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Living Cationic Polymerization of Isobutyl Vinyl Ether by Hydrogen Iodide/Lewis Acid Initiating Systems: Effects of Lewis Acid Activators and Polymerization Kinetics[1]

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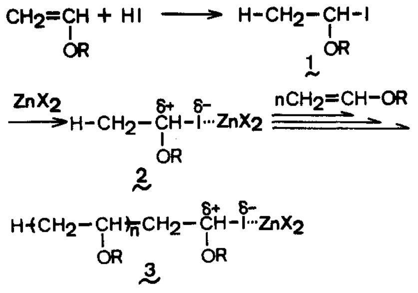
ABSTRACT: Eight initiating systems (HI/MX_n), each of which consists of hydrogen iodide and a metal halide ($MX_n = ZnI_2, ZnBr_2, ZnCl_2, SnI_2, SnCl_2, MgCl_2, BF_3OEt_2, SnCl_4$), have been employed for possible living cationic polymerization of isobutyl vinyl ether. Zinc and tin(II) halides all led to well-defined living polymerizations in toluene and in methylene chloride at −40 °C; in particular, zinc halides also permitted similar living processes in toluene even at room temperature (+25 °C). Under these conditions, the number-average molecular weights ($\bar{M}_n$) of the polymers were directly proportional to monomer conversion and inversely proportional to the initial concentration of hydrogen iodide but independent of that of MX_n. The stability of the living ends at +25 °C slightly decreased in the order $ZnI_2 > ZnBr_2 > ZnCl_2$. With $MgCl_2$, in contrast, polymerization hardly occurred under similar conditions, whereas the use of stronger Lewis acids (BF_3OEt_2 and $SnCl_4$) resulted in nonliving polymers. Kinetic studies with the HI/ZnX_2 initiating systems (X = I, Br, Cl) showed the rate of the living polymerizations to be first order with respect to monomer, hydrogen iodide, and ZnX_2 and thereby confirmed that hydrogen iodide serves as an initiator which generates the growing species and that MX_n serves as an activator which promotes its living propagation.

Introduction

Binary initiating systems (HI/I_2 and HI/ZnI_2) that consist of hydrogen iodide and a weak Lewis acid (iodine or ZnI_2) have been shown to permit well-defined living cationic polymerizations of vinyl ethers[2,4] as well as *p*-methoxystyrene.[5] The binary nature of these systems is of critical importance for attaining the living processes:[6] As visualized in Scheme I, hydrogen iodide undergoes, prior to the onset of the polymerization, quantitative electrophilic addition to the vinyl group of monomer to form an initiating adduct 1 with a carbon–iodine (C–I) bond that is per se unable to propagate. The Lewis acid component (MX_n) in turn activates the dormant C–I linkage through an electrophilic interaction so as to start the living propagation. Therefore, hydrogen iodide and the Lewis acid are termed "initiator" and "activator", respectively.[2,7]

Scheme I



The initiator/activator mechanism elicits two important questions: (1) What is the range of activators (MX_n) that are suited for the HI-mediated living polymerization? Namely, how do the structure and acidity of MX_n affect the living nature of the reaction? (2) What is the kinetics of the living polymerization that involves a consecutive activation of the dormant C–I terminal? This study specifically focuses on these subjects.

To answer the first question, we employed the following eight Lewis acids as potential activators for the living polymerization of isobutyl vinyl ether (IBVE) in the presence of hydrogen iodide: (A) ZnI_2, $ZnBr_2$, $ZnCl_2$, SnI_2, $SnCl_2$, $MgCl_2$; (B) BF_3OEt_2, $SnCl_4$. Group A consists of divalent metal halides that are relatively weak Lewis acids unable to polymerize IBVE by themselves. The two compounds of group B, being stronger Lewis acids commonly used for cationic polymerization, are employed for comparison with those of group A. For these MX_n's, we will discuss the effects of the central metals (M = Zn, Sn, Mg, B), the accompanying halogens (X = I, Br, Cl), and their Lewis acidity on living IBVE polymerization.

The kinetics of the living polymerization by HI/I_2 has been studied by us[6,8] and more recently by Cho and McGrath[9] and by Fontanille and his co-workers.[10] Although our spectroscopic and kinetic study has allowed us to formulate the initiator/activator scheme, whereas the latter two groups have determined the orders of reaction with respect to monomer, hydrogen iodide, and iodine for selected vinyl ethers, the kinetic details of the living polymerizations by the HI/MX_n systems still remain obscure. Perhaps the HI/I_2 combination does not fit best such a purpose; the direct initiation as well as the strong complexation of monomer by iodine apparently render the kinetics undesirably complicated. The second part of this study is, therefore, directed toward establishing the kinetics of the (living) polymerization of IBVE by the HI/MX_n systems that turned out to be free from the difficulty associated with the HI/I_2 counterpart.

Experimental Section

Materials. ZnX_2 (X = I, Br, Cl) (Aldrich, purity >99.99–99.999%), SnI_2 (Mitsuwa, purity >99%), $SnCl_2$ (Aldrich, purity >99.99%), and $MgCl_2$ (Wako, purity >97%) were used as received; they were vacuum dried at least overnight just before use and handled in the dark under dry nitrogen.[2,5] Commercial BF_3OEt_2 and $SnCl_4$ (Wako) were distilled under reduced pressure over calcium hydride and stored in ampules under dry nitrogen.

IBVE (Tokyo Kasei) was washed with 10% aqueous sodium hydroxide solution and then water, dried overnight over potassium hydroxide, and distilled twice over calcium hydride before use. Anhydrous hydrogen iodide was purified and used as an *n*-hexane solution as previously reported.[4] Acetone was dried overnight with anhydrous magnesium sulfate and doubly distilled before use. Toluene, methylene chloride (CH_2Cl_2), *n*-hexane, and diethyl ether as solvents and carbon tetrachloride and *n*-heptane as internal standards for gas chromatography were purified by the usual methods[4] and distilled twice over calcium hydride just before use.

Procedures. Polymerizations were carried out under dry nitrogen in baked glass tubes equipped with a three-way stopcock; the polymerization solution was 5.0 mL in volume. The reactions were initiated by adding sequentially a prechilled hydrogen iodide solution (in *n*-hexane; 0.50 mL) and an MX_n solution to a monomer solution [in toluene or CH_2Cl_2; 0.38 M (5.0 vol %)] kept at the polymerization temperature. Solid MX_n's were dissolved either in ether (ZnX_2; 0.50 mL) or in acetone (SnI_2, $SnCl_2$, and $MgCl_2$; 0.25 mL) depending on their solubility; liquid metal halides (BF_3OEt_2 and $SnCl_4$) were dissolved in the same solvent (0.50 mL) as for IBVE monomer. After a certain period, the polymerization was terminated with prechilled ammoniacal methanol (2.0 mL). Monomer conversion was determined from its residual concentration measured by gas chromatography with carbon tetrachloride or *n*-heptane as an internal standard (0.25 mL). The polymer yield by gravimetry was in good agreement with gas chromatographic conversion.

The quenched reaction mixtures were washed with 10% aqueous sodium thiosulfate solution and then with water to remove initiator residues, evaporated to dryness under reduced pressure, and vacuum dried to give the product polymers. The molecular weight distribution (MWD) of the polymers was measured by size-exclusion chromatography (SEC) equipped with three polystyrene gel columns (Shodex AC-802 and A-804 × 2). The $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ values of the polymers were calculated from SEC eluograms on the basis of a polystyrene calibration.

Results and Discussion

1. Polymerization of IBVE by HI/ZnX_2: Effects of the Halogens on Zinc.

Recently we have found that the HI/ZnI_2 initiating system induces living polymerizations of IBVE[2] and *p*-methoxystyrene.[5] This section describes the extension of this finding to the use of three zinc halides (ZnX_2; X = I, Br, Cl) in order to study the effects of the halogens attached to zinc on the IBVE polymerization by the HI/ZnX_2 systems.

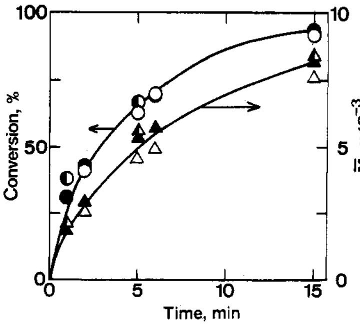


Figure 1. Time–conversion and time–$\bar{M}_n$ curves for the polymerizations of IBVE by HI/ZnX_2 in toluene at 0 °C: $[M]_0$ = 0.38 M; $[HI]_0$ = 5.0 mM; $[ZnX_2]_0$ = 0.10 mM. ZnX_2: (○, △) ZnI_2; (◐, ▲) $ZnBr_2$; (●, ▲) $ZnCl_2$.

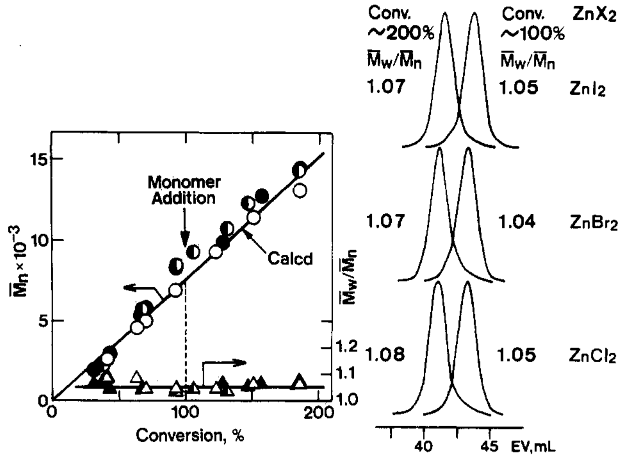


Figure 2. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of poly(IBVE) obtained with HI/ZnX_2 in monomer-addition experiments in toluene at 0 °C: $[M]_0$ = 0.38 M; $[HI]_0$ = 5.0 mM; $[ZnX_2]_0$ = 0.10 mM. The molar amount of the second IBVE feed is the same as in the first. The superposed MWD curves for each ZnX_2 are for the samples obtained before and after the second monomer addition (conversion ca. 100% and 200%, respectively). The diagonal solid line in the $\bar{M}_n$–conversion profile indicates the calculated $\bar{M}_n$ assuming the formation of one living polymer per mole of hydrogen iodide (eg 3). ZnX_2: (○, △) ZnI_2; (◐, ▲) $ZnBr_2$; (●, ▲) $ZnCl_2$.

Polymerization in Toluene. IBVE was polymerized by using the three zinc halides as activators in conjunction with hydrogen iodide (initiator); ZnX_2 was dissolved in ether because of its insolubility in toluene (see Experimental Section). We soon found not only HI/ZnI_2 but HI/$ZnBr_2$ and HI/$ZnCl_2$ as well to be effective to living polymerization of IBVE in a wide temperature range from −40 to +25 °C. Figure 1 shows the time–conversion and time–$\bar{M}_n$ curves for the reactions at 0 °C. Irrespective of the kind of ZnX_2, quantitative polymerizations occurred without an induction phase at almost identical rates. The polymerization mixtures were all homogeneous and colorless throughout; ZnX_2 alone did not polymerize IBVE at all under these conditions.

As shown in Figures 2 and 3 (for 0 and +25 °C, respectively), the number-average molecular weights ($\bar{M}_n$) of the polymers increased in direct proportion to monomer conversion, independent of polymerization temperatures and of the halogens in ZnX_2. The $\bar{M}_n$ values, though based on a polystyrene calibration, are in excellent agreement with the calculated values assuming that one polymer

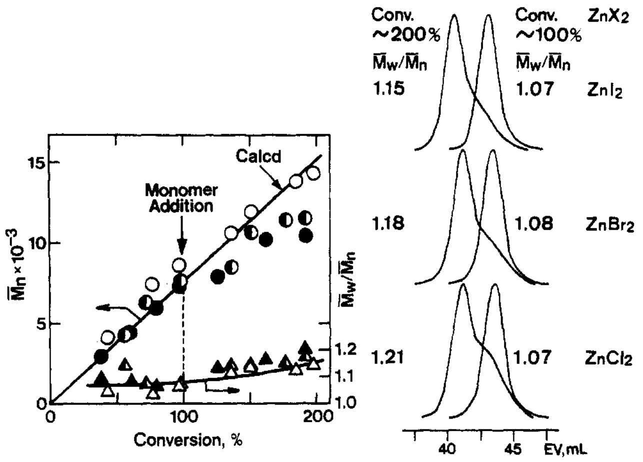


Figure 3. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of poly(IBVE) obtained with HI/ZnX_2 in monomer-addition experiments in toluene at +25 °C: $[M]_0 = 0.38$ M; $[HI]_0 = 5.0$ mM; $[ZnX_2]_0 = 0.10$ mM. The molar amount of the second IBVE feed is the same as in the first. The superposed MWD curves for each ZnX_2 are for the samples obtained before and after the second monomer addition (conversions ca. 100% and 200%, respectively). The diagonal solid line in the $\bar{M}_n$–conversion profile indicates the calculated $\bar{M}_n$ assuming the formation of one living polymer per mole of hydrogen iodide (eq 3). ZnX_2: (○, △) ZnI_2; (◐, ◭) $ZnBr_2$; (●, ▲) $ZnCl_2$.

chain forms per mole of hydrogen iodide (the solid lines in Figures 2 and 3). Throughout all these polymerizations, the MWDs of the polymers all stayed very narrow ($\bar{M}_w/\bar{M}_n < 1.1$), independent of monomer conversion. Virtually the same results were obtained at −40 °C.

The living nature of these polymerizations was further demonstrated by so-called "monomer-addition" experiments where fresh feeds of IBVE were added to completely polymerized reaction mixtures. The added IBVE feeds were smoothly polymerized at nearly the same rate as that before the monomer addition. At temperatures below 0 °C (e.g., Figure 2), the $\bar{M}_n$'s of the polymers continue to increase in direct proportion to monomer conversion and are very close to the calculated values for living polymers (one polymer chain per mole of hydrogen iodide; the solid lines in Figures 2 and 3). The MWDs again remain very narrow ($\bar{M}_w/\bar{M}_n < 1.1$). In the monomer-addition experiments at +25 °C (Figure 3), however, the MWDs of the polymers obtained after the second monomer addition exhibited slight tailings in the low molecular weight region, and the extent of the tailing increased in the order $ZnI_2 < ZnBr_2 < ZnCl_2$.

Thus, when coupled with hydrogen iodide, not only ZnI_2 but $ZnBr_2$ and $ZnCl_2$ as well turned out to induce perfect living polymerization of IBVE in toluene below 0 °C. Similar living processes are feasible at +25 °C, although the stability of the living polymer, as judged from the monomer-addition experiments, depended on the halogens in ZnX_2 in the order $ZnI_2 > ZnBr_2 > ZnCl_2$. Such an effect of the halogens may be partly due to the halogen exchange (e.g., $\sim\!\sim CH–I\cdots ZnX_2 \rightleftarrows \sim\!\sim CH–X\cdots ZnIX$; X = Br, Cl) that may occur when $ZnBr_2$ or $ZnCl_2$ interacts with the growing CH–I terminal derived from hydrogen iodide. The resulting C–Br or C–Cl terminal would be less reactive than the C–I counterpart and hence reluctant to propagate even when activated by ZnIX or ZnX_2.

Polymerization in Methylene Chloride. The polymerizations of IBVE by the HI/ZnX_2 systems were also carried out at −40 to +25 °C in CH_2Cl_2, a more polar solvent. In the reaction at −40 °C (Figure 4A), the polymer molecular weights were directly proportional to conversion and in excellent agreement with the calculated values for living polymers (the solid line). The MWD of the polymers remained very narrow ($\bar{M}_w/\bar{M}_n < 1.1$) over the whole conversion range. Similar results were obtained for the polymerizations at −15 and 0 °C. In contrast, elevating polymerization temperature to +25 °C resulted in nonliving processes where, irrespective of the type of ZnX_2, the increase in $\bar{M}_n$ leveled off at higher conversion, while the MWD of the polymers became progressively broader (Figure 4B). Thus, living polymerizations by HI/ZnX_2 are possible only at low temperatures (−40 to 0 °C) in CH_2Cl_2, where the higher polarity of the solvent renders the propagating species more ionically dissociated and thereby less stable than in toluene. The increased dissociation of the growing end may also account for the fact that the polymerizations at +25 °C are not living, independent of the halogens in ZnX_2; whether or not the halogen exchange occurs (see above), such a dissociated species would be unstable.

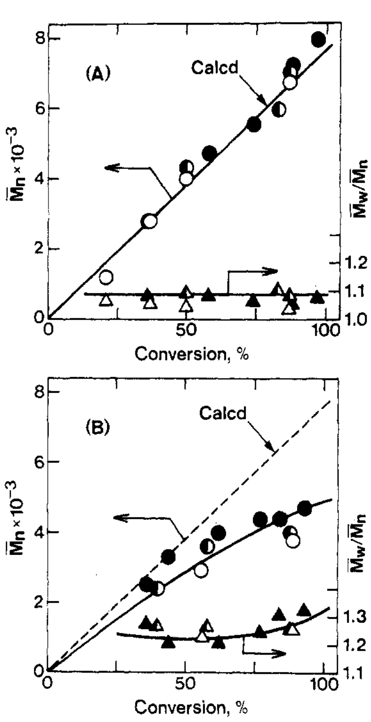


Figure 4. $\bar{M}_n$–conversion plots for poly(IBVE) obtained by HI/ZnX_2 in CH_2Cl_2 at −40 (A) and +25 °C (B): $[M]_0 = 0.38$ M; $[HI]_0 = 5.0$ mM; $[ZnX_2]_0 = 0.20$ mM (0.10 mM for $ZnCl_2$ in B). The diagonal solid (A) and broken (B) lines indicate the calculated $\bar{M}_n$ assuming the formation of one living polymer per mole of hydrogen iodide (eq 3). ZnX_2: (○, △) ZnI_2; (◐, ◭) $ZnBr_2$; (●, ▲) $ZnCl_2$.

2. Polymerization by HI/MX_n: Effects of the Central Metals in MX_n. The nature of the HI/MX_n systems may be affected by the central metal M in MX_n as well as by the accompanying halogens X. In addition to ZnX_2, therefore, we employed the halides of tin(II), tin(IV), magnesium, and boron as MX_n's to be coupled with hydrogen iodide.

HI/SnX_2 Initiating Systems (X = I, Cl). The polymerization of IBVE by HI/SnX_2 was carried out in toluene at −40 or +25 °C, where SnX_2 was dissolved in acetone instead of in ether where it is insoluble (see Experimental Section). Both HI/SnI_2 and HI/$SnCl_2$ initiating systems readily polymerized IBVE to quantitative conversion without an induction phase. Table I shows the times to reach 50% conversion. HI/SnX_2 gives slower polymerizations than the corresponding HI/ZnX_2 does under the same conditions at −40 °C. The polymerization mixtures with SnX_2 were yellow and homogeneous at +25 °C, but a trace of the tin halide precipitated at −40 °C

Table I
IBVE Polymerization by HI/MX$_n$ Systems in Toluene:[a] Time for 50% Conversion

	time at polymn temp	
MX$_m$ (mM)	-40 °C	+25 °C
ZnI$_2$ (1.0)[b]	5.7 h	~3 min
SnI$_2$ (1.0)[b]	38 h	~1 min
SnCl$_2$ (1.0)[b]	11 h	~3 min
MgCl$_2$ (5.0)[b]	no polymn	39 h
BF$_3$OEt$_2$ (0.10)	3.1 h	
SnCl$_4$ (1.0)	6.3 h	

[a] [IBVE]$_0$ = 0.38 M (5.0 vol %); [HI]$_0$ = 5.0 mM. [b] The polymerization solution contains 5.0 vol % of acetone as the solvent for MX$_n$.

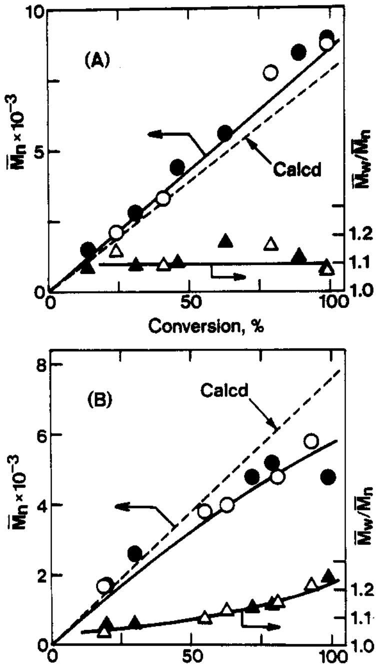


Figure 5. $\bar{M}_n$–conversion plots for poly(IBVE) obtained by HI/SnX$_2$ in toluene at -40 (A) and +25 °C (B): [M]$_0$ = 0.38 M; [HI]$_0$ = 5.0 mM; [SnX$_2$]$_0$ = 1.0 mM. The diagonal broken lines indicate the calculated $\bar{M}_n$ assuming the formation of one living polymer per mole of hydrogen iodide (eq 3). SnX$_2$: (○, △) SnI$_2$; (●, ▲) SnCl$_2$.

upon addition to a monomer solution. Control experiments carried out in the absence of hydrogen iodide showed that SnX$_2$ alone does not polymerize IBVE at all.

As shown in Figure 5A, the $\bar{M}_n$'s of the polymers, obtained at -40 °C with either SnI$_2$ or SnCl$_2$, increase in direct proportion to conversion, and they are in excellent agreement with the calculated values assuming that one polymer chain forms per mole of hydrogen iodide. It is important that the $\bar{M}_n$ values for SnI$_2$ and SnCl$_2$ led to a single straight line, which demonstrates the polymer molecular weights to be independent of the kind of tin(II) halide activators.

In sharp contrast, however, the $\bar{M}_n$'s for +25 °C did not increase linearly with conversion, being slightly smaller than the calculated values at high conversions (Figure 5B), and the polymers' MWD became broader with increasing conversion.

Very similar results were obtained for the HI/SnX$_2$ mediated polymerizations in CH$_2$Cl$_2$. Thus, the HI/SnX$_2$ systems lead to living polymers in both toluene and CH$_2$Cl$_2$ at -40 °C but not at +25 °C. The latter failure contrasts with the successful living processes by HI/ZnI$_2$ in toluene at the same higher temperature (see Figure 3).

Table II
Living Polymerization of IBVE by HI/MX$_n$ Initiating Systems: Effects of MX$_n$ and Reaction Conditions[a]

	solv. and temp			
	toluene		CH$_2$Cl$_2$	
MX$_n$	-40 °C	+25 °C	-40 °C	+25 °C
ZnI$_2$	O[c]	O	O[c]	×
ZnBr$_2$	O[c]	O[d]	O[c]	×
ZnCl$_2$	O[c]	O[d]	O[c]	×
SnI$_2$	O	×	O	×
SnCl$_2$	O	×	O	×
MgCl$_2$	no polymn	×	no polymn	×
SnCl$_4$	×	×	×	×
BF$_3$OEt$_2$	×	×	×	×
I$_2$[b]	O[c]	×	O[c]	×

[a] O, living; ×, not living. Living polymerization is defined as a reaction where the $\bar{M}_n$ of the product polymer increases proportionally to monomer conversion and further increases in the same fashion on addition of a second monomer feed at the end of the first-stage polymerization. [b] From ref 2. [c] Living polymerization is possible also at -15 and 0 °C. [d] After a second monomer addition, the MWD of the polymer shows a tailing in the lower molecular weight region; as a result, the $\bar{M}_n$-conversion plot deviates from linearity in the second-state polymerization (see Figure 3).

Other HI/MX$_n$ Systems. Effects of the Lewis acidity of MX$_n$ on the IBVE polymerization by the HI/MX$_n$ systems were observed clearly with MX$_n$ = MgCl$_2$, BF$_3$OEt$_2$, and SnCl$_4$. MgCl$_2$, the weakest Lewis acid among the eight MX$_n$'s employed, proved unsuited for polymerizing IBVE in the presence of hydrogen iodide. Even when it was charged at a concentration (5.0 mM; [HI]$_0$ = 5.0 mM) 50 times higher than that for ZnX$_2$, no polymers were obtained in 30 h in toluene at -40 °C; only oligomers ($\bar{M}_n$ ca. 10^3) with broad MWDs slowly formed at +25 °C, though the monomer was consumed almost quantitatively within 130 h in toluene and within 3 h in CH$_2$Cl$_2$.

The stronger Lewis acids, BF$_3$OEt$_2$ and SnCl$_4$, also failed to give well-defined living processes when employed with hydrogen iodide (5.0 mM) in toluene at -40 °C. At a low concentration (0.10 mM), BF$_3$OEt$_2$ resulted in a slow polymerization (100% conversion in 24 h), whereas no reactions took place with SnCl$_4$, which led to a slow polymerization at a higher concentration (1.0 mM; 100% conversion in 55 h). Whenever polymers formed, they had multipeaked broad MWDs with $\bar{M}_w/\bar{M}_n$ in the range 3–10, suggesting the occurrence of polymerization by the metal halides alone (with adventitious water as protogen) even when their concentrations were much lower than that of hydrogen iodide.

3. Scope of Living Polymerization of IBVE by HI/MX$_n$. Table II summarizes the overall results obtained in the first half of this study. Five mild Lewis acids of zinc and tin(II) in conjunction with hydrogen iodide were found to induce well-defined living polymerization of IBVE in toluene below 0 °C or CH$_2$Cl$_2$ at -40 °C as HI/I$_2$ does. Among these initiating systems, the HI/ZnX$_2$ pairs excel in that they permit living IBVE polymerization to occur also at room temperature (+25 °C) where the HI/I$_2$ and HI/SnX$_2$ systems are unsuccessful.

Equally important, the range of reaction conditions for perfectly living polymerization depends clearly on the central metals of MX$_n$ [Zn > Sn(II) ≫ Mg, B, Sn(IV)] and, to a minor extent, on the accompanying halogens (e.g., ZnI$_2$ > ZnBr$_2$ > ZnCl$_2$). Such trends appear to be related to the variation in the Lewis acidity of the MX$_n$'s. These effects of the MX$_n$ activators in turn demonstrate that they play a crucial role in controlling the (living) nature of the propagating species that originates from hydrogen iodide,

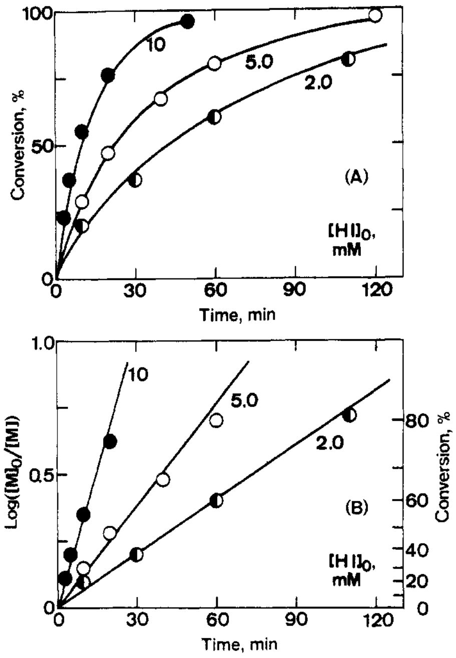


Figure 6. Time–conversion curves (A) and first-order plots (B) for the IBVE polymerization by $HI/ZnBr_2$ in toluene at −40 °C at variable HI concentrations: $[M]_0 = 0.38$ M; $[ZnBr_2]_0 = 0.20$ mM. $[HI]_0$ (mM): (●) 10; (○) 5.0; (◐) 2.0.

and this conclusion reinforces the validity of our initiator/activator mechanism shown in Scheme I.

4. Kinetics of Living Polymerization by HI/MX_n. The clean living polymerizations of IBVE by the HI/ZnX_2 initiating systems prompted us to pursue kinetic studies that principally focus on the roles of hydrogen iodide and ZnX_2 as well as the order of reaction with respect to monomer The absence of polymerization by ZnX_2 alone (see above) offers a particular advantage over the HI/I_2 counterpart where iodine may not only act as activator but also initiate polymerization by itself. A similar but less extensive study has been reported for HI/ZnI_2 by us;[2] therefore, $ZnBr_2$ was primarily used as an activator herein.

Polymerization Rate. Two series of kinetic experiments were carried out for the $HI/ZnBr_2$ mediated polymerization of IBVE in toluene at −40 °C: In one series, the initial concentrations of the monomer ($[M]_0$) and the zinc salt ($[ZnBr_2]_0$) were kept constant, whereas that of hydrogen iodide ($[HI]_0$) was varied (Figure 6); the other series involved constant $[M]_0$ and $[HI]_0$ but variable $[ZnBr_2]_0$ (Figure 7). As shown in the time–conversion profiles, the overall rate of monomer consumption monotonically increased with increasing $[HI]_0$ (Figure 6A) or with increasing $[ZnBr_2]_0$ (Figure 7A). In both series, the polymerizations proved to be of first order with respect to monomer, as clearly demonstrated by the linear first-order plots (log ($[M]_0/[M]$) vs time; [M] is the monomer concentration at time t) given in Figures 6B and 7B. Thus,

$$-d[M]/dt = k_1[M] \qquad (1)$$

where k_1 represents a first-order rate constant.

Orders of Reaction. The dependences of the rate constant k_1 on the concentrations of hydrogen iodide and zinc bromide were then determined by plotting its values against $[HI]_0$ or $[ZnBr_2]_0$. The k_1 values proved to be directly proportional to both $[HI]_0$ (Figure 8A) and $[ZnBr_2]_0$ (Figure 8B) and led to

$$-d[M]/dt = k_3[M][HI]_0[ZnBr_2]_0 \qquad (2)$$

where k_3 is an externally third-order rate constant.

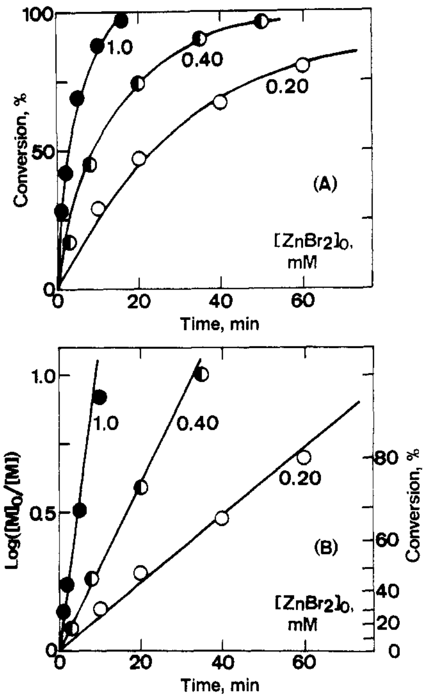


Figure 7. Time–conversion curves (A) and first-order plots (B) for the IBVE polymerization by $HI/ZnBr_2$ in toluene at −40 °C at variable $ZnBr_2$ concentrations: $[M]_0 = 0.38$ M; $[HI]_0 = 5.0$ mM. $[ZnBr_2]_0$ (mM): (●) 1.0; (◐) 0.40; (○) 0.20.

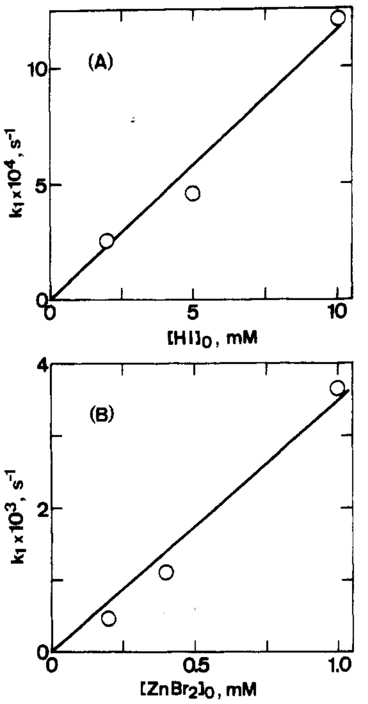


Figure 8. First-order rate constant k_1 (eq 1) for the polymerization by $HI/ZnBr_2$ in toluene at −40 °C, as a function of $[HI]_0$ (A) or $[ZnBr_2]_0$ (B): (A) $[M]_0 = 0.38$ M, $[ZnBr_2]_0 = 0.20$ mM, data from Figure 6B; (B) $[M]_0 = 0.38$ M, $[HI]_0 = 5.0$ mM, data from Figure 7B.

Polymer Molecular Weight. In spite of the variations of $[HI]_0$ and $[ZnBr_2]_0$, the polymerizations in the above two series were invariably living, where the molecular weights ($\bar{M}_n$) of the product polymers were directly proportional to monomer conversion and the MWDs were almost monodisperse with $\bar{M}_w/\bar{M}_n$ well below 1.1 (see, for example, Figure 9). More important, the $\bar{M}_n$'s at the same conversions are inversely proportional to $[HI]_0$ (Figure 9A), but they are independent of $[ZnBr_2]_0$ (Figure 9B), and in

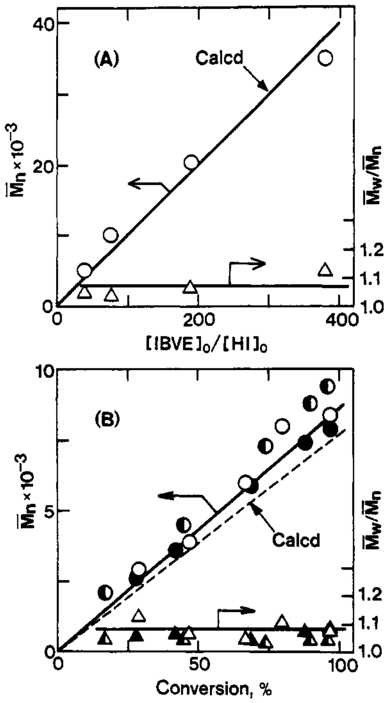


Figure 9. $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ values of poly(IBVE) obtained with $HI/ZnBr_2$ in toluene at -40 °C at variable HI (A) or $ZnBr_2$ (B) concentrations: (A) plotted against the $[M]_0/[HI]_0$ ratio, $[M]_0 = 0.38$ M, $[HI]_0 = 2.0$–10 mM, $[ZnBr_2]_0 = 0.20$ mM, conversion 100%; (B) plotted against conversion, $[M]_0 = 0.38$ M, $[HI]_0 = 5.0$ mM, $[ZnBr_2]_0 = 0.20$–1.0 mM. The diagonal solid (A) and broken (B) lines indicate the calculated $\bar{M}_n$ assuming the formation of one living polymer per mole of hydrogen iodide (eq 3).

all cases they are in excellent agreement with the calculated values assuming that one living polymer forms per mole of hydrogen iodide; namely,

$$\bar{M}_n = (\text{weight of IBVE consumed per liter})/[HI]_0 \qquad (3)$$

Virtually the same results as described above (eq 1–3) were obtained for the polymerizations by HI/ZnI_2, $HI/ZnCl_2$, HI/SnI_2, and $HI/SnCl_2$ under similar conditions. Thus, irrespective of the type of initiating systems, the living IBVE polymerizations by HI/ZnX_2 and HI/SnX_2 (X = I, Br, Cl) follow the same simple kinetics, which is fully consistent with Scheme I where hydrogen iodide and zinc or tin(II) halides serve as initiator and activator, respectively.

Comparison between HI/MX_n and HI/I_2. A few years ago, we showed, rather qualitatively, the living polymerizations of IBVE and related alkyl vinyl ethers by HI/I_2 to exhibit kinetic features similar to those observed for HI/MX_n in this study;[6,8] i.e., the overall reaction rate increases with increasing initial concentrations of hydrogen iodide ($[HI]_0$) and iodine ($[I_2]_0$) (eq 2), and the $\bar{M}_n$ of the living polymers is inversely proportional to $[HI]_0$ but independent of $[I_2]_0$ (eq 3).

Quite recently, two research groups have independently investigated the kinetics of the HI/I_2 initiated polymerizations of *n*-butyl[9] and 2-chloroethyl[10] vinyl ethers. Both of them again observed first-order dependences of the reaction rate on $[HI]_0$ and $[I_2]_0$ but found that the polymerizations were nearly zeroth order with respect to monomer. For the HI/I_2 initiated polymerization of IBVE in *n*-hexane, we also obtained a linear time–conversion profile that indicates a zeroth-order reaction for monomer concentration (see Figure 1, ref 4a). This last finding is in sharp contrast to the clearly first-order kinetics for the HI/ZnX_2 and HI/SnX_2 initiating systems (eq 1).

Noting the nearly zeroth-order rate dependence on monomer, the two groups threw doubt on our initiator/activator reaction scheme (Scheme I) and proposed an alternative propagation mechanism where a vinyl ether–iodine complex ($M{\cdot}I_2$; activated monomer) reacts with a growing C–I terminal that is *not* activated by iodine.[9,10] As Cho and McGrath themselves pointed out correctly,[9] however, the zeroth-order polymerization holds *either* when a noncomplexed monomer attacks an iodine-activated C–I terminal (Scheme I) *or* when a complexed monomer attacks a nonactivated C–I terminal, *only if* the complexation of a vinyl ether with iodine is thermodynamically favored ($[\text{free } I_2] \ll [M{\cdot}I_2]$).

Another mechanism that leads to a zeroth-order polymerization has been proposed by Fontana and Kidder,[11,12] where the rate-determining propagation step consists of a rearrangement of a growing end–monomer complex that is in equilibrium with the two components. This mechanism, however, does not account for the observed first-order rate dependence on the iodine concentration (cf. eq 2) and hence is invalid for the HI/I_2 initiating system.

Our recent study[13] has revealed that the living polymerizations of vinyl ethers by HI/I_2 are either of first order or of zeroth order with respect to monomer, depending on the types of vinyl ethers and reaction media, which may affect the complexation equilibrium between iodine and the monomer. Evidently, such an activator–monomer complexation is absent or at least kinetically negligible in the first-order living polymerizations by the HI/MX_n initiating systems, and thus they are simpler in kinetics and mechanism than the HI/I_2 initiated counterpart.

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Registry No. IBVE (homopolymer), 9003-44-5; IBVE, 109-53-5; HI, 10034-85-2; ZnI_2, 10139-47-6; $ZnBr_2$, 7699-45-8; $ZnCl_2$, 7646-85-7; SnI_2, 10294-70-9; $SnCl_2$, 7772-99-8; $MgCl_2$, 7786-30-3; BF_3OEt_2, 109-63-7; $SnCl_4$, 7646-78-8.

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