

Ring-Opening Copolymerization of Maleic Anhydride with Propylene Oxide by Double-Metal Cyanide

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ABSTRACT: Ring-opening copolymerization of maleic anhydride (MA) with propylene oxide (PO) was successfully carried out by using double-metal cyanide (DMC) based on $Zn_3[Co(CN)_6]_2$. The characteristics of the copolymerization are presented and discussed in this article. The structure of the copolymer was characterized with IR and 1H -NMR. Number-average molecular weight (M_n) and molecular weight distribution (MWD) of the copolymer were measured by GPC. The results showed that DMC was a highly active catalyst for copolymerization of MA and PO, giving high yield at a low catalyst level of 80 mg/kg. The catalytic efficiency reached 10 kg polymer/g catalyst. Almost alternating copolymer was obtained when monomer charge molar ratio reached $MA/PO \geq 1$. The copolymerization can be also carried out in many organic solvents; it was more favorable to be carried in polar solvents such as THF and acetone than in low-polarity solvents such as diethyl ether

and cyclohexane. The proper reaction temperature carried in the solvents was between 90 and 100 °C. The M_n was in the range of 2000–3000, and it was linear with the molar ratio of conversion monomer and DMC catalyst. The reactivity ratio of MA and PO in this reaction system was given by the extended Kelen–Tudos equation: $\eta = [r_1 + (r_2/\alpha)]\xi - (r_2/\alpha)$ at some high monomer conversion. The value of reactivity ratio $r_1(MA) = 0$ for MA cannot be polymerized itself by DMC catalyst, and $r_2(PO) = 0.286$. The kinetics of the copolymerization was studied. The results indicated that the copolymerization rate is first order with respect to monomer concentration. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1788–1792, 2004

Key words: catalysts; copolymerization; double-metal cyanide; kinetics; polycarbonates

INTRODUCTION

Cyclic acid anhydrides were first reported to form copolymers with cyclic ethers in the presence of anionic and cationic catalysts at high temperatures by Fischer et al. in the 1960s,^{1–3} as a more efficacious method than polycondensation to produce unsaturated polyesters. It was testified by Hilt et al. that copolymers obtained by an anionic mechanism exhibited higher tendency toward alternation and higher molecular weight (M_n) in comparison with those obtained by cationic mechanism.⁴ Then, copolymerization of cyclic acid anhydrides with cyclic ethers in the presence of organometallic catalyst such as diethyl zinc was postulated by Inoue et al. to proceed via an anionic-coordination mechanism in 1969.⁵ In the following three decades, ring-opening copolymerization of maleic anhydride (MA) with propylene oxide (PO) was successfully carried out by using ethyl zinc compounds $ROZnEt$,⁶ AlR_3 ,⁷ $Mg(OEt)_2$,⁸ Fe-Al- α , α' -dipyridyl catalyst,⁹ and rare earth complex.¹⁰ All of those catalytic systems, however, cannot simulta-

neously get high yield and highly alternating copolymer.

Double-metal cyanide (DMC) complexes are well-known catalysts for alkene–oxide polymerization with high activity.^{11,12} With 5 years of research on alkene–oxide polymerization with DMC complex,^{13–15} we carried ring-opening copolymerization of MA with PO with this catalyst in this article. The characteristics of the copolymerization was presented and discussed in this article. The structure of the copolymer was characterized with IR and 1H -NMR. Number-average molecular weight (M_n) and molecular weight distribution (MWD) of the copolymer were measured by gel permeation chromatography (GPC).

EXPERIMENTAL

Materials

DMC complex based on $Zn_3[Co(CN)_6]_2$ was obtained according to our previously reported method.¹² MA, tetrahydrofuran (THF), dichloromethane, acetone, cyclohexane, and diethyl ether are analytically pure grade reagents. PO was refined by being circumfluenced with CaH_2 and distilled before use.

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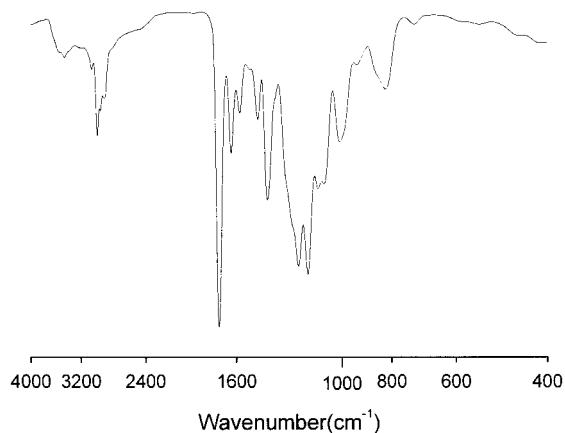


Figure 1 Infrared spectrum of MA-PO copolymer.

Copolymerization experiment

Bulk copolymerization

A 200-ml autoclave was charged with a certain amount of MA and DMC catalyst; then it was stripped by vacuum and purged several times with nitrogen to remove traces of water and oxygen in the autoclave. Now PO was added. The mixture was stirred and heated to 100°C. The reaction was stopped at a proper pressure.

Solution copolymerization

A certain amount of MA, PO, and DMC catalyst were dissolved in organic solvent; then, the solution was transferred to a 200-ml autoclave that had been stripped by vacuum and purged several times with nitrogen. The mixture was stirred and heated to 100°C. The reaction was then stopped at a proper pressure. The obtained reaction slurry was stripped under high vacuum at 50°C to remove the remaining solvent.

The content of the reaction vessel was purged several times with 50°C distilled water until neutral to remove the remaining MA monomer and cyclohexane to remove minute PO homopolymer. Then, the solution was heated at 50°C under high vacuum for a few hours to remove the remaining water and cyclohexane to achieve the purified MA-PO copolymer.

Measurement

Infrared spectra were recorded for film samples cast on KBr disk from THF solution by a Vector-22 IR spectrometer. ¹H-NMR spectra were obtained on an Avance DMX500 spectrometer with CDCl₃ as a solvent. *M_n* and MWD of copolymers were measured by a Waters 150-C instrument, operated at 35°C with THF

as an eluant. Polystyrene standards with low polydispersities were used to generate a calibration curve.

RESULTS AND DISCUSSION

Characterization of copolymer

The MA-PO copolymer prepared in room temperature by using DMC complex, was a yellow semisolid content. It can be solved in almost all polar solvents, but not in water and cyclohexane.

Figure 1 shows the IR spectrum of MA-PO copolymer. Some characteristic absorptions of an unsaturated polyester are exhibited in it: 1730 cm⁻¹ [$\nu_{C=O}$ (ester)], 1640 cm⁻¹ [$\nu_{C=C}$], 1213 cm⁻¹, and 1164 cm⁻¹ [ν_{C-O-C} (ester)]. There are also some faintly characteristic absorptions of PO homopolymer [i.e., 1082 cm⁻¹ and 1113 cm⁻¹ ν_{C-O-C} (ether)], but the characteristic absorption of polyanhydride at 1810 cm⁻¹ does not appear in the IR spectrum, because DMC cannot make MA polymerize itself. All of the above factors can be also indicated in ¹H-NMR spectrum as shown in Figure 2 (δ ppm): 6.23–6.29 [CH=CH], 5.12–5.26 [OCH (ester)], 4.14–4.26 [OCH₂ (ester)], 3.41–3.53 [OCHCH₂ (ether)], 1.28–1.33 [—CH₃ (ester)], 1.13–1.18 [—CH₃ (ether)]. Hereto, it was proved that the unsaturated polyester was composed of MA-PO alternating segments and a few PO self-propagation segments.

Characteristic features of DMC-catalyzed MA-PO copolymerization

The lowest temperature at which the DMC complex catalyzed MA-PO copolymerization is about 70°C. The reaction time was long; it took more than 16 h to complete the copolymerization at 100°C, and the induction period was more than 6 h. The copolymerization can also be carried out in many organic solvents. Table I shows the copolymerization results carried in

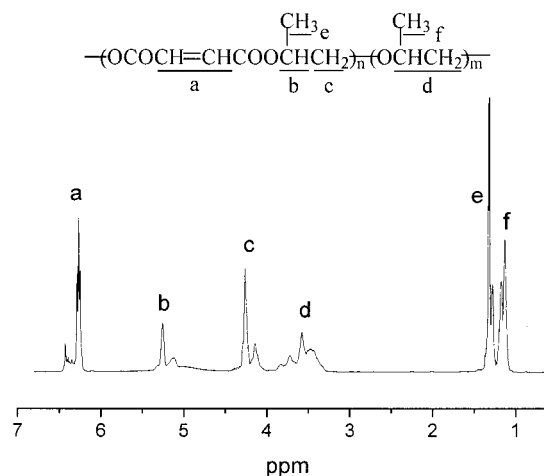


Figure 2 ¹H-NMR spectrum of MA-PO copolymer.

TABLE I
Effect of Solvent on MA-PO Copolymerization

Solvent	Conversion (%)	M_w/M_n	M_n
THF	96.7	1.37	3181.6
Acetone	92.8	1.48	2867.2
Cyclohexane	84.3	1.65	3306.7
Diethyl ether	81.2	1.50	2899.5
Dichloromethane	66.4	1.71	2668.2

Monomer charge MA/PO = 1.0(mol), temperature = 90 ± 2 °C, total monomer concentration = 5 mol/L, reaction time = 16 h, catalyst level (concentration in a mixture of monomer MA and PO on a solid $Zn_3[Co(CN)_6]_2$ weight basis) = 80 mg/kg.

five different polarity solvents: THF, acetone, diethyl ether, cyclohexane, and dichloromethane. It indicated that it was more favorable to get high yield in polar solvents such as THF and acetone than in low-polarity solvents such as diethyl ether and cyclohexane, but the M_n and MWD were close to each other.

The effect of temperature, catalyst level, and reaction time on MA-PO copolymerization was listed in Table II. It shows that it was not only in bulk copolymerization but in solution copolymerization that the reaction rate and conversion were increased with heightened temperature. When the temperature was lower than 100°C, the M_n and conversion were synchronously increased with temperature. M_n was, on

the contrary, sharply declined at 115°C and MWD broadened in comparison with that carried at 100°C in bulk copolymerization ($M_n = 2140$, MWD = 2.03). We guess that a rapid exchange reaction of active species to monomers was easier to carry at high temperature. Another factor in common polymerization was that the active chain-propagation reaction was high with respect to increasing temperature. So, chain-propagation reaction and exchange reaction of active species to monomers were a pair of competitors in this copolymerization system. Once the temperature was not so high (e.g., <100°C), chain-propagation reaction was more active than exchange reaction of active species to monomers; then, M_n was synchronously increased with respect to increasing temperature. The other way around was that exchange reaction of active species to monomers was easier to carry than chain-propagation reaction at high temperature, 115°C, for example; so, M_n declined and MWD broadened. The case carried in solvent was the same but better than in bulk copolymerization. Maybe the active species-monomers exchange reaction was not so high in solvent as in bulk copolymerization.

Another unexpected factor in this copolymerization was that M_n was not synchronously increased with reaction time and monomer conversion, which was different from PO homopolymerization with the same catalyst.¹³⁻¹⁵ We supposed that the chain-propagation reaction was more active than the exchange reaction of

TABLE II
Effect of Reaction Conditions on MA-PO Copolymerization

Temperature (°C)	Catalyst level (mg/kg)	Reaction time (h)	Conversion (%)	M_w/M_n	M_n
60 ^a	100	20	—	—	—
70 ^a	100	20	47.1	2.34	1968.4
85 ^a	80	16	63.7	1.54	2384.5
100 ^a	80	16	91.3	1.58	3021.9
115 ^a	80	12	97.8	2.03	2140.3
60	80	20	—	—	—
70	80	16	54.3	1.72	2240.9
80	80	16	73.5	1.66	2685.6
90	80	16	95.1	1.38	3363.6
100	80	14	98.2	1.42	2998.7
115	80	14	99.6	1.69	2677.8
90	40	20	—	—	—
90	60	16	59.2	1.76	2730.9
90	80	16	95.1	1.35	3363.6
90	100	16	98.2	1.68	2897.6
90	200	14	99.6	1.96	1321.5
90	400	14	99.6	2.23	787.8
90	80	6	—	—	—
90	80	8	21.5	1.72	2212.3
90	80	12	67.3	1.53	2675.5
90	80	16	95.1	1.35	3363.6
90	80	20	98.7	1.34	3378.8

Monomer charge MA/PO = 1 (mol), solvent; THF, total monomer concentration = 5 mol/L.

^a Polymerization without solvent.

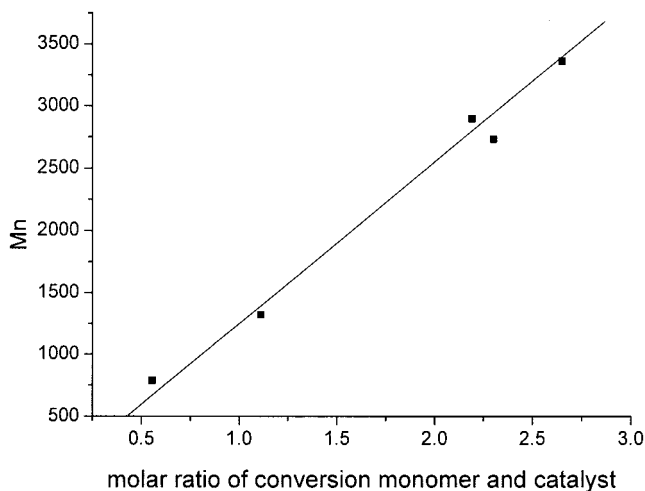


Figure 3 Dependence of M_n on molar ratio of conversion monomer and catalyst.

active species to monomers at initial stage of copolymerization, but the case was reversed at the upper stage. Possibly the tendency of active species on polymer chains to transfer to monomers was in direct proportion to the length of chain, so M_n was lower than 4000 in any copolymerization cases we carried, and MWD was also low.

Although M_n was not so high, and reaction time was somewhat long, beyond 16 h, the DMC complex was yet a highly active catalyst for MA–PO copolymerization. The catalytic activity on MA–PO copolymerization was quite higher than known catalytic systems, such as ROZnEt ,⁶ AlR_3 ,⁷ $\text{Mg}(\text{OEt})_2$,⁸ $\text{Fe-Al-}\alpha,\alpha'$ -dipyridyl catalyst,⁹ and rare earth complex.¹⁰ The catalytic efficiency of those catalysts was universally lower than 1 kg polymer/g catalyst, and that of DMC complex reached 10 kg polymer/g catalyst. It carried the copolymerization well when the catalyst level was 60 mg/kg; the higher the catalyst level was, the faster the copolymerization reaction and the higher the monomer conversion was given. Once the catalyst level was 100 mg/kg, after 16 h reaction, monomer conversion reached 98.2%, but M_n was, on the contrary, lower than that carried at catalyst level of 80 mg/kg. Further research on the relationship of catalyst level and M_n indicated that M_n was nearly linear with the molar ratio of conversion monomer and DMC catalyst, as shown in Figure 3.

Molar ratio of MA unit to PO unit in copolymer can be determined from peak area ratio of $\text{HC}=\text{CH}$ in MA and CH_3 in PO in $^1\text{H-NMR}$ spectrum. The result of the monomer charge molar ratio of MA and PO on yield and copolymer composition was listed in Table III. It showed that the copolymer was almost alternating when the monomer charge molar ratio $\text{MA/PO} \geq 1$. Because MA cannot polymerize itself by DMC complex, only two reactions, MA–PO alternating copoly-

merization and PO homopolymerization, happened in the reaction system. The molar ratio of MA unit to PO unit in copolymer was higher than the molar ratio of MA/PO in feed when the monomer charge molar ratio $\text{MA/PO} < 1$, so the active species of PO terminal was easier to react with MA than with PO. That is a precondition to carry an alternating MA–PO copolymerization.

Therefore, as discussed above, the DMC complex was an available catalyst for alternating MA–PO copolymerization.

Reactivity ratio of MA and PO in the reaction system

It is available to get the reactivity ratio of MA and PO in the reaction system by extended Kelen–Tudos equation¹⁶ at some high monomer conversion.

The extended Kelen–Tudos equation is as follows:

$$\eta = \left(r_1 + \frac{r_2}{\alpha} \right) \xi - \frac{r_2}{\alpha} \quad \eta = \frac{G}{\alpha + F} \quad \xi = \frac{F}{\alpha + F}$$

$$\alpha = (F_{\max} \times F_{\min})^{1/2} \quad G = \frac{Y - 1}{Z} \quad F = \frac{Y}{Z^2}$$

$$Z = \frac{\lg(1 - \xi_1)}{\lg(1 - \xi_2)} \quad \xi_2 = \frac{W(\mu + X)}{(\mu + Y)} \quad \xi_1 = \frac{\xi_2 Y}{X}$$

where X and Y are the molar ratio of monomer 1 (MA) and monomer 2 (PO) in feed and MA unit to PO unit in copolymer, respectively, W is weight conversion, μ is the molecular weight ratio of PO to MA. X , Y , and W were given in Table IV, so the other parameters can be obtained from the above equations. Because MA cannot be polymerized itself by DMC complex, $r_1(\text{MA}) = 0$ and the extended Kelen–Tudos equation was changed to $\eta = (r_2/\alpha)(\xi - 1)$. η is linear with ξ , so $r_2(\text{PO})$ can be given from the slope of the line, 0.286.

TABLE III
Effect of Monomer Charge Ratio of MA and PO on Copolymerization

PO/MA	Conversion (%)	M_w/M_n	M_n	Copolymer composition (%)	
				F_{MA}	F_{PO}
2	86.8	2.37	2981.8	38.0	62.0
3/2	85.6	1.98	2827.9	43.6	56.4
1	88.7	1.35	3063.9	48.7	51.3
2/3	60.3	1.49	2896.1	49.6	50.4
0.5	38.1	1.54	2968.3	50.1	49.9
0	—	—	—	—	—

Polymerization without solvent, temperature = $90 \pm 2^\circ\text{C}$, reaction time = 16 h, catalyst level = 80 mg/kg.

TABLE IV
Copolymer Composition at Different Monomer Charge Ratios

PO/MA	Conversion (%)	Copolymer composition (%)	
		F_{MA}	F_{PO}
2	15.7	41.3	58.7
3/2	16.3	44.2	55.8
1	20.2	46.4	53.6
2/3	6.8	48.0	52.0
0.5	5.0	50.1	49.9

Polymerization without solvent, temperature = 90 ± 2 °C, catalyst level = 80 mg/kg.

Kinetics of the copolymerization

Eight copolymerizations were carried with the same polymerization conditions at one time: molar ratio in feed MA/PO = 1, catalyst level of 80 mg/kg, 90°C, THF as solvent. The reaction was stopped at different times: then the relationship of polymer yield and reaction time was given, as shown in Figure 4. It took more than 16 h to complete the copolymerization, and the induction period was more than 6 h. We studied the relationship of conversion (c) and reaction time (t) before 16 h. $\ln 1/(1-c)$ was linear with t , as shown in Figure 5. Therefore, the copolymerization rate is first order with respect to monomer concentration.

CONCLUSION

DMC complex was, compared with other known catalytic systems, a highly active catalyst for copolymerization of MA and PO, giving high yield at a low catalyst

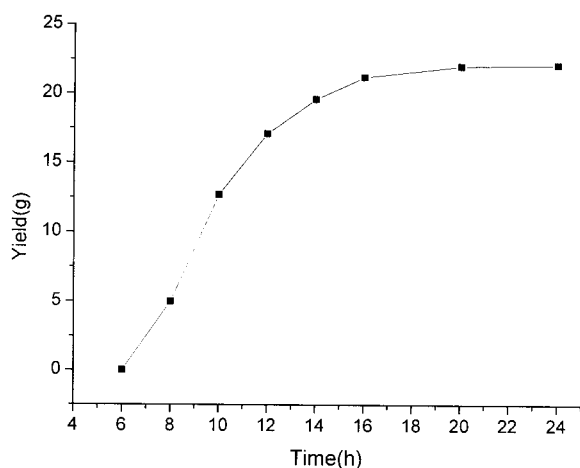


Figure 4 Dependence of copolymer yield on reaction time. Monomer charge MA/PO = 1 (mol); catalyst level = 80 mg/kg, temperature = 90 ± 2 °C, THF as solvent, total monomer concentration = 5 mol/L.

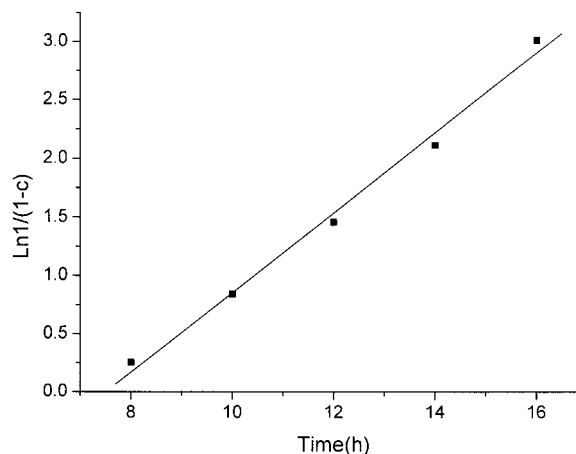


Figure 5 Dependence of monomer conversion on reaction time. Monomer charge MA/PO = 1 (mol), catalyst level = 80 mg/kg, temperature = 90 ± 2 °C, THF as solvent, total monomer concentration = 5 mol/L.

level of 80 mg/kg. The catalytic efficiency reached 10 kg polymer/g catalyst. Almost alternating copolymer was gained when monomer charge molar ratio MA/PO ≥ 1 . The copolymerization can also be carried out in many organic solvents; it was favorable to be carried in polar solvents such as THF and acetone. The proper reaction temperature carried in solvent was between 90 and 100°C. The reactivity ratio of MA and PO in this reaction system was given by the extended Kelen–Tudos equation at some high monomer conversion. The value of reactivity ratio $r_1(MA) = 0$ for MA cannot be polymerized itself by DMC complex, and $r_2(PO) = 0.286$. The kinetics of the copolymerization were studied. The results indicated that the copolymerization rate is first order with respect to monomer concentration.

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