

Polymerization of Tetrahydrofuran Initiated by Heteropolyacid in the Presence of Substituted Oxirane

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Received 2 September 1999; accepted 14 January 2000

ABSTRACT: Both propylene oxide and epichlorohydrin could effectively promote the polymerization of tetrahydrofuran initiated with a heteropolyacid, $H_3PW_{12}O_{40}$, in low concentration. Water or butylene glycol was used to control the molecular weight of the product in the range of 1000–3000. The promotion activity of propylene oxide was similar to that of ethylene oxide and better than that of epichlorohydrin, especially when water was introduced. The polymerization started upon addition of propylene oxide or epichlorohydrin. After the polymerization stopped, it could be reinitiated with the addition of a new portion of propylene oxide or epichlorohydrin. The products were found to be copolyether glycol with hydroxyl groups at both ends. The melting point of the polymer obtained by using propylene oxide promoter was about 20°C lower than that of polytetramethylene ether glycol having the same molecular weight. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 3239–3246, 2000

Key words: tetrahydrofuran; heteropolyacid; propylene oxide; epichlorohydrin; polymerization promoter

INTRODUCTION

In the last decade, heteropolyacids (HPAs), as a new kind of cationic polymerization initiators, which are easily available, not particularly corrosive, recoverable, and reusable, have drawn extensive attentions.^{1–6} However, the initiation activity of HPA for tetrahydrofuran (THF) polymerization is low.^{1–3} When the concentration of HPA is low, very long polymerization time is needed, and the molecular weight of the product is much higher than that of commercial products.¹

In order to promote the initiation activity, in the previous article,⁷ a small amount of ethylene oxide (EO) was introduced into the polymerization system. EO could effectively promote THF

polymerization initiated by $H_3PW_{12}O_{40}$ (PW_{12}) in low concentration, the molecular weight of the product could be controlled in the range of 1000–3000 by varying the concentration of water or low molecular weight diol, and the yield reached 50–70% per cycle. In the present article, we continued the study on the substituted oxirane promoters, that is, propylene oxide (PO) and epichlorohydrin (ECH), which can be manipulated and stored more conveniently than EO, because of their higher boiling temperatures. In addition, from the methyl group of PO and the chloromethylene group of ECH, we can obtain more structure information of products in the spectra of nuclear magnetic resonance.

EXPERIMENTAL

Materials

THF (AR grade, ≥ 99.5) was dried by refluxing over sodium metal and diphenylketone until the

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Contract grant sponsor: Doctoral Program Foundation of Chinese Institution of High Education.

Journal of Applied Polymer Science, Vol. 77, 3239–3246 (2000)
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Table I Determination of *K* Values for Copolyethers

No.	Content of Oxirane Moieties in Copolyether (mol %)	$\bar{M}_{n(s)}$ ($\times 10^{-3}$)	$\bar{M}_{n(NMR)}^a$ ($\times 10^{-3}$)	$\bar{M}_{n(VPO)}$ ($\times 10^{-3}$)	<i>K</i> ^b
PO					
1	14.2	4.73	2.16		0.46
2	14.9	3.40	1.71	1.70	0.50
3	15.1	3.57	1.78	1.76	0.50
4	15.6	5.78	2.75		0.48
5	12.3	5.88	2.85		0.48
6	15.6	2.90	1.52	1.50	0.51
7	15.4	2.97	1.52	1.49	0.51
					0.49 ^c
ECH					
8	7.3	2.21	1.11	1.06	0.49
9	6.8	2.79	1.39		0.50
10	7.0	3.44	1.72		0.50
11	9.6	2.93	1.45	1.54	0.51
12	8.9	3.19	1.62	1.60	0.50
					0.50 ^c

^a Calculated from ¹H-NMR spectrum shown in Figures 3 and 4.

^b $K = \bar{M}_{n(NMR)}/\bar{M}_{n(s)}$ or $\bar{M}_{n(VPO)}/\bar{M}_{n(s)}$.

^c Mean value of *K*.

color of the liquid became blue and then distilled. EO ($\geq 98\%$) was used as received. PO (AR grade, $\geq 99\%$) and ECH (AR grade, $\geq 95\%$) were distilled over CaH₂. Butylene glycol (BG; AR grade) was dried over 5-Å molecular sieves and distilled at reduced pressure. H₃PW₁₂O₄₀ · nH₂O was obtained from Chemistry Institute of Henan and heated at 300°C for 3 h before use.

Polymerization

Oxirane and water or BG were added into a three-necked flask containing THF, which had been cooled to 0–2°C. Subsequently the anhydrous PW₁₂ was added with stirring. At the end of the reaction, 0.5*N* NaOH (aq) in sixfold of moles of PW₁₂ was added to terminate the polymerization. After unreacted THF was evaporated off, and the colorless product was extracted with toluene, washed with water, and dried in vacuum for 4 h at 110°C.

Analysis

¹H-NMR spectra were recorded at room temperature on a Bruker (Billerica, MA) ARX-400 NMR spectrometer (measured at 400 MHz) with CDCl₃ as solvent.

The number-average molecular weight of copolymer, $\bar{M}_{n(VPO)}$, was determined in acetone at

37°C on a vapor pressure osmometer Knauer-VPO_(German) that was calibrated with sucrose octaacetate and for each sample four concentrations of polyether glycol were used in the range of 10–110 g/kg (acetone).

Number-average molecular weight $\bar{M}_{n(s)}$ and molecular weight distribution index \bar{M}_w/\bar{M}_n (\bar{M}_w is weight-average molecular weight and \bar{M}_n is number-average molecular weight) of the copolyether were determined at 35°C by gel permeation chromatography on Waters Associates (Milliford, MA) Model HPLC/GPC 515 liquid chromatography, equipped with a refractive index detector, HT2+HT3+HT4μ–Styragel columns and calibrated with standard polystyrene, using THF as the eluent and a flow rate of 1.0 mL/min. The number-average molecular weight of copolyether, $\bar{M}_{n(gp\bar{c})}$, was evaluated from $\bar{M}_{n(s)}$ by the equation: $\bar{M}_{n(gp\bar{c})} = K\bar{M}_{n(s)}$, where *K* is a constant.⁸ By analysis of the products containing PO moieties around 12.3–15.6 mol %, we determined the conversion factor *K* to be 0.49 for $\bar{M}_{n(s)}$ in the range of 2.9–5.9 × 10³ (as shown in Table I). The conversion factor *K* of products containing ECH moieties about 6.8–9.6 mol % was 0.50 for $\bar{M}_{n(s)}$ in the range of 2.2–3.5 × 10³.

The melting point (*T*_m) and glass transition temperature (*T*_g) of copolymer were measured on a TA Instruments differential scanning calorime-

Table II Polymerization of THF Initiated by PW₁₂ in the Presence of PO or ECH

No.	Polymerization Condition ^a			Conversion (%)	$\bar{M}_{n(gpc)}$ ($\times 10^{-3}$)	\bar{M}_w/\bar{M}_n
	[oxirane] (mol L ⁻¹)	[H ₂ O]/[PW ₁₂] (molar ratio)	Time (h)			
PO						
1	1.00	0	2	31.3	9.31	2.13
2	1.00	0	4	69.5	9.70	1.52
3	1.00	0	5	79.2	11.1	1.52
4	1.00	10	4	69.9	6.32	1.55
5	1.00	15	4	65.8	5.29	1.60
6	1.00	30	3	57.0	3.02	1.56
7	1.00	30	4	58.0	3.28	1.55
8 ^b	1.00	30	6	58.7	2.83	1.48
9 ^b	1.00	30	7	60.3	2.88	1.47
10	1.14	30	4	57.7	2.32	1.52
11	1.14	30	5	60.8	2.46	1.47
12	0.57	10	4	51.7	3.61	1.59
13	0.57	10	5	53.1	4.05	1.56
ECH						
14	1.00	0	4	62.0	8.85	1.71
15	1.00	10	4	56.4	4.61	1.48
16	1.00	10	6	69.2	5.30	1.54
17	1.00	10	8	75.2	8.55	1.54
18	1.00	15	4	28.5	2.18	1.56
19	1.00	15	5	40.0	2.32	1.65
20	1.00	15	6	49.6	2.49	1.55
21 ^c	1.00	5	3.5	82.0	4.50	1.76
22 ^c	1.00	15	5	74.6	2.35	1.55
23 ^c	1.00	15	6	85.0	2.59	1.55
24 ^c	1.00	20	6	49.7	1.60	1.42

^a Bulk polymerization at 0–2°C, [PW₁₂] = 6.14 × 10⁻³ mol L⁻¹.

^b BG was used instead of water.

^c [PW₁₂] = 1.54 × 10⁻² mol L⁻¹.

ter (Model 2010; New Castle, DE) at a temperature elevation speed of 10°C/min.

RESULTS AND DISCUSSION

Promotion Effect of PO and ECH on the Polymerization

It can be seen from Table II, that both PO and ECH are effective promoters for the polymerization of THF initiated with PW₁₂ in low concentration (PW₁₂/THF = 0.02 or 0.05 by weight). High conversion could be obtained in 4–5 h (see Nos. 2, 3, and 14 in Table II), in comparison with the 500-h reaction time that was needed as reported in the literature.¹

By introducing and adjusting the amount of water or diol in the polymerization system, the

molecular weight of the polymer could be controlled in the range of 600–3000. The conversion could reach around 60% after 4–7 h polymerization (see Nos. 8–11 and 22 and 23 in Table II), in comparison with <35% conversion when as high as PW₁₂/THF = 0.5 (by weight) was used without oxirane promoter.⁹

Effect of Water on the Promotion Activities of EO, PO, and ECH

From Figure 1 it can be seen that with increasing the amount of water, which was used as the molecular weight controller, the conversion of the polymerization decreased, especially for ECH-promoted polymerization. There are two probable factors that may cause the significant decrease of the promotion activity of ECH: whether a slow

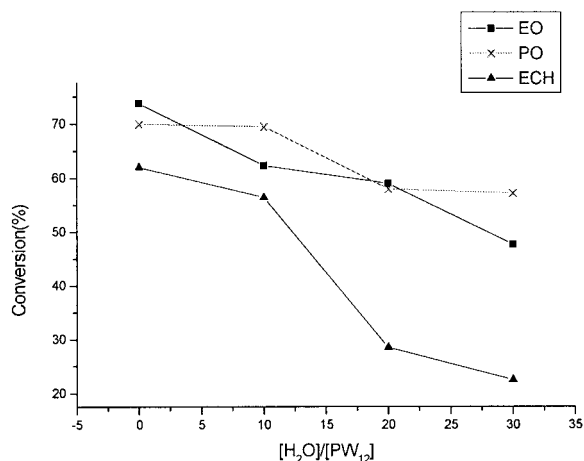


Figure 1 Effect of water on the conversion of THF polymerization in the presence of promoter at 0°C $[PW_{12}] = 6.14 \times 10^{-3} \text{ mol L}^{-1}$, $[EO] = [PO] = [ECH] = 1.00 \text{ mol L}^{-1}$.

rate of initiation or a slow rate of propagation. In order to ascertain which factor is the determining one, we did the kinetic study.

In Figure 2, the slopes of the two kinetic straight lines are nearly the same. The values of rate constant of propagation (k_p) could be calculated according to the equation of chain propagation reaction¹⁰ [Eq. (1)] on the assumption of concentration of propagating species $[P^*] = 3[PW_{12}]$ to be quite close to each other, that is 5.73×10^{-3} and $5.54 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$ for the polymerization promoted by PO and ECH, respectively, with an introduced amount of water $[H_2O] = 10[PW_{12}]$. Thus, the propagation rate did not decrease when water was introduced:

$$\ln \frac{[THF]_0 - [THF]_e}{[THF]_t - [THF]_e} = \int_0^t k_p [P^*] dt \quad (1)$$

where $[THF]_0$, $[THF]_t$ and $[THF]_e$ are the concentration of time = 0, t , and equilibrium (to be 1.70 mol/L)^[11], respectively.

However, the line for ECH promoter in Figure 2 showed an induced period. During this period the polymerization rate was slow, and the propagating species concentration $[P^*]$ gradually increased until $[P^*] = 3[PW_{12}]$. Therefore, the decrease in the promotion activity of ECH must be caused mainly by the slow rate of propagating species formation, that is, by the slow rate of initiation. Considering the weaker basicity of ECH with respect to that of EO or PO, the protons

from PW_{12} reacted with ECH relatively slowly and faced the competition reaction with water and diol derived from ECH and water.¹² Moreover, the protonated ECH, as pointed out by Okamoto¹² in the study on ECH homopolymerization with the presence of a diol, reacts much faster with the diol than with ECH monomer itself. Therefore, it is reasonable to say that in our polymerization system once the protonated ECH species formed, they should evade the attack of water and diol, even in a small amount, to react with THF, resulting in the formation of propagating chain.¹⁰ So an induced period of initiation is needed to give rise to $[P^*] = 3[PW_{12}]$ and is the determining factor leading to the significant decrease in the promotion activity of ECH, especially when water was introduced.

Dormancy and Reinitiation of the THF Polymerization in the Presence of PO or ECH

In previous article¹⁰ we have reported that the polymerization of THF initiated by PW_{12} in low concentration did only proceed in the presence of promoter EO, and the propagating chains did not terminate after the complete consumption of EO, but transformed into dormant species. The reaction behavior for PO or ECH promoter is similar to that of EO. After the polymerization stopped, it could be re-initiated by the addition of a further portion of PO or ECH (Table III).

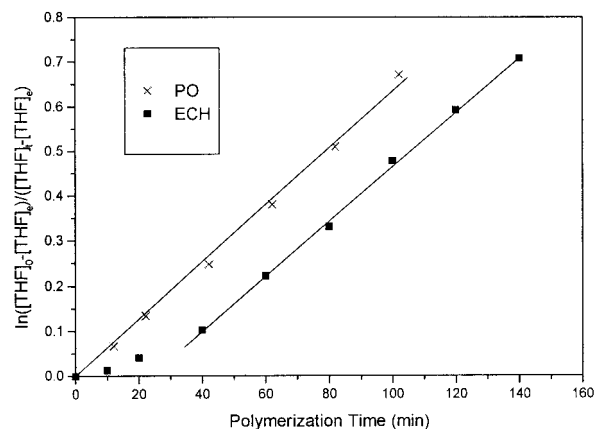


Figure 2 Kinetics of the bulk polymerization of THF initiated with PW_{12} in the presence PO or ECH at 0–2°C. $[PW_{12}] = 6.14 \times 10^{-3} \text{ mol L}^{-1}$, $[H_2O]/[PW_{12}] = 10$, $[PO] = [ECH] = 0.50 \text{ mol L}^{-1}$, $[THF]_e = 1.7 \text{ mol L}^{-1}$.¹¹

Table III Polymerization of THF with Stepwise Addition of Oxirane

No.	Polymerization Condition ^a			Conversion (%)	$\bar{M}_{n(gpc)}$ ($\times 10^{-3}$)	\bar{M}_w/\bar{M}_n
	[oxirane] (mol L ⁻¹)	[H ₂ O]/[PW ₁₂] (molar ratio)	Time (h)			
PO						
1	0.57	35	6	41.6	1.99	1.50
2	0.57	35	10	41.7	2.03	1.49
3	0.57	35	48	41.5	2.06	1.50
4	No. 3 +0.57	–	6	85.2	2.52	1.51
5	0.28	15	24	24.2	1.98	1.54
6	No. 5 +0.14	–	24	34.9	1.87	1.54
ECH						
7	0.50	35	6	13.0	1.17	1.47
8	0.50	35	10	21.6	1.29	1.37
9	0.50	35	24	60.0	1.90	1.60
10	0.50	35	48	61.3	1.76	1.57
11	No. 10 +0.50	–	6	86.4	2.09	1.51
12 ^b	0.50	20	24	68.5	2.06	1.47
13 ^b	No. 12 +0.50	–	24	87.4	2.12	1.45

^a Bulk polymerization at 0–2°C, [PW₁₂] = 6.14 × 10⁻³ mol L⁻¹.

^b [PW₁₂] = 1.54 × 10⁻² mol L⁻¹.

Characterization of the Copolyethers

According to ¹H-NMR spectrum and VPO analysis, the hydroxyl end-group functionality (\bar{f}) of products is close to 2.0 as shown in Table IV.

Spectral assignments of a typical ¹H-NMR spectrum of the product composed of THF and PO moieties by spin-decoupling technique are shown in Figure 3. H(a): 5.27 ppm; H(b): 4.38 ppm; H(c):

Table IV Average Hydroxyl End-Group Functionality (\bar{f}) of Products

No.	Polymerization Condition ^a			Conversion (%)	$\bar{M}_{n(VPO)}$ ($\times 10^{-3}$)	$\bar{M}_{n(NMR)}$ ($\times 10^{-3}$) ^b	\bar{f}^c
	[oxirane] (mol L ⁻¹)	Time (h)	[H ₂ O]/[PW ₁₂] (molar ratio)				
PO							
1 ^d	1.00	6	60	38.0	1.50	1.52	1.97
2 ^d	1.00	7	60	38.3	1.49	1.52	1.96
3 ^e	0.57 × 2	4	30	47.0	1.70	1.71	1.99
4 ^e	0.57 × 2	6	30	56.9	1.76	1.78	1.98
5	1.14	4	30	57.7	2.10	2.16	1.94
ECH							
6 ^f	1.00	7	30	16.5	1.06	1.11	1.91
7 ^f	1.00	5	20	33.6	1.54	1.45	2.12
8 ^f	1.00	6	20	49.7	1.60	1.62	1.98

^a Bulk polymerization at 0–2°C, [PW₁₂] = 6.14 × 10⁻³ mol L⁻¹.

^b Calculated from ¹H-NMR spectrum shown in Figures 3 and 4.

^c $\bar{f} = \bar{M}_{n(VPO)}/[\bar{M}_{n(NMR)}/2] = [\bar{M}_{n(VPO)}/\bar{M}_{n(NMR)}] \times 2$.

^d BG was used instead of water.

^e PO was divided into two parts, and the second part was added after 2 h after the first one was introduced.

^f [PW₁₂] = 1.54 × 10⁻² mol L⁻¹.

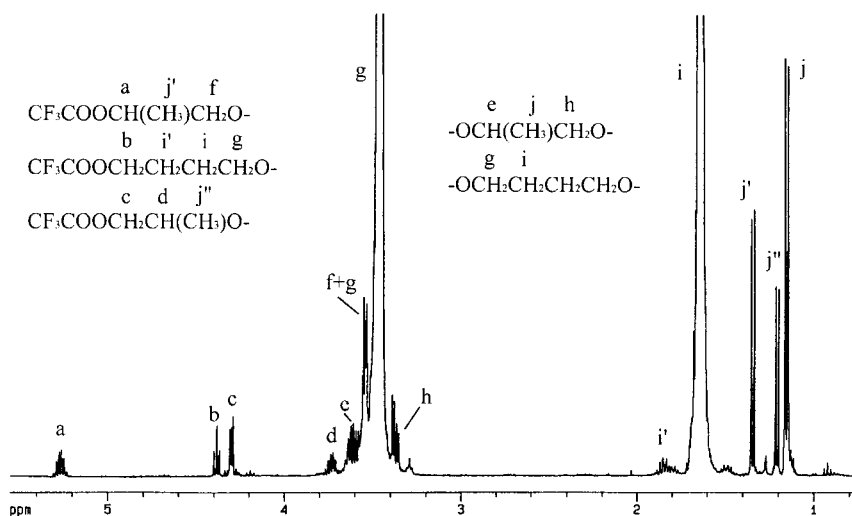


Figure 3 $^1\text{H-NMR}$ chemical shift assignments of copolyether after esterifying with $(\text{CF}_3\text{CO})_2\text{O}$ (Run No. 2 in Table V).

4.30 ppm; H(d): 3.72 ppm; H(e): 3.58 ppm; H(f): 3.53 ppm; H(g): 3.53, 3.48 ppm; H(h): 3.34 ppm; H(i'): 1.82 ppm; H(i): 1.62 ppm; H(j'): 1.33 ppm; H(j''): 1.20 ppm; H(j): 1.13 ppm.

A typical $^1\text{H-NMR}$ spectrum of the product composed of ECH and THF moieties is shown in Figure 4. H(a): 5.32 ppm; H(b): 4.38 ppm; H(c), H(d), H(e), H(f), H(g): 3.61–3.82 ppm; H(h): 3.48 ppm; H(i'): 1.82 ppm; H(i): 1.63 ppm.

In Table V, the content of PO moieties in chains is about twice as high as that of PO in feed; however, the content of ECH moieties is near or lower than that of ECH fed, inferring that the

rate of PO incorporation into the polymer chains is faster than that of ECH. From the ratio of oxirane moieties at the chain ends and in chains ($-\text{OxOH}/-\text{Ox}-$), the copolyethers containing ECH moieties are different from those having PO moieties in that most of ECH moieties attached to hydroxyl end-groups, while for PO moieties the ratio is only about 0.4–0.5, denoting also that the amount of ECH incorporating into chains by copolymerization is relatively small. The percentages of $-\text{OxOH}$ both for PO and ECH promoters were higher than 50% of the total amount of hydroxyl end-groups. This finding is similar to that

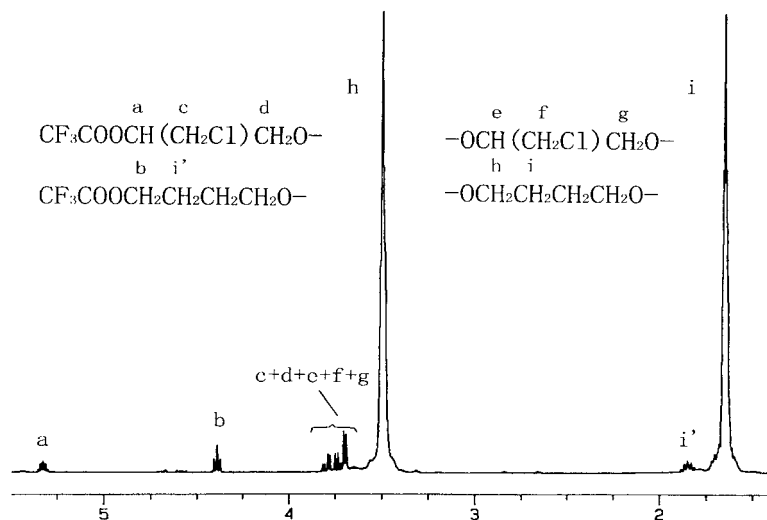


Figure 4 $^1\text{H-NMR}$ chemical shift assignments of copolyether after esterifying with $(\text{CF}_3\text{CO})_2\text{O}$ (Run No. 10 in Table V).

Table V Chain Structure Analysis of Products by ¹H-NMR (Figs. 3 and 4)

No.	Polymerization Condition ^a			Conversion (%)	Oxirane Moieties in Chains (mol %)	$\frac{-OxOH}{-Ox-}$ (mol %)	$\frac{-OxOH}{-OH}$ (mol %)	$\frac{-OxOH_{pr}}{-OxOH_{sec}}$ (molar ratio)	$\bar{M}_n(NMR)$ ($\times 10^{-3}$)
	Oxirane in Feed (mol %)	$\frac{[H_2O]}{[PW_{12}]}$	Time (h)						
PO									
1	9.0	30	4	57.7	14.2	37	83	0.66	2.16
2 ^b	4.5 × 2	30	4	47.0	14.9	44	83	0.69	1.71
3 ^b	4.5 × 2	30	6	56.9	15.1	44	86	0.69	1.78
4 ^c	7.6	30	6	58.7	15.6	37	90	0.61	2.75
5 ^c	7.6	30	7	60.2	12.3	36	90	0.67	2.85
6 ^c	7.6	60	6	38.0	15.6	49	84	0.71	1.52
7 ^c	7.6	60	7	38.3	15.4	49	85	0.73	1.52
ECH									
8	8.4	35	4	23.6	6.8	83	59	0	1.39
9	8.4	35	6	37.4	7.0	95	77	0	1.72
10 ^d	8.4	30	7	16.5	7.3	68	59	0	1.11
11 ^d	8.4	20	5	33.6	9.6	79	74	0	1.45
12 ^d	8.4	20	6	49.7	8.9	83	81	0	1.62

^a Bulk polymerization at 0–2°C, $[PW_{12}] = 6.14 \times 10^{-3}$ mol L⁻¹.

^b PO was divided into two parts, and the second part was added after 2 h after the first one was introduced.

^c BG was used instead of water.

^d $[PW_{12}] = 1.54 \times 10^{-2}$ mol L⁻¹.

for THF polymerization by EO promoter and may infer that all the chains started with PO or ECH moieties as in the case of EO promoter, where all chains started with EO moieties.¹⁰ The molar ratio of primary and secondary hydroxyl end-groups ($-OxOH_{pr}/-OxOH_{sec}$) formed by PO is found to be around 1 : 2. The polyether obtained by using ECH as promoter possesses 60–80 mol % secondary hydroxyl groups and 20–40 mol % primary ones. The primary hydroxyls exclusively attached to THF moieties, and those formed from ECH could not be detected by ¹H-NMR analysis.

The glass transition temperature (T_g) of the copolymer containing 14–16 mol % of PO moieties within the molecular weight range of 1500–2800 was found to be –83°C or so, and the melting temperature was in the range of 10.8–15.2°C. The melting temperature was lower nearly 20°C as compared with polytetramethylene ether glycol having the same molecular weight,¹³ indicating the less crystallite perfection in the copolyether, which is preferable for the soft segment use in the preparation of elastomer.^{3,14} Besides, although there are some secondary hydroxyl end-groups in polyether obtained by using PO as promoter, the polyether can be used as well for preparation of polyurethane products, as pointed out in the lit-

erature¹⁵ for polyether having secondary hydroxyls derived from PO.

CONCLUSIONS

1. PO and ECH could effectively promote the polymerization of THF initiated with PW_{12} in low concentration. Water or diol could be used to control the molecular weight of products.
2. The promotion activity of PO was similar to that of EO and better than that of ECH, especially when water was introduced.
3. PO or ECH was necessary in the initiation of THF polymerization to start the propagating chains, and after the polymerization stopped, it could be reinitiated by the addition of a supplementary portion of PO or ECH.

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