

RANDOM COPOLYMER OF PROPYLENE OXIDE AND ETHYLENE OXIDE PREPARED BY DOUBLE METAL CYANIDE COMPLEX CATALYST

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Abstract Copolymerization of propylene oxide (PO) and ethylene oxide (EO) using double metal cyanide (DMC) complex as the catalyst was carried out. The structure of random copolymers was confirmed by ^{13}C -NMR and IR spectra. ^1H -NMR analysis shows that the EO content in the copolymer is the same as that in the initial monomer feed. Moderate molecular weight copolymers with various EO content were obtained and their values of molecular weight distribution (MWD) fell in the range of 1.21–1.55. It was found that the molecular weight of copolymers is controlled by the mass ratio of EO + PO to initiator moles used. The reaction rate as well as polymer yield decrease with increasing EO content in the feed composition.

Keywords Propylene oxide, Ethylene oxide, Double metal cyanide complex

INTRODUCTION

Copolymers of ethylene oxide (EO) and propylene oxide (PO) are of considerable technical importance. Their block copolymer and random copolymer have been widely used in the manufacture of polyurethanes and surfactants^[1]. These commercial polymers are currently prepared using conventional base catalysts, such as alkali metal hydroxides (*e.g.* KOH). A number of studies^[2–5] have shown that abstraction of a methyl proton can hardly be avoided during base-catalyzed polymerization of PO. As a consequence of this abstraction reaction which is generally referred to as the chain transfer reaction, the number-average molecular weight (M_n) of obtained polymer is relatively low and its molecular weight distribution (MWD) is broadened. Under the conditions used for the industrial production of polypropylene glycol, the limiting value of M_n is less than 3000. This chain transfer reaction does not occur in the polymerization of EO, but it will occur in the copolymerization of EO and PO^[6]. Indeed, conventional catalyst such as KOH cannot produce high quality PO/EO copolymer with $M_n > 5000$ if more than about 20% PO is present in the monomer feed.

Double metal cyanide (DMC) compounds are well known catalyst for alkene-oxide polymerization and synthesis of polyether polyols^[7–9]. Compared with KOH catalyst, DMC catalysts can give high-quality polyether polyols (*e.g.* polyoxypropylene polyols) that have low unsaturation and MWD. Moreover, unlike many other catalysts, DMC catalysts are not air- and moisture sensitive. It is generally recognized that DMC is superior to the base catalysts traditionally used in industry. However, there are only few reports on DMC catalyzed copolymerization of EO and PO.

In the present work, relatively high molecular weight copolymers of EO and PO were prepared and the structure of random copolymers was elucidated by IR and ^{13}C -NMR. Characteristic features of the copolymerization were also investigated to understand the action mode of DMC catalytic system.

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EXPERIMENTAL

Materials

$K_3Co(CN)_6$ (Acros, 95%) was recrystallized before use, $ZnCl_2$ (analytical reagent), $ZnSO_4 \cdot 7H_2O$ (analytical reagent) and *tert*-butyl alcohol (98%) were used without further purification. PPG-400, a commercial polyoxypropylene diol oligomer (catalyzed by KOH $M_n \sim 400$) was used as the initiator. PO and EO oxide (> 99.8% pure) were used as received.

Preparation of DMC Catalysts

3 g $K_3Co(CN)_6$ was dissolved in a mixture of 50 g distilled water and 6 g *tert*-butyl alcohol (solution 1). Solution 2 was prepared by dissolving 16 g $ZnCl_2$ in a mixture of 40 g distilled water and 12 g *tert*-butyl alcohol. Solution 1 and 2 were mixed together in a round-bottom flask using a mechanical stirrer and a white precipitate was formed. Then, the slurry was stirred for another 40 min, and was pressure filtered. The solid catalyst was isolated, and redispersed with vigorous stirring in a mixture of 50 g *tert*-butyl alcohol and 50 g distilled water. After all the solids were suspended in this solution, the mixture was stirred for 20 min. The solids were again isolated by pressure filtration. This process was repeated several times. Finally, the solids were reslurried in 50 g *t*-BuOH, after which 1 g $ZnSO_4 \cdot 7H_2O$ in 2 g H_2O was added with rapid stirring. The obtained slurry was aged for a few days and directly used as a catalyst.

Polymerization Experiment

PPG-400 initiator (40 g) and DMC catalyst were transferred to a 1 L reactor which had been purged several times with nitrogen. The mixture was stirred and heated to 100°C, and was evacuated for 20 min to remove traces of water from PPG-400. Then the mixture was heated to 115°C. Mixed monomers (10 g) of PO and EO were added. Additional mixed monomer was gradually added when an accelerated pressure drop occurred in the reactor, which indicates the initiation of the catalysis. The polymerization reaction was stopped when the catalyst no longer showed any activity (a constant pressure was observed). The remaining EO and PO were removed under reduced pressure.

Measurement

Wide-angle X-ray diffraction (WAXD) pattern of the DMC catalyst was obtained by means of a Rigaku D/MAX-B X-ray diffractometer using Cu K α radiation and with a scanning of 3°/min in the scanning range of 30–70°. The elemental analysis of catalysts was performed by using a Hitachi 180–50 atomic absorption spectrophotometer. The M_n of the polymer was determined by using a Knauer vapor phase osmometer (THF as solvent). The MWD was measured using a Waters 150-C instrument, operated at 25°C, with a set at 10^4 , 10^3 and 500 Å columns. Polystyrene standards with low polydispersities were used to generate a calibration curve. ^{13}C -NMR spectra of the polymer were performed on a Avance DMX 500 (500 MHz) spectrometer with $CDCl_3$ as the solvent. Infrared spectra of the catalysts were recorded on a Vector-22 IR spectrometer.

RESULTS AND DISCUSSION

Characterization of DMC Catalyst

The analytical data of catalyst paste obtained are as follows: Zn = 2.71%, Co = 1.03%, and K = 12 ppm. This result means that the paste catalyst contains about 5.68 wt% $Zn_3[Co(CN)_6]_2$ (90% yield based on $K_3Co(CN)_6$), 0.86% $ZnCl_2$ and 1.28 wt% $ZnSO_4$, the remainder being a mixture of *tert*-butyl alcohol and H_2O . Figure 1(a) shows the WAXD pattern of DMC catalyst (vacuum-dried). For comparison, the crystal structure of $ZnSO_4 \cdot 7H_2O$ and the DMC catalyst which was prepared without added $ZnSO_4 \cdot 7H_2O$ were also investigated, respectively. The catalyst has predominantly sharp lines, which indicates a relatively high crystallinity. It is obvious that the crystalline phase was ascribed to $Zn_3[Co(CN)_6]_2$ since there were no peaks related to $ZnSO_4$ in the pattern. Unfortunately, this crystal structure modification of $Zn_3[Co(CN)_6]_2$ can not be identified by using the standard Joint Committee on Powder Diffraction File (JCPDF) library files.

Polymerization Procedure

Figure 2 shows a plot of the mixed monomer consumption versus the reaction time. These polymerization reactions exhibited a relatively short induction period (from about 10 min to about 1/2 h). This is in contrast with the long induction period (several hours) as reported by some patents^[10, 11]. The reaction rate, as well as the consumed monomer mass is almost proportional to the amount (or concentration) of catalyst, other conditions being kept the same. In all these cases, the reaction rate decreases gradually with the incremental monomer addition. Finally, further consumption of the monomer was limited, and this indicates the presence of a termination process.

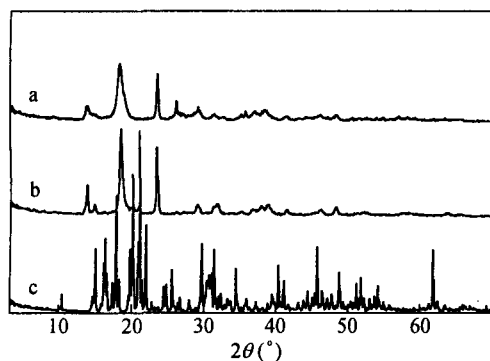


Fig. 1 WAXD patterns of DMC complex
(a) Catalyst;
(b) Catalyst without $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$;
(c) $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$

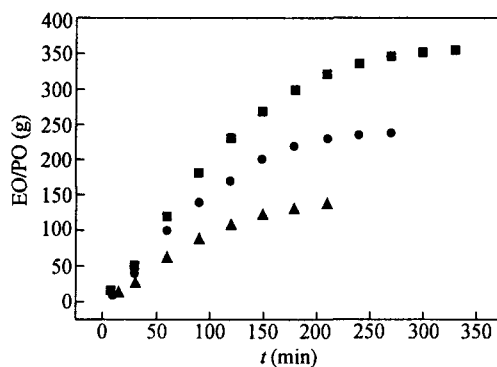


Fig. 2 Copolymerization of PO and EO with different amounts of catalyst
40 g PPG-400 as initiator, $f_{\text{EO}} = 0.572$ at $115 \pm 2^\circ\text{C}$
■ 0.04 g, ● 0.03 g, ▲ 0.018 g

Structure of Copolymer

Figure 3 shows the ^{13}C -NMR spectrum of EO/PO copolymer. To designate a particular carbon concisely, the following notations are adopted: (1) EO units are designated as E and PO as P, the arrow running from the CH_2 tail to the $\text{CH}(\text{CH}_3)$ head. (2) The unit in which the carbon locates is indicated by underlining. Within a P unit, the symbols t and s distinguish the CH and CH_2 carbons, respectively. If an E unit is at the center of a symmetrical sequence, the carbons are identical and no distinction is necessary. If the sequence is unsymmetrical, the E CH_2 s are not identical, in this case CH_2 s are designated by a or b representing respectively the left- and right hand CH_2 in the sequence as written.

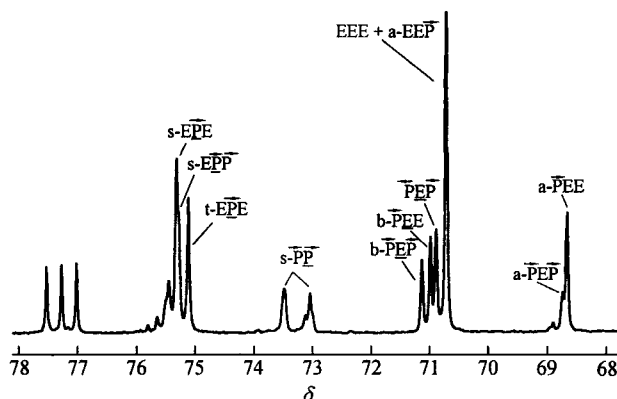


Fig. 3 ^{13}C -NMR spectrum of EO/PO copolymer ($F_{\text{EO}} = 0.521$)

The main-chain CH and CH₂ resonances which were found to be sensitive to chain stereochemistry and sequence structure are briefly discussed, whereas the CH₃ resonances are much less informative (the fraction of spectrum concerning the CH₃ (δ 17.1–18.5) is omitted).

The spectrum is divided into four regions, I–IV, covering the range (in CDCl₃) δ_c 68.5–69.2 (CH₂), 70.4–71.2 (CH₂), 72.8–73.8 (CH₂) and 74.8–75.8 (CH₂ + CH). The main peaks were assigned mainly in the form of triad respectively. Region III consists of four clearly resolved CH₂ peaks at δ_c 70.7, 70.9, 71.0 and 71.1. Among them, the most intense peak is assigned to (EEE + a-EPE) and the fourth peak at δ_c 71.1 (b-PPE) is not observed in the spectra of EO/PO block copolymer. Region IV also contains a minor peak at δ_c 68.74 (a-PPE) which is not observed in the block copolymer regardless ABA- or BAB type. Thus, these mixed-feed copolymer adducts have a random distribution of EO unit.

Figure 4 shows the infrared spectra of the copolymer. The infrared adsorption at 970 cm⁻¹, which can not be observed in the block copolymer, is associated with the following structure: RO–CH₂CH(CH₃)–O–CH₂CH₂–. It is most likely that the CH₃ rocking mode vibration accounts for this absorption. Therefore, the analytic result of infrared spectra of the copolymer also supports the above-discussed fact.

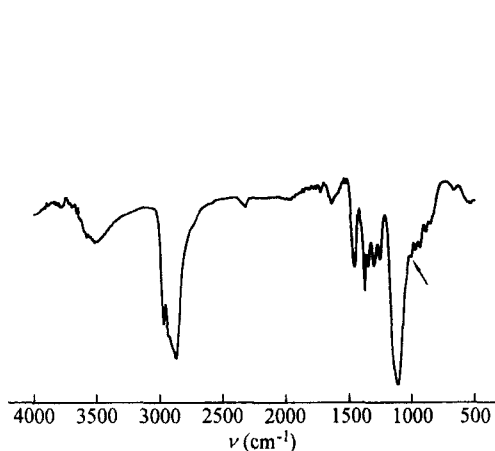


Fig. 4 Infrared spectrum of EO/PO copolymer ($F_{EO} = 0.521$)

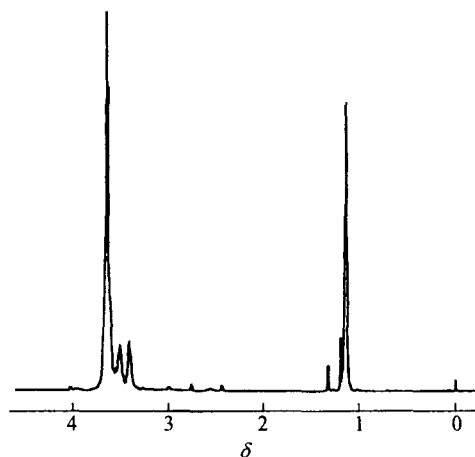


Fig. 5 ¹H-NMR spectrum of EO/PO copolymer ($F_{EO} = 0.521$)

Table 1. Copolymerization of EO and PO with DMC catalyst ^a

f_{EO}	F_{EO}	M_n (vp0)	M_n (exp.)	M_w/M_n
0	0	5890	6750	1.22
0.305	0.267	4185	3680	1.31
0.305	0.285	5712	4850	1.25
0.305	0.281	7625	9120	1.28
0.415	0.377	3681	4590	1.55
0.415	0.369	6737	7500	1.51
0.572	0.521	6529	8200	1.44

^a Conditions: $T = 115 \pm 2^\circ\text{C}$; initiator = 40 g; catalyst = 0.55 g (based on weight of $\text{Zn}_3[\text{Co}(\text{CN})_6]_2$ solids)

Controlled Copolymerization of EO and PO

A series of polymerizations were carried out with different f_{EO} (mole fraction of EO in the initial feed) and the results are summarized in Table 1. A ¹H-NMR spectrum of freshly prepared sample in CDCl₃ is shown in Fig. 5. The resonances at δ 0.9 and 3.1–3.4 are ascribed to CH₃ protons and backbone protons (CHO and CH₂O) respectively. Since the oxypropylene unit contributes with 3 protons each in the two signals, $I_{\text{backbone}} - I_{\text{methyl}}$ corresponds to the contribution of EO only. I_{methyl} corresponds to 3 protons and $I_{\text{backbone}} - I_{\text{methyl}}$ to 4 protons. Thus, the mole fraction of EO unit in the copolymer (F_{EO}) was calculated as follows:

$$f_{EO} = ((I_{\text{backbone}} - I_{\text{methyl}})/4)/((I_{\text{backbone}} - I_{\text{methyl}})/4 + I_{\text{methyl}}/3)$$

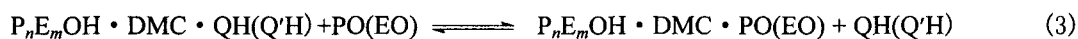
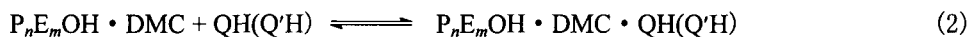
$$= (I_{\text{backbone}} - I_{\text{methyl}})/(I_{\text{backbone}} + 1/3 I_{\text{methyl}})$$

From Table 1, it can be seen that the EO content in the copolymer is close to that in the initial monomer feed. M_n expected in the absence of transfer reaction was calculated as the ratio of mass of EO + PO to initiator moles used in preparation. The good agreement between the observed M_n (measured by VPO) and the expected M_n indicates that the initiation and propagation proceed quantitatively from initiators. In other words, polymerization proceeds in a controlled manner under these conditions. It should be stressed that the amount of initiator greatly exceeded that of the catalyst (in these cases, the molar ratio of initiator to catalyst is as high as 10^3 or higher). Thus, it seems impossible that all the chain ends are permanently active during polymerization. Taking into account this fact and yet the relatively narrow MWD of copolymer, it appears reasonable that every active species must be associated with many different chains at any time during polymerization. The question then arises how a particular active species activates so many different molecular chains. Undoubtedly, as reported in our previous papers^[12, 13], a rapid exchange reaction must be existing between active polymer species and other inactive chains (equation 1):



where $Q'H$ denotes an inactive chain, P denotes an oxypropylene unit, $CH_2CH(CH_3)O-$ and E denotes an oxyethylene unit, CH_2CH_2O- . The number of growing chains is fixed by the original molar amount of initiator as a result of this rapid exchange reaction. Accordingly, the molecular weight of polymers formed is consistent with the calculation based on the monomer to initiator ratio (M/I) and not on the monomer to catalyst ratio (M/C) (provided they are calculated on basis of M/C , $M_{n, \text{calc}}$ as high as several tens of thousands would be reached). In the event this exchange reaction is rapid with respect to the polymer propagation growth, the MWD of product is expected to remain narrow. On the other hand, a slight increase in molecular weight distribution (MWD) was found for copolymer with higher EO content. This result is contrary to general observation during the anionic copolymerization of EO and PO that the value of MWD decreases with increasing EO content in feed.

Figure 6 shows the effect of initial feed composition on the reaction rate of copolymerization. Apparently, the polymerization reaction rate slowed down when a high EO content was employed in the feed composition. Moreover, the polymer yield was dramatically lowered with increasing f_{EO} (Table 2), *e.g.*, the polymer yield of polyoxyethylene polyols was about one fourteenth of that of polyoxypropylene polyols. This observation seems somehow unexpected since, in general, EO is more reactive than PO during the ring-opening polymerization. In addition, it can be seen from Table 2 that the molar ratio of initiator to catalyst (I/C) has certain effect on the polymer yield. The low I/C gives somewhat higher yield than the higher I/C . In other words, the initiator has a depressive effect on the polymer yield. This depressive effect is probably due to a competition between the initiator and the catalyst with the monomer for coordination to the active site. A complex may be formed when the active site is coordinated by hydroxyl oxygens of the initiator or the inactive species (equation 2, where QH denotes a initiator) and monomer must substitutes for it before the chain propagating (equation 3). When more initiator was used, it would hinder the coordination of monomer to the active site; the yield is therefore decreased.



It is worth noting that the copolymer prepared with $f_{EO} = 0.789$ became turbid. As the GPC trace of this polyols in Fig. 7 shows, a little peak emerges in the higher molecular weight region. This fraction of the polyether polyol product was easily isolated by precipitation from dimethyl ether, and water-soluble white solids which were identified to be a relatively high molecular weight polyoxyethylene were obtained. In other words, when high feed f_{EO} was employed, DMC catalyst will preferentially generate polyoxyethylene homopolymer. The

reason for this phenomenon needs further investigation.

Table 2. Effect of initial feed composition on copolymerization of EO and PO^a

f_{EO}	Molar ratio $\times 10^{-3}$ (initiator/ $Zn_3[Co(CN)_6]_2$)	Yield kg polymer/g of $Zn_3[Co(CN)_6]_2$	M_n (vpo)	Appearance
0	1.60	30.2	8510	Clear
0.305	1.60	14.1	3346	Clear
0.305	0.80	16.5	7625	Clear
0.415	1.60	10.6	2895	Clear
0.415	0.40	12.8	8571	Clear
0.572	1.60	8.5	2126	Clear
0.572	0.40	9.8	7219	Clear
0.789	1.60	4.5	1165	Slight turbid
1	1.60	2.1	758	Turbid

^a Other conditions as described in Table 1

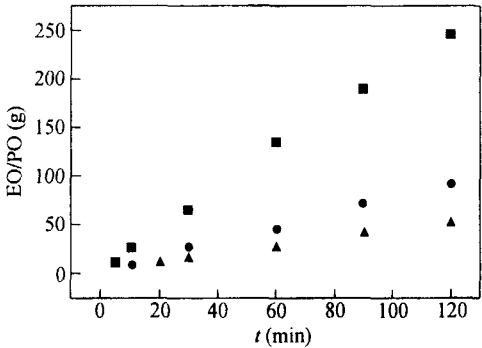


Fig. 6 Effect of mole fraction of EO in the initial feed on EO/PO copolymerization
Catalyst = 0.08 g, other conditions as described in Fig. 2
■ 0.305 g; ● 0.572 g; ▲ 0.789 g

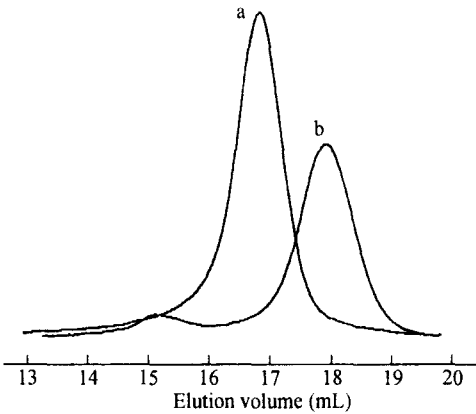


Fig.7 GPC elution curves of PO/EO copolymers prepared with different f_{EO}
a) $f_{EO} = 0.572$ ($M_n = 1826$, $M_w/M_n = 1.21$)
b) $f_{EO} = 0.789$ ($M_n = 1165$)

CONCLUSION

The DMC catalyst is very effective for the copolymerization of propylene oxide and ethylene oxide. Random copolymers with relatively high molecular weight and moderate MWD could be prepared. By using this catalyst system, polymerization proceeds in controlled manner. Polymerization reaction rate as well as polymer yield decrease with increasing EO content in initial feed composition. The initiator has a two-fold effect on the course of copolymerization. First, it directly participates in the control of polymer molecular weight. Second, it has a depressive effect on the polymer yield. In general, the DMC catalytic approach is a powerful and practical method for preparing moderate molecular weight EO/ PO copolymer.

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