# Effective Promotion of Tetrahydrofuran Polymerization Initiated with Heteropolyacid

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**ABSTRACT:** Tetrahydrofuran was polymerized using the heteropolyacid $H_3PW_{12}O_{40}$ as the initiator and ethylene oxide as the promoter, which effectively increased the rate and conversion of the polymerization. Water and butylene glycol were used to control the molecular weight of the product in the range of 1000–3000. The polymer was found to be polyether glycol containing 10–22 mol % oxyethylene moieties with hydroxyl groups at both chain ends. The melting point was $\sim$ 10°C lower compared to polytetramethylene ether glycol having the same molecular weight. The concentration of active species remained unchanged in the main period of the polymerization, indicating the absence of chain termination. The values of the chain propagation rate constant of tetrahydrofuran polymerization at 0 and 20°C were found to be $3.78 \times 10^{-3}$ and $1.98 \times 10^{-2}$ L mol$^{-1}$ s$^{-1}$, respectively, which are close to the rate constant of chain propagation of tetrahydrofuran on ionic active species. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2303–2308, 1999

**Key words:** tetrahydrofuran; ring-opening polymerization; heteropolyacid; promotion; ethylene oxide

## INTRODUCTION

Cationic ring-opening polymerization of tetrahydrofuran (THF) was first observed in the late 1930s.[1,2] Since then it has been studied extensively,[3–5] and the polymer of medium molecular weight (600–3000) having hydroxyl groups at both chain ends is commercially important in the preparation of polyurethane and polyester elastomers. However, the polymer is commonly prepared by using superacids (fluorosulfuric acid, perchloric acid–acetic anhydride, fuming sulfuric acid, etc.) as the polymerization catalysts. Aside from the requirement for acid-resistant construc-

tion materials, there are the problems of neutralization and disposal of the by-product salts. In the last decade, various research groups found the heteropolyacids (HPAs) to be efficient initiators of cationic polymerization.[6–13] HPAs are strong acids with complex polyanions, which are formed by condensation of more than two different mononuclear oxoanions. Because of the unique structure, HPAs possess high acid strength and stable polyanions and could exhibit a pseudoliquid phase. These behaviors are particularly important in cationic polymerization, especially in the polymerization of THF. These initiators are also of interest because they are easily available, nonvolatile, not particularly corrosive, stable in open air, and soluble in a number of organic solvents; furthermore, they can be recovered and reused.

There are only a few reports in the open literature that deal with the application of HPAs in the ring-opening polymerization of THF, and

**Table I    Determination of *K* Value for Copolyether of THF and EO**

| No. | Content of EO Moieties in Copolyether (mol %)[a] | $\overline{M_n}$ (s) $\times 10^{-3}$ | $\overline{M_n}$ (NMR)[b] $\times 10^{-3}$ | $\overline{M_n}$ (VPO) $\times 10^{-3}$ | $K$[c] |
|---|---|---|---|---|---|
| 1 | 9.8 | 1.72 | 1.00 | 0.97 | 0.56 |
| 2 | 11.1 | 2.70 | 1.66 | 1.71 | 0.63 |
| 3 | 12.1 | 4.00 | 2.34 | | 0.58 |
| 4 | 13.2 | 5.88 | 3.56 | | 0.60 |
| 5 | 22.5 | 2.41 | 1.51 | | 0.63 |
| 6 | 20.6 | 2.22 | 1.40 | | 0.63 |
| 7 | 10.7 | 2.04 | 1.17 | 1.14 | 0.56 |
| 8 | 10.3 | 3.12 | 1.86 | 1.81 | 0.58 |
| | | | | | 0.60 (mean value) |

[a] Calculated from $^1$H-NMR spectrum as shown in Figure 2 $[(I_{3.48-4.49} - I_{1.62-1.85})/I_{3.48-4.49}] \times 100\%$, (where $I$ is the integrated area.)

[b] Calculated from $^1$H-NMR spectrum as shown in Figure 2(b): $18 + [(I_{3.48-4.49} - I_{1.62-1.85}) \times 44 + I_{1.62-1.85} \times 72]/(I_{4.39} + I_{4.49})$, where $I$ is the integrated area.

[c] $K = \overline{M_n}$ (NMR)$/\overline{M_n}$ (VPO)$/\overline{M_n}$ (s).

some problems remained unsolved. The efficiency of the initiator is low,[6] so a large amount of initiator (HPA/THF = 0.25–1.0 by weight) has to be used to get a suitable reaction rate and a polymer with medium molecular weight.[7–10] In addition, the mechanism of polymerization is still not clear. In the present work the polymerization of THF initiated with $H_3PW_{12}O_{40}$ ($PW_{12}$) was investigated in the presence of a small amount of ethylene oxide (EO). EO is well known in THF polymerization initiated with $BF_3$ as a polymerization promoter[14–17] due to the ease of ring opening of the high strain three-member ring. The efficiency of the catalyst was dramatically increased and the amount of the catalyst used was reduced.

## EXPERIMENTAL

### Materials

THF (AR grade, 99.5%) was dried over 5-Å molecular sieves for a week and then distilled over $CaH_2$. EO (98%) was used as received. Butylene glycol (BG) and ethylene glycol (EG) were distilled at reduced pressure. $H_3PW_{12}O_{40} \cdot nH_2O$ (Chemistry Institute of Henan) was heated at 300°C for 3 h before use.

### Polymerization

The polymerization was performed with a procedure similar to the one described in our previous article.[17] A given quantity of EO (dissolved in THF) and water or BG were added to THF in a

three-necked flask, which was cooled to a required temperature, and subsequently the anhydrous $PW_{12}$ was added with stirring under nitrogen. At the end of the reaction, 6 equiv of $0.05N$ NaOH (with respect to $PW_{12}$) was added to terminate the polymerization. After the unreacted THF was evaporated off, the colorless product was extracted with toluene, washed with water, and dried in a vacuum for 3 h at 100–120°C.

### Analysis

The number average molecular weight of the copolymer, $\overline{M_n}$ (VPO), was determined in acetone at 37°C on a Knaver-VPO vapor pressure osmometer. The number average molecular weight, $\overline{M_n}$ (s), and molecular weight distribution ($\overline{MWD} = \overline{M_w}/\overline{M_n}$) of the copolyether were determined with gel permeation chromatography (GPC) on a Waters Associates LC/GPC 512 liquid chromatograph calibrated with standard polystyrene and equipped with a refractive index detector and 500, $10^3$, and $10^4$ ultrastyragel columns. THF was used as the eluent at room temperature and a flow rate of 1.0 mL/min. The $\overline{M_n}$ of the copolyether, $\overline{M_n}$ (GPC), was evaluated from the $\overline{M_n}$ (s) by the equation $\overline{M_n}$ (GPC) $= K \overline{M_n}$ (s), where $K$ is a constant.[18] By analysis of the products containing EO moieties of around 9.8–22.5 mol % prepared from copolymerization of THF with EO (3.2–16 mol % based on the amount of THF charged) initiated with $PW_{12}$, we determined the conversion factor $K$ to be 0.60 for $\overline{M_n}$ (s) in the range of $1.7–5.9 \times 10^3$, which is shown in Table I.

The $^1$H-NMR spectrum was recorded at room temperature on a Bruker ARX-400 NMR spectrometer (measured at 400 MHz) with CDCl$_3$ and tetramethylsilane as the solvent and standard, respectively. The melting point ($T_m$) of the copolymer was measured on a Shimadzu DSC-50 instrument at a temperature elevation speed of 4°C min$^{-1}$.

Gas chromatography (GC) was performed on a Shimadzu GC-9A gas chromatograph equipped with a split/splitless injector, a flame ionization detector, and a Shimadzu C-R1B data system for data processing. The components of the polymerization were separated on a quartz capillary column (25 m × 0.25 mm i.d.) coated with OV-225. High pure hydrogen was used as the carrier gas at a velocity of 40 cm s$^{-1}$. The column temperature was held at 55°C and the injector at 240°C.

## RESULTS AND DISCUSSION

The reaction mixture was heterogeneous after the solid PW$_{12}$ was added to the THF. But when EO was added and the molar ratio of H$_2$O/PW$_{12}$ was higher than 5.0, the reaction system became homogeneous and then it converted into heterogeneous at a later stage of polymerization as most of the water and EO was consumed.

### Promotion Effect of EO on Polymerization

It can be seen from Table II that EO is an effective promoter for the polymerization of THF initiated with PW$_{12}$. High conversion (60–80%) could be obtained with a low concentration of PW$_{12}$ (PW$_{12}$/THF = 0.02 by weight) in 3.5–7 h (see nos. 1–8 in Table II) in comparison with when 30% conversion at as high as HPA/THF = 0.5 (by weight) was used or a 500-h reaction time was needed as reported in the literature.[6,8] Similar to our comparative run with the absence of EO under the same conditions, no polymer could be detected after 24 h of polymerization.

Although EO can effectively promote the polymerization of THF, the molecular weight of the copolyether is higher than that required for commercial use. By adjusting the concentration of water in the polymerization system, the molecular weight of the polymer can be controlled. Varying the molar ratio of H$_2$O/PW$_{12}$ in the range of 0–30, the molecular weight of the product was remarkably decreased with an increasing amount

of water, and the conversion of the polymerization remained higher than 60% after 4–5 h of reaction (see nos. 8–13 in Table II).

It is also noteworthy that with a molar ratio of H$_2$O/PW$_{12}$ being as high as 30.0, the polymerization proceeds normally and offers a high conversion up to 68.3% and products of medium molecular weight. But in the absence of EO, with the molar ratio of H$_2$O/HPA being 7.2, the polymer yield was only 2.3%; as the ratio reached 15, no polymer could be obtained as reported in the literature,[8] even when the amount of HPA up to HPA/THF = 0.5 (by weight) was used instead of the 0.02 we used in runs shown in Table II.

BG has a similar effect on controlling the molecular weight of the product (compare nos. 14–16 with 10 – 13 in Table II).

The molecular weight of the product decreased from $4.0 \times 10^3$ to $0.9 \times 10^3$ as the concentration of PW$_{12}$ increased from 6.14 to $15.35 \times 10^{-3}$ mol L$^{-1}$ (see nos. 9, 17, and 18 in Table II) and increased with conversion (compare nos. 1, 2, and 3; nos. 4, 5, and 6; nos. 19, 20, and 21; nos. 22, 23, and 24). As the reaction temperature increased from −5 to 10°C (see nos. 19–24 in Table II), the reaction rate increased, but the conversion and the molecular weight of the final products remained similar to each other.

### Characterization of Copolymer

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

The melting points of the copolyether containing 10–22 mol % of EO moieties with molecular weights from 1000 to 2900 were found to be in the range of 12.4–21.0°C, which was lower by more than 10°C compared to polytetramethylene ether glycol having the same molecular weight.[19] This indicates the less perfect crystallite in the copolyether, which is preferable for soft segment use in the preparation of elastomer.[10]

A typical $^1$H-NMR spectrum of the product is shown in Figure 1. The chemical shifts in Figure 1(a) are assigned as follows: 3.72 ppm for H(a), H(a'); 3.64 ppm for H(b), H(c), H(d), H(e); 3.57 ppm for H(g); 3.49 ppm for H(f), H(h'); 3.41 ppm for H(h); 2.86 ppm for H(i); and 1.62 ppm for H(j), H(j'). After esterification of the copolyether with (CF$_3$CO)$_2$O (an excess of (CF$_3$CO)$_2$O was added directly to the NMR tubes containing the copolyether), the peak i at 2.86 ppm disappeared, indicating that the hydroxyl groups were completely

**Table II   Polymerization of THF Initiated with PW$_{12}$ in Presence of EO**

| No. | Polymerization Condition[a] | | Time (h) | Conversion (%) | $\overline{M}_n$ (GPC) $\times 10^{-3}$ | $\overline{\text{MWD}}$ |
| | [EO] (mol L$^{-1}$) | [H$_2$O]/[PW$_{12}$] (Molar Ratio) | | | | |
|---|---|---|---|---|---|---|
| 1 | 1.00 | 0 | 3.5 | 59.1 | 12.5[b] | 2.6 |
| 2 | 1.00 | 0 | 5.0 | 73.8 | 20.0[b] | 2.1 |
| 3 | 1.00 | 0 | 7.0 | 75.4 | 20.0[b] | 2.2 |
| 4[c] | 1.00 | 0 | 1.0 | 65.0 | 12.5[b] | 2.1 |
| 5[c] | 1.00 | 0 | 3.5 | 77.9 | 20.0[b] | 2.1 |
| 6[c] | 1.00 | 0 | 7.0 | 78.2 | 20.0[b] | 1.8 |
| 7 | 2.01 | 0 | 2.5 | 56.9 | 5.4 | 3.1 |
| 8 | 2.01 | 0 | 6.0 | 84.0 | 6.7 | 3.0 |
| 9 | 2.01 | 5 | 3.8 | 74.3 | 4.0 | 2.1 |
| 10 | 2.01 | 15 | 2.0 | 37.8 | 2.6 | 1.7 |
| 11 | 2.01 | 15 | 6.0 | 64.4 | 5.0 | 1.5 |
| 12 | 2.01 | 30 | 3.0 | 59.7 | 2.1 | 2.0 |
| 13 | 2.01 | 30 | 8.5 | 68.3 | 2.5 | 1.6 |
| 14[d] | 1.00 | 15 | 5.5 | 53.5 | 3.5 | 1.6 |
| 15[d] | 1.00 | 15 | 7.0 | 58.3 | 3.5 | 1.7 |
| 16[d] | 2.01 | 15 | 3.5 | 76.7 | 4.0 | 1.7 |
| 17[c] | 2.01 | 5 | 1.6 | 65.8 | 1.5 | 1.7 |
| 18[e] | 2.01 | 5 | 1.0 | 72.7 | 0.9 | 1.7 |
| 19[f] | 2.01 | 5 | 0.5 | 7.1 | 1.7 | 1.7 |
| 20[f] | 2.01 | 5 | 3.8 | 61.3 | 3.5 | 2.1 |
| 21[f] | 2.01 | 5 | 10.5 | 80.0 | 6.7 | 1.9 |
| 22[g] | 2.01 | 5 | 0.5 | 23.0 | 2.4 | 2.8 |
| 23[g] | 2.01 | 5 | 1.0 | 62.2 | 6.7 | 1.6 |
| 24[g] | 2.01 | 5 | 2.0 | 79.9 | 7.5 | 1.8 |

[a] Bulk polymerization at 0–2°C, [PW$_{12}$] = 6.14 $\times$ 10$^{-3}$ mol L$^{-1}$.
[b] $\overline{M}_n$ (s) instead of $\overline{M}_n$ (GPC).
[c] [PW$_{12}$] = 15.35 $\times$ 10$^{-3}$ mol L$^{-1}$.
[d] BG was used instead of water.
[e] [PW$_{12}$] = 30.7 $\times$ 10$^{-3}$ mol L$^{-1}$.
[f] Polymerization at −5°C.
[g] Polymerization at 10°C.

esterified [Fig. 1(b)]. The proton resonance of the methylene group at the $\alpha$ position adjacent to the hydroxyl end groups shifted from 3.64 and 3.72 to 4.39 and 4.49 ppm, respectively, due to the esterification. These were assigned according to the literature[20] and by using the spin-decoupling technique. Based on the integrated area of each peak, the content of EO moieties in the copolymer chains and the $\overline{M}_n$ (NMR) could be calculated (Tables I, III).

## Kinetics Study

The polymerization mixtures were withdrawn at a certain reaction time and the concentrations of THF were directly analyzed by GC.

In the cationic polymerization of THF, the chain propagation equation is given by

$$-\frac{d[\text{THF}]}{dt} = k_p[P^*]([\text{THF}] - [\text{THF}]_e) \quad (1)$$

where [THF], [THF]$_e$, and [P$^*$] are the instantaneous, equilibrium monomer, and propagating species concentrations, respectively, and $k_p$ is the rate constant of the propagation reaction. Integration of eq. (1) with respect to time gives

$$\ln\frac{[\text{THF}]_o - [\text{THF}]_e}{[\text{THF}]_t - [\text{THF}]_e} = \int_{t_o}^{t} k_p[P^*] \, dt \quad (2)$$

**Table III   Hydroxyl End-Group Functionality $(\bar{f})$ of Polyether Glycol**

| No. | Polymerization Condition[a] | | Conversion (%) | Content of EO Moieties in Chains[b] (mol %) | $\overline{M}_n$ (NMR)[b] $\times 10^{-3}$ | $\overline{M}_n$ (VPO) $\times 10^{-3}$ | $\bar{f}$[c] |
|-----|---------------|----------|-----|------|------|------|------|
| | [EO] (mol L$^{-1}$) | Time (h) | | | | | |
| 1 | 2.01 | 0.5 | 7.3 | 10.7 | 1.17 | 1.14 | 1.95 |
| 2 | 2.01 | 1.0 | 16.3 | 10.3 | 1.86 | 1.81 | 1.95 |
| 3 | 2.01 | 1.5 | 26.3 | 11.2 | 2.21 | 2.26 | 2.04 |
| 4[d] | 1.00 | 0.5 | 7.5 | 9.8 | 1.00 | 0.97 | 1.94 |
| 5[d] | 1.00 | 1.0 | 20.4 | 11.1 | 1.66 | 1.71 | 2.06 |

[a] Bulk polymerization at 0–2°C, [PW$_{12}$] = 6.14 $\times 10^{-3}$ mol L$^{-1}$, [H$_2$O]/[PW$_{12}$] = 15.
[b] Calculated with the same method described in Table I.
[c] $\bar{f} = [\overline{M}_n \text{ (VPO)}/\overline{M}_n \text{ (NMR)}] \times 2$.
[d] BG was used instead of water.

where [THF]$_o$ and [THF]$_t$ are the THF concentrations at $t = 0$ and $t$, respectively.

A plot of $\ln([\text{THF}]_o - [\text{THF}]_e)/([\text{THF}]_t - [\text{THF}]_e)$ versus the polymerization time gave a straight line (Fig. 2). The linear relationship clearly shows good agreement with eq. (2), indicating [P*] is constant and there was no loss of active centers in

the polymerization. The rate constants of the chain propagation ($k_p$), on the assumption of Bednarek et al.[6] that each of the three protons of HPA starts a chain (i.e., that the concentration of active species [P*] = 3[PW$_{12}$]), were found to be 3.78 $\times 10^{-3}$ L mol$^{-1}$ s$^{-1}$ at 0°C and 1.98 $\times 10^{-2}$ L mol$^{-1}$ s$^{-1}$ at 20°C, respectively. These values are in good agreement with the propagation rate constant of THF on ionic species.[18,21,22]

A detailed structure analysis of the copolyether based on the NMR spectrum and study of the polymerization mechanism of this system will be published in the future.



**Figure 1**   $^1$H-NMR spectra (the 1.0–5.0 ppm region only) of copolyether (1500) containing 22.5 mol % of EO moieties (a) before and (b) after esterification with (CF$_3$CO)$_2$O.



**Figure 2**   Kinetics of the polymerization of THF initiated with PW$_{12}$ in the bulk. [PW$_{12}$] = 6.14 $\times 10^{-3}$ mol L$^{-1}$, [EO] = 2.01 mol L$^{-1}$. (a) 20°C, [EG]/[PW$_{12}$] = 15, [THF]$_e$ = 2.96 mol L$^{-1}$ and (b) 0°C, [H$_2$O]/[PW$_{12}$] = 30, [THF]$_e$ = 1.7 mol L$^{-1}$. The [THF]$_e$ values are from Ofstead.[23]

## CONCLUSIONS

1. EO is an efficient promoter for the polymerization of THF initiated with $PW_{12}$. High conversion of copolyether could be easily obtained within a polymerization time of 4–5 h and a low concentration of $PW_{12}$ of around 2–5 wt % based on the total amount of THF charged.

2. Water or BG could be used to adjust the molecular weight of the products. The polymerization proceeded well, even when the molar ratio of $H_2O/PW_{12}$ reached 30, and the product with medium molecular weight could be prepared in high yield.

3. The copolymer has a hydroxyl group at both chain ends and a lower melting point in comparison with polytetramethylene ether glycol having the same molecular weight.

4. The polymerization proceeds through macrocations without a chain termination reaction.

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