Macromolecules **1985,** *18,* 611–616

(9) Saegusa, T.; Ikeda, H.; Hirayanagi, S.; Kimura, Y.; Kobayashi, S. *Macromolecules* **1975**, *8*, 259.

(10) Silverstein, R. M.; Bassler, G. C.; Morril, T. C. "Spectroscopic Identification of Organic Compounds", 4th ed.; Wiley: New York, 1981.

(11) Pouchert, C. J. "The Aldrich Library of NMR Spectra", 2nd ed.; Aldrich Chemical Co.: Milwaukee, WI, 1984.

(12) Kortum, G.; Vogel, W.; Andrussow, K. "Dissociation Constants of Organic Acids in Aqueous Solution"; Butterworths: London, 1961.

Mechanism of Living Polymerization of Vinyl Ethers by the Hydrogen Iodide/Iodine Initiating System

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ABSTRACT: The initiation/propagation mechanism of the living polymerization of isobutyl vinyl ether (IBVE) initiated by a mixture of hydrogen iodide and iodine (HI/I_2 initiator) was investigated by NMR and UV/visible spectroscopy in nonpolar media at low temperatures below −15 °C. The initial reaction is the quantitative addition of HI to IBVE to yield a 1:1 adduct (1), $CH_3CHIOCH_2CH(CH_3)_2$. Adduct 1 (or HI) itself can hardly polymerize IBVE but, in the presence of iodine, it does induce a polymerization that yields monodisperse living polymers, the molecular weight of which is determined only by the initial HI concentration. ^1H NMR analysis of the polymerization mixture showed that the living polymers bear a CH–I terminal analogous to that of 1. UV/visible spectroscopy indicated the presence of a constant concentration of unreacted iodine throughout the reaction. From these results, a new polymerization mechanism has been proposed, in which the CH–I bond of 1 is first activated by the electrophilic interaction of added iodine with the terminal iodine and IBVE monomer inserts into the activated CH–I linkage. The resultant dimeric species has again a CH–I terminal that is in turn activated by iodine to allow the insertion of IBVE. Thus, the living polymers form via the successive insertion of the monomer into the covalent CH–I end activated by iodine. The difference between the polymerizations by HI/I_2 initiator and by iodine alone was also discussed on the basis of the proposed mechanism.

Introduction

Quite recently, we have reported the living polymerization of a series of vinyl ethers initiated by a mixture of hydrogen iodide (HI) and iodine, in which monodisperse living polymers with controlled molecular weight are obtained.[1,2] The living processes were also applied to synthesize novel di-[2] and triblock[3] copolymers and amino-functionalized poly(vinyl ethers).[3]

The living polymerization of vinyl ethers by HI/I_2 initiator differs clearly from the conventional cationic polymerization initiated by iodine itself.[1] For instance, even in nonpolar solvents the former proceeds without an induction phase that is usually involved in the latter, and well-defined living polymers can be obtained only with HI/I_2 initiator. Immediate questions arising from these facts are the following: What is the nature of the propagating species derived from the HI/I_2 initiating system that leads to the living processes? What is the difference in mechanism between the polymerizations by HI/I_2 and iodine alone? This study is to unravel these problems.

The mechanism of the iodine-initiated polymerization of vinyl ethers and related monomers has long been discussed mostly on the basis of kinetic investigations,[4-7] none of which, however, provided direct evidence on the nature of the propagating species therein. Ledwith and Sherrington[8] observed by UV spectroscopy equilibrium formation of an adduct (substituted 1,2-diiodoethane) between iodine and isobutyl vinyl ether (IBVE) in methylene chloride and suggested that the diiodo compound would dissociate in the presence of iodine to give an ionic propagating species. A later study by Johnson and Young[9] also indicated the presence of a similar diiode in the polymerization of *n*-butyl vinyl ether by iodine. According to Giusti et al.,[10-12] on the other hand, the adduct between styrene and iodine is inactive per se and may release HI that in turn initiates polymerization. Although these previous studies indicate the intervention of iodine–vinyl ether (or styrene) adducts in the polymerization by iodine, their role in initiation and propagation processes remains unknown.

In this study, we applied NMR and UV/visible spectroscopy, coupled with kinetic measurements, to analyze directly the polymerization systems of IBVE initiated by HI/I_2 and iodine. HI was found to form quantitatively a 1:1 adduct (α-iodo ether; eq 1) with IBVE. We also found that the C–I bond of the HI–IBVE adduct is activated by added iodine and that propagation proceeds via the reaction of IBVE with the activated C–I bond. This mechanism consistently accounts for the difference between the polymerizations by HI/I_2 and iodine alone.

Experimental Section

Materials. IBVE and polymerization solvents [*n*-hexane and carbon tetrachloride (CCl_4)] were purified as described previously.[1] Anhydrous hydrogen iodide was obtained by the dehydration of a 57% aqueous solution (Wako Chemicals) with phosphorus pentoxide[10] and stored as an *n*-hexane or CCl_4 solution in ampules in the dark at −20 °C.[1] Iodine (Wako Chemicals) was sublimed over potassium iodide and stored under dry nitrogen in the dark.

Polymerization Procedures. Reactions and polymerization of IBVE were carried out under dry nitrogen in a test tube equipped with a three-way stopcock.[1] The number-average molecular weight ($\bar{M}_n$) and molecular weight distribution (MWD) of the product polymers were measured by vapor pressure osmometry and gel permeation chromatography, respectively, as described.[1]

NMR Spectroscopy. ^1H and ^{13}C NMR spectra (89.55 and 22.5 MHz, respectively) were recorded on a Jeol FX-90Q Fourier-

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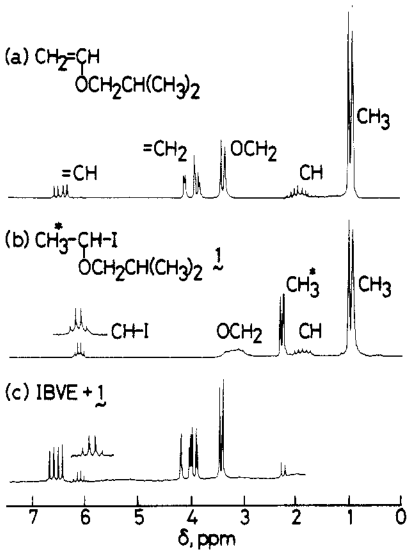
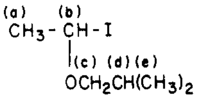


Figure 1. ^{1}H NMR spectra at −25 °C: (a) IBVE (170 mM) in CCl_4; (b) an equimolar mixture of IBVE (300 mM) and HI (300 mM) (adduct 1) in CCl_4; (c) a mixture of IBVE (125 mM) and HI (12.5 mM) in *n*-hexane.

Table I
^{1}H and ^{13}C NMR Chemical Shifts (δ) of Adduct 1 in CCl_4 at −25 °C



$$\overset{(a)}{CH_3}-\overset{(b)}{CH}-I \quad \big|_{(c)}\ O\overset{}{CH_2}\overset{(d)}{CH}(\overset{(e)}{CH_3})_2$$

	a	b	c	d	e
^{1}H	2.23	6.05	2.9–3.3	1.6–2.1	0.93
^{13}C	30.99	78.72	80.19	27.42	19.45

transform spectrometer with a variable-temperature probe insert (acetone-d_6 capillary for internal locking). Aliquots of a reaction solution were transferred under dry nitrogen via a dry syringe into a septum-capped NMR sample tube (5-mm o.d.) filled with dry nitrogen, which was then placed in the thermostated probe insert. For ^{1}H NMR spectra in *n*-hexane, the signals of the solvent were saturated by irradiating (homogated decoupling) them at their resonance frequency to enhance the signal-to-noise ratio. The run time for one spectrum was ca. 2 min, short enough to neglect safely the progress of polymerization during the spectral accumulation.

UV/Visible Spectroscopy. UV/visible spectra were recorded on a Shimadzu UV-190 double-beam spectrometer. Reactions for spectroscopic studies were performed under dry nitrogen in a quartz cell fitted with a three-way stopcock (optical path, 1 cm). The cell was immersed in a methanol bath maintained at the desired temperature, and quickly inserted into the cell chamber of the spectrometer in a dark room. The time required for each scan was ca. 40 s and hence the extent of the reaction therein was negligible.

Results

Before spectroscopic studies on the living polymerization initiated by HI/I_2 initiator, we first examined the interaction of IBVE with HI or iodine alone.

1. Reaction of Hydrogen Iodide with IBVE in Nonpolar Media. Equimolar Reaction. When IBVE was treated with an equimolar amount of HI in a nonpolar solvent (*n*-hexane or CCl_4) in the temperature range of −25 to −78 °C, a covalent 1:1 adduct, 1-iodoethyl isobutyl ether (1), was quantitatively formed (eq 1). Figure 1 (a and b)

$$CH_2{=}CHOCH_2CH(CH_3)_2 + HI \rightarrow \underset{1}{CH_3CHIOCH_2CH(CH_3)_2} \quad (1)$$

shows typical ^{1}H NMR spectra of IBVE and adduct 1 in CCl_4 at −25 °C. ^{13}C NMR chemical shifts of 1 are listed in Table I. Very similar ^{1}H and ^{13}C NMR spectra were obtained in *n*-hexane at −25 °C.

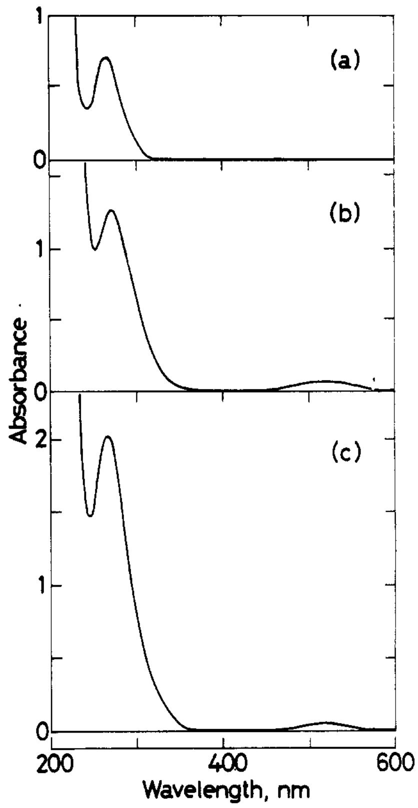


Figure 2. UV/visible spectra in *n*-hexane at −25 °C: (a) $[IBVE]_0$ = 50 mM, $[HI]_0$ = 0.60 mM; (b) $[IBVE]_0$ = 50 mM, $[I_2]_0$ = 0.60 mM; (c) $[IBVE]_0$ = 50 mM, $[HI]_0 = [I_2]_0$ = 0.60 mM. The spectra remained unchanged until the end of the reactions.

On addition of HI to an IBVE solution, the vinyl protons of the monomer (δ 3.8–4.3 and 6.2–6.6) (Figure 1a) immediately disappeared and in turn signals due to the α-iodo ether 1 were observed (Figure 1b), e.g., the quartet at 6.0 ppm for >CHI and the doublet at 2.2 ppm for CH_3CHI. Signals of other products were absent, and no polymers formed during the reaction. The ^{13}C NMR chemical shift values were also consistent with 1, being in good agreement with the calculated values based on conventional chemical shift parameters.[13]

Reaction of HI with Excess IBVE. Adduct 1 was also obtained quantitatively when HI was mixed with a 10-fold excess of IBVE in *n*-hexane at −25 °C (Figure 1c). The ^{1}H NMR spectrum of the reaction mixture showed the coexistence of 1 and unreacted IBVE in the absence of polymers and other products. These observations are consistent with our previous result[1] that the attempted polymerization of IBVE by HI alone in *n*-hexane at −15 °C ($[IBVE]_0$ = 0.38 M, $[HI]_0$ = 5.0 mM) is so sluggish (or negligible) that no polymers form within 2 days.[14]

Figure 2a illustrates the UV/visible spectrum of a mixture of IBVE and HI in *n*-hexane at −25 °C. The spectrum exhibited a single absorption centered at 270 nm, the absorbance of which was proportional to the initial HI concentration (Figure 3). The molar absorption coefficient (ϵ_{max}) of this peak was determined to be 1.13×10^3 M^{-1} cm^{-1} by assuming a quantitative reaction of HI. The observed absorption maximum (λ_{max}) and ϵ_{max} are close to the literature data for the n → σ* transition of alkyl iodides (e.g., $RCH(CH_3)I$, λ_{max} = 260 nm, ϵ_{max} = 5.8×10^2 M^{-1} cm^{-1}, in ethanol[15]). Therefore, the UV analysis also supported the

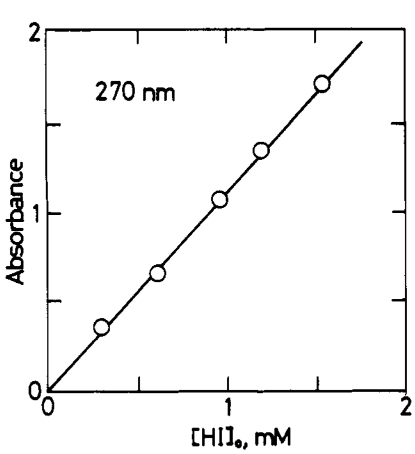


Figure 3. Absorbance at 270 nm of IBVE/HI mixtures as a function of the initial HI concentration: $[IBVE]_0 = 50$ mM, in *n*-hexane at −25 °C.

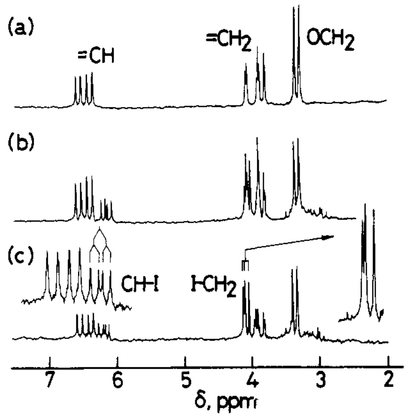


Figure 4. ^1H NMR spectra of IBVE (a) and a polymerization solution with iodine (b and c) in *n*-hexane: $[IBVE]_0 = 83$ mM; $[I_2]_0 = 25$ mM. Temperature and reaction time: (a) −50 °C; (b) −50 °C, 10 min; (c) −15 °C, 22 min.

formation of 1 from HI and IBVE in nonpolar solvents.

2. Polymerization by Iodine in *n*-Hexane. NMR Spectroscopy. We have already reported the clear differences between the polymerizations of IBVE initiated by HI/I_2 and iodine (see Introduction).[1] To clarify these differences further, a polymerization mixture of IBVE with iodine was analyzed by ^1H NMR spectroscopy in the temperature range −50 to −15 °C (Figure 4). In these experiments, an iodine solution was added to excess IBVE in *n*-hexane at −78 °C ($[IBVE]_0 = 83$ mM, $[I_2]_0 = 25$ mM) and a series of NMR spectra were recorded while the temperature was gradually raised.

The first spectrum obtained at −50 °C (Figure 4b; 10 min after mixing) showed a doublet of doublet at 6.1 ppm (J = 5.2 and 8.3 Hz) and a multiplet at 3.8–4.0 ppm overlapping with the vinyl signals of IBVE (cf. Figure 4a). From its splitting pattern and chemical shift, the signal at 6.1 ppm is assignable to the α-proton (CHI) of the 1:1 adduct between iodine and IBVE (2, eq 2). The dd

$$CH_2{=}CHOCH_2CH(CH_3)_2 + I_2 \rightarrow \underset{\mathbf{2}}{ICH_2CHIOCH_2CH(CH_3)_2} \quad (2)$$

pattern of this signal results from the chemical-shift nonequivalent β-protons (ICH_2) of 2, which also give overlapping doublets at 3.8–4.0 ppm. Similar ABX-type spectra have been observed for 1,2-dibromo-1-phenylethane ($BrCH_2CH(C_6H_5)Br$)[16] and 1-bromo-2-iodo-1-isobutoxyethane ($ICH_2CH(O\text{-}i\text{-}Bu)Br$).[17] The absence of lower-field resonances (δ >7) in Figure 4 further shows that the observed product is not an iodonium ion[18] but covalent diiodo adduct 2.

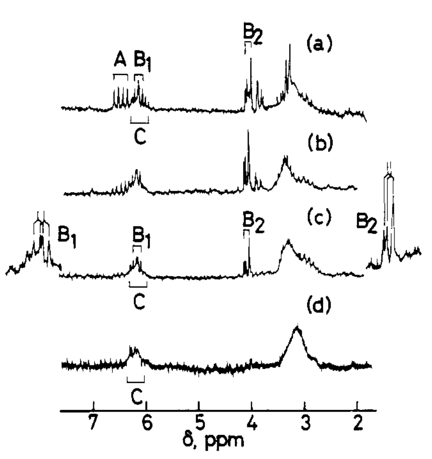


Figure 5. ^1H NMR spectra of a polymerization solution of IBVE initiated by HI/I_2 in *n*-hexane: $[IBVE]_0 = 42$ mM; $[HI]_0 = [I_2]_0 = 12.5$ mM. Temperature and reaction time: (a) −70 °C, 5 min; (b) −50 °C, 21 min; (c) −50 °C, 26 min; (d) −30 °C, 31 min.

Upon a gradual rise of temperature to −15 °C (Figure 4c), the polymerization of IBVE proceeded (decrease in the vinyl protons), but adduct 2 was still observable and its concentration virtually unchanged until the end of the polymerization.

UV/Visible Spectroscopy. Figure 2b shows the UV/visible spectrum of the polymerization solution with iodine at −25 °C. Immediately after iodine was mixed with excess IBVE in *n*-hexane, a strong absorption appeared at 270 nm along with that of the unreacted iodine (520 nm). At this stage no polymers formed and ca. 13% of the initially supplied iodine remained in the solution. The 270-nm band was very similar to that of adduct 1 (Figure 2a) but the ϵ_{max} was nearly doubled. It has been reported[18] that an α,ω-diiodo alkane (IRI) exhibits a UV absorption at nearly the same position as the corresponding monoiodo alkane (HRI) whereas the ϵ_{max} is twice that of the latter. Therefore, the observed absorption is assignable to the diiodo adduct 2, which was also observed by ^1H NMR (Figure 4).

The absorbance of the 270-nm band remained almost unchanged until all the monomer had been polymerized. The concentration of unreacted iodine (520-nm band) also stayed nearly constant throughout the polymerization. At the end of the reaction, however, the absorption of iodine increased considerably and the reaction mixture became turbid (see below).

Thus, the NMR and UV analyses showed that in the IBVE polymerization by iodine alone, adduct 2 is produced and remains intact throughout the reaction. Another important finding is the presence of unreacted iodine at a nearly constant concentration (ca. 13% of $[I_2]_0$). The unreacted iodine may be free or weakly interacting (π-complexed) with IBVE monomer.

3. Polymerization by HI/I_2 Initiator in *n*-Hexane. NMR Spectroscopy. After establishing the formation of adduct 1 by HI and adduct 2 by iodine from IBVE, we then studied spectroscopically the living polymerization of this monomer by the HI/I_2 initiating system in *n*-hexane.

Figure 5 illustrates a series of ^1H NMR spectra of a polymerization solution with HI/I_2 initiator ($[IBVE]_0 = 42$ mM, $[HI]_0 = [I_2]_0 = 12.5$ mM). The reaction mixture was prepared at −70 °C and the temperature was gradually raised to −30 °C. Adduct 1 was quantitatively formed immediately after the addition of HI to a monomer solution at −70 °C (cf. Figure 1b). When iodine was added to

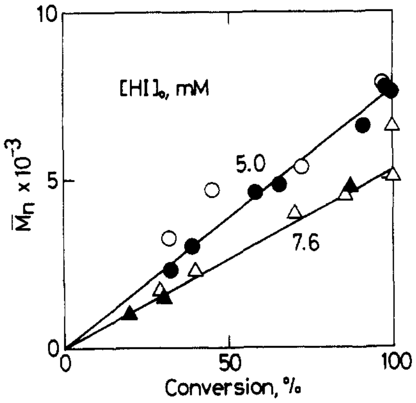


Figure 6. $\bar{M}_n$ vs. conversion relationships for poly(IBVE) obtained by HI/I_2 initiator in *n*-hexane at -25 °C at $[IBVE]_0$ = 0.38 M. $[HI]_0$ and $[I_2]$ (mM): (●) 5.0, 5.0; (○) 5.0, 10; (▲) 7.6, 7.6; (△) 7.6, 5.0.

this mixture at the same temperature (Figure 5a), the resonance of the α-proton of **1** (peak C; 6.0–6.3 ppm) became broader, and concurrently the signals of adduct **2** (peaks B_1 and B_2) appeared. Peak B_1 (CHI) is seen at 6.1–6.3 ppm as a doublet of doublet overlapping with broad peak C (cf. Figure 4b); peak B_2 (CH_2I, 4.0–4.2 ppm) is also overlapping with the vinyl proton signals. Thus, adducts **1** and **2** were found to coexist at the beginning of the polymerization by HI/I_2. The broadening of peak C indicates that the CHI unit of adduct **1** is incorporated into a polymer terminal (~~~$CH_2CH(O$-*i*-Bu)I) as the polymerization proceeds. Separate experiments showed that such a broadening of peak C did not occur when iodine was mixed with adduct **1** in the absence of IBVE monomer.

Upon a gradual rise in temperature to -50 °C (Figure 5b,c), polymerization of IBVE further proceeded, as indicated by the decrease of the vinyl protons (e.g., peak A) relative to those of **1** and **2**. Importantly, peaks B_1 and C due to the CHI units were still observed until all the monomer had depleted (Figure 5c). After 5 min from the end of the polymerization, however, the diiodo compound **2** (peaks B_1 and B_2) completely disappeared, while peak C (CHI units) remained unchanged (Figure 5d).[19] This indicates that adduct **1** or the CHI unit of the living polymer end exists consistently throughout the living polymerization by HI/I_2.

NMR measurements extended to lower field (up to 18 ppm) failed to detect any ionic (carbenium, oxonium,[8] or halonium[18]) species during and after the polymerization.

UV/Visible Spectroscopy. Figure 2c illustrates the UV/visible spectrum of a polymerization solution initiated by HI/I_2 in *n*-hexane at -25 °C ($[IBVE]_0$ = 50 mM, $[HI]_0$ = 0.60 mM). As already described (Figure 2a), a mixture of IBVE and HI shows an absorption at 270 nm. Addition of iodine to this mixture led to an increase in absorbance of this band, and the absorption of iodine was also observed at 520 nm. The absorbance at 270 nm was close to the sum of those of adducts **1** (Figure 2a) and **2** (Figure 2b) obtained at the same concentrations of HI and iodine. The concentration of unreacted iodine, determined from the 520-nm band, remained virtually constant throughout the reaction and was nearly the same as that observed for the iodine-initiated polymerization (cf. Figure 2b).

These facts support the coexistence of adduct **1** (and its polymeric homologues) and adduct **2** in the polymerization by HI/I_2. The UV/visible analysis also revealed that a constant amount of the added iodine remains unreacted until the end of the living process.

Effect of HI/I_2 Concentration Ratios. To obtain a further insight into the roles of HI and iodine in the living polymerization by HI/I_2 initiator, IBVE was polymerized at different concentration ratios of the two components ($[HI]_0$ and $[I_2]_0$). Figure 6 shows the $\bar{M}_n$ vs. conversion plots for poly(IBVE) thus obtained. All of the polymers exhibited a nearly monodisperse MWD ($\bar{M}_w/\bar{M}_n \le 1.1$) and their $\bar{M}_n$'s were directly proportional to conversion (living polymerization).

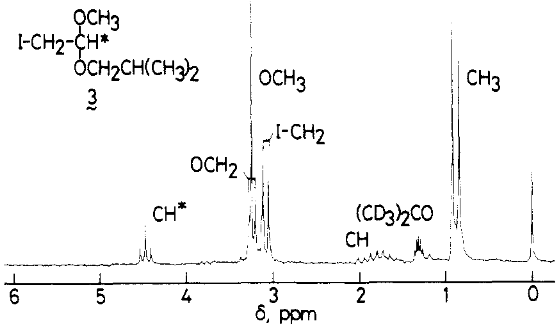


Figure 7. ^1H NMR spectrum of acetal **3** (10 mM) in CCl_4 at +30 °C.

Within the range of the $[HI]_0/[I_2]_0$ ratios examined, the $\bar{M}_n$ vs. conversion plots for the same $[HI]_0$ fell on a single straight line passing through the origin, irrespective of $[I_2]_0$, and the observed $\bar{M}_n$ values were in good agreement with those calculated with the assumption that one HI molecule yields one living chain. Therefore, the polymer molecular weight is dependent only on $[HI]_0$ and independent of $[I_2]_0$. The overall reaction rate, however, increased with increasing $[I_2]_0$ at the same $[HI]_0$. These results indicate that HI is solely responsible for the formation of the living propagating species, whereas iodine accelerates its propagation.

Methanolysis of Iodine–IBVE Adduct 2. The NMR spectra shown in Figure 5 indicate the inertness of adduct **2** in the polymerization by HI/I_2. This implies that this diiodo compound should exist in the reaction mixture even at a high IBVE conversion. To confirm this conclusion, we isolated **2** by converting it into the corresponding, more stable acetal (**3**, eq 3 below) via methanolysis. Thus, IBVE was polymerized by HI/I_2 initiator at -25 °C in *n*-hexane ($[IBVE]_0$ = 0.38 M, $[HI]_0 = [I_2]_0$ = 10 mM), and the reaction was quenched with ammoniacal methanol immediately after its completion. Fractionation of the products by preparative gel permeation chromatography gave a low-molecular-weight compound soluble in methanol, along with poly(IBVE) ($\bar{M}_n \sim 3600$, $\bar{M}_w/\bar{M}_n = 1.06$).

On the basis of its ^1H NMR spectrum (Figure 7), this product was identified as an acetal (**3**) derived from adduct **2** (eq 3). Peak assignments were as follows: δ 4.4–4.6 (t),

$$\underset{\mathbf{2}}{ICH_2CHIO\text{-}i\text{-}Bu} \xrightarrow[-HI]{CH_3OH} \underset{\mathbf{3}}{ICH_2CH(OCH_3)O\text{-}i\text{-}Bu} \quad (3)$$

OCHO; 3.44 (s), OCH_3; 3.2–3.4 ppm (d), ICH_2. Acetal **3** most likely forms via the reaction of adduct **2** with methanol followed by elimination of HI (eq 3). The isolated yield of **3** was about 50 mol % relative to the iodine initially supplied, and roughly corresponded to the consumption of the iodine (87 mol %) determined by UV/visible spectroscopy (Figure 2c), when a loss of **3** during its isolation and workup was taken into consideration. The successful isolation of **3** further shows the existence of **2** even at the end of the polymerization by HI/I_2.

Discussion

The above-described results obtained for the living polymerization of IBVE by HI/I_2 initiator are summarized as follows:

(1) Prior to the polymerization, HI adds quantitatively to IBVE to yield adduct **1** (eq 1; Figure 1).

(2) HI or **1** alone can hardly polymerize IBVE (no polymers in 2 days).

(3) Addition of iodine to an apparently quiescent mixture of IBVE and HI, however, induces a polymerization without an induction phase and yields monodisperse living polymers. The CHI terminal groups are observable throughout the living process (Figure 5).

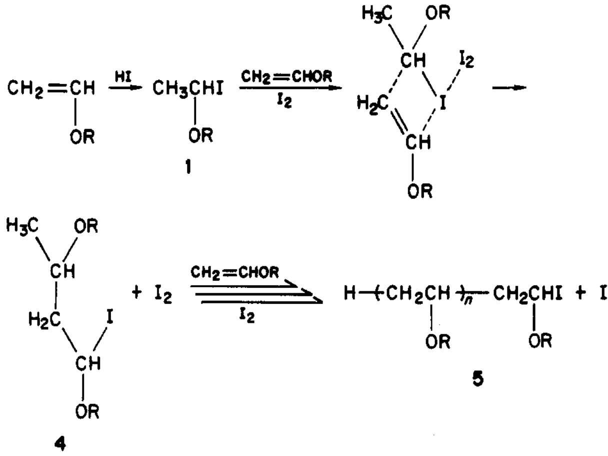
(4) The added iodine in part forms adduct **2** (eq 2) which remains intact throughout the living polymerization and can be isolated as acetal **3** via methanolysis (Figure 7). The remainder of the iodine stays free in the reaction mixture at a constant concentration.

(5) Adduct **2** forms also in the polymerization by iodine alone (Figure 4), in which a part of iodine remains unreacted. The iodine-initiated polymerization involves a slow initiation, as indicated by the presence of an induction phase.[1]

(6) The $\bar{M}_n$ of the living polymer produced by HI/I_2 initiator is dependent only on the HI concentration and independent of the iodine concentration (Figure 6).

Results 2 and 3 indicate that added (free) iodine "activates" adduct **1** so as to initiate polymerization. NMR analysis (result 3) showed the presence of CHI terminals similar to that of **1** throughout the reaction, and these end groups may also be activated by iodine.

On the basis of these facts, we now propose a propagation mechanism illustrated in eq 4 for the HI/I_2-initiated living polymerization ($R = CH_2CH(CH_3)_2$). The initial reaction is the formation of adduct **1** from IBVE and HI (eq 1). The C–I bond of **1** is then activated by the electrophilic interaction of (free) iodine with the terminal iodine, and propagation proceeds via the insertion of IBVE monomer into the activated C–I bond. The resulting dimeric species (**4**) again has a C–I terminal bond that is in turn activated by iodine. Successive insertion of the monomer into the activated C–I end eventually leads to living polymer **5**. Note that this growing polymer **5** and adduct **1** have the C–I terminals almost identical in nature.



(4)

According to the UV/visible spectroscopic analysis (Figure 2), added iodine partly forms adduct **2** and partly stays free, probably in equilibrium with **2**; and the free iodine acts as an "activator" for the C–I terminals. Since the $\bar{M}_n$ of the living polymer is determined by the HI concentration only (result 6), initiation by adduct **2** should be negligible as long as reaction 4 proceeds. Apparently, the CH(OR)–I bond of **2** is much less reactive than those of **1**, **4**, and **5**, because of the electron-withdrawing iodine on the β-carbon. If a concurrent initiation by **1** and **2** took place, the resulting polymer would show a broad MWD, rather than the nearly monodisperse MWD actually observed.[1]

The main factor leading to living polymers in the HI/I_2-initiated polymerization may be that, during most of its lifetime, the propagating end bears a stable covalent structure that in turn prevents chain transfer (β-proton elimination) and termination. This stable propagating end, however, must be "activated" by iodine so that its electrophilic addition (propagation) to IBVE can take place. Interestingly, a similar propagation mechanism involving an activated covalent bond has recently been proposed for the group-transfer (living) polymerization of methacrylate monomers,[20] in which an O–Si bond is activated by a nucleophilic anion (as catalyst), whereas in the HI/I_2-initiated process the terminal CH–I bond is activated by electrophilic iodine.

The activation of a covalent carbon–halogen bond is not unusual in cationic polymerization. For example, initiation by the alkyl halide/Lewis acid system (e.g., *tert*-butyl chloride/$Al(C_2H_5)_2Cl$) involves the activation (dissociation) of the C–halogen bond of the alkyl halide by an electrophilic Lewis acid. The living polymerization by HI/I_2 is, however, unique in that not only the initiation process but "each" propagation step requires the activation by iodine.

The propagation mechanism shown in eq 4 is also applicable to the polymerization by iodine alone. In this reaction, adduct **2** is first formed and this diiodide may be activated by remaining iodine so that IBVE can insert into its CH(OR)–I bond. Since **2** is much less reactive than **1** (see above), the initiation is slower than in the HI/I_2-initiated polymerization, and thus the polymerization by iodine shows an induction phase. Once **2** reacts with IBVE, the resultant propagating end is essentially identical with that of **4** or **5**, more reactive than **2**. Therefore, the polymerization progressively accelerates and finally proceeds at nearly the same rate as in the HI/I_2-initiated process. This has in fact been observed in our previous study (see Figure 1, ref 1).

The existence of covalent propagating species was first proposed by Gandini and Plesch for the polymerization of styrene by perchloric acid.[21] According to their "pseudocationic" mechanism,[22] polystyryl esters of protonic acids in general and polystyryl perchlorate in particular might be the propagating species and styrene might insert into the carbon–oxygen bond of the esters. We have already shown[23] that at least one of the proposed ester species (polystyryl trifluoroacetate) itself cannot polymerize styrene, and there has been a dispute on the possibility of the propagation reaction via a covalent (ester) intermediate. Interestingly, in a recent study Plesch suggested the importance of the activation of the inherently inactive trifluoroacetate to induce polymerization of styrene.[24] It has also been reported that even an ester of a stronger acid (polystyryl perchlorate) is by itself "dormant" toward styrene at −78 °C and capable of polymerizing only more nucleophilic monomers (aziridines) at higher temperature.[25]

Another example of a possible covalent intermediate has been proposed for the polymerization of styrene and related monomers by iodine.[10-12] According to Giusti et al., iodine adds to styrene to form an α,β-diiodo compound (similar to **2**), but the diiodostyrene per se is inactive and releases HI that in turn initiates polymerization. These authors also suggested[10,11] the formation of HI–monomer adducts and the activation of their C–I bonds by iodine. It should be pointed out, however, that the iodine-initiated polymerizations of the aromatic monomers yield not living polymers but only oligomers in polar media and thus differ clearly from our living polymerization of vinyl ethers in nonpolar solvents.

The present study has provided the first direct spectroscopic evidence for the propagation reaction involving the activation of a covalent species in "cationic" polymerization of vinyl compounds, and this mechanism is of key importance for the formation of perfect living polymers. As we previously pointed out,[23] covalent species per se are not capable of polymerizing monomers, but they can react electrophilically with a carbon–carbon double bond when activated (e.g., by iodine) or when highly nucleophilic monomers are employed.[25] Therefore, this work has accounted for the longstanding apparent contradiction between the pseudocationic theory[21,22] and our experimental results on the styrene polymerization by trifluoroacetic acid.[23]

Registry No. 1, 95314-34-4; 3, 95314-33-3; HI, 10034-85-2; I_2, 7553-56-2; IBVE, 109-53-5.

References and Notes

(1) Miyamoto, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1984**, *17*, 265.
(2) Miyamoto, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1984**, *17*, 2228.
(3) Miyamoto, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1985**, *18*, 123.
(4) Eley, D. D.; Saunder, J. *J. Chem. Soc.* **1952**, 4167.
(5) Eley, D. D.; Seabrooke, A. *J. Chem. Soc.* **1964**, 2226.
(6) Eley, D. D.; Isack, F. L.; Rochester, C. H. *J. Chem. Soc. A* **1968**, 872, 1651.
(7) Higashimura, T.; Kanoh, N.; Okamura, S. *Makromol. Chem.* **1961**, *47*, 35 and subsequent papers.
(8) Ledwith, A.; Sherrington, D. C. *Polymer* 1971, *12*, 344.
(9) Johnson, A. F.; Young, R. N. *J. Polym. Sci., Polym. Symp.* **1976**, *56*, 211.
(10) (a) Giusti, P.; Pice, G.; Andruzzi, F. *Makromol. Chem.* **1966**, *98*, 170. (b) Cerrai, P.; Andruzzi, F.; Giusti, P. *Ibid.* **1968**, *117*, 128.
(11) Giusti, P.; Andruzzi, F. *J. Polym. Sci., Part C* **1968**, *16*, 3797.
(12) Maschio, G.; Cerrai, P.; Giusti, P. *Polym. Bull.* **1982**, *8*, 147; **1983**, *10*, 321.
(13) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. "Spectroscopic Identification of Organic Compounds", 4th ed.; Wiley: New York, 1981; Chapter 5.
(14) Some polymers were obtained after 1 month.[1] It is not clear at present whether the polymerization was initiated by HI per se or by a mixture of HI and iodine, the latter of which might form in situ via the oxidation/decomposition of the acid.
(15) Haszeldine, R. N. *J. Chem. Soc.* **1953**, 1764.
(16) Morrison, R. T.; Boyd, R. N. "Organic Chemistry", 4th ed.; Allyn and Bacon: Boston, MA, 1983; p 709.
(17) Miyamoto, M.; Sawamoto, M.; Higashimura, T., unpublished results (1983); δ 6.0 (dd, CH_2I) and 3.8–3.9 (dd, CHBr), $J = 3.9$ and 8.5 Hz (*n*-hexane, −10 °C).
(18) Olah, G. A.; Ballinger, J. M.; Brinich, J. *J. Am. Chem. Soc.* **1968**, *90*, 2587.
(19) After the disappearance of adduct **2**, the polymerization solution turned turbid and an insoluble material formed. No further attempts were made to identify this product.
(20) Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1983**, *105*, 5706.
(21) (a) Gandini, A.; Plesch, P. H. *Proc. Chem. Soc., London* **1964**, 240. (b) Gandini, A.; Plesch, P. H. *J. Polym. Sci., Part B* **1965**, *3*, 127.
(22) As a recent review on this subject, see, for example: Gandini, A.; Cheradame, H. *Adv. Polym. Sci.* **1980**, *34/35*, 1.
(23) Sawamoto, M.; Masuda, T.; Higashimura, T.; Kobayashi, S.; Saegusa, T. *Makromol. Chem.* **1977**, *178*, 389.
(24) Obrecht, W.; Plesch, P. H. *Makromol. Chem.* **1981**, *182*, 1459.
(25) Bossaer, P. K.; Goethals, E. J.; Hackett, P. J.; Pepper, D. C. *Eur. Polym. J.* **1977**, *13*, 489.

Two-Step Synthesis of Alkyl- and Alkenylbenzoxazole Polymers

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ABSTRACT: The conversion of several commercial and new AB monomers to polyamides and polybenzoxazoles was carried out through a two-step process. The monomers include 3-hydroxy-4-aminobenzoic acid and its 4,3 isomer, the analogous derivative of phenylacetic acid, 3-hydroxy-4-aminocinnamic acid and its isomer, and the two hydrocinnamic acid derivatives with HO and NH_2 in the 3- and 4-positions. Treatment of these monomers with a triphenylphosphine reaction mixture led to formation of polyamides containing hydroxyl substituents on the aromatic rings of the backbones. These polymers were characterized by IR, ^{13}C NMR, and TGA. Thermal cyclization of the polyamides gave the corresponding polybenzoxazoles in excellent yields and with viscosities up to 2.1 dL/g. IR was used to monitor the dehydration process and to characterize the polybenzoxazoles. TGA data for these polyheteroaromatics indicate reasonable thermal stability for the all-aromatic polymers as well as those containing alkene and a single methylene group in the polymer backbone. The two polymers containing CH_2CH_2 backbone units displayed catastrophic weight loss over a very narrow temperature range. This behavior is attributed, in part, to a thermal unzipping of the polymer backbone. Carbon NMR data are presented on new monomers and polyamides.

Introduction

Polymers with heteroaromatic repeat units have been known for many years to exhibit good thermal and oxidative stability. Polybenzimidazoles,[1] polybenzothiazoles,[2] and polybenzoxazoles[3] were first reported in the late 1950s and early 1960s and have since been under widespread investigation. Both AA–BB and AB monomer systems have been employed in the synthesis of high molecular weight polymers.[4] The thermal stability in nitrogen atmosphere of the completely aromatic AB polymers prepared from the various 3,4-disubstituted benzoic acid derivatives reportedly decreased in the order benzimidazole > benzothiazole > benzoxazole.[4] In air, however, the reported order of stability for AA–BB polymers was benzo-

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