

Preparation of Polytetrahydrofuran Monomethacrylate Macromonomers by Cationic Ring-Opening Polymerization of Tetrahydrofuran

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Received 13 July 1999; accepted 14 October 1999

ABSTRACT: Polytetrahydrofuran monomethacrylate (MA-PTHF) macromonomer was prepared by cationic ring-opening polymerization (CROP) of tetrahydrofuran (THF) using boron trifluoride etherate ($\text{BF}_3 \cdot \text{OEt}_2$) as initiator and epichlorohydrin (ECH) as promoter. Two kinds of transfer agents were used: methacrylic acid (represented as TA1), and a mixture of methacrylic acid and sodium methacrylate (represented as TA2). The effects of polymerization conditions on molecular weight and molecular weight distribution of macromonomers were studied in this article, when the composition of reactants was kept constant. Under the same conditions, the molecular weight of macromonomer using TA2 is lower than that using TA1, which indicates that TA2 is more active than TA1. The molecular weight of MA-PTHF macromonomer varies with the polymerization time before transfer agents were added (T1), but molecular weight distribution remains constant. When T1 is limited in 30 min, the apparent number-average molecular weight of MA-PTHF increases significantly with the increase of T1, and ranges from 5000 to 18,000. Hence, the molecular weight of MA-PTHF macromonomer can be controlled by varying T1. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 810–815, 2000

Key words: tetrahydrofuran; cationic ring-opening polymerization; transfer agent; macromonomer; molecular weight control

INTRODUCTION

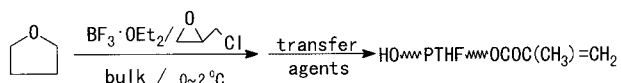
Recently, considerable progress has been made in understanding the mechanism of cationic ring-opening polymerization (CROP) of heterocyclic compounds. CROPs have been classified into three categories:¹ (1) living or almost living polymerizations (no or slow termination); (2) polymer-

izations showing a reversible termination; (3) polymerizations showing irreversible termination. These polymerizations of the first category allow optimal control of polymer structure, such as the incorporation of functional end groups by end-capping reactions, which is also one of the basic methods to prepare macromonomers.² But only several CROPs are performed on a commercial scale. In this respect, tetrahydrofuran (THF) is one of the most important monomers. Its polymerization is probably the most widely studied and best-known CROP.³

Some polytetrahydrofuran (PTHF) macromonomers with different end groups have been

Correspondence to: Y. Peng.
Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 59773019.

Journal of Applied Polymer Science, Vol. 77, 810–815 (2000)
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Scheme 1 Transfer agents: TA0: distilled water, TA1: methacrylic acid, TA2: mixture of sodium methacrylate and methacrylic acid.

synthesized.⁴⁻⁸ Among them, the research group of Asami prepared polytetrahydrofuran monomethacrylate (MA-PTHF) using triethyloxonium tetrafluoroborate as an initiator and sodium methacrylate as a terminator.⁶ Although the molecular weight distribution was very narrow, the yield of MA-PTHF was very low.

The mechanism of cationic ring-opening polymerization of THF using boron trifluoride etherate ($\text{BF}_3 \cdot \text{OEt}_2$) as an initiator and epichlorohydrin (ECH) as a promoter is well understood.⁹⁻¹¹ On this theoretical basis, we tried to prepare the MA-PTHF macromonomer according to Scheme 1 using $\text{BF}_3 \cdot \text{OEt}_2$ as an initiator and ECH as a promoter. Two kinds of transfer agents were used to induce a methacrylate end group. One was methacrylic acid (MA, represented as TA1), and the other was a mixture of methacrylic acid and sodium methacrylate (represented as TA2). To compare with hydroxy end-capped polytetrahydrofuran (HO-PTHF), we used water as a transfer agent (represented as TA0) in the control experiment.

It was found that THF could undergo living cationic polymerization when the conversion is kept low,¹ less than 25%. The polymerization has the characteristics of long-lived propagating species and narrow molecular weight distributions, which make it possible to control molecular weight of PTHF. The common method to control the molecular weight of polymers is varying the recipe, such as the ratio of the initiator and monomer. As a different method to other common methods, we tried to prepare the MA-PTHF macromonomer with different molecular weights by varying polymerization conditions, for example, polymerization time before transfer agents were added, and reaction time and temperature after transfer agents were added. So we designed experiment procession as shown in Scheme 2 and investigated the effects of polymerization conditions on molecular weight and molecular weight distribution of the MA-PTHF macromonomer.

EXPERIMENTAL

Materials

Anhydrous THF was used in the polymerization. THF (AR) was dried with calcium hydride for a week, and then refluxed with sodium wire in the presence of a trace of benzophenone until a blue color was obtained. It was distilled just before use.

$\text{BF}_3 \cdot \text{OEt}_2$ (AR) was purified before use by adding 2% (wt %) dry ether and then distilling from calcium hydride under reduced pressure (b.p. $46^\circ\text{C}/10$ mmHg).

Epichlorohydrin (AR) was distilled from calcium hydride before use.

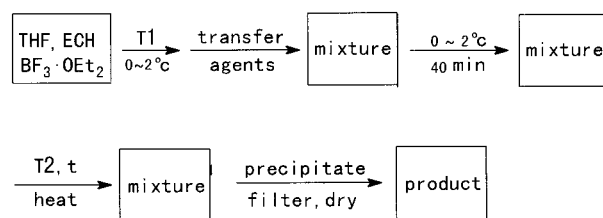
MA (AR) was dried with calcium chloride and then distilled under vacuum with 0.1% (wt %) hydroquinone as inhibitor before use.

Sodium methacrylate was obtained and purified according to a procedure described in ref 6.

Synthesis of the MA-PTHF Macromonomer

Polymerization reactions were carried out in stirred flasks with condenser pipes. An indicated amount of initiator and promoter were added to anhydrous THF under dry nitrogen atmospheres at $0\sim 2^\circ\text{C}$. Reaction temperatures were controlled with appropriate baths. After a period of reaction time (T1), two kinds of transfer agents were injected into the reaction mixture. Keeping the polymerization at $0\sim 2^\circ\text{C}$ for 40 min, the reaction mixtures were heated to certain temperatures (t) for certain periods of time (T2), and then poured into dilute sodium hydrate solution. After precipitating completely, the products were filtered and washed with distilled water to neutrality, and dried at room temperature.

In the control experiment, except that distilled water was used as the terminator, all other experimental steps were the same as above.



Scheme 2 ECH: epichlorohydrin, T1, reaction time before adding the transfer agent, T2: reaction time after heating, t : temperature, transfer agents: see Scheme 1.

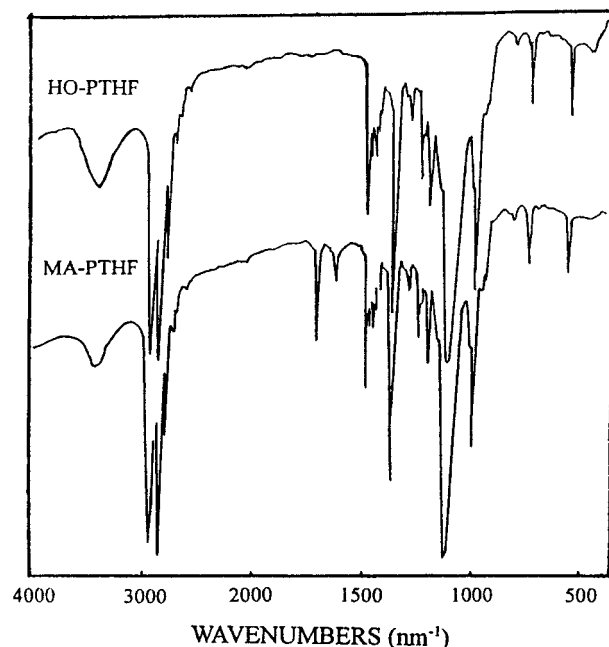


Figure 1 FTIR spectra of the OH-PTHF polymer and the MA-PTHF macromonomer.

Analysis

Fourier transform infrared (FTIR) analysis was performed on a Nicolet MX-1 FTIR spectrometer, and the samples were coated on a KBr disk.

$^1\text{H-NMR}$ spectra were recorded on a Bruker AC-P 400-MHz spectrometer and deuteriochloroform was employed as the solvent. Chemical shifts were measured relative to tetramethylsilane.

Size-exclusion chromatography (GPC) was performed on a PL-GPC 210 instrument with two PL Gel mixed B columns and a refractive index detector. The samples were dissolved in butanone, and the measurements were carried at 40°C . The molecular weights and molecular weight distributions of macromonomers were determined relative to polystyrene standards.

The hydroxyl and methacrylic functionality was determined according to a procedure described in refs. 12 and 13.

RESULTS AND DISCUSSION

Characterization of the MA-PTHF Macromonomer

Following the process shown in Scheme 2, a series of MA-PTHF macromonomers were synthesized. Although polymerization conditions are different,

all of MA-PTHF macromonomers show the same FTIR and $^1\text{H-NMR}$ spectra. Because TA1 and TA2 have the same counterion, methacrylate ion, their termination products should have the same chemical structures.

To test the methacrylate end group of MA-PTHF macromonomers conveniently, we also synthesized HO-PTHF polymers as comparison samples. The FTIR spectra and $^1\text{H-NMR}$ spectra of MA-PTHF and HO-PTHF are shown in Figures 1 and 2, respectively. In contrast with the FTIR spectrum of HO-PTHF polymer, the spectrum of MA-PTHF macromonomer in Figure 1 shows two different absorption peaks at the wave numbers ranging from 1500 to 1800 cm^{-1} . The peak at 1637 cm^{-1} represents the stretching vibration of the $\text{C}=\text{C}$ group. The peak at 1718 cm^{-1} is due to the stretching vibration of the $\text{C}=\text{O}$ group of the ester. By comparing the MA-PTHF macromonomer with the corresponding HO-PTHF polymer in Figure 2, peaks a–b are assigned to the methacrylate end group protons, and peak c to methylene protons of the PTHF chain closest to the methacrylate end group. The average functionality of methacrylate end groups of the MA-PTHF macromonomers is close to 1. The average functional-

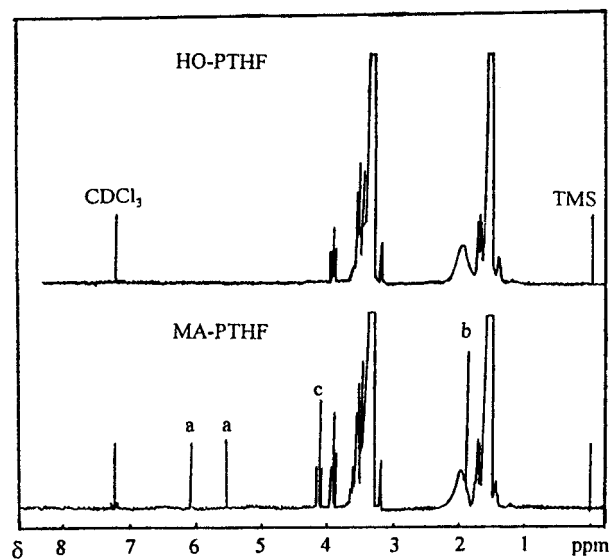


Fig. 2 $^1\text{H-NMR}$ spectra of MA-PTHF and HO-PTHF

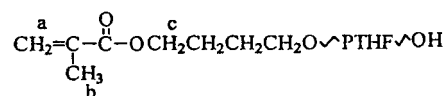


Figure 2 $^1\text{H-NMR}$ spectra of the HO-PTHF polymer and the MA-PTHF macromonomer.

Table I Polymerization Conditions^a and Conversion of THF

Reaction Time		Temperature <i>t</i> /°C	Conversion %(W/W)		
T1/min	T2/h		TA1 ^b	TA2 ^c	TA0 ^d
60	4	25	57.5	53.0	54.1
30	4	25	56.5	50.1	52.6
20	4	25	55.2	51.9	45.2
15	4	25	52.3	49.9	24.7
0	4	25	57.5	57.7	—
15	4	35	55.6	53.4	30.1
15	6	35	52.7	49.1	30.1
15	8	35	55.1	51.1	29.1
15	10	35	57.2	52.4	30.0
15	4	45	52.3	55.0	31.1
15	4	55	51.3	51.5	28.1

^a [BF₃ · OEt₂]/[THF] = 3%; [ECH] = [BF₃ · OEt₂].

^b TA1: 1.0 mL, methacrylic acid dissolved in 5.0 mL THF.

^c TA2: 0.2 g sodium methacrylate suspended in a mixture of 0.8 mL methacrylic acid and 5.0 mL THF.

^d TA0: 0.20 mL distilled water.

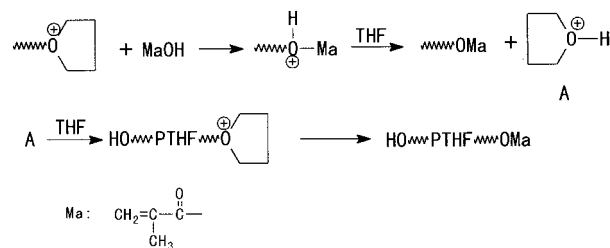
ity ratios of methacrylate end groups to hydroxyl groups for the same macromonomer were also determined to be close to 1. From the above analysis, the synthesized MA-PTHF macromonomer contains one methacrylate end group, and the structure of the MA-PTHF macromonomer is in accord with the expected one shown in Scheme 1.

Effect of Different Transfer Agents on Polymerization Conversion of THF

The polymerization conditions and conversions of THF are shown in Table I. As shown in Table I, when other conditions are constant, the conversions of THF using three transfer agents increase with reaction time T1, except for T1 = 0. This fact is in accord with the general living cationic ring-opening polymerization process; in other words, the propagating species of this polymerization system are long lived.

If TA1 or TA2 was added at the beginning of polymerization, namely T1 = 0, the conversion values of THF are close to 58%. This value is higher than others that T1 is larger than 0 min. Owing to the supply of protons, the function of a small amount of methacrylic acid in these two transfer agents may be considered as a catalyst at the same time. Hence, we believe the reaction process is as shown in Scheme 3. We also estimated that the molecular weight distribution of the macromonomer might be broadened because of the following propagation of oxonium ion A.

When reaction time T1 is kept constant at 15 min, the conversion of THF using distilled water as a transfer agent is lower than that using other two transfer agents. These facts can be attributed to the activity of the transfer agents. As a common terminator, water often shows high activity in organic solvents that are miscible with water. Methacrylic acid or sodium methacrylate exists mainly as a contact ion pair in THF. Because sodium methacrylate has higher effective charge density, we presume that TA2 may show a higher activity than TA1. But we did not find obvious evidence in Table I to support it. The conversion values using TA2 are only slightly lower than those using TA1. This can be attributed to methacrylic acid, which is present in both transfer agents. As we mentioned before, methacrylic acid, as a proton supplier, can catalyze the polymerization of THF, and so suppress the effect of sodium methacrylate.

**Scheme 3**

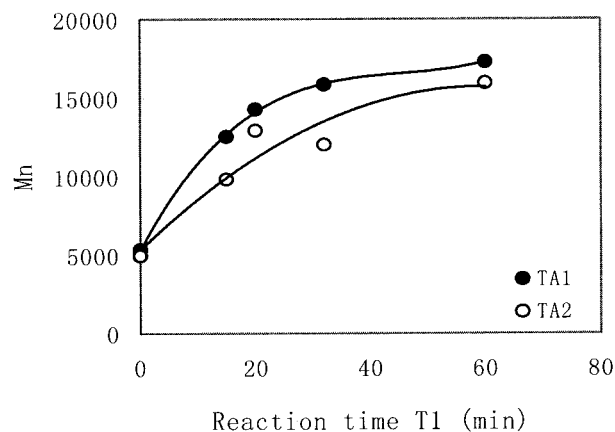


Figure 3 Effect of reaction time T_1 on apparent number-average molecular weight of the MA-PTHF macromonomer (M_n).

Effect of Polymerization Conditions on the Molecular Weight and Macromolecular Weight Distribution of the MA-PTHF Macromonomer

The common methods to control molecular weight are varying the stoichiometry of polymerization systems, such as the ratio of the initiator to monomer. In this article, we try to prepare MA-PTHF macromonomers with different molecular weights by varying the reaction times T_1 and T_2 , and reaction temperature t , under constant stoichiometry.

The effects of polymerization conditions on molecular weight and molecular weight distribution of MA-PTHF macromonomers are shown in Figures 3–8. As shown in Figure 3, the molecular weight of the MA-PTHF macromonomer decreases significantly with decreasing the reaction

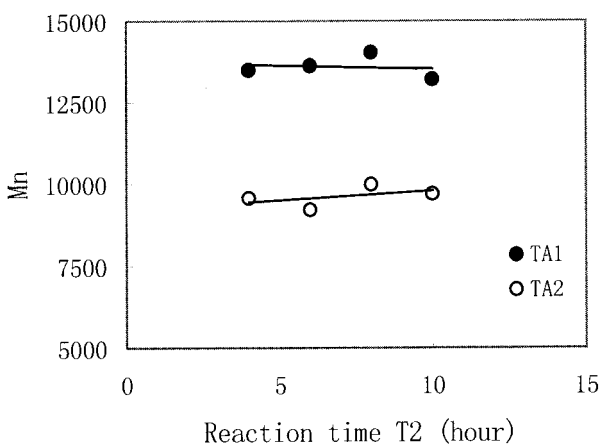


Figure 4 Effect of reaction time T_2 on apparent number-average molecular weight of the MA-PTHF macromonomer (M_n).

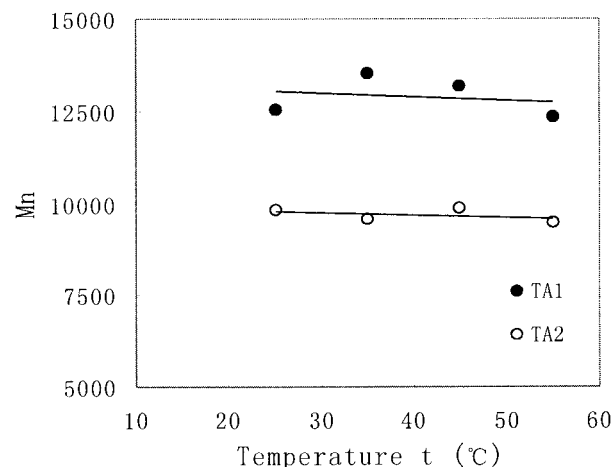


Figure 5 Effect of temperature t on apparent number-average molecular weight of the MA-PTHF macromonomer (M_n).

time T_1 . For TA1 and TA2, the tendency is similar. When T_1 is within 30 min, the molecular weight of MA-PTHF macromonomers increased significantly with T_1 . When T_1 is more than 30 min, the increase of the molecular weight of MA-PTHF macromonomers is not as significant. This fact indicates that propagating species were long lived, and the termination before the addition of the transfer agents is slower than the propagation. After the transfer agents were added, the propagation species were terminated by counter ion of the transfer agents. MA-PTHF macromonomers with molecular weights ranging from about 5000 to 18,000, as determined relative to polystyrene standards, were prepared.

On the contrary, reaction time T_2 and temperature t have little effect on the molecular weight of MA-PTHF macromonomers. This phenomenon

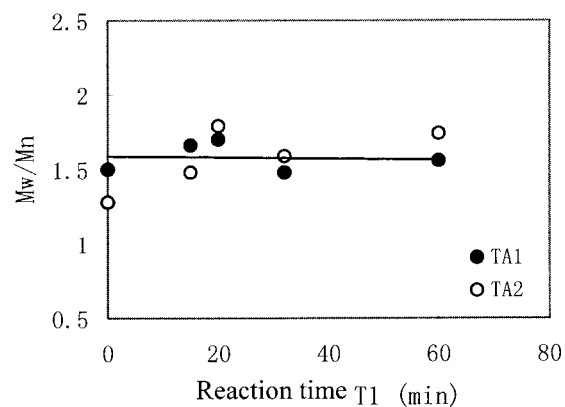


Figure 6 Effect of reaction time T_1 on molecular weight distribution of the MA-PTHF macromonomer (M_w/M_n).

can be attributed to the experimental step that the reaction mixture was kept at 0–2°C for 40 min after transfer agents were added. It kept the temperature of polymerization and termination constant for a period of time. We estimated that the termination of transfer agents almost approached completeness in this period. So the molecular weight of the MA-PTHF macromonomer would not be affected by the following heating and extended reaction time.

As shown in Figures 3–5, molecular weights of the MA-PTHF macromonomer using TA1 are lower than those using TA2. This fact is in accord with the presumption that TA2 is more effective than TA1 in the termination reaction.

As shown in Figures 6–8, molecular weight distributions are constantly about 1.6, and it shows little change with the polymerization conditions. Because the molecular weight dispersity indexes of macromonomers are less than 2, the attack of propagating species to TA1 or TA2 is more important than to the polymer chain. Although the polymerization conversion is not low, about 50%, this polymerization still shows characteristics of living polymerization. Therefore, MA-PTHF macromonomers with different molecular weights and relatively narrow molecular weight distributions can be prepared by this polymerization system.

CONCLUSIONS

MA-PTHF macromonomers can be prepared by cationic ring-opening polymerization of THF using $\text{BF}_3 \cdot \text{OEt}_2$ as an initiator, ECH as a promoter, and TA1 and TA2 as transfer agents. TA2 is more effective than TA1. When T1 is less than 30 min,

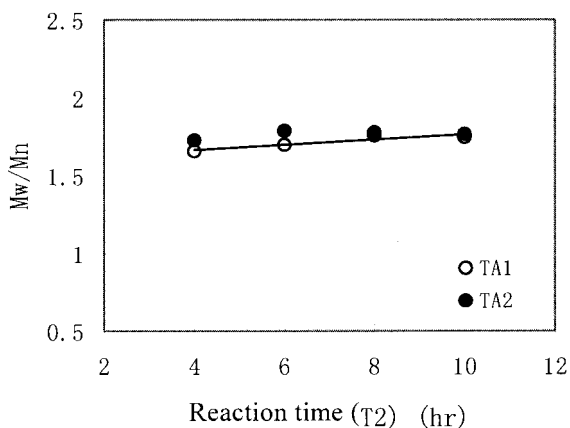


Figure 7 Effect of reaction time T2 on molecular weight distribution of the MA-PTHF macromonomer (M_w/M_n).

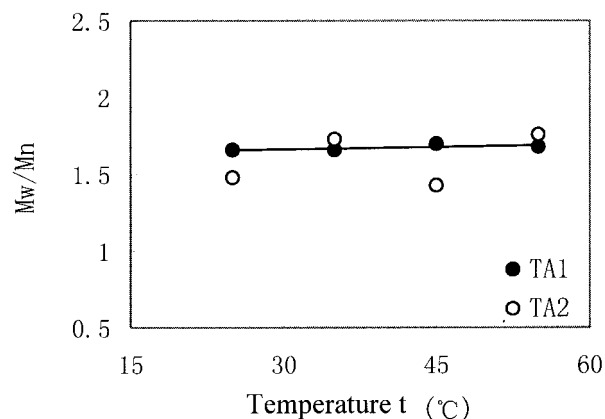


Figure 8 Effect of temperature t on molecular weight distribution of the MA-PTHF macromonomer (M_w/M_n).

the molecular weight of MA-PTHF macromonomers increases with increasing the T1. Although adding transfer agents cause the broad molecular weight distribution of MA-PTHF macromonomers, less than 2, the process is still almost a living CROP. Hence, the molecular weight of MA-PTHF macromonomer can be controlled by varying T1. The molecular weight of MA-PTHF ranges from 5000 to 18,000, and their dispersity indexes are kept about 1.6.

The National Natural Science Foundation of China is gratefully acknowledged for financial support (Grant No. 59773019).

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