

Kinetics of the Copolymerization of Alkylene Oxides with Glycidyl Methacrylate

Gulnare Ahmetli,¹ Ahmet Kocak,² Zafer Yazicigil²

¹Department of Chemical Engineering, Selcuk University, Campus, 42031 Konya, Turkey

²Department of Chemistry, Selcuk University, Campus, 42031 Konya, Turkey

Received 24 January 2007; accepted 1 May 2007

DOI 10.1002/app.27069

Published online 30 August 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: In the present study, the kinetics of copolymerization reaction of propylene oxide (PO) and butylene oxide (BO) with glycidyl methacrylate (GMA) in the presence of $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ catalyst were investigated. The kinetic parameters and activation energy of the copolymerization reaction were calculated. The amounts of reacting PO, BO, and GMA during copolymerization were determined by chromatographic method, because the same copolymerization conditions were carried out for them. It was determined that the copolymerization rate of PO (r_0) and BO (r_0) was

higher than that of GMA, but activation energy (E) of GMA was higher than that of PO and BO. The rate of reaction, the rate constant, and activation energy were calculated from the amount of copolymer obtained with respect to time. The structures of synthesized copolymers were determined by the spectral and chemical analysis methods. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 3710–3715, 2007

Key words: kinetics (polymer); copolymerization; alkylene oxides; glycidyl methacrylate

INTRODUCTION

The synthesis of oligomers having polyfunctional groups is one of the current subjects in polymer chemistry. As known from the literature, the unsaturated oligoesters are synthesized from the copolymerization of alkylene oxides (AOs) with anhydrides, chloroanhydrides, and esters of unsaturated monocarbonic acids.^{1–7} A novel copolymer containing chiral epoxy residues was prepared by free radical initiated copolymerization of glycidyl methacrylate with ethylene glycol dimethacrylate (GMA) in high yield.⁸

In our previous studies, the copolymerization of propylene oxide (PO) with GMA in the presence of the cationic catalyst was investigated and unsaturated oligomers were synthesized in high yields. The synthesized unsaturated oligomers (oligoesters including unsaturated ester groups) are used in the derivation of polymer materials having high adhesion properties and resistant to thermodestruction.⁹

But there are limited studies on the influence of different parameters on the kinetics of reactions with AOs and acrylates. In one of the earliest studies, Sorokin and Babkina studied copolymerization kinetics of butyl- and glycidyl methacrylate with methacrylic

acid.¹⁰ Kinetics of the copolymerization of glycidyl methacrylate and styrene were studied by Kochnov and Sorokin.¹¹

Effect of polar compounds on copolymerization of PO and tetrahydrofuran (THF) was studied by Komratov et al. It was found that propionaldehyde and sodium perchlorate have a marked effect not only on the kinetics of copolymerization of PO and THF initiated by BF_3 , but also on the molecular weight characteristics of the copolymer obtained.¹²

Using kinetic observations (polymerization of styrene and isoprene initiated by LiC_{12} , or of ethylene oxide by KC_{24}), Gole et al. showed that the propagation rate constants are slower than that in homogeneous media, and that the efficiency of the initiator depends on the kind of monomer or graphite and the influence of the diffusion phenomena in the interlayer spacing of the lamellar compound during the course of polymerization.¹³

Langlois et al. investigated the effect of *tert*-butyl acrylate/macromonomer molar ratio, the nature of the polylactic acid end group (acid or ester functionality), and the temperature on the kinetics of hydrolytic degradation.¹⁴

In this study, the reaction kinetics of the cationic copolymerization of PO and butylene oxide with GMA in the presence of $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ were investigated. Because of the structure and the activity of monomers, the amounts of reacting monomers during copolymerization were determined by chromatographic method. The rate, rate constant, and activation energy of each component in the copolymerization reaction with respect to the amount of

Correspondence to: G. Ahmetli (ahmetli@selcuk.edu.tr).

Contract grant sponsor: Selcuk University Scientific Research Foundation; contract grant number: 2005/05401034.

monomers obtained in the copolymerization reaction and time were calculated.


EXPERIMENTAL

Materials

Glycidyl methacrylate (GMA), propylene oxide (PO), butylene oxide (BO), dioxane as solvent, and cationic catalyst $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ were purchased from Merck (Darmstadt, Germany).

Measurements and analysis

The IR spectrums of synthesized copolymers films were recorded with UNICAM SP 1025 spectrometer.

Determination of epoxy group ()

To determine the percentage of the epoxy groups in PO-GMA and BO-GMA oligomers, the epoxy group in the sample was cleaved with an excess of HCl and then the remaining HCl was back titrated with KOH (0.1N).

The epoxy group was calculated by the following equation:

$$\text{Epoxy groups, \%} = (V_1 - V_2) \times 0.0043 \times 100/m$$

where V_1 is the volume of the added 0.1N KOH used for titration of control (mL), V_2 is the volume of the added 0.1N KOH used for titration of sample (mL), m is the amount of the sample analyzed (g), 0.0043 is the number of epoxy groups corresponding to 1 mL of 0.1N KOH.¹⁵

Determination of double bonds

The number of double bonds in oligomer was determined by titration method. The sample (0.2–0.4 g) in a stoppered-vial was dissolved in 15 mL of ethanol at 50–60°C. Twenty-five milliliters of an iodine solution (2.57 g iodine in 100 mL of ethanol) and 200 mL of water at 30–35°C was added to the afore-mentioned mixture. The mixture in stoppered-vial was sufficiently shaken and allowed to stand in the dark for 5 min. Then, the excess iodine was back-titrated with a solution of 0.1N $\text{Na}_2\text{S}_2\text{O}_3$, using starch indicator. In the same conditions, a control titration was also performed without sample. Titration was continued until the blue color of solution was disappeared. The iodine value (I.V.) was calculated using the following equation:

$$\% \text{I.V.} = \frac{(V_1 - V_2) \times 0.012697}{m} \times 100$$

where V_1 is the volume of 0.1N $\text{Na}_2\text{S}_2\text{O}_3$ used for control titration (mL), V_2 is the volume of 0.1N

$\text{Na}_2\text{S}_2\text{O}_3$ used for titration with sample (mL), 0.012697 is the amount of iodine corresponding to 1 mL of 0.1N $\text{Na}_2\text{S}_2\text{O}_3$ (g), and m is the amount of oligomer sample (g).

Determination of molecular weight

The molecular weights of the synthesized copolymers were determined via the gel chromatography method.

Kinetics of copolymerization reaction of PO and GMA with chromatographic method

The kinetics of copolymerization reaction of PO with GMA in the presence of catalyst $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ in dioxane solution at a constant temperature in the reaction, which has closed system and used magnetic mixer under the dry nitrogen atmosphere, was investigated. The rate of the copolymerization reaction (r_0), the rate constant (k), and activation energy (E) were observed.

Hundred milliliters of dioxane was added to the reactor, which was put in thermostat; the temperature of the medium was decreased to 0°C (273 K); they were solved in the medium of dry nitrogen by mixing 2.9 g (0.05 mol) of PO and 7.1 g of (0.05 mol) GMA. After 0.142 g (0.001 mol) $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ catalyst was added to the mixed reaction solution, at zero time and regular time intervals (10 min), 1 mL aliquot was withdrawn from the reaction mixture, and the amounts of PO and GMA in the reaction were calculated with chromatographic methods. The copolymerization kinetics was investigated due to the amount of PO and GMA in the reaction.

The rate of copolymerization reaction r_0 ($\text{mol L}^{-1} \text{s}^{-1}$) with respect to PO and GMA was calculated from the graph of mol/L amount of PO and GMA in the copolymerization reaction versus time. From the rate of the reactions PO and GMA at a constant temperature, rate constant (k) was calculated. For this reason, at different temperatures, the rates of the reaction were observed and the activation energy of the reaction [E (cal)] was estimated by the graph method from the rate constant ($-\log k$).

The copolymerization kinetics of BO with GMA in the presence of $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ was investigated by the same method and kinetic parameters were determined.

RESULTS AND DISCUSSION

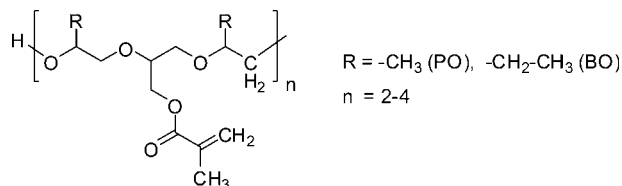
Chemical structures of unsaturated oligomers were determined via IR spectrum of oligomers. In the IR spectrum, characteristic bands appeared in the regions of 1620 and 1635 cm^{-1} for $\text{C}=\text{C}$, 1700

TABLE I
The Effect of the Copolymerization Conditions to the Molecular Mass Distributions of the Unsaturated Oligomers

AO : GMA mol ratio	BF ₃ ·O (C ₂ H ₅) ₂ (mol)	T (K)	M _w		M _n		M _w /M _n	
			I	II	I	II	I	II
3 : 1	0.010	273	930	840	520	470	1.78	1.79
3 : 1	0.010	268	860	780	500	450	1.73	1.73
1 : 1	0.010	273	787	700	455	410	1.72	1.70
3 : 1	0.005	273	540	490	370	300	1.46	1.63
1 : 2	0.010	273	620	530	390	330	1.59	1.60
3 : 1	0.010	283	1050	970	600	500	1.75	1.84

I: with PO and GMA; II: with BO and GMA.

and 1735 cm⁻¹ for C=O, and 1065 cm⁻¹ for -C-O-C-.



As it was seen from the determination of the molecular mass distribution of the synthesized unsaturated oligomers via gel chromatographic method, molecular weight of the oligomers changed between $M_n = 370$ and 520 , and $M_w = 540$ and 930 due to the amount of catalyst and mol ratio of the PO and GMA used in the copolymerization at low temperature (273 K). When the temperature was increased to 10°C, molecular weights were determined as $M_n = 600$; $M_w = 1050$ at 283 K (Table I).

The similar results were obtained from copolymerization of BO with GMA under same reaction conditions. However, molecular weights ($M_w = 840$ – 970) of unsaturated oligomers, obtained from the copolymerization of BO with GMA, were less than those of oligomers ($M_w = 930$ – 1050), obtained from the copolymerization of PO with GMA (Table I).

The copolymerization kinetics of AOs with GMA in the presence of catalyst BF₃·O(C₂H₅)₂ were investigated with the chromatographic methods according to the amount of components in the reaction at the following conditions: for [AO]₀ 0.25–1.50 mol/L, for [GMA]₀ 0.5–1.0 mol/L, and for [BF₃·O(C₂H₅)₂]₀ 0.005–0.020 mol/L at 268–283 K. The results of copolymerization reaction kinetic, which was made between monomers having different nature (PO, BO, and GMA) in the presence of BF₃·O(C₂H₅)₂ catalyst, were demonstrated in Tables II and III and Figures 1 and 2.

As was seen in Table II and Figure 1, the copolymerization rate of PO increased from 2.7×10^{-5} to

TABLE II
Copolymerization Reaction Kinetics of PO with GMA in the Presence of BF₃·O(C₂H₅)₂ Catalyst

[PO] ₀ (mol/L)	[GMA] ₀ (mol/L)	[BF ₃ ·O(C ₂ H ₅) ₂] ₀ (mol/L)	T (K)	r ₀ (×10 ⁵ mol L ⁻¹ s ⁻¹)	
				PO	GMA
0.25	0.5	0.010	273	2.74	1.0
0.50	0.5	0.010	273	7.4	1.9
1.00	0.5	0.010	273	16.6	2.4
1.50	0.5	0.010	273	22.4	4.1
1.50	1.0	0.010	273	15.7	2.1
1.50	0.5	0.005	273	13.3	2.5
1.50	0.5	0.020	273	40.7	10.0
1.50	0.5	0.010	268	16.7	2.9
1.50	0.5	0.010	283	28.8	6.0

k (×10⁴ L mol⁻¹ s⁻¹)

	268 K	273 K	283 K	E (kJ/mol)
PO	2.23	3.06	3.84	22.36
GMA	0.22	0.55	0.80	53.50

22.4×10^{-5} mol L⁻¹ s⁻¹ and the copolymerization rate of GMA increased from 1.0×10^{-5} to 4.1×10^{-5} mol L⁻¹ s⁻¹ when [PO]₀ increased from 0.25 to 1.50 mol/L under the reaction conditions $T = 273$ K, [BF₃·O(C₂H₅)₂]₀ = 0.010 mol/L. The copolymerization rate of BO with GMA was less than that of PO under same conditions, and the copolymerization rate of BO ranges from 1.83×10^{-5} to 18.45×10^{-5} mol L⁻¹ s⁻¹ and that of GMA ranges from 0.96×10^{-5} to 3.40×10^{-5} mol L⁻¹ s⁻¹.

The copolymerization rate of PO ranges from 13.3×10^{-5} to 40.7×10^{-5} mol L⁻¹ s⁻¹ and the copoly-

TABLE III
Copolymerization Reaction Kinetics of BO with GMA in the Presence of BF₃·O(C₂H₅)₂ Catalyst

[BO] ₀ (mol/L)	[GMA] ₀ (mol/L)	[BF ₃ ·O(C ₂ H ₅) ₂] ₀ (mol/L)	T (K)	r ₀ (×10 ⁵ mol L ⁻¹ s ⁻¹)	
				BO	GMA
0.25	0.5	0.01	273	1.83	0.96
0.50	0.5	0.01	273	5.76	1.87
1.00	0.5	0.01	273	12.30	2.10
1.50	0.5	0.01	273	18.45	3.40
1.50	1.0	0.01	273	12.16	3.60
1.50	0.5	0.005	273	11.75	2.00
1.50	0.5	0.02	273	30.15	8.20
1.50	0.5	0.01	268	12.15	2.30
1.50	0.5	0.01	283	23.41	4.25

k (×10⁴ L mol⁻¹ s⁻¹)

	268 K	273 K	283 K	E (kJ/mol)
BO	1.59	2.45	3.11	30.88
GMA	0.31	0.45	0.56	36.74

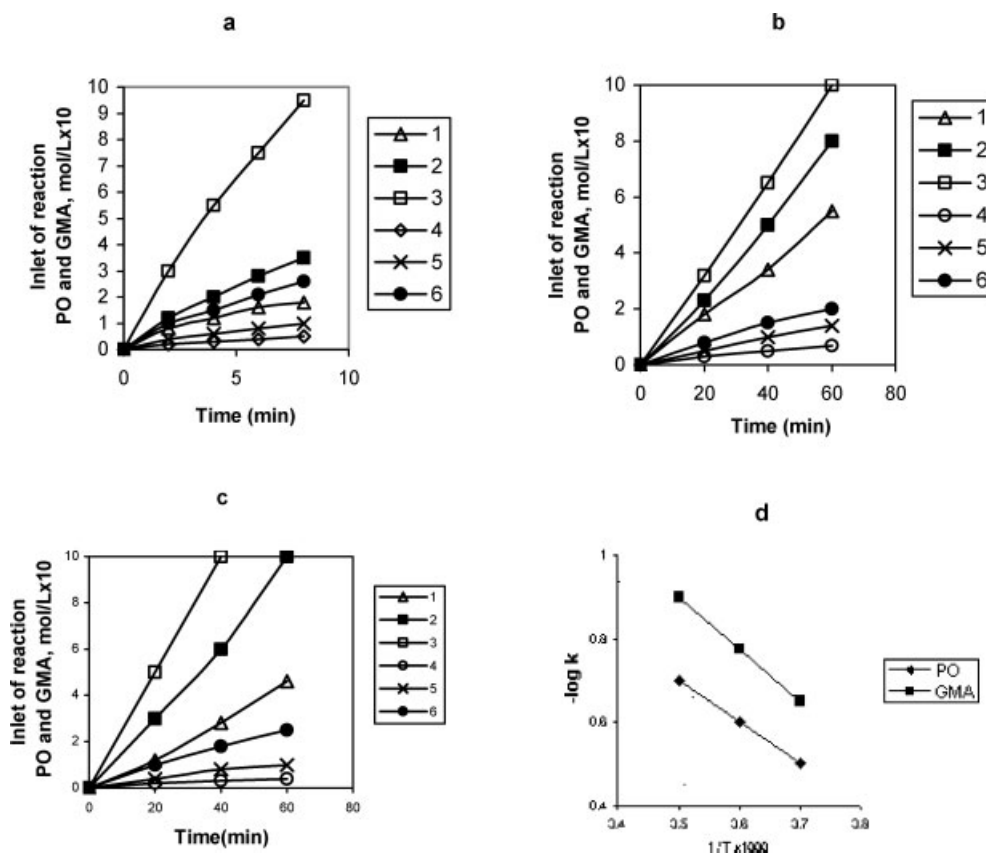


Figure 1 (a–c) Copolymerization kinetics of PO with GMA in the presence of $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ catalyst; Curves 1–3 for PO; Curves 4–6 for GMA. (a) The effect of PO and GMA mol ratio: $T = 273$ K; $[\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2]_0 = 0.01$ mol/L; PO : GMA = 0.5 : 1.0 (1 and 4); 1 : 1 (2 and 5); 3 : 1 (3 and 6). (b) The effect of temperature: $[\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2]_0 = 0.01$ mol/L; PO : GMA = 1.5 : 0.5; $T = 268$ K (1 and 4); 273 K (2 and 5); 283 K (3 and 6); (c) The effect of $[\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2]_0$: $T = 273$ K; PO : GMA = 1.5 : 0.5; $[\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2]_0 = 0.005$ mol/L (1 and 4); 0.01 mol/L (2 and 5); 0.02 mol/L (3 and 6). (d) A graph of $-\log k$ versus $(1/T) \times 10^3$ ($T =$ temperature).

merization rate of GMA ranges from 2.5×10^{-5} to 10.0×10^{-5} mol L^{-1} s^{-1} , when $[\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2]_0$ increased from 0.005 to 0.020 mol/L in the medium of reaction. Consequently, the reaction rate of PO with GMA was higher than that of BO with GMA under same reaction conditions.

The optimum reaction conditions for the copolymerization of AO with GMA obtained according to results presented in Figures 1 and 2 and Tables II and III are the following: $[\text{AO}]_0$: 1.50 mol/L; $[\text{GMA}]_0$: 0.50 mol/L; $[\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2]_0$: 0.020 mol/L; T : 273 K.

The rate constants (k) for the copolymerization reaction of AOs with GMA was calculated by using following equation at 268–283 K, as shown in Tables II and III.

$$r_0 = [\text{AO}]_0 [\text{GMA}]_0 [\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2]_0$$

The activation energy of the copolymerization reaction was calculated by plotting $-\log k$ versus $(1/T) \times 10^3$. The activation energy of the reaction was calculated as 22.36 kJ/mol for PO and 53.50 kJ/

mol for GMA from the slope (Table II and Fig. 1). As it is shown in Table II and Figure 1, the activation energy of PO is 2.5 times lower than that of GMA. Because of the structure of PO, it has more reaction ability than GMA in the copolymerization reaction.

The activation energy of the copolymerization of PO with GMA ($E = 22.36$ kJ/mol) was lower than that of copolymerization of BO with GMA ($E = 30.88$ kJ/mol). Namely, it was determined that the copolymerization reaction with PO was faster than copolymerization reaction with BO.

As seen from the obtained results that the copolymerization reaction of AOs with GMA at the same kinetic conditions, the copolymerization reaction rate (r_0) and reaction rate constant (k) of the AO is higher about 4 and 10 times than that of GMA, respectively. In order to obtain the best yield, optimum conditions were determined. These conditions: mol ratio of AO : GMA is 3 : 1, temperature is 273 K and amount of catalyst is 0.01 mol.

The kinetic parameters of both reactions were determined to be obeying the same kinetic order in

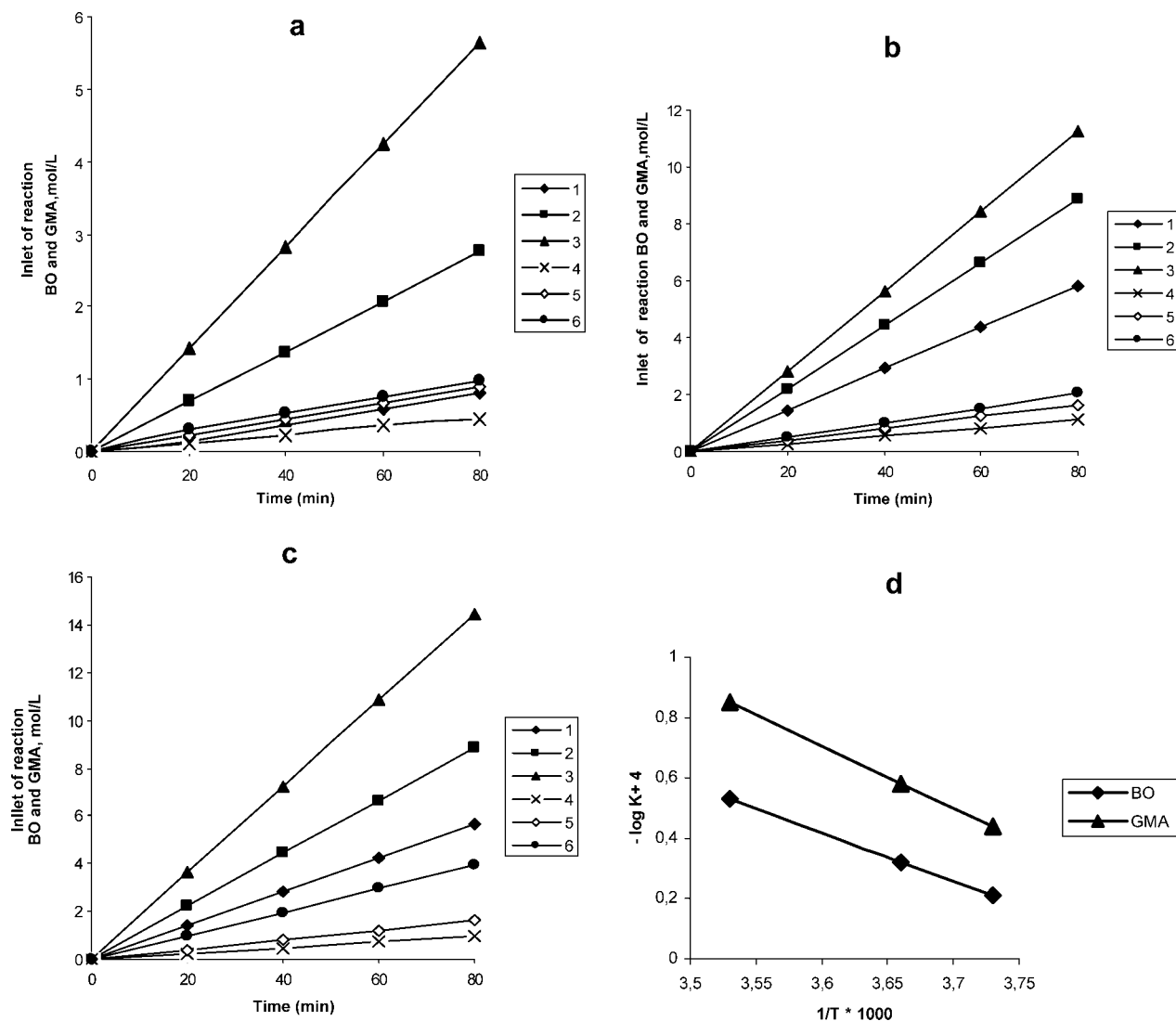
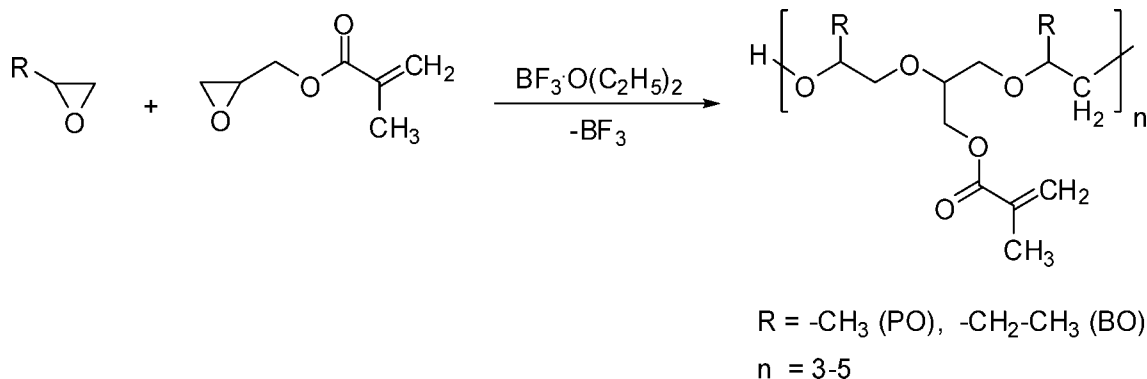


Figure 2 (a–c) Copolymerization kinetics of BO with GMA in the presence of $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ catalyst; Curves 1–3 for BO; Curves 4–6 for GMA. (a) The effect of BO and GMA mol ratio: $T = 273 \text{ K}$; $[\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2]_0 = 0.01 \text{ mol/L}$; BO : GMA = 0.5 : 1.0 (1 and 4); 1 : 1 (2 and 5); 3 : 1 (3 and 6). (b) The effect of temperature: $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2]_0 = 0.01 \text{ mol/L}$; BO : GMA = 1.5 : 0.5; $T = 268 \text{ K}$ (1 and 4); 273 K (2 and 5); 283 K (3 and 6). (c) The effect of $[\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2]_0$: $T = 273 \text{ K}$; BO : GMA = 1.5 : 0.5; $[\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2]_0 = 0.005 \text{ mol/L}$ (1 and 4); 0.01 mol/L (2 and 5); 0.02 mol/L (3 and 6). (d) A graph of $-\log k$ versus $(1/T) \times 10^3$ ($T = \text{temperature}$).



Scheme 1 Copolymerization reaction of PO and BO with GMA in the presence of catalyst $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$.

spite of the differences of kinetic parameters. The structure of unsaturated oligomers was determined by using chemical and spectral analysis methods. The copolymerization of PO and BO with GMA in the presence of $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ catalyst occurred not only as a result of the peaks of unsaturated oligomers in the IR spectrums, but also as a result of determined low amount of epoxy groups and high amount double bonds in the structure of oligomers via chemical analysis methods. The amount of epoxy groups and double bonds in oligomers were 7.3% and 15.4% for PO-GMA, and 3.23% and 20.68% for BO-GMA, respectively.

This caused the synthesis of unsaturated oligomers, which has the following structure, via ring-opening copolymerization of the epoxide cycles of both monomers (Scheme 1).

CONCLUSIONS

In the determination of kinetic parameters of copolymerization reaction of PO, BO, and GMA that is certified in $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ as a catalyst, it is seen that PO is faster in the copolymerization reaction and less activation energy was consumed for the copolymerization reaction. It was determined that the copolymerization reaction rate (r_0) and reaction rate constant (k) of copolymerization for PO and BO were 4

and 10 times more, respectively, while their activation energy were 2.5 times lower than that of GMA's under same cationic copolymerization conditions.

References

1. Grigorovskaya, B.; Begun, B.; Tixomirov, N.; Tugov, I. *J Plastmassy* 1991, 2, 51.
2. Bulai, A.; Slonim, I.; Filippenko, D.; Khrenova, N. *Polym Sci USSR* 1988, 30, 8, 1874.
3. Chen, S.; Zhang, P.; Chen, L. *Prog Org Coat* 2004, 50, 4, 269.
4. Maeda, Y.; Nakayama, A.; Kawasaki, N.; Hayashi, K.; Aiba, S.; Yamamoto, N. *Polymer* 1997, 38, 18, 4719.
5. Penchek, P.; Valchak, E.; Smolovik, E. *J Plastmassy* 1977, 6, 11.
6. Zak, A.; Gorin, Y.; Rogina, E. *Zh Prikl Khim* 1980, 11, 2623.
7. Aliyev, S.; Vezirov, Sh.; Zeynalova, E.; Bagirova, Sh. *USSR Pat.* 1,439,110 (1988).
8. Rolland, A.; Heralut, D.; Touchard, F.; Saluzzo, C.; Duval, R.; Lemaire, M. *Tetrahedron* 2001, 12, 811.
9. Vezirov, Sh.; Aliyev, S.; Ibragimova, M.; Ahmetli, G. *USSR Pat.* 1,740,377 (1994).
10. Sorokin, M.; Babkina, M. *Polym Sci USSR* 1967, 9, 1012.
11. Kochnov, I.; Sorokin, M. *Polym Sci USSR* 1965, 7, 2100.
12. Komratov, G.; Barzykina, R.; Korovina, G. *Polym Sci USSR* 1980, 22, 2571.
13. Gole, J.; Merle, G.; Pascault, J. P. *Synth Met* 1982, 4, 269.
14. Langlois, V.; Vallee-Rehel, K.; Peron, J.; le Borgne, A.; Walls, M.; Guerin, Ph. *Polym Degrad Stabil* 2002, 76, 411.
15. Ahmetli, G.; Kocak, A.; Sen, N.; Kurbanli, R. *J Adhes Sci Technol* 2006, 20, 1431.