

Living Cationic Polymerization of Vinyl Ethers in the Presence of Iodomethyl Methyl Ether and Zinc Iodide

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Abstract: Living cationic polymerization behaviors of isobutyl vinyl ethers (IBVE), initiated by iodomethyl methyl ether (IMME)/zinc iodide (ZnI_2) have been investigated. The polymerization was carried out at 0, -15, and -30°C in toluene. It was found that the rate of polymerization increased as the IMME concentration increased and decreased as temperature decreased. 100% conversion was always achieved without exception. Furthermore, the number-average molecular weight (\bar{M}_n) of polymers increased in direct proportion to monomer conversion. The molecular weights of polymers were in good agreement with the theoretical values, calculated on the basis that one polymer chain was formed by one IMME molecule and the values of polydispersity index are always less than 1.2, revealing the living nature. The living nature was also confirmed by synthesis of poly(IBVE-*b*-TBVE) by subsequent monomer addition of *t*-butyl vinyl ether (TBVE).

Keywords: Living cationic polymerization, Vinyl ether, Iodomethyl methyl ether, Zinc iodide, Block copolymer

Introduction

Much attention has been paid to the living cationic polymerization since the absence of chain breaking reactions such as chain transfer or termination in this system makes it possible to design molecular structure of the polymers obtainable from cationically polymerizable monomers such as isobutylene and vinyl ethers. It has been reported that cumyl diacetate/boron triacetate initiating systems are very effective for living cationic polymerization of isobutylene[1-3] and hydrogen iodide/iodine[4], hydrogen iodide/zinc iodide systems[5,6] are effective for the living cationic polymerization of vinyl ethers where the polymerization proceeds via the adduct formation by the reaction and the polymerization is initiated by the activation of C-I bond of the adduct by Lewis acid MX_n in the absence of chain breaking.

Protonic acids used in the living cationic polymerization are hydrogen halide (HX, X = Cl, Br, I)[7], trimethylsilyl halide ($(CH_3)_3SiX$, X = Cl, Br, I)[8], aliphatic and aromatic acid (CF_3COOH , CH_3COOH , C_6H_5COOH , etc.)[9-12] and phosphoric and phosphinic acid ($(PhO)_2POOH$, $(Ph)_2POOH$, etc.)[13]. The Lewis acids used for this purpose are zinc halides (ZnX_2 , X = Cl, Br, I)[14], tin halide (SnX_4 , X = Cl, Br, I)[10-13] and ethylaluminum dichloride ($EtAlCl_2$)[15].

In this article, we report the living cationic polymerization of IBVE, initiated by IMME/zinc iodide initiating system that makes it possible to omit the handling of hydrogen iodide gas.

Experimental

Materials

Reagent grade IBVE and TBVE (Aldrich) were washed

successively with 10% aqueous sodium hydroxide solution and distilled water. IBVE and TBVE were purified by distillation. Reagent grade iodomethyl methyl ether (Tokyo Kasei) and zinc iodide (Aldrich) were used as received. Zinc iodide was stored in a desiccator until used after drying under reduced pressure at room temperature. Toluene and diethyl ether were purified by distillation.

Procedures

Polymerization was carried out in the dry box equipped with a low temperature bath. The reaction was initiated by the successive addition of IMME and zinc iodide in diethyl ether into monomer in toluene. After addition of each reagent, the mixture was thoroughly mixed using vortex mixer. After certain period of the reaction, polymer was precipitated by addition of ammoniacal 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

The \bar{M}_n and MWD of polymers were determined by gel permeation chromatography (Spectra-Physics SP8430) using tetrahydrofuran as a solvent (10^5 , 10^4 , 10^3 polystyrene gel columns in series. Flow rate: 1.0 ml/min). Polystyrene standard was used for the calibration.

Brucker NMR spectrometer (Brucker 250) was used for 1H -NMR analysis of the polymer using chloroform-*d*.

Results and Discussion

Figure 1 shows time-conversion curves of IBVE polymerization carried out at various temperatures. The rate of polymerization decreases as temperature decreases and 100% conversion is achieved without exception in these

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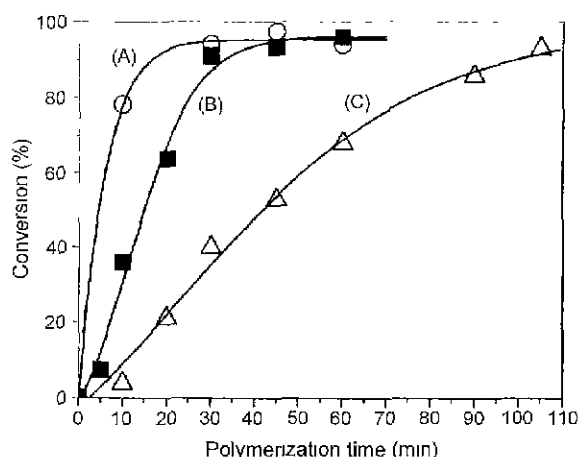


Figure 1. Time-conversion curves of polymerization of IBVE at different polymerization temperatures: $[M] = 1.6$ M, $[IMME] = 4.9$ mM, $[ZnI_2] = 0.167$ mM, polymerization temp.: (A) 0°C , (B) -15°C , (C) -30°C .

experimental conditions. This suggests that polymerization proceeds until complete consumption of the monomer. The apparent activation energy of the polymerization, obtained from the Arrhenius plot, gives a value of 4.2 kJ/mol, which is in good agreement with reported value.

Figure 2 shows the relationship between the number average molecular weight (\bar{M}_n) and polydispersity index of the resulting polymer, obtained from the polymerization carried out at 0, -15 , -30°C . It is evident that \bar{M}_n values of polymers are in direct proportion to % conversion and the values of MWD are always less than 1.2 ($\bar{M}_w/\bar{M}_n \leq 1.2$). Furthermore, experimental \bar{M}_n values are on the theoretical curves (not shown), which are drawn on the assumption that the number of polymer molecules equals to the number of IMME molecules. However, the deviation of the experimental data from the theoretical values becomes significant as polymerization temperature increases. These facts strongly suggest the living nature of the polymerization, i.e., the polymerization of IBVE is initiated by the instantaneous reaction of IMME with monomer and the propagating species is the activated C-I bond by activator, zinc iodide. The deviation of experimental data from the theoretical curve is probably due to the consumption of propagating species by the reaction with basic impurity, such as water molecule.

Figure 3 shows time-conversion curves of polymerization of IBVE, carried out at -15°C in the presence of various IMME concentrations. The rate of polymerization decreases as the concentration of IMME decreases and when the concentration of IMME is lower than 0.66 mM, conversion curve is leveled off at around 70% conversion, which indicates that a part of IMME is consumed by side reaction such as nucleophilic attack of the basic impurities to the cationic propagating species.

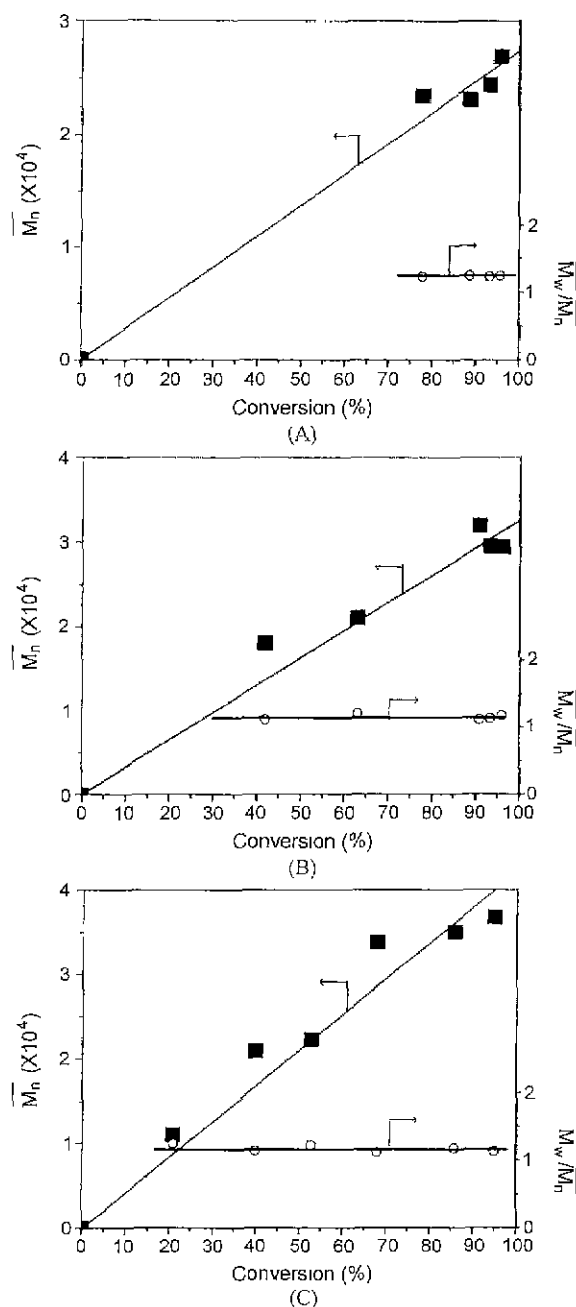


Figure 2. Conversion versus \bar{M}_n and MWD curves of polymerization of IBVE at different polymerization temperatures: $[M] = 1.6$ M, $[IMME] = 4.9$ mM, $[ZnI_2] = 0.167$ mM, polymerization temp.: (A) 0°C , (B) -15°C , (C) -30°C .

Figure 4 shows the relationships of \bar{M}_n and MWD versus % conversion. The \bar{M}_n values increase with increasing % conversion, while MWD values keep almost constant. Furthermore, the molecular weights of the resulting polymers are in good agreement with theoretical values that are calculated by the molar ratio of monomer and IMME.

The living nature of this polymerization is confirmed by

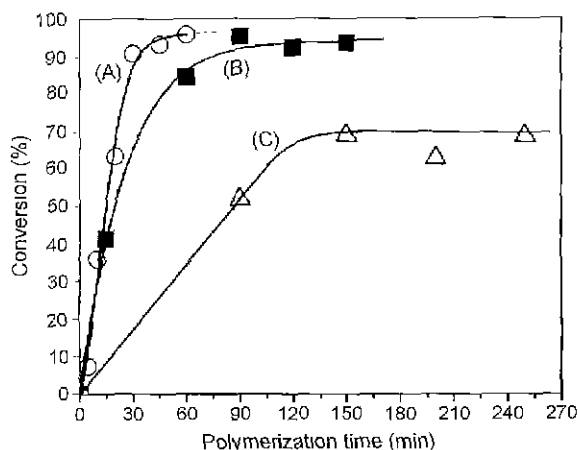


Figure 3. Time-conversion curves of polymerization of IBVE at different IMME concentrations: $[M] = 1.6 \text{ M}$, $[\text{ZnI}_2] = 0.167 \text{ mM}$, polymerization temp.: -15°C , $[\text{IMME}]$: (A) 4.9 mM, (B) 2.3 mM, (C) 0.66 mM.

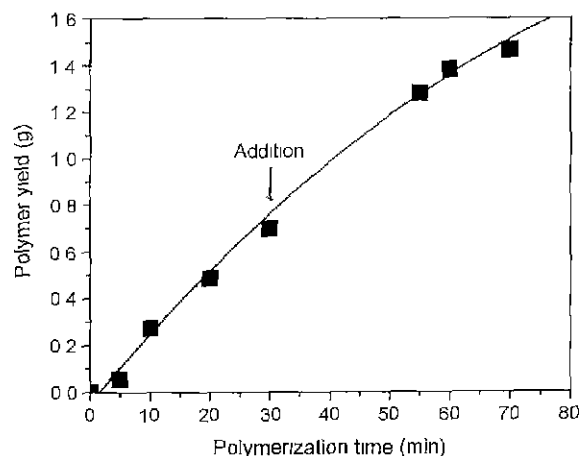


Figure 5. Evidence of the living nature of the poly(IBVE). Fresh IBVE was added to the cationic poly(IBVE) system when the conversion reaches 85%: $[M] = 1.6 \text{ M}$, $[\text{IMME}] = 4.9 \text{ mM}$, $[\text{ZnI}_2] = 0.167 \text{ mM}$, polymerization temp.: -15°C .

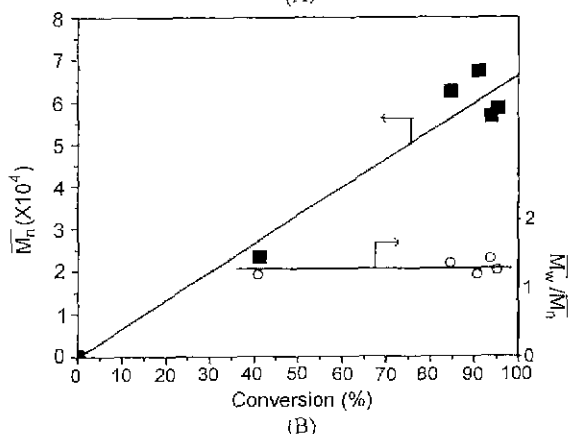
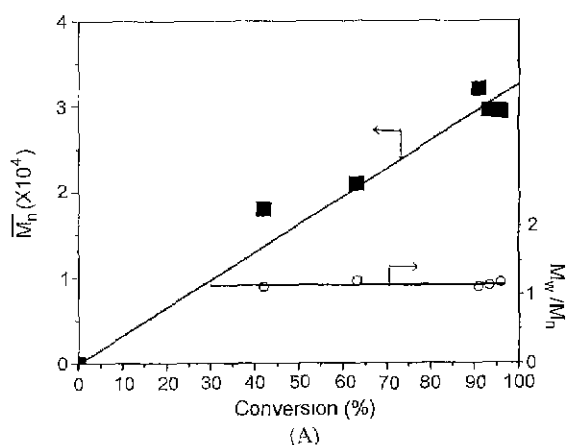


Figure 4. Conversion versus \bar{M}_n and MWD curves of polymerization of IBVE at different IMME concentrations: $[M] = 1.6 \text{ M}$, $[\text{ZnI}_2] = 0.167 \text{ mM}$, polymerization temp.: -15°C , $[\text{IMME}]$: (A) 4.9 mM, (B) 2.3 mM.

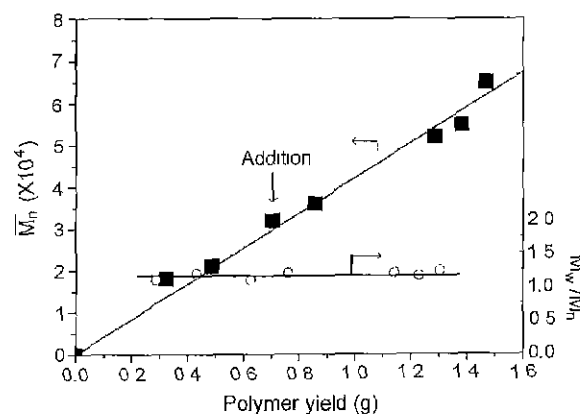


Figure 6. Polymer yield versus \bar{M}_n and MWD curves of polymerization of IBVE. Fresh IBVE was added to living cationic poly(IBVE) system when the conversion reaches 85%: $[M] = 1.6 \text{ M}$, $[\text{IMME}] = 4.9 \text{ mM}$, $[\text{ZnI}_2] = 0.167 \text{ mM}$, polymerization temp.: -15°C

monomer addition techniques. Fresh IBVE monomer was added to the polymerization system when the conversion reaches 85%. Figures 5 and 6 clearly show that after fresh IBVE monomer was added, polymer yield and \bar{M}_n increased simultaneously. It reveals that the propagating cationic species maintain the activity even in the later stage of the polymerization. The rate of polymerization of freshly added monomer is almost same with that of original polymerization system.

The living nature of the system was also confirmed by subsequent monomer addition method to obtain diblock copolymer of IBVE and TBVE, i.e., TBVE was added to the living cationic polymerization of IBVE system when the conversion reaches 85%. Figure 7 shows the polymer yield

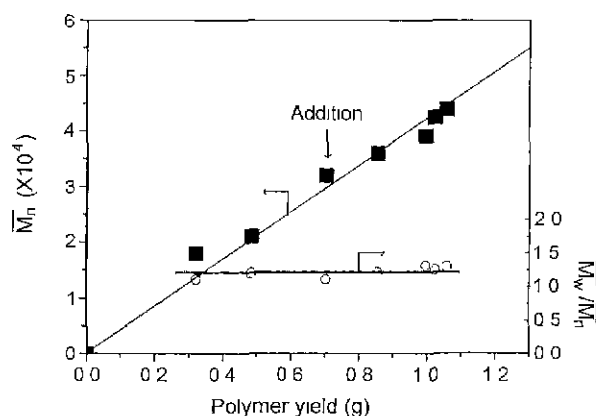


Figure 7. Polymer yield versus \bar{M}_n and MWD curves of copolymerization of IBVE and TBVE. TBVE was added to living cationic poly(IBVE) system when the conversion of IBVE reaches 85%: $[M] = 1.6$ M, $[IMME] = 4.9$ mM, $[ZnI_2] = 0.167$ mM, polymerization temp.: -15°C .

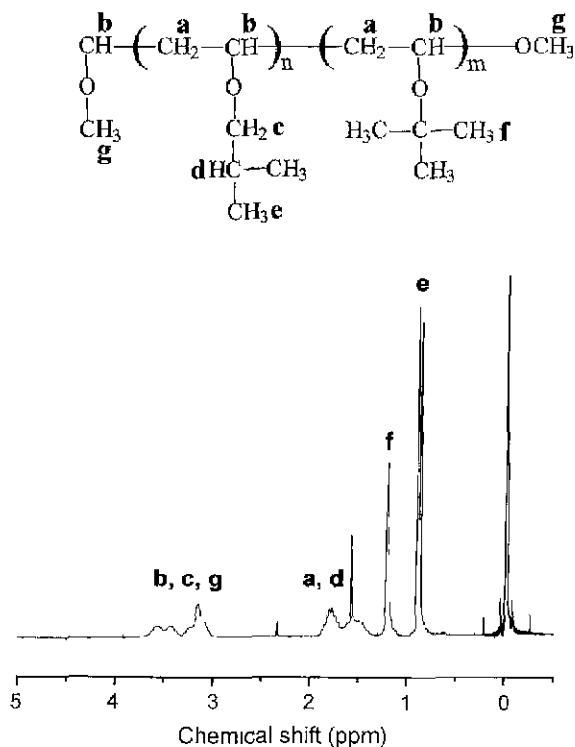


Figure 8. $^1\text{H-NMR}$ Spectrum of poly(IBVE-b-TBVE): $[M] = 1.6$ M, $[IMME] = 4.9$ mM, $[ZnI_2] = 0.167$ mM, polymerization temp.: -15°C , polymer yield: 1.026 g.

versus \bar{M}_n of the polymer curve. The increase in the polymer yield and \bar{M}_n of the resulting polymer indicates that TBVE is initiated by living cationic poly(IBVE). $^1\text{H-NMR}$ spectrum of the copolymer is shown in Figure 8, which also reveals that poly(IBVE-b-TBVE) can be successfully synthesized by this polymerization system.

Conclusions

Living cationic polymerization behaviors of IBVE in the presence of iodomethyl methyl ether (IMME) and zinc iodide (ZnI_2) have been investigated. The achievement of 100% conversion and increase in number average molecular weight of the resulting polymer with the increase in % conversion strongly suggested the living nature of this system. The MWD values of the polymers are always below 1.2. As the concentration of IMME increased, the number average molecular weight of the resulting polymer decreased, however, the rate of polymerization increased. The living nature of the system was confirmed by monomer addition technique and synthesis of diblock copolymer.

Acknowledgement

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