

# Photoinduced Living Cationic Polymerization of Tetrahydrofuran. I. Living Nature of the System and Its Application to the Diblock Copolymer Synthesis

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Received 16 May 1997; accepted 3 September 1997

**ABSTRACT:** The living nature of cationic polytetrahydrofuran (THF), photoinduced in the presence of diphenyliodonium hexafluorophosphate (initiator), was investigated. In the bulk polymerization of THF, the linear relationship between percent conversion and the number-average molecular weight of the resulting polymer strongly suggests the living nature of this polymer and this was confirmed by the monomer addition technique, that is, cationic poly(THF) is capable of initiating a newly added monomer. The loss of the living nature of the cationic poly(THF) in a polar solvent, dichloromethane, is explained in terms of the stabilization of the five-membered cyclic oxonium ion, a propagating species of cationic polymerization of THF, by ion-pair formation with a less nucleophilic counterion, hexafluorophosphate. Based on the living nature of cationic poly(THF), a diblock copolymer, composed of THF and *N*-2-(hydroxyethyl)ethyleneimine (HEEI) was synthesized by subsequent monomer addition method; however, it was found that the HEEI block of the copolymer has a nonlinear structure. The factors affecting the structure of the HEEI block are also discussed. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 611–618, 1998

**Key words:** living polymer; photocationic initiator; ion pair; diblock copolymer; subsequent monomer addition

## INTRODUCTION

The living polymers of ionic polymerizations have been the subject of extensive study for several decades because of their potential utility for molecular design. In living polymer systems in which chain transfer or termination is absent, it has been reported that polymers of a well-defined structure, such as monodispersed polymers,<sup>1</sup> block copolymers,<sup>2</sup> and star-shaped polymers,<sup>3</sup> may be successfully synthesized, for example, for living anionic polymerization.

The living cationic polymer system has been studied less in contrast with the living anionic system due to the difficulty in finding a suitable means to stabilize the reactive cationic growing chain end. Recently, several reports concerning living cationic polymerizations and their applications to the synthesis of polymers of well-defined structures such as the synthesis of block copolymers and star-shaped polymers<sup>4,5</sup> have been published. The living nature was ascribed to a tight association of the cationic propagating species by the counteranion.<sup>4</sup>

It was known earlier that the polymerization of tetrahydrofuran (THF) occurs via a living cationic processes due to the moderate reactivity and stability of the five-membered cyclic oxonium species.<sup>6,7</sup>

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*Journal of Applied Polymer Science*, Vol. 69, 611–618 (1998)  
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Furthermore, the degradative reaction of the cationic growing species to the polymer occurs to a very limited extent due to the higher basicity of the monomer than that of the polymer chain. Thus, the cationic polymerization of THF is one of the best-defined examples. The cationic living nature of poly(THF) has been applied to the synthesis of terminally functional poly(THF),<sup>8,9</sup> block copolymers by sequential polymerization,<sup>10,11</sup> block copolymers by terminal functionalization followed by polymerization,<sup>12</sup> block copolymers by an ion-coupling reaction,<sup>13</sup> and graft copolymers.<sup>14</sup> In these systems, the living nature of cationic poly(THF) was attributed to the stabilization of the cationic propagating species of the cyclic oxonium ion by ion-pair formation with a less nucleophilic complex metal halide counteranions<sup>15</sup> such as hexafluorophosphate, hexafluoroarsenate, and tetrafluoroborate.

In this study, we report on a photoinduced cationic living polymerization system of THF in the presence of a well-known photocationic initiator, diphenyliodonium hexafluorophosphate, and its application to the synthesis of a poly(THF)-based diblock copolymer.

## EXPERIMENTAL

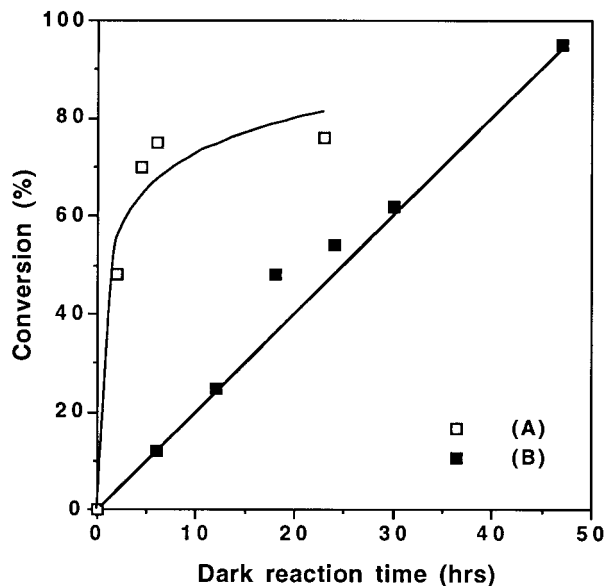
### Materials

The monomers, tetrahydrofuran (THF) and *N*-2-(hydroxyethyl)ethylene-imine (HEEI, Aldrich Chemical Co.), were purified by distillation on LiAlH<sub>4</sub>. Diphenyliodonium hexafluorophosphate, a photocationic initiator, was synthesized by the method described elsewhere.<sup>16</sup>

### Photopolymerization

A proper amount of the monomer was introduced into a Pyrex ampule by trap-to-trap distillation on a high vacuum line where the dried photocationic initiator was placed and then the ampule was sealed off after degassing. Polymerization samples were irradiated with a 500-W high-pressure Hg lamp (Ushio UI-501-C), followed by a dark reaction at 2°C for further reaction. After completion of the reaction, the ampule was opened and polymer was precipitated in excess methanol. Percent conversion was determined by gravimetry.

In the case of the poly(THF-*b*-HEEI) diblock copolymer synthesis, the second component of the copolymerization, HEEI, was added to the photoinduced living cationic poly(THF) by a microsyringe in order to avoid the contact of HEEI with



**Figure 1** Dark reaction time versus conversion curves of THF polymerization. Irradiation was carried out at 0°C for 10 min and by a dark reaction at (A) 28°C and (B) 2°C, respectively, in the presence of  $5 \times 10^{-2} M$  initiator.

air. The procedures for the diblock synthesis after the second monomer addition were quite the same as that of the THF homopolymerization.

### Analysis

The molecular structures of the poly(THF) and poly(THF-*b*-HEEI) were identified by a Nicolet 520 FTIR (cast film) and a Bruker AN-300 NMR spectrophotometer using DMSO-*d*<sub>6</sub> for poly(THF) and acetic acid-*d*<sub>4</sub> for poly(THF-*b*-HEEI). The molecular weight determination of poly(THF) was measured by GPC (Spectra Physics SP 8430, RI detector) using THF as a solvent (flow rate: 0.5 mL/min; columns: 10<sup>4</sup>, 10<sup>3</sup>, 500A in series).

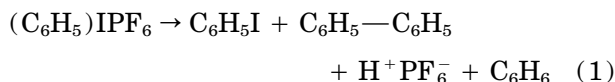
## RESULTS AND DISCUSSION

### Living Nature of Bulk THF Polymerization

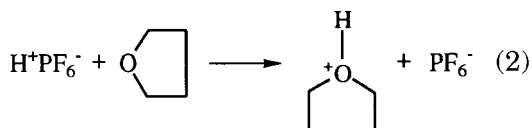
The samples, prepared under strictly dried conditions on a high vacuum line, were stored in the dark after photoirradiation for 10 min at 0°C. Figure 1 shows the percent conversion of poly(THF) as a function of the dark reaction time. The conversion increases with the dark reaction time; however, 100% was never attained in any run. After the conversion reaches its final value, no further increase in percent conversion was ob-

served even when the dark reaction time was extended. No polymer was obtained from the sample prepared in wet open air. The inhibition effect of a basic impurity such as water implies the ionic nature of the system. It has been well known that photoinduced cationic initiation in the presence of an initiator proceeds via a cationic mechanism. Polymerization is initiated by the direct addition of a proton, a photolytic product of the initiator,<sup>16</sup> to the oxygen atom of a five-membered cyclic ether to give a cyclic oxonium ion, followed by propagation due to the nucleophilic attack of THF on the cyclic oxonium ion as shown below:

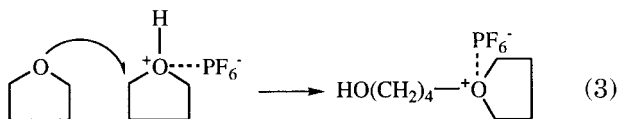
*Generation of protonic acid by photoirradiation:*



*Initiation by direct addition of proton to the oxygen atom of THF:*

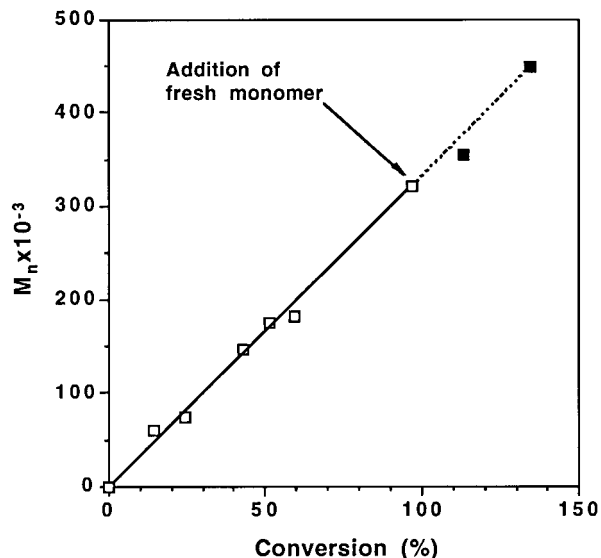


*Propagation by nucleophilic attack of THF:*



Comparison of the results at 0 and 28°C reveals a higher final conversion and a lower rate of polymerization at a lower dark reaction temperature. It is worthy to mention that the rate of polymerization is very low when compared with that of the production of the initiating species,  $\text{HPF}_6$ . Even at the high dark reaction temperature of 28°C, it takes longer than 20 h to reach the final conversion, whereas the production of protonic acid by photoirradiation is completed within 10 min.

Figure 2 shows the relationship between percent conversion and the number-average molecular weight of the resulting poly(THF) in this bulk polymerization system. The linear relationship between the two parameters provides evidence of the living nature of this polymerization system. It is believed that in this polymerization a rapid photoinduced cationic initiation is followed by propagation at a relatively low rate in the absence of chain transfer and termination processes,

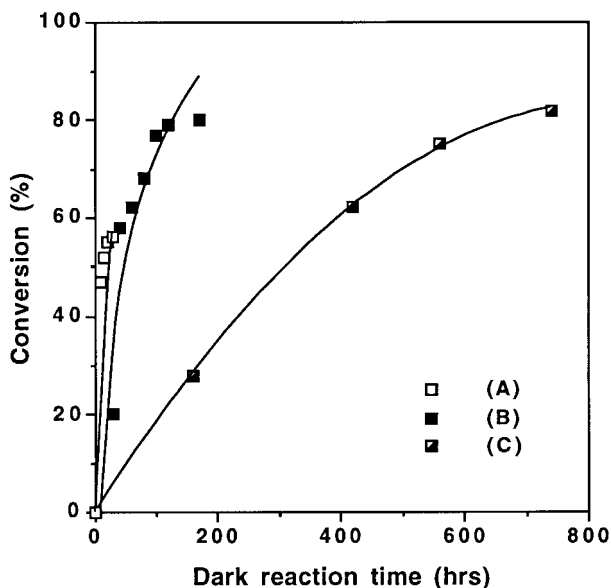


**Figure 2** Dependence of the number-average molecular weight of poly(THF) on percent conversion. Irradiation was carried out at 0°C for 10 min, followed by a dark reaction at 2°C in the presence of  $5 \times 10^{-2} M$  initiator. The second portion of the monomer was added.

which results in an increase in the molecular weight, keeping pace with percent conversion.

The living nature of the system was confirmed by the monomer addition method: To a photoinduced bulk polymerization system of THF, in which the conversion reached a final value of 95% at 2°C, freshly distilled THF was introduced through a breakable seal. The living nature of the photoinduced poly(THF) was checked by the capability of the living polymer chain end to initiate the newly added monomer. Increases in both the polymer yield and molecular weight of the polymer were observed as shown in Figure 2, revealing that the polymer chain end retains its activity to initiate the newly added monomer even after the conversion of the original monomer to the polymer reaches its final value. It is also recognized that the linear relationship between the conversion and the molecular weight of the resulting polymer is still valid in the polymerization of the newly added monomer.

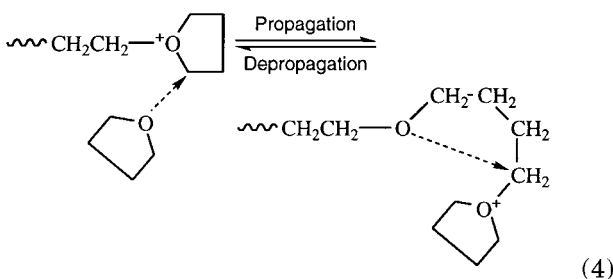
Although the activity of the propagating chain end is maintained throughout the whole course of the reaction, the conversion never reached 100% in any run. After the time-conversion curves leveled off, no further increase in percent conversion was observed even if the dark reaction time was extended. This fact, together with the negative dependence of the final conversion on the dark reaction temperature, leads us to a conclusion that an equilibrium between propagation and de-



**Figure 3** Time-conversion curves of photocationic solution polymerization of THF (9.85M) in dichloromethane in the presence of 0.04M initiator carried out in the dark at various temperatures after photoirradiation at 0°C for 10 min: (A) 28°C; (B) 2°C; (C) -14°C.

propagation is established in this system as has been reported in the catalytic cationic polymerization.<sup>17</sup> The lower value of final conversion at higher temperature is explainable when we consider the exothermic nature of the polymerization, that is, the equilibrium is shifted toward depolymerization at higher temperature.

*Equilibrium between propagation and depropagation:*



#### Loss of the Living Nature in Solution Polymerization

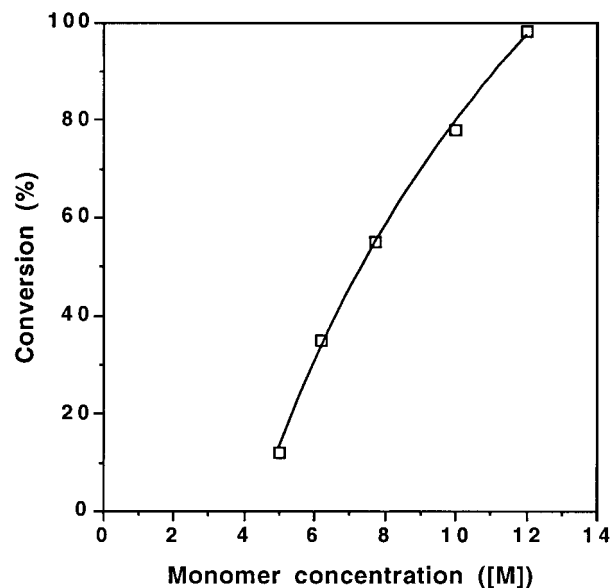
This is supported by the results obtained from the solution polymerization. Figure 3 shows time-conversion curves of the solution polymerization of THF in the polar solvent, dichloromethane, at 0°C. From the figure, it is evident that the final

conversion value in the solution polymerization is always lower than that of the corresponding bulk polymerization. The decrease in the monomer concentration due to the addition of solvent makes the equilibrium shift to the direction of depolymerization, as expected.

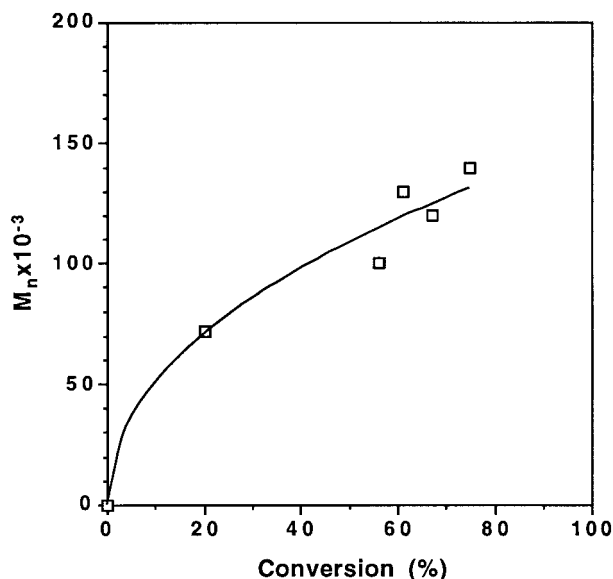
Figure 4 shows the dependence of the final conversion value in the solution polymerization on the monomer concentration. Actually, no polymer was obtained when the monomer concentration was lower than 4.2M.

Figure 5 shows the relationship between percent conversion and the number-average molecular weight of the resulting polymer in the solution polymerization. The deviation from the linearity indicates that the living nature is partly lost due to the presence of the polar solvent.

It has been reported that the propagating species responsible for the cationic propagation is stabilized by ion-pair formation with a less nucleophilic complex metal halide anion.<sup>15</sup> It is believed that the cationic propagating species of the five-membered cyclic oxonium ion, having a moderate reactivity, is stabilized by ion-pair formation with a less nucleophilic counterion, hexafluorophosphate, supplied from the initiator. Since the cationic propagating species is so stable, any degradative reaction such as chain transfer to the polymer backbone is depressed to a very limited extent



**Figure 4** Percent conversion as a function of monomer concentration in photocationic solution polymerization of THF in dichloromethane in the presence of  $4 \times 10^{-2}M$  initiator. The reaction mixtures were kept in the dark at 2°C for 144 h after photoirradiation at 0°C for 10 min.



**Figure 5** Relationship between percent conversion and the number-average molecular weight of the resulting polymer in photocationic solution polymerization of THF in dichloromethane in the presence of  $4 \times 10^{-2} M$  initiator, carried out in the dark at  $2^\circ\text{C}$  after photoirradiation at  $0^\circ\text{C}$  for 10 min. Monomer concentration:  $9.85 M$ .

because of the higher basicity of cyclic monomer than that of the linear polymer. Thus the cationic propagation proceeds preferentially to give a living poly(THF).<sup>18</sup> In the presence of the polar solvent, however, the propagating species in the ion-paired state is dissociated to a free ion which is reactive enough for chain transfer or termination. Accordingly, the living nature is lost in the solution polymerization.

#### Synthesis of Poly(THF-*b*-HEEI) Diblock Copolymer by Sequential Monomer Addition

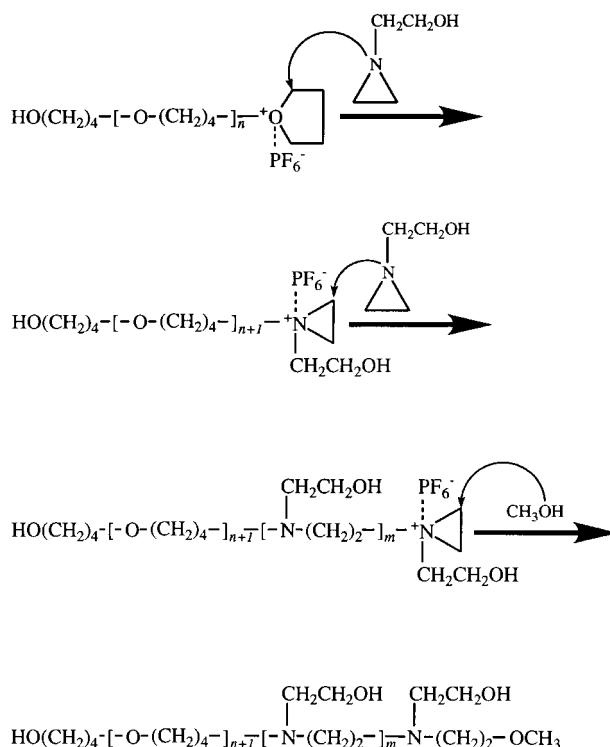
Based on the living nature of the photoinduced living cationic poly(THF), an attempt was made to synthesize the diblock copolymer of THF and HEEI by the sequential addition method as shown in Scheme 1. It was expected that when fresh HEEI is added to a photoinduced living cationic poly(THF), ring-opening polymerization of HEEI would be initiated cationically by the cyclic oxonium ion located at the end of living cationic poly(THF), finally giving a poly(THF-*b*-HEEI) diblock copolymer of a well-defined structure.

HEEI, dried thoroughly on  $\text{CaH}_2$ , was added to photoinduced living cationic poly(THF), which was allowed to stand in the dark for 6 h at  $2^\circ\text{C}$  after photoirradiation for 10 min at  $0^\circ\text{C}$ , by a mi-

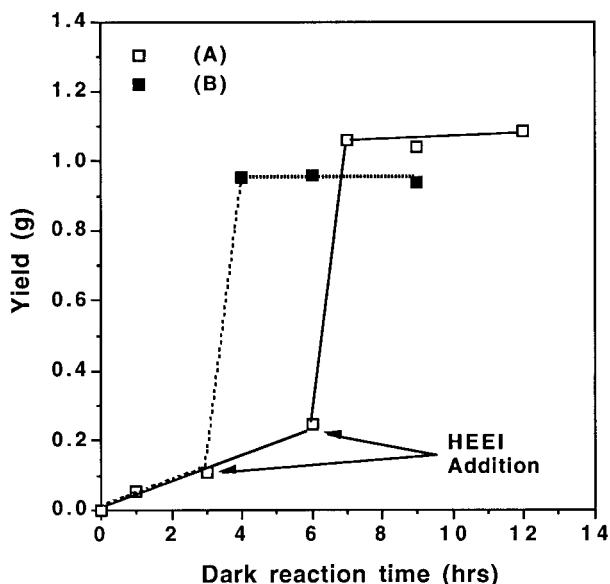
croscopy in order to avoid the HEEI contacting humid air. It was impossible to extend the dark reaction time of THF polymerization longer than 6 h because the viscosity of the living poly(THF) was too high to mix homogeneously with the second monomer. When HEEI was added in the open air, no diblock copolymer was obtained, revealing the ionic nature of the system.

Figure 6 shows the results of the block copolymerization when the second monomer, HEEI, was added to the living cationic poly(THF), which was allowed to stand in the dark for 3 and 6 h at  $2^\circ\text{C}$  after 10-min photoirradiation. The results are shown as a weight increase due to HEEI addition as a function of the reaction time. The polymerization of HEEI initiated by the living cationic poly(THF) was so drastic that it was impossible to control the reaction temperature. The larger the HEEI addition, the larger was the increase in the polymer yield observed. Although the reaction proceeds vigorously, the polymerization of HEEI did not proceed until complete consumption of HEEI and the percent conversion of HEEI to the polymer shows an almost constant value of around 76% irrespective of the amount of HEEI added.

The final values of the conversion of HEEI to the polymer are summarized in Table I. The in-



**Scheme 1** Synthetic route of poly(THF-*b*-HEEI).



**Figure 6** Time-yield curves of poly(THF-*b*-HEEI) copolymerization by sequential monomer addition technique. Fresh HEEI was added to living poly(THF) when a dark reaction was carried out for (A) 6 h and (B) 3 h after photoirradiation. ( $[THF]/[HEEI] = 1$ ).

complete consumption of HEEI in the copolymerization is believed to be due to the loss of the activity of the cationic propagating species, aziridinium ion. Almost the same value of the final conversion was observed in the cationic polymerization of HEEI, photoinitiated in the presence of the same initiator at various temperatures ranging from 0 to 50°C. The fact that the final conversion value is independent of the temperature means that the incomplete consumption of HEEI is not dependent on the equilibrium established between the propagation and depropagation in the living polymerization because it is thought that the equilibrium is shifted toward the direction of depropagation in the exothermic reaction. Therefore, it is believed that the incomplete consumption of HEEI in the block copolymerization is due to the loss of activity of the cationic propagating species before the monomer is completely consumed by the process of chain transfer or termination. This indicates that the cationic propagating species of HEEI, even in the form of an ion pair with  $PF_6^-$ , is so reactive that chain transfer or termination takes place.

It is known that the cationic propagation step of *N*-alkylaziridines is a nucleophilic attack of the nitrogen of the monomer on the active species. However, this attack can also occur with a nitrogen of the polymer molecule. The formed branched or cyclic quaternary ammonium ion is unreactive

toward propagation; therefore, the concentration of the cationic propagating species becomes lower, as polymerization proceeds, to produce the more basic acyclic amino groups. This explains the observed decrease in the rate of polymerization. Accordingly, it is believed that this is the real termination reaction in the cationic polymerization of HEEI. As a consequence, the polymerizations of *N*-alkylaziridines generally do not proceed to completion and do not lead to high molecular weight polymers.<sup>19</sup> It was shown later that the nature of the nitrogen substituent plays a predominant role in the rate of the termination reaction between the aziridinium group and an amino function of its own polymer chain forming a macrocyclic ammonium end group. *N*-Butylaziridine, having a bulky *N*-substituent, is the exception which exhibits the character of a living polymer. Actually, there is a termination reaction; however, it is so slow compared with propagation that, at almost quantitative conversion, almost all polymer chains still possess an active center.<sup>20,21</sup>

The  $^1H$ -NMR spectrum of the block copolymer is shown in Figure 7. The spectrum is composed of many complicated proton signals including those signals at 3.5 and 1.6 ppm due to the THF block and at 2.7 and 3.6 ppm for the HEEI<sup>22</sup> block of a linear structure, implying that the HEEI block has a nonlinear structure. The  $^1H$ -NMR spectrum of poly(HEEI), obtained from the photoinduced cationic polymerization of HEEI in the presence of the same initiator, is almost the same as that of the diblock copolymer. It is thought that the nonlinear structure of the HEEI block of the diblock copolymer also gives evidence that chain

**Table I** Conversion of HEEI in Block Copolymerization at Various Conditions

Run No.	Dark Reaction Time of THF <sup>a</sup> (h)	Amount of HEEI Added <sup>b</sup>	Conversion (%)
1	6	1.0 : 1.0	75.2
2		1.0 : 0.2	79.7
3		1.0 : 0.1	77.2
4	3	1.0 : 1.0	77.5
5		1.0 : 0.2	78.6
6		1.0 : 0.1	74.9

$[I] = 5 \times 10^{-2} M$ ; photoirradiation at 0°C for 10 min for the photoinitiation of THF. Fresh HEEI was added to the living poly(THF) after the THF polymerization was settled for 3 and for 6 h in the dark at 2°C.

<sup>a</sup> Homopolymerization of THF.

<sup>b</sup> Mol ratio of THF : HEEI.

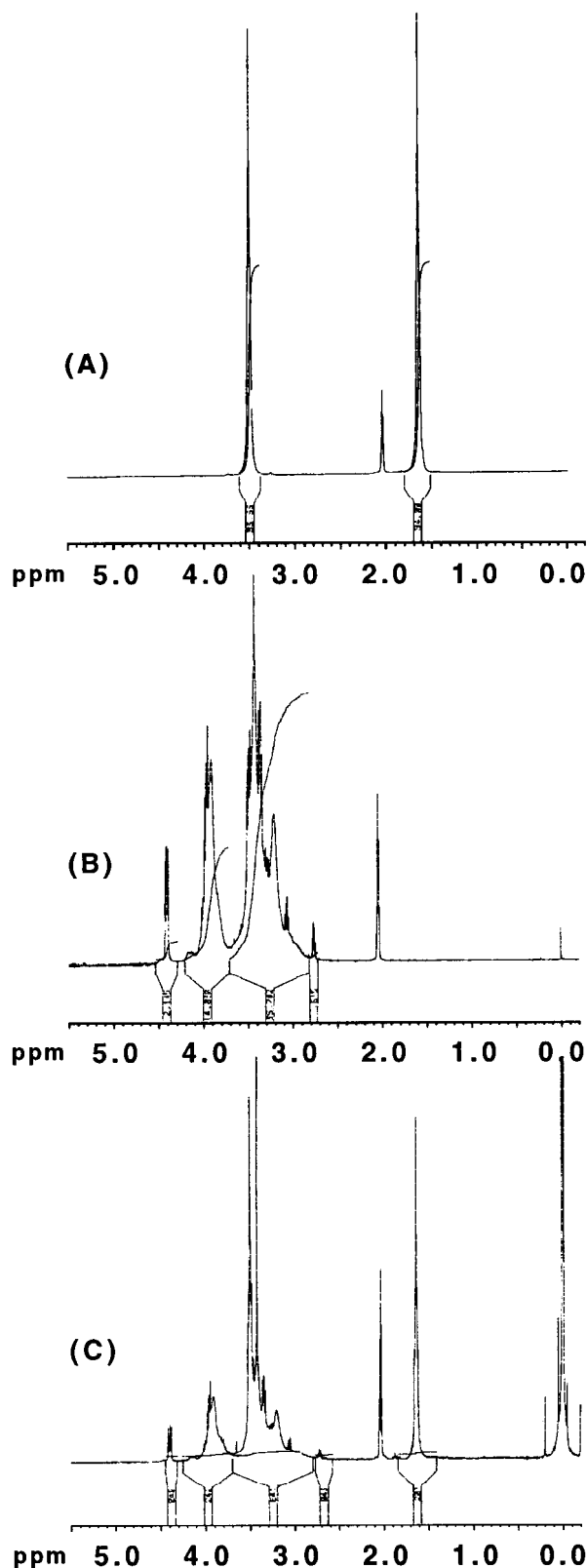


Figure 7  $^1\text{H-NMR}$  spectra of (A) poly(THF), (B) poly(HEEI), and (C) poly(THF-*b*-HEEI).

transfer or termination operates in the cationic propagation step of HEEI.

## CONCLUSIONS

A photoinduced living cationic poly(THF) was investigated and used as a macromolecular cationic initiator for the synthesis of a poly(THF-*b*-HEEI) diblock copolymer. The living nature of the photoinduced cationic poly(THF) was demonstrated by the linear relationship between percent conversion and the number-average molecular weight of the resulting polymer and was confirmed by the monomer addition method. However, it was found that the living nature is partially lost in a polar solvent, dichloromethane. This led us to a conclusion that the living nature of the cationic poly(THF) is due to the increased stability of the five-membered cyclic oxonium ion, the propagating species of the cationic polymerization of THF, by ion-pair formation with hexafluorophosphate, supplied from the initiator. Loss of the living nature in the polar solvent is ascribed to the dissociation of the ion-paired cation to the free cation which is so reactive that chain transfer or termination can take place. It has been found that the HEEI block in the diblock copolymer has a nonlinear complicated structure, which reveals a competitive nucleophilic attack of nitrogen of the monomer and polymer on the cationic propagating sites of HEEI.

## REFERENCES

1. M. Szwarc, M. Levy, and R. Milkovich, *J. Am. Chem. Soc.*, **78**, 2656 (1956).
2. L. J. Fetters, *J. Polym. Sci. C*, **26**, 1 (1969).
3. T. Fujimoto and M. Nagasawa, *Macromolecules*, **11**, 673 (1978).
4. M. Sawamoto, S. Asoshima, and T. Higashimura, *Makromol. Chem. Macromol. Symp.*, **13/14**, 513 (1988).
5. R. Faust and J. P. Kennedy, *J. Macromol. Sci. A*, **21**, 595 (1987).
6. G. Prukmayr and K. Wu, *Macromolecules*, **6**, 33 (1973).
7. M. P. Dreyfuss and P. Dreyfuss, *J. Polym. Sci. A-1*, **4**, 2179 (1966).
8. P. Dreyfuss and J. P. Kennedy, *J. Polym. Sci. Lett. Ed.*, **14**, 139 (1976).
9. T. Fujimoto, M. Kawahashi, M. Nagasawa, and A. Takahashi, *Polym. J.*, **11**, 193 (1979).
10. J. L. Lambert and J. Goethals, *Makromol. Chem.*, **133**, 289 (1970).

11. Y. Tezuka and E. J. Goethals, *ACS Polym. Prepr.*, **22**, 313 (1981).
12. Y. Yamashita and K. Chiba, *Polym. J.*, **4**, 200 (1973).
13. D. H. Richards, S. B. Kingstone, and T. Souel, *Polymer*, **19**, 68 (1978).
14. R. Asami, M. Takaki, Y. Harima, and H. Tsuzuki, *Polym. J.*, **13**, 141 (1981).
15. S. Mah, Y. Yamamoto, and K. Hayashi, *J. Phys. Chem.*, **87**, 287 (1982).
16. J. V. Crivello and J. H. W. Lam, *J. Polym. Sci. Chem. Ed.*, **16**, 1441 (1978).
17. T. Saegusa, H. Imai, and S. Matsumoto, *J. Polym. Sci. A-1*, **6**, 459 (1968).
18. H. R. Kricheldorf, Ed., *Handbook of Polymer Synthesis*, Part A, Marcel Dekker, New York, 1991, p. 521.
19. G. D. Jones, D. C. McWilliams, and N. A. Braxton, *J. Org. Chem.*, **30**, 1994 (1965).
20. E. J. Goethals, E. N. Schacht, P. Bruggeman, and P. Bossaer, ACS Symposium Series 59, American Chemical Society, Washington, DC, 1977, p. 1.
21. M. V. Velde and E. J. Goethals, *Makromol. Chem. Macromol. Symp.*, **6**, 271 (1986).
22. B. L. Rivas, *Eur. Polym. J.*, **27**, 1165 (1991).