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Copolymerization of tetrahydrofuran and propylene oxide

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Summary

Copolymerization of tetrahydrofuran and propylene oxide catalyzed by modified $H_2SO_4.SO_3$ system has been studied. Sodium perchloride was used to replace perchloric acid as co-catalyst. The copolymerization rate was obviously accelerated when using the new $H_2SO_4.SO_3$ -$NaClO_4$ catalyst system. The reaction became less sensitive to the moisture.

Introduction

Poly(tetramethylene oxide) glycol has been widely used as soft segment in synthesizing multiblock copolymers, such as poly(ether-urethane)and poly(ether-ester). Poly(tetramethylene oxide) glycol with molecular weight above 2000, however, has been found to be easily crystallized, which influences greatly the properties of the corresponding block copolymers, e.g. the elasticity, toughness etc.(1). Therefore, the attempt has been made to decrease the degree of crystallinity through copolymerization of tetrahydrofuran with propylene oxide. BF_3- diol (2,3) and $SbCl_5$ -diol (4) are usually utilized as catalyst system for the copolymerization. But the conversion of copolymerization remained at low level when the PO content was low [3] . The functionality of end hydroxy group was much less than 2 (4). Moreover, the end groups consisted of mainly secondary alcohols (2). Zhang et al. (5) studied the copolymerization of THF and PO catalyzed with fuming sulfuric acid-$HClO_4$ system, and got higher conversion at low PO/THF feed ratio and better product properties.

The present work describes the copolymerization of PO with THF catalyzed with both $H_2SO_4.SO_3$ -$HClO_4$ and $H_2SO_4.SO_3$ -$NaClO_4$ systems over a wide range of PO/THF ratios. The effects of the comonomer feed ratio on PO/THF ratio in copolymer as well as the effect of catalyst amount on the molecular weight of copolymer have been observed. The improvement of catalyst system is also discussed.

Experimental

1. Materials

Tetrahydrofuran(THF)(from Beijing Chemical Company) was dried over 4 A molecular sieves for a week, refluxed in the presence of CaH_2 for 2 to 3 hrs. and distilled under the protection of nitrogen. Propylene oxide(PO)(the product of Shanghai Reagent Company) was treated as the above method. Fuming sulfuric acid, from Beijing Chemical Company was

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diluted with sulfuric acid to certain concentration. Perchloric acid (70%), sodium perchlorate ($NaClO_4 . H_2O$) were used as received. Anhydrous $NaClO_4$ was prepared by heating $NaClO_4 . H_2O$ at 130-150 °C under vacuum for 2 to 3 hrs.

2. Copolymerization of THF and PO

Copolymerization of THF and PO was carried out according to the ref.(5). 50 g. of THF and certain amount of $NaClO_4$ or $HClO_4$ were put into a flask stirring at -2 - 0 °C. $H_2SO_4.SO_3$ was dropwisely added within 20 min. PO was dropwisely added 5 minutes after the addition of catalyst. Polymerization was stopped by adding water into the flask. The unreacted monomers were removed by evaporation. The crude product obtained was dried at 100-120 °C/10-20 mm Hg for 4 hrs.

3. Characterization of the THF-PO copolymer[P(THF-co-PO)]

The number average molecular weights(MWs) of the copolymers were measured from end group analysis by acetylation with acetic anhydride in pyridine(1:9 v/v) (5). They were also checked by vapor pressure osmometry(VPO)(OQ-08 vapor pressure osmometer) in chloroform at 30 °C. The composition of copolyether was analysized by NMR spectrometer in $CDCl_3$ and calculated by the following equation:

$$PO\% = \frac{nMp}{mMt + nMp} \quad 100\%$$

Mp: Molecular weight of PO unit
Mt: Molecular weight of THF unit

Results and Discussion

1. Copolymerization of THF and PO catalyzed with $H_2SO_4.SO_3$ -$HClO_4$

Zhang et al (5) reported that the compositions of THF-PO copolymers were similar to the monomer feed ratios when the PO content in the comonomer was below 15%. In this work, monomer feed ratio varies over a wide range. It is found that the PO content in copolymer increases with increasing the PO% in monomer feed ratio. Then the PO% in copolymer keeps at a relatively constant level when PO% in comonomer is above 30% . Table 1. shows that as PO/THF feed ratio enhanced from 0.10 to 0.50, the PO content in copolymer reaches only 21.9% . More than half of the PO molecules were not incorporated in the copolymer chain.

Table 1. Composition of P(THF-co-PO)

PO/THF(g./g.)	PO% in copolymer*	MW x 10^{-3}
0.10	6.6	2.16
0.20	10.7	1.86
0.30	23.2	1.37
0.40	19.9	1.32
0.50	21.9	1.04

* Weight percent, determined by NMR
21% $H_2SO_4.SO_3$: 20 %, $HClO_4$: 4 %.

Although the reported data about reactivity ratio of PO/THF copolymerization by several researchers are quite different (4,6), there is a strong tendency that PO is more active than THF. Accordingly, the copolymer should contain higher PO percent. But the opposite results were gained in the present work. This may be due to the formation of PO cyclic oligomers, which was reported to produce easily at higher PO/THF ratio in the absence of diol (3).

The increase of PO% in feed ratio causes the descent of molecular weight of the copolymer as illustrated in Table 2. This may be probably ascribed to the side reactions of PO.

2. Copolymerization of THF and PO catalyzed by $H_2SO_4.SO_3$ -$NaClO_4$ system

Copolymerization of THF and PO catalyzed by $H_2SO_4.SO_3$ -$HClO_4$ system requires longer reaction time, usually 6-8 hrs to reach the equilibrium conversion. It is probably caused by water existed in $HClO_4$. We have improved the property of the catalyst by using $NaClO_4$ to replace $HClO_4$. It is found that the polymerization rate was obviously accelerated. The copolymerization may achieve 40-50 % conversion within only two hours. The reaction system is also not very sensitive to the moisture. In order to get a series of copolymers with different PO contents, we have studied the effects of different variables on the composition and molecular weight of the copolymer, such as PO/THF feed ratio, $H_2SO_4.SO_3$ concentration, and the amount of $NaClO_4$.

2-1. Effect of PO/THF feed ratio on the composition of the copolymer

The effect of PO/THF feed ratio on the composition of the copolymer initiated by $H_2SO_4.SO_3$ -$NaClO_4$ system is similar to that of initiated by $H_2SO_4.SO_3$ -$HClO_4$ as demonstrated in Table 3.

It is apparent that the PO% in copolymer was enhanced as PO/THF feed ratio increased at the beginning. When the PO/THF ratio was higher than 0.40, the PO content remained at relatively constant level even up to 2/1 PO/THF ratio, and the polymerization conversion dropped down gradually. As mentioned above, there were maybe some PO cyclic oligomers formed during the reaction and eliminated during purification. Further study is needed to confirm this explanation. The fact that PO/THF ratio displays the same effect on copolymer composition regardless of catalyst system indicates that the change in catalyst system only alter the reaction rate, but not effect the mechanism of copolymerization.

Table 3. Composition of P(THF-co-PO)

PO/THF(g./g.)	PO% in copolymer*	Conversion%
0.10	6.5	56.2
0.20	13.6	57.8
0.40	19.2	34.5
0.70	19.1	28.2
0.80	23.9	29.7
0.125	18.4	18.1
0. 20	17.7	14.3

* Weight percent, determined by NMR

21% $H_2SO_4.SO_3$; 20%, $NaClO_4$: 4%.

2-2. Effect of PO/THF feed ratio on the MW of P(THF-co-PO)

The PO/THF feed ratio not only influences the conversion and composition of the copolymer but also change greatly the MW of the copolymer. As PO/THF ratio increased, the MW dropped down quickly when using $NaClO_4$ or $NaClO_4$ H_2O as cocatalyst(Fig. 1, Table 4).

Under the same condition, PO/THF feed ratio revealed less effect on the MW of the copolymer in the presence of $HClO_4$ (70%). However, the MW of the copolymer was always higher than that initiated by $HClO_4$ (70%). Apparently, water content in $HClO_4$ (70%) played a predominate role in controlling the molecular weight of the copolymer.

Table 4. Effect of PO/THF feed ratio on the MW of P(THF-co-PO)

PO * (%)	$HClO_4$ Conversion%	$MWx10^{-3}$	$NaClO_4$ Conversion%	$MWx10^{-3}$	$NaClO_4 H_2O$ Conversion%	$MWx10^{-3}$
0	/	/	48.7	2.94	50.2	2.74
10	40.5	1.23	56.2	1.92	43.6	1.91
20	39.0	1.05	57.8	1.67	65.5	1.50
30	46.2	1.16	45.1	1.11	33.6	1.00

*Based on THF .
21% $H_2SO_4.SO_3$: 20%, $NaClO_4$: 4 %.

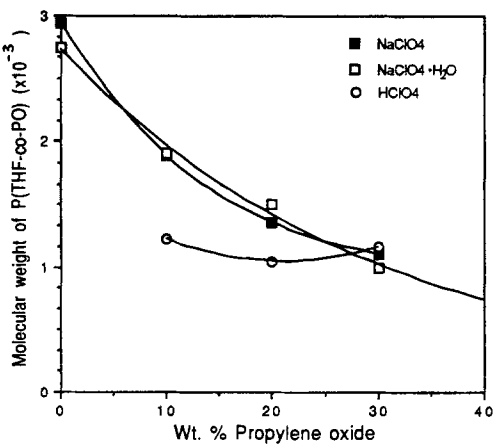

Fig. 1 Effect of PO/THF feed ratio on the Molecular Weight of P(THF-co-PO)

21% $H_2SO_4.SO_3$: 20%, $NaClO_4$: 4 %

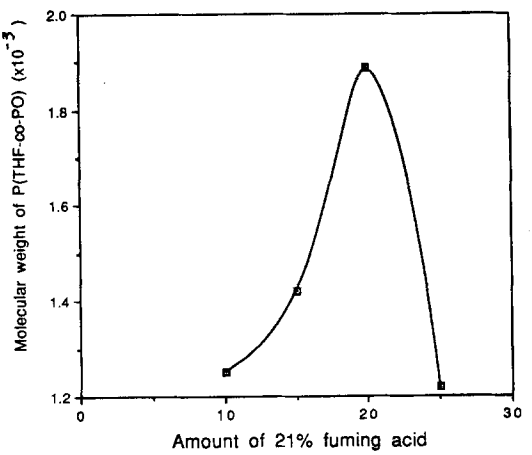

Fig. 2 Effect of fuming acid amount on the molecular weight of P(THF-co-PO)

PO/THF: 0.1, NaClO4: 4%

2-3. Effects of $H_2SO_4.SO_3$ amount and concentration on the MW of P(THF-co-PO)

Fig. 2 and Table 5 summarize the results of copolymerization initiated with different $H_2SO_4.SO_3$ amount. The MW of the copolymer increased first as $H_2SO_4.SO_3$ amount increased, then the MW reached a maxium. The further increase in $H_2SO_4.SO_3$ amount resulted in a sharp descending in MW. There is an optimum amount of $H_2SO_4.SO_3$ in the copolymerization for the high MW polymer.

Table 5. Effect of $H_2SO_4.SO_3$ amount on the MW of P(THF-co-PO)

21% $H_2SO_4.SO_3$ (%)	Conversion%	MWx10^{-3}
10	46.2	1.25
15	51.8	1.42
20	54.9	1.89
25	55.4	1.22

PO/THF(g/g): 0.1, $NaClO_4$: 4 %.

Table 6. Effect of $H_2SO_4.SO_3$ concentration on the MW of P(THF-co-PO)

$H_2SO_4.xSO_3$ Concentration (%)	$NaClO_4$ Conversion%	MWx10^{-3}	$NaClO_4$ H_2O Conversion%	MWx10^{-3}
21	54.9	1.89	43.6	1.91
25	55.4	1.38	51.3	1.83
28	52.3	1.56	53.8	2.02

PO/THF(g/g): 0.1, $H_2SO_4.SO_3$: 20 %, $NaClO_4$: 4 %.

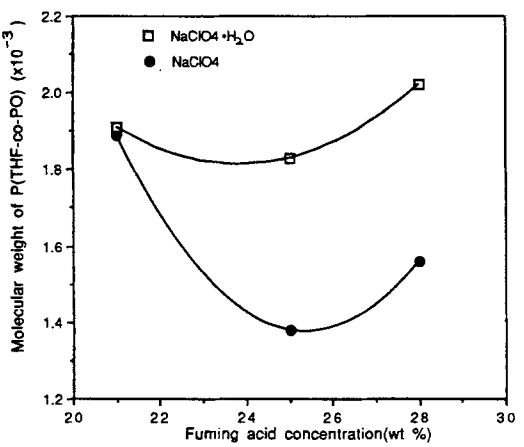

Fig. 3 Effect of fuming acid concentration on the molecular weight of P(THF-co- PO)

PO/THF: 0.1. $H_2SO_4SO_3$ 20%

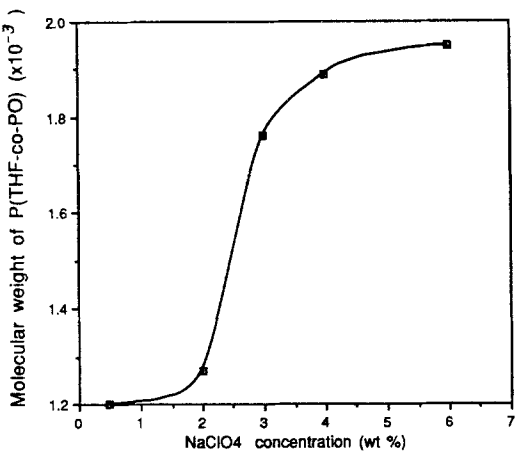

Fig. 4 Effect of NaClO4 concentration on the molecular weight of P(THF-co-PO)

PO/THF: 0.1, 21% fuming acid: 20%

The concentration of $H_2SO_4.SO_3$ also influenced the MW of the copolymer especially in $H_2SO_4.SO_3$ -$NaClO_4$ initiated system(Table 6, Fig. 3). From Table 6, we may see that the MW decreased with increasing $H_2SO_4.SO_3$ concentration. After a minimun, the MW was raised when $H_2SO_4.SO_3$ concentration reached 28%. However, the effect of $H_2SO_4.SO_3$ was greatly reduced when using $NaClO_4$- H_2O as cocatalyst. The reason is unknown.

2-4 . Effect of $NaClO_4$ amount on MW of P(THF-co-PO)

Fig. 4 and Table 7 show the effect of $NaClO_4$ amount on the MW of the copolymer. The MW of the copolymer increased sharply with an increase in $NaClO_4$ amount. Then it reached a plateau as seen in Fig. 4. When the $NaClO_4$/THF ratio , however was higher than 0.05, the rate of copolymerization was too fast to control. In this case, the explosive polymerization happened readily producing polymers with dark color.

Table 7. Effect of $NaClO_4$ amount on the MW of P(THF-co-PO)

$NaClO_4$(%)	Conversion%	MWx10^{-3}
0.5	44.6	1.20
2.0	38.5	1.27
3.0	53.8	1.76
4.0	54.9	1.89
6.0	49.7	1.95

PO/THF(g/g): 0.1, 21% $H_2SO_4.SO_3$: 20 %.

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