Photoinduced Living Cationic Polymerization of Tetrahydrofuran. II: Synthesis of Four-Armed Star-Shaped Poly(tetrahydrofuran)

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ABSTRACT: A four-armed star-shaped poly(tetrahydrofuran) (THF) having a pentaerythritol unit at the center of the molecule was synthesized from photoinduced cationic copolymerization of THF and pentaeryithritol tetrakis(3,4-epoxybutanoate) (PETE) in the presence of diphenyliodonium hexafluorophosphate. It was found that the molecular weight of the resulting polymer increases with increasing percent conversion and the rate of cationic polymerization of THF is remarkably increased by the addition of PETE when the concentration of PETE is kept much lower than that of THF. A similar enhancement effect was also observed in the photoinduced cationic polymerization of THF in the presence of epichlorohydrin (ECH). The enhancement effect of ECH and PETE was ascribed to the increased concentration of the cationic propagating species due to a rapid protonation process. The living nature was explained in terms of the stabilization of the cationic growing chain end by ion pair formation. Accordingly, the arm length of the polymer was determined by the molar ratio of THF and PETE. However, the polymer of well-defined structure was only obtainable in the early stage of the reaction because chain transfer to the polymer process plays an important role when the concentration of the polymer becomes high. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 2637–2644, 1999

Key words: photoinduced living cationic polymerization; tetrahydrofuran; poly(tetrahydrofuran)

INTRODUCTION

In an earlier article[1] we investigated the living nature of the photoinduced cationic poly(tetrahydrofuran) [poly(THF)] and based on this study a THF-based diblock copolymer was synthesized by the sequential monomer addition method. A linear relationship between the conversion and the number average molecular weight of the resulting polymer indicates that the cationic poly(THF) has a living nature (i.e., the chain transfer or termination process is absent in this system) and this was ascribed to the stabilization of the five-membered cyclic oxonium ion, which is responsible for the cationic polymerization of THF, by ion pair formation with the less nucleophilic complex metal halide anion.

Although much attention has been paid to the potential utility of the living nature for the synthesis of terminally functional poly(THF),[2] THF-based block copolymers,[3–5] and graft copolymers,[6] any attempt to synthesize a star-shaped poly(THF) has not been made.

In this article we report on a new synthetic route of a four-armed star-shaped poly(THF) by photoinduced living cationic polymerization of
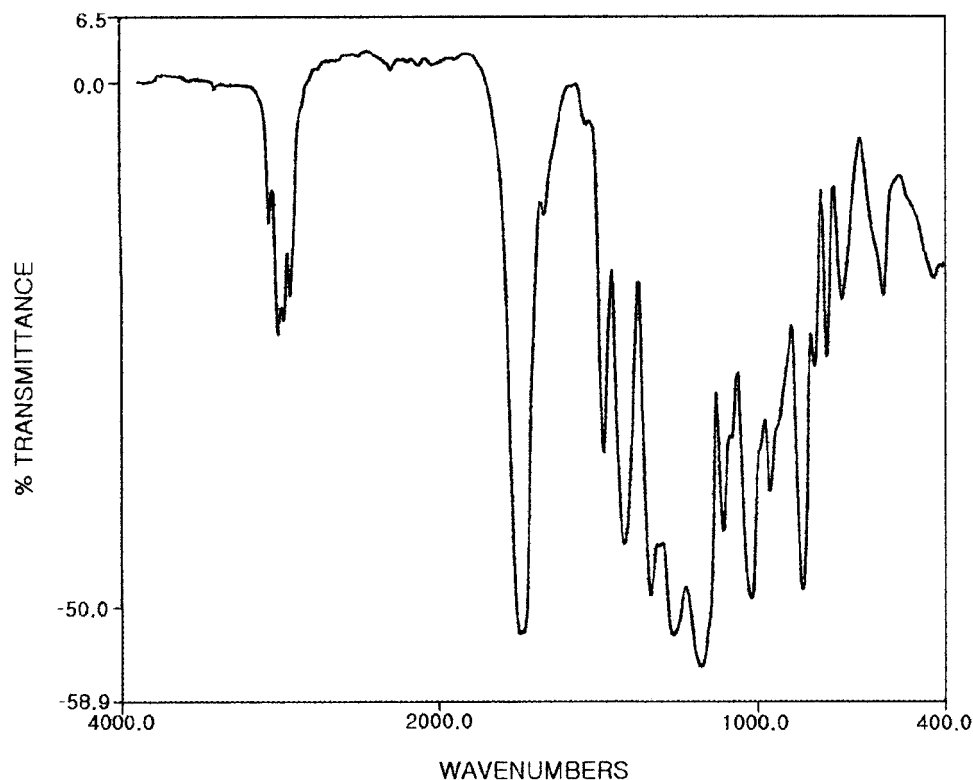
Figure 1   FTIR spectrum of PETE.

THF in the presence of pentaerythritol tet-rakis(3,4-epoxybutanoate) (PETE).

EXPERIMENTAL

Materials

Monomers, THF, and epichlorohydrin (ECH) were purified by the conventional fractionation method.[1] Diphenyliodonium hexafluorophosphate, a well-known photocationic initiator, was synthesized by the method described elsewhere.[7]

Synthesis of PETE

PETE was used as the second component of the copolymerization and was synthesized by epoxidation of PE tetravinyl acetate (PETVA). The PE was esterified with vinyl acetic acid at 140°C for about 4.5 h. Dichloromethane (30 mL) containing m-chloroperoxybenzoic acid (CPBA, 39.4 g) was added dropwise to the PETVA (8.2 g, 20 mmol), and it was allowed to react for 42 h while being agitated. Unreacted CPBA was precipitated by the successive addition of sodium sulfite and 10% aqueous sodium bicarbonate solution and then isolation by filtration (72% yield). The evidence

that PETE was duly synthesized via this method was confirmed by FTIR spectroscopy using an AgBr cell. The absorption bands at 3059 and 3001 cm^{-1} were due to C—H stretching vibration of the cyclic ether, at 2970 cm^{-1} were due to aliphatic C—H stretching vibration, at 1736 cm^{-1} were due to the ester group, and at 1099 cm^{-1} were due to C—O stretching vibration of the cyclic ether as shown in Figure 1.

PETE was also identified by ^{1}H-NMR and ^{13}C-NMR. ^{1}H-NMR (300 MHz, CDCl$_3$): δ = 2.48–2.57 (m, 8H, O=CC$\underline{H}_2$), 2.87 (q, J = 13.5/4.7 Hz, 4H, CHC$\underline{H}_2$O), 2.85 (q, J = 2.4 Hz, 4H, CHC$\underline{H}_2$O), 3.24–3.30 (m, 4H, C$\underline{H}$CH$_2$O), 4.21 (d, J = 2.2 Hz, 8H, CC$\underline{H}_2$O) ppm; ^{13}C-NMR (75 MHz, CDCl$_3$): δ = 37.75 (O=C$\underline{C}$H$_2$), 42.10 [$\underline{C}$(CH$_2$O)$_4$], 6.58 (CH$\underline{C}$H$_2$O), 47.65 ($\underline{C}$HCH$_2$O), 62.16 (C$\underline{C}$H$_2$O) ppm.

Photopolymerization

Samples for irradiation were prepared by introducing a certain amount of THF into a Pyrex ampoule by trap to trap distillation where dried initiator and PETE were placed and the ampoules were sealed off after repeated degasing on a high vacuum line. After polymerization samples were

irradiated at 0°C for a certain period, they were allowed to stand in the dark at 2°C for further reaction. A 500-W high pressure Hg lamp (Ushio UI-501-C, Japan) without any filter was used as a light source. After the reaction in the dark was completed the ampoule was opened and the contents were poured into excess methanol to precipitate the polymer. The percent conversion to polymer was determined by gravimetry. Because the conversion is independent of the duration of the photoirradiation when it exceeds 10 min, it is thought that the photolysis of the initiator is completed within 10 min and so the time of photoirradiation was fixed at 10 min throughout the whole experiment.

Analysis

The structure of the resulting polymer was investigated with a Nicolet 520 FTIR (cast film) and Bruker AM-300 NMR spectrometer using DMSO-d_6 as the solvent. The number average molecular weights of the resulting polymers were determined by GPC (Spectra Physics SP 8430, RI detector) using THF as the solvent (0.5 mL/min flow rate, 10^4, 10^3, and 500 Å columns in series). The GPC was calibrated using poly(THF) standards of various molecular weights (Polymer Laboratories Ltd.).

## RESULTS AND DISCUSSION

Effect of ECH Addition

The effect of ECH addition to the photoinduced cationic polymerization of THF is shown in Figure 2, which shows that the rate of polymerization of THF, a five-membered cyclic ether, is drastically increased by the addition of a small amount of ECH, a three-membered cyclic ether (curve A). It is well known that the ring opening polymerization of a five-membered cyclic ether is promoted in the presence of a three-membered cyclic ether and it is attributed to the increased concentration of the five-membered cyclic oxonium ion, which is a propagating species of the cationic polymerization of THF. The explanation is that the five-membered cyclic oxonium ion in the presence of ECH is produced via a nucleophilic attack of THF to the cationic center, which is produced by the preferential attack of the proton to ECH with a higher rate due to its high ring strain of a three-membered cyclic ether [eqs. (1–3)]. However, in the absence of ECH the production of the five-
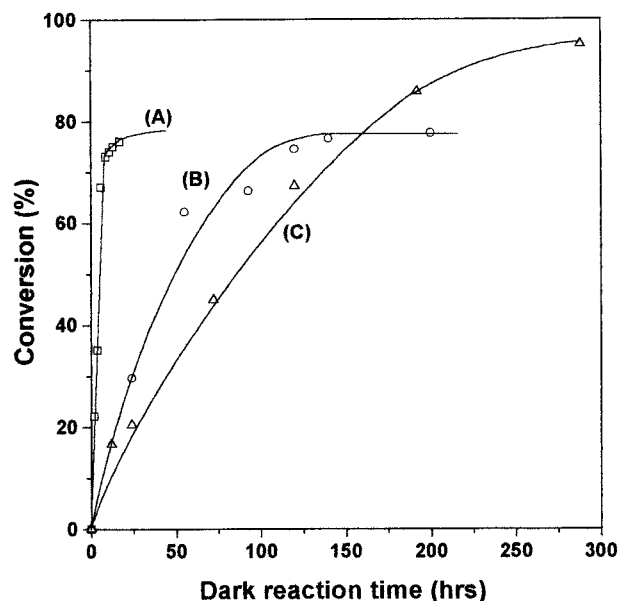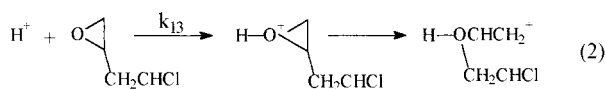

Figure 2   The effect of ECH on the photocationic solution polymerization of THF in dichloromethane in the presence of $4 \times 10^{-2}M$ initiator. The reaction mixture was kept in the dark at 2°C after photoirradiation at 0°C for 10 min. Monomer concentration: 9.85M; (A) in the presence of 2.2 mol % ECH, (B) in the absence of ECH, and (C) in the presence of an equimolar amount of ECH.

membered cyclic oxonium ion proceeds via a direct protonation of THF whose rate is much lower than that of the protonation of ECH [eq. (4), Fig. 2, curve B]. The conversion curves of both systems are leveled off at a similar conversion value, indicating that the final conversion value is not affected by ECH. The leveling off of the curve at a certain value of conversion in the cationic polymerization of THF is explained in terms of an equilibrium established between propagation and depropagation in the living cationic polymerization of THF.[1] In the system containing a large amount of ECH, on the contrary, the polymerization is retarded and the final conversion reaches 90% without leveling of the curve (Fig. 2, curve C), implying that the polymerization mechanism in this system is different from that in the absence of ECH.
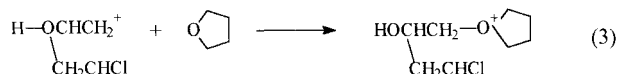
The production of a protonic acid by photolysis of the initiator is

$$(C_6H_5)_2IPF_6 \longrightarrow H^+ + PF_6^- + \cdots \cdots \qquad (1)$$
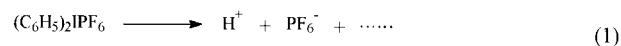
The production of the five-membered cyclic oxonium ion in the presence of ECH has a preferential attack of the proton to ECH as

$$H^+ \ + \ O \overset{}{\underset{CH_2CHCl}{\triangleleft}} \ \xrightarrow{k_{13}} \ H\!-\!O^- \overset{}{\underset{CH_2CHCl}{\triangleleft}} \ \longrightarrow \ H\!-\!OCHCH_2^+ \underset{CH_2CHCl}{} \tag{2}$$

and a nucleophilic attack of THF to the cationic center as

$$H\!-\!OCHCH_2^+ \underset{CH_2CHCl}{} \ + \ O\!\!\bigcirc \ \longrightarrow \ HOCHCH_2\!-\!O^+\!\!\bigcirc \underset{CH_2CHCl}{} \tag{3}$$
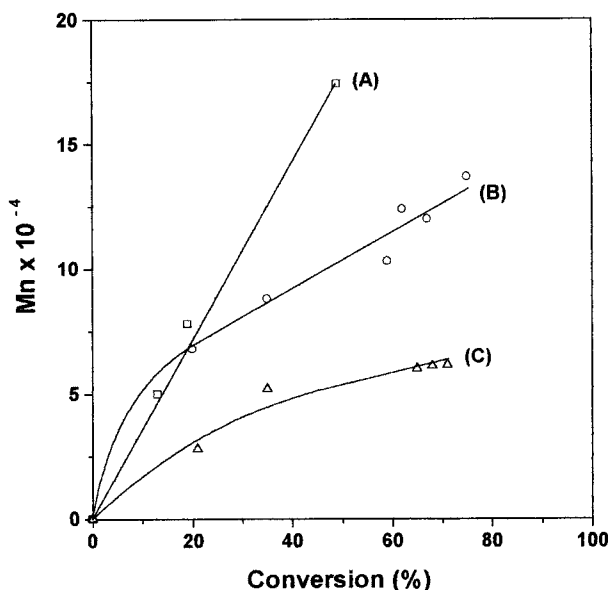
The production of the five-membered cyclic oxonium ion in the absence of ECH by direct protonation of THF is as follows:

$$H^+ \ + \ O\!\!\bigcirc \ \xrightarrow{k_{15}} \ H\!-\!O^+\!\!\bigcirc \tag{4}$$
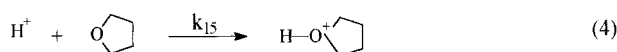
where $k_{13} \gg k_{15}$.

Figure 3 shows the relationship between the percent conversion and the number average molecular weight of the resulting polymer in the solution polymerization. Our earlier data[1] in bulk polymerization is also shown for the sake of comparison. The linear relationship between two parameters that was observed in the bulk polymerization (Fig. 3, curve A) is no longer valid in the solution polymerization (Fig. 3, curve B) and the degree of deviation from the linearity becomes more significant when ECH is added to the solution polymerization system (Fig. 3, curve C). The linear relationship that is an indication of the living nature was attributed to the stabilization of the cationic growing chain end of the five-membered cyclic oxonium ion by ion pair formation with the less nucleophilic hexafluorophosphate anion supplied from the initiator. This led us to conclude that the partial loss of the living nature in the presence of the polar solvent can be ascribed to the dissociation of the stable ion-paired cationic growing chain end to a free cation that is so reactive that chain transfer or termination takes place. The living nature of the system is not lost because of the presence of the small amount of ECH. It is explainable when we assume that ECH is almost consumed in the preferential protonation process; therefore, the cationic propagation is the same as that of THF homopolymerization: the cationic propagation proceeds exclusively by the nucleophilic attack of THF to the cationic growing chain end occupied by the five-membered cyclic oxonium ion. In such a case the equilibrium is established between propagation and depropagation at the cationic growing chain end as was observed in the photoinduced living cationic bulk polymerization of THF. The establishment of an equilibrium is believed to be not only based on the absence of chain transfer or termination due to the stabilization of the cationic propagation species by ion-pair formation but is also attributed to the small enthalpy change of ring opening of the five-membered cyclic oxonium ion, which results in the low ceiling temperature[3] of the THF polymerization [83°C, eq. (5)]. This gives an explanation of why the time-conversion curves of THF in the absence or presence of the small amount of ECH is leveled off when the monomer concentration decreases to a certain value where an equilibrium is reached between propagation and depropagation.

However, in the ECH rich system it is thought that ECH is not completely consumed in the rapid protonation process; therefore, there is a possibility that the cationic growing chain end is occupied by the unreacted ECH. In such a case, chain transfer or termination can operate at the reactive cationic growing chain end, which is occupied by an ECH unit, because of the high reactivity of the three-membered cyclic oxonium ion or carbonium ion, a ring opening product of the former [eq. (6)].


Figure 3 The relationship between the percent conversion and the number average molecular weight of the resulting polymer in photoinduced cationic polymerization of THF in the presence of $4 \times 10^{-2}M$ initiator under various conditions: (A) bulk polymerization in the absence of ECH, (B) solution polymerization in dichloromethane in the absence of ECH, and (C) solution polymerization in dichloromethane in the presence of 2.2 mol % ECH. [THF] = 9.85M.

The living nature is apparent when the cationic growing chain end is occupied by an ion-paired five-membered cyclic oxonium ion:

$$(5)$$
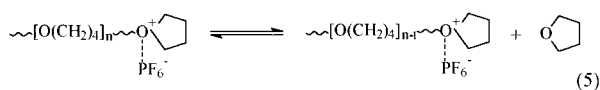
The living nature is lost when the cationic growing end is occupied by the reactive ECH.

Chain transfer or termination

$$(6)$$
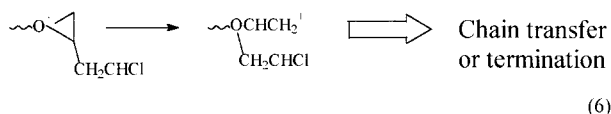
Synthesis of Four-Armed Star-Shaped Poly(THF)

Based on the fact that the production of the five-membered cyclic oxonium ion, which is the propagating species of cationic THF polymerization in the presence of the small amount of ECH, proceeds via a rapid protonation of a three-membered cyclic ether, synthesis of a four-armed star-shaped poly(THF) by photoinduced cationic polymerization of THF in the presence of a small amount of PETE was attempted. As shown in Scheme 1, it is expected that in the presence of a small amount of PETE the oxirane unit of PETE is almost consumed in the rapid protonation process when its concentration is kept much lower than that of THF to give a three-membered cyclic oxonium ion. The cationic initiating species of THF, a five-membered cyclic oxonium ion, is produced by the nucleophilic attack of THF to the cationic center of a three-membered cyclic oxonium ion or a carbonium ion. Furthermore, the cationic growing chain end occupied by the five-membered cyclic oxonium ion is stabilized by ion-pair formation with hexafluorophosphate, which enables the formation of a four-armed star-shaped living cationic poly(THF). In order to prevent the dissociation of the ion-paired cationic propagating species to a more reactive free cation, the polymerization was carried out in the bulk state without using any solvent. As a consequence, it was expected that a living cationic poly(THF) with four arms would be obtained and whose arm length is determined by the molar ratio of THF and the oxirane unit of PETE. Synthesis of a four-armed poly(THF) by a subsequent monomer addition method (i.e., the addition of PETE to the photoinduced living cationic poly(THF)] was tried; however, the results were unsatisfactory because of the high viscosity of the
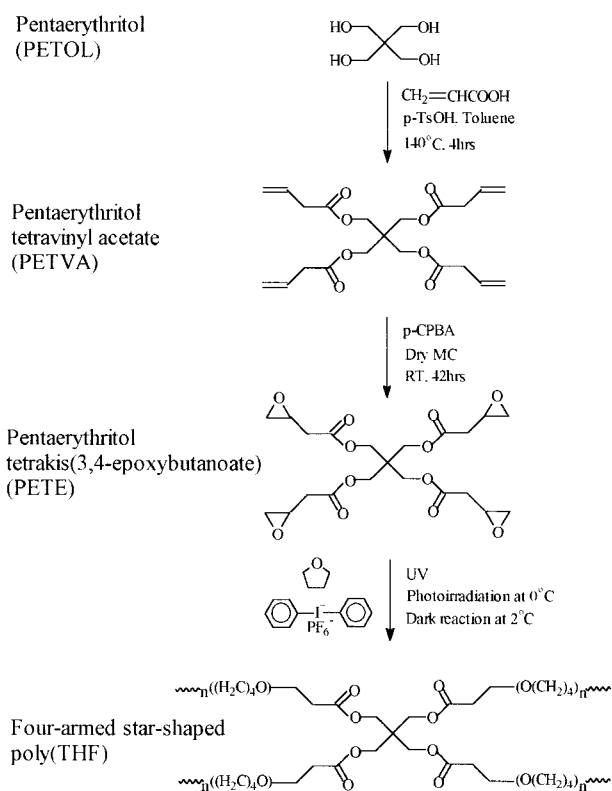
Scheme 1 Synthetic route of the four-armed star-shaped poly(THF).

living cationic poly(THF) in the bulk state, which interferes with the homogenous mixing of the two components.

Comparison of the time-conversion curves shown in Figure 4 reveals that the rate of polymerization of THF is drastically enhanced by the addition of PETE. This indicates that the five-membered cyclic oxonium ion that is responsible for the cationic polymerization of THF is produced indirectly by the nucleophilic attack of THF to the cationic center of the three-membered cyclic oxonium ion of PETE. This can be confirmed by IR spectroscopy of the oligo(THF) obtained just after the photoirradiation. The presence of an absorption band at around 1740 cm^{-1} due to the ester group of PETE in the IR spectrum supports the idea of the production of cationic propagating species via the rapid protonation of the three-membered cyclic ether unit of PETE.

The initiation via preferential protonation of the oxirane unit of PETE followed by the nucleophilic attack of THF to the cationic center to produce a cationic growing chain end occupied by the five-membered cyclic oxonium ion proceeds as follows:

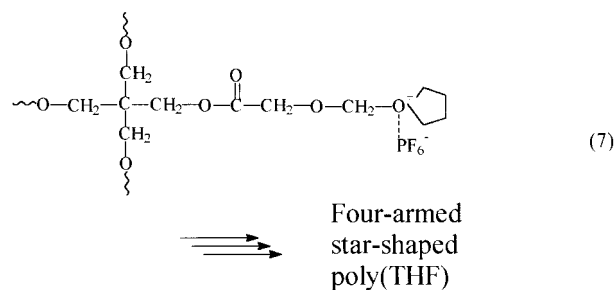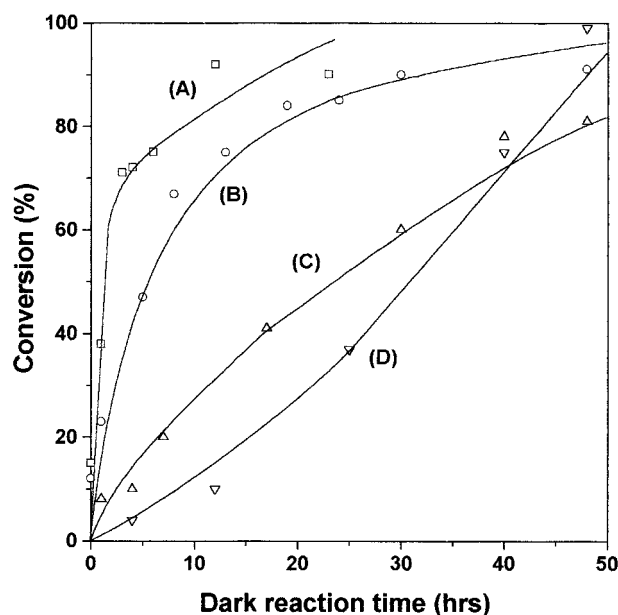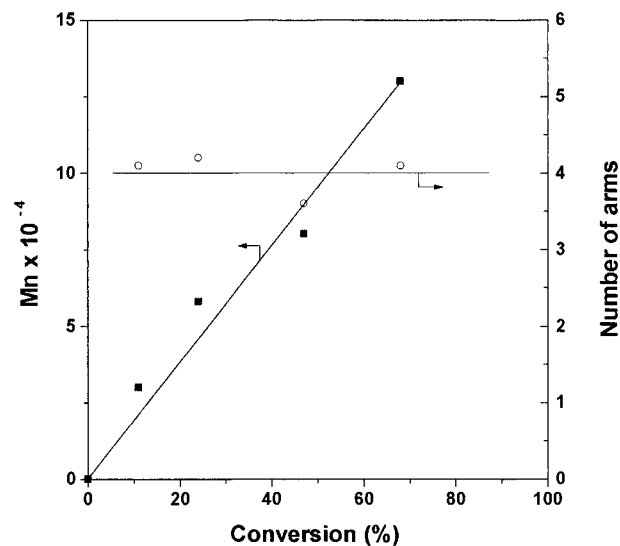Four-armed
star-shaped
poly(THF)

(7)

Figure 5 shows the relationship between the percent conversion and number average molecular weight of the resulting polymer of the polymerization system containing PETE. Although the relationship between the two parameters deviates slightly from linearity, the molecular weight increases with increasing percent conversion, indicating that the living nature is still retained even in the presence of PETE. This also implies that the cationic propagation proceeds mainly by the nucleophilic attack of THF to the ion-paired growing chain end, which is occupied by the five-membered cyclic oxonium ion. As it is in the cationic homopolymerization of THF, after most of the oxirane unit of PETE is consumed in the early stage of the reaction by the rapid protonation process. However, the slight deviation

Figure 5 Dependence of the number average molecular weight and number of arms of the resulting polymers on percent conversion. [THF]/[PETE] = 1000.

from linearity in the presence of PETE implies there is a possibility that the chain end is occupied by the unreacted oxirane unit of PETE.

Figure 6 shows the gel content of the product as a function of the dark reaction time together with time-conversion curves. The insoluble portion of the polymer to toluene increases with an increasing percent conversion that implies that
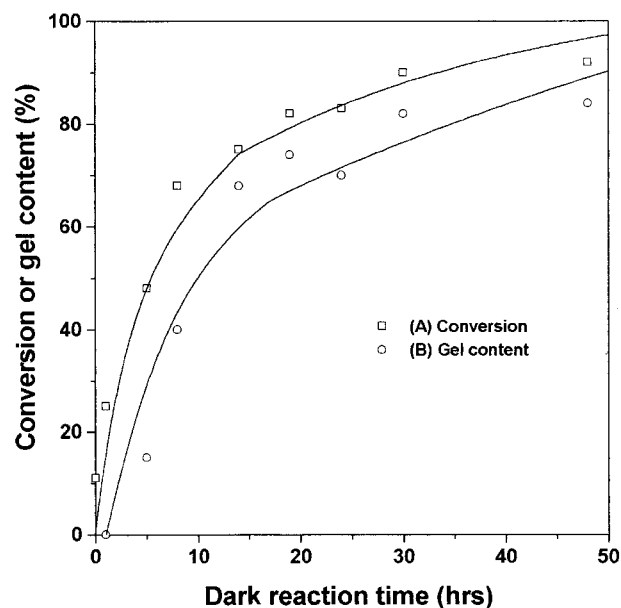

Figure 4 Time-conversion curves of the bulk polymerization of THF in the dark in the presence or absence of PETE after photoirradiation for 10 min at 0°C. [Initiator] = $5 \times 10^{-3}M$. The composition is expressed as [THF]/[PETE] (A) 500, (B) 1000, (C) 5000, and (D) in the absence of PETE.

Figure 6 Gel content as a function of dark reaction time in photoinduced cationic polymerization of THF in the presence of PETE. [THF]/[PETE] = 1000.
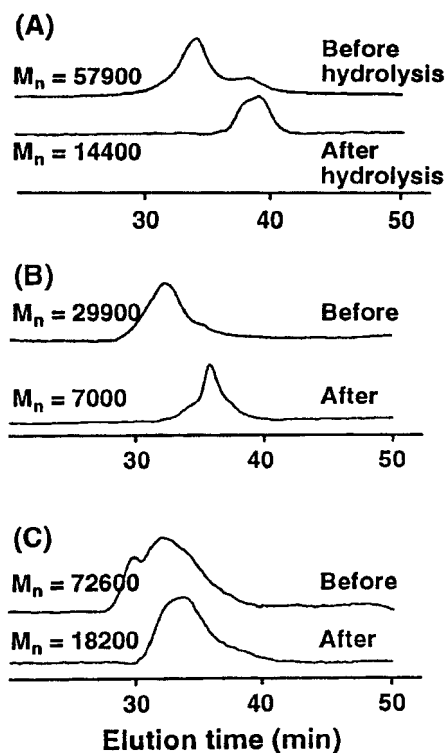
Figure 7 Comparisons of GPC traces of the polymers before and after alkaline hydrolysis.

chain transfer to the polymer plays an important role when the polymer concentration becomes high in the later stage of the reaction. This also gives an explanation of why the living nature is partially lost in the cationic THF polymerization system containing PETE.

Some examples of GPC traces of the original polymers and their alkaline treated products are shown in Figure 7. Because the ester linkage of

the PETE unit in the polymer is expected to be cleaved by the alkaline treatment, the ratio of the number average molecular weight of the polymer before and after alkaline treatment gives the number of arms of the star-shaped polymer. The polymers were refluxed in a 10% aqueous NaOH solution for 10–12 h in a flask equipped with a condenser. The number average molecular weight of the polymer was determined by GPC. The results are summarized in Table I. The values scattered around 4 reveals that the star-shaped poly-(THF) with four arms and whose arm length is determined by the molar ratio of THF and the oxirane unit of PETE was successfully obtained from this system. However, the four-armed star-shaped poly(THF) of well-defined structure, which was free of crosslinking, was only obtainable in the early stage of the reaction of low conversion.

CONCLUSIONS

A four-armed star-shaped poly(THF) was synthesized by photoinduced cationic polymerization of THF in the presence of a small amount of PETE. The remarkable increase in the rate of polymerization in the presence of ECH was attributed to the increased concentration of the cationic propagating species that is produced via a preferential protonation of the oxirane unit. The preferential protonation of the three-membered cyclic ether was also confirmed in THF polymerization in the presence of ECH. The living nature of the system was ascribed to the stability of the cationic growing chain end occupied by the ion-paired five-

Table I   Results of Photoinduced Cationic Polymerization of THF in Presence of PETE

		Molecular Weight				
[THF]/[PETE]	Dark Reaction Time (h)	Before Alkaline Hydrolysis	After Alkaline Hydrolysis	Conversion (%)	No. Arms	Remarks
5,000	1	82,000	20,000	8	4.1	—
	4	90,000	22,000	11	4.1	—
	8	206,000	45,000	22	4.6	—
	30	227,000	53,000	61	4.3	Gel formed
1,000	0	30,000	7,000	11	4.2	—
	1	58,000	14,500	24	4.0	—
	4	80,000	23,000	47	3.4	—
	8	130,000	32,000	68	4.1	Gel formed
500	1	47,000	13,000	38	3.6	—
	4	72,000	18,000	72	4.0	—

membered cyclic oxonium ion after the oxirane unit of PETE was almost consumed in the preferential protonation process.

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