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Chang G. Cho[a]; James E. McGrath[a]
[a] Department of Chemistry Polymer Materials and Interfaces Laboratory, Virginia Polytechnic Institute and State University, Blacksburg, Virginia

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KINETIC STUDY OF THE POLYMERIZATION OF ALKYL VINYL ETHERS BY HI/I_2 CATALYST

CHANG G. CHO and JAMES E. McGRATH

Department of Chemistry
Polymer Materials and Interfaces Laboratory
Virginia Polytechnic Institute and State University
Blacksburg, Virginia 24061

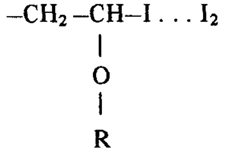
ABSTRACT

The polymerization of alkyl vinyl ethers initiated by hydrogen iodide and iodine catalyst has been studied in detail. The polymerization showed living behavior in nonpolar solvents at low (-15°C) temperatures as reported earlier by others. The observed rate of polymerization under the reaction conditions was linearly dependent on the initial concentration of hydrogen iodide and iodine, respectively. However, the monomer concentration did not influence the rate of polymerization (apparent zero order). From the observed rate equation, two possible reaction schemes were proposed and attempts were made to distinguish them by using UV/visible spectroscopy and ^{13}C-NMR spectroscopy. In both schemes a reversible interaction between monomer and an iodine molecule was postulated as a necessary elemental reaction to fit the observed expression for rate of polymerization. From the spectroscopic analysis results, the interaction between the iodide compound (chain end) and the iodine molecule seems to be very weak compared to the interaction between monomer and the iodine molecule.

INTRODUCTION

Alkyl vinyl ethers have long been known to polymerize readily with iodine since Wislicenus [1] reported these types of reactions in 1878. This work was extended by Giusti and Andruzzi [2], who used iodine as a catalyst and hydrogen iodide as a "cocatalyst" for styrene polymerizations. They observed that the degree of polymerization was inversely proportional to the initial amount of hydrogen iodide in the styrene polymerization.

Recently, Higashimura et al. [3, 4] reported the living polymerization of a series of alkyl vinyl ethers initiated by a mixture of hydrogen iodide and iodine. The degree of polymerization of the poly(alkyl vinyl ethers) was inversely proportional to the initial amount of hydrogen iodide, and the molecular weight distributions (MWD) were quite narrow. The propagating chain end was proposed to have a relatively stable covalentlike structure, such as **1**, which is activated for polymerization by iodine.



$$-CH_2-\underset{\substack{|\\ O\\ |\\ R}}{CH}-I\ldots I_2$$

1

There are relatively few kinetic measurements of the polymerization of alkyl vinyl ethers initiated by the hydrogen iodide-iodine system, which is in marked contrast to the wealth of data available for iodine-initiated polymerizations. A kinetic investigation appeared necessary in order to establish reliable data which could be used to generate possible mechanistic reaction schemes. In the present work, rates of polymerizations of *n*-butyl vinyl ether (nBVE) and ethyl vinyl ether (EVE) were measured, and the effects of hydrogen iodide, iodine, and monomer concentrations on the rates of polymerizations were determined and expressed as rate equations. In conjunction with spectroscopic measurements, the observed rate equation has been analyzed in an attempt to gain information about the polymerization reaction.

EXPERIMENTAL

Materials

n-Butyl vinyl ether (Aldrich) and ethyl vinyl ether (Polysciences) were washed three times with 5% aqueous sodium hydroxide solution and subsequently with distilled water until the pH became neutral. These monomers were dried over potassium hydroxide pellets, fractionally distilled over calcium hydride (through a 150-mm column packed with glass beads of 5 mm diameter), and then finally distilled over sodium metal under dry argon. *n*-Hexane (Baker, HPLC Grade) was treated with concentrated sulfuric acid, washed thoroughly with water, and dried over anhydrous sodium sulfate. Thereafter, it was distilled over sodium metal under dry argon. Carbon tetrachloride (Fisher, spectral analyzed) was distilled over calcium hydride under dry argon. Hydrogen iodide was obtained from a 57% solution (Aldrich) by dehydration with phosphorus pentoxide [2] and stored as a *n*-hexane or carbon tetrachloride solution in a freezer (-20°C). For a normality determination, the solution was extracted with distilled water, then titrated with 0.1 *N* alcoholic potassium hydroxide solution by using a Fisher automatic titrator. Iodine (Fisher, resublimed) was purified by sublimation from the mixture of iodine with potassium iodide and ignited lime.

Procedures

Polymerizations of alkyl vinyl ethers were carried out in septum-stoppered flasks in a bath which was protected from light. The bath temperature was controlled by a Neslab immersion cooler.

Polymerization was initiated by the addition of hydrogen iodide solution to the monomer solution, followed by the injection of the iodine solution. Reaction time was taken to start at the moment when the iodine solution was injected. After a given time, the polymerization was quenched by injecting a triethylamine-methanol (2/6 v/v) solution.

In order to measure the yield, the unreacted monomer and solvent in the quenched reaction mixture were removed by rotary evaporator, and the polymer mixture was dried in a vacuum oven (1 torr) at ~55°C for 3 d. In the yield calculation, the weight of the initiator was subtracted from the total dried weight.

For analysis of the polymers, the products were dissolved in *n*-hexane, washed with 5% aqueous sodium thiosulfate solution, then with distilled water, and dried over anhydrous sodium sulfate. Then, the solvent was removed under vacuum by a rotary evaporator. Molecular weights and distributions of the polymers were measured by gel permeation chromatography (GPC) using polystyrene standards. Number-average molecular weights were also measured directly by vapor-phase osmometry (VPO).

NMR Spectroscopy

^{13}C-NMR spectra (50.3 MHz) were recorded on a Bruker WP-200SY spectrometer in CCl_4 at -20°C with deuterated acetonitrile as a locking solvent in a 5-mm (od) inner tube. All solutions were transferred under dry nitrogen via dry syringes into a septum-capped NMR sample tube (10 mm o.d.) which was placed in a low-temperature bath (-20°C). Then, the NMR sample tube was cooled in a Dry-Ice/acetone bath in order to avoid undesirable temperature build-up during the transfer to the NMR probe. Proton decoupled ^{13}C-NMR spectra were obtained with nuclear Overhauser enhancement. ^{1}H-NMR spectra were recorded on a Bruker WP-270SY spectrometer at room temperature.

UV/Visible Spectroscopy

UV/visible spectra were recorded on a Perkin-Elmer 552 spectrophotometer. Solutions were injected via dry syringes into a septum-stoppered quartz cell which was placed in a methanol bath (-21°C). Enough time was allowed to attain temperature equilibrium, then the cell was quickly inserted into the cell chamber of the spectrophotometer. The cell chamber was purged with dry argon throughout this experiment to prevent possible moisture condensation. A fast scan speed (480 nm/min) was used in order to minimize the temperature change of the cell during the measurement.

RESULTS

The addition of hydrogen iodide (HI) to the double bond of a monomer (M) was very rapid. This fact was checked with NMR by the addition of a stoichiometric amount of hydrogen iodide to the monomer in carbon tetrachloride solution. The resultant compound was the addition product $CH_3CHI{-}O{-}$alkyl (RI). This observation was very similar to that of Higashimura et al. [4]. However, at room temperature the RI seems to be un-

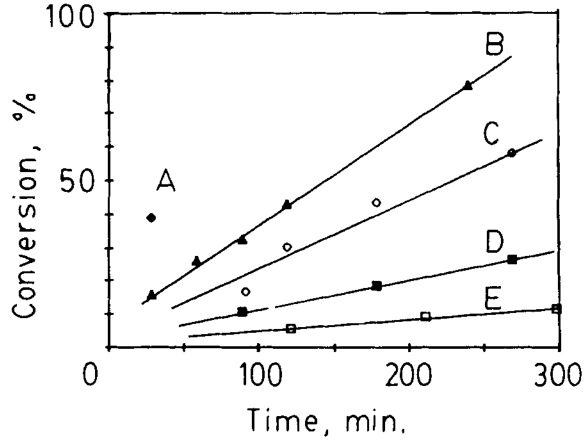


FIG. 1. Time-conversion plots of nBVE polymerization at various temperatures in *n*-hexane: $[M]_0 = 1.77$ mol/L, $[HI]_0 = 8.73$ mmol/L, $[I_2]_0 = 8.49$ mmol/L; (A) -5°C, (B) -16°C, (C) -25°C, (D) -35°C, (E) -45°C.

stable, and the instability is a function of the nature of R. Proton NMR spectra of the compound in $CCl_4/CDCl_3$ solution (3/1 v/v) was observed to change, and the NMR peaks became quite different after about 2 h.

The color of the iodine disappeared as soon as the iodine solution was injected into the polymerization system. Only a slight yellow tint was observed, and this color did not appear to change until the polymerization was nearly complete. When the reaction mixture was quenched by the triethylamine-methanol mixture during the polymerization, the color turned to orange and slowly disappeared.

Figure 1 shows some kinetic curves of the polymerization of nBVE with constant iodine, hydrogen iodide, and monomer concentrations at different reaction temperatures in *n*-hexane. The plots of percent conversion versus time afforded straight lines, with decreasing slopes as the polymerization temperature was decreased. The rate of polymerization (R_p) showed a zero-order dependence on the monomer concentration.

For further confirmation of the effects of monomer concentration on the polymerization, the initial concentration of the monomer was reduced to 0.17 mol/L from 1.7 mol/L. Still, the time versus conversion plot showed a linear relationship (Fig. 2). When the reaction medium was changed from hexane to carbon tetrachloride, the rate of polymerization increased. EVE showed a

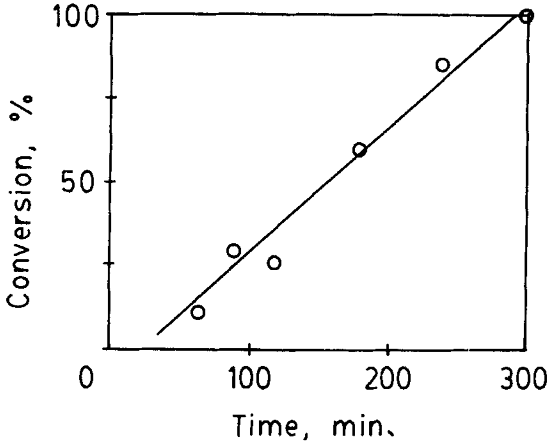


FIG. 2. Time-conversion plot of nBVE polymerization at low monomer concentration in *n*-hexane: $[M]_0 = 0.173$ mol/L, $[HI]_0 = 2.42$ mmol/L, $[I_2]_0 = 2.31$ mmol/L, temperature = -15.5°C.

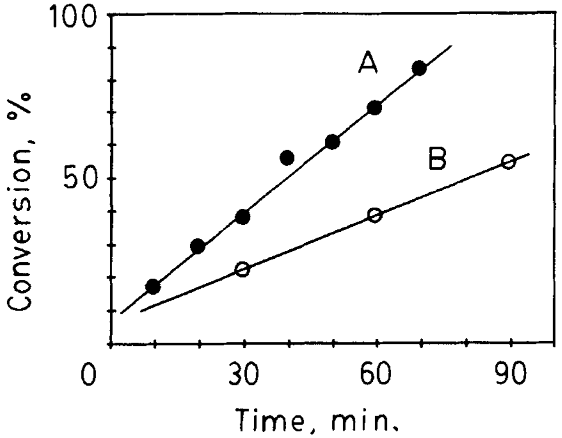


FIG. 3. Time-conversion plots of nBVE and EVE polymerizations in CCl_4: $[M]_0 = 1.77$ mol/L, $[HI]_0 = 8.7$ mmol/L, $[I_2]_0 = 8.5$ mmol/L, temperature = -16°C; (A) EVE, (B) nBVE.

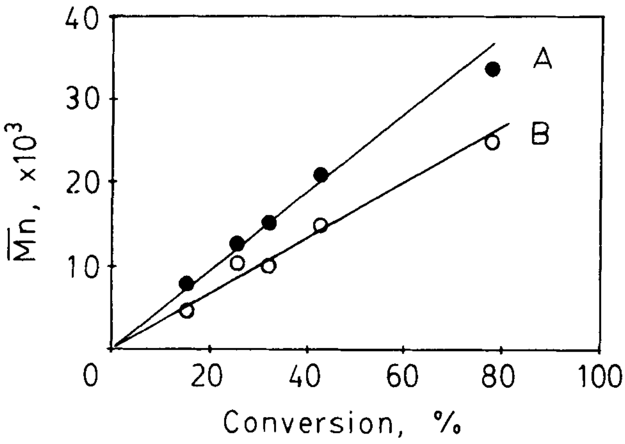


FIG. 4. Conversion-$\bar{M}_n$ plot of poly(nBVE) obtained at -16°C in *n*-hexane: $[M]_0$ = 1.77 mmol/L, $[HI]_0$ = 8.73 mmol/L, $[I_2]_0$ = 8.49 mmol/L; (A) GPC with polystyrene standard, (B) VPO.

more rapid polymerization than nBVE, as indicated in Fig. 3. However, deviation from a straight line occurred due to the inaccurate temperature control of the polymerization bath in this case.

Figure 4 shows the dependence of the number-average molecular weight ($\bar{M}_n$) of poly(nBVE) on the conversion. The polymer molecular weight was directly proportional to the conversion for a given condition. Also, the molecular weight distributions (MWD) were quite narrow (Fig. 5) as expected in a living polymerization.

To determine the effects of iodine concentration on the polymerization, the concentration of hydrogen iodide and monomer were fixed, and the ratio of iodine to hydrogen iodide was varied. Figure 6 shows the dependence of the polymerization conversion of nBVE on the initial ratio of iodine to hydrogen iodide for a given polymerization time. Conversion and $\bar{M}_n$ of the polymer were linearly proportional to the initial concentration of iodine. When no iodine was added, polymerization did not occur. The concentrations of active species calculated from conversion/$\bar{M}_n$ were essentially equal to the initial hydrogen iodide concentrations.

In these experiments the following facts were observed: 1) living polymerization; 2) zero-order dependence of R_p on the monomer concentration; 3) first-order dependence of R_p on the initial iodine concentration; 4) first-order

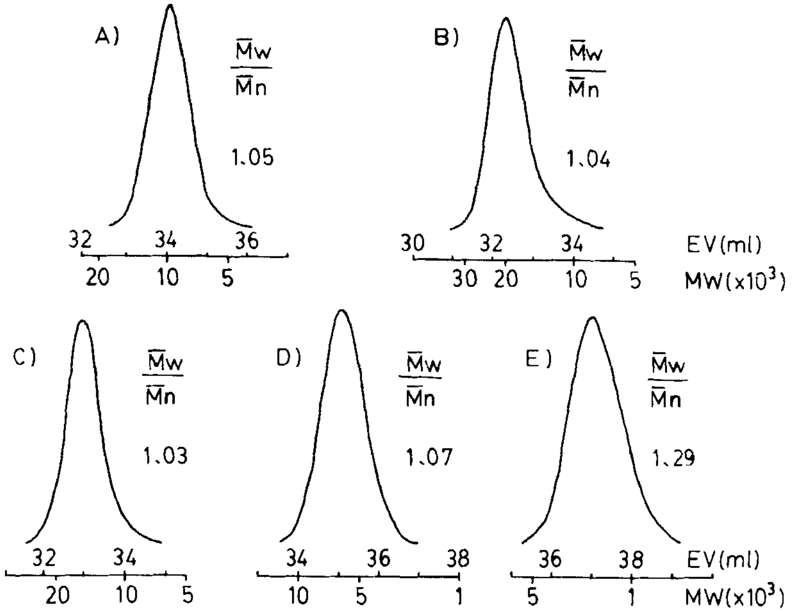


FIG. 5. MWD of poly(nBVE) obtained at various temperatures in *n*-hexane. Temperature (% conversion): (A) -5°C (39), (B) -15.5°C (100), (C) -25°C (58), (D) -35°C (27), (E) -45°C (12).

dependence of R_p on the initial hydrogen iodide concentration. Thus, the observed rate of polymerization could be expressed as

$$R_p = k_{pzn}[I_2]_0[HI]_0 \tag{1}$$

where $[I_2]_0$ is the initial concentration of iodine and $[HI]_0$ is the initial concentration of hydrogen iodide. The apparent rate constant of the polymerization, k_{pzn}, and the experimentally determined rate constants of the polymerization are shown in Table 1.

The overall activation energy of the polymerization of nBVE in *n*-hexane was calculated from an Arrhenius plot and found to be about 9.1 kcal/mol (38 kJ/mol). This value is very similar to the 9.7 kcal/mol which was obtained earlier from the polymerization of nBVE in heptane using a metal sulfate-sulfuric acid complex catalyst [5] and to the 10.0 kcal/mol obtained from the polymerization of 2-ethylhexyl vinyl ether in petroleum ether using

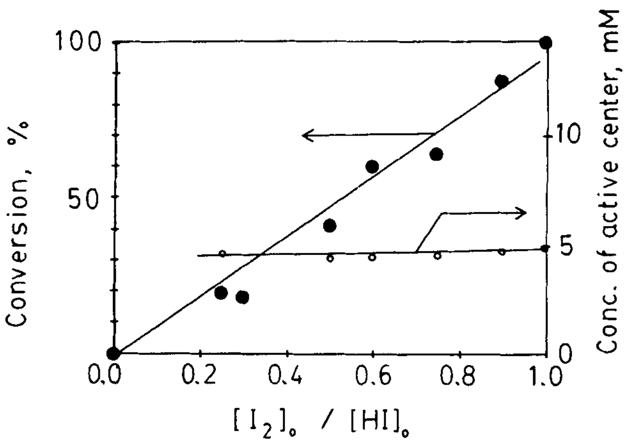


FIG. 6. Effect of initial ratio of iodine/hydrogen iodide on the conversion of poly(nBVE), and concentration of active center: $[M]_0$ = 0.773 mol/L, $[HI]_0$ = 5.13 mmol/L, reaction temperature = -15.5°C; reaction time = 5 h, solvent = *n*-hexane.

TABLE 1. Apparent Propagation Rate Constant (k_{pzn}) of nBVE and EVE in the Polymerization Initiated by HI/I_2 Catalyst (L/mol•min)

		Temperature, °C			
		-16	-25	-35	-45
nBVE	*n*-Hexane	71	52	21	7.8
	CCl_4	137			
EVE	CCl_4	271			

iodine [6]. However, it is higher than the values (~6 to ~7 kcal/mol) reported for polymerizations initiated with free ion salts [7-9].

DISCUSSION

This polymerization reaction consists of several elementary reactions, and the combination of the major elementary reactions appears to fit the observed rate of polymerization.

One possible major reaction is the reversible equilibrium between iodine and monomer. This equilibrium (equilibrium constant $K_{1\text{eq}}$) has been studied by many workers [10], and the majority of the reports conclude that a charge-transfer complex is formed.

$$\text{M (monomer)} + I_2 \overset{K_{1\text{eq}}}{\rightleftharpoons} \text{C (complex)}. \tag{2}$$

Also, it has been suggested that the reversible equilibrium may not be truly a charge-transfer complexation, but rather, could involve reversible diiodide formation [11, 12].

$$C + I_2 \longrightarrow ICH_2CH(OR)I + I_2. \tag{3}$$

Both opinions could be reasonable, depending on the relative reactivity of the diiodide with monomer compared to the propagation reaction. If the reactivity of the diiodide was similar to that of the iodide, the diiodide formation would increase the total concentration of iodides and should lead to broader molecular weight distributions. This has not been observed in these HI/I_2 initiated systems. To comply with the observed living nature of the polymerization, under the given polymerization conditions, the possible diiodide formation reaction [11, 13] between iodine and the complex would have to be slow enough to be neglected. This reaction would only become significant if the amount of iodine is large compared to that of hydrogen iodide. Slow diiodide formation could explain the induction periods observed by many workers in the polymerizations of alkyl vinyl ethers initiated with iodine only. If the reactivity of the diiodide is very low compared to that of the iodide [4], reversible diiodide formation would not significantly increase the number of propagating chain ends and the observed living behavior is explainable. Also, the initiation reaction for simple iodine-initiated polymerization is porbably not the reaction of Eq. (3), but it could involve the dimeric iodide formed by the reaction between diiodide and iodine molecule in the presence of monomer.

In this work the disappearance of the iodine color seems to be consistent with the formation of a "charge transfer complex, C," whose identity is somewhat different from a normal charge-transfer complex, due to its exceptionally strong interaction (heat of reaction, ΔH = -33 kcal/mol) and reversible equilibrium [11]. The structure of the complex may be similar to that of the diiodide structure in a classical reaction coordinate, but, in any event, the iodine must be in close contact in order to attain fast equilibrium.

In addition to the complexation between monomer and iodine, the iodine could also form another charge transfer complex $RI{-}I_2$ with the iodide compounds, RI, in the reaction system.

$$RI + I_2 \xrightleftharpoons{K_{2eq}} RI{-}I_2. \tag{4}$$

This equilibrium (equilibrium constant K_{2eq}) could be assumed reasonably from the fact that iodine acts as a Lewis acid and can attract an iodide ion to make a triiodide ion as in the equilibrium

$$KI + I_2 \rightleftharpoons KI_3.$$

The equilibrium constant toward the KI_3 formation has been reported to be ~740 *in an aqueous medium* at room temperature [14]. Likewise, the iodine molecule will attract iodine in the carbon–iodine bond, but the extent of the attraction will depend on the nature of the carbon–iodine bond. This complexation will be further discussed below.

Identification of the correct reaction scheme relies on defining the propagation reactions. One possible propagation mode is (A), the reaction between charge-transfer complex C and iodide compound RI. Another possibility is (B), the insertion of a monomer into the activated carbon–iodine bond in the complex. The former reaction (A) can be assumed to be due to the nature of the charge-transfer complex. The exceptionally strong interaction (and the corresponding ΔH [11]) and reversible equilibrium between iodine and monomer suggest that the complex has the possibility of being somewhat activated, which is different from the idea of an inactive [15] complex. If iodine is present on one side of the charge-transfer complex, an imaginary transition state, a six-membered ring structure as proposed for a typical pseudocationic polymerization [16], can be drawn for the propagation reaction. The importance of the complexation between monomer and catalyst was also reported in the polymerization of styrene initiated by perchloric acid [17]. For example, the polymerization of styrene by trifluoroacetic acid, it has been reported that the reaction cannot be represented by a single, simple equation [18]. These reports imply that there has to be some route for activation of chain ends which differs from conventional activation routes. On the other hand, the latter reaction (B) will be very similar to a conventional ionic propagation or propagation in which the propagating chain end is activated by catalyst [19, 20].

Kinetic Reaction Schemes

Fast addition of hydrogen iodide (HI) to a monomer (M) leads to an iodide compound (RI), and the reactivity of the monomeric iodide RI is assumed to be equal to that of polymeric iodide. Here, the total concentration of iodide compounds is designated as $[RI]_0$, and $[RI]_0 = [HI]_0$ from the living nature of this polymerization. Both propagation modes mentioned above fit the observed zero-order dependence of R_p on the monomer concentration. Also, the combination of these two leads to the same result. The following are the possible two reaction schemes.

Reaction Scheme A

The chain grows via interaction between the monomer-iodine charge-transfer complex and the iodide compound.

Iodide formation:

$$M + HI \longrightarrow RI. \tag{5}$$

Complexation of I_2:

$$M + I_2 \xrightleftharpoons{K_{1eq}} C. \tag{2}$$

Chain growth:

$$RI + C \xrightarrow{k_p} RI + I_2, \tag{6}$$

where k_p = rate constant of propagation reaction.

Rate of polymerization:

$$R_p = k_p[\mathrm{RI}][\mathrm{C}] = k_p[\mathrm{HI}]_0[\mathrm{C}]. \tag{7}$$

From the equilibrium constant, [C] becomes

$$[\mathrm{C}] = K_{1\mathrm{eq}}[\mathrm{M}][\mathrm{I_2}], \tag{8}$$

and the total concentration of iodine becomes the initial concentration of iodine, then,

$$[\mathrm{I_2}]_0 = [\mathrm{C}] + [\mathrm{I_2}]. \tag{9}$$

From Eqs. (8) and (9),

$$[\mathrm{C}] = K_{1\mathrm{eq}}[\mathrm{I_2}]_0[\mathrm{M}]/(1 + K_{1\mathrm{eq}}[\mathrm{M}]). \tag{10}$$

Then, by the substitution of Eq. (10) into Eq. (7), the rate of polymerization becomes

$$R_p = k_pK_{1\mathrm{eq}}[\mathrm{HI}]_0[\mathrm{I_2}]_0[\mathrm{M}]/(1 + K_{1\mathrm{eq}}[\mathrm{M}]), \tag{11}$$

$$\cong k_p[\mathrm{HI}]_0[\mathrm{I_2}]_0, \quad \text{for } K_{1\mathrm{eq}}[\mathrm{M}] \gg 1. \tag{12}$$

Reaction Scheme B

The chain grows via insertion of a monomer into the activated carbon–iodine bond.

Iodine formation:

$$\mathrm{M + HI \longrightarrow RI.} \tag{5}$$

Complexation of I_2:

$$\mathrm{M + I_2} \xrightleftharpoons{K_{1\mathrm{eq}}} \mathrm{C}, \tag{2}$$

$$\mathrm{RI + I_2} \xrightleftharpoons{K_{2\mathrm{eq}}} \mathrm{RI{-}I_2}. \tag{13}$$

Chain growth:

$$\mathrm{RI{-}I_2} + \mathrm{M} \xrightarrow{k_p'} \mathrm{RI{-}I_2}, \tag{14}$$

where k_p' = rate constant of the propagation reaction.

Rate of polymerization:

$$R_p = k_p'[\mathrm{M}]\,[\mathrm{RI{-}I_2}]. \tag{15}$$

From the equilibrium constants,

$$[\mathrm{C}] = K_{1\mathrm{eq}}[\mathrm{I_2}\,[\,]\mathrm{M}]. \tag{8}$$

$$[\mathrm{RI{-}I_2}] = K_{2\mathrm{eq}}[\mathrm{RI}]\,[\mathrm{I_2}]. \tag{16}$$

And from the mass balance of $[\mathrm{I_2}]_0$ and $[\mathrm{RI}]_0$,

$$[\mathrm{I_2}]_0 = [\mathrm{I_2}] + [\mathrm{C}] + [\mathrm{RI{-}I_2}] \tag{17}$$

and

$$[\mathrm{RI}]_0 = [\mathrm{RI}] + [\mathrm{RI{-}I_2}]. \tag{18}$$

Then it becomes

$$\begin{aligned}[\mathrm{RI{-}I_2}] &= K_{2\mathrm{eq}}[\mathrm{RI}]_0[\mathrm{C}]/(K_{2\mathrm{eq}}[\mathrm{C}] + K_{1\mathrm{eq}}[\mathrm{M}]),\\ &\cong K_{2\mathrm{eq}}[\mathrm{RI}]_0[\mathrm{C}]/(K_{1\mathrm{eq}}[\mathrm{M}]), \quad \text{for } K_{1\mathrm{eq}}[\mathrm{M}] \gg K_{2\mathrm{eq}}[\mathrm{C}],\end{aligned} \tag{19}$$

and

$$[\mathrm{I_2}]_0 = [\mathrm{C}] + [\mathrm{RI{-}I_2}] + [\mathrm{C}]/(K_{1\mathrm{eq}}[\mathrm{M}]). \tag{20}$$

Then, from Eqs. (19) and (20),

$$[\mathrm{RI{-}I_2}] \cong K_{2\mathrm{eq}}[\mathrm{RI}]_0[\mathrm{I_2}]_0/(1 + K_{2\mathrm{eq}}[\mathrm{RI}]_0 + K_{1\mathrm{eq}}[\mathrm{M}]). \tag{21}$$

By substitution of Eq. (21) into Eq. (15),

$$R_p \cong k_p' K_{2\mathrm{eq}}[\mathrm{RI}]_0[\mathrm{I}_2]_0[\mathrm{M}]/(1 + K_{2\mathrm{eq}}[\mathrm{HI}]_0 + K_{1\mathrm{eq}}[\mathrm{M}]), \tag{22}$$

$$\cong (k_p' K_{2\mathrm{eq}}/K_{1\mathrm{eq}})[\mathrm{HI}]_0[\mathrm{I}_0]_0, \quad \text{for } K_{1\mathrm{eq}}[\mathrm{M}] >> (1 + K_{2\mathrm{eq}}[\mathrm{HI}]_0). \tag{23}$$

The primary difference in the above schemes is in the rate constant expressions. In Case A, k_p is equal to the observed rate constant, but in Case B, k_p' is determined by the relative magnitudes of $K_{1\mathrm{eq}}$ and $K_{2\mathrm{eq}}$ for an observed rate constant. If the ratio $K_{2\mathrm{eq}}/K_{1\mathrm{eq}}$ is small, k_p' has to be large. For a conventional anionic [21] or cationic [22] polymerization, the rate of polymerization becomes larger as charge separation increases. Similarly, the more the carbon–iodine bond is activated by the iodine molecule, the closer the structure of the iodide will be to I_3^-, and k_p' will be larger.

$K_{1\mathrm{eq}}$ at a certain temperature can be calculated from the van't Hoff plot by using a literature value of $K_{1\mathrm{eq}}$ and the corresponding ΔH [11]. At -20°C, the calculated $K_{1\mathrm{eq}}$ is ~254, and this increases as the temperature decreases.

In order to estimate the value of $K_{2\mathrm{eq}}$, a series of UV/visible spectroscopic measurements were performed. In Fig. 7 the absorption bands of CH_3CHI–O–nBu (RI) and iodine appeared at 270 and 510 nm, respectively. Figure 8 shows the UV/visible spectra of the mixture of RI and iodine. The absorption peaks at 300-400 nm, where the triiodide ion absorption peak is reported to occur [12, 15], increased only slightly as the ratio of iodine/RI increased. The iodine band and the RI band did not show any distinctive change after they were mixed, except for a slight shift of λ_{max} of RI. The absorption peak at 300-400 nm may originate from the structure which is similar to the triiodide compound. If the structure of the complex is similar to that of the triiodide ion, the molar absorptivity would be expected to be large because that of the triiodide ion is of the order of 10^4 in an aqueous solution [23]. In that case, the equilibrium constant, $K_{2\mathrm{eq}}$, should be very small. However, more than one charge-transfer complex could exist in this system, so that only a qualitative estimation is possible with the given experimental data.

The complex formation would lead to the activation of the carbon–iodine bond where charge separation of the bond occurs. The resultant ionic character of the bond could be studied by the NMR chemical shift difference between the iodide compound and the corresponding complex, by using the following equation [24, 25]:

$$d_z = 160z, \tag{24}$$

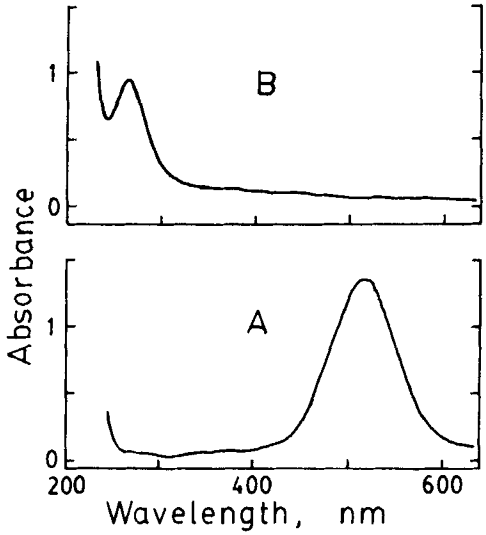


FIG. 7. UV/visible spectra of iodine and $CH_3CHI-O-nBu$ in *n*-hexane at -21°C: (A) iodine, 1.5 mmol/L; (B) $CH_3CHI-O-nBu$, 1.0 mmol/L.

where d_z is the ^{13}C chemical shift after elimination of ring current portion and z is the charge on carbon. In Fig. 9, the chemical shift of the carbon attached to the iodine atom (peak f) shifted 0.83 ppm downfield by the addition of 0.5 equivalents of iodine. From the above equation, the calculated degree of overall activation is clearly very small. If complexation of the iodide compound consists of only one equilibrium, such as in Eq. (13), two interpretations are possible. One is the case where almost all of the iodide compound is inactive and only a quite small portion of the iodide compound is activated, like a free ion pair. The other is the case where a large portion of the iodide compound forms a complex with only weak interaction. In the complexation, however, the strength of the complexation as well as the equilibrium constant K_{2eq} would be determined by the negative charge density of the iodine atom of the carbon–iodine bond. The small shift in the ^{13}C-NMR spectra suggests that the strength and the equilibrium constant are small values. By contrast, if the complexation consists of multistep equilibria, then the interpretation becomes more complicated. For all cases, however, the interaction between iodide compound and iodine molecule appears to be very weak compared to the interaction between monomer and the iodine molecule.

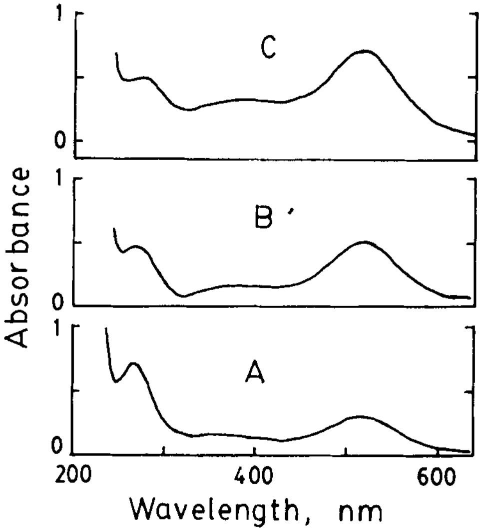


FIG. 8. UV/visible spectra of the mixture of $CH_3CHI-O-nBu$ and iodine in *n*-hexane at -21°C. $[CH_3CHI-O-nBu]/[iodine]$, (mmol/L)/(mol/L): (A) 0.80/0.31, (B) 0.67/0.51, (C) 0.57/0.65.

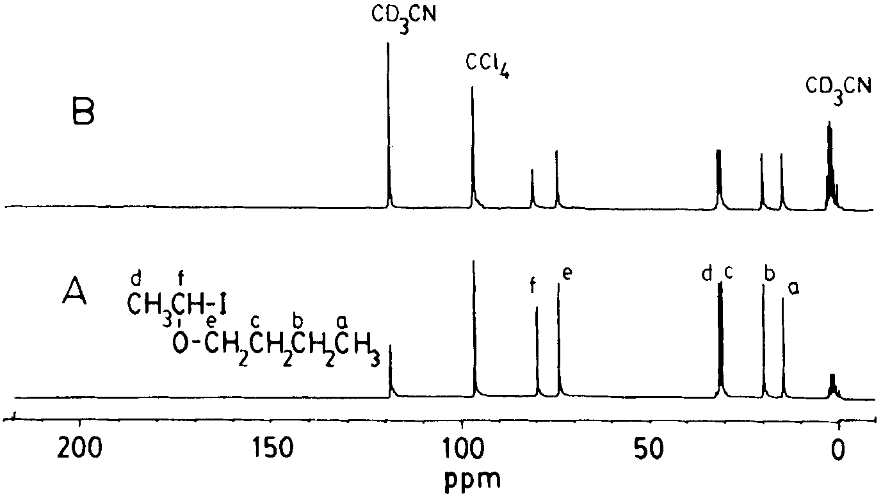


FIG. 9. ^{13}C-NMR spectra of $CH_3CHI-O-nBu$ and its mixture with iodine in carbon tetrachloride at -20°C: (A) [RI], 0.47 mol/L; (B) [RI]/[iodine], (0.12 mol/L)/(0.06 mol/L).

Thus, in the polymerization, almost all of the iodine should form a charge-transfer conplex with monomer and only a very small amount of the iodine could produce a charge-transfer complex with the iodide compound. Then the rate constant k_p' in Scheme B has to be large enough compared to that of conventional cationic polymerization to comply with the observed rate constant.

CONCLUSIONS

The observed rate of polymerization of alkyl vinyl ethers could be explained well by the introduction of charge-transfer complexation between monomer and iodine, regardless of the detailed identity of the complex. At least two propagation modes could be proposed, and the identity, reactivity, and role of the monomer–iodine charge-transfer complex are thought to be important in the polymerization. In one of the proposed modes, the complex participates in the propagation reaction. However, in the other, the complex becomes inactive and only a small portion of the iodide chain end would be activated by iodine. However, at present there is no strong evidence which could eliminate either one of the proposed propagation modes. More systematic investigation of the propagating chain end could perhaps reveal the real polymerization pathway in these interesting systems.

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