

# Control of Molecular Weight in Tetrahydrofuran Polymerization Initiated by Heteropolyacid

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**ABSTRACT:** Both anhydrous and hydrated heteropolyacid can be used to initiate the tetrahydrofuran polymerization in the presence of ethylene oxide promoter, in regard to the crystallization water of the hydrated one as a part of the extra-added water for controlling the molecular weight. The polyether glycol having number-average molecular weight of  $2000 \pm 100$  or  $1000 \pm 50$  was prepared in yield beyond 50% by the process without neutralization or neutralization and washing with water after polymerization, respectively. A modified equation based upon conversion of polymerization and concentrations of molecular weight controller and heteropolyacid with a correction factor for predicting the number-average molecular weight of the product was given. The products were characterized by nuclear magnetic resonance, gel permeation chromatography, and differential scanning calorimetry analyses. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 269–275, 2001

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

## INTRODUCTION

The polymerization of tetrahydrofuran (THF) was first studied in the late 1930s<sup>1,2</sup> and since then it has been studied extensively.<sup>3–5</sup> Polytetrahydrofuran with hydroxyl end groups in the number-average molecular weight range of 1000–3000, especially  $2000 \pm 100$  or  $1000 \pm 50$ , has become a large-scale commercial product, used mainly as the flexible polyether segment in elastomeric polyurethanes and polyesters.<sup>5</sup>

Recently, we have reported that THF polymerization initiated by heteropolyacid (HPA)– $H_3PW_{12}O_{40}$  ( $PW_{12}$ ), which is not particularly corrosive, recoverable, and reusable, in low concen-

trations (2–10 wt % with respect to THF), could be efficiently promoted by ethylene oxide (EO); the yield reaches 50–70% per cycle. The number-average molecular weight of product can be controlled in the range 1000–3000 by varying the concentration of water or low molecular weight diol.<sup>6</sup> Besides, we inferred eq. (1) to predict the number-average molecular weight of product<sup>7</sup>:

$$\begin{aligned} \bar{M}_{n(\text{calc})} &= \frac{\Delta[\text{THF}] \times 72 + \Delta[\text{EO}] \times 44}{3[\text{PW}_{12}] + [\text{H}_2\text{O}]} + 18 \\ &= \frac{\Delta[\text{THF}] \times 72 + \Delta[\text{EO}] \times 44}{(3 + A) \times [\text{PW}_{12}]} + 18 \quad (1) \end{aligned}$$

where  $A = [\text{H}_2\text{O}]/[\text{PW}_{12}]$ ,  $\Delta[\text{THF}] \times 72 + \Delta[\text{EO}] \times 44 \approx W_{\text{polymer}}$  (weight of polymer obtained).

However, the yield of polymerization decreased below 30% in preparation of polyether having molecular weight of 1000, and the calculated molec-

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ular weight according to eq. (1) fairly deviated from the found one. In the present article the approaches aimed at the above problems were described.

## EXPERIMENTAL

### Materials

THF (AR grade,  $\geq 99.5$ ) was refluxed over sodium metal and diphenylketone until the color of the liquid became blue and then distilled. EO ( $\geq 98\%$ ). Ethyl ether (Eth, AR grade) and cyclohexane (CH, AR grade) were used as received. Butylene glycol (BG; AR grade) was dried over 5 Å molecular sieves and distilled under reduced pressure. Hexamethylene glycol (HG) was dried in vacuum.

### Purification<sup>8</sup> of Commercial PW<sub>12</sub>

One hundred grams of PW<sub>12</sub> was dissolved in 80 mL water; then Eth (about 80 mL) was slowly added to coordinate the PW<sub>12</sub> until three phases occurred. The lowest phase consisting of PW<sub>12</sub>, water, and Eth was isolated. After evaporating Eth off and drying at 110–120°C for 24 h, PW<sub>12</sub> with 6 crystallization water (PW<sub>12</sub> · 6H<sub>2</sub>O) was obtained. PW<sub>12</sub> · 6H<sub>2</sub>O was heated at 110°C for 24 h on a vacuum line in a vessel fitted with a side-arm containing P<sub>2</sub>O<sub>5</sub> to get PW<sub>12</sub> · 4H<sub>2</sub>O. The anhydrous PW<sub>12</sub> was obtained by heating PW<sub>12</sub> · 4H<sub>2</sub>O at 170°C on the same vacuum apparatus for 24 h.

### Polymerization

#### Method 1

EO and water or low molecular weight diol were added into a three-necked flask containing THF, which had been cooled to 0–2°C. Subsequently, the anhydrous PW<sub>12</sub> was added with stirring. At the end of the reaction, 0.5 mol/L NaOH (aq) in sixfold of moles of PW<sub>12</sub> was added to terminate the polymerization. After unreacted THF was evaporated off, extracted the product with CH and washed with water until pH 7. Evaporated CH off and the product was dried in vacuum for 4 h at 110°C.

#### Method 2

The process was similar to method 1, except that the PW<sub>12</sub> phase was isolated after polymerization, and then water in half volume of polymer-

ization solution was added. After unreacted THF was evaporated off, the product was extracted with CH and washed with water until pH 7. CH was evaporated off and the product was dried in vacuum for 4 h at 110°C.

#### Method 3

The process was similar to method 2, except that the residual portion of PW<sub>12</sub> after separation of the PW<sub>12</sub> phase was precipitated by introducing Eth in half volume of polymerization solution. As the unreacted THF and uncoordinated Eth were evaporated off, the product was dried in vacuum for 4 h at 110°C.

### Analysis

The crystallization water of PW<sub>12</sub> was analyzed by weight loss on TA Instruments SDT2960 Simultaneous TGA-DTA (New Castle, DE).

<sup>1</sup>H-NMR spectra were recorded at room temperature on a Bruker (Billerica, MA) ARX-400 NMR spectrometer (measured at 400 MHz) with CDCl<sub>3</sub> as solvent.

Molecular weight distribution index  $\bar{M}_w/\bar{M}_n$  ( $\bar{M}_w$  is the weight-average molecular weight and  $\bar{M}_n$  is the number-average molecular weight) of the copolyether was determined at 35°C by gel permeation chromatography (GPC) on Waters Associates (Milliford, MA) Model high performance liquid chromatography (HPLC)/GPC 515 liquid chromatography, equipped with a refractive index detector, HT2+HT3+HT4 $\mu$ -Styragel columns and calibrated with standard polystyrene, using THF as the eluent and a flow rate of 1.0 mL/min.

Hydroxyl number, acid number, and number-average molecular weight  $\bar{M}_{n(\text{found})}$  were measured by titration.<sup>9</sup>

Hydroxyl number: The amount of 0.8–1 g copolyether and 2 mL acetic anhydride–pyridine solution (1:9 in volume) were placed in a 100 mL flask equipped with air condenser. After 1 h of heating at 90–100°C, introduced 2 mL water and kept at 90–100°C for 10 min. Then the solution was cooled and several drops of phenolphthalein were added. The solution was titrated by 0.1 mol/L NaOH (aq) and the consumed volume of NaOH (aq) was  $V$  mL. In a separate test without polyether, the consumed volume of NaOH (aq) by 2 mL acetic anhydride–pyridine solution was  $V_0$  mL.

Hydroxyl number (mgKOH/g)

$$= (V_0 - V) \times N \times 56.1/G$$

where  $N$  is the mole concentration of NaOH and  $G$  is the weight of polymer sample.

Acid number: The solution of 0.8–1g polyether and 10 mL toluene–alcohol (1:1 in volume) was titrated with 0.01 mol/L NaOH–alcohol solution and the consumed volume of alkali solution was  $V$  mL. The consumed volume of alkali solution by 10 mL toluene–alcohol in the absence of polyether was  $V_0$  mL.

Acid number (mgKOH/g)

$$= (V - V_0) \times N \times 56.1/G$$

$$\bar{M}_{n(\text{found})} = 56.1 \times f \times 1000/$$

$$(\text{hydroxyl number} + \text{acid number}) \quad (2)$$

where  $f$  is the hydroxyl end group functionality, which was verified to be 2.<sup>6</sup>

The acid numbers of two samples having the same hydroxyl number 56 mg KOH/g were determined to be 0.027 and 0.056 mg KOH/g, respectively, which were much smaller than hydroxyl numbers. So eq. (2) could be abbreviated as

$$\bar{M}_{n(\text{found})} = 56.1 \times f \times 1000/\text{hydroxyl number} \quad (3)$$

The melting point ( $T_m$ ) of copolymer was measured on a TA Instruments differential scanning calorimeter (Model 2010; New Castle, DE) at a temperature elevation speed of 10°C/min.

## RESULTS AND DISCUSSION

### The Catalytic Activity of Hydrated PW<sub>12</sub>

We noticed that various HPA hydrates in low concentration used as catalyst were less effective

in the THF homopolymerization. For example, HPA having 15–20 molecules water of crystallization cannot start absolutely the THF polymerization as shown by Bednarek et al.<sup>10</sup> In our results the polymerization yield and molecular weight of the product decreased as the crystallization water in HPA increased (compare no. 1 with no. 3 in Table I). Due to the reduced catalytic activity of the hydrates, so far only the anhydrous HPAs have been used in the THF polymerization studies.<sup>10–13</sup> The crystallization water in hydrates offers the protons from H<sub>5</sub>O<sub>2</sub><sup>+</sup> cations or larger aggregator if more water molecules are present in the hydrated HPA,<sup>14</sup> and the different water content in the HPA crystal may also change the anion packing. By linking the neighboring anions the protons act as the initiator center.<sup>15</sup> In our experimental results we can get the relatively quantitative interpretation for the behavior of crystallization water in HPA. As the same total number of water in the polymerization system including the crystallization water of hydrated HPA and the extra added water was used in the reaction, the polymerization initiated by PW<sub>12</sub>, PW<sub>12</sub> · 4H<sub>2</sub>O, or PW<sub>12</sub> · 6H<sub>2</sub>O offered nearly the same yield and molecular weight of product (Table I, nos. 2–4). So we can conclude that the crystallization water behaves just like the water extra-added into the polymerization system and together with the extra-added water plays the role of molecular weight controller. The rate of initiation reaction in the THF homopolymerization using HPA catalyst in low concentration is rather slow,<sup>10</sup> so the existence of chain transfer agent will make the polymerization difficult or impossible. However, in our experiments promoter was added, so the THF polymerization proceeded smoothly even in the presence of chain transfer agent.<sup>16</sup> Therefore, the hydrates can also

**Table I** Reaction Behavior of Crystallization Water of PW<sub>12</sub>

No.	Polymerization Condition <sup>a</sup>			Time (h)	Yield (%)	$\bar{M}_n^c$
	$\frac{[\text{H}_2\text{O}]_{\text{cryst. b}}}{[\text{PW}_{12}]}$	$\frac{[\text{H}_2\text{O}]_{\text{added}}}{[\text{PW}_{12}]}$	$\frac{[\text{H}_2\text{O}]_{\text{total}}}{[\text{PW}_{12}]}$			
1	0	10	10	3	73.5	3303
2	0	14	14	3	66.0	2800
3	4	10	14	3	66.1	2869
4	6	8	14	3	65.6	2865

<sup>a</sup> By method 1 polymerization, [EO] = 2.00 mol/L, [PW<sub>12</sub>] = 1.54 × 10<sup>-2</sup> mol/L.

<sup>b</sup> Molecules of crystallization water per PW<sub>12</sub> molecule.

<sup>c</sup> According to <sup>1</sup>H-NMR spectra.

be used as the catalyst, taking into account the crystallization water as a part of extra-added water, instead of anhydrous PW<sub>12</sub>, and so the complication rising from PW<sub>12</sub> decomposition due to the prolonged treatment at high temperature in order to get the anhydrous one could be avoided.

### Preparation of Polyether Glycol Having Number-Average Molecular Weight of 3000–7000

It can be seen from Table II that the polyether glycol having number-average molecular weight of 3000–7000 could be obtained in high yield by the polymerization method 1, which was used in our previous paper.<sup>6</sup> The molecular weights calculated by eq. (1) ( $\bar{M}_{n(\text{calc})}$ ) were similar to those found ( $\bar{M}_{n(\text{found})}$ ) (nos. 1–5). Besides, it can also be noticed that with decreasing the molecular weight of polyether the difference between  $\bar{M}_{n(\text{found})}$  and  $\bar{M}_{n(\text{calc})}$  increased, i.e., the  $R$  value increased (Nos. 6 and 7), which would be discussed hereinafter.

### Preparation of Polyether Glycol Having Number-Average Molecular Weight of 2000

Polymerization method 1 was characteristic of decomposing PW<sub>12</sub> by NaOH after polymerization, which evaded the loss of polyether adsorbed by PW<sub>12</sub>. However, some Na<sup>+</sup> could be wrapped in the polyether, which may influence the reaction with isocyanates in the preparation of polyure-

thane.<sup>17</sup> The other defect of method 1 is that PW<sub>12</sub> was not recycled and reused.

In order to overcome the above-mentioned defects of method 1, we devised method 2. The feature of method 2 is that, after polymerization the PW<sub>12</sub> catalyst phase<sup>18</sup> was separated by centrifugal machine. The separated catalyst phase could be reused directly for initiation of another batch of polymerization after the estimation of amounts of PW<sub>12</sub> and THF in it. And since there was no NaOH introduced in the posttreatment, the procedure for getting rid of Na<sup>+</sup> could be ruled out.

From Table III we can see that the polyether glycol having number-average molecular weight of 2000 ± 100, as required commercially,<sup>19</sup> could be obtained in yield above 50% (Table III, nos. 5–7) by method 2. However,  $\bar{M}_{n(\text{calc})}$  calculated by eq. (1) showed some deviation from  $\bar{M}_{n(\text{found})}$ . So we modified the eq. (1) by introducing a correction factor  $R$  as follows:

$$\begin{aligned} \bar{M}_n &= \left( \frac{\Delta[\text{THF}] \times 72 + \Delta[\text{EO}] \times 44}{3[\text{PW}_{12}] + [\text{H}_2\text{O}]} + 18 \right) \times R \\ &= \left( \frac{W_{\text{polymer}}}{3[\text{PW}_{12}] + [\text{H}_2\text{O}]} + 18 \right) \times R \quad (4) \end{aligned}$$

All the values of  $R$  were greater than 1.0 when method 2 was adopted (see Table III). Comparing the data of nos. 1 in Tables I and II, it can be seen that the values of  $R$  were different by using different posttreatment methods under the same po-

**Table II** Preparation of Polyether Glycol by Method 1

No.	Polymerization Condition <sup>a</sup>				Yield (%)	$\bar{M}_n$		$R^c$
	[EO] (mol L <sup>-1</sup> )	[PW <sub>12</sub> ] × 10 <sup>-3</sup> (mol L <sup>-1</sup> )	$\frac{[\text{H}_2\text{O}]}{[\text{PW}_{12}]}$	Time (h)		Found <sup>b</sup>	Calc.	
1	0.50	6.14	5	2.0	36.3	6360	6660	1.0
2	1.00	6.14	5	1.5	54.9	4020	4150	1.0
3 <sup>d</sup>	1.00	6.14	15	5.5	53.5	3560	3600	1.0
4	2.00	15.4	10	3	73.5	3303	3247	1.0
5 <sup>e</sup>	2.00	15.4	10	3	68.0	3471	3031	1.1
6 <sup>f</sup>	2.00	15.4	14	3	66.1	2869	2258	1.3
7 <sup>g</sup>	2.00	15.4	20	4	57.1	1943	1430	1.4

<sup>a</sup> By polymerization method 1.

<sup>b</sup> According to <sup>1</sup>H-NMR spectra.

<sup>c</sup>  $R = \bar{M}_{n(\text{found})} / \bar{M}_{n(\text{calc})}$ .

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

<sup>e</sup> PW<sub>12</sub> phase was isolated after polymerization.

<sup>f</sup> PW<sub>12</sub> · 4H<sub>2</sub>O was used.

<sup>g</sup> PW<sub>12</sub> · 6H<sub>2</sub>O was used.

**Table III** Preparation of Polyether Glycol by Method 2

No.	Polymerization Condition <sup>a</sup>		Yield (%)	$\bar{M}_n$		$R^c$
	[H <sub>2</sub> O]/[PW <sub>12</sub> ]	Time (h)		Found <sup>b</sup>	Calc.	
1	10	3	66.0	3820 <sup>d</sup>	2942	1.3
2	14	3	66.0	3120 <sup>d</sup>	2254	1.4
3	17	2.5	56.3	2376	1639	1.4
4	20	2.5	52.2	2185	1325	1.6
5	22	2.5	55.0	2058	1285	1.6
6	22	2.5	53.0	2070	1239	1.7
7	22	2.5	53.0	1943	1239	1.6
8	25	6	46.2	1580	968	1.6
9	30	4	35.9	1568	645	2.4
10 <sup>e</sup>	40	4	19.7	1269	282	4.5

<sup>a</sup> [EO] = 2.00 mol L<sup>-1</sup>, [PW<sub>12</sub>] = 1.54 × 10<sup>-2</sup> mol L<sup>-1</sup>.

<sup>b</sup> According to eq. (3).

<sup>c</sup>  $R = \bar{M}_{n(\text{found})}/\bar{M}_{n(\text{calc})}$ .

<sup>d</sup> According to <sup>1</sup>H-NMR.

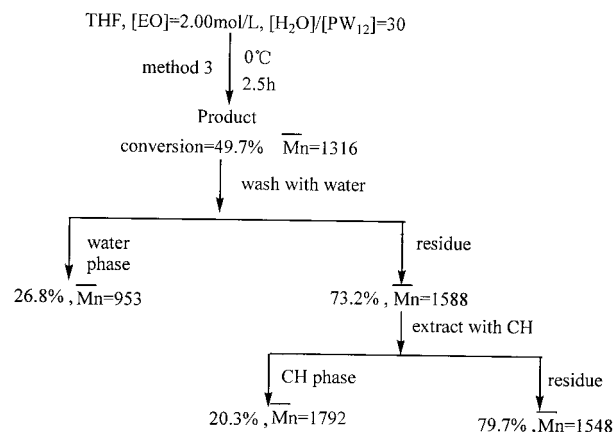
<sup>e</sup> HG instead of water.

lymerization condition. When method 1 was adopted, that is, NaOH was introduced to destroy PW<sub>12</sub> after polymerization,  $\bar{M}_{n(\text{calc})}$  according to eq. (1) and  $\bar{M}_{n(\text{found})}$  of the product were almost the same, i.e.,  $R = 1.0$ . When method 2 without neutralization by NaOH in the posttreatment was used, the value of  $R$  became 1.3. The deviation of  $R$  from 1.0 must be due to the fact that the PW<sub>12</sub> was not destroyed, but isolated as the catalyst phase, containing some polyether glycol of lower molecular weight that was subsequently lost and led to the lower yield and the lower  $\bar{M}_{n(\text{calc})}$  calculated according to eq. (1). The loss of the portion of lower molecular weight resulted in the higher  $\bar{M}_n$  of the product ( $\bar{M}_{n(\text{found})}$ ). Thus the value of  $R$  became higher than 1.0. Besides, from the data in Table III it can also be noticed that with decreasing the molecular weight of polyether the difference between  $\bar{M}_{n(\text{found})}$  and  $\bar{M}_{n(\text{calc})}$  increased, i.e.,  $R$  value increased (Table III, nos. 9 and 10), which must be related to the polarity of product and would be discussed hereinafter. The average value of  $R$  was obtained to be 1.6 for preparing the polyethers having  $\bar{M}_n$  around 2000 (Table III, nos. 3 and 8), or say, the molecular weight of polyethers could be predicted by multiplying  $\bar{M}_{n(\text{calc})}$  calculated according to eq. (1) by 1.6.

#### Preparation of Polyether Glycol Having Number-Average Molecular Weight of 1000

For preparation of polyether of  $\bar{M}_n$  around 1000 by method 2 even the amount of water as the

molecular weight controller was used in 40-fold of PW<sub>12</sub> moles, the  $\bar{M}_n$  of the product was still high, such as 1269, and the yield of polymerization already decreased below 20% (Table III, no. 9). Thus, it was impossible to obtain the polyether having  $\bar{M}_n$  1000 in high yield by method 2. In the procedure we noticed that some polyether did not dissolve in CH and the emulsifying effect with water was serious, resulting in difficulty to separate the CH phase from water phase. The above phenomena could be explained by the increase of polarity of polyether glycol with decreased molecular weight. In order to prevent the loss of polyether glycol caused by the incomplete extraction of CH and separation of CH phase, we devised



**Scheme 1** Soluble and residual parts of polyester in water and CH.

**Table IV** Preparation of Polyetherglycol by Method 3

No.	Polymerization Condition <sup>a</sup>			Yield (%)	$\bar{M}_n$		$R^d$
	[EO] (mol/L)	$\frac{[\text{H}_2\text{O}]}{[\text{PW}_{12}]}$	Time (h)		Found <sup>b</sup>	Calc. <sup>c</sup>	
1 <sup>e</sup>	1.00	30	1.5	33.0	926	594	1.6
2	2.00	40	2.5	51.0	1041	701	1.5
3	2.00	40	2.5	50.0	1006	688	1.5
4	2.00	40	2.5	50.0	1017	688	1.5
5 <sup>f</sup>	2.00	40	2.5	51.0	1046	701	1.5
6	3.00	40	2.5	66.0	1100	902	1.2
7	2.00	30	2.5	53.0	1213	943	1.3

<sup>a</sup>  $[\text{PW}_{12}] = 1.54 \times 10^{-2} \text{ mol L}^{-1}$ .<sup>b</sup> Determined by eq. (3).<sup>c</sup> Calculated by eq. (1).<sup>d</sup>  $R = \bar{M}_{n(\text{found})}/\bar{M}_{n(\text{calc})}$ .<sup>e</sup> HG was used instead of water.<sup>f</sup>  $\text{PW}_{12} \cdot 6\text{H}_2\text{O}$  was used.

method 3, which was characteristic of removing the residual  $\text{PW}_{12}$  by the coordination with Eth evading the extraction of CH and the washing with water. In order to verifying that the extraction of CH and washing with water may cause the loss of polyether of lower  $\bar{M}_n$  portion, we did the model experiment with a polyether sample prepared by method 3. The results are shown in Scheme 1.

It can be seen from Scheme 1 that 26.8% polyether of lower molecular weight could be washed off by water, and a significant amount of polyether of lower molecular weight was also lost due to the incomplete extraction with CH. Therefore CH could no more be used for the preparation of polyether with  $\bar{M}_n$  around 1000.

The polyether glycol having  $\bar{M}_n$  1000 was obtained conveniently in yield beyond 50% (Table

IV, nos. 2–5) by method 3, and the  $\bar{M}_n$  of the products could be controlled in the range of  $\pm 50$  as required commercially.<sup>19</sup> The average value of  $R$  was determined to be 1.5. The deviation from 1.0 may be explained by procedures of separation of  $\text{PW}_{12}$  phase and  $\text{PW}_{12}$ –Eth complex phase, which could lead to the loss of some polyether of lower molecular weight.

### Characterization of Copolyether Glycol

As EO moieties was incorporated into the chain of polyether, the melting temperatures of copolymers of  $\bar{M}_n = 1000$  and 2000 were about 20°C lower than those of polytetramethylene glycols having the same molecular weight (Table V), which are 25–33 and 28–40°C, respectively,<sup>19</sup> and both were lower than room temperature,

**Table V** Characterization of Copolyether Glycol

No.	$\bar{M}_n$	Content of EO Moieties in Chains		$\frac{[\text{—EOH}^a]}{[\text{—E—}]}$ (mol %)	$\frac{[\text{—TEOH}]^b/[\text{—EEOH}]}{[\text{—TOH}]}$	$\frac{[\text{—EOH}]^c}{[\text{—TOH}]}$	$T_m$ (°C)	$\bar{M}_w/\bar{M}_n$
		(mol %)	(wt %)					
1 <sup>d</sup>	1017	26.9	18.4	41.4	5.1	4.0	7.8	1.36
2 <sup>e</sup>	1943	22.7	15.2	25.3	4.2	4.6	11.9	1.37

<sup>a</sup> Content of hydroxyl end groups attached to EO moieties toward total EO moieties in chain.<sup>b</sup> Molar ratio of THF and EO moieties attached to hydroxyl end groups formed by EO.<sup>c</sup> Molar ratio of hydroxyl end groups attached to EO moieties and THF moieties.<sup>d</sup> See Table IV, no. 4.<sup>e</sup> See Table III, no. 7.

which is preferable for handling the soft segment use in the preparation of elastomer.<sup>20-22</sup> The values of  $\bar{M}_w/\bar{M}_n$  for both copolyethers are relatively narrow, which will benefit the low temperature resilience of polyurethane prepared thereby.<sup>18</sup>

By the analysis of <sup>1</sup>H-NMR spectra of copolyethers esterified with trifluoroacetic anhydride,<sup>6</sup> some structure information was obtained and listed in Table V.

## CONCLUSIONS

1. Both anhydrous and hydrated heteropolyacid can be used to initiate the tetrahydrofuran polymerization in the presence of EO, in regard to the crystallization water of the hydrated one as a part of the extra-added water for controlling the molecular weight.
2. The polyether glycol having number-average molecular weight of  $2000 \pm 100$  was prepared by method 2 with the polymerization yield beyond 50%.
3. The polyether glycol of number-average molecular weight  $1000 \pm 50$  was prepared by method 3, and the polymerization yield was around 50%.
4. The molecular weight of polymerization product could be predicted by eq. (4) based upon conversion of polymerization and concentrations of molecular weight controller and heteropolyacid with the correction factor  $R$ , which is 1.0, 1.5, or 1.6 for products of  $\bar{M}_n = 3000-7000$ , 1000, or 2000, respectively.
5. The melting point of product of  $\bar{M}_n = 1000$  or 2000 is about 20°C lower than that of polytetramethylene glycol having the same molecular weight and is lower than room temperature, which is preferable for handling the soft segment use in the preparation of elastomer.
6. The molecular weight distribution for both products of  $\bar{M}_n = 1000$  and 2000 is relatively narrow. The values of  $\bar{M}_w/\bar{M}_n$  are around 1.4, which are benefit low temperature resilience of polyurethane prepared thereby.

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