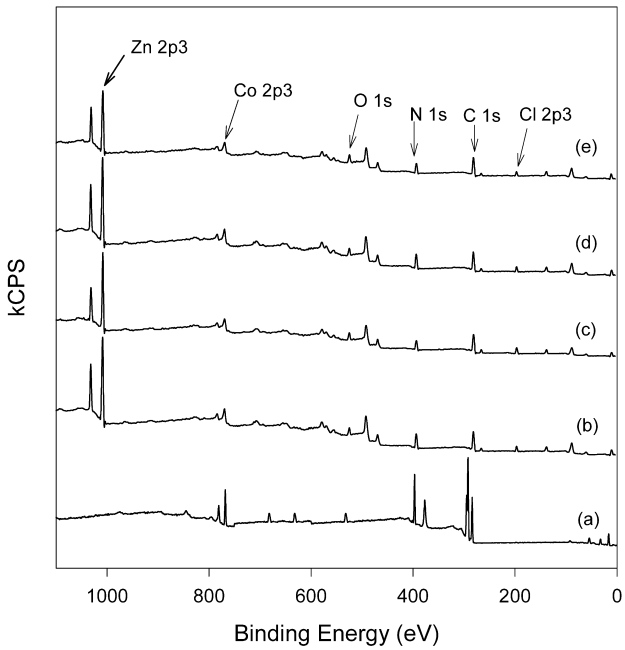

Fig. 1. XPS spectra of (a) $K_3[Co(CN)_6]_2$, and DMC catalysts: (b) **DMC-1**, (c) **DMC-2**, (d) **DMC-3**, and (e) **DMC-4**.

In this study excess amount ([Zn]/[Co] = 10) of $ZnCl_2$ was used for the preparation of catalysts. The small amount of Cl 2p present in the catalyst surface indicates that stoichiometric amount of $ZnCl_2$ is reacted to form a desired complex and most of excess $ZnCl_2$ was disappeared. The presence of unreacted $ZnCl_2$ has been reported to be one of an important factor to achieve high catalytic activity, even if the exact mechanism remains uncertain [3]. In order to check this we washed the catalyst repeatedly by water during the catalyst preparation to remove the unreacted

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

Compound	Zn 2p3		Co 2p3		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] %	
$ZnCl_2$	1023.7												
$K_3[Co(CN)_6]_2$			781										
DMC-1	1020	18.32	780	12.51	530	3.86	396	22.18	283	40.25	197	2.89	0.21
DMC-2	1020	16.6	777	7.44	530	8.42	397	14.97	283	48.93	197	3.60	0.50
DMC-3	1021	19.22	778	8.84	530	7.01	397	20.45	283	42.04	197	2.43	0.37
DMC-4	1021	16.76	777	6.66	530	9.61	397	16.12	283	48.40	197	2.45	0.57

$ZnCl_2$. DMC catalyst prepared by this procedure was really inactive at all.

Infrared spectra of $K_3[Co(CN)_6]_2$ and catalysts (Fig. 3 and Table 2) showed a shift of the ν(CN) band at 2198.4, 2192.3, 2195.9 and 2194.9 cm^{-1} for **DMC-1**, **DMC-2**, **DMC-3**, and **DMC-4**, respectively, instead of 2133.4 cm^{-1} for $K_3[Co(CN)_6]_2$. The ν(CN) of free CN^- is 2080 cm^{-1} [12]. 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. Electron donation tends to raise the ν(CN) since electrons are removed from the 5σ orbital, which is weakly antibonding, while π-back-bonding tends to decrease the ν(CN) because the electrons enter into the antibonding $2p\pi^*$ orbital. In general, CN^{-1} is a good s-donor and a poorer p-acceptor. Thus the ν(CN) of the complexes are generally higher than the value for free CN^-. A slight ν(CN) shift to lower frequencies from **DMC-1** catalyst to the other catalysts (**DMC-2**, **DMC-3**, and **DMC-4**) seems to be the effect of elecronegativity. Since the electronegativity of Zn is become smaller as the coordinated amount of bulky co-complexing agent (PPG or PTMEG) 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-3** > **DMC-4** > **DMC-2**. These results demonstrate that the cyanide ligands are oriented linearly between the divalent Zn atoms and the Co atoms with the C atoms toward the Co atom. The divalent Zn atoms are linked to the Co atoms by cyanide bridging as shown in Fig. 2.

Alteration of the crystal structure can be shown by X-ray diffraction patterns to be dependent on the different surfaces. Fig. 4 shows typical power X-ray diffraction curves of the catalysts of the present study. The X-ray patterns for **DMC-1** made in the presence of ^{t}BuOH complexing agent resemble the pattern for highly crystalline zinc hexacyanocobaltate hydrate [11,13]. **DMC-2**, **DMC-3** and **DMC-4** catalysts, which are synthesized in the presence of ^{t}BuOH complexing agent and co-complexing agent (PPG or PTMEG), 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 $Zn_3[Co(CN)_6]_2$ [11,13]. This means that **DMC-2**, **DMC-3** and **DMC-4** catalysts with PPG or PTMEG co-complexing agent are substantially amorphous compared with **DMC-1** catalyst. The crystallinity of the catalyst may strongly influence the catalytic activity. As already mentioned the 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**, **DMC-3** and **DMC-4** catalysts have been

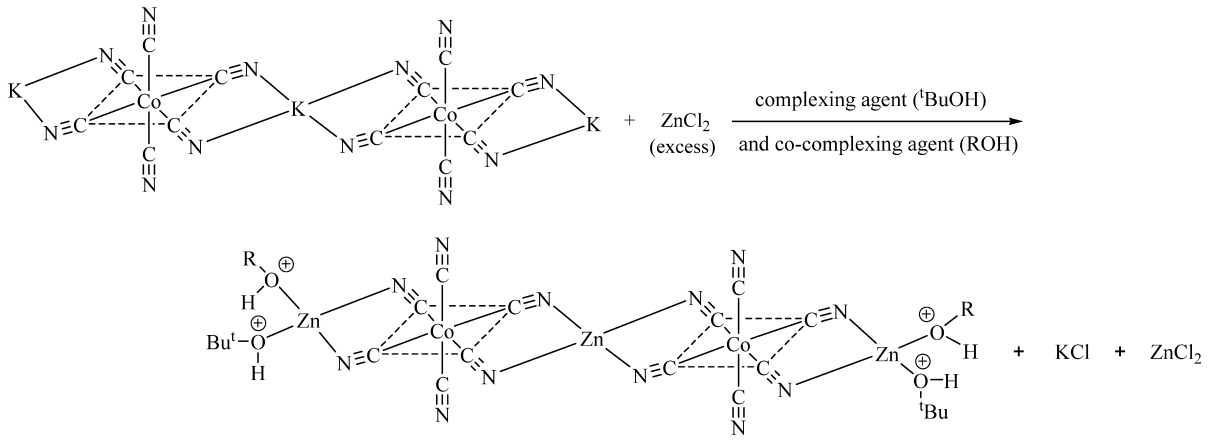

Fig. 2. Plausible structure of DMC catalyst prepared by using ^{t}BuOH (complexing agent) and co-complexing agent.

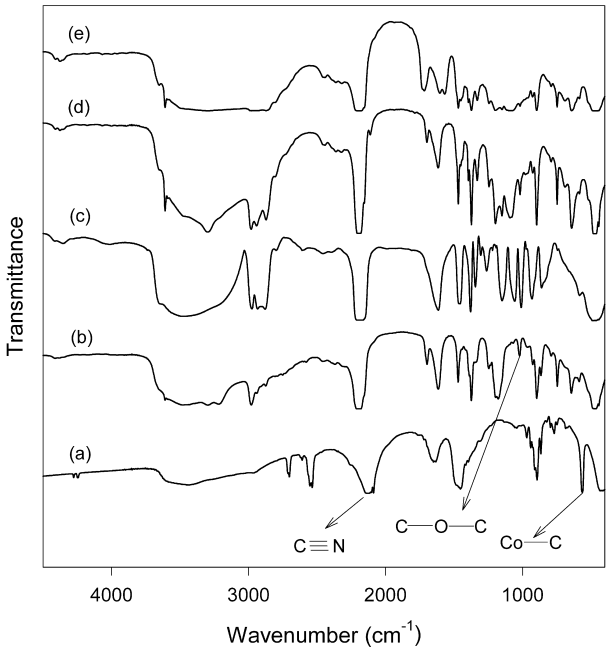

Fig. 3. Infrared spectra of (a) $K_3[Co(CN)_6]_2$, and DMC catalysts: (b) **DMC-1**, (c) **DMC-2**, (d) **DMC-3**, and (e) **DMC-4**.

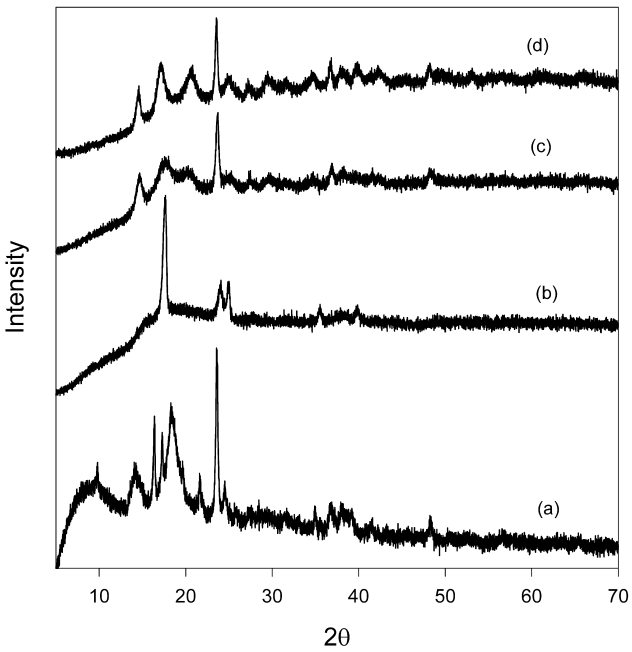

Fig. 4. XRD patterns of DMC catalysts: (a) **DMC-1**, (b) **DMC-2**, (c) **DMC-3**, and (d) **DMC-4**.

carried out at the temperature range between 95 and 130 °C by keeping the pressure of the reactor constant at 10 psig. There have been no reports on the detailed rate profiles of PO polymerization by using DMC catalysts. Fig. 5 shows polymerization rate profiles obtained by **DMC-1**, **DMC-2**, **DMC-3** and **DMC-4** catalysts in the presence of PPG-700 as an initiator at 115 °C. The catalytic activity as a maximum rate ($R_{p,max}$) was in the order of **DMC-4** ($R_{p,max}$ = 2672 g-POP/g-cat *h*, POP = polyoxypropylene diol) > **DMC-1** ($R_{p,max}$ = 1720 g-POP/g-cat h) > **DMC-3** ($R_{p,max}$ = 1316 g-POP/g-cat h) > **DMC-2** ($R_{p,max}$ = 869 g-POP/g-cat h). Even if there is a big difference in the activity among the catalysts, it can be identified that all catalysts have some common features: (1) the catalysts have prolonged induction period before activation and (2) the catalysts show bell-type rate profiles—very fast propagation reaction to reach maximum rate once they are activated, followed by rapid deactivation. Unlike KOH catalyst, DMC catalysts must normally be activated before the propylene oxide can be added continuously to the reactor. Catalyst activation is inferred from a drop in propylene oxide partial pressure in the reactor. The induction period was longer than 250 min with **DMC-1** catalyst and the time decreased to 60 min, 190 min, and 160 min with **DMC-2**, **DMC-3** and **DMC-4** catalysts, respectively. The induction time is shorten by using more weakly coordinating complexing agents such as PPG and PTMEG. The order of strength of coordination of complexing agent, **DMC-1** > **DMC-3** > **DMC-4** > **DMC-2**, agrees with the length of induction period.

Considering the result of catalyst characterization and PO polymerization, the reaction scheme for the PO

Table 2
Characterization of DMC catalysts by infrared spectra shown in Fig. 3

Compound	ν(Co–C)	ν(C–O)	ν(C≡N)
$K_3[Co(CN)_6]_2$	563.5	–	2133.4
DMC-1	475.2	1187.9	2198.4
DMC-2	474.8	1151.9	2192.3
DMC-3	472.4	1151.4	2195.9
DMC-4	470.9	1150.3	2194.9

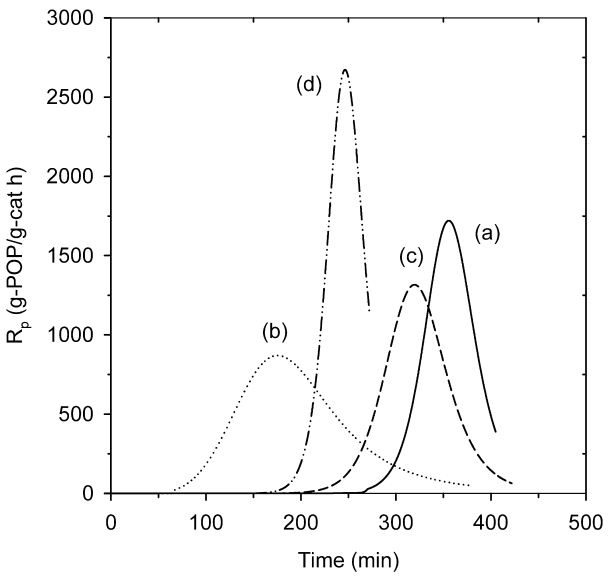

Fig. 5. Polymerization rate curves obtained by using DMC catalysts at T_p = 115 °C : (a) **DMC-1**, (b) **DMC-2**, (c) **DMC-3**, and (d) **DMC-4**. The amount of PPG-700 initiator added was 70 g and the catalyst amount used per batch was 0.1 g.

polymerization using heterogeneous DMC catalysts in the presence of initiator can be postulated as shown in Fig. 6 diagrammatically. In the case of heterogeneous catalytic polymerization using an initiator whose functionality are selected based on the final application, the polymerization centers are formed in two stages: (i) the formation of active sites S^* from a dormant site S in the catalyst surface by the initiator, followed by (ii) the formation of a polymerization center C^* from an active site and a PO monomer unit. Once the polymerization center formed the monomer is inserted to give high molecular weight polymers. Active intermolecular 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 fast exchange reaction with the initiator molecule, resulting in the delay of the formation of polymerization centers (C^*).

In order to further investigate the rate behavior of the DMC catalysts, polymerizations were carried out at a T_p range between 95 and 130 °C. Figs. 7–9 show polymerization rate (R_p) versus time curves obtained by **DMC-2**, **DMC-3** and **DMC-4** catalysts, respectively. Generally the induction time becomes shorten as T_p increases due to a faster formation of polymerization center at high T_p. The catalytic activity showed maximum at 115 °C for **DMC-2**, **DMC-4** catalysts, while it increased monotonously from 95 °C to 130 °C for **DMC-3** catalyst. These results demonstrate that the activity and thermal stability of

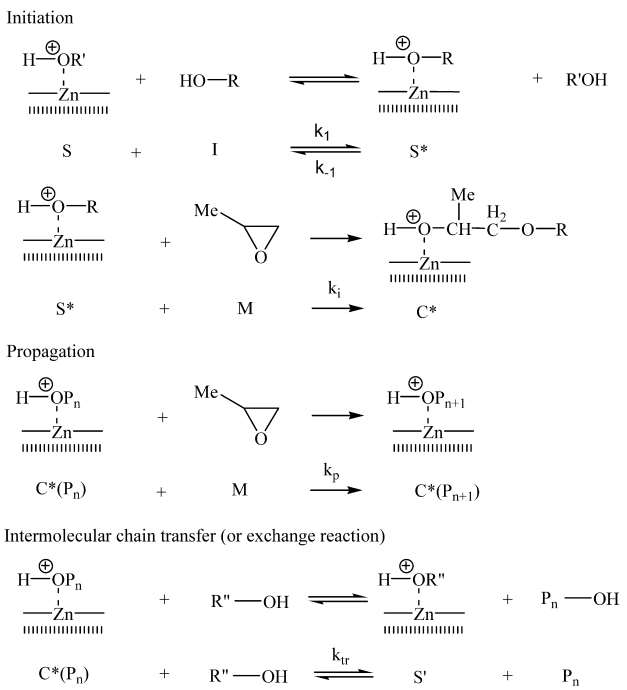

Fig. 6. Mechanism of DMC-catalyzed ring-opening polymerization of propylene oxide.

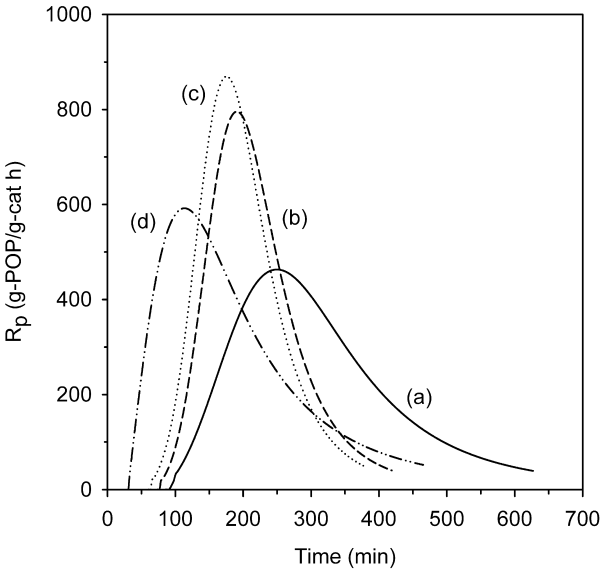

Fig. 7. Polymerization rate curves obtained by **DMC-2** catalyst at various polymerization temperatures of (a) 95 °C, (b) 105 °C, (c) 115 °C, and (d) 130 °C. The amount of PPG-700 initiator added was 70 g and the catalyst amount used per batch was 0.1 g.

polymerization centers depend on the type and the amount of complexing agent.

As expected from polymerization mechanism illustrated in Fig. 6, the type of initiator is one of parameters influencing the kinetics of polymerization. In order to investigate this factor polymerization behavior was compared by using different initiator compounds of similar molecular weight: i.e. trifunctional glycerol propoxylate (molecular weight = 725) which results in POP triol and bifunctional PPG-700 which result in POP diol. As shown in

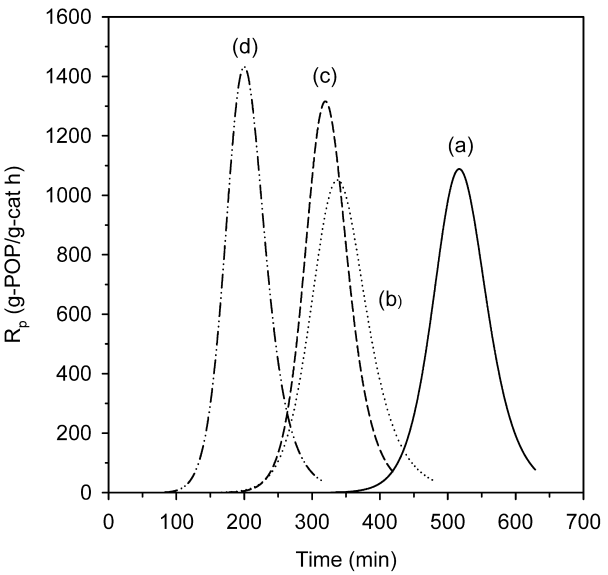

Fig. 8. Polymerization rate curves obtained by **DMC-3** catalyst at various polymerization temperatures of (a) 95 °C, (b) 105 °C, (c) 115 °C, and (d) 130 °C. The amount of PPG-700 initiator added was 70 g and the catalyst amount used per batch was 0.1 g.

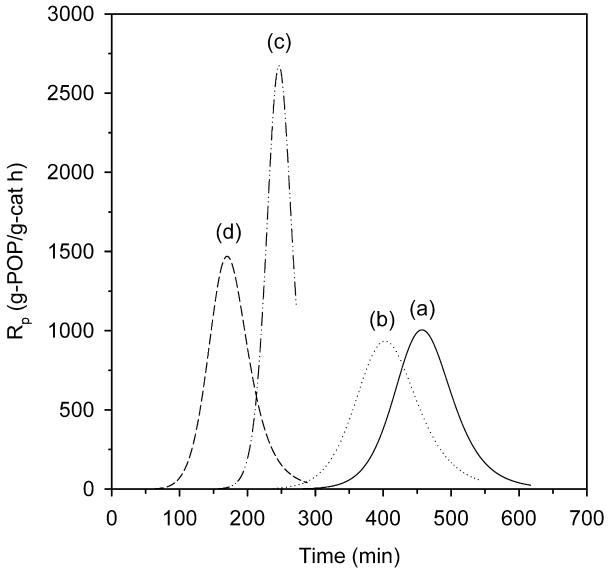

Fig. 9. Polymerization rate curves obtained by **DMC-4** catalyst at various polymerization temperatures of (a) 95 °C, (b) 105 °C, (c) 115 °C, and (d) 130 °C. The amount of PPG-700 initiator added was 70 g and the catalyst amount used per batch was 0.1 g.

Fig. 10, R_p and induction time change not so much according to the type of the initiator. However, independent polymerization results showed that simple molecules such as ethylene glycol (EG) and glycerol (GL) resulted in no polymerization activity. The DMC·EG and DMC·GL surface sites (S^*) formed by the replacement of DMC·CA (complexing agent) sites (S) are strongly coordinated not enough to attack PO monomer to generate polymerization center (C^*). As a result initiators that have good coordination ability, such as amine, urea, low carbon acid, and alcohol, would act as inhibitors. It is therefore understandable that initiators should have a reasonable molecular weight and bulkiness not to be strongly coordinated to the dormant sites as a result of their hindrance effect. However, it seems that the functionality of the initiators is not a significant factor in the polymerization, on condition that they are similar structured molecule of a similar molecular weight. Detailed study on the effect of initiator on the polymerization behavior is a good theme for the further study and is to be reported elsewhere.

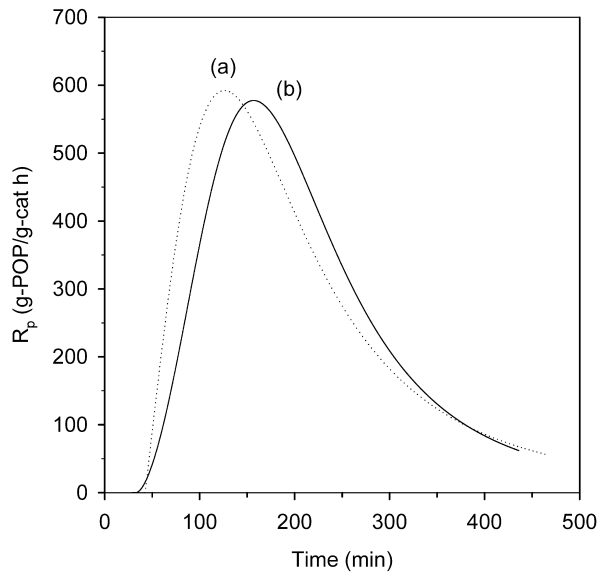

Fig. 10. Polymerization rate curves obtained by using **DMC-2** catalyst at $T_p = 115$ °C by using different initiator: (a) PPG-700 and (b) glycerol propoxylate. The amount initiator added was 70 g and the catalyst amount used per batch was 0.1 g.

3.3. Characterization of polyoxypropylene

The catalysts of the present study are 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 [14]. 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 as illustrated in Fig. 11. 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 3 shows 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 not reduced so much by using **DMC-2** catalyst. However, **DMC-3** and **DMC-4** catalysts with PTMEG as a co-complexing agent give polyols having ultra-low monol,

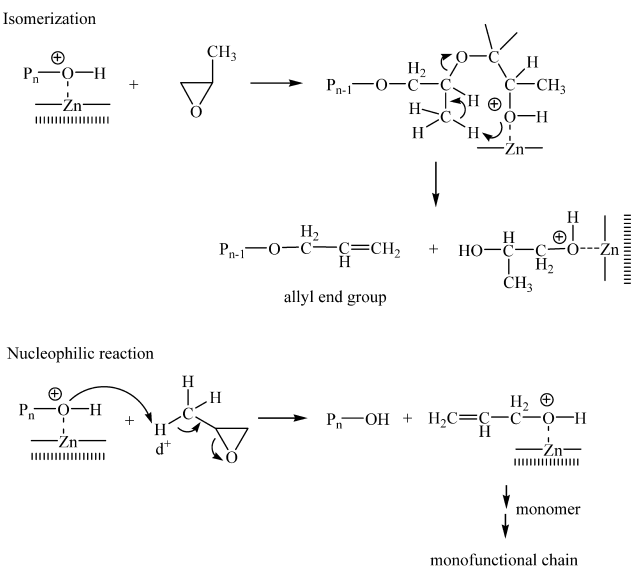

Fig. 11. Illustrative reactions resulting in the formation of monofunctional polymer chains.

Table 3
Results of ring-opening polymerization of PO catalyzed by double metal cyanide complexes

Catalyst	Polym. temp (°C)	Activity		Unsaturation (mequiv./g)	OHV		GPC	
		R_p [a]	$R_{p,max}$ [a]		OH value (mg KOH/g)	M_n (g/mol)	M_n (g/mol)	MWD
DMC-1	115	790	1720	0.017	35.0	3620	3730	1.43
DMC-2	95	198	463	0.022	27.9	4020	3710	1.58
	105	297	796	0.023	28.4	3950	3700	1.48
	115	343	869	0.026	30.5	3680	3470	1.36
	130	256	592	0.027	34.8	3220	3200	1.29
	130[b]	267	578	0.019	55.4	3040	3290	1.31
DMC-3	95	176	1088	0.003	23.8	4710	4830	1.02
	105	232	1051	0.004	24.1	4650	4840	1.03
	115	257	1316	0.005	24.2	4640	4880	1.04
	130	348	1432	0.006	24.3	4610	4810	1.02
DMC-4	95	180	1005	0.004	24.2	4640	4950	1.03
	105	201	935	0.005	24.3	4610	4940	1.04
	115	427	2672	0.004	24.9	4510	4740	1.04
	130	390	1470	0.005	26.2	4280	4290	1.10

The initiator is bi-functional polypropylene glycol.
[a] The unit is g-POP/g-cat h.
[b] The initiator for this run is tri-functional glycerol propoxylate.

0.003–0.006 meq/g. Even if the level of unsaturation increases slightly according to the polymerization temperature (see **DMC-2** and **DMC-3** in Table 3), it may be said that T_p is not a decisive factor to control the level of unsaturation. The ultra-low monol levels of **DMC-3** and **DMC-4** 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 other words the choice of complexing agent plays an important role in suppressing reactions to form the unsaturated chains. However, it still remains uncertain what type of complexing agent and what kind of interaction between the complexing agent and catalyst surface lead to such a low level of unsaturation.

Active isomerization and chain transfer reactions during polymerization by using **DMC-1** and **DMC-2** catalysts led to POP of relatively broad molecular weight distribution (MWD) as shown in Table 3. However, **DMC-3** and **DMC-4** catalysts produced POP of very narrow MWD (MWD = 1.02–1.10). Furthermore, the molecular weight of polymers obtained by **DMC-3** and **DMC-4** catalysts at low T_p is consistent with the calculation on the basis of the monomer-to-initiator ratio, i.e.

$$M_{n,calcd} = M_{n,init}\left(1 + \frac{M}{I}\right) = 700\left(1 + \frac{400}{70}\right) = 4700 \quad (1)$$

where $M_{n,init}$ is the molecular weight of initiator, M, total weight (g) of monomer added, and I, weight (g) of initiator used. We have initiated by using 70 g of initiator and stopped polymerization after adding 400 g of monomer. These results reveal that the moles of produced polymers are almost equivalent to the moles of the initiator and that each of the initiators added participates in propagation. In addition there were few new polymer chains being introduced during polymerization either from initiation reactions or by chain transfer reactions. It is evident that the broader MWD and bigger deviation from the calculated molecular weight by **DMC-1** and **DMC-2** catalysts is ascribed to more active isomerization and chain transfer reactions.

The very narrow MWD value of polymer can generally be achieved by controlled ionic polymerization in a living mode [15–17]. 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 (see Fig. 6). As a result of the exchange reaction the dormant sites (S') and transient dead-polymer chains (P_n-OH) which can be rapidly reactivated are generated. If the exchange reaction is faster than propagation reaction, the number of growing polymer chains keeps constant depending on the initial amount of initiator, resulting in polymers of narrow MWD. Slow exchange reaction should result in generating polymer chains with different chain length.

NMR spectroscopy is usually the method of choice for unraveling the microstructure details of polymers. POP may show region and stereo-irregularities since propylene oxide monomer has a chiral center and two types of ring cleavage are possible. Because POP repeat unit contains three protons

(two methylene and one methine) whose resonances overlap extensively, it has not been possible to use ^{1}H NMR spectroscopy to determine the microstructure of POP. ^{13}C NMR generally offers the potential for greater spectroscopic resolution when compared to ^{1}H NMR and might be expected to be better suited for the analysis of polyol microstructure. The representative carbon-13 NMR spectrum of **DMC-1** catalyzed POP of its unsaturation content of 0.017 meq/g is shown in Fig. 12 for methylene and methine regions. There was extensive overlap of resonances in the case of methyl carbon. The methine and methylene carbons all display chemical shift sensitivity to the stereochemistry of the polymer chain. The methylene carbon displays a clear sensitivity to the diad stereochemical relationship between neighboring chiral centers but exhibits little longer range sensitivity as shown in Fig. 12. The chiral methine carbon shows clear seperation of the triads, expect that the two heterotactic sequences are not resolved.

The assignment for the chemical shift for these head-to-tail carbons is given in Table 4 [18–22]. Note that carbon-13 NMR analysis data of **DMC-3** catalyzed POP diol of its unsaturation content of 0.004 meq/g and KOH-catalyzed POP diol of its unsaturation content of 0.035 meq/g are also summarized in Table 4 for the comparison. According to the quantitative analysis of methine stereosequence all polyols are characterized by atactic, even though the randomness of the backbone as a sum of *mr* and *rm* triad is somewhat different each other. The backbone of POP produced by KOH catalyst is more random than those produced by DMC catalysts. It is interesting to note that the POP diol containing very low unsaturation content show higher syndiotactic triad (as *rr*) sequence than that produced by KOH catalyst. The *rr* tiad value of POP of its unsaturation content 0.004 meq/g is also larger than that of DMC-catalyzed POP of its unsaturation content of 0.017 meq/g. The stereoregularity of POP might be an important factor in the final applications and seems to be a good theme for further study.

The possibility of mixing of the methine and methylene carbons was checked by the use of the DEPT techniques. The DEPT technique permits spectral editing in such a manner that one can produce spectra containing only a

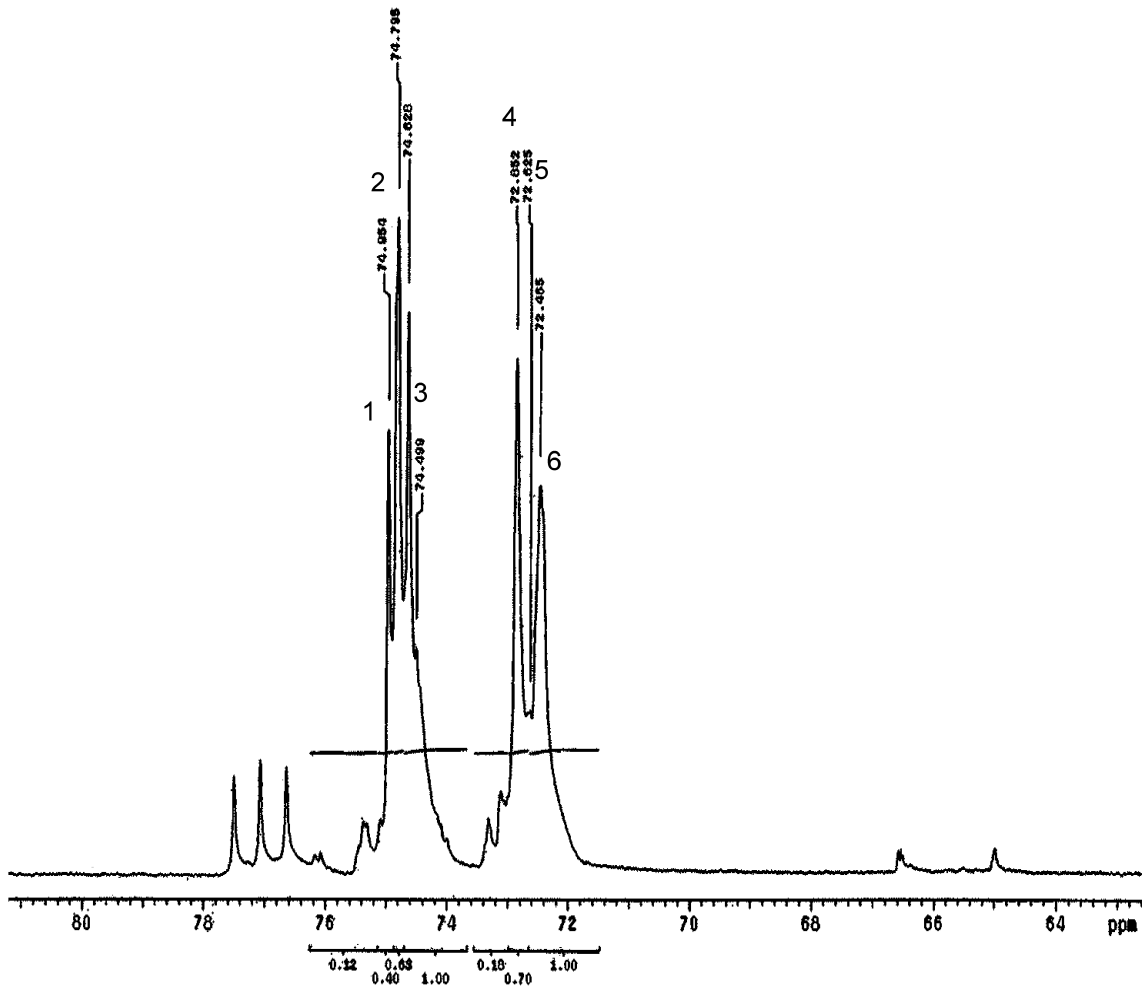

Fig. 12. The methylene and methine regions of ^{13}C NMR spectrum of **DMC-2** catalyzed POP (unsaturation content = 0.017 meq/g). The assignments of the peak indicated by numbers are given in Table 4.

Table 4
Stereochemical characterization of various POPs by ^{13}C NMR spectroscopy

Peak. no.[a]	Chemical shift (ppm)	Carbon type	Relative amount (mol%)			Stereosequence
			POP 1[b]	POP 2[b]	POP 3[b]	
1	74.95	CH	27.2	25.9	19.7	*mm*
2	74.79	CH	38.8	29.3	31.0	*mr* + *rm*
3	74.62	CH	34.0	44.8	49.3	*rr*
4	72.85	CH_2	–	–	–	*m*
5	72.62	CH_2	–	–	–	*r*
6	72.46	CH_2	–	–	–	*r*

[a] Peak numbers are in Fig. 12.
[b] KOH-catalyzed POP 1 (unsaturation content = 0.035 mequiv./g) was donated by SK Company (Korea), and POP 2 (unsaturation content = 0.017 mequiv./g) was synthesized by **DMC-1** catalyst at 115 °C and POP 3 (unsaturation content = 0.004 mequiv./g) by **DMC-4** at 115 °C.

specific carbon. In Fig. 13 we show the results of the DEPT measurement on polyol 2 for methine, methylene and methyl carbons. The most interesting feature of the DEPT analysis could be found by observing methine and methylene carbons. There are clearly methine carbon resonances in the upfield region generally thought to contain exclusively methylene resonances and also there are methylene resonances in the downfield portion of the spectra generally thought to contain only methine resonances. These unexpected resonances are ascribed to the existence of regio-irregular sequences due to head-to-head or tail-to-tail insertion of propylene oxide. Thus, it can be said that DMC catalysts lead to a polymer having predominantly region-regular head-to-tail enchainment.

3.4. The nature of the active sites of DMC catalyst

The insolubility of the DMC catalyst makes intensive investigations, especially using spectroscopic methods, on the characteristics of active sites difficult. Here we gather some indirect evidences to discuss on the mechanism of this complex system. From the results shown above, it is assumed that the DMC catalyzed polymerizations present two different characters, i.e. coordinative and cationic ones. As evidences for the cationic characters, following statements can be made, i.e. (1) addition of HCl to the reactor did not kill the active sites completely, (2) $Zn_3[Co(CN)_6]_2$ compound showed no activity before complexing agents containing oxygen atom were not coordinated cationically, (3) m.w. of polymers obtained by DMC catalysts was almost consistent with the calculation on the basis of the monomer-to-initiator ratio, and (4) DMC catalyzed POP showed very narrow MWD around unity. Evidences for the coordinative characters can also be collected, i.e. (1) coordination of different type of complexing agent led to quite different polymerization behaviors including activity and initiation time, (2) increase of loading of complexing agent increased supported amount of complexing agent, resulting in the change of polymerization behavior, (3) amount of unsaturation in POP depended on the type of complexing agents, and (4) DMC catalyzed POP were characterized by high head-to-tail regiosequence. Some evidences mentioned above may also come from the combination of both cationic and coordination nature of active sites. In summary the active sites of DMC-catalyzed polymerization of propylene oxide have both cationic and coordinative characters.

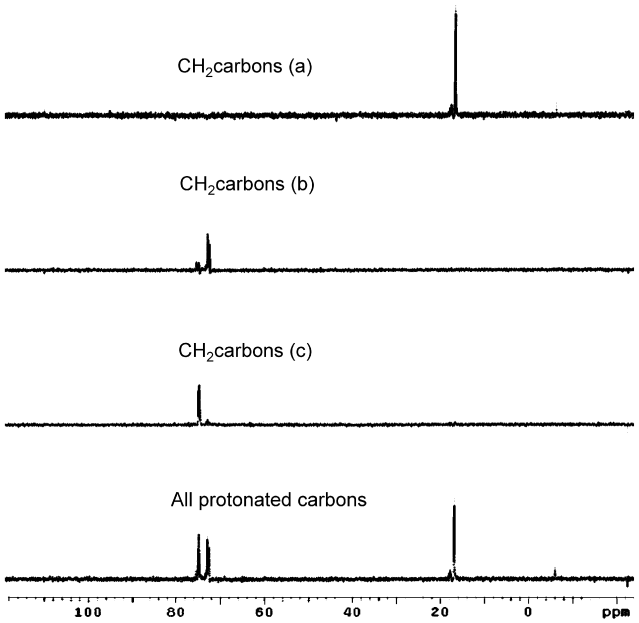

Fig. 13. ^{13}C NMR DEPT spectra of **DMC-2** catalyzed POP sample shown in Fig. 12.

3.5. Mechanical properties of polyurethane elastomers

In order to investigate the basic performance of POP's produced in this study as a raw material for polyurethane elastomers, we have prepared various polyurethane elastomers by controlling the weight contents of the hard segment in the polyurethane to 29 wt% [23]. DMC-catalyzed POPs and PTMEG have polyether backbones, which inherently impart excellent hydrolytic stability and microbial resistance to polyurethanes. PTMEG has in general higher reactivity primary hydroxyl groups and can therefore be used in both one-shot and prepolymer processing. DMC-catalyzed polyols, with their secondary hydroxyl groups,

Table 5
Mechanical properties of POP-based polyurethane elastomers

Run no.	Catalyst	POP used		Tensile strength (kg_f/cm^2)			Elongation (%)	T_g (°C)[a]
		M_n	Unsaturation (mequiv./g)	@ 100%	@ 300%	@ break		
1	KOH[b]	3600	0.035	34.1	–	51.8	213	−67
2	**DMC-1**	3620	0.017	39.6	66.4	85.6	450	n.d.
3	**DMC-2**	3680	0.026	42.3	–	65.5	298	–
4	**DMC-4**	4510	0.004	47.8	90.1	169.3	807	−68
5	PTMEG[b]	2000	–	54.6	103.7	193.8	862	−62

[a] Measured by DSC.
[b] Commercially available grade (SKC Company, Korea).

need to be prereacted with MDI to form a prepolymer. In this study we prepared the elastomers according to the same synthetic method requiring prepolymer.

The stress–strain behavior of polyurethane elastomers fabricated with POP's produced by conventional KOH catalyst and DMC catalysts was investigated and summarized in Table 5. PTMEG-based polyurethane was also synthesized for the comparison. Excess 4,4-MDI was used to prepare the prepolymers, and then cured with 1,4-butanediol. The tensile behavior of a strained thermoplastic elastomer generally depends on the size, shape, and concentration of the hard domain, intermolecular bonding within the hard domains, and the ability of the soft segment to crystallize under strain [3,14,23]. If we assume these factors are not the decisive ones since all samples were prepared by using POP with similar molecular weight at the same conditions, the unsaturation level of POP seems to deeply influence elastomer properties. Lower unsaturation content clearly has a positive effect on all elastomer mechanical properties. Dramatic property improvements are seen comparing elastomer based on KOH-catalyzed POP with that of DMC-based POP. For example, the tensile strength at break of elastomer increases from 51.8 (KOH-catalyzed) to 169.3 kg_f/cm^2 (**DMC-4**-catalyzed), In addition elongation increases from 213% (KOH-catalyzed) to 807% (**DMC-4**-catalyzed). It is interesting to note in Table 5 that the tensile strength and the elongation of elastomers are deeply dependent on the unsaturation level of POP and that the tensile properties of elastomers based on DMC-4-catalyzed POP are almost comparable to those of PTMEG-based elastomer. According to dynamic mechanical thermal analysis the glass transition temperature of elastomers based on DMC-catalyzed POP is similar to that of elastomers based on PTMEG, resulting in polyurethanes that remain flexible in cold, harsh environments. Detailed analysis of the properties of elastomeric materials is still ongoing and is to be reported elsewhere.

4. Conclusion

A series of DMC catalysts were synthesized by changing the type and the amount of co-complexing agents and utilized for the polymerizations of propylene oxide. The catalytic activity, initiation time, and the unsaturation level in POP were very sensitive to the type of co-complexing agents 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 catalysts. DMC catalyst prepared by using $K_3[Co(CN)_6]_2$ and $ZnCl_2$ in the presence of ^{t}BuOH as a complexing agent and PTMEG as a co-complexing agent showed very high activity ($R_{p,max}$ = 2672 g-POP/g-cat) in PO polymerization. The resulting POPs were characterized by ultra-low unsaturation level (0.003–0.006 meq/g) and by narrow molecular weight distribution (MWD = 1.02–1.04). According to some indirect evidences, the active sites of DMC-catalyzed polymerization of PO had both cationic and coordinative characters.

Analysis of the POP using ^{13}C NMR spectroscopy showed that the POPs have a random distribution of the configurational sequences and head-to-tail regiosequence, even if the amount of [*rr*] triad of POP produced by DMC catalyst was larger than that of POP by conventional KOH catalyst. The distortionless enhancement by polarization transfer analysis showed that there exist regioirregular sequences as well. Investigation of mechanical properties of methylene diisocyanate/1,4-butanediol cured polyurethane elastomers using various POPs showed that the unsaturation content contained in POP was a very important factor. Lower unsaturation content clearly has a positive effect on all elastomer mechanical properties. Tensile properties of elastomers based on POP with ultra-low unsaturation content were almost comparable to those of PTMEG-based elastomer.

Acknowledgements

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