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Tuning of activity, induction period and polymer properties of double metal cyanide catalyzed ring-opening polymerizations of propylene oxide by using quaternary ammonium salts

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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 (^{t}BuOH) as a complexing agent. The catalytic activity and the induction period for PO polymerizations catalyzed by DMC are tunable by using various quaternary ammonium salts (QAS) as external additives. The DMC/QAS binary catalyst improves polymer properties as well such as molecular weight, molecular weight distribution, viscosity, and unsaturation level.

Keywords: Double metal cyanide catalyst; Propylene oxide; Quaternary ammonium salts

1. Introduction

The polyols produced by the ring-opening polymerization (ROP) of propylene oxide (PO) are one of the core raw materials for various polyurethane (PU) applications. Most of the current PO based polyols (PPG) are being produced by simple base catalysts like KOH. The PPG produced through a base-catalyzed process has been studied as a soft segment material for foams, with less spectacular properties for elastomers [1]. However, in the early 1990s, advances in zinc hexacyanocobaltate-based double metal cyanide (DMC) catalyst used to produce PPG diols, resulted in a substantial improvement in the levels of polyfunctionality and molecular weight (MW), a narrowing of the molecular weight distribution (MWD), and a lowering of viscosity [2–5]. The resulting PPG polyols of narrow MWD and ultra-low monol content (<0.02 meq/g) allow them to yield PU with superior mechanical properties.

While DMC catalysts offer significant advantages over conventional base catalysts, they must be activated for a long time (e.g. several hours) at high temperatures above 100 °C together with starter (or initiator) molecules, usually low MW PPG polyols, which control the functionality of the resulting polyols, before PO monomer can be added continuously to the reactor for propagation. This long induction period increases cycle time, which undercuts the economic advantage of the DMC-catalyzed polymerizations. In addition, initial heating of the catalyst during the long induction period at high temperature can reduce its activity or deactivate it completely [6]. Numerous trials have been made to make up this shortcoming of DMC catalysts by modifying formulations of the catalyst, remaining unsolved.

In this report, we show a simple but very effective way to tune polymer properties as well as polymerization activity and induction period by combining DMC catalyst with quaternary ammonium salts (QASs) as simple external additives.

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2. Experimental

2.1. Materials

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 PPG (MW = 700) was also purchased from Aldrich and used as received after drying (at 110 °C for 6 h under vacuum). Polymerization grade of PO was donated by SKC (Korea). Quaternary ammonium salts such as tetrapropyl ammonium chloride (TPACl), tetrabutyl ammonium chloride (TBACl), tetrahexyl ammonium chloride (THACl), tetraoctyl ammonium chloride (TOACl), tetradodecyl ammonium chloride (TDACl), tetrabutyl ammonium iodide (TBAI), and tetrabutyl ammonium bromide (TBABr), were purchased from Fluka and used without further purification.

2.2. Preparation of catalysts and polymerization of PO

For the preparation of DMC catalyst, 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. A solution of complexing agents comprised of water (1 mL) and ^{t}BuOH (20 mL) was added to the resulting mixture, 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. Elemental analysis: Zn, 20.3; Co, 7.9; Cl, 4.9; C, 34.0; H, 5.8; O, 14.6; N, 12.5.

Polymerization of PO was carried out by using 1 L autoclave (Parr) at 115 °C. The reactor was charged with 70 g of PPG-700 starter, predried at 110 °C under vacuum over 6 h, catalyst (0.1 g) and a prescribed amount of QAS, and then purged several times with nitrogen. Then 15 g of PO monomer was introduced into the reactor at a polymerization temperature. Additional monomer was added 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 for a facile agitation. The pressure of the reactor was kept constant at 0.7 bar throughout a polymerization run.

2.3. Characterizations

X-ray photoelectron spectroscopy (XPS) analysis of the catalysts was performed on an ESCALAB 250 induced electron emission spectrometer with Al Kα (1486.6 eV, 12 mA, 20 kV) X-ray sources. Infrared (IR) spectra were recorded on a Shimadzu 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. Elemental analysis was carried out on DMC catalysts. Samples were analyzed in triplicate lots. The expected relative error for Zn, Co, Cl, C, H, and N is ±3% and oxygen was obtained by subtraction. Elemental analysis of Zn, Co, and Cl was obtained by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), on an Agilent 7500 ICP-MS. Elemental analysis for C, H and N was performed by combustion analysis, on a Perkin Elmer CHN Analyzer (Model 2400).

^1H and ^{13}C NMR spectra of polyols were performed on a Varian Gemini 2000 & HP5P (300 MHz) with $CDCl_3$ as a solvent. All chemical shifts are reported in parts per million (δ) relative to tetramethylsilane. 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 [6]. The total degree of unsaturation of polyols was measured by titration method according to ASTM D2847 [6]. 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 in tetrahydrofuran (THF) 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 repeated three times each and the averages of the readings were taken for the analysis of the data.

3. Results and discussion

3.1. Characterization of DMC catalyst

In general the DMC catalyst is comprised of a metal ion (M^1) which forms a strong bond to oxygen and a metal (M^2) cyanide salt, e.g., $[M^1]_n[M^2(CN)_6]_m$, Prussian blue analogues. Prussian blue analogues possess structures based upon a simple cubic $M^1[M^2(CN)_6]$ framework, in which octahedral $[M^2(CN)_6]^{n-}$ complexes are linked via octahedrally coordinated, nitrogen-bound $[M^2]^{n+}$ ions [7,8]. By combining $[M^1]^{2+}$ ions with $[M^2(CN)_6]^{3-}$ complexes, one can generate even more porous Prussian blue analogues of formula $M^1_3[M^2(CN)_6]_2 \cdot xH_2O$. One of the most preferable catalyst precursors for the ROP of PO is zinc hexacyanocobaltate(III) wherein interactions with bridging cyanide ligands and/or coordinatively unsaturated metal centers lead to higher adsorption enthalpies, featuring vacancies at one-third of the hexacyanocobaltate sites [9]. As with aromatic bridges, the polarizable π-electron clouds of the cyanide bridges in these materials can be expected to have some affinity for incoming PO monomer. The monomer may also be able to interact with the open coordination sites on the Zn^{2+} ions arising upon removal of the bound water molecules. However, highly crystalline $Zn_3[Co(CN)_6]_2 \cdot 12H_2O$ compound prepared by reacting an aqueous solution of $K_3[Co(CN)_6]$ with aqueous solution of $Zn(NO_3)_2$ according to literature procedure [9–11] was inactive for PO polymerization.

To achieve high activity with these catalysts, an organic coordinating reagent is also required, such as an alcohol. In fact, the water molecules filling the resulting cavities can be replaced upon reacting with complexing agents to leave the cobalt-cyanide framework intact. Accordingly the DMC catalysts prepared by reacting an aqueous solution of potassium hexacyanocobaltate(III) ($K_3[Co(CN)_6]$), excess amount of zinc chloride ($ZnCl_2$), and tertiary butyl alcohol (^{t}BuOH) as an organic complexing agent are expected to have the general formula: $Zn_3[Co(CN)_6]_2 \cdot xZnCl_2 \cdot yH_2O \cdot z$ complexing agents. Results of elemental analysis shows that DMC catalyst has an approximate molecular formula of $Zn_{2.3}Cl_{1.0}[Co(CN)_6]_{1.0} \cdot 2.0{}^tBuOH \cdot 1.0H_2O$, assuming a mole fraction of CN/Co = 6.0 and no additional CN or HCN was present. The catalysts were found to be insoluble in water and all common organic solvents. The solid-state (KBr) infrared spectra of DMC catalyst revealed the ν(CN) bands at 2131 cm^{-1} of $K_3[Co(CN)_6]$ and at 2187 cm^{-1} of Prussian blue analogue $Zn_3[Co(CN)_6]_2 \cdot 12H_2O$ compound were shifted to 2198 cm^{-1} (Fig. 1). The ν(CN) shift to higher frequencies demonstrates that the CN^- ion acts not only as a σ-donor by donating electrons to the cobalt, but also as an electron donor by chelating to zinc metal to form a Zn–Co double metal complex bridged with CN groups.

The crystal structure of Prussian blue analogues, $Zn_3[Co(CN)_6]_2 \cdot 12H_2O$ was resolved by many authors [10,11]. The basic structure of this network solid can be described as octahedral $Co-C_6$ units surrounded by tetrahedral $Zn-N_4$ units, with water molecules filling the interstitial cavities. According to XRD analysis of $Zn_3[Co(CN)_6]_2 \cdot 12H_2O$ compound and DMC catalyst (Fig. 2), $Zn_3[Co(CN)_6]_2$ compound was fully consistent with the usual Prussian blue structure type, displaying sharp, intense peaks, while DMC catalyst have broad peaks between 13.5° and 22.5° 2θ, which are associated with relatively sharp peaks at about 23.6° 2θ, demonstrating that the DMC catalyst is poorly crystalline due to the framework collapse. The crystallinity of the catalyst may influence the catalytic activity, since it changes according to the presence of complexing agents and excess Zn. Thus, polymerizations of PO with free $ZnCl_2$, $ZnCl_2$ activated with ^{t}BuOH and highly crystalline $Zn_3[Co(CN)_6]_2 \cdot 12H_2O$ compound showed no activity.

XPS is sensitive to detect the chemical composition of the surface structures so that it is a good tool to characterize insoluble catalysts. Fig. 3 shows XPS spectra of DMC catalysts. The binding energy of zinc atom (the $2p^3$ XPS line at 1023.7 eV) in $ZnCl_2$ shifted to lower values, 1021.3 eV for the DMC catalyst and 1020.6 eV for $Zn_3[Co(CN)_6]_2 \cdot 12H_2O$ compound. The formation of zinc hexacyanocobaltate-based catalyst led the binding energy of zinc atom in $ZnCl_2$ to shift towards lower values. As the electron withdrawing power of the ligands bound to Zn atom decreases due to the substitution of Cl ligands for CN ligands and the coordination of complexing agents to coordinatively unsaturated Zn metal centers led to the chemical shift to lower values. It is noted that there exist considerable amounts of free zinc halides (Cl $2p^3$) in DMC catalysts as already demonstrated by elemental analysis. Peak assigned to Co $2p^3$ in $K_3Co(CN)_6$ also shifts from 781 eV to 777 eV for the DMC catalyst.

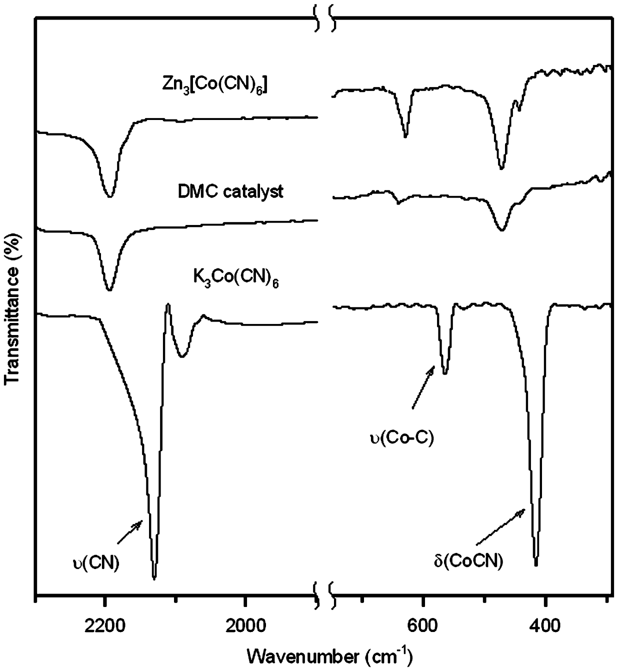


Fig. 1. Infrared spectra of $K_3[Co(CN)_6]$ and Zn–Co double metal cyanide (DMC) catalyst.

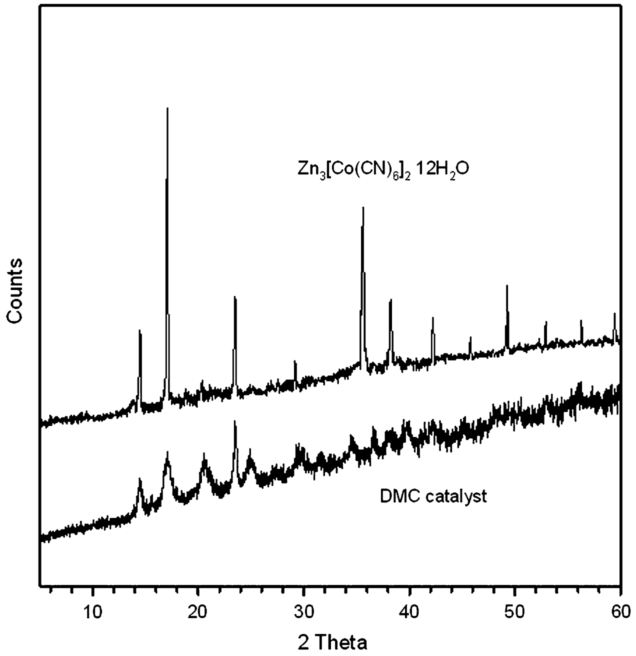


Fig. 2. X-ray powder diffraction patterns of $Zn_3[Co(CN)_6]_2 \cdot 12H_2O$, Zn–Co double metal cyanide (DMC) catalyst.

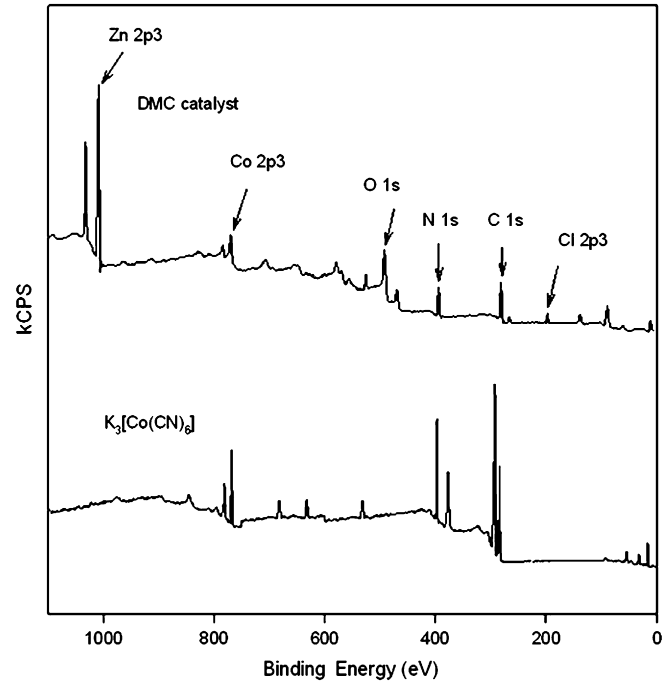


Fig. 3. XPS spectra of $K_3[Co(CN)_6]$ compound, Zn–Co double metal cyanide (DMC) catalyst.

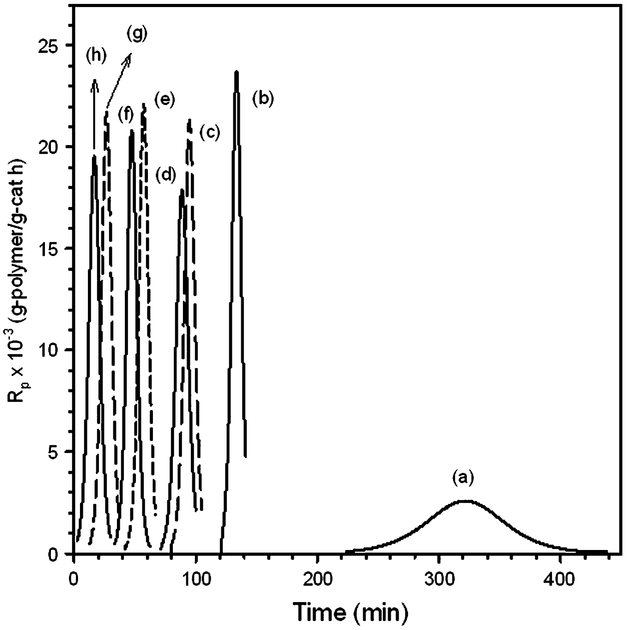


Fig. 4. Polymerization rate curves obtained by using Zn–Co double metal cyanide (DMC) catalyst and DMC/quaternary ammonium salt (QAS) binary catalysts: (a) DMC catalyst alone, (b) DMC/tetrapropyl ammonium chloride, (c) DMC/tetrabutyl ammonium chloride, (d) DMC/tetrabutyl ammonium bromide, (e) DMC/tetrahexyl ammonium chloride, (f) DMC/tetrabutyl ammonium iodide, (g) DMC/tetraoctyl ammonium chloride, and (h) DMC/tetradodecyl ammonium chloride. Polymerization conditions: temperature = 115 °C, PPG starter = 70 g, catalyst = 0.1 g (0.4 mmol Zn), and QAS = 0.5 mmol.

3.2. PO polymerizations and characterization of the resulting polymers

The goal of this research is to develop catalyst systems with tunable activity and preactivation (or induction) period. In fact there have been a lot of catalyst systems showing high activity [6,12]. These highly active DMC catalysts were prepared by variations of known procedures for making DMC, such as by combination of various starting materials including complexing agents, reaction parameters, filtration and/or drying. Even if rather tedious and careful procedures are needed to obtain highly active catalysts in low yield, DMC catalysts show very high activity once they are activated. Fig. 4 shows rate profiles of semi-batch polymerizations of PO by DMC catalyst. The rate curves were obtained by dividing the amount of PO consumption by polymerization time and by catalyst amount (0.1 g). Note that all polymerizations were stopped when total PO consumption reached 400 g for facile agitation. Low polymerization rates at the end of polymerizations demonstrate that polymerizations are deactivated to a different degree according to the catalyst systems. DMC catalyst (Fig. 4(a)) shows high activity (the maximum polymerization rate $R_{p,max} = 2588$ g-polymer/g-cat h) with decline of the rate profile after reaching $R_{p,max}$ most likely due to initial heating of the catalyst for a prolonged period at high temperature for activation. Note that we stopped the polymerization runs when total amount of PO monomer added reached 400 g for facile agitation. Taking a careful look at a rate curve obtained by DMC catalyst, it is also found that DMC catalyst is characterized by long induction period: i.e. it takes 321 min (t_{max}) to reach $R_{p,max}$. Evidently this long induction period undercuts the economic advantage of the DMC-catalyzed polymerizations. In order to overcome these shortcomings of DMC catalyst, we tried binary catalyst system using QAS as an external catalyst component. This trial was motivated by a recent report by Lu and Wang [13], in which they found chiral [(salcy)-$Co^{III}X$]/QAS binary catalyst was highly efficient for the copolymerization of CO_2 with PO to afford completely alternating copolymers. We also revisit the mechanism of PO polymerization initiated by base catalyst such as KOH, where no induction period was observed. 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.

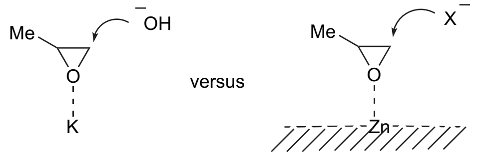


Fig. 4 shows rate profiles of semi-batch polymerizations of PO by DMC/QAS binary catalysts, changing the size of cation and the type of anion in QAS. It is evident that binary catalyst systems combining DMC catalyst with QAS are a simple and efficient way of tuning induction period as well as activity. By adding 0.5 mmol of QAS ([QAS]/[Zn] = 1.25) together with DMC catalyst the activity increases remarkably, so that $R_{p,max}$ increases from 2588 for DMC catalyst alone to 23,663

Table 1
Results of ring-opening polymerization of propylene oxide catalyzed by double metal cyanide (DMC) catalysts and DMC/quaternary ammonium salt binary catalysts[a]

Catalyst	$R_{p,max}$[b]	t_{max}[b](min)	M_n[c] (g/mol)	MWD[c]	Unsaturation (meq/g)[d]	Viscosity at 25 °C (cP)[e]
DMC only	2588	321	4800	1.47	0.018	1870
DMC/TPACl	23,663	133	6600	1.35	0.011	1320
DMC/TBACl	21,301	95	6100	1.28	0.011	1260
DMC/THACl	22,115	57	6200	1.37	0.012	1400
DMC/TOACl	21,705	13	6100	1.41	0.013	1490
DMC/TDACl	19,550	10	6200	1.26	0.013	1370
DMC/TBABr	17,874	88	6500	1.27	0.007	1210
DMC/TBAI	20,827	47	6300	1.29	0.009	1270

[a] Polymerization conditions as in Fig. 4.

[b] Maximum polymerization rate ($R_{p,max}$) in g-polymer/g-cat h and time to reach $R_{p,max}$ (t_{max}).

[c] Measured by gel permeation chromatography using a Waters 150 instrument operated at 25 °C in tetrahydrofuran solvent using polystyrene standards.

[d] Total degree of unsaturation of polyols measured by titration method according to ASTM D2847.

[e] Measured by a Brookfield viscometer model DV III (Brookfield Instruments), with a spindle no. 21.

g-polymer/g-cat h for DMC/TPACl binary catalyst (see Table 1 as well). In addition, as the alkyl groups of QAS become bulkier with the same anions (Cl^-), the induction period becomes shorter remarkably. As a result, the time to reach $R_{p,max}$ becomes short from 321 min for DMC catalyst alone to 10 min for DMC/TDACl binary catalyst. Comparing polymerizations with DMC catalyst combined with TBACl (Fig. 1(c)), TBABr (Fig. 4(d)) and TBAI (Fig. 4(f)) in order to investigate the effect of anions, all catalysts show very high activities; however, the effectiveness decreased in order of $I^- > Br^- > Cl^-$, considering both activity and induction period. A more detailed investigation of the effect of anions is ongoing by changing them with BF_4^-, PF_6^-, etc.

Investigation on the effect of QAS amount on polymerization was performed by DMC catalyst [0.1 g (0.4 mmol Zn)] combined with various amounts of TOACl from 0.01 to 2.0 mmol at the similar conditions employed in Fig. 4 (see Fig. 5). Even if the best results were obtained at around 0.5 mmol of TOACl, considering both activity and induction period, a very small amount (e.g. 0.01 mmol) of TOACl was enough to increase activity ($R_{p,max} = 21{,}682$ g-polymer/g-cat h) and shorten the induction period (e.g. $t_{max} = 26$ min). The induction period begins to increase and the activity decreases with an excess amount of TOACl (e.g. 2.0 mmol; [TOACl]/[Zn] = 5): i.e. $R_{p,max} = 17{,}910$ g-polymer/g-cat h at $t_{max} = 26$ min. Controlled polymerization runs with QASs alone in the absence of DMC catalyst showed no activity, demonstrating anions or cations in QAS are not actual active sites.

It is interesting to note that the use of QAS as an external additive improves polymer properties as well. The MW of polyols increases and the MWD becomes narrower as shown in Table 1. All polyols produced by DMC/QAS binary catalysts produce polyols with higher MW (>6100) and lower MWD (<1.41) than DMC catalyst alone. In general M_n values increased with decrease of QAS concentration, since anions of QAS may react with monomer (*vide infra*). Especially, the level of unsaturation, which is one of the decisive parameters to yield high-performance PU elastomers requiring high level of difunctionality, becomes improved. Monofunctional PPG polyols resulting from unsaturation act as termination during the development of PU elastomer MW upon chain extension with either diols or diamines. The elastomers thus produced have inferior mechanical properties [1]. Essentially all PPG polyols produced here by DMC catalysts showed much lower unsaturation level (<0.02 meq/g) than conventional based catalyzed PPG polyols due to reduced isomerizations and terminations leading to allyl end groups. As shown in Table 1, DMC catalyst produces polyol with unsaturation level of 0.018 meq/g and DMC/TBABr binary catalyst produces polyol with ultra-low unsaturation level of 0.007 meq/g. The viscosity of polyol, which is an important property during handling and producing polyurethane products, decreases from 1870 cP for DMC catalyst alone to less than 1500 cP for DMC/QAS binary catalysts. It is expected that the viscosity is dependent on many

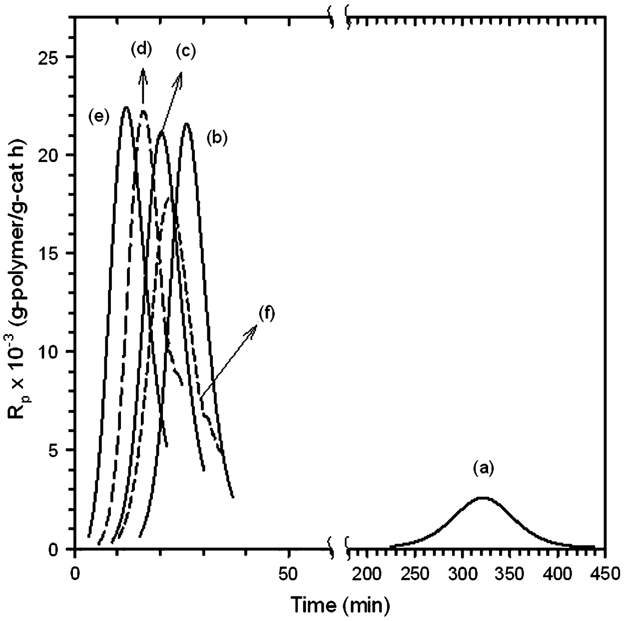


Fig. 5. Polymerization rate curves obtained by using binary catalyst systems composed of Zn–Co double metal cyanide catalyst (0.1 g; 0.4 mmol Zn) and various amounts of tetraoctyl ammonium chloride: (a) none, (b) 0.01, (c) 0.05, (d) 0.1, (e) 0.5, and (f) 2.0 mmol. Polymerization conditions: temperature = 115 °C, PPG starter = 70 g, and catalyst = 0.1 g.

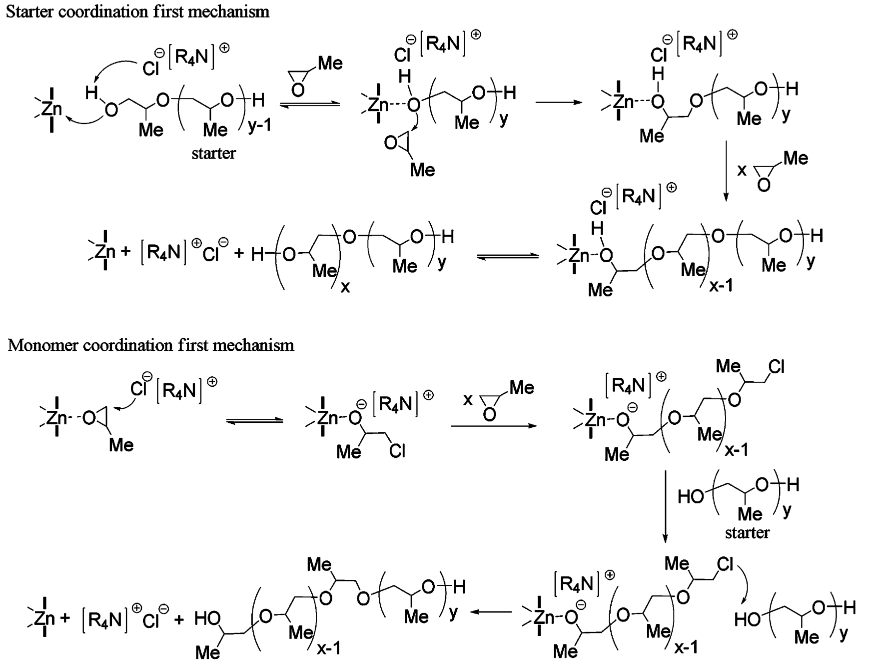
parameters such as MW, MWD and unsaturation level of polymer. Even if it is hard to conclude the effect of individual parameter on viscosity, the decreased viscosity might be caused by combined effect of narrow MWD and low unsaturation level.

3.3. Mechanism of polymerizations by DMC/QAS binary catalysts

Based on the results of this study, we propose mechanisms for a binary catalyst system: starter coordination first mechanism and monomer coordination first mechanism (Scheme 1). In the starter coordination first mechanism, it is assumed that anions of QAS should help starter molecules to be coordinated to zinc active sites by nucleophilic attack. The attack of acid hydrogen from OH group by Cl anions of QAS may also help starter molecules to be coordinated with Zn catalyst. However, Cl anions are very weak bases, and moreover the basicity of Br and I anions is lower than Cl anions. Therefore, replacing of Cl anion with Br or I anion should prolong the induction period; however, observed results are opposite, demonstrating starter coordination first mechanism seems to be unreasonable. In addition, if starter coordination first mechanism is true, the change of starter concentration should induce the change of induction period. However, a series of polymerization runs carried out by changing the amount of difunctional PPG starter in the range of 10 g to 200 g by fixing [PPG]/[QAS] and [QAS]/[Zn] and [QAS]/[Zn] molar ratios to 200 and 1.25, respectively, showed the induction period was independent of the amount of PPG starter. It may be another evidence that the PPG starter plays no important role in forming active sites at the early period of polymerization.

In monomer coordination first mechanism, the DMC catalyst is proposed to serve as an electrophile for complexing PO, and the anion of the QAS serves as a nucleophile. The attack of a nucleophile leads to ring opening of the PO with subsequent addition of POs until the propagating chains terminate by the action of the PPG starter molecules. 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 QAS for the nucleophilic attack of PO. Bulky QAS cations activate anions by increasing the distance separating the cation from anion in the ion pair [e.g., $\mathrm{Na^{+}{-}Br^{-}}$ ($r = 285$ nm) versus $\mathrm{Bu_4N^{+}{-}Br^{-}}$ ($r = 0.628$ nm)] [14], which in turn will lower the energy of activation. A large bulky ('soft') QAS cation makes the required anion activation easier for initiation. As a result, the binary catalyst system using TDACl, the QAS of the bulkiest ammonium ion in this study, showed the fastest activation with high activity.

As a means of gathering evidences for monomer coordination first mechanism, PO polymerization was performed without adding PPG starter. No conspicuous change in the induction period was observed in these polymerization conditions. Fig. 6 shows ^{13}C NMR spectrum of the resulting polymer. It was possible to detect polyether having Cl group at one chain end ($-CH_2Cl$ at 51 ppm) and hydroxyl group at the other chain end (methine carbon in $-CH_2CH(CH_3)OH$ in the spectral region 65.5–67 ppm) [15], demonstrating monomer coordination first mechanism is more plausible. Even if it may be the case, the actual polymerization mechanism should be more complex and more similar mechanisms should run at the same time, depending on the concentration of QAS, DMC and starter. According to the quantitative analysis of methine, methylene and methyl stereosequence by ^{13}C



Scheme 1. Mechanisms proposed for ring-opening polymerization of propylene oxide catalyzed by Zn–Co double metal cyanide/quaternary ammonium salt binary catalyst system.

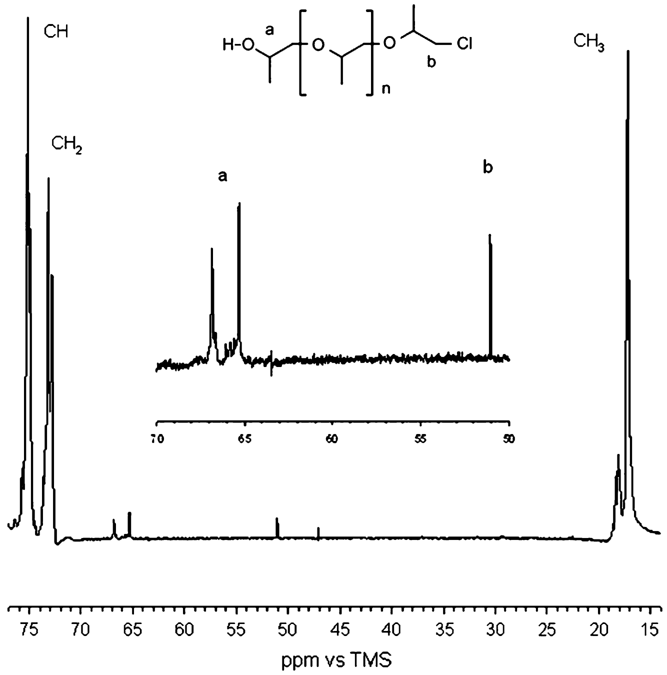


Fig. 6. ^{13}C NMR spectrum of poly(propylene oxide) prepared by double metal cyanide catalyst (0.1 g; 0.4 mmol Zn)/tetraoctyl ammonium chloride (0.5 mmol) binary catalyst at 115 °C in the absence of PPG starter.

NMR [15], all PPG polyols were characterized by atactic configuration, even though the randomness of the backbone as a sum of *mr* and *rm* triad is somewhat different from each other. In addition, all DMC catalyst systems led to PPG polyols with highly regioregular head-to-tail enchainment.

The presence of an excess amount of QAS (e.g. 2.0 mmol of TOACl in Fig. 5) makes the induction period longer, probably due to the competitive nucleophilic attack of PO monomers with Cl^- anions to Zn active sites. The Cl^- attack will stabilize the sites by forming Zn–Cl bonds so that PO monomers cannot coordinate. In order to check the coordinative nature of the DMC-catalyzed polymerization, we carried out a series of polymerizations changing the catalyst concentration from 50 ppm to 320 ppm based on catalyst concentration in final polymer products. As the catalyst concentration increases, the polymerization rate increases monotonously ($R_p \propto [Zn]$) within our experimental range. It demonstrates that the incoming monomer added coordinatively to bonds between growing polymer chain and zinc active sites as follows:

$$\underset{\text{active site}}{Zn{-}P_n} + \text{Propylene oxide} \xrightarrow{k_p} Zn{-}P_{n+1} \tag{1}$$

in which P_n is a growing polymer chain, and k_p is a rate constant of propagation. This type of propagation is a typical step that can be found in the metal-catalyzed coordination polymerizations.

4. Conclusion

A typical DMC catalyst was prepared by reacting $ZnCl_2$ and $K_3[Co(CN)_6]$ in the presence of ^{t}BuOH as a complexing agent. The DMC catalyst of the molecular formula of $Zn_{2.3}Cl_{1.0}[Co(CN)_6]_{1.0}\cdot 2.0{}^tBuOH\cdot 1.0H_2O$ is poorly crystalline due to the framework collapse from crystalline Prussian blue analogues, $Zn_3[Co(CN)_6]_2\cdot 12H_2O$ compound. This catalyst showed high activity ($R_{p,max} = 2588$ g-polymer/g-cat h) in PO polymerizations; however, long induction period (e.g. $t_{max} = 321$ min) and severe deactivation after some period of polymerization runs were recorded. These shortcomings of DMC catalysts were improved by using binary catalysts combining DMC with various quaternary ammonium salts. As a result, DMC/TDACl binary catalyst showed very high activity ($R_{p,max} = 19{,}550$ g-polymer/g-cat h) with negligible induction period ($t_{max} = 10$ min). The nucleophilic attack of anions in QAS helped PO monomers to coordinate zinc active sites and to lead ring opening of the PO with subsequent addition of PO. The use of external QAS additives improved various polymer properties as well. Thus, all polyether polyols produced by the binary catalyst systems had stereoirregular structure with highly head-to-tail enchainment and were characterized by high MW (>6100) with narrow MWD (<1.41) and very low unsaturation level (<0.013 meq/g).

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