Photo-induced Living Cationic Polymerization of Isobutyl Vinyl Ether in the Presence of Various Combinations of Halides of Diphenyliodonium and Zinc Salts in Methylene Chloride

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Abstract: Living nature of photoinduced cationic polymerization of isobutyl vinyl ether (IBVE) in the presence of various combinations of diphenyliodonium halide (DPIX), a photocationic initiator and zinc halide (ZnX_2) in methylene chloride has been investigated. Attainment of 100 % conversion and a linear relationship between % conversion and number average molar mass of the resulting polymer, strongly suggests the living nature of this system. Livingness of the polymerization system was observed irrespective to the type of halide anion of the initiator and zinc salts unless the reaction temperature is not higher than −30 °C. The rate of polymerization decreases in the order of iodide > bromide > chloride when halide salt of DPIX and ZnX_2 are used. It is postulated that the cationic initiation is started by the insertion of weakly basic monomer in to the activated C-X terminal of the monomer adduct which is a reaction product of monomer and HX, a photolytic product of DPIX, formed in situ during the photo-irradiation process. It was concluded that polymerization is initiated by the insertion of weakly basic monomer into activated C-X terminal of monomer adduct due to the pulling action of ZnX_2, which successively producing a new polarized C-X terminal for the propagation in cationic nature. This led us to a conclusion that the living nature of this cationic polymerization is ascribable to the polarized C-X growing terminal, which is stable enough to depress the processes of chain transfer or termination process.

Keywords: Living polymerization, Cationic polymerization, Photo polymerization, Poly(vinyl ethers)

Introduction

Living polymer systems have been the subject of extensive study in order to obtain polymers having well defined structures, i.e., polymer having narrow molar mass [1-11], and functional terminal groups [12-15]. However, it is very rare to find any attempt to obtain living cationic polymers via photo-induced polymerization [16]. We reported that a living cationic poly(IBVE)(PIBVE) can be prepared successfully using combination of iodomethyl methyl iodide and zinc iodide which is advantageous of omission of a procedure to handle dry gaseous protonic acid required in the preparation of monomer-acid adduct [17] This idea is extended to living cationic polymerization of isobutyl vinyl ether via photo-induced system in the presence of various halides of diphenyliodonium in conjunction with zinc salts.

Experimental

Materials

Reagent grade IBVE (Aldrich) was washed successively with 10 % aqueous sodium hydroxide solution and distilled water. IBVE was purified by distillation. Reagent grades diphenyliodonium iodide (DPII, Tokyo Kasei), diphenyliodonium bromide (DPIBr, Tokyo Kasei), diphenyliodonium chloride (DPICl, Tokyo Kasei), zinc iodide (ZnI_2, Aldrich), zinc bromide ($ZnBr_2$, Aldrich) and zinc iodide ($ZnCl_2$, Aldrich)

were used as received. DPIX and ZnX_2 were stored in a desiccator until used after drying under reduced pressure at room temperature. Methylene chloride (CH_2Cl_2, Oriental Chemical Company) was purified by conventional distillation.

Polymerization and Polymer Characterization

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

Characterization

Number average molar mass ($\overline{M_n}$) and its distribution (MWD) of the resulting polymer were determined using gel permeation chromatography (GPC, Spectra-Physics SP8430). Details of the characterization has been given elsewhere [17].

Results and Discussion

Figure 1 shows time-conversion curves of photo-induced polymerization of IBVE in CH_2Cl_2, carried out in the dark at various temperatures after photo-irradiation. Photo-irradiation
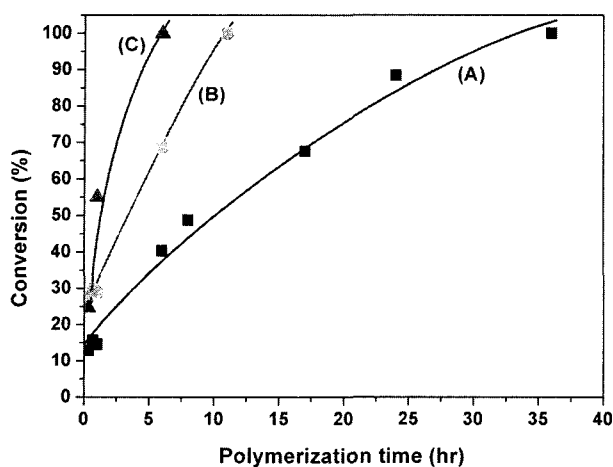
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Figure 1. Time-conversion curves of photo-induced polymerization of IBVE, carried out at various temperatures in the presence of DPII; conc.: [IBVE] 1.42 M, [DPII] 0.907 mM, [ZnI_2] 1.16 mM, polymerization was carried out in the dark at various temperatures after irradiation for 10 min at −78 °C, temperature: (A) −30 °C, (B) −15 °C, (C) 0 °C.
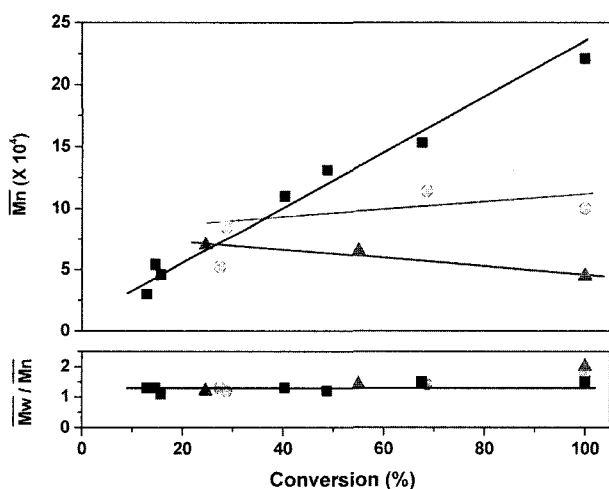

Figure 2. Plot of % conversion vs $\overline{M_n}$ and MWD of photo-induced polymerization of IBVE in the presence of DPII; reaction conditions are same as those given in Figure 1. Temperature: (■) −30°C, (●) −15 °C, (▲) 0 °C.

was carried out for 10 min at −78 °C in the presences of DPII and ZnI_2. Polymerization proceeds very rapidly to give 12 % of conversion during the irradiation period of 10 min. It is evident that the rate of polymerization increases as temperature increases and the polymerizations proceed until the full consumption of the monomer in the dark in the whole range of the concentrations of monomer and DPII and temperature of the experiment.

The relationship between the number-average molar mass of the resulting polymer ($\overline{M_n}$) and % conversion is shown in Figure 2 whose reaction conditions are same as those given
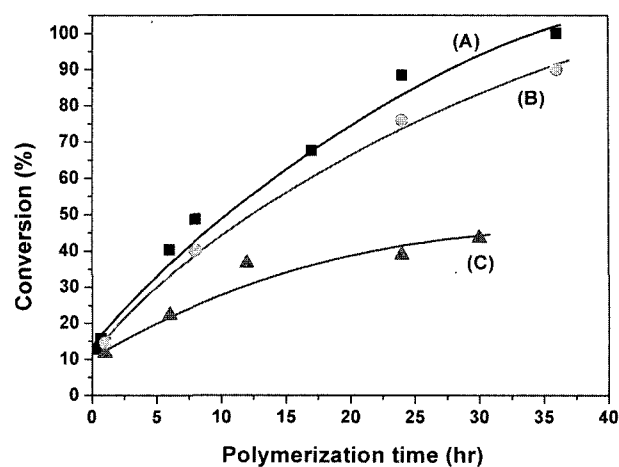

Figure 3. Time-conversion curves of photo-induced polymerization of IBVE carried out at −30 °C in the presence of DPII using various zinc halides. Reaction conditions are same as those given in Figure 1; activator used ZnI_2 (A), $ZnBr_2$ (B), $ZnCl_2$ (C).

in Figure 1. The linear dependence of the number average molar mass on % conversion in the polymerizations, carried out at −30 °C strongly suggests the living nature of this photo-induced polymerization system. On the other hand, dependence on % conversion of those carried out at the temperatures higher than −30 °C evidently deviates from the linearity and $\overline{M_n}$ values keep almost constant throughout full conversion range. This reveals that the activity of the propagating species is no more maintained, probably due to the operation of the chain breaking processes such as chain transfer or termination.

Figure 3 shows comparison of the time-conversion curves of the polymerizations, carried out in the presence of various ZnX_2 in conjunction with DPII, showing that there is no significant difference in the rate of polymerization as well as in the final conversion between the systems where ZnI_2, $ZnBr_2$ except $ZnCl_2$. Remarkable decreases in both rate of polymerization and final conversion value (less than 45 % even under prolonged reaction time) is observed when zinc chloride is used.

The dependences of $\overline{M_n}$ on % conversion, obtained from the photo-induced polymerization, carried out in the presence of DPII in conjunction with various zinc halides are compared in Figure 4. A linear dependence of the molar mass on % conversion is observed from the systems where $ZnBr_2$ or ZnI_2 is used, however, it was impossible to confirm the linearity of $ZnCl_2$ system due to the difficulty in obtaining a polymer at higher conversion range.

Time-conversion curves of photo-induced polymerization in the presence of DPIBr in conjunction with various zinc halides are also compared in Figure 5. Although, the rate of polymerization in the presence of $ZnBr_2$ and $ZnCl_2$ is much lower than that of ZnI_2 system, however, it is noteworthy to
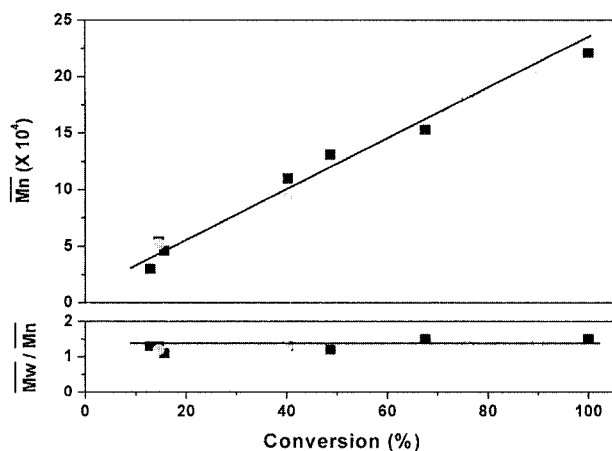
Figure 4. Plot of conversion vs $\overline{M_n}$ and MWD of photo-induced polymerization of IBVE in the presence of DPII using different type of activator, carried out −30 °C; reaction conditions are same as those given in Figure 1. Activator used ZnI_2 (■), $ZnBr_2$ (●).
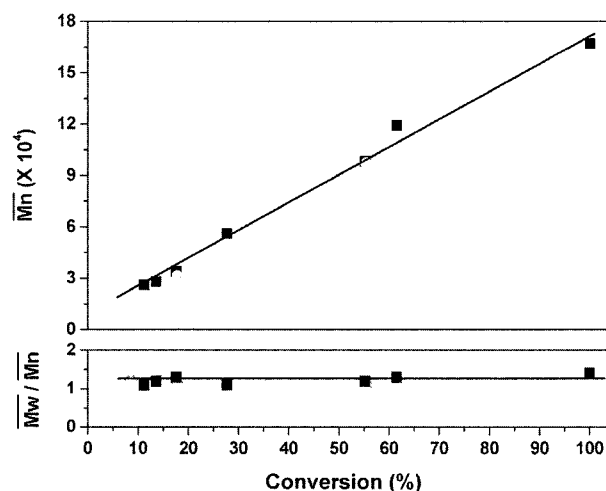

Figure 6. Plot of conversion vs $\overline{M_n}$ and MWD of photo-induced polymerization of IBVE in the presence of DPIBr using various type of zinc halide, carried out −30 °C; reaction conditions are same as those given in Figure 1. Activator used ZnI_2 (■), $ZnBr_2$ (●).
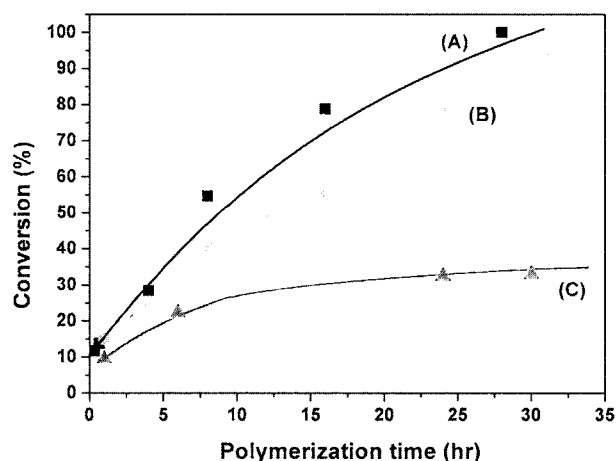

Figure 5. Time-conversion curves of photo-induced polymerization of IBVE, in the presence of DPIBr using various zinc halides, carried out at −30 °C; reaction conditions are same as those given in Figure 1. Activator used ZnI_2 (A), $ZnBr_2$ (B), $ZnCl_2$ (C).
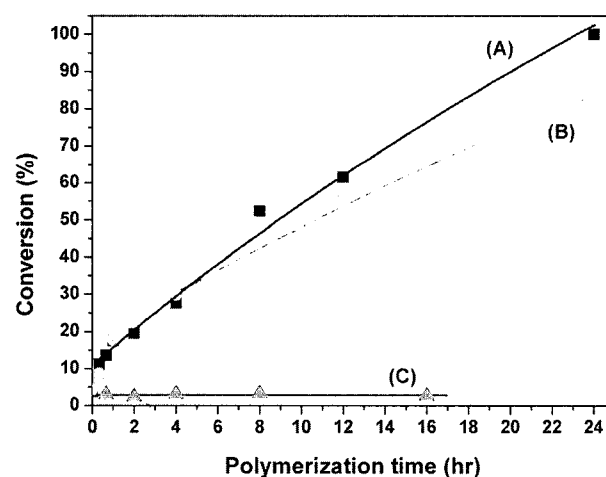

Figure 7. Time-conversion curves of photo-induced polymerization of IBVE in the presence of DPICl, carried out at −30 °C; reaction conditions are same as those given in Figure 1. Activator used ZnI_2 (A), $ZnBr_2$ (B), $ZnCl_2$ (C).

mention that the polymerization proceeds until the full monomer consumption and $\overline{M_n}$ increases linearly with increasing % conversion is also observed in $ZnBr_2$ system as shown in Figure 6, furthermore, the data of the two systems of ZnI_2 and $ZnBr_2$ lies on a same straight line, implying that the mode of propagation in the two systems is almost identical even though there is a remarkable difference in the rate of polymerization.

The living nature of the photo-induced polymerization in the presence of DPICl in conjunction with various zinc halides was also investigated. Time-conversion curves and $\overline{M_n}$ dependence on % conversion is given in Figures 7 and 8, respectively. Although, the rate of polymerization in the presence of DPICl is much lower than those of corresponding

DPII and DPIBr systems, the dependence of $\overline{M_n}$ on % conversion shows linear relation and the data lies on a same straight line with those obtained from $ZnBr_2$ and ZnI_2 systems in low conversion area, as shown in Figure 8. This led us a conclusion that living nature of the system is not so severely affected by the type of halide anion of both initiator and zinc halide, only rate of polymerization is remarkably influenced by the type of halide anion used in both initiator and activator. The rate of polymerization decreases in the order of iodide > bromide >> chloride.

Based on the facts mentioned earlier, it is proposed that photo-induced cationic initiation process comprises of the
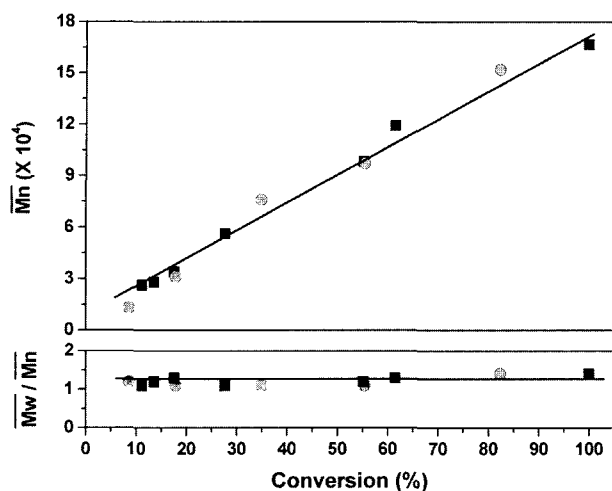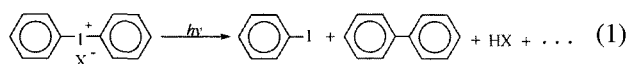
Figure 8. Plot of conversion vs $\overline{M_n}$ and MWD of photo-induced polymerization of IBVE in the presence of DPICl, carried out -30 °C; reaction conditions are same as those given in Figure 1. Activator used ZnI_2 (■), $ZnBr_2$ (●).
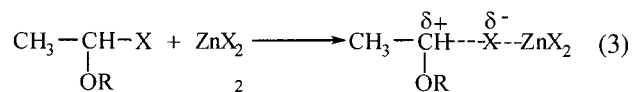

Figure 9. Comparison of ^{1}NMR spectra of IBVE and DPII in DMSO-d_6/acetonitrile solution before and after photo irradiation; concentrations of [DPII] 9.07 mM, [IBVE] 0.142 M, (A) IBVE in DMSO-d_6/acetonitrile, (B) IBVE in acetonitrile was added to a solution of DPII in DMSO-d_6/acetonitrile, irradiated for 10 min at 0 °C.

processes;

Firstly, production of HX by photolysis of DPIX [16],

$$\langle\bigcirc\rangle\!-\!{}^+_{X^-}\!\langle\bigcirc\rangle \xrightarrow{h\nu} \langle\bigcirc\rangle\!-\!{}_1 + \langle\bigcirc\rangle\!-\!\langle\bigcirc\rangle + HX + \cdots \quad (1)$$

Followed by formation of monomer adduct with of HX, a photolytic product of DPIX with monomer,

$$HX + CH_2 = \underset{\underset{OR}{|}}{CH} \longrightarrow CH_3 - \underset{\underset{OR}{|}}{CH} - X \quad (2)$$
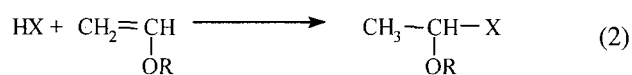
Formation of activated monomer-HX adduct by complex formation with ZnX_2.

$$CH_3 - \underset{\underset{OR}{|}}{CH} - X + ZnX_2 \longrightarrow CH_3 - \underset{\underset{OR}{|}}{\overset{\delta+}{CH}} \cdots \overset{\delta-}{X} - ZnX_2 \quad (3)$$

It was postulated that the living polymerization in cationic nature proceeds via the sequences, 1) formation of monomer-HX adduct by the reaction of the monomer with hydrogen halide, a photolytic product of DPII which is formed in situ during the photo-irradiation, 2) polarization of C-X terminal of the monomer adduct by the pulling action of ZnX_2, 3) Insertion of weakly basic monomer between activated C-X bond of the adduct by nucleophilic attack, 4) formation of a new polarized C-X terminal 5) successive insertion of the monomer and formation of activated C-X growing terminal for propagation in cationic nature. Therefore, it is concluded that ZnX_2 plays a role to activate the C-X terminal, which allows the insertion of the monomer in this polymerization system. It is believed that the living nature of this system is ascribable to the stability of the polarized C-X growing
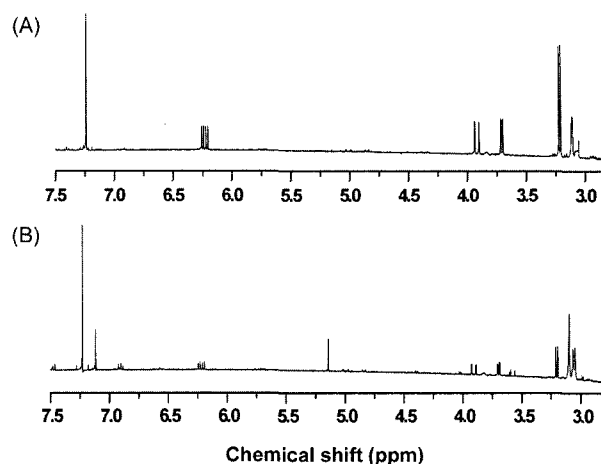
terminal which is unstable enough to allow the propagation process but also stable enough to depress the chain breaking processes such as termination or chain transfer as reported earlier for the living cationic polymerization of IBVE initiated by HI-ZnI_2 [5-7].

Formation of monomer adduct in this photo-induced system was confirmed by proton NMR spectroscopy. As shown in Figure 9, it is evident that proton signal newly appeared at 7.15 ppm by mixing of fresh monomer to the DPII solution in toluene due to C-I bond formation [4-6].

It has been reported that living P(IBVE) can be successfully prepared via catalytic polymerization initiated by HI- ZnI_2 initiating system, carried out at 0 °C [5-7,17]. However, livingness was not observed in this photo-induced system. The livingness is observed only when the reaction temperature is kept below -30 °C in this photo-induced system. Therefore, dependence of the living nature on the concentration of ZnI_2 and temperature has been carried out in order to clarify the reason that brings the contradiction of two reports.

The effect of ZnI_2 concentration on the relationship between $\overline{M_n}$ and % conversion in the polymerizations, carried out at 0 °C in the presence of various concentration of ZnI_2 is compared in Figure 10. It is evident that that in the polymerization carried out at 0 °C, $\overline{M_n}$ is no longer dependent on % conversion when the concentration of activator exceeds a certain value, however, linear increase in $\overline{M_n}$ with increasing % conversion is observed when the concentration of the activator is kept very low less than 0.35 mM.

Living nature of the polymerization, carried out at 0 °C in the presence of low concentration of the activator was confirmed as shown in Figure 11. The linear dependence of $\overline{M_n}$ on % conversion demonstrates the livingness is maintained
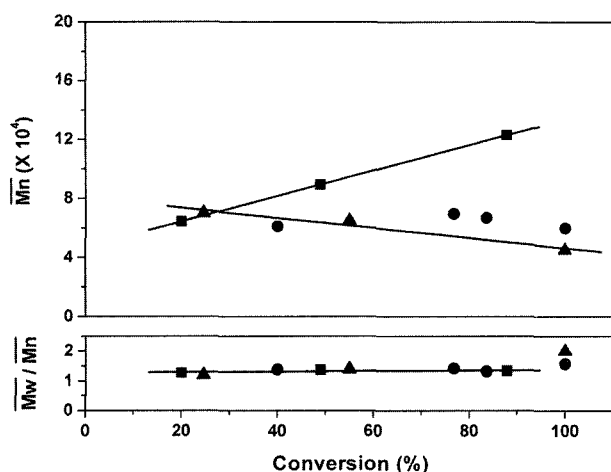
Figure 10. Dependence of $\overline{M_n}$ on % conversion in photo induced polymerization of the IBVE, carried out at 0 °C in methylene chloride in the presence of various concentration of ZnI_2; $[ZnI_2]$ (mM): 0.35 (■), 0.58 (●), 1.16 (▲). Other reaction conditions are same as those given in Figure 1.
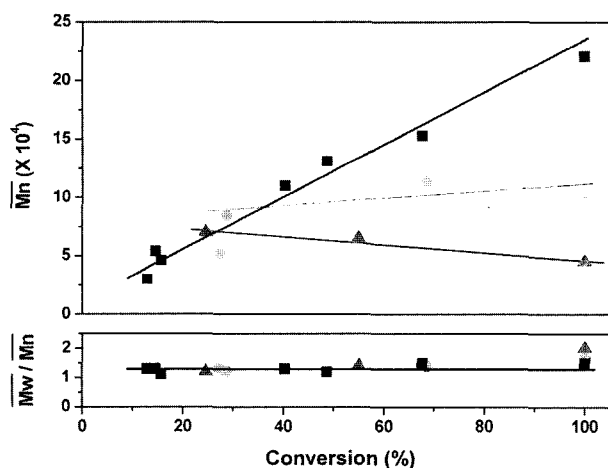

Figure 11. Comparison of relationship between $\overline{M_n}$ and % conversion in photo induced polymerization of IBVE carried out at 0 °C and −30 °C in methylene chloride; Temperature and $[ZnI_2]$ (mM): (▲) 0 °C, 0.35, (■) −30 °C, 1.16. Other reaction conditions are same as those given in Figure 1.

at this relatively high temperature when the concentration of the activator is kept below a critical value, although slope of the plot of $\overline{M_n}$ versus % conversion is much smaller than that of −30 °C. The linear dependence of $\overline{M_n}$ on % conversion of the polymerization carried out at −30 °C in the presence of large amount of the activator is shown together in the Figure for the sake of comparison. This gives us an explanation for the contradiction of the two reports is originated from the difference in the level of ZnI_2 concentration. This phenomenon concerning the loss of living nature is explainable when we assume an equilibrium established between polarized and dissociated growing C-X terminal and loss of livingness is

related with the possibility of chain breaking process, i.e., chain breaking is depressed when the growing terminal exists in stable polarized C-X, however, chain breaking is operative when the growing C-X terminal is dissociated to yield a very reactive carbocation. This is supported by the facts that the loss of livingness is observed under the conditions where equilibrium is shifted toward the direction of dissociated growing terminal with increasing temperature, concentration of the activator and polarity of the reaction media.

Even though reaction rate is greatly affected by the type of halide anion of both initiator and activator used, it is evident that the living nature of the system is not so greatly dependent on the type of halide anion. The insensitiveness of the living nature to the type of halide anions of both initiator and activator used is not fully understood, however, it is explainable when we assume the occurrence of rapid halide ion exchange is undertaken between growing and dormant polymer terminal containing halogen atom and zinc salt during whole course of the reaction. It is also postulated that decrease in the slope of $\overline{M_n}$ versus % conversion plot with increasing temperature is interpreted as a result of increased halide anion exchange rate at higher temperature [18], as proposed in the following equation where A and B are expressed various halide ions.

$$\text{wwwwCH}_2\text{—CH—B} + \text{ZnA}_2 \rightleftharpoons \text{wwww CH}_2\text{—CH—A} + \text{ZnAB}$$
$$\qquad\qquad | \qquad\qquad\qquad\qquad\qquad\qquad\qquad | $$
$$\qquad\qquad \text{OR} \qquad\qquad\qquad\qquad\qquad\qquad\text{OR}$$

Conclusions

A new synthetic method of the preparation of living cationic PIBVE via photo-induced polymerization of isobutyl vinyl ether in the presences of various combinations of diphenyl-iodonium halides and zinc halides in methylene chloride has been successfully developed. Controllability of the molar mass having low polydispersity of the resulting polymer, which is determined by the molar ratio of monomer and initiator, furthermore, the linear dependence of number average molar mass on conversion gives a strong evidence for the living nature of this system irrespective to the type of halide anion of both initiator and zinc salt used. On the contrary, the rate of polymerization is greatly affected by the type of halide of both initiator and zinc salt used. The rate of polymerization decreases in the order of iodide, bromide and chloride.

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