

Bottleneck for Reactive Molar Mass in the Polymerization of Propylene Oxide Initiated with Potassium *t*-Butoxide

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ABSTRACT: The anionic polymerization of propylene oxide was investigated with potassium *t*-butoxide as an initiator, and the solvent hexamethyl phosphoric triamide was used in controlling experiments. The relative molar mass limit of the products was determined as about 2700, and the C=C double bond was found to exist by NMR. *In situ* Fourier transform infrared spectroscopy was used to monitor the whole polymerization process until the absorbance reached a constant value and the system reached equilibrium. However, propylene oxide still existed in the system, and alkoxide was detected in the reaction system

by ²³Na-NMR. On the basis of these results, we deduced that the residual alkoxide was not active enough to initiate propylene oxide polymerization in the near end of the polymerization. Therefore, there might have been another factor that limited the increase of the relative molar mass of poly(propylene oxide) in addition to chain transfer. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 3656–3660, 2009

Key words: anionic polymerization; FTIR; molecular weight distribution/molar mass distribution; NMR; polyethers

INTRODUCTION

Poly(propylene oxide) has been widely used in many fields, and its preparation via anionic polymerization has been extensively investigated from many points of view, including the as chain-transfer process, kinetics and isomerization of allyl ether, initiators, additives, molecular weight, and stereo regularity.^{1–10}

Because the relative molar mass of poly(propylene oxide) is very important for its application, the control of the molecular weight of poly(propylene oxide) has been a key problem in the anionic polymerization of propylene oxide. Until now, nearly all involved researchers have believed that the chain-transfer reaction was the main factor limiting the polymeric chain propagation.¹¹ The alkoxide ion formed by elimination is, of course, capable of initiating a new chain, now capped at one end by an allyl ether group. The maximum relative molar mass of a base-catalyzed propylene oxide polymer is limited by the ratio of the propagation constant (k_p) to the transfer constant (k_{tr}), as shown in Scheme 1.

Simons and Verbanee¹² suggested that the rearrangement of allyl ethers to propenyl ethers (Scheme 2) under basic conditions existed and resulted in the two kinds of end groups.

Gee et al.¹³ pointed out that isopropenyl ethers might be formed from another rearrangement reaction, as shown in Scheme 3.

In this study, the anionic polymerization of propylene oxide was investigated with potassium *t*-butoxide as the initiator, and we found that the coexistence of propylene oxide monomer and an alkoxide initiator in the reaction system, which implied that the residual alkoxide was not active enough to initiate the propylene oxide polymerization in the near end of polymerization process. There may, therefore, be another factor limiting the increase of relative molar mass in addition to chain transfer.

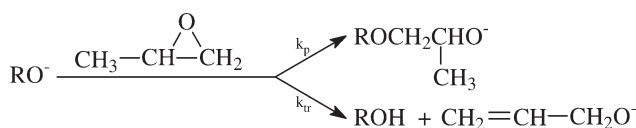
EXPERIMENTAL

Materials

Potassium *t*-butoxide was purchased from Alfa Aesar (Heysham, England), and sodium salt was purchased from Sinopharm Chemical Reagent Co. (Shanghai, China) both were used as received. Propylene oxide was purchased from Sinopharm Chemical Reagent Co. and purified by distillation in the presence of calcium hydroxide; hexamethyl phosphoric triamide (HMPT) was purchased from

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Scheme 1

Sinopharm Chemical Reagent Co. and was purified by vacuum distillation in the presence of calcium hydroxide.

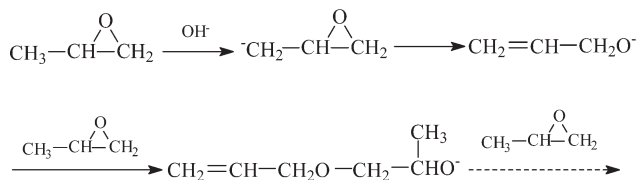
Preparation and characterization of poly(propylene oxide)

All of the reactions were carried out at 308 K as follows: a flask containing potassium *t*-butoxide was pumped into a vacuum and filled with argon three times. Propylene oxide was added, stirred with a magnetic stirrer, and maintained for a given period of time. Different relative molar masses were designed as 1000–5000 by variation of the molar ratios of potassium *t*-butoxide to propylene oxide.

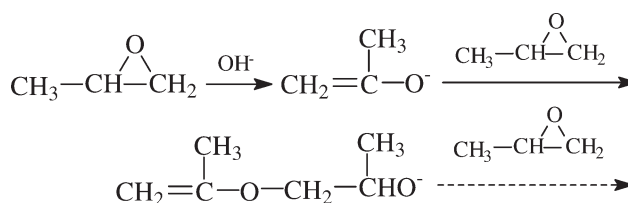
Moreover, polymerization was done with the polar solvent HMPT as follows: after argon replacement, propylene oxide was added to the HMPT solution containing potassium *t*-butoxide to run the polymerization. Different relative molar masses were designed as 1000–4000 by variation of the molar ratios of potassium *t*-butoxide to propylene oxide.

After the polymerization, sodium chloride was first added to the mixture and stirred strongly. Then, ^{23}Na -NMR, recorded on a Bruker AVANCEII400 spectrometer (Fallanden, Switzerland), was used to analyze the reaction mixture, which had been precipitated for 12 h. After that, the reaction was terminated by the addition of pure water. The polyether was extracted by ether and washed with pure water three times to remove potassium hydroxide and sodium salt before it was dried in a vacuum oven.

In situ Fourier transform infrared spectroscopy (Mettler–Toledo IC10 React IR spectrometer, Columbia, MD) was used to monitor the polymerization process until the absorbance reached a constant value and the system reached equilibrium. The number-average relative molar mass was measured by NMR. Gel permeation chromatography/multi-angle static laser light scattering (Wyatt Dawn Heleos ana-



Scheme 2



Scheme 3

lyzer, Santa Barbara, CA) was used to measure the distribution of the relative molar mass with tetrahydrofuran as the eluent.

RESULTS AND DISCUSSION

IR and ^1H -NMR analysis

The IR and ^1H -NMR spectra of poly(propylene oxide) (run 1, Table I) are shown in Figures 1 and 2, respectively.

From Figure 1, the band at 3500 cm^{-1} was assigned to $-\text{OH}$ stretching, and that at 1103 cm^{-1} was assigned to $\text{C}-\text{O}-\text{C}$ stretching. The assignments of all of the chemical shifts shown in Figure 2 are given in Table I, which were very similar to Yu et al.'s viewpoint.⁵

Relative molar mass limit and chain transfer

Different stoichiometric ratios of potassium *t*-butoxide to propylene oxide were used. Figure 3 shows the relative molar mass [number-average molecular weight (M_n)] of poly(propylene oxide) with the changes in the theoretical value and the relative molar mass distribution (polydispersity index). The existence of HMPT influenced the relative molar mass very little and only made its distribution lower. Take runs 3 and 8 as examples. The contrast of molar mass distribution, that is, the effects of HMPT, is shown in Figure 4.

In runs 1, 2, 6, and 7, the experimental value of the relative molar mass was very similar to the designed one. However, for runs 3–5, 8, and 9, it made a great difference. That is, when the relative molar mass [calculated number-average molecular weight ($M_{n,\text{calc}}$)] was designed as larger, its experimental value was limited to around 2700.

There was no doubt that the chain transfer limited chain propagation. The $\text{C}=\text{C}$ bond, a sign of chain-transfer occurrence, was clearly found to exist from the ^1H -NMR spectra (Table I, runs a–c). The values of the transfer constant were calculated according to Ding et al.'s⁹ method. The results show that the chain transfer increased remarkably in runs 3–5, which limited the relative molar mass increases (Table II).

TABLE I
 $^1\text{H-NMR}$ Spectral Assignments for Poly(propylene oxide) in CDCl_3

Run	δ (ppm)	Peak split	Assignment
a	5.87	Multiplet	Allyl end group, $\text{CH}_2=\text{CHCH}_2\text{O}-$
b	5.25, 5.16	Two doublets	Allyl end group, $\text{CH}_2=\text{CHCH}_2\text{O}-$
c	3.98	Doublet	Allyl end group, $\text{CH}_2=\text{CHCH}_2\text{O}-$
d	3.89	Multiplet	Hydroxyl end group, $-\text{CH}_2\text{CH}(\text{CH}_3)-\text{OH}$
e	3.53	Multiplet	Backbone units, $-\text{OCH}_2\text{CH}(\text{CH}_3)-$
f	3.38	Multiplet	Backbone units, $-\text{OCH}_2\text{CH}(\text{CH}_3)-$
g	3.15	Triplet	Hydroxyl end group, $-\text{CH}_2\text{CH}(\text{CH}_3)-\text{OH}$
h	1.14	Singlet	Initiator end group, $(\text{CH}_3)_3\text{COCH}_2\text{CH}(\text{CH}_3)-$
i	1.11	Multiplet	Side groups, $-\text{OCH}_2\text{CH}(\text{CH}_3)-$

Ineffective alkoxide initiator

However, from the *in situ* Fourier transform infrared spectra, after 24 h of polymerization, the absorbance of propylene oxide was still quite obvious [Fig. 5(B)]. That happened in runs 3–5, 8, and 9, in which the experimental relative molar mass was much lower than the designed one. It seemed that the alkoxide initiator was eventually inert and could not initiate propylene oxide to polymerize. The main absorbances of the epoxy groups at 828 cm^{-1} in run 2 and 3 are shown in Figure 5. Those depict the concentration reduction of propylene oxide.

In run 2, propylene oxide was nearly completely consumed after 16 h. However, in run 3, the absorbance of propylene oxide remained obvious from beginning to end. This might have resulted because of two reasons: (1) the alkoxide was not effective enough for the polymerization to proceed, and (2) it was changed into potassium hydroxide during the reaction process.

Confirmation by $^{23}\text{Na-NMR}$

Attempts were made to prove the existence of the intermediate, potassium alcoholate, in run 3, but it was very difficult to accomplish directly. So a substi-

tuted method of ion exchange was used after polymerization as follows: sodium chloride (twice the amount of potassium *t*-butoxide) was introduced to make potassium alcoholate change into sodium alcoholate, and the upper liquor was used to do $^{23}\text{Na-NMR}$ research after precipitation. All of the $^{23}\text{Na-NMR}$ spectra were collected in the solvent of deuterated dimethyl sulfoxide and tested quickly to prevent secondary reaction.

It was obvious that sodium alkoxide definitely existed in run 2 because propylene was completely consumed. So the NMR spectra of runs 2 and 3 are shown for comparison in Figure 6. The NMR spectra of sodium chloride, sodium *t*-butoxide, and sodium hydroxide are also given in Figure 6. The chemical shifts (δ 's) were 3.080 (run 2), 3.081 (run 3), 0.903 (sodium chloride), -0.795 (sodium *t*-butoxide), and 0.955 (sodium hydroxide).

It is well known that the chemical shift varies with different sodium salts in aprotic solvents. After the interference of sodium chloride, sodium *t*-butoxide, and sodium hydroxide was excluded, the peak value of $\delta = 3.08$ was the chemical shift of sodium alkoxide. It showed the existence of oxyalkyl instead of hydroxide in runs 2 and 3.

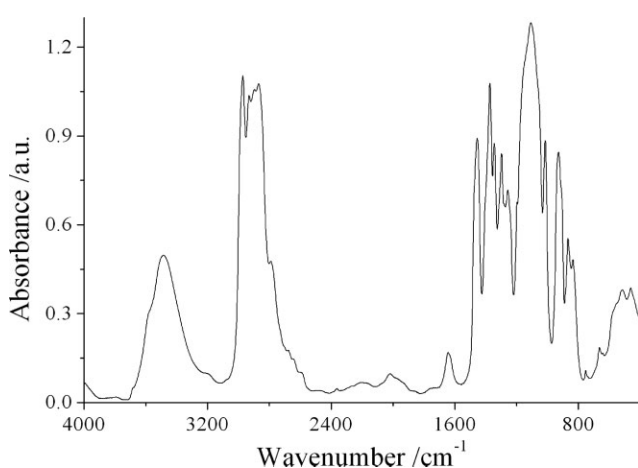


Figure 1 IR spectrum of poly(propylene oxide).

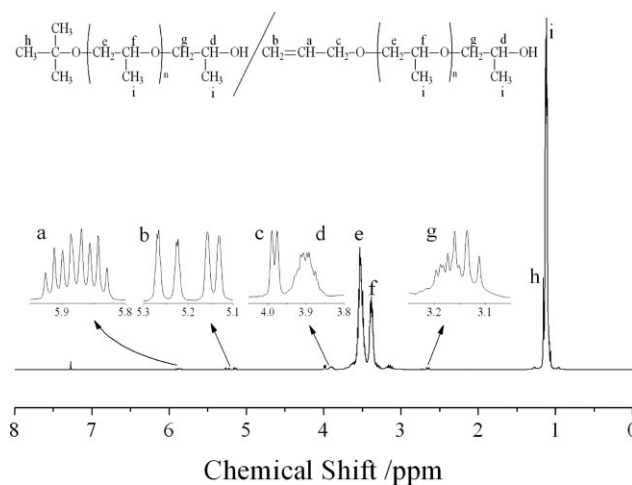


Figure 2 $^1\text{H-NMR}$ spectrum of poly(propylene oxide).

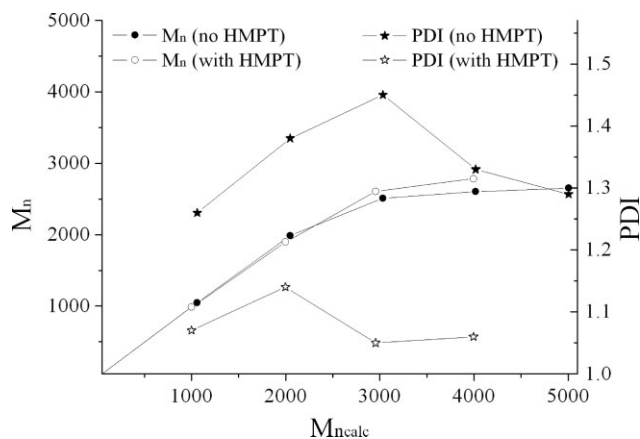


Figure 3 Relative molar masses and molar mass distributions of poly(propylene oxide) with different polymerization methods.

To further verify the chemical shift of oxyalkyl, the upper liquor was moved to another flask before a small quantity of water was added. After the liquor was stirred mildly for 12 h, ^{23}Na -NMR was

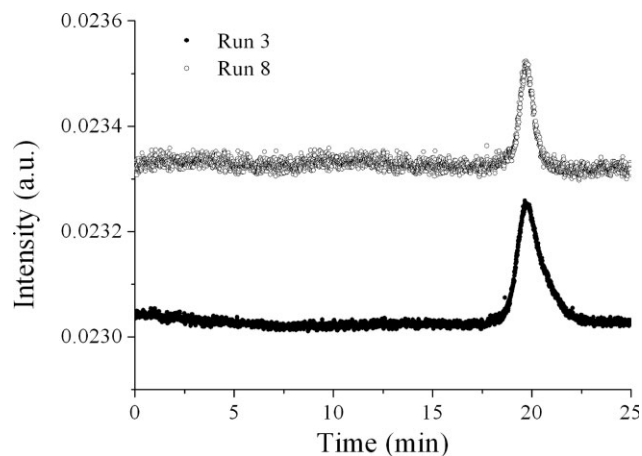


Figure 4 Diagram of the relative molar mass distribution for runs 3 and 8.

used to characterize the reaction mixture. As predicted, the chemical shift transferred to $\delta = 0.931$, which implied that the alkoxide changed into sodium hydroxide.

TABLE II
Chain-Transfer Constants of Poly(propylene oxide) for Different Polymerization Methods

Run	r^a	HMPT (mol %) ^b	$M_{n,calc}$	Chain-transfer constant $\times 10^3$
1	17 : 1	—	1060	0.79
2	34 : 1	—	2046	0.83
3	51 : 1	—	3032	3.97
4	68 : 1	—	4018	7.85
5	85 : 1	—	5004	10.3
6	16 : 1	50	998	0.82
7	33 : 1	50	1997	1.53
8	49.7 : 1	50	2955	2.63
9	67.6 : 1	50	3994	6.31

^a Molar ratio of propylene oxide to potassium *t*-butoxide.

^b HMPT is a polar solvent substitute for dimethyl sulfoxide because dimethyl sulfoxide can react slowly with potassium *t*-butoxide.¹⁴

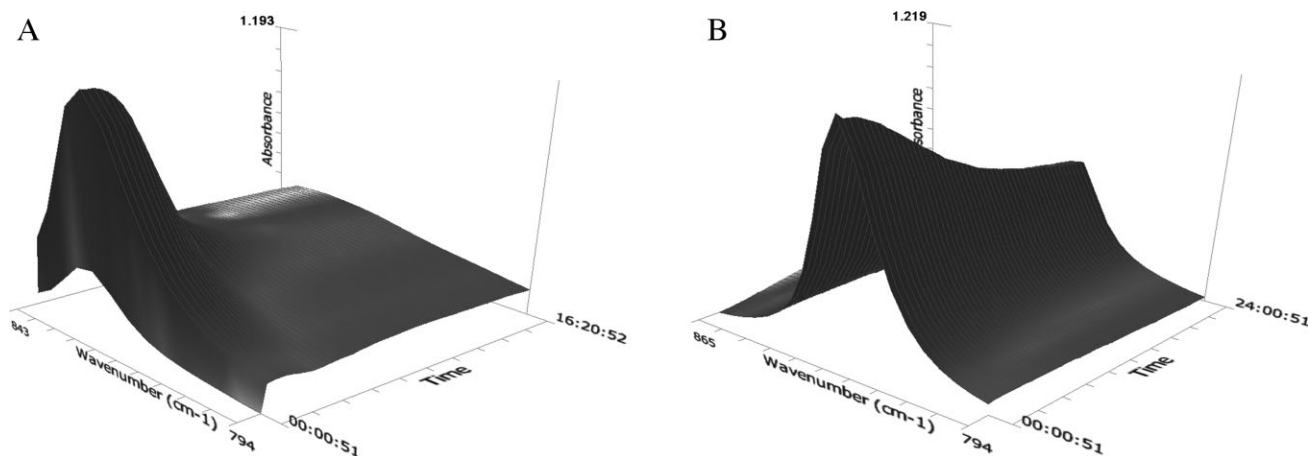


Figure 5 Reactive IR spectra of propylene oxide absorbance at 828 cm^{-1} in different runs: (A) run 2 and (B) run 3.

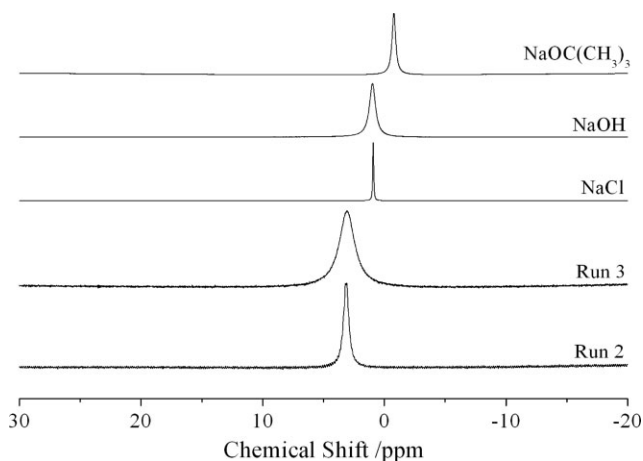


Figure 6 ^{23}Na -NMR spectra of the reaction mixtures in runs 2 and 3.

CONCLUSIONS

The upper limit of the relative molar mass of poly(propylene oxide) was determined as around 2700. The C=C bond was clearly observed by ^1H -NMR, which showed that the chain transfer could have a large influence on the increase of relative molar mass.

However, the alkoxide initiator was found in the reaction system, which was not active enough to initiate the polymerization of the monomer. We deduced that the alkoxyl anion became inert with the growth of the polymer chain, and it also limited

the increase of the polymer molar mass. Some further studies on why it came into being and how to make it effective will be carried out in the future.

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