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Tuning of the activity and induction period of double metal cyanide catalyzed ring-opening polymerizations of propylene oxide by using ionic liquids

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Abstract

Polymerizations of propylene oxide (PO) have been carried out by using double metal cyanide (DMC) catalyst prepared by reacting $ZnCl_2$ and $K_3[Co(CN)_6]$ in the presence of *tert*-butyl alcohol as a complexing agents. The DMC catalyst of the molecular formula, $Zn_{2.3}Cl_{1.0}[Co(CN)_6]_{1.0}{\cdot}2.0\ ^tBuOH{\cdot}1.0H_2O$, is characterized by gas sorption measurements, infrared spectroscopy and X-ray powder diffraction. The structure of DMC catalyst with negligible surface area and broadened X-ray diffraction peaks is different from that of Prussian blue analogue, $Zn_3[Co(CN)_6]_2{\cdot}12H_2O$ of microporous crystalline materials. The PO polymerization behavior is tunable by combining it with various imidazolium based ionic liquids (ILs) as external additives. Thus, (1) they make the zinc-monomer bond faster activated during the initial stage of polymerization, (2) they make the zinc-monomer bond more active, (3) they stabilize the polymerization centers and prevent their decomposition, and (4) they improve important polymer properties such as molecular weight, viscosity and unsaturation level. The maximum rate of polymerization ($R_{p,max}$) of DMC catalyst increases from 2587 to 27,222 g-polymer/g-cat h by combining with 1-ethyl-3-methylimidazolium chloride (emimCl, [emimCl]/[Zn] = 1.25) at 115 °C. The induction period as the time to reach $R_{p,max}$ becomes short from 321 min for DMC catalyst to 29 min for DMC/emimCl binary catalyst. The unsaturation value of polyol (0.017 mequiv./g) produced by DMC decreases to 0.005 mequiv./g by simply combining with IL. The molecular weight polyol produced by DMC catalyst increases from $M_n = 3700$ to more than 6000, and the viscosity of polyol decreases by combining with ILs.

Keywords: Catalysis; Epoxides; Polyol; Propylene oxide; Ring-opening polymerization; Transition metal catalysis

1. Introduction

Prussian blue analogues possess structures based upon a simple cubic $M[M'(CN)_6]$ framework, in which octahedral $[M'(CN)_6]^{n-}$ complexes are linked via octahedrally coordinated, nitrogen-bound M^{n+} ions [1,2]. Double metal cyanide (DMC) complexes base upon $Zn_3[Co(CN)_6]_2$ framework are well-known catalyst for the polymerization of epoxides and the synthesis of propylene oxide (PO) based polyether polyols (PPGs) that are one of the main raw materials in a wide range of polyurethane applications [3–16].

Recent improvements have made DMC catalysts much more attractive for commercial manufacture of polyether polyols since they give high-quality PPG products that have low level of unsaturation, narrow molecular weight distribution (MWD) and low viscosity, especially compared to conventional base catalysts [4–8,12,13]. While DMC catalysts offer attractive advantages over most widely used base catalysts such as KOH and CsOH, they must be activated for a long time before the polymerization starts [13,17–20]. Long induction period, say several hours, increases cycle time and therefore undercuts the economic advantage of faster polymerizations. In addition, heating the catalyst for a prolonged period at high polymerization temperature above 100 °C can reduce its activity or deactivate it completely [5–8,12,13].

Numerous trials have been made to make up this shortcoming of DMC catalysts by modifying formulations of the catalyst, requiring tedious procedures and thus remaining unsolved. In this study we show a simple method

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tuning the polyol properties as well as the activity and the induction period of DMC-catalyzed PO polymerizations by combining DMC catalyst with imidazolium-based ionic liquids (ILs).

2. Experimental

2.1. Material

All materials such as potassium hexacyanocobaltate(III) ($K_3[Co(CN)_6]$), zinc chloride ($ZnCl_2$), and tertiary butyl alcohol (^{t}BuOH) were purchased from Aldrich and used without further purification. Difunctional polypropylene glycol (molecular weight = 700; PPG) was also purchased from Aldrich and used as received after drying (at 110 °C for 6 h under vacuum). Polymerization grade of propylene oxide (PO) were donated by SKC (Korea). ILs such as 1-ethyl-3-methylimidazolium chloride (emimCl), 1-butyl-3-methylimidazolium chloride (bmimCl), 1-hexyl-3-methylimidazolium chloride (hmimCl), 1-ethyl-3-methylimidazolium tetrafluoroborate ($emimBF_4$), 1-butyl-3-methylimidazolium tetrafluoroborate ($bmimBF_4$), 1-hexyl-3-methylimidazolium tetrafluoroborate ($hmimBF_4$), and 1-ethyl-3-methylimidazolium hexafluorophosphate ($emimPF_6$) were purchased from Fluka and used without further purification.

2.2. Preparation of catalyst

Typical DMC catalyst using ^{t}BuOH as a complexing agent has been prepared according to the literature procedures [17]. A solution of $ZnCl_2$ (13.63 g, 0.1 mol) in water (100 mL) and ^{t}BuOH (20 mL) mixture was added to a solution of $K_3[Co(CN)_6]$ (3.32 g, 0.01 mol) in water (40 mL) over 60 min at 50 °C with vigorous agitation using a mechanical stirrer. To the resulting cake separated by centrifugation a solution of comprised of water (1 mL) and ^{t}BuOH (20 mL) was added, and then stirred for 3 min. The mixture was centrifuged and the resulting catalyst cake was dried at 60 °C under vacuum to a constant weight.

2.3. Polymerization

Polymerization of PO was carried out by using 1 L autoclave (Parr) at various temperatures. The reactor was charged with 70 g of PPG-700 starter, catalyst (0.1 g, 0.4 mmol of Zn) and a prescribed amount of IL, and then purged several times with nitrogen. The mixture was heated to 100 °PC and evacuated for over 6 h with vigorous agitation in order to remove traces of water contained in the reaction mixture. Then 15 g of PO monomer was introduced into the reactor at a polymerization temperature (typically 115 °C). Additional monomer was begun to add continuously 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 to allow facile agitation. The pressure of the reactor kept constant at 0.7 bar throughout a polymerization run.

2.4. Characterizations

Infrared (IR) spectra were recorded on a Shimadzu IRPrestige-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 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. Element analysis was carried out on DMC catalyst. The expected relative error for Zn, Co, Cl, C, H, and N is ±3% and oxygen was obtained by subtraction. Element analysis of Zn, Co, and Cl was obtained by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), on a Agilent 7500 ICP-MS. Element analysis for C, H and N was performed by combustion analysis, on a Perkin Elmer CHN Analyzer (Model 2400). For the gas sorption measurements, sample tubes of a known weight were loaded with 200–400 mg of sample and sealed using a transeal. Samples were degassed at 100 °C for 24 h on a Micromeritics ASAP 2020 analyzer until the outgas rate was no more than 1 mTorr/s. The degassed sample and sample tube were weighed precisely and then transferred back to the analyzer (with the transeal preventing exposure of the sample to air after degassing). The outgas rate was again confirmed to be no more than 1 mTorr/s. Measurements were performed at 77 K in a liquid nitrogen bath.

The total degree of unsaturation of polyols was measured by titration method according to ASTM D2847. Molecular weight (MW) and its distribution (MWD) was measured using a Waters 150 instrument operated at 25 °PC, with a set at 10^4, 10^3, and 500 Å columns in tetrahydrofuran solvent. Polystyrene standards with low polydispersity were used to generate a calibration curve. The viscosity of polymer was measured at 30 °C. A Brookfield viscometer model DV III (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 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 performing the experiments, the samples were deaerated. The viscosity measurements were each repeated three times and the averages of the readings were used for the analysis of the data.

3. Results and discussion

3.1. Characterization of catalyst

One of the highly crystalline Prussian blue analogues, $Zn_3[Co(CN)_6]_2{\cdot}xH_2O$ compound, can be prepared by reacting an aqueous solution of $K_3[Co(CN)_6]$ with an aqueous solution of $Zn(NO_3)_2$ according to literature procedure [21] and its structure can be described as shown in Fig. 1 [1,2,22–24]. In this structure, charge balance with the Zn^{2+} ions leads to

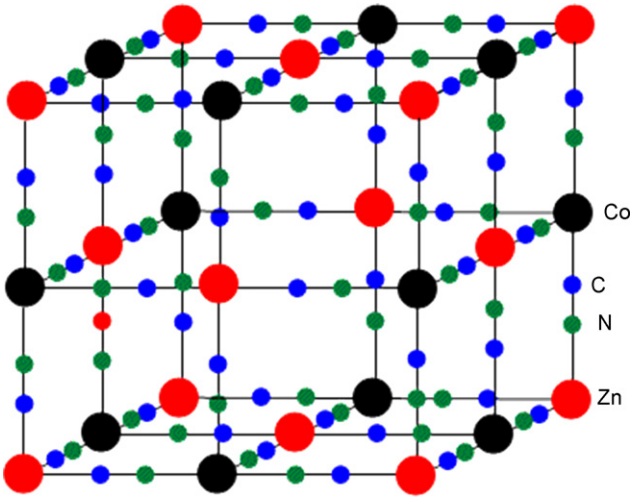


Fig. 1. Stereoscopic drawing of the ordered structural representation of $Zn_3[Co(CN)_6]_2{\cdot}12H_2O$. Water molecules are not shown for simplicity.

vacancies at one-third of the $[Co(CN)_6]^{3-}$ sites in the framework [22–24]. The water molecules fill the resulting cavities as Zn^{2+}-bound and solvate and they can be removed upon heating to leave the cobalt-cyanide framework intact [2]. If complexing agents such as alcohol are used together with water during the preparation of the complexes, they are also able to interact with the open coordination sites on the Zn^{2+} ions arising upon substitution of the bound water molecules.

The complexation of bulky alcohol such as ^{t}BuOH may result in framework collapse. This could be identified by comparing X-ray powder diffraction patterns of the samples prepared in different procedures (Fig. 2). The X-ray powder diffraction pattern of the hydrated forms of $Zn_3[Co(CN)_6]_2$ compound was fully consistent with the usual Prussian blue structure type, displaying sharp, intense peaks. However, the DMC compound prepared by using ^{t}BuOH as a complexing agent showed significantly broadened peaks, suggesting a much smaller crystallite size and/or a lowering of the crystallinity. Propylene oxide polymerization runs with the fully crystalline $Zn_3[Co(CN)_6]_2{\cdot}xH_2O$ compound showed no activity, demonstrating the complexing agent and the crystal structure of the compound play important roles in the polymerization.

Elemental analyses by laser ablation inductively coupled plasma mass spectrometry confirmed the composition of the hydrated forms of $Zn_3[Co(CN)_6]_2$ compound and the DMC compound containing ^{t}BuOH as $Zn_3[Co(CN)_6]_2{\cdot}12H_2O$ and $Zn_{2.3}Cl_{1.0}[Co(CN)_6]_{1.0}{\cdot}2.0$ ^{t}BuOH·1.0H_2O (DMC catalyst), respectively. In order to compare the structure of these compounds, the porosity of the dehydrated samples by heating at 100 °C for 24 h under dynamic vacuum was probed via nitrogen sorption measurements performed at 77 K. $Zn_3[Co(CN)_6]_2{\cdot}12H_2O$ compounds showed typical Type I sorption isotherms characteristic of microporous materials (see Fig. 3). The surface area, calculated by applying the BET model to the data, was 690 m^2/g, which is much higher than the 49 m^2/g estimated for dehydrated Prussian blue [25], suggesting that the cobalt-cyanide frameworks remain largely intact upon dehydration. However, the DMC catalyst complexed with ^{t}BuOH exhibiting broadened X-ray diffraction peaks (Fig. 2), the variations in surface area are only slight and are likely due to differences in the unit cell volumes and perhaps the degree of framework collapse.

DMC complexes could be identified since they exhibited sharp ν(CN) at 2200–2000 cm^{-1} according to IR spectroscopy. Thus, the ν(CN) band at 2131 cm^{-1} in $K_3[Co(CN)_6]$ was shifted to 2198 cm^{-1} for the DMC catalyst. The ν(CN) shift to higher frequencies demonstrates that the CN^- ion acts as not

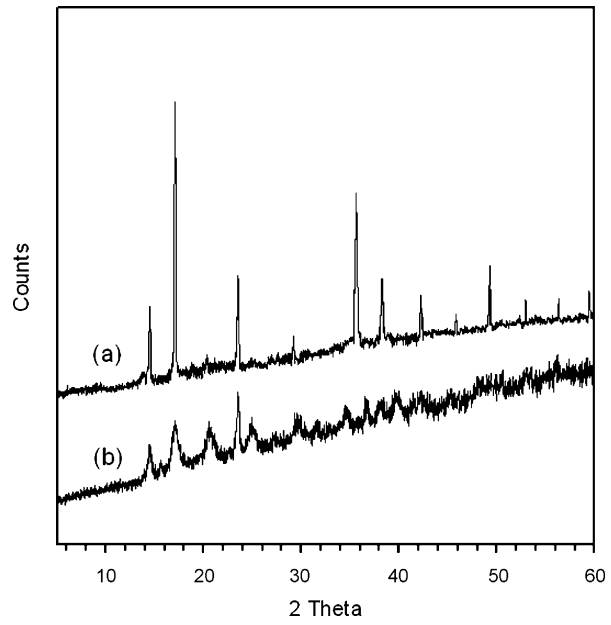


Fig. 2. X-ray powder diffraction data for (a) $Zn_3[Co(CN)_6]_2{\cdot}12\ H_2O$ and (b) DMC catalyst of the molecular formula, $Zn_{2.3}Cl_{1.0}[Co(CN)_6]_{1.0}{\cdot}2.0$ ^{t}BuOH·1.0H_2O.

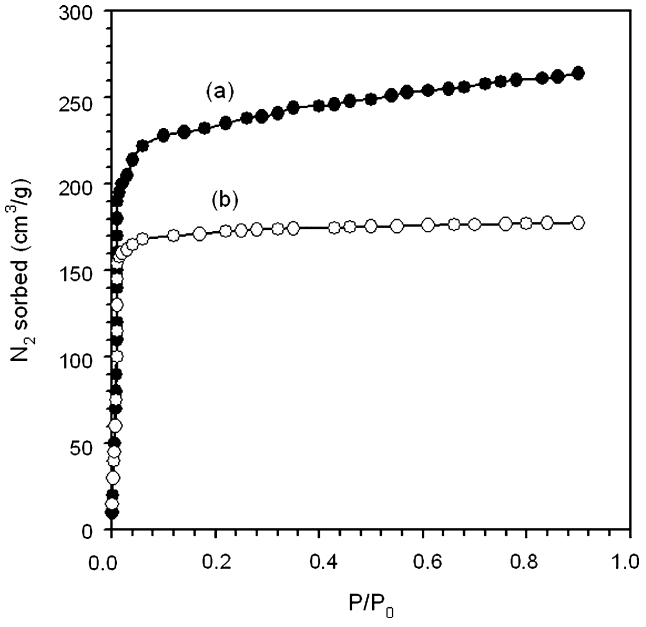


Fig. 3. Nitrogen sorption isotherm for (a) $Zn_3[Co(CN)_6]_2{\cdot}12H_2O$ and (b) DMC catalyst of the molecular formula, $Zn_{2.3}Cl_{1.0}[Co(CN)_6]_{1.0}{\cdot}2.0$ ^{t}BuOH·1.0H_2O at 77 K.

only a σ-donor by donating electrons to the cobalt but also an electron donor by chelating to zinc metal to form a Zn–Co double metal complex bridged with CN groups.

3.2. Polymerizations of PO and characterization of the resulting polymers

In order to investigate the performance of the DMC catalyst for the ring-opening polymerization of PO, semi-batch polymerizations were carried out at various temperatures. As illustrated in Fig. 4, the DMC catalysts show high activity at all temperatures of this study once it is activated. The maximum rate of polymerization ($R_{p,max}$) is 2166, 2074, 2587, and 2851 g-polymer/g-cat h at 95, 105, 115, 130 °C, respectively. In all polymerizations catalytic activity was somewhat declined, the more at higher temperature, at the end period of polymerization, most likely due to initial heating of the catalyst for a prolonged period at high temperature for activation. Taking a look at the polymerization rate profiles carefully, it can be seen that it needs a long induction period (IP) before polymerization starts. The IP value is 85, 170, 180, and 355 min at 130, 115, 105, and 95 °C, respectively. The time to reach $R_{p,max}$ is 519, 342, 321, and 204 min at 95, 105, 115, 130 °C, respectively. Evidently the prolonged induction period is not attractive as an effective catalyst and a decline of activity at the end period of polymerization run needs to be improved. The long induction period undercuts the economic advantage of the DMC-catalyzed polymerizations. Numerous ways are possible to solve this shortcoming of DMC catalysts by controlling preparation parameters as well as by screening of their compositions by modifying formulation, requiring tedious procedures and remaining unsolved [4–13,15–18].

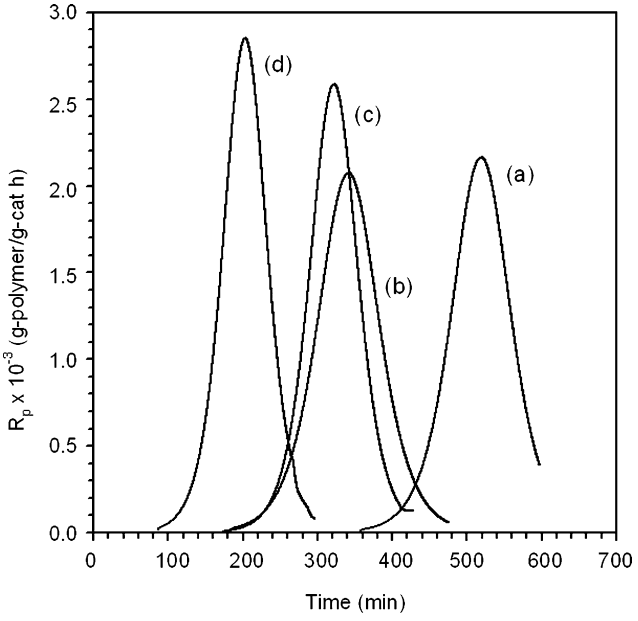
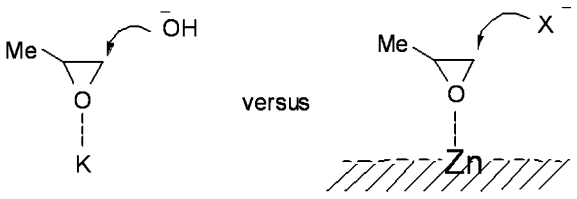


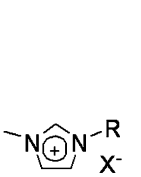
Fig. 4. Polymerization rate curves obtained by DMC catalyst at various polymerization temperatures of (a) 95 °C, (b) 105 °C, (c) 115 °C, and (d) 130 °C. Polymerization conditions: temperature = 115 °C, PPG starter = 70 g, catalyst = 0.1 g.

In order to overcome these problems we revisit the mechanism of PO polymerization initiated by base catalyst such as KOH, where no induction period is observed (Scheme 1). Assuming potassium atom is corresponding to zinc atom, it is easy to generate an idea to speed up the activation. As the OH anions make nucleophilic attack to make the PO monomer ring opened, the addition of the second anionic species together with the DMC catalyst may help fast activation. This idea was tested by using ionic liquids (ILs). We chose ILs due to some of their peculiar properties, such as negligible vapor pressure, ability to dissolve organic and polymeric materials and high thermal stability. IL is now the commonly accepted term for low-melting salts (melting-point typically <100 °C) obtained by the combination of large organic cations with a variety of anions. Although estimates vary, there is no doubt that the number of combinations of anions and cations that can give rise to potential ILs is vast. Here we chose imidazolium cations, differently substituted, associated with anions like [Cl], [BF_4], and [PF_6] (Scheme 2).

Fig. 5 shows rate profiles of PO polymerizations obtained by DMC/IL binary catalysts. It is evident that binary catalyst systems combining DMC catalyst with IL are a simple and efficient way of tuning the induction period. The IP value decreases from 170 min for DMC catalyst to 40, 18, 16, 14, 8, 4, and 1 min for DMC/bmimCl, DMC/hmimCl, DMC/emimBF_4, DMC/emimCl, DMC/ bmimBF_4, DMC/emimPF_6, and DMC/ hmimBF_4 catalysts, respectively. Thus the time to reach maximum rate becomes short from 321 min for DMC catalyst to 15 min for DMC/hmimBF_4 binary catalyst (Table 1). In addition, as summarized in Table 1, the catalytic activity was increased remarkably by simply combining 0.5 mmol of IL ([IL]/[Zn] = 1.25) together with DMC catalyst. For example, the $R_{p,max}$ value (27,222 g-polymer/g-cat h) of DMC/emimCl catalyst was larger than that (2587 g-polymer/g-cat h) of DMC catalyst by more than 10 times. The severe activity decline of



Scheme 1. Comparison of activation of KOH catalyzed PO polymerization with that of DMC catalyzed polymerization combined with ionic liquids.



R	X	
C_2H_5	Cl	emimCl
C_4H_9	Cl	bmimCl
C_6H_{13}	Cl	hmimCl
C_2H_5	BF_4	emimBF_4
C_4H_9	BF_4	bmimBF_4
C_6H_{13}	BF_4	hmimBF_4
C_2H_5	PF_6	emimPF_6

Scheme 2. Ionic liquids used in this study.

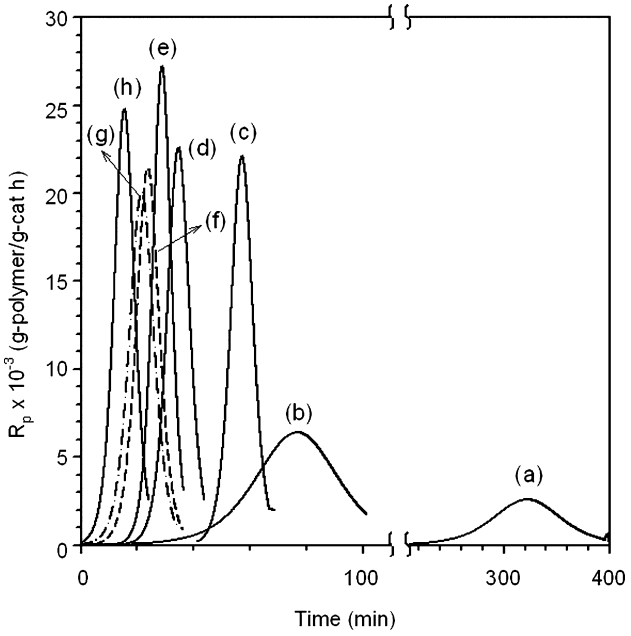


Fig. 5. Polymerization rate profile obtained by DMC catalyst at 115 °C (a) and those by DMC catalyst combined with various ionic liquids (ILs) of (b) 1-hexyl-3-methylimidazolium chloride, (c) 1-butyl-3-methylimidazolium chloride, (d) 1-ethyl-3-methylimidazolium tetrafluoroborate, (e) 1-ethyl-3-methylimidazolium chloride, (f) 1-butyl-3-methylimidazolium tetrafluoroborate, (g) 1-ethyl-3-methylimidazolium hexafluorophosphate, and (h) 1-hexyl-3-methylimidazolium tetrafluoroborate. Polymerization conditions: temperature = 115 °C, PPG starter = 70 g, catalyst = 0.1 g, and IL = 0.5 mmol ([IL]/[Zn] = 1.25).

the DMC catalyst at the end of the polymerization was also remarkably reduced by the addition of IL, most probably due to shortened exposure at high temperature (115 °C) during activation period. These results demonstrate that our original idea shown in Scheme 1, in which anions may speed up the activation of DMC catalyst, was reasonable.

Controlled polymerization tests with only ILs in the absence of DMC catalyst gave no activities at various IL concentrations, demonstrating anions and/or cations in ILs cannot initiate PO polymerization. According to Fig. 5 and Table 1, the activity of DMC/IL binary catalyst systems decreases emimCl > bmimCl > hmimCl when the anion is Cl, $hmimBF_4 > emimBF_4 \geq bmimBF_4$ when the anion is BF_4, and $emimCl > emimBF_4 \geq emimPF_6$ when the cation is emim. Even if it is hard to explain the effect of IL on PO polymerization behavior mechanistically with the data collected in this study, it is expected that the reaction rate is affected by the properties of the attacking anion, by its polarizability and its nucleophilicity (or basicity). These properties of ILs are strongly dependent on the mutual fit of the cation and anion, in term of size, geometry and charge distribution although, within a similar class of salts, small changes in the shape of uncharged, covalent regions of the ions may have an important influence. Therefore, more detailed studies are needed to explain the effect of the IL type on PO polymerization.

Investigation on the effect of IL amount on polymerization was performed by DMC/$hmimBF_4$ binary catalyst by changing the amounts of $hmimBF_4$ from 0.01 to 1.0 mmol at the similar conditions employed in Fig. 5. Note that the amount DMC catalyst added per batch is 0.1 g (0.4 mmol as Zn). Fig. 6 shows average polymerization rate ($R_{p,avg}$) and $R_{p,max}$ versus [$bmimBF_4$] plots. Even if the highest activity was recorded at around 0.4 mmol of $bmimBF_4$ ([$bmimBF_4$]/[Zn] ≈ 1), a very small amount (e.g. 0.05 mmol) of $bmimBF_4$ was enough to increase the activity remarkably. Addition of excess amount of $bmimBF_4$ ([$bmimBF_4$]/[Zn] = 2.5) does not increase the activity any more. Considering a possible mechanism of active sites formation (Scheme 1), we may suppose that the polymerization centers (C^*) are formed in two ways: (i) the formation of active sites S^* from a dormant zinc surface site combined by IL, followed by the formation of C^* from the active site S^* and monomer, and (ii) the formation of C^* from a dormant zinc surface site directly combined with PO monomers without the help of IL. In this sense, a Langmuir-type dependence of the formation of C^* on [IL] can be postulated:

$$[C^*] = [C^*]_{Zn} + [C^*]_{IL} = [C^*]_{Zn} + [S^*]\left(\frac{K[IL]}{1 + K[IL]}\right) \quad (1)$$

where $[C^*]_{Zn}$ is a total number of polymerization centers formed regardless of IL, $[C^*]_{IL}$ is a total number of polymer-

Table 1
Results of ring-opening polymerization of propylene oxide catalyzed by double metal cyanide (DMC) catalysts of the molecular formula, $Zn_{2.3}Cl_{1.0}[Co(CN)_6]_{1.0}\cdot 2.0\ ^tBuOH\cdot 1.0\ H_2O$, and DMC/ionic liquid (IL) binary catalysts[a]

Ionic liquid	$R_{p,max}/R_{p,400\ g}$[b] (g-pol/g-cat h)	$t_{max}/t_{400\ g}$[c] (min)	M_n[d]	MWD[d]	Unsaturation[e] (mequiv./g)	Viscosity[f] (cP)
Not added	2587/86	321/438	3700	1.43	0.017	1790
emimCl	27,222/3122	29/36	6100	1.45	0.010	1310
bmimCl	22,115/1950	57/68	6300	1.58	0.010	1270
hmimCl	6409/1751	78/101	6600	1.43	0.012	1450
$emimBF_4$	22,618/2600	35/43	6900	1.36	0.011	1300
$bmimBF_4$	21,450/888	24/36	6700	1.35	0.008	1180
$hmimBF_4$	24,811/2589	15/24	6700	1.49	0.005	1250
$emimPF_6$	20,090/1077	22/34	6800	1.40	0.015	1150

[a] Polymerization conditions: temperature = 115 °C, PPG starter = 70 g, catalyst = 0.1 g, and IL = 0.5 mmol ([IL]/[Zn] = 1.25).
[b] Maximum rate of polymerization ($R_{p,max}$) and rate of polymerization at the moment total amount of PO added reach 400 g ($R_{p,400\ g}$).
[c] Time to reach $R_{p,max}$ (t_{max}) and time to reach $R_{p,400\ g}$ ($t_{400\ g}$).
[d] Measured by gel permeation chromatography using a Waters 150 instrument operated at 25 °C in tetrahydrofuran solvent.
[e] Total degree of unsaturation of polyols measured by titration method according to ASTM D2847.
[f] Measured by a Brookfield viscometer model DV III (Brookfield Instruments), with a spindle no. 21.

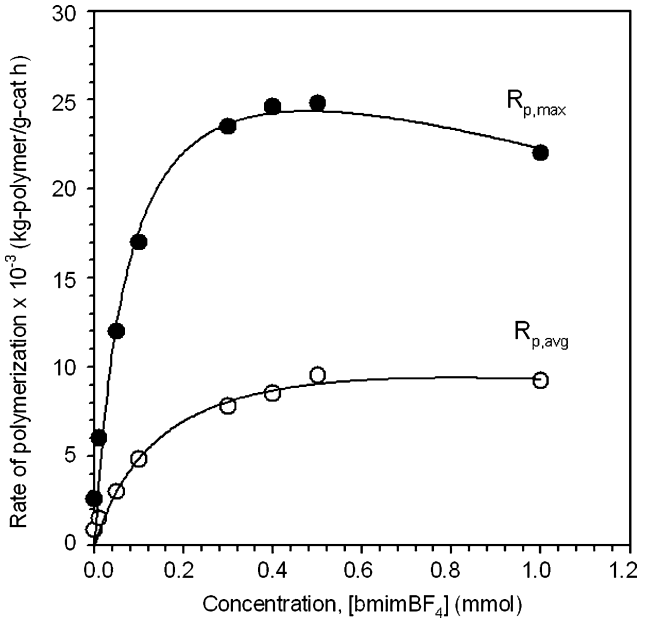


Fig. 6. Dependence of the rate of polymerization (as maximum polymerization rate ($R_{p,max}$) and average polymerization rate over a polymerization period ($R_{p,avg}$)) on concentration of ionic liquid (as 1-butyl-3-methylimidazolium tetrafluoroborate (bmimBF$_4$)). Solid lines imply a Langmuir-type dependence of R_p on [bmimBF$_4$]. Polymerization conditions: temperature = 115 °C, PPG starter = 70 g, and catalyst = 0.1 g (0.4 mmol Zn).

ization centers formed by combining with IL, and K is an equilibrium constant. By assuming rate of propagation $R_p = k_p[C^*][M]$, where k_p is a rate constant of propagation and $[M]$ is a monomer concentration, we could fit (solid line in Fig. 6) both $R_{p,max}$ versus [hmimBF$_4$] and $R_{p,avg}$ versus [hmimBF$_4$] data successfully.

Based on above results and reported results [26,27], the presence of IL as part of the complex, even if its presence is not an essential condition for DMC catalyzed polymerizations, is attractive for a number of reasons: (1) it makes the zinc-monomer bond faster activated during the initial stage of polymerization, (2) it makes the zinc-monomer bond more active for polymerization, and/or (3) it stabilizes the polymerization centers and prevent its decomposition. More surprisingly, it improved important polymer properties such as molecular weight, viscosity and unsaturation level as shown in Table 1. In fact, these properties are the most important ones characterizing DMC catalysts differentiating from conventional base catalysts such as KOH. It is well known that base catalyzes not only the addition of PO to the growing polymer chain, but also a side reaction in which propylene oxide isomerizes to allyl alcohol [15,16]. Allyl alcohol acts as a monofunctional starter resulting in the production of the propoxylated allyl alcohol, often referred to as monol. The monols are also generated by other types of side reactions [15,16]. Since each monol molecule also contains a terminal double bond, the amount of monol present in the polyol can be quantified by measuring the unsaturation level. Typically KOH catalyzed polyols are characterized by high level of unsaturation (0.03–0.10 mequiv./g), so that they have limited applications as high performance polyurethane products [28]. As shown in Table 1, the unsaturation value of polyol produced by DMC, 0.017 mequiv./g, is lower than that of polyol produced by base catalyst, and the value decreases remarkably by combining with IL. For example, DMC/hmimBF$_4$ catalyst produced polyol with ultra low unsaturation level, 0.005 mequiv./g. The MW of polyols produced by DMC catalyst increases from $M_n = 3700$ to more than 6000 by combining with ILs. All polyols are characterized by narrow MWD, from 1.35 to 1.58. The viscosity of polymer, important property during handling and reacting with isocyanate compounds, also decrease by combining with ILs.

Here, we have demonstrated that the activity and the induction period of DMC catalyst are tunable by combining with ILs by assuming DMC catalyst serves as an electrophile for complexing PO monomer and the anion of IL serves as a nucleophile. Evidently the notable activity and the rapid activation originate from the cooperative actions of both the zinc active sites for PO coordination and the anions of IL for the nucleophilic attack of PO (Scheme 1). However, detailed mechanistic study, is not so easy because of insoluble nature of DMC catalyst, is needed to explain the effect of IL on DMC catalyzed polymerization behavior and on the resulting polymer properties.

4. Conclusions

The structure of DMC catalyst of the molecular formula, $Zn_{2.3}Cl_{1.0}[Co(CN)_6]_{1.0}\cdot 2.0\ ^tBuOH\cdot 1.0H_2O$, prepared by reacting $ZnCl_2$ and $K_3[Co(CN)_6]$ in the presence of ^{t}BuOH as a complexing agents was different from that of typical Prussian blue analogue, $Zn_3[Co(CN)_6]_2\cdot 12H_2O$, prepared in the absence of ^{t}BuOH. Even though the latter compound showed no activity in PO polymerizations, the former compound showed high activity with a long induction period. The activity and the induction period of PO polymerizations catalyzed by DMC were tunable by combining with ILs as external additives. As a result the $R_{p,max}$ of DMC catalyst was increased from 2587 to 27,222 g-polymer/g-cat h by combining with emimCl ([emimCl]/[Zn] = 1.25) at 115 °C and the induction period as the time to reach $R_{p,max}$ becomes remarkably short from 321 min for DMC catalyst to 15 min for DMC/hmimBF$_4$ ([hmimCl]/[Zn] = 1.25) binary catalyst. By combining DMC catalyst with ILs, the important properties of polyol such as the degree of unsaturation, MW, and viscosity were also tunable. The unsaturation value of polyol (0.017 mequiv./g) produced by DMC decreased to 0.005 mequiv./g by simply combining with IL. The MW of polyol produced by DMC catalyst increased from $M_n = 3700$ to more than 6000 by combining with ILs, and the viscosity of polyol decreased by combining with ILs.

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