

# Synthesis and Characterization of Linear Asymmetrical Poly(propylene oxide) Diol

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**ABSTRACT:** Linear asymmetrical poly(propylene oxide) was synthesized through four-step reactions: selective benzylation, alcohol exchange reaction, propylene oxide anionic polymerization, debenylation. One terminal of the asymmetrical polymer chains is alcohol hydroxyl and the other is phenol hydroxyl. It was characterized with infrared (IR) and <sup>1</sup>H Nuclear Magnetic Resonance (<sup>1</sup>H-NMR). Peaks at 1.11, 3.38, and 3.53 ppm were attributed to side groups (—OCH<sub>2</sub>CH(CH<sub>3</sub>)—), backbone units (—OCH<sub>2</sub>CH(CH<sub>3</sub>)—) and (—OCH<sub>2</sub>CH(CH<sub>3</sub>)—) of poly(propylene oxide), respectively. Molecular weight and molecular weight distribution were measured with <sup>1</sup>H-NMR and laser light scattering (LLS), which showed that the linear asymmetrical

poly(propylene oxide) was mono-disperse (PDI = 1.02–1.07). Then, its carbamate reaction with phenyl isocyanate was studied; the reaction rate constants for phenol hydroxyl and alcohol hydroxyl of poly(propylene oxide) were  $k_1 = 0.209 \text{ mol L}^{-1} \text{ min}^{-1}$  and  $k_2 = 0.051 \text{ mol L}^{-1} \text{ min}^{-1}$ . There was a great reactivity difference for two types of hydroxyls in asymmetrical poly(propylene oxide), contrasting to the single carbamate reaction rate constant of symmetrical poly(propylene oxide) ( $k_3 = 0.049 \text{ mol L}^{-1} \text{ min}^{-1}$ ). © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 1095–1099, 2010

**Key words:** asymmetrical poly(propylene oxide); anionic polymerization; carbamate reaction; kinetics

## INTRODUCTION

Poly(propylene oxide) is an important material in polyurethane (PU) industry, and its preparation via anionic polymerization has been intensively investigated.<sup>1–6</sup> At present, most polyethers are synthesized with diol or polyol as substrate.<sup>7–9</sup> Chain propagation starts from two or more hydroxyls during the polymerization of epoxide, such as ethylene oxide, propylene oxide etc. The obtained polyethers are symmetrical and contain only alcohol terminal hydroxyl.

Other studies showed that different hydroxyls in polyethers, such as alcohol and phenol, had different chemical properties when reacting with isocyanate.<sup>10–13</sup> For example, the phenol-isocyanate reaction, namely, the blocking and unblocking reaction of isocyanate, is an equilibrium reaction. A substantial number of references have covered its applica-

tions in many aspects,<sup>14</sup> while there is no similar reaction taking place in alcohol-isocyanate system.

With the development of PU coatings, more and more attention has been paid to synthesize PU with new-type monomers,<sup>15–18</sup> such as various polyethers, polyesters, and diisocyanates. However, few investigations were reported on asymmetrical polyethers with different hydroxyls. In this article, we aim to explore a method for the preparation of asymmetrical poly(propylene oxide) with potassium alcoholate as initiator. One terminal of the polymer chain is alcohol hydroxyl and the other is phenol hydroxyl. Then, its carbamate reaction with phenyl isocyanate was studied and compared with symmetrical poly(propylene oxide)-phenyl isocyanate reaction.

## EXPERIMENTAL

### Materials

4-Hydroxyphenethyl alcohol, symmetrical poly(propylene oxide) ( $M_n = 3500$ ) and phenyl isocyanate were purchased from Sigma–Aldrich, St. Louis, Missouri; potassium *t*-butoxide was purchased from Alfa Aesar, Heysham, England; benzyl bromide, potassium carbonate and 10% palladium on carbon were purchased from Sinopharm Chemical Reagent, Shanghai, China; and all of them were used as

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received. Propylene oxide, acetone and cyclohexane were purchased from Sinopharm Chemical Reagent, Shanghai, China, and purified by distillation in the presence of calcium hydroxide; hexamethylphosphorotriamide (HMPT) was purchased from Sinopharm Chemical Reagent, Shanghai, China, and purified by vacuum distillation in the presence of calcium hydroxide.

### Measurements

IR spectra were recorded on an IR Prestige-21 spectrometer (Shimadzu Corporation, Kyoto, Japan). *In situ* FTIR spectra were recorded on a React IR IC10 spectrometer (Mettler Toledo International, Columbia, Maryland).  $^1\text{H-NMR}$  spectra were recorded on an AVANCE II 400 spectrometer (Bruker BioSpin, Fallanden, Switzerland) with tetramethylsilane as internal reference. Number-average molecular weight was calculated from  $^1\text{H-NMR}$  spectra and molecular weight distribution was measured on a DAWN HELEOS laser light scattering analyzer (LLS) (Wyatt Technology Corporation, Santa Barbara, CA) with tetrahydrofuran as eluent. GC spectra were recorded on a GC-14C spectrometer (Shimadzu Corporation, Kyoto, Japan) with column temperature, oven temperature and detector temperature at 363, 423, and 403 K, respectively.

### Synthesis of asymmetrical poly(propylene oxide)

#### Synthesis of 4-(benzyloxy)benzyl alcohol (I)

A mixture of 4-hydroxybenzyl alcohol (12.0 mmol) and potassium carbonate (15.0 mmol) in acetone (100 mL) was reacted with benzyl bromide (10.0 mmol) and refluxed for 6 h. After reaction finished, the mixture was washed with potassium hydroxide solution (3.0 mol/L) for three times and extracted with EtOAc. The organic layer was concentrated and dried in a vacuum oven.

4-(Benzyloxy)benzyl alcohol (I): IR ( $\text{cm}^{-1}$ ): 3332.99, 3032.10, 2870.08, 1608.63, 1510.26, 1458.18, 1382.96, 1244.09, 1170.79, 1002.98.  $^1\text{H-NMR}$   $\delta$ (DMSO-*d*6): 4.40(d, 2H,  $\text{CH}_2\text{OH}$ ), 5.03(t, 1H,  $\text{CH}_2\text{OH}$ ), 5.09(s, 2H,  $\text{OCH}_2\text{Ph}$ ), 6.96(d, 2H), 7.23(d, 2H), 7.38–7.43(m, 5H).

#### Preparation of potassium 4-(benzyloxy)benzyl alcoholate initiator(II)

Potassium *t*-butoxide (10.0 mmol) and I (10.0 mmol) were mixed in cyclohexane (150 mL) and reacted at the azeotropic point of tertiary butanol–cyclohexane system. cyclohexane is the entrainer to remove the product—tertiary butanol. After 12 h, about 100 mL liquid was distilled out. The mixture was transferred to another flask and concentrated under vacuum to remove residual solvent.

Potassium 4-(benzyloxy)benzyl alcoholate (II):  $^1\text{H-NMR}$   $\delta$ (DMSO-*d*6): 4.40(s, 2H,  $\text{CH}_2\text{OK}$ ), 5.09(s, 2H,  $\text{OCH}_2\text{Ph}$ ), 6.96(d, 2H), 7.23(d, 2H), 7.38–7.43(m, 5H).

#### Synthesis of Poly(propylene oxide) alcohol(III)

A flask containing II (10.0 mmol) was replaced with argon for three times. To this was added propylene oxide (0.255 mol) and HMPT (30.0 mL) with magnetic stirring. Polymerization was maintained at 308 K and argon atmosphere. Pure water was added after reaction finished. The product was extracted with ether, washed with pure water and finally dried in a vacuum oven. The designed molecular weight was 1000, 1500, 2000, and 2500.

Poly(propylene oxide) alcohol (III): IR ( $\text{cm}^{-1}$ ): 3468.01, 2972.31, 2870.08, 1610.56, 1510.26, 1456.26, 1375.25, 1296.16, 1242.16, 1109.07, 1014.56.  $^1\text{H-NMR}$   $\delta$ ( $\text{CDCl}_3$ ): 1.11(m, side groups,  $-\text{OCH}_2\text{CH}(\text{CH}_3)-$ ), 3.38(m, backbone units,  $-\text{OCH}_2\text{CH}(\text{CH}_3)-$ ), 3.53(m, backbone units,  $-\text{OCH}_2\text{CH}(\text{CH}_3)-$ ), 4.44(s, 2H,  $\text{CH}_2\text{O}$ ), 5.03(s, 2H,  $\text{OCH}_2\text{Ph}$ ), 6.90(d, 2H), 7.13(d, 2H), 7.32–7.42(m, 5H).

#### Synthesis of asymmetrical poly(propylene oxide)(IV)

A solution of III (110 mg) in MeOH (10 mL) was reacted with hydrogen stream on 300 mL/min, using 10% palladium on carbon (11 mg) as catalyst. The reaction lasted for 20 h at room temperature. After reaction finished, the product was filtered, concentrated and dried in a vacuum oven.

Asymmetrical poly(propylene oxide) (IV):IR ( $\text{cm}^{-1}$ ): 3475.73, 2972.31, 2870.08, 1616.35, 1516.05, 1452.40, 1375.25, 1298.09, 1269.16, 1111.00, 1014.56.  $^1\text{H-NMR}$   $\delta$ ( $\text{CDCl}_3$ ): 1.11(m, side groups,  $-\text{OCH}_2\text{CH}(\text{CH}_3)-$ ), 3.38(m, backbone units,  $-\text{OCH}_2\text{CH}(\text{CH}_3)-$ ), 3.53(m, backbone units,  $-\text{OCH}_2\text{CH}(\text{CH}_3)-$ ), 4.44(s, 2H,  $\text{CH}_2\text{O}$ ), 6.90(d, 2H), 7.13(d, 2H).

### Studies on carbamate reactions

The *in situ* FTIR spectrometer, React IR IC10, was used for reaction kinetics studies. Clean and dry air was flowed into the instrument continuously. To eliminate the interference of impurities, the background spectra were recorded until the absorbance of all impurities was constant.

Asymmetrical poly(propylene oxide) (IV, 1.458 g) and DMSO (6 mL) were poured into the flask and heated to 297 K under nitrogen atmosphere. Then the stoichiometric phenyl isocyanate (0.4 mL) was added and the reaction began. Data were collected every 15 seconds. The resolution was  $8\text{ cm}^{-1}$  and scan region was 4000–650  $\text{cm}^{-1}$ .

Likewise, symmetrical poly(propylene oxide) (3.698 g) was reacted with phenyl isocyanate (0.2

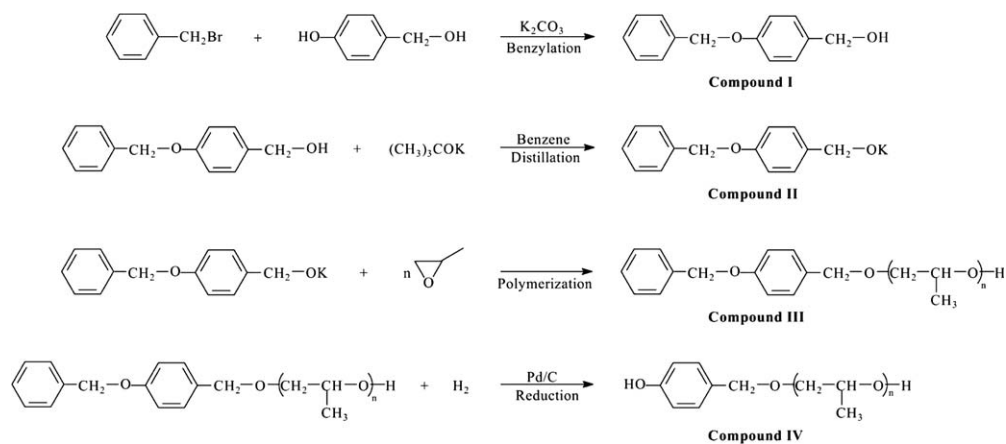


Figure 1 Synthetic route of asymmetrical poly(propylene oxide).

mL) in DMSO (4 mL) at 297 K. *In situ* FTIR spectrometer was used to monitor the reaction, and the test conditions were the same as aforementioned.

## RESULTS AND DISCUSSION

The synthetic route of asymmetrical poly(propylene oxide) was shown in Figure 1.

In Figure 1, asymmetrical poly(propylene oxide) was synthesized with potassium 4-(benzyloxy)benzyl alcoholate as initiator. Because of its high substituted reactivity and low initiated reactivity, phenol hydroxyl in 4-hydroxybenzyl alcohol must be protected. In our method, benzyl bromide was used to protect phenol hydroxyl before polymerization, and hydrogen stream was used to get rid of protective groups with Pd/C catalyst.

### Purification of 4-(benzyloxy)benzyl alcohol

A lot of studies have been reported about selective benzylation on phenol when both phenol and alcohol are in the same reaction conditions. So we did not make a detailed study. It was worth noting that 4-hydroxybenzyl alcohol was a little excessive during the reaction, to make benzyl bromide reacted completely. Therefore, it must be removed after reaction finished.

An effective purification method is column chromatography on silica, using ethyl acetate and hexane as mixed eluent. However, Fauq<sup>19</sup> reported that the volume ratio of ethyl acetate to hexane was 1 : 2, yet Lee<sup>20</sup> reported that the volume ratio of ethyl acetate to hexane was 2 : 1. After experimental study, we find that Lee's method reached better separation efficiency.

In fact, we used another purification method. Potassium hydroxide solution was used to wash reaction mixture and 4-hydroxybenzyl alcohol was also

completely removed. This method seemed more convenient when lots of products were needed.

### Preparation of potassium 4-(benzyloxy)benzyl alcoholate initiator

The reaction of potassium *t*-butoxide and 4-(benzyloxy)benzyl alcohol is a balance. Tertiary butanol must be removed to make the equilibrium shift rightwards. Because the boiling points of reactants and tertiary butanol were adjacent, ordinary distillation was inappropriate and reactive rectification must be used. Different solvents including benzene, toluene and cyclohexane were used as entrainer to remove tertiary butanol. To determine their effect, Gas Chromatography was used to analysis time dependent mass fraction of tertiary butanol in distillation cut (Fig. 2).

As was shown in Figure 2, the mass fraction in benzene was very low and it took relative long time to remove tertiary butanol completely. While the mass fraction in cyclohexane reduced extremely

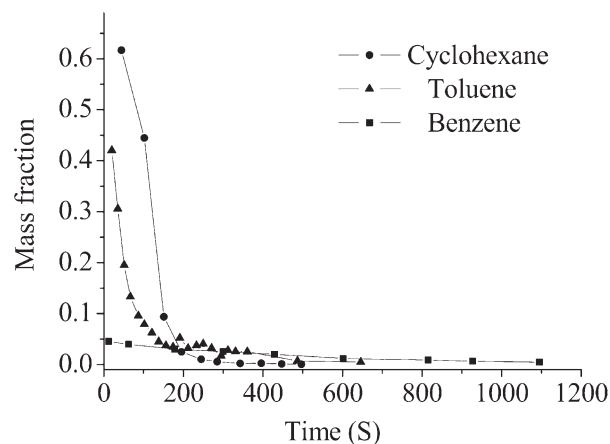


Figure 2 Mass fraction of tertiary butanol in cyclohexane, toluene and benzene.

**TABLE I**  
Molecular Weight and its Distribution of Asymmetrical Poly(propylene oxide)

Runs	$\bar{M}_{n,calc}$	$\bar{M}_n$	PDI	Yield (%) <sup>a</sup>
1	1000	982	1.02	40.5
2	1500	1450	1.02	37.8
3	2000	1868	1.05	38.2
4	2500	2208	1.07	34.7

<sup>a</sup> Overall yield after four-step reaction.

sharp: it took only 400 s to remove tertiary butanol from more than 60% to zero. The efficiency of toluene was in the middle. Therefore, cyclohexane was chosen to react with potassium *t*-butoxide.

### Synthesis of asymmetrical poly(propylene oxide)

Before debenylation, multiple peaks at 7.32–7.4 ppm and single peak at 5.03 ppm are attributed to aryl and methylene protons derived from benzyl bromide. Double peaks at 6.90 ppm, 7.13 ppm and single peak at 4.44 ppm are attributed to aryl and methylene protons derived from 4-hydroxybenzyl alcohol.

A lot of researches have been reported about debenylation reaction,<sup>21</sup> so we also did not make a detailed study. After debenylation, multiple peaks at 7.32–7.4 ppm and single peak at 5.03 ppm were absent. That is, benzyl was removed and phenol hydroxyl generated. Double peaks at 6.90 ppm, 7.13 ppm and single peak at 4.44 ppm were still obvious, which could also confirm the presence of phenol hydroxyl indirectly. Moreover, peaks at 1.11, 3.38, and 3.53 were attributed to side groups (–OCH<sub>2</sub>CH(CH<sub>3</sub>)–), backbone units (–OCH<sub>2</sub>CH(CH<sub>3</sub>)–) and (–OCH<sub>2</sub>CH(CH<sub>3</sub>)–) of poly(propylene oxide), respectively.

Number-average molecular weight ( $\bar{M}_n$ ) was calculated by <sup>1</sup>H-NMR, according to Ding's method.<sup>22</sup> Molecular weight distribution (PDI) was measured by LLS. Their results were shown in Table I.

Different stoichiometric ratios of potassium alcoholate to propylene oxide were designed (Table I). Compared with the designed molecular weight ( $\bar{M}_{n,calc}$ ), the experimental value ( $\bar{M}_n$ ) was a little lower. The reason was attributed to the chain-transfer reaction or inert initiator, which had been studied in our former article.<sup>23</sup> A special polar solvent, HMPT, was used to dissolve potassium alcoholate initiator and make the polymerization homogeneous, so Mono-disperse poly(propylene oxide) was acquired. Moreover, the overall yield after four-step synthesis was about 35%.

### Kinetic studies on carbamate reaction

As is known to all, Beers-Lambert Law could only be used for the solution of low concentration. When highly concentrated solution was concerned, we must examine the linear relationship between ab-

sorbance (*A*) and concentration (*C*). As was shown in Figure 3, the –NCO absorbance at 2273 cm<sup>–1</sup> varied with different isocyanate concentration in DMSO, and linear relationship appeared correct only when the concentration was lower than 1.0 mol/L. So 0–1.0 mol/L was used in the following kinetic studies.

Thus, the measured absorbance (*A*) is directly proportional to the sample concentration,

$$A = K \cdot C \quad (1)$$

where *K* is the linear-slope in Figure 3.

To obtain the rate constants, it is assumed that there is no side reaction. Hence the isocyanate conversion (*p*) can be calculated from absorbance.

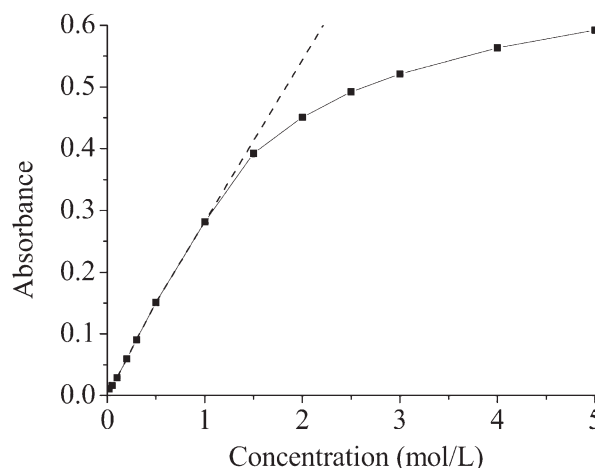
$$\begin{aligned} \text{Isocyanate conversion (p)} &= \frac{[\text{NCO}]_0 - [\text{NCO}]_t}{[\text{NCO}]_0} \\ &= 1 - \frac{[\text{NCO}]_t}{[\text{NCO}]_0} = 1 - \frac{A_t}{A_0} \quad (2) \end{aligned}$$

where  $[\text{NCO}]_0$  and  $[\text{NCO}]_t$  are the isocyanate concentrations at time zero and certain reaction moment *t*; *A*<sub>0</sub> and *A*<sub>*t*</sub> are the intensity of –NCO absorption at time zero and certain reaction moment *t*, respectively.

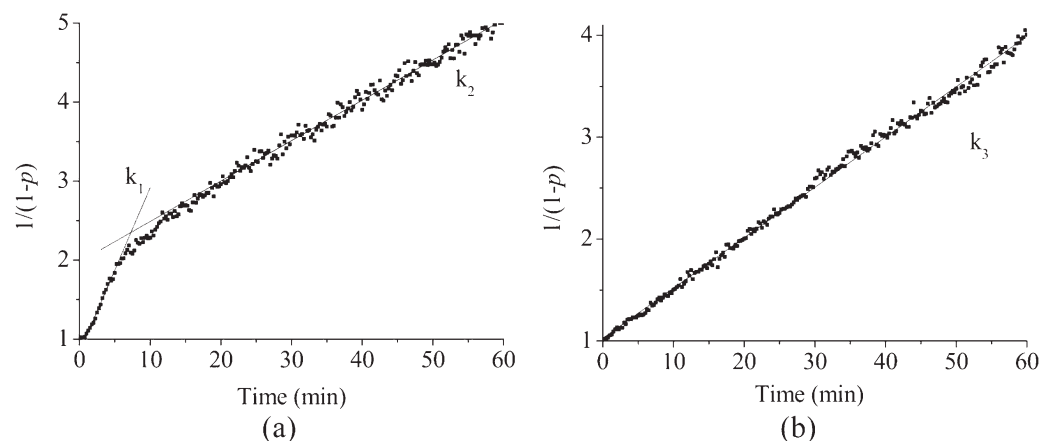
When the stoichiometric ratio is used, the total isocyanate concentration can be given in the general *n*th-order expression as a relationship of time-dependence<sup>24</sup>; for the *n*th-order kinetic equation, when  $[\text{NCO}] = [\text{OH}]$ , it can be expressed as

$$\begin{aligned} \frac{dp}{dt} &= k \cdot [\text{NCO}]^a \cdot [\text{OH}]^b = k \cdot [\text{NCO}]^{a+b} \\ &= k \cdot (1 - p)^{a+b} = k \cdot (1 - p)^n \quad (3) \end{aligned}$$

here *k* is apparent rate constant, which depends on the reaction temperature. Parameter *n* is the reaction order.



**Figure 3** Relationship between absorbance and concentration of –NCO at 2273 cm<sup>–1</sup>.



**Figure 4** Relationship between  $1/(1-p)$  and time for carbamate reaction: (a) asymmetrical poly(propylene oxide); (b) symmetrical poly(propylene oxide).

Assuming it is a second-order process, we can use the  $n$ th-order approach to model the reaction kinetics as follows:

$$\frac{1}{1-p} = k \cdot t + b \quad (4)$$

Figure 4 showed the experimental points for the relationship between  $1/(1-p)$  and reaction time  $t$ . In Figure 4(a), the asymmetrical poly(propylene oxide) was synthesized from Run 3, Table I. A reasonable linear relationship could be achieved according to eq. (4) if the reaction was divided into two stages. It indicated that phenol hydroxyl and alcohol hydroxyl in asymmetrical poly(propylene oxide) had different reactivity when reacting with phenyl isocyanate ( $k_1 = 0.209 \text{ mol L}^{-1} \text{ min}^{-1}$  and  $k_2 = 0.051 \text{ mol L}^{-1} \text{ min}^{-1}$ ). However, there was no reactivity difference in symmetrical poly(propylene oxide) [Fig. 4(b)], which was purchased from Sigma–Aldrich. The apparent rate constant was invariable ( $k_3 = 0.049 \text{ mol L}^{-1} \text{ min}^{-1}$ ).

## CONCLUSIONS

In conclusion, linear asymmetrical poly(propylene oxide) has been successfully synthesized through the procedures of selective benzylation, alcohol exchange reaction, propylene oxide anionic polymerization, debenylation. One terminal of the polymer chains is alcohol hydroxyl and the other is phenol hydroxyl.

Furthermore, its carbamate reaction with phenyl isocyanate was studied. Kinetic data showed there was a great reactivity difference between phenol hydroxyl and alcohol hydroxyl in asymmetrical poly(propylene oxide). The reaction rate constants for the two stages at 297 K were  $k_1 = 0.209 \text{ mol L}^{-1} \text{ min}^{-1}$  and  $k_2 = 0.051 \text{ mol L}^{-1} \text{ min}^{-1}$ . The linear asymmetrical poly(propylene oxide) may be has special applications in the preparation of PU.

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