(15) Kurihara, S.; Ikeda, T.; Tazuke, S. *Jpn. J. Appl. Phys., Part 2* **1988**, *27*, L1791.
(16) Ikeda, T.; Horiuchi, S.; Karanjit, D. B.; Kurihara, S.; Tazuke, S. *Macromolecules*, preceding paper in this issue.
(17) Ikeda, T.; Itakura, H.; Lee, C. H.; Winnik, F. M.; Tazuke, S. *Macromolecules* **1988**, *21*, 3536.
(18) Broer, D. J.; Finkelmann, H.; Kondo, K. *Makromol. Chem.* **1988**, *189*, 185.
(19) Watanabe, J.; Krigbaum, W. R. *Macromolecules* **1984**, *17*, 2288.
(20) Flory, P. J.; Ronca, G. *Mol. Cryst. Liq. Cryst.* **1979**, *54*, 311.

Lifetime of Living Polymers in Cationic Polymerization. 1. Methodology and Application to the HI/I_2-Initiated Living Cationic Polymerization

Won Ok Choi, Mitsuo Sawamoto, and Toshinobu Higashimura*

Department of Polymer Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan. *Received January 5, 1989; Revised Manuscript Received May 25, 1989*

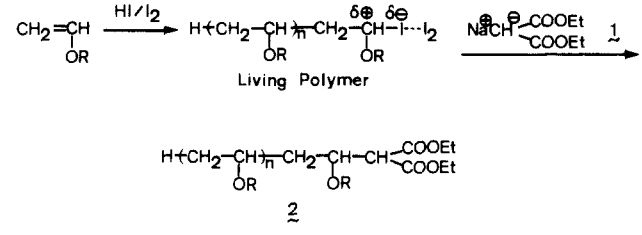
ABSTRACT: An end-capping method using sodiomalonic ester (1) as a quencher was shown to permit the determination of the concentration ([P*]) of living ends in the polymerization of isobutyl vinyl ether initiated by the hydrogen iodide/iodine (HI/I_2) system in toluene or methylene chloride at 0 to −40 °C. The terminal malonate group, thus attached to the polymer chain, could be determined by ^1H NMR spectroscopy, from the concentration of which [P*] was obtained. Throughout the polymerizations, the living-end concentration remained constant against monomer conversion and equal to the initial concentration of hydrogen iodide ($[P^*] = [HI]_0$), and the same relation held for the second-stage polymerizations that were started by adding a fresh feed of monomer to completely polymerized reaction mixtures. After the complete consumption of the monomer, however, the living end turned out to decay progressively with time, in first order with respect to [P*], and by following this decay its lifetime could be determined. The half-life of the living end, even in the absence of monomer, was relatively long, ranging from 40 to 1000 min (17 h). The decay process was slower at lower temperature but accelerated at higher iodine concentrations.

Introduction

Living polymers, by definition,[1a] have a lifetime that is long enough to permit their propagation to continue without chain transfer and termination over the time span of polymerization, as evidenced by a progressive increase in polymer molecular weight, in direct proportion to monomer conversion, as well as the formation of block polymers upon sequential addition of monomers. This definition, however, does not necessarily imply that living polymers per se should possess an infinite lifetime. They may be "killed" by purposefully added quenching agents or may undergo a spontaneous side reaction(s), particularly after the complete consumption of monomer.[1b] In cationic vinyl polymerization, for example, the quenchers include a variety of basic compounds, such as methanol, water, and amines.[2]

For some years we have been pursuing a number of living cationic polymerizations of vinyl monomers.[3] For example, a variety of vinyl ethers can be polymerized into well-defined living polymers by the hydrogen iodide/iodine (HI/I_2) initiating system.[4,5] A question that has frequently been asked but is yet unanswered is, how long is the lifetime of our living polymers (propagating species)? This is a problem of particular importance, because the lifetime is a direct measure of the stability of the growing carbocations that are no doubt the key to living cationic processes[3] and because its answer would in turn give further insight into the principles of initiator design of living cationic polymerization and into the methodology of related polymer syntheses like block copolymerization. Furthermore, the lifetime of growing carbocations in cationic polymerization has not been measured extensively, despite our attempt by stopped-flow spectroscopy.[6] This series of investigations is thus directed toward uncovering the lifetime of living propagating species in cationic polymerization of vinyl ethers and related monomers.

Scheme I
End Capping of Living Poly(IBVE) with Sodiomalonic Ester 1 (R = Isobutyl)



The simplest way to measure the lifetime of a growing species involves determination of its concentration as a function of time, thereby following its decay process, if any. As we have established quite recently (Scheme I),[7] sodiomalonic ester (1; diethyl malonate sodium salt) reacts quantitatively with the living poly(vinyl ether) growing ends that are generated by the HI/I_2 initiating system. Each polymer chain (2) thereby carries a malonate terminal group, the ^1H NMR analysis of which would in turn lead to the living-end concentration ([P*]). Specifically for vinyl ether polymerization, the carbanionic nature of the quencher 1 is beneficial and perhaps essential to an accurate determination of [P*], because the resulting carbon–carbon terminal bond of 2 is much more stable than the corresponding oxygen-, sulfer-, nitrogen-, and

0024-9297/90/2223-0048$02.50/0

phosphorus-carbon linkages to be formed from, respectively, alcohols and phenols[8] (or naphthols[9]), thiophenes,[10] amines,[11,12] and phosphines,[13] all of which have thus far been employed as end-capping agents in cationic polymerization; particularly when located adjacent to the vinyl ether's alkoxyl pendant group, these heterojunctions are often susceptible to decomposition under the acidic conditions of cationic polymerization.

In our series of lifetime studies, therefore, we have decided to employ the carbanion salt 1 as an end-capping agent for the determination of [P*] and the lifetime of cationically generated living polymers. This first paper concerns the establishment of our methodology and its application to the living cationic polymerization of isobutyl vinyl ether (IBVE) initiated by the HI/I_2 system.

Experimental Section

Materials. Commercial IBVE was washed with 10% aqueous sodium hydroxide solution and then water, dried over potassium hydroxide pellets, and distilled over calcium hydride before use; gas chroamtographic purity was >99.5%. Anhydrous hydrogen iodide (as *n*-hexane solution) and iodine were obtained and purified as reported.[4] Solvents [toluene, methylene chloride (CH_2Cl_2), and *n*-hexane] and the internal standard for gas chromatography (carbon tetrachloride) were purified by the usual methods[4] and distilled over calcium hydride at least twice just before use. Sodiomalonic ester 1 (ca. 200 mM in 1,4-dioxane) was prepared from diethyl malonate and sodium hydride as described elsewhere[7] and stored in ampules under dry nitrogen.

Procedures. Living cationic polymerization of IBVE was initiated with the HI/I_2 system under dry nitrogen in baked Schlenk tubes equipped with three-way stopcocks[4] and then terminated by addition of an excess of 1 (50-fold molar excess over hydrogen iodide) with vigrous manual stirring. For some control runs, ammonical methanol was used as quenching agent.

The quenched reaction mixtures were washed successively with 10% aqueous sodium thiosulfate solution and deionized water, evaporated to dryness under reduced pressure at room temperature, and vacuum dried overnight to give the produced polymers. The number-average molecular weight ($\bar{M}_n$) and polydispersity ratio ($\bar{M}_w/\bar{M}_n$) of the products were determined by size-exclusion chromatography (SEC) in chloroform on a Jasco Trirotar chromatograph: columns, Shodex polystyrene gels K-802, -803, and -804 (8 mm i.d. × 300 mm each); refractive index and ultraviolet (254 nm) dual detection.

Polymer samples for structural analysis and [P*] determination were further purified, to be free from the unreacted end-capping agent and other low-molecular-weight residues, by preparative SEC on a Jasco Trirotar chromatograph and a Jasco Megapak 201 polystyrene gel column (25 mm i.d. × 500 mm) in chloroform. ^1H NMR spectra of the samples were recorded at 300 MHz (Varian VXR-300) or 90 MHz (Jeol FX-90Q) in $CDCl_3$ at room temperature. Integrated NMR peak areas were obtained by the cut-and-weigh method on enlarged spectra.

Results and Discussion

Determination of Living-End Concentration [P*]. The HI/I_2-initiated living polymerization was carried out at −15 °C in toluene; the initial concentrations of hydrogen iodide and iodine were 10 and 5.0 mM, respectively. At varying intervals, the reaction was quenched with an excess of the carbanion salt 1 ($[HI]_0/[1] = 1/50$). At the identical reaction times, the polymerization was also terminated with ammoniacal methanol. The experiments by the two methods gave practically the same time-conversion curves (Figure 1). Independent of the type of quenching agents, the MWDs of the polymers were invariably very narrow and almost monodisperse ($\bar{M}_w/\bar{M}_n <$ 1.1; e.g., Figure 2). These facts show the termination process (Scheme I) by 1 to be clean, quantitative, and instantaneous.

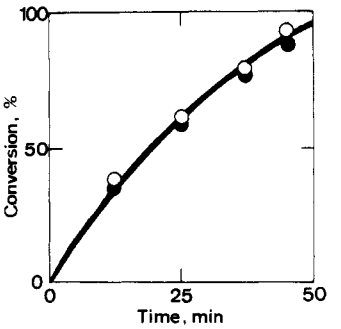


Figure 1. Time–conversion curve for the living IBVE polymerization by HI/I_2 in toluene at −15 °C, quenched with (●) sodiomalonic ester 1 or (○) methanol: $[M]_0$ = 0.38 M; $[HI]_0$ = 10 mM; $[I_2]_0$ = 5.0 mM.

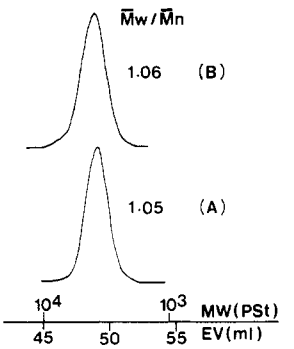


Figure 2. MWD of poly(IBVE) obtained with HI/I_2 in toluene at −15 °C: $[M]_0$ = 0.38 M; $[HI]_0$ = 10 mM; $[I_2]_0$ = 5.0 mM; IBVE conversion ≥90%. Quencher: (A) sodiomalonic ester 1; (B) methanol. $\bar{M}_w/\bar{M}_n$ ratios as indicated.

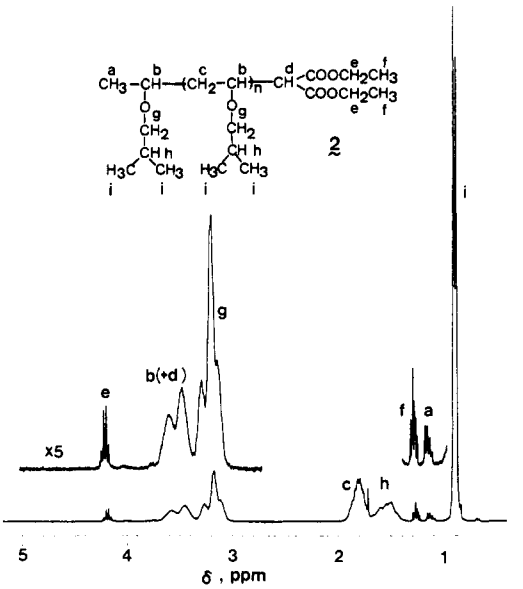


Figure 3. 300-MHz NMR spectrum of poly(IBVE) 2 end capped with sodiomalonic ester1; polymerization by HI/I_2 in toluene at −15 °C: $[M]_0$ = 0.38 M; $[HI]_0$ = 10 mM; $[I_2]_0$ = 5.0 mM; IBVE conversion = 93 %; $\bar{M}_n$ = 3900 (by SEC); $\bar{M}_w/\bar{M}_n$ = 1.10. $[P^*]/[HI]_0$ = 0.98.

Figure 3 shows a typical 300-MHz ^1H NMR spectrum of the polymers obtained after the termination with 1. In addition to the signals of poly(IBVE), the spectrum exhibits the characteristic absorptions of the malonate terminal group (e and f) and is fully consitent with the structure expected for polymer 2 (Scheme I); resonances assignable to byproducts or other terminal groups were absent. The corresponding 90-MHz spectra showed similar features.[7]

Table I
End-Capping Analysis of the Living IBVE Polymerization by HI/I_2 in Toluene at −15 °C[a,b]

	monomer conv, %			
	49.6	85.4	93.0	^{1}H NMR
[terminal malonate]/$[HI]_0$	0.99	0.98	0.98	300 MHz
	1.02	1.00	1.02	90 MHz
[living polymer]/$[HI]_0$[c]	1.04	1.01	0.97	
$\overline{DP}_n$(calcd)[d]	18.5	31.9	34.7	
$\overline{DP}_n$(obsd)[e]	17.8	31.7	35.8	

[a] $[M]_0$ = 0.38 M, $[HI]_0$ = 10.2 mM, $[I_2]_0$ = 5.0 mM. [b] The products were analyzed by 300-MHz ^{1}H NMR spectroscopy (e.g., Figure 3), unless otherwise specified; see text for the details of determination of the listed values. [c] [terminal methyl group]/$[HI]_0$. [d] $[M]_0$(% conv/100)/$[HI]_0$. [e] $[M]_0$(% conv/100)/[terminal methyl group].

The peak intensity ratio of the terminal methylene protons (e) to those of the methylene and methine units of poly(IBVE) (b and g) gives the concentration of the terminal malonate group (in mol/L): [terminal malonate] = $[M]_0$(% conv/100) × (3/4)[e/(b + g)], where $[M]_0$ is the initial monomer concentration. For convenience, this value is then compared with the initial concentration of hydrogen iodide ($[HI]_0$) to give the ratio [terminal malonate]/$[HI]_0$, the typical values of which are listed in Table I as a function of IBVE conversion.

The [terminal malonate]/$[HI]_0$ values based on 300- and 90-MHz NMR spectroscopy were in excellent agreement with each other, and thus the end-group analysis was routinely carried out by 90-MHz ^{1}H NMR spectroscopy. The experimental error for this method is estimated to be ±5%, and according to separate experiments, the lowest detectable [terminal malonate] was 1 mM for polymers with $\bar{M}_n$ below 10^4.

More important, these data show that throughout the polymerization, the concentration of the terminal malonate group remains constant and equal to the initial HI concentration: [terminal malonate] = $[HI]_0$.

The 300-MHz ^{1}H NMR spectra also gave a well-resolved signal (a, Figure 3) of the terminal methyl group that arises from the addition of hydrogen iodide to the double bond of the IBVE monomer.[5] The intensity ratio of this peak to those of the main-chain protons (peaks b and g) then leads to the concentration of the living polymer chains ([living polymer] = [terminal methyl] = $[M]_0$(% conv/100) × [a/(b + g)]), along with the degree of polymerization ($\overline{DP}_n$(obsd) = $[M]_0$(% conv/100)/[living polymer]). As seen in Table I, the living polymer concentration is equal to the initial concentration of hydrogen iodide, and accordingly, the observed $\overline{DP}_n$ is in excellent agreement with the calculated value ($\overline{DP}_n$ = $[M]_0$(% conv/100)/$[HI]_0$), which is based on the assumption that one living chain is formed from one molecule of hydrogen iodide.

The data collected in Table I thus show that the following equation holds independent of IBVE conversion: [terminal malonate] = [living polymer] = $[HI]_0$. The same conclusion that [living polymer] is constant and equal to $[HI]_0$ has been reached,[4,5] though indirectly, on the basis of the number of living polymer chains determined from their $\bar{M}_n$. Therefore, we can determine the concentration [P*] of living ends from that of the terminal malonate group: [P*] = [terminal malonate].

Effect of Hydrogen Iodide Concentration. Supporting evidence for the validity of our end-capping method for [P*] determination was provided by a series of experiments carried out in toluene at −15 °C at variable hydrogen iodide concentrations $[HI]_0$ but at constant concentrations of monomer and iodine ($[M]_0$ and $[I_2]_0$, respectively). The results of the end-capping analysis and related data are summarized in Figure 4 (for samples obtained at ca. 100% conversion).

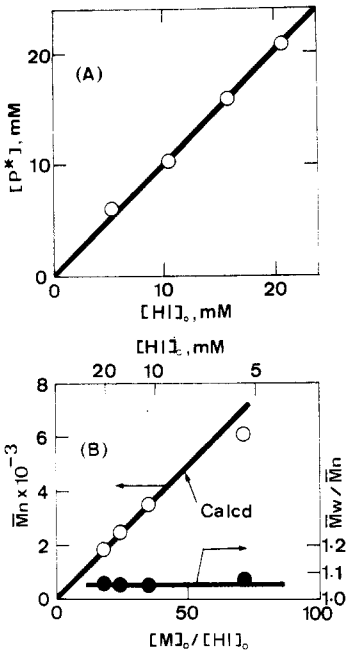


Figure 4. Effects of the initial hydrogen iodide concentration ($[HI]_0$) on (A) the living-end concentration ([P*] = [terminal malonate]) and (B) the molecular weight ($\bar{M}_n$) of polymers in the IBVE polymerization by HI/I_2 in toluene at −15 °C: $[M]_0$ = 0.38 M; $[HI]_0$ = 5–20 mM; $[I_2]_0$ = 0.50 mM; conversion = 100%. The diagonal straight line in (B) indicates the calculated $\bar{M}_n$ values assuming that one living chain forms per hydrogen iodide: $\bar{M}_n$(calcd) = (weight of reacted IBVE per liter)/$[HI]_0$.

At all hydrogen iodide concentrations employed, the [P*] values (=[terminal malonate]) were invariably equal to $[HI]_0$ (Figure 4A). In accordance with this relation, polymer molecular weights ($\bar{M}_n$) were not only inversely proportional to $[HI]_0$ but also very close to the calculated $\bar{M}_n$ values, assuming the formation of one living polymer chain per hydrogen iodide (Figure 4B).[5] Independent of $[HI]_0$, the polymerizations were all living and gave polymers of very narrow MWDs (Figure 4B) but were increasingly accelerated at higher $[HI]_0$. Very similar results have been obtained by us in methylene chloride solvent.[7] A separate series of experiments further showed that at a fixed $[HI]_0$ but at variable iodine concentrations ($[I_2]_0/[HI]_0 \leq 1$), the molecular weight of the living poly(IBVE) is independent of $[I_2]_0$.[5]

Monomer Addition Experiments. In truly living polymerization, all polymer chains resume propagation upon addition of a second feed of monomer, which is evidenced by a linear increase in $\bar{M}_n$ that further continues during the second-stage polymerization, and this characteristic is also the case for the IBVE polymerization by the HI/I_2 initiating system;[4,5] see Figure 5A. The living-end concentration ($[P^*]/[HI]_0$) was then determined by our method in such sequential monomer addition experiments. As shown in Figure 5B, the observed [P*] was constant and almost the same as the initial HI concentration, both before and after the second monomer addition where polymer molecular weight is directly proportional to monomer conversion.

The results summarized in Figures 1–5 thus demonstrate that the end capping with the carbanion salt 1 provides a convenient method to determine the living-end

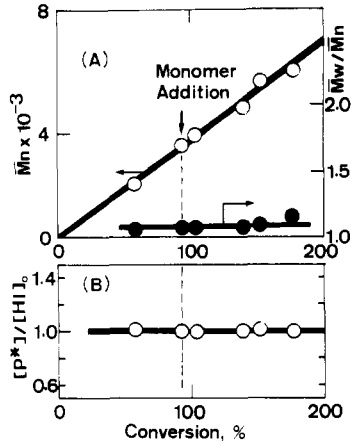


Figure 5. Conversion dependence of living-end concentration ($[P^*]/[HI]_0$), $\bar{M}_n$, and $\bar{M}_w/\bar{M}_n$ for poly(IBVE) obtained with HI/I_2 in toluene at −15 °C before and after a second monomer addition: $[M]_0 = [M]_{added} = 0.38$ M; $[HI]_0 = 10$ mM; $[I_2]_0 = 5.0$ mM.

concentration [P*] in the HI/I_2-mediated polymerization of IBVE. The data further confirm the mechanism of this living process[5] (Scheme I) in which hydrogen iodide is solely responsible for the generation of the growing species, one living chain being formed per hydrogen iodide molecule ($[P^*] = [HI]_0$), and each polymer carries a carbon–iodine terminal bond.

In spite of this simple relationship, however, it should be noted that, as we have proposed and indeed confirmed experimentally,[5] the hydrogen iodide generated carbon–iodine terminal must be activated by molecular iodine so as to undergo living propagation and that in this study the polymerizations were carried out mostly at an iodine concentration one-half that of hydrogen iodide ($[I_2]_0/[HI]_0 = 0.50$). The deficiency in iodine for the termials therefore renders at least half of them to remain "unactivated" or "dormant" at each moment when propagation occurs; namely, *not* all of the potentially growth-active polymers can propagate simultaneously. As the reaction proceeds, however, each polymer chain should have a statistically equal chance of propagation (or equal availability to iodine), otherwise the products would not possess nearly monodisperse MWDs and the molecular weight would not be solely controlled by the hydrogen iodide concentration (see above).

The fact that [terminal malonate] = $[HI]_0$ in turn means that the quencher 1 reacts *undiscriminately* with *all* of the terminal carbon–iodine linkages, either activated by iodine or unactivated (dormant). For simplicity, we hereafter call all these activated and unactivated (but potentially growth-active) forms as "living propagating species".

Lifetime of the Living Polymers. After establishing the method for [P*] determination, we then applied it to measure the lifetime and possible decay of the living polymers of IBVE generated by the HI/I_2 system under various conditions. It is of particular interest how long the living growing end can survive in the absence of monomer. Thus, the reaction mixtures of the living polymers were allowed to stand after the polymerization was completed, and [P*] was followed as a function of standing time.

Figure 6 presents a typical set of the ^1H NMR spectra of malonate-capped poly(IBVE) samples that were obtained immediately before and long after the end of the polymerization in toluene at −15 °C. Under these conditions, the reaction was completed in 50 min (sample A, Figure 6), but some of the runs (samples B and C) were deliberately quenched later, up until 200 min or four times the time span of the polymerization. The series of the spectra show a progressive decrease in the malonate terminal (living end) with increased standing time. The $[P^*]/[HI]_0$ values, obtained from these NMR spectra, were then plotted against time in Figure 7 (open circles).

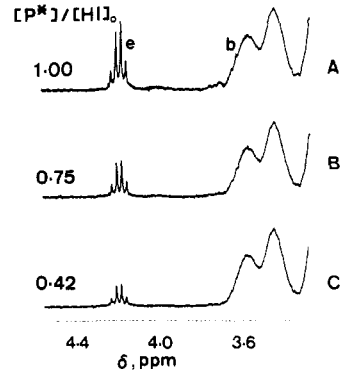


Figure 6. Expanded 300-MHz NMR spectra [terminal $-COOCH_2-$ (e) and main-chain $>CHO-$ (b)] of malonate-capped poly(IBVE) samples, showing a decrease in the terminal malonate group due to the decay of the living end in the absence of monomer. Polymerization by HI/I_2 in toluene at −15 °C: $[M]_0 = 0.38$ M; $[HI]_0 = 10$ mM; $[I_2]_0 = 5.0$ mM. Reaction time (min): (A) 50 (conversion = 100%); (B) 100; (C) 200. $[P^*]/[HI]_0$ values as indicated; see Figure 7 (open circles).

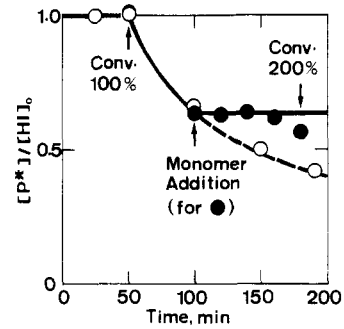


Figure 7. Living-end concentration ($[P^*]/[HI]_0$) as a function of time in the IBVE polymerization by HI/I_2 in toluene at −15 °C: (●) with second monomer addition 50 min after the end of the first-stage polymerization; (○) without the monomer addition. $[M]_0 = [M]_{added} = 0.38$ M; $[HI]_0 = 10$ mM; $[I_2]_0 = 5.0$ mM.

In sharp contrast to its constancy during the reaction ($[P^*] = [HI]_0$), the living-end concentration turned out to start decreasing monotonically soon after the complete depletion of monomer; after 200 min (or 150 min after conversion reached 100%), [P*] reduced to less than 50% of the value for 50 min. As shown in Figure 8, the decay process was of first order with respect of [P*], suggesting a spontaneous deactivation (see below). Figure 8 also demonstrates a good reproducibility of our experiments even in such a decay process.

In another series of experiments (Figure 7, closed circles), second feeds of IBVE were added to the reaction mixtures at 100 min where ca. 35% of the living end had been deactivated. A second-stage polymerization immediately occurred at a slightly lower rate than in the first, and the added monomer was completely polymerized 80 min after its addition (indicated as 200% conversion in Figure 7). Throughout this stage, [P*] maintained the level ($[P^*]/[HI]_0 = 0.65$) that was observed at the point of the second monomer addition, indicating the livingness of the second-phase reaction.

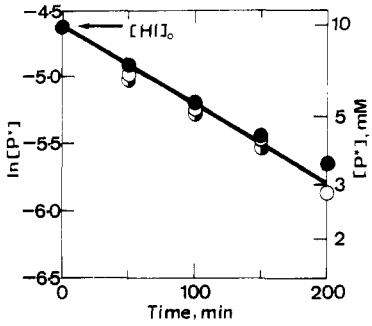


Figure 8. First-order plots of [P*] for the decay of the living end in toluene at −15 °C (cf. Figure 7, open circles): $[M]_0$ = 0.38 M; $[HI]_0$ = 10 mM; $[I_2]_0$ = 5.0 mM. The abscissa indicates the time after the complete consumption of monomer (50 min from initiation under these conditions). The data points appearing with different symbols show the results of replicated experiments.

These results led to two important conclusions: First, they further confirm the applicability of the end capping with **1** to [P*] determination. Namely, the carbanion salt **1** reacts quantitatively and specifically with the living chain ends that can propagate upon a second supply of monomer; if **1** combined nonspecifically with not only living ends but also other growth-inactive species (such as terminal olefins arising from β-proton elimination; see below), the observed [P*] values would not decrease but would remain constant or even increase beyond $[HI]_0$.

Second, in the absence of monomer, the HI/I_2-generated living species turned out to be not very stable but decay relatively quickly in toluene at −15 °C. The data in Figure 7 for the monomer addition experiment suggest that the presence of unreacted IBVE may be necessary for maintaining the livingness of the growing ends. We speculate that the electron-rich double bond and/or the ether oxygen of the monomer stabilize the electrophilic growing end through weak coordination or solvation. Such a possibility of the stabilization of the living end is currently being studied in our laboratories.[14]

Effects of Reaction Conditions on Lifetime. Following the [P*] determination in toluene at −15 °C, similar experiments were carried out under a variety of reaction conditions, in order to examine the effects of polymerization temperature, solvent polarity (toluene versus CH_2Cl_2), and initial concentration of iodine ($[I_2]_0$). Separate experiments confirmed that under all these conditions, the HI/I_2-mediated IBVE polymerizations are invariably living.

Figure 9 plots the $[P^*]/[HI]_0$ values, as a function of time, for the polymerizations in toluene and CH_2Cl_2 in the temperature range from 0 to −40 °C. In all cases, the living-end concentrations remain unchanged and very close to $[HI]_0$ as long as unreacted IBVE was present in the reaction mixtures. Soon after the complete depletion of the monomer, in contrast, the decrease in [P*] started where the rate of the decay depended on the reaction conditions.

All these decay processes, as that in toluene at −15 °C, were found to be of first order with respect of [P*], giving straight ln [P*]–time plots (cf. Figure 8); i.e., $-d[P^*]/dt = k[P^*]$, where k is a constant. The lifetime (half-life, $t_{1/2}$) of the living end was then obtained from the slope (k) of the first-order plot [$t_{1/2} = (\ln 2)/k$]; $t_{1/2}$ refers to the time at which [P*] is reduced to one-half its original value $[HI]_0$. Table II lists typical $t_{1/2}$ values thus determined.

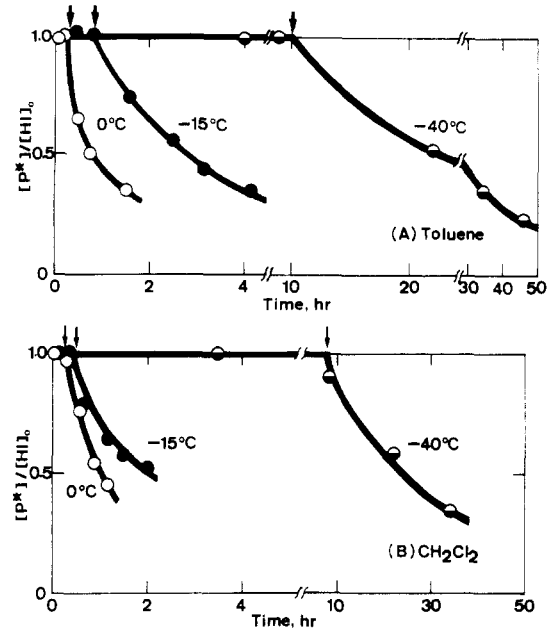


Figure 9. Living-end concentration ($[P^*]/[HI]_0$) as a function of time in the IBVE polymerizations by HI/I_2 in (A) toluene and (B) CH_2Cl_2: $[M]_0$ = 0.38 M; $[HI]_0$ = 10 mM; $[I_2]_0$ = 5.0 mM (in toluene) or 0.20 mM (in CH_2Cl_2). Polymerization temperature (°C): (○) 0; (●) −15; (◒) −40. The vertical arrows indicate the time for 100% conversion for each temperature.

Table II
Lifetime ($t_{1/2}$) of the Living Ends in the IBVE Polymerization by HI/I_2 ($[M]_0$ = 0.38 M)

solvent	$[HI]_0$, mM	$[I_2]_0$, mM	temp, °C	$t_{1/2}$,[a] min	rel lifetime[b]	entry
toluene	10	5.0	−40	950	24	1
	10	3.0	−15	160	4.0	2
	10	5.0	−15	120	3.0	3
	10	7.0	−15	49	1.2	4
	10	5.0	0	40	1.0	5
CH_2Cl_2	10	0.20	−40	1030	23	6
	10	0.10	−15	130	2.9	7
	10	0.20	−15	65	1.5	8
	10	0.30	−15	52	1.2	9
	10	0.20	0	44	1.0	10

[a] Half-life: $t_{1/2} = (\ln 2)/k$, where k is defined as $-d[P^*]/dt = k[P^*]$; see text and Figures 7 and 8. [b] Half-life relative to the $t_{1/2}$ value for 0 °C (entry 5 for toluene or entry 10 for CH_2Cl_2).

The observed lifetimes range from 40 to 1000 min (17 h), and consistent with the living nature of the polymerization, they are much longer than those of unstable (nonliving) growing carbocations, which are estimated to be from milliseconds[15–17] to a few seconds.[6] It should also be stressed that the lifetime determination herein is based on the decay of the living ends in the *absence* of monomer. Inspection of Figure 8 clearly shows that such a decay does not occur in the *presence* of monomer (conversion < 100%), under which condition the HI/I_2-generated growing species does survive long enough to maintain [P*] constant and equal to $[HI]_0$.

As expected, the living end has a longer lifetime at a lower polymerization temperature; note the more than 20-fold increase on going from 0 to −40 °C in both toluene and CH_2Cl_2.

Effects of Iodine on Lifetime. The lifetime was found to depend also on the iodine concentration $[I_2]_0$, being shorter at a higher $[I_2]_0$ ($[HI]_0$ constant), irrespective of solvent polarity (entries 2–4 and 7–9, Table II). This effect of iodine renders comparison of the data for toluene and CH_2Cl_2 solvents practically impossible, because

at the same $[HI]_0$ and $[I_2]_0$, the living polymerization in toluene is considerably slower than in CH_2Cl_2 and hence needs much higher concentrations of iodine to obtain reasonably high reaction rates.

The effect of $[I_2]_0$ on the lifetime, however, indeed indicates that the halogen accelerates the decay of the living end. As discussed already in this and other papers,[5] the role of iodine in the HI/I_2-initiated polymerization is to electrophilically activate the terminal carbon–iodine bond in order to trigger living propagation. This interaction may increase the electrophilicity of not only the growing carbocationic site but also its β-hydrogen and may thereby promote its elimination as a proton.

Nevertheless, the progressive decrease in [P*] (Figures 7 and 9) shows that the decay process does not yield acidic or electrophilic byproducts that may react with the added malonate anion. Although the initial β-proton elimination from the growing end certainly regenerates hydrogen iodide, the resulting olefinic polymer terminal perhaps undergoes a secondary series of dealcoholation reactions (with the acid)[18] that give polyene structures by which the liberated hydrogen iodide is also trapped to form unreactive delocalized cations.

In conclusion, this study has demonstrated that the end-capping with sodiomalonic ester **1** affords a convenient method for the determination of the concentration and lifetime of living ends in the HI/I_2-mediated IBVE polymerization. We are currently studying the applicability of this method to a variety of living cationic polymerizations that we have recently developed.[3] Another area of our future investigations[14] will invole the decay process of the living ends, first found in this study, the mechanism of which should be discussed in relation to the roles of unreacted monomer and iodine therein that are briefly speculated in this paper but not experimentally verified.

Acknowledgment. We thank Messrs. H. Ushio and K. Matsumura of Unitika Research Laboratories, Inc., Kyoto, Japan, for measuring the 300-MHz NMR spectra.

References and Notes

(1) Szwarc, M. *Carbanions, Living Polymers, and Electron-Transfer Processes*; Interscience: New York, 1968; (a) pp 16 ff; (b) p 646.
(2) Kennedy, J. P.; Marechál, E. *Carbocationic Polymerization*; Interscience: New York, 1982; pp 216 ff.
(3) For a recent review, see: Higashimura, T.; Aoshima, S.; Sawamoto, M. *Makromol. Chem., Macromol. Symp.* **1988**, *13/14*, 457.
(4) Miyamoto, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1984**, *17*, 265, 2228.
(5) Higashimura, T.; Miyamoto, M.; Sawamoto, M. *Macromolecules* **1985**, *18*, 611.
(6) Higashimura, T.; Sawamoto, M. *Polym. Bull. (Berlin)* **1978**, *1*, 11.
(7) Sawamoto, M.; Enoki, T.; Higashimura, T. *Macromolecules* **1987**, *20*, 1.
(8) Saegusa, T.; Matsumoto, S. *J. Polym. Sci., Part A-1* **1968**, *6*, 1559.
(9) Sawamoto, M.; Furukawa, A.; Higashimura, T. *Macromolecules* **1983**, *16*, 518.
(10) Higashimura, T.; Kusano, H.; Masuda, T. Okamura, S. *J. Polym. Sci., Part B* **1971**, *9*, 463.
(11) Miyamoto, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1985**, *18*, 123.
(12) Sawamoto, M.; Enoki, T.; Higashimura, T. *Polym. Bull. (Berlin)* **1987**, *18*, 117.
(13) Brzezińska, K.; Chwiałkowska, W.; Kubisa, P.; Matyjaszewski, K.; Penczek, S. *Makromol. Chem.* **1977**, *178*, 2491.
(14) Choi, W. O.; Sawamoto, M.; Higashimura, T. *Macromolecules*, submitted for publication (part 4 of this series).
(15) Lorimer, J. P.; Pepper, D. C. *Proc. R. Soc. London, Ser. A* **1976**, *351*, 551.
(16) Kunitake, T.; Takarabe, K. *Polym. J.* **1978**, *10*, 105; *Macromolecules* **1979**, *12*, 1061.
(17) Sawamoto, M.; Higashimura, T. *Macromolecules* **1978**, *11*, 328; **1978**, *11*, 501; **1979**, *12*, 581.
(18) Aoshima, S.; Higashimura, T. *Polym. J.* **1984**, *16*, 249.