

# Tetrahydrofuran Polymerization Initiated by Heteropolyacid in the Presence of Ethylene Oxide: Reaction Behavior of Water and Glycol

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**ABSTRACT:** The reaction behavior of water and low molecular weight glycol in tetrahydrofuran polymerization initiated by  $H_3PW_{12}O_{40}$  in the presence of ethylene oxide has been studied. A lot of water was used in the hydrolysis reaction of ethylene oxide at the early stage of the polymerization and transformed into ethylene glycol (EG), which was consumed subsequently through a chain transfer reaction. EG was more reactive both than 1,4-butylene glycol and hexamethylene glycol toward propagating species, and the reaction rate constants at 0°C were determined by GC to be 0.142,  $8.83 \times 10^{-2}$ , and  $5.53 \times 10^{-2} \text{ L} \cdot \text{mol}^{-1} \text{ s}^{-1}$ , respectively. The molecular weight of the product can be predicted by an equation based upon conversion of polymerization and the concentrations of molecular weight controller and  $H_3PW_{12}O_{40}$ . © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 1821–1826, 1999

**Key words:** tetrahydrofuran; cationic ring-opening polymerization; heteropolyacid; ethylene oxide; molecular weight prediction

## 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,<sup>1–6</sup> but the initiation activity of HPA for tetrahydrofuran (THF) polymerization is very low.<sup>1–3</sup> Recently, we found  $H_3PW_{12}O_{40}$  ( $PW_{12}$ ) in low concentration could effectively initiated the polymerization of THF in the presence of ethylene oxide (EO), and the molecular weight of the products could be controlled by the concentration of water or low molecular weight glycol.<sup>7</sup> There is no chain termination reaction, and the concentration of

propagating species was maintained constant during the polymerization. With the molar ratio of  $H_2O/PW_{12}$  being as high as 30, the polymerization proceeded normally, and offered a high conversion up to 68.3% and products with molecular weight around 2000.

Although in the polymerization of THF initiated by HPA in high concentration in the absence of EO as reported in the literature,<sup>2</sup> water was believed to participate in the initiation reaction, and the polymerization activity increased as the molar ratio of  $H_2O/PW_{12}$  increased from 0 to 7. But as the ratio reached 15, no polymer could be obtained even when the amount of  $PW_{12}$  charged was as large as half the weight of THF.<sup>2,4</sup> Thus the reaction behavior of water, which may be quite different from that reported in the literature, together with the reaction behavior of low molecular weight glycol was investigated in the present article.

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## EXPERIMENTAL

### Materials

THF (AR grade,  $\geq 99.5\%$ ) was dried over five molecular sieves for a week and then distilled over  $\text{CaH}_2$ . EO ( $\geq 98\%$ ) was used as received. Butylene glycol (BG), hexamethylene glycol (HG), and ethylene glycol (EG) were dried over five molecular sieves and distilled at reduced pressure.  $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot n\text{H}_2\text{O}$  was supplied by Chemistry Institute of Henan and heated at  $300^\circ\text{C}$  for 3 h to become anhydrous before use.<sup>6</sup>

### Polymerization

A given quantity of EO (dissolved in THF) and water or glycol were added to a three-necked flask containing THF, which had been cooled to a required temperature, and the anhydrous  $\text{PW}_{12}$  was added with stirring under nitrogen. At the end of the reaction, 0.05N NaOH (aq) in sixfold of mol of  $\text{PW}_{12}$  was added to terminate the polymerization. After the unreacted monomers were evaporated off, the colorless product was extracted with toluene, washed with water, and dried in vacuum for 3 h at  $100\text{--}120^\circ\text{C}$ .

### Analysis

$^1\text{H-NMR}$  spectra were recorded at room temperature on a Bruker ARX-400 NMR spectrometer (measured at 400 MHz) with tetramethylsilane (TMS) as standard and  $\text{CDCl}_3$  as solvent. The molecular weight of polymer,  $M_n(\text{gpc})$  was evaluated by the procedure described in the previous article.<sup>7</sup>

Gas chromatography (GC) was performed on a Shimadzu GC-9A gas chromatograph equipped with a split/splitless injector, flame ionization detector (FID), and a Shimadzu C-R1B data system for data processing. Components of the polymerization were separated on a quartz capillary column ( $25\text{ m} \times 0.25\text{ mm i.d.}$ ) coated with OV-225. High pure hydrogen was used as carrier gas at a velocity of 40 cm/s. The injector was held at  $240^\circ\text{C}$ . The column was held at  $120^\circ\text{C}$  initially, then programmed to  $160^\circ\text{C}$  after 2.1 min at a temperature elevation speed of  $10^\circ\text{C}$  per min.

## RESULTS AND DISCUSSION

### Reaction Behavior of Water

Water was used as molecular weight controller in EO promoted polymerization of THF as reported

in the previous article.<sup>7</sup> The polymerization conversion after the same reaction time decreased with increasing the concentration of water (compare Nos. 1, 3, and 5; 2, 4, and 6; 7 and 8 in Table I). When the anhydrous  $\text{PW}_{12}$  was used after heating at  $300^\circ\text{C}$  for 3 h without addition of water, i.e., in the absence of water, the polymerization was feasible and reached the conversion as high as 83.5% (Table 1). However, in the absence of EO there was no polymerization product could be detected after 24 h under similar reaction conditions shown in Table I. Therefore, unlike EO, water is not necessary for the initiation reaction to start the polymer chains in the reaction system, but retards the polymerization. These behaviors of water are different from those in THF polymerization initiated by HPA in high concentration as reported in the literature,<sup>2,6</sup> where the water was described to form the pseudoliquid phase with HPA, coordinating with THF to start the polymerization chains. However, in the polymerization of THF initiated by  $\text{PW}_{12}$  in low concentration as we discuss here and in our previous work,<sup>7</sup> the pseudoliquid phase is not necessary for the polymerization because the pseudoliquid phase forms only when the ratio of  $[\text{H}_2\text{O}]/[\text{PW}_{12}]$  is in the range of 1 to 15, but this ratio is only zero in runs 1, 2, and 8 and equal 30 in runs 6 and 14 in Table I.

To study the reaction behavior of water in EO promoted THF polymerization, the component of the polymerization mixture was analyzed by GC, and EG was detected at the initial reaction stage of the polymerization (Fig. 1). It is well known that water may react with EO to form EG in the presence of acid catalyst as shown in eq. (1). According to the rate of EG formation at the initial stage of reaction in Figure 1, the apparent second-order hydrolysis rate constant of EO ( $k^{\text{app}}$ ) at  $0^\circ\text{C}$  was calculated to be  $3.0 \times 10^{-4}\text{ L} \cdot \text{mol}^{-1}\text{s}^{-1}$ . This value is much smaller than the chain transfer reaction rate constant of EG, which is  $1.42 \times 10^{-1}\text{ L} \cdot \text{mol}^{-1}\text{s}^{-1}$  as discussed in the next section of this article.

Thus, some of the EG must be consumed during its formation. After a 48-min reaction, the amount of EG formed from 82% of water could be detected, indicating that most of water in the reaction system took part in hydrolysis reaction of EO at the earlier reaction stage. EG was consumed quickly in the subsequent reaction process to form an hydroxyl end group of the polyether as shown by eq. (2b). Only a very small amount of water might be consumed by eq. (2a).

**Table I** Effect of Water and Low Molecular Weight Glycol on the Polymerization of THF

No	Polymerization Condition <sup>a</sup>			Conversion (%)	$\bar{M}_n$ (gpc) $\times 10^{-3}$	$\bar{M}_w/\bar{M}_n$
	[EO] $\text{mol} \cdot \text{L}^{-1}$	$[\text{H}_2\text{O}]/[\text{PW}_{12}]$ (Molar Ratio)	Time (h)			
1	2.01	0	1.0	19.0	5.0	1.92
2	2.01	0	4.0	83.5	6.0	3.59
3	2.01	15	1.0	16.3	1.9	1.71
4	2.01	15	4.0	65.0	4.0	1.52
5	2.01	30	1.0	16.3	1.4	1.69
6	2.01	30	4.0	64.2	2.4	1.69
7	1.00	15	4.0	59.0	4.3	1.91
8	1.00	0	4.0	73.8	12.0	2.08
9 <sup>b</sup>	1.00	30 <sup>c</sup>	3.0	14.5	1.01 <sup>f</sup>	1.31
10 <sup>b</sup>	2.01	30 <sup>c</sup>	6.0	30.2	1.11 <sup>f</sup>	1.25
11	1.00	15 <sup>d</sup>	0.5	7.5	1.00 <sup>f</sup>	2.57
12	1.00	15 <sup>d</sup>	1.0	20.4	1.66 <sup>f</sup>	1.82
13 <sup>b</sup>	2.01	30 <sup>e</sup>	0.5	30.8	1.07 <sup>f</sup>	2.42
14 <sup>b</sup>	2.01	30 <sup>e</sup>	2.4	70.4	1.20 <sup>f</sup>	1.67

<sup>a</sup> Bulk polymerization at 0–2°C,  $[\text{PW}_{12}] = 6.14 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ .

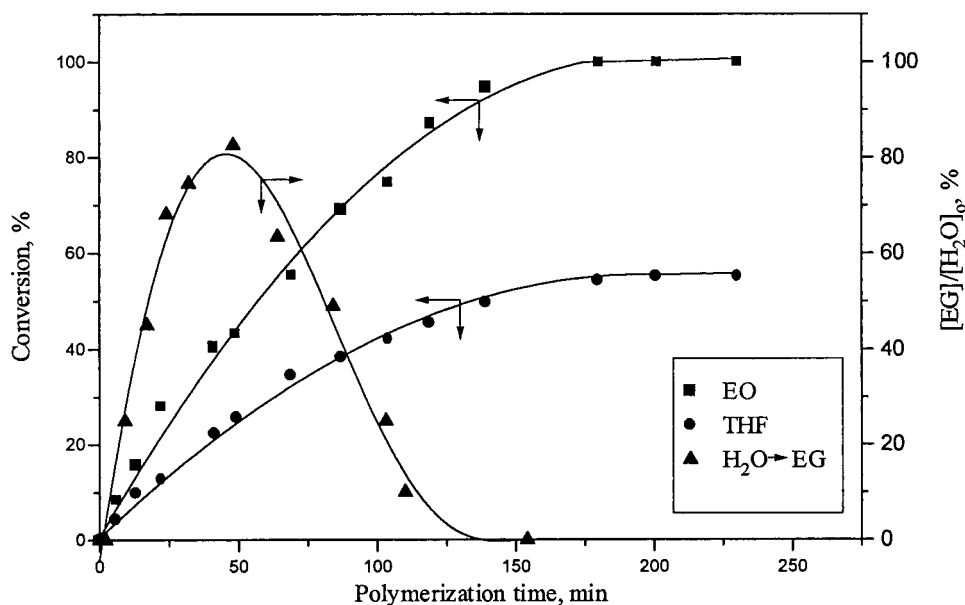
<sup>b</sup>  $[\text{PW}_{12}] = 1.52 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$ .

<sup>c</sup> EG was used instead of water.

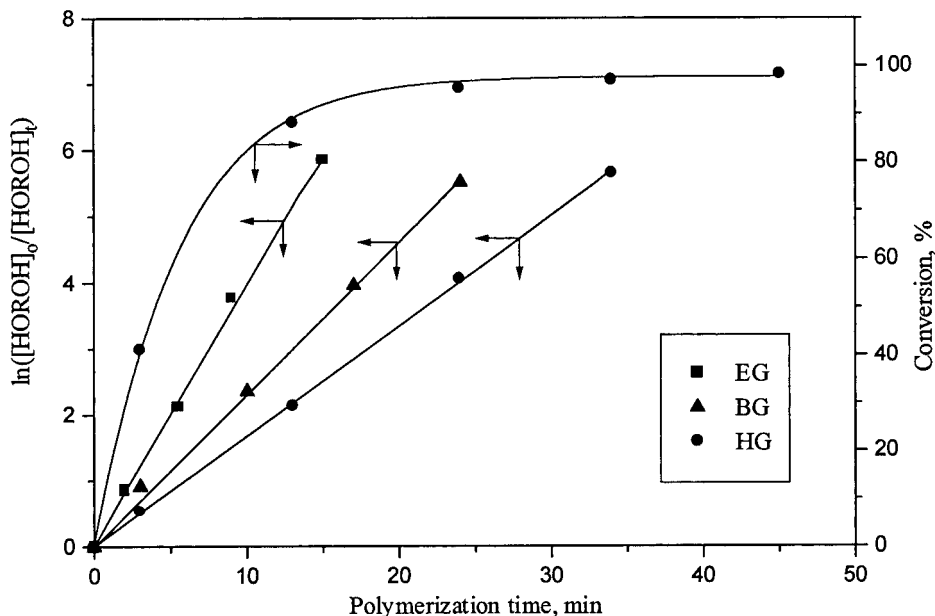
<sup>d</sup> BG was used instead of water.

<sup>e</sup> HG was used instead of water.

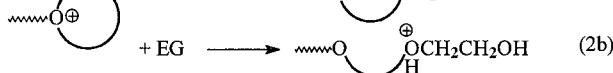
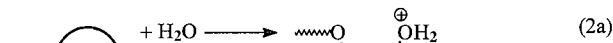
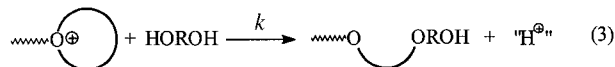
<sup>f</sup> Calculated from <sup>1</sup>H-NMR spectra by the same method described in the previous article.<sup>7</sup>



**Figure 1** Reaction behavior of water in THF bulk polymerization at 0°C.  $[\text{PW}_{12}] = 6.14 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ ,  $[\text{EO}] = 2.01 \text{ mol} \cdot \text{L}^{-1}$ ,  $[\text{H}_2\text{O}]/[\text{PW}_{12}] = 30$ .



**Figure 2** Kinetics of low molecular weight glycol reaction in THF bulk polymerization at 0°C.  $[PW_{12}] = 1.54 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$ ,  $[\text{EO}] = 2.01 \text{ mol} \cdot \text{L}^{-1}$ ,  $[\text{HOROH}]/[\text{PW}_{12}] = 30$ .



where HOROH represents EG, BG, or HG. The kinetic equation is

$$-\frac{d[\text{HOROH}]}{dt} = k[P^*][\text{HOROH}] \quad (4)$$

where  $[P^*]$  is the concentration of propagating species. Integration of eq. (4) with respect to time gives eq. 5

$$\ln \frac{[\text{HOROH}]_0}{[\text{HOROH}]_t} = \int_0^t k[P^*] dt \quad (5)$$

### Reaction Behavior of Low Molecular Weight Glycol

The low molecular weight glycol, such as EG, BG, or HG, has a similar effect on controlling the molecular weight of polymerization product as water (Nos. 9–14 in Table I). The variation of components during polymerization, monitored by GC analysis, showed that EG, BG, or HG was exhausted at the early stage of the reaction (Fig. 2), inferring the transfer reaction of propagating chains with the low molecular weight glycol was fast.

Because in the presence of glycol without EO there was no polymerization that could be observed under conditions shown in Table I or Figure 2, the polymerization could not be initiated by low molecular weight glycol, which might be consumed mainly through chain transfer reaction, as shown in eq. (3).

The linear semilogarithmic plots through origin for EG, BG, and HG (Fig. 2) indicated that the experiment results fitted eq. 5 well, and verified the reliability of eq. (3). In our previous work<sup>7</sup> we reported that during the polymerization there was no chain termination reaction and  $[P^*]$  maintained constant, i.e.,  $[P^*] = 3[PW_{12}]$ . From the slopes of the kinetics lines in Figure 2, the transfer reaction rate constants at 0°C were found to be 0.142,  $8.83 \times 10^{-2}$  and  $5.53 \times 10^{-2} \text{ L} \cdot \text{mol}^{-1}\text{s}^{-1}$  for EG, BG, and HG, respectively, which are

**Table II** Verification of the Prediction of Molecular Weight of Copolyether

No	Polymerization Conditions <sup>a</sup>			Conversion (%)	Content of EO Moieties in Chains (mol %) <sup>b</sup>	$\bar{M}_n \times 10^{-3}$	
	[EO] (mol · L <sup>-1</sup> )	[H <sub>2</sub> O]/[PW <sub>12</sub> ]	Time (h)			Calc.	Found <sup>b</sup>
1	1.00	15 <sup>c</sup>	1.0	20.4	11.1	1.71	1.66
2	1.00	15 <sup>c</sup>	5.5	53.5	13.2	3.60	3.56
3	1.00	5	1.5	54.9	12.0	4.15	4.02
4	2.01	0	0.3	5.1	8.99	2.69	2.71
5	2.01	30	7.0	67.2	19.2	3.22	3.04
6	2.01	30	8.5	68.3	20.6	3.27	3.00
7	0.50	5	2.0	36.3	6.4	6.66	6.36

<sup>a</sup> Bulk polymerization at 0°C, [PW<sub>12</sub>] = 6.14 × 10<sup>-3</sup> mol · L<sup>-1</sup>.

<sup>b</sup> Calculated from <sup>1</sup>H-NMR spectra.<sup>7</sup>

<sup>c</sup> BG was used instead of water.

much higher than the propagation rate constant of THF (3.78 × 10<sup>-3</sup> L · mol<sup>-1</sup>s<sup>-1</sup>).<sup>7</sup> It is interesting to note that with increase of the molecular weight of glycol, the rate constant towards propagating species decreased, due to the increase of chain length. Thus, with the progress of polymerization the polymer chain length became longer, and the hydroxyl groups at the polymer chain ends must be more difficult to react with propagating species due to the difficulty of movement of hydroxyl end groups of intertwined long chains. In fact, the molecular weight distribution of most products was relatively narrow, sometimes the index ( $\bar{M}_w/\bar{M}_n$ ) was smaller than 1.3–1.5 (Table I), inferring that the possibility of transfer reaction of the hydroxyl end group of chains with propagating species to start a new propagating chain subsequently was small, at least at the later stage of polymerization.

### Molecular Weight Control of the Products

The hydroxyl groups at the polymer chain ends mainly came from water or glycol charged (each water or glycol molecule offered two hydroxyl end groups). Some of the hydroxyls were introduced from the initiator (its amount was equal to [P\*], i.e., 3[PW<sub>12</sub>]). Other ones were introduced by water in the final quenching process. Because of absence of chain termination and constancy of the concentration of active species in the polymerization,<sup>7</sup> the amount of hydroxyls introduced in the final quenching process was also equal to [P\*]. So the total concentration of the hydroxyl end groups in the polymer was equal to the sum of hydroxyl concentrations from the above-mentioned three sources, i.e., 2[P\*] + 2[HOROH] or 2[P\*] + 2[H<sub>2</sub>O].

In general, the hydroxyl content of the polymerization product remains constant for conversion higher than 30% after all the water or glycol in the polymerization mixture was incorporated into the polymer chains according to eqs. (2) and (3). As we have already verified that the hydroxyl end group functionality of the products is equal to 2.0,<sup>7</sup> the molecular weight of the product could be calculated by the following equation:

$$\bar{M}_n = \frac{\Delta[\text{THF}] \times 72 + \Delta[\text{EO}] \times 44}{(3 + \mathbf{R}) \times [\text{PW}_{12}]_0} + 18 \quad (6)$$

where **R** is the molar ratio of water or glycol to PW<sub>12</sub>.

From the results of molecular weight determination for a series of runs in Table II, we found that the molecular weights found are in agreement with those calculated. The errors may be mainly caused by unexpected amounts of water introduced from the original materials. Thus, the molecular weight of the product can be predicted by eq. (6).

### CONCLUSIONS

1. Water was consumed mainly at the early stage of polymerization through the reaction with EO to form EG.
2. Low molecular weight glycol was found to be more reactive towards the propagating species than THF, and consumed at the early stage of polymerization.
3. The transfer reaction constants of EG, BG, and HG towards propagating species were

found to be 0.142,  $8.83 \times 10^{-2}$ , and  $5.53 \times 10^{-2} \text{ L} \cdot \text{mol}^{-1}\text{s}^{-1}$ , respectively, which indicated the activity of hydroxyl group decreases as the molecular weight of glycol increased.

4. Molecular weights of the products calculated on the basis of conversion of polymerization and concentrations of molecular weight controller and initiator were close to those experimentally found.

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