Living Cationic Polymerization of Isobutyl Vinyl Ether (II): Photoinduced Living Cationic Polymerization in a Mixed Solvent of Toluene and Diethyl Ether

Soonhong Kwon, Younsung Lee, Hyunjeong Jeon, Kyuchan Han, Soukil Mah

Department of Textile Engineering, Inha University, Yonghyun-dong 253, Nam-Ku, Inchon 402–751, Korea

Received 10 February 2003; accepted 31 March 2005
DOI 10.1002/app.22619

ABSTRACT: A new method of preparation of living cationic polymer of isobutyl vinyl ether via photoinduced polymerization in the presence of diphenyliodonium iodide (DPII, initiator) and zinc iodide in a mixed solvent of toluene/diethyl ether, which was irradiated at −78°C for short period, was completed within 15 min. The reaction was allowed for further reaction in the dark until monomer was fully consumed. It was found that increase in the conversion of monomer to polymer during the irradiation is very limited. Confirmation of the linear dependence of number-average molar mass of resulting polymer on % conversion together with the fact that polymerization proceeds until monomer consumption, and controllability of number-average molar mass of resulting polymer, depending on the molar ratio of monomer and initiator, strongly suggests the living nature of this polymerization, unless reaction temperature becomes higher than 0°C, i.e., the absence of chain breaking process. The narrow molar mass distribution, whose polydispersity index values are less than 1.2, reveals that the rate of initiation where irradiation is usually completed within 15 min is much faster than that of propagation in cationic nature in this system. Effect of some major factors, such as solvent polarity and temperature, on the living nature of the polymerization was also investigated. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3581–3586, 2006

Key words: living polymerization; cationic polymerization; photopolymerization; poly(vinyl ethers)

INTRODUCTION

Much attention has been paid to develop new method of preparation of living poly(vinyl ethers) via cationic polymerization to obtain polymer having well-defined structures[1–13]; however, any attempt to prepare the living polymer via a photoinduced polymerization is very rare except our previous report concerning on the preparation of living cationic poly(isobutyl vinyl ether) (PIBVE) via a photoinduced polymerization in the presence of diphenyliodonium iodide and zinc iodide, followed by the dark reaction carried out at temperature below −30°C in methylene chloride.[14] This led us to a conclusion that the propagating species having polarized C—I terminal, which is responsible for the cationic propagation, is not stable enough to suppress the chain breaking process when the reaction is carried out at the temperature higher than −15°C in a polar medium. In this article, we report a new method of the preparation of living cationic P(IBVE) via a photoinduced polymerization in the presences of diphenyliodonium iodide, a well-known photocationic initiator, in conjunction with zinc iodide in toluene, a nonpolar medium, and its mixed solvent with diethyl ether, a polar component. It was found that living nature of the system is appeared in the polymerization system when temperature is kept below 0°C.

EXPERIMENTAL

Materials

Reagent grade monomer, isobutyl vinyl ether (IBVE, Aldrich), toluene (Oriental Chemical Co.), and diethyl ether (Oriental Chemical Co.) used as solvents were purified by conventional distillation and dried on CaH_2 just before use. Reagent grade diphenyliodonium iodide (DPII, Tokyo Kasei) and zinc iodide (Aldrich) were used as received after drying under reduced pressure at room temperature. Details concerning the materials have been given elsewhere.[14]

Polymerization

A sealed Pyrex ampoule containing strictly dried monomer, mixed solvent of toluene and diethyl ether, DPII, and ZnI_2, after repeated degassing by freeze-thaw techniques, was photoirradiated using a 500 W high mercury lamp (Ushio UI-501-C) at −78°C for

---

Correspondence to: S. Mah (simah@inha.ac.kr).

Contract grant sponsor: Inha University, Inchon, Korea; contract grant number: 22,688−01.

Journal of Applied Polymer Science, Vol. 101, 3581–3586 (2006)

certain period and then allowed to stand in the dark for further polymerization. The resulting polymer was precipitated by addition of ammonical methanol, and the polymer was thoroughly washed successively with 10% aqueous sodium thiosulfate solution and distilled water and then dried under reduced pressure at room temperature. Percent conversion was determined by gravimetry.

Characterization

Determinations of number-average molar mass ($\bar{M}_n$) and molar mass distribution (MWD) of the resulting polymers were carried out using gel permeation chromatography (GPC, Spectra-Physics SP8430). Details of the characterization has been given in elsewhere.[14]

RESULTS AND DISCUSSION

Figure 1 shows time–conversion curves of the polymerization of IBVE, photoinduced in the presence of DPII and zinc iodide in a mixed solvent of toluene/diethyl ether (9/1, v/v). Same composition of the solvent is used throughout the whole experiment in this article unless noted otherwise. The polymerization was carried out in the dark at various temperatures after it was irradiated 40 min at of −78°C to prevent conversion of monomer to polymer less than 16%, during the period of irradiation. Figure 1 clearly shows that polymerization proceeds until the full consumption of the monomer and the rate of polymerization increases as reaction temperature in the dark increases, irrespective to the length of the irradiation period. Therefore, it is believed that the polymerization up to full monomer conversion is taken place in the dark reaction by any active propagating species that is generated in situ by photolysis of DPII, a well-known photocationic initiator during the irradiation. It was also confirmed that no polymer was resulted from the photoinduced polymerization systems in the absence of DPII, revealing that DPII is an efficient cationic initiator for cationically polymerizable monomers.

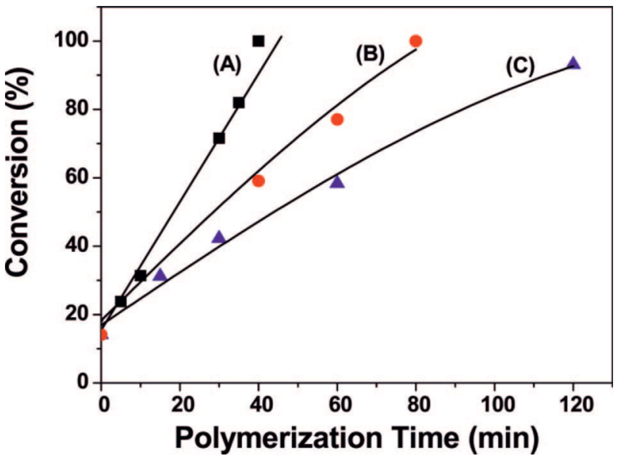


Figure 1 Time–conversion curves of IBVE polymerization carried out in the dark at various temperatures after photoinduction in the presence of DPII and zinc iodide at −78°C for 40 min. Concentrations: [IBVE] = 1.42M, [DPII] = 0.907 mM, [ZnI2] = 1.16 mM, Temperature: (A) 20°C, (B) 0°C, and (C) −15°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

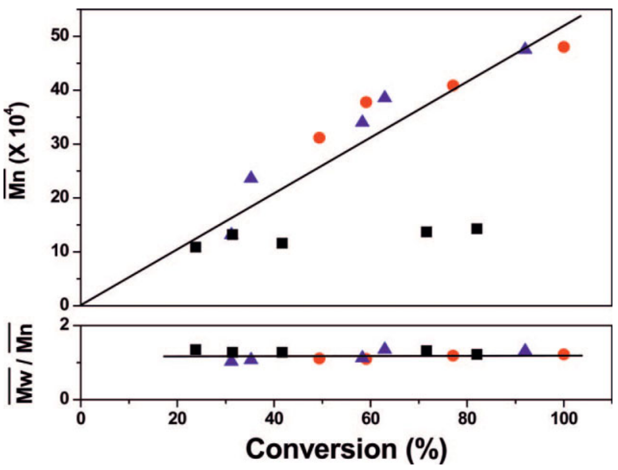


Figure 2 Plot of $\bar{M}_n$ and % conversion of IBVE polymerization carried out in the dark at various temperatures after photoinduction in the presence of DPII and zinc iodide at −78°C for 40 min. Reaction conditions are same with those given in Figure 1. Temperature: ● −15°C, ▲ 0°C, and ■ 20°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 2 shows the dependence of $\bar{M}_n$ and MWD of the resulting polymer on % conversion of the photoinduced polymerizations whose reaction conditions are same with those given in Figure 1. The plot of $\bar{M}_n$ of the resulting polymer versus % conversion is linear over the entire conversion range strongly, which suggests the living nature of this system unless reaction temperature is not higher than 0°C, however, deviation from the linearity between two parameters is observed in the polymerizations carried out at higher temperature than 0°C, and the extent of deviation becomes more significant with increasing temperature, indicating that the activity of the propagation is not maintained at constant value at temperature region higher than 0°C, probably because of the operation of chain breaking process such as chain transfer or termination. Furthermore, it is interesting to note that polymer having very narrow MWD is obtainable from this system. As shown in the figure, MWD of the resulting polymers, expressed in polydispersity index, gives values less than 1.2. It is postulated that the narrow molar mass of the resulting polymer is a consequence of faster initiation, which is completed within 10–20 min, and slower propagation, which takes several hours for full monomer consumption,

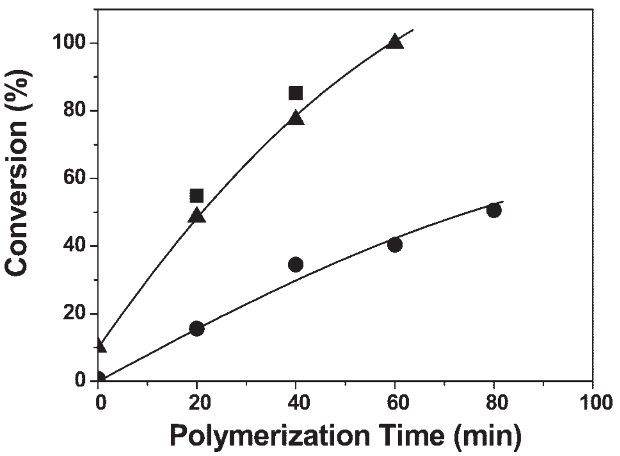


Figure 3 Time–conversion curves of IBVE polymerization carried out in the dark at 0°C after photoinduction in the presence of various concentrations of DPII at −78°C for 10 min. Concentrations: [IBVE] = 1.42*M*, [ZnI$_2$] = 1.16 m*M*. Concentrations of [DPII]: (●) 0.45 m*M*; (▲) 0.907 m*M*; (■) 0.81 m*M*.

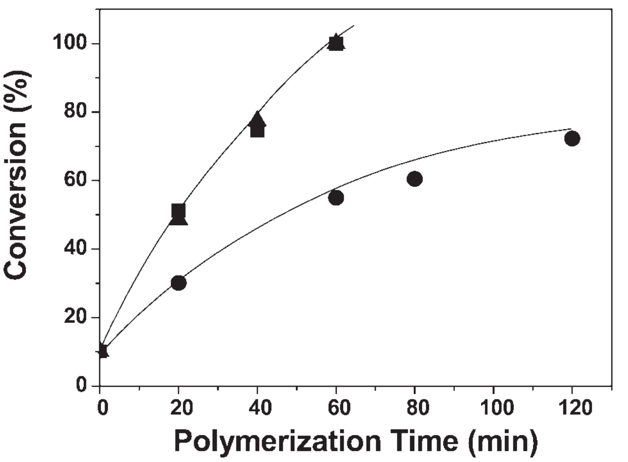


Figure 5 Time–conversion curves of IBVE polymerization carried out in the dark at 0°C after photoinduction in the presence of various concentrations of zinc iodide at −78°C for 10 min. Concentrations: [IBVE] = 1.42*M* and [DPII] = 0.907 m*M*. Concentrations of [ZnI$_2$] = ● 0.58 m*M*, ▲ 1.160 m*M*, and ■ 2.32 m*M*.

and maintaining of the propagating concentration of the propagating species throughout the whole course of polymerization because of the absence of chain breaking process.

Two time–conversion curves of the polymerizations carried out in the presence of different levels of DPII concentrations are compared in Figure 3. The remarkable increase in the rate of polymerization with increasing DPII concentration reveals that HI, a photolytic product of DPII, plays an important role in the initiation process of IBVE, as previously reported.[14]

Figure 4 shows a comparison of the dependence of $\bar{M}_n$ on % conversion of the polymerizations containing different levels of DPII concentrations, shown in Figure 3. Comparison of two $\bar{M}_n$ values obtained at same conversion clearly reveals that polymer having higher molar mass is resulted from the system of lower concentration of DPII; meanwhile, it also shows that MWD of the polymer, which shows almost constant polydispersity index value, is not affected by DPII concentration.

Time–conversion curves and the relationship between $\bar{M}_n$ and % conversion of the polymerization in the presence of two different levels of ZnI$_2$ concentration are compared in Figures 5 and 6, respectively, revealing that although remarkable enhancement ef-

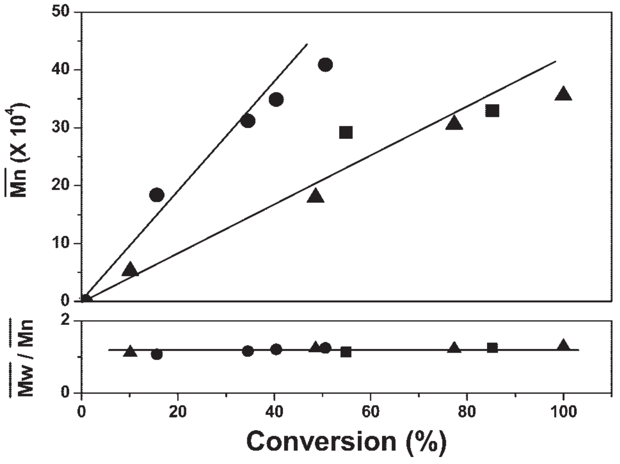


Figure 4 Plot of $\bar{M}_n$ and % conversion of IBVE polymerization carried out in the dark at 0°C after photoinduction in the presence of various concentrations of DPII at −78°C for 10 min. Concentrations: [IBVE] = 1.42*M* and [ZnI$_2$] = 1.16 m*M*. Concentrations of [DPII] = ● 0.45 m*M*, ▲ 0.907 m*M*, and ■ 1.81 m*M*.

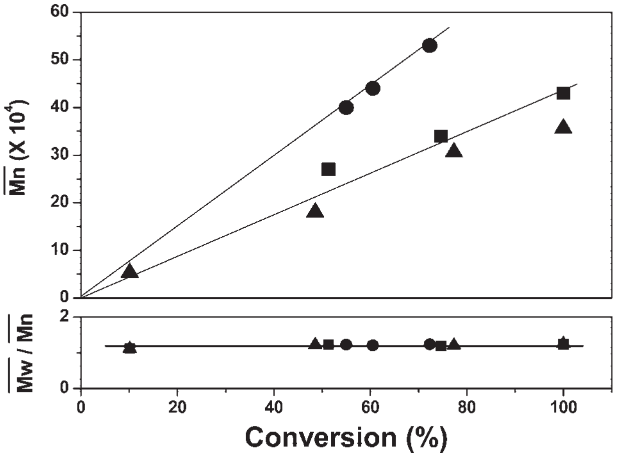


Figure 6 Plot of $\bar{M}_n$ and % conversion of IBVE polymerization carried out in the dark at 0°C after photoinduction in the presence of various concentrations of zinc iodide at −78°C for 10 min. Concentrations: [IBVE] = 1.42*M*, [DPII] = 0.907 m*M*. Concentrations of [ZnI$_2$] = ● 0.58 m*M*, ▲ 1.160 m*M*, and ■ 2.32 m*M*.

fect of ZnI_2 on increasing polymerization rate, however, molar mass of the resulting polymer is not dependent on ZnI_2. This indicates that ZnI_2 plays a role as an activator in this system to increase in the rate of polymerization.

The living nature of this polymerization system is further demonstrated by the monomer addition technique (Fig. 7). The equal amount of fresh monomer with originally fed portion of monomer was added to the polymerization system where the % conversion of original batch reaches at around 100%. The increase in both polymer yield and $\bar{M}_n$ of the resulting polymer to form a straight line with same slope indicates that the activity of the propagating species is still maintained even after the monomer originally fed is fully consumed without loss of activity due to chain breaking process.

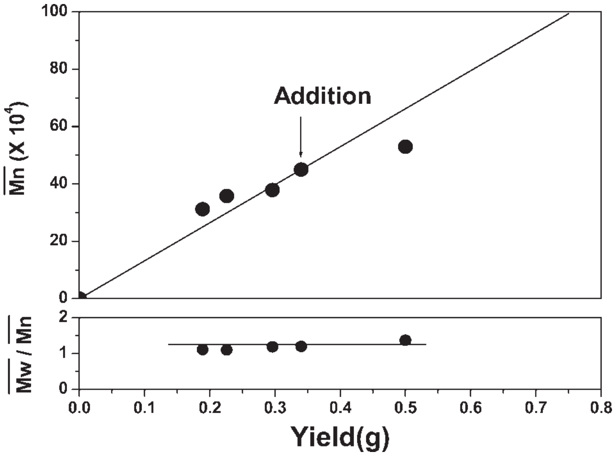
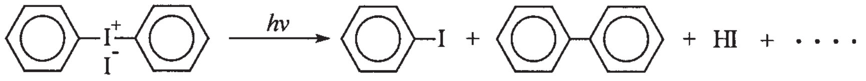


Figure 7 An evidence of the living nature confirmed by subsequent monomer addition method. Equal amount of fresh monomer was added to the system when the conversion of original feed reaches around 90%. Concentrations of originally fed [IBVE] = 1.42*M*, [DPII] = 0.907 m*M*, and [ZnI_2] = 1.16 m*M*. Temperature: 0°C. Photoirradiation was carried out at −78°C for 40 min before the dark reaction.

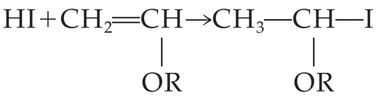
Summarizing the results aforementioned, it is postulated that initiation takes place via the process of monomer-HI adduct formation, by reaction between monomer and HI, a photolytic product of DPII[15,16] (Eqs. (1), (2)), followed by activation of C—I terminal of the adduct by the pulling action of ZnI_2. The polarized C—I terminal of the monomer-adduct, then, allows the insertion monomer to form a new polarized C—I terminal for cationic initiation (Eq. (2)). This is followed by successive insertion of monomer for cationic propagation (Eq. (3)). It was explained that polarized C—I terminal is stable enough to suppress chain breaking processes; however, also reactive enough to attack the carbon–carbon double bond of cationically polymerizable monomer to realize the living cationic polymerization in the absence of chain transfer or termination process [eqs. (3) and (4)].[2,3,6–12]

Equation 1 Generation of protonic acid, HI due to photolysis of DPII



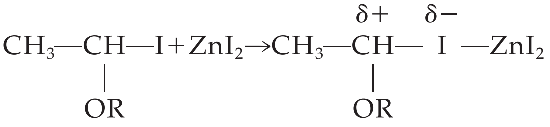
(1)

Equation 2. Formation of monomer–HI adduct



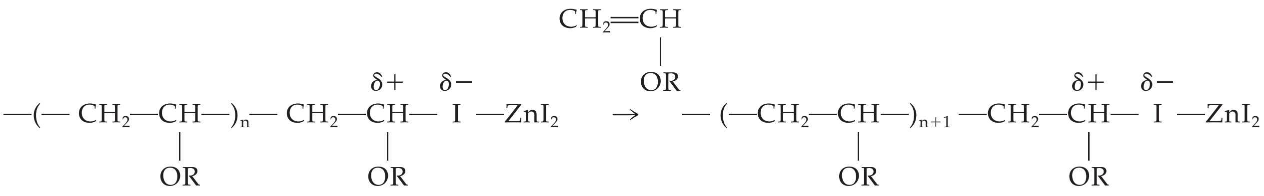
$$\mathrm{HI}+\mathrm{CH_2}{=}\underset{\substack{|\\ \mathrm{OR}}}{\mathrm{CH}}\rightarrow\mathrm{CH_3}{-}\underset{\substack{|\\ \mathrm{OR}}}{\mathrm{CH}}{-}\mathrm{I} \qquad (2)$$

Equation 3. Activation of C—I terminal by the pulling action of ZnI_2



$$\mathrm{CH_3}{-}\underset{\substack{|\\ \mathrm{OR}}}{\mathrm{CH}}{-}\mathrm{I}+\mathrm{ZnI_2}\rightarrow\mathrm{CH_3}{-}\underset{\substack{|\\ \mathrm{OR}}}{\overset{\delta+}{\mathrm{CH}}}{-}\overset{\delta-}{\mathrm{I}}{-}\mathrm{ZnI_2} \qquad (3)$$

Equation 4. Cationic propagation by polarized C—I growing end



$$-(-\mathrm{CH_2}{-}\underset{\substack{|\\ \mathrm{OR}}}{\mathrm{CH}}-)_n-\mathrm{CH_2}{-}\underset{\substack{|\\ \mathrm{OR}}}{\overset{\delta+}{\mathrm{CH}}}-\overset{\delta-}{\mathrm{I}}-\mathrm{ZnI_2}\ \xrightarrow{\mathrm{CH_2}=\underset{\substack{|\\ \mathrm{OR}}}{\mathrm{CH}}}\ -(-\mathrm{CH_2}{-}\underset{\substack{|\\ \mathrm{OR}}}{\mathrm{CH}}-)_{n+1}-\mathrm{CH_2}{-}\underset{\substack{|\\ \mathrm{OR}}}{\overset{\delta+}{\mathrm{CH}}}-\overset{\delta-}{\mathrm{I}}-\mathrm{ZnI_2} \qquad (4)$$

Formation of monomer adduct in this photoinduced system was confirmed by ^1H NMR spectroscopy. As shown in Figure 8, it is evident that proton signal newly appeared at 7.15 ppm by mixing of fresh monomer with toluene solution of DPII due to C—I bond of monomer–HI adduct.[6–12]

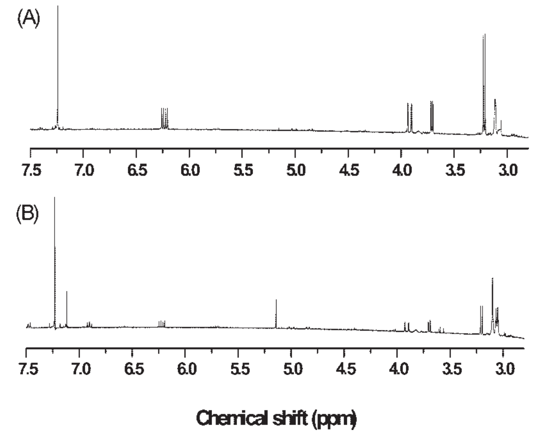


Figure 8 Comparison of ^{1}NMR spectra of IBVE and DPII in DMSO-d_6/acetonitrile solution before and after photo irradiation. Concentrations of [DPII] = 9.07 mM, [IBVE] = 0.142M. (A) IBVE in DMSO-d_6/acetonitrile. (B) IBVE in acetonitrile was added to photo irradiated solution of DPII in DMSO-d_6/acetonitrile for 10 min at 0°C.

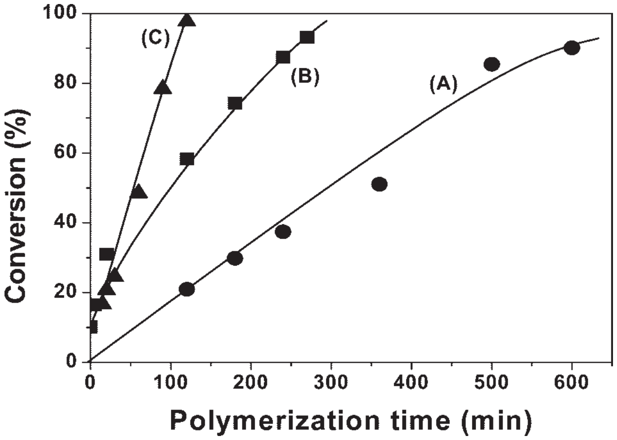


Figure 9 Time–conversion curves of IBVE polymerization carried out in the dark at 0°C in a mixed solvent of toluene/diethyl ether after photoinduction in the presence of DPII and zinc iodide at −78°C for 10 min. Concentrations: [IBVE] = 1.42M, [DPII] = 0.907 mM, [ZnI$_2$] = 1.16 mM. Solvent used: (A) toluene, (B) mixed solvent: toluene/diethyl ether (9/1) (v/v), and (C) diethyl ether.

If this is the case, number–average molar mass of resulting polymer is determined by the molar ratio of monomer and HI, a protonic acid, produced in situ as a photolytic product of DPII, whose concentration at the time of the completion of irradiation equals to or is proportional to that of DPII. Therefore, theoretical values of $\bar{M}_n$, determined by the molar ratio of monomer and DPII, on the basis of assumption that one polymer molecule is formed from one molecule of DPII are compared with those of corresponding experimental values. The results are summarized in Table I. The inverse relation of molar mass and concentration of DPII that appeared in experimental results is in good agreement with theoretical expectation; however, it is evident that experimental data always give larger values than those of theoretical values, and the ratio of theoretical value/experimental value gives values scattered around 0.55. It is postulated that the incoincidence of two sets of data might be ascribable to quantum yield of HI production in photolytic process of DPII being less than unity. It is deemed that a further detailed study is required in this regard.

Solvent effect on the living nature of the polymerization has also been investigated. Two time–conversion curves of polymerizations carried out in a mixed solvent of toluene and diethyl ether are shown in Figures 9 and 10, respectively. The comparison of the curves reveals that the rate of polymerization increases as diethyl ether content of the mixed solvent increases. Meanwhile, it is also evident that a deviation from the linear relationship between the two parameters due to the loss of living propagating center is observed as diethyl ether content increases in a mixed solvent; however, it is worth noting that a large increase in the rate of polymerization is attainable with minimum loss of the living nature when the volume fraction of diethyl ether is kept below 0.11 in the mixed solvent. It is postulated that the polarized C—I propagating terminal in cationic nature is in equilibrium state with certain dissociated form, which is not

TABLE I
Comparison of Experimental and Theoretical $\bar{M}_n$ Values

Solvent used	Final conversion (%)	Experimental	Theoretical	Experimental/theoretical
Diethyl ether	97.7	262,000	153,000	1.71
Toluene(9)/diethyl ether(1) (v/v)	93.2	294,000	146,000	2.01
Toluene	90.2	241,000	142,000	1.63

Theoretical $\bar{M}_n$ values are calculated from the molar ratio of [monomer]/[DPII], assuming that one polymer molecule is resulted from one initiator molecule. Polymerization was carried out at 0°C in the dark after photoirradiation, carried out at −78°C for 10 min.

Concentrations: [IBVE] = 1.42M, [DPII] = 0.907 mM, and [ZnI$_2$] = 1.16 mM.

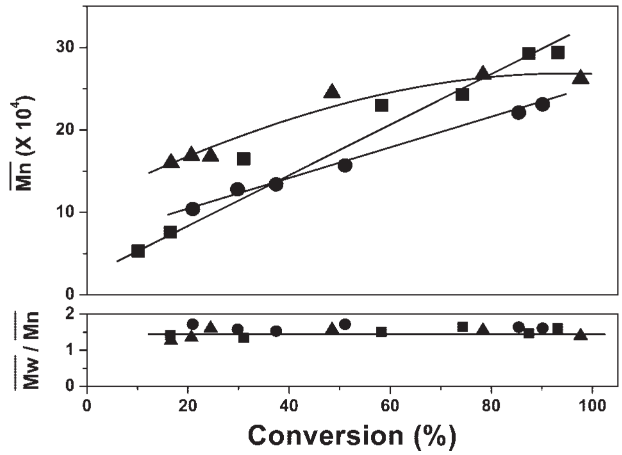
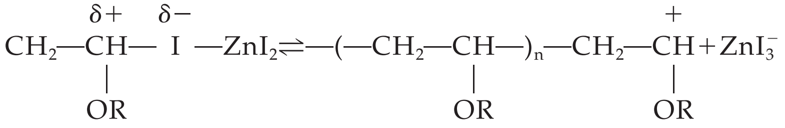


Figure 10 Plot of $\bar{M}_n$ and % conversion of IBVE polymerization carried out in the dark at 0°C in the mixed solvent of toluene/diethyl ether after photoinduction in the presence of DPII and zinc iodide at −78°C for 10 min. Concentrations: [IBVE] = 1.42*M*, [DPII] = 0.907 m*M*, and [ZnI_2] = 1.16 m*M*. Solvent used: ● toluene, ■ mixed solvent: toluene/diethyl ether (9/1) (v/v), and ▲ diethyl ether.

stable enough to suppress chain breaking processes such as chain transfer to monomer and termination processes. In such circumstances, chain breaking process cannot be suppressed because of the higher reactivity of the carbocationic propagating center in free ion or loose ion pair state, which results in the increase in rate of polymerization and loss of living nature of the system. It is also expected that the equilibrium is further shifted toward the direction of the dissociated form, which consists of carbocationic center and ZnI_3^- counterion[17] [eq. (5)], which is much more stable than that of I^- and expected to be a counterion formed in the absence of ZnI_2; therefore, carbocationic center is more stabilized by the presence of less nucleophilic counterion ZnI_3^-. Finally, it is interesting to mention that the optimum conditions for the polymerization, i.e., polymerizations showing the highest rate of polymerization with minimum loss of the living nature is observed from the mixed solvent system, consisting of toluene/diethyl ether (9/1) in volume ratio.

Equation 5. Dissociation to free carbocation and less nucleophilic counterion


$$\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{OR}}}{\overset{\delta+}{\mathrm{CH}}}-\overset{\delta-}{\mathrm{I}}-\mathrm{ZnI_2}\rightleftharpoons-(-\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{OR}}}{\mathrm{CH}}-)_n-\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{OR}}}{\overset{+}{\mathrm{CH}}}+\mathrm{ZnI_3^-} \qquad (5)$$

CONCLUSIONS

A new method of preparation of living cationic IBVE polymer has been successfully developed via photoinduced polymerization in the presences of DPII and ZnI_2. A linear dependence of number–average molar mass of the resulting polymer on % conversion strongly suggests the living nature of the system. It was found that PIBVE having very narrow molar mass distribution whose polydispersity index is less than 1.2 and whose number–average molar mass is easily controllable by adjusting the molar ratio of monomer and initiator is obtainable from this system.

References

1. Matyjaszewski, K.; Sawamoto, M. In Cationic Polymerization, Mechanisms, Synthesis, and Applications; Matyjaszewski, K., Ed.; Marcel Dekker: New York, 1996; Chapter 5.
2. Miyamoto, M.; Sawamoto, M.; Higashimura, T. Macromolecules 1985, 18, 123.
3. Sawamoto, M.; Enoki, T.; Higashimura, T. Macromolecules 1987, 20, 1.
4. Cho, C. G.; McGrath, J. E. Polym Prepr (Am Chem Soc Div Polym Chem) 1987, 28, 356.
5. Verma, A.; Nielsen, A.; Bronk, J. M.; McGrath, J. E.; Riffle, J. S. Makromol Chem Macromol Symp 1991, 47, 239.
6. Shohi, H.; Sawamoto, M.; Higashimura, T. Macromolecules 1991, 24, 4926.
7. Shohi, H.; Sawamoto, M.; Higashimura, T. Macromolecules 1992, 25, 58.
8. Hashimoto, T.; Iwao, S.; Kadaira, T. Makromol Chem 1993, 194, 2323.
9. Fukui, H.; Sawamoto, M.; Higashimura, T. J Polym Sci Part A: Polym Chem 1994, 32, 2699.
10. Fukui, H.; Sawamoto, M.; Higashimura, T. Macromolecules 1994, 27, 1297.
11. Sawamoto, M.; Shohi, H.; Sawamoto, H.; Higashimura, T. J Macromol Sci Pure Appl Chem 1994, A31, 1609.
12. Fukui, H.; Sawamoto, M.; Higashimura, T. Macromolecules 1995, 28, 3756.
13. Kwon, S.; Lee, Y.; Mah, S. Fibers Polym 2001, 2, 9.
14. Kwon, S.; Lee, Y.; Jeon, H.; Mah, S. Fibers Polym, submitted.
15. Crivello, J. V.; Lam, J. H. W. J Polym Sci Polym Chem Ed 1979, 17, 977.
16. Crivello, J. V.; Lam, J. H. W. J Polym Sci Polym Chem Ed 1979, 17, 1047.
17. Odian, G. Principles of Polymerization, 3rd ed.; Wiley: New York, 1991; Chapter 5.