

DICATIONICALLY LIVING CHAINS: COPOLYMERIZATION OF TETRAHYDROFURAN WITH PROPYLENE OXIDE AND SYNTHESIS OF THE TELECHELIC OLIGOMERS*

ZHANG Hongzhi (张鸿志), MENG Xiansheng (孟宪胜) and FENG Xinde (冯新德)
(*Department of Chemistry, Peking University, Beijing*)

ABSTRACT

The living chains were obtained in the bulk copolymerization of tetrahydrofuran (THF) with propylene oxide (PO) (10–20 wt. %) initiated by adipoyl chloride (AC)– AgClO_4 ($[\text{AC}]_0 = 0.02$ – $0.09 \text{ mol} \cdot \text{l}^{-1}$) catalyst at -10 – 0°C without chain termination and transfer reactions. The estimation of reactivity ratios gave values of 0.8 ± 0.2 and 0.08 ± 0.03 for THF and PO, respectively. The functionality of living chains with 10% PO in the feed is close to 2. Four different telechelic THF–PO copolymers with amine or hydroxyl end-groups $[\text{P}(\text{THF-co-PO})\text{R}]$, where $\text{R} = \text{—NHBu}$, —NHPh , —NEt_2 or —OH were synthesized.

The living polymerization of tetrahydrofuran (THF) has been widely investigated^[1]. But little is known about the living nature of THF copolymerization. It is an interesting subject whether we can obtain the living chains in the THF–propylene oxide (PO) copolymerization in spite of the side reactions such as cyclization and isomerization reactions. It is also important for obtaining the copolyether with lower tendency towards crystallization in comparison with that of homopolyether. Its incorporation into the block polyurethanes or block polyesters as the soft segments may modify the low temperature properties of the products.

The polymerization of THF initiated by BF_3 at 20°C is a living one^[2], but as 10% PO was added to the reaction system, all the reactive copolymer chains died in a period of 4 hrs^[3]. However, we successfully obtained the dicationically living chains in the THF–PO copolymerization by AC– AgClO_4 catalyst at lower temperatures and synthesized four different telechelic oligomers thereof.

EXPERIMENTAL

Materials. PO (A.R. grade) was dried over $3 \text{ \AA}$ molecular sieves, and after refluxing over calcium hydride for 5–6 hrs. was distilled twice under nitrogen atmosphere. Its purity was verified by gas chromatography. Diethylamine (C.P. grade) was dried with sodium hydroxide and twice distilled over calcium hydride under nitrogen. Other chemical reagents were purified as described in our previous papers^[2,3].

Copolymerization. The copolymerization was performed with the similar procedure of the THF homopolymerization^[4]. The adipoyl chloride (AC)– AgClO_4 catalyst system with 3–10 mol % of AgClO_4 in excess was added to the THF–PO monomer mixture. The concen-

* Received July 30, 1985

trations of living chains $[P^*]$ and reactive centers $[RC]$ were determined by the phenoxyl end capping method^[8]. The conversions for runs 11C, 12C and 15C were estimated according to our previous work^[4] and for other runs by extracting the product with CH_2Cl_2 solvent^[3].

The preparation of telechelic oligomers and dicationically living copolyether chains and the determination of the equivalent of the end-groups (E_g) were carried out as described previously^[6,9].

The reactivity ratios were calculated by the intersection method from the copolymer compositions determined with ^1H -NMR spectra at about 10% copolymerization conversion.

The molecular weight of the copolyether ($\bar{M}_n$) was evaluated from that by GPC calibrated with standard polystyrene ($\bar{M}_s$) using the Waters 150C/GPC with μ -styragel columns ($10^3+10^4+10^5 \text{ \AA}$) in $CHCl_3$ at $30^\circ C$ or with μ -bondagel E125 and μ -Porasil GPC $60 \text{ \AA}$ columns in DMF containing 3g $NaNO_3$ per liter at $45^\circ C$ according to the equation: $\bar{M}_n = K\bar{M}_s$. In the literature the constant K was calculated from the data of the unperturbed mean square end-to-end distance^[10]. With the aid of the typical hydroxyl end capped copolyethers containing 10% PO ($\bar{M}_n = 2.4 \times 10^3$) and 20% PO ($\bar{M}_n = 1.3 \times 10^3$)^[11] we determined the K values: in $CHCl_3$ is 0.55 and in DMF is 0.82. With the aid of the phenoxyl end capped copolyethers obtained in parallel copolymerization runs for preparing hydroxyl terminated copolyethers ($\bar{M}_n = 3.5 \times 10^3$ and 4.0×10^3), we determined the K values: in $CHCl_3$ is 0.505 and in DMF is 0.93.

The molecular weight distribution was characterized by GPC calibrated with standard polystyrene without corrections for chromatogram broadening.

^1H -NMR spectra were recorded on the Varian, FT-80A NMR spectrometer with $CDCl_3$ as solvent.

RESULTS AND DISCUSSION

1. The living nature of the copolyether chains

Figure 1 shows the relationship between the concentration of reactive centers $[RC]$ and the reaction time. It is observed that $[RC]$ remains almost constant in the bulk THF-PO

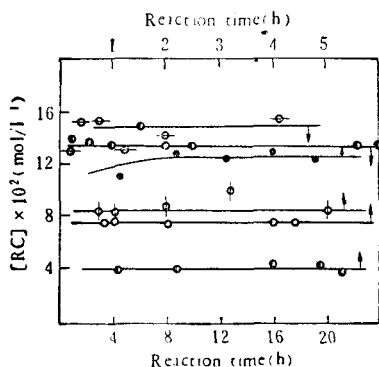


Fig. 1 $[RC]$ and reaction time relationship

○ run 5C: PO 10%, $[AC]_0$ 0.09 mol/l, $0^\circ C$; ● 7C: 20%, 0.093 mol/l, $0^\circ C$;
● 12C: 20%, 0.09 mol/l, $-10^\circ C$; ○ 9C: 10%, 0.045 mol/l, $0^\circ C$; ○ 2C: 10%,
0.053 mol/l, $0^\circ C$; ● 11C: 10%, 0.0224 mol/l, $-10^\circ C$.

(10–20 wt%) copolymerization initiated by AC–AgClO₄ catalyst ([AC]₀ = 0.02–0.09 mol/l) at –10–0°C. Obviously, the copolymerization proceeds without being interrupted by chain termination reaction.

In the absence of both chain transfer and termination reactions the molecular weight of the product of copolymerization can be estimated by equation (1)^[2]:

$$\overline{MW} = \frac{\text{density of system (g/ml)} \times \text{conv.} \times 1000}{[P^*]} \quad (1)$$

Densities of THF–PO mixtures when PO = 20%: $d_4^0 = 0.8985$ and $d_4^{-10} = 0.9087$; when PO = 10%: $d_4^0 = 0.8994$ and $d_4^{-10} = 0.9141$.

According to Eq. (1) the plot of $\overline{MW}$ vs. conversion is a straight line since $[P^*]$ is a constant. As it was expected, we obtained the linear dependence in Fig. 2. Therefore the chain

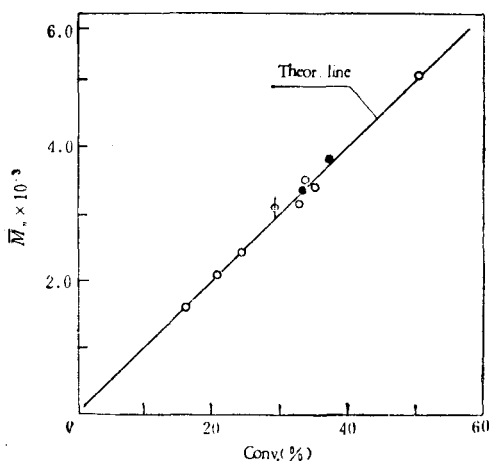


Fig. 2 Dependence of $\overline{M}_n$ on the conversion
 ○ 5C, ● 7C and ◐ 12C, for their reaction conditions see footnote of Fig. 1.
 ◐ 8C: PO 15%, [AC]₀ 0.093 mol/l, 0°C.

transfer reaction can also be excluded. The good correspondence between the experimental and theoretical lines assuming $[AC]_0 = [P^*]$ indicates the initiator efficiency (I_f) is equal to one. That means, in the copolymerization every AC molecule gives one living chain.

The value of $\overline{M}_w/\overline{M}_n$ of the sample 4C obtained at the conversion of 16.4% is 1.4.

2. The functionality ($\bar{f}$) of the living chains

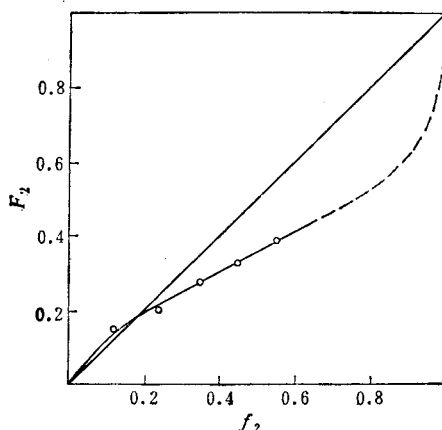
As $\bar{f} = \overline{MW}/E_q$, for samples of 10% PO the difunctionality of the chains can be verified either by $\overline{M}_{calc}$ calculated from the data of conversion according to Eq. (1) or by $\overline{M}_n$ determined by GPC (Tab. 1). The explanation of the lower $\bar{f}$ values for that of 15–20% PO in the feed needs further studies.

3. The reactivity ratios

The r_1 and r_2 values for THF (M_1) and PO (M_2) copolymerization were determined by the intersection method to be 0.8 ± 0.2 and 0.08 ± 0.03 , respectively, which are close to $r_1 = 0.50$

Table 1 Functionality of the living chains in THF-PO copolymerization

Run	PO in feed (wt%)	[AC] ₀ (mol/l)	Temperature (°C)	Conv. (%)	$E_q \times 10^{-3}$	$\overline{MW}$	
						$\overline{M}_{calc}^*$	$\overline{M}_n$
4C-3	10	0.09	-10	27.8	1.25	2.8	2.3
4C-4	10	0.09	-10	35.0	1.75	3.5	
4C-7	10	0.09	-10	49.5	2.5	5.0	
5C-2	10	0.09	0	20.8	1.25	2.1	2.1
5C-6	10	0.09	0	50.6	2.85	5.1	5.1
7C-7	20	0.093	0	32.8	2.25	3.1	3.1
7C-10	20	0.093	0	35.1	2.35	3.4	3.4
8C-4	15	0.092	0	28.9	2.1	2.8	3.1
11C-5	10	0.0224	-10	8.2	1.7	3.3	
15C-1	10	0.092	-10	34.5	1.8	3.5	3.4
15C-2	10	0.092	-10	37.0	1.9	3.8	3.8

* calculated from eq. (1) assuming $[P^*] = [AC]_0$ Fig. 3 THF(M₁)-PO(M₂) copolymer composition curve
[AC]₀ = 0.09 mol/l, 0°C.

and $r_2=0.05$ for the copolymerization initiated by $BF_3 \cdot THF$ in the absence of diols^[12]. The copolymer composition curve is given in Fig. 3.

4. Synthesis of the telechelic oligomers

The telechelic oligomers of polyethers are very important for the preparation of block copolymers^[13]. We have already reported the synthesis of several telechelic homopoly-THF with secondary amine end-groups^[6]. In this work we describe the synthesis of telechelic copolyethers, P (THF-co-PO)R, where R = NHBu, NPh, NEt₂ or OH by the following reactions:

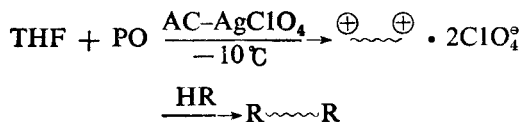


Table 2 The functionality of the telechelic copolyethers P(THF-co-PO)R

R	[AC] ₀ (mol/l)	[AgClO ₄] ₀ (mol/l)	Time (h)	Conv. (%)	E _q × 10 ⁻³	$\overline{MW} \times 10^{-3}$	
						$\overline{M}_{\text{calc}}$	$\overline{M}_n$
NHBu	0.092	0.194	3.9	34.5	1.8	3.45	3.4
NHBu	0.092	0.194	4.0	37.0	2.2	3.85	3.85
NEt ₂	0.092	0.194	4.0	37.0	2.1	3.85	3.85
NHPh	0.038	0.082	9.6	44.8	5.2	10.4	10.4
OH	0.038	0.082	45.5		2.45		4.6

Tab. 2 demonstrates that the functionalities of all the four different telechelic THF-PO copolymers are close to 2 ($\bar{f} = \overline{MW}/E_q$).

The present method for obtaining P(THF-co-PO)OH is different from the copolymerization initiated either by BF₃-diol or SbCl₅-diol or by H₂S₂O₇-HClO₄ catalyst system with the peculiarities i.e. the end-groups of the copolyether are predominantly primary hydroxyls (around 70–80%) and the $\overline{MW}$ reached 4.6×10^3 , whereas the share of primary alcohols in the copolyether by BF₃-diol or SbCl₅-diol is only about 26% and the $\overline{MW}$ of the copolyether by H₂S₂O₇-HClO₄ is lower than 2000^[11].

Acknowledgement We are grateful to acknowledge the partial support by the Science Fund of the Chinese Academy of Sciences.

REFERENCES

- [1] Dreyfuss, P., "Poly(tetrahydrofuran)", Gordon and Breach Sci. Publ., New York, 1983.
- [2] 張鴻志、董嘉揚、王彥樂、曾憲森、馮新德，高分子通訊，1985 (4)，258.
- [3] 張鴻志、李秉明、馮新德，高分子通訊，1980 (4)，251.
- [4] 張鴻志、馮新德，高分子通訊，1981 (5)，326.
- [5] Комратов, Т. Н., Барцукина, Р. А. и Коровна, Г. В., *Высоком. Соед.*, 1980, A22, 2342.
- [6] Tseng, S.S., Zhang, H.Z. and Feng, X.D., *Polym. Bull.*, 1982, (8), 219.
- [7] Розенберг, Б. А., Людвиг Е. В., Гантмахер, А. Р. и Медведев, С. С., *Высоком. Соед.*, 1964, 6, 2035.
- [8] Saegusa, T. and Matsumoto, S., *J. Polym. Sci.*, 1968, A-1, 6, 1559.
- [9] 莊野利三、辻野孝、八兵義和，工業化學雜誌(日本)，1958, 61, 1348.
- [10] Croucher, T.G. and Wetton, R.E., *Polymer*, 1976, 17, 205.
- [11] 張鴻志、高國楨、王英、馮新德，高分子通訊，1981, (6) 429.
- [12] Alvarez, E.J., Hornof, V. and Blanchard, L. P., *J. Polym. Sci.*, 1972, A-1, 10, 1895.
- [13] Smith, S. and Hubin, A. J., *U.S. Pat.* 3,824,220, 1974; *U.S. Pat.* 3,631,199, 1971.