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Living Polymerization of Isobutyl Vinyl Ether with the Hydrogen Iodide/Iodine Initiating System

Masaaki Miyamoto, Mitsuo Sawamoto, and Toshinobu Higashimura*

Department of Polymer Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan. *Received March 24, 1983*

ABSTRACT: Living polymerization of isobutyl vinyl ether (IBVE) was achieved with an equimolar mixture of hydrogen iodide (HI) and iodine in *n*-hexane at −15 °C to give nearly monodisperse poly(IBVE). The number-average molecular weight ($\bar{M}_n$) of the polymers increased in direct proportion to monomer conversion and to the reciprocal of the initial HI concentration. Their molecular weight distribution (MWD) remained nearly monodisperse ($\bar{M}_w/\bar{M}_n \lesssim 1.1$) throughout the reaction. The polymerizations in other solvents (CH_2Cl_2 and toluene), in contrast, were not living and yielded polymers having broader MWD ($\bar{M}_w/\bar{M}_n$ = 1.4–2.0), the $\bar{M}_n$ of which did not increase with conversion. Iodine alone could not effect a truly living IBVE polymerization in *n*-hexane; the $\bar{M}_n$ of the product polymers increased only slightly with conversion. The polymerization by HI alone in *n*-hexane was much slower than that by the HI/I_2 initiating system. Interestingly, addition of iodine to a quiescent mixture of HI and IBVE led to a rapid polymerization that yielded nearly monodisperse polymers.

Introduction

In the cationic polymerization of vinyl monomers, the propagating carbocations are usually so unstable that they tend to undergo chain-transfer and termination reactions, and thus living polymers and monodisperse polymers have seldom been obtained yet. In spite of these difficulties, our previous work showed that *p*-methoxystyrene,[1,2] isobutyl vinyl ether (IBVE),[3] and *N*-vinylcarbazole,[4] when polymerized by iodine initiator, generate long-lived propagating species at low temperature in nonpolar solvents. The long lifetime of the growing intermediate was indicated by the increase of the number-average molecular weight ($\bar{M}_n$) of produced polymers along with increasing monomer conversion. However, these reactions cannot be regarded as truly "living" polymerizations, because, first, the number of polymer chains produced per unit initiator increases as the polymerizations proceed and, second, the polymers are not monodispersed; these facts indicate the involvement of chain transfer and/or initiation slower than propagation.

Related studies by other research groups on vinyl ether polymerizations also failed to achieve truly living cationic processes. For example, Sawamoto and Kennedy[5] recently reported that when IBVE or methyl vinyl ether was added slowly and continuously to an initiator solution the $\bar{M}_n$ of product polymers increased with the amount of the added monomers ("quasi-living" polymerization). Johnson and Young[6] found that the $\bar{M}_n$ of poly(*n*-butyl vinyl ether) obtained with iodine increased on sequential addition of the monomer to a completely polymerized reaction mixture ("pseudoliving" polymerization). In these examples, however, the $\bar{M}_n$ of the polymers was not proportional to the total amount of added monomers, and their molecular weight distributions (MWD) were rather broad ($\bar{M}_w/\bar{M}_n$ = 1.4–1.7).

One of the reasons for the failure of truly living polymerization with iodine initiator may be its slow initiation. In these investigations, therefore, we used hydrogen iodide (HI), in conjunction with equimolar iodine, to effect living polymerization of IBVE. Since hydrogen iodide has a greater dissociation constant than iodine, the HI/I_2 initiating system will lead to faster initiation than iodine alone does. IBVE was employed as monomer, which generates a stable propagating species and is highly polymerizable even at low temperature. Hydrogen iodide has been reported to accelerate the iodine-initiated polymerizations of styrene and related monomers,[7–9] in which long-lived/living propagating species have not yet been obtained.

We succeeded in a nearly perfect living polymerization of IBVE with an equimolar mixture of hydrogen iodide and iodine as an initiating system and obtained monodisperse poly(IBVE) with a controlled molecular weight.

Experimental Section

Procedures. Polymerization was carried out in the dark under dry nitrogen in a vessel equipped with a three-way stopcock. The concentration of adventitious water in the reaction mixture was in the range 0.2–0.3 mM (by Karl Fischer titration). The reaction was initiated by adding an initiator solution (HI/I_2, HI, or I_2) to a monomer solution and terminated after a certain interval by

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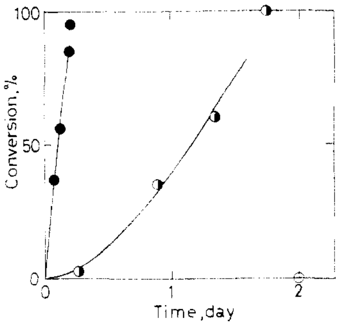

Figure 1. Time–conversion curves for the polymerization of IBVE in *n*-hexane at −15 °C and $[M]_0 = 0.38$ M. Initiator: (○) HI (5.0 mM); (◑) I_2 (5.0 mM); (●) HI/I_2 (5.0 mM each).

adding ammoniacal methanol. An equimolar mixture of hydrogen iodide and iodine in *n*-hexane was used as the HI/I_2 initiating system. The concentration of hydrogen iodide in the initiator solution was determined by extracting the acid with deionized water and subsequently titrating the aqueous phase with a standard sodium hydroxide solution, bromthymol blue being the indicator. The conversion of IBVE was measured by gas chromatography with carbon tetrachloride as internal standard and also by gravimetry of the product; the conversion values by the two methods were in good agreement.

The quenched reaction mixture was washed with aqueous sodium thiosulfate solution, evaporated to dryness under reduced pressure, and vacuum dried to give product polymers. Their MWD was measured by gel permeation chromatography (GPC) in chloroform on a Jasco Trirotar high-performance liquid chromatograph equipped with two polystyrene gel columns (Shodex H-2002 and H-2004, 21.5-mm i.d. × 500 mm each). The polydispersity ratio ($\bar{M}_w/\bar{M}_n$) was calculated from GPC curves on the basis of a polystyrene calibration. The $\bar{M}_n$ of the polymers was measured by vapor pressure osmometry (VPO) in benzene at 30 °C on a Hitachi-117 molecular weight apparatus.

Materials. Commercial IBVE was washed with aqueous sodium hydroxide solution and then water and was distilled twice over calcium hydride before use. Hydrogen iodide was obtained from a 57% aqueous solution (Wako Chemicals) by dehydration with phosphorus pentaoxide[8] and stored as an *n*-hexane solution (ca. 200 mM) in ampules in a freezer. Iodine (Wako Chemicals, guaranteed reagent, purity >99.9%) was used without further purification. Solvents (methylene chloride, toluene, and *n*-hexane) were purified by the usual methods and distilled twice over calcium hydride before use.

Results and Discussion

Polymerization in *n*-Hexane. IBVE was polymerized with the HI/I_2 initiating system at a low temperature (−15 °C) in a nonpolar alkane solvent (*n*-hexane). The molar ratio of hydrogen iodide to iodine was unity in all experiments of this study. For comparison, we also polymerized IBVE with hydrogen iodide or iodine alone otherwise under the same conditions.

Figure 1 shows the time–conversion curves obtained with the three initiators (HI/I_2, HI, and I_2). The conversion curve with HI/I_2 completely differed from those with HI or I_2 alone. The polymerization with HI/I_2 proceeded without an induction period and faster than that with iodine. Hydrogen iodide alone induced a very slow polymerization, giving virtually no polymer in one day and a ca. 70% conversion in one month. Interestingly, separate experiments showed that addition of iodine (5.0 mM) to a very slowly polymerizing mixture of IBVE (0.38 M) and hydrogen iodide (5.0 mM) effected a polymerization which followed almost the same time course as that initiated with an equimolar HI/I_2 mixture (5.0 mM each). The acceleration by the addition of iodine suggests that the added halogen interacts with the iodine atom in the propagating end formed by hydrogen iodide and thereby weakens its interaction with the terminal carbon.

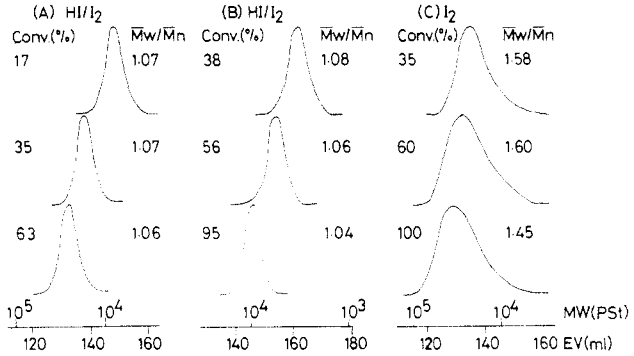

Figure 2. MWD of poly(IBVE) obtained with HI/I_2 (A and B) or iodine (C) in *n*-hexane at −15 °C and $[M]_0 = 0.38$ M: (A) $[HI]_0 = [I_2]_0 = 1.2$ mM; (B) $[HI]_0 = [I_2]_0 = 5.0$ mM; (C) $[I_2]_0 = 5.0$ mM. Conversions and $\bar{M}_w/\bar{M}_n$ ratios as indicated.

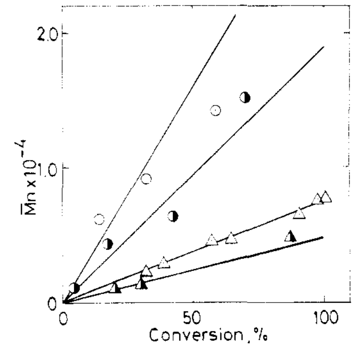

Figure 3. $\bar{M}_n$ vs. conversion relationships for poly(IBVE) obtained with HI/I_2 initiating systems in *n*-hexane at −15 °C, $[M]_0 = 0.38$ M, and $[HI]_0 = [I_2]_0$. $[HI]_0$ (mM): (○) 1.2; (◑) 2.0; (△) 5.0; (▲) 7.6. The straight lines indicate the $\bar{M}_n$ values for living polymerization calculated by $\bar{M}_n = 100.2[M]_{consumed}/[HI]_0$.

Figure 2 illustrates the MWD of the polymers produced by HI/I_2 and iodine. The MWD with HI/I_2 stayed nearly monodisperse ($\bar{M}_w/\bar{M}_n \lesssim 1.1$) and shifted obviously toward higher molecular weight without tailing as the polymerization proceeded. On the other hand, the MWD with iodine was broader ($\bar{M}_w/\bar{M}_n = 1.4$–$1.6$) and shifted only slightly with increasing IBVE conversion. The polymers obtained with HI alone or with sequentially added HI and iodine (vide supra) exhibited a nearly monodisperse MWD, similar to those with HI/I_2.

Figure 3 shows the relationships between conversion and the $\bar{M}_n$ of polymers obtained with equimolar HI/I_2 initiating mixtures at different initial concentrations. The MWD of the produced polymers was nearly monodisperse irrespective of the initiator concentrations employed ($[HI]_0 = [I_2]_0 = 1.2$–7.6 mM; see Figure 2A,B). The $\bar{M}_n$ was directly proportional to conversion at any HI concentration in this range, although some deviations from linearity could be seen for the values at low HI concentrations and high conversions. The straight lines in Figure 3 indicate the calculated $\bar{M}_n$ values for living polymers when they are formed quantitatively from hydrogen iodide. The agreement between the experimental and calculated values is quite satisfactory, indicating that the $\bar{M}_n$ of poly(IBVE) obtained with HI/I_2 is proportional to the reciprocal of the HI concentration.

The number of polymer molecules (N) produced per unit initiator can be calculated according to eq 1, where $\overline{DP}_n$

$$N = [M]_{consumed}/\overline{DP}_n[C]_0 \qquad (1)$$

means the number-average degree of polymerization (by VPO) and $[C]_0$ the initial concentration of initiator. Line a in Figure 4 shows the dependence of N on monomer conversion for the polymerization with HI/I_2; in this case

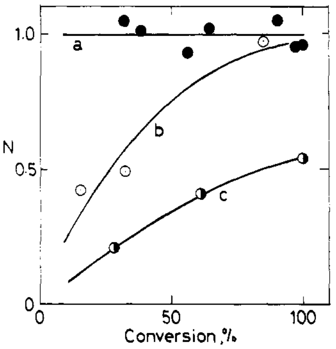

Figure 4. Relationships between conversion and N, the number of poly(IBVE) chains produced per unit initiator (eq 1), at -15 °C and $[M]_0 = 0.38$ M. Initiator and solvent: (a) HI/I_2 (5.0 mM each), n-hexane; (b) I_2 (5.0 mM), toluene; (c) I_2 (5.0 mM), n-hexane.

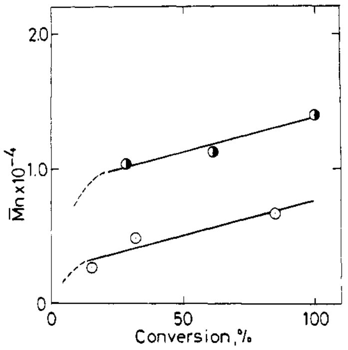

Figure 5. $\bar{M}_n$ vs. conversion relationships for poly(IBVE) obtained with iodine at -15 °C, $[M]_0 = 0.38$ M, and $[I_2]_0 = 5.0$ mM. Solvent: (◑) n-hexane; (○) toluene.

the initial HI concentration was taken as $[C]_0$.

The N values were nearly unity and remained almost constant up to high conversions. This, coupled with the $\bar{M}_n$ data in Figure 3, demonstrates that in the polymerization by HI/I_2 chain transfer and termination are absent while initiation is quantitative and faster than propagation. Thus, the HI/I_2 initiating system led to an almost perfect living polymerization of IBVE.

On the other hand, the $\bar{M}_n$ of polymers obtained with iodine alone increased only slightly with conversion, and the $\bar{M}_n$ vs. conversion plot did not pass through the origin (Figure 5; data for $[I_2]_0 = 5.0$ mM only). The N values were much smaller than unity and gradually increased as the polymerization proceeded (Figure 4c). Since the initiation by iodine in nonpolar media is thought to be bimolecular with respect to the initiator,[10,11] N should be less than 0.5 in living polymerization. The observed N values could thus be ascribed to a slow initiation. Figures 4c and 5, therefore, indicate that the IBVE polymerization with iodine differs from that with HI/I_2.

Polymerization in Other Solvents. To clarify whether n-hexane solvent is indispensable to the living polymerization by the HI/I_2 system, IBVE was polymerized in other solvents (toluene and CH_2Cl_2) with HI/I_2, HI, and iodine as initiators. Figures 6 and 7 show the time–conversion curves for the polymerizations with HI/I_2 and iodine, respectively. Hydrogen iodide alone gave results almost identical with those for HI/I_2 in these solvents. The MWDs of the polymers formed are illustrated in Figure 8.

The polymerizations in CH_2Cl_2 with the three initiators were all so fast as to be completed within 1 min ($[C]_0 = 5.0$ mM). The MWDs of the produced polymers were fairly broad ($\bar{M}_w/\bar{M}_n = 1.5$–$2.0$) and did not shift as the polymerization proceeded. The number of polymer chains, N (eq 1), was much larger than unity and increased considerably with increasing conversion; for example, with HI/I_2 (1.0 mM each) $N = 1.7$ (conversion 83%) and 2.3 (100%). These results indicate that in CH_2Cl_2 none of the three initiators can effect living IBVE polymerization because of frequent chain transfer. The absence of living polymerization in polar solvents has also been reported for p-methoxystyrene[1,2] and N-vinylcarbazole.[4]

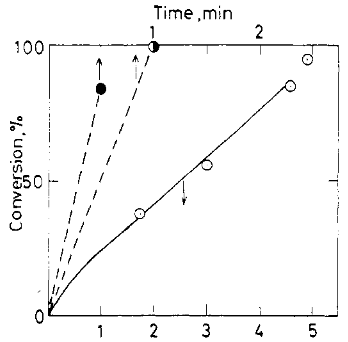

Figure 6. Time–conversion curves for the polymerization of IBVE with the HI/I_2 initiating system at -15 °C, $[M]_0 = 0.38$ M, and $[HI]_0 = [I_2]_0$. Solvent and $[HI]_0$ (mM): (○) n-hexane, 5.0 (from Figure 1); (◑) toluene, 2.0; (●) CH_2Cl_2, 1.0.

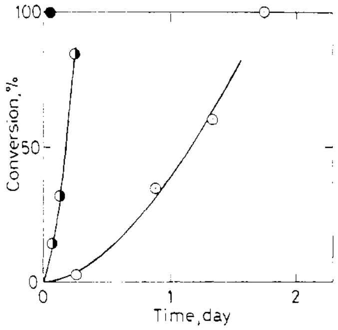

Figure 7. Time–conversion curves for the polymerization of IBVE with iodine at -15 °C, $[M]_0 = 0.38$ M, and $[I_2]_0 = 5.0$ mM. Solvent: (○) n-hexane (from Figure 1); (◑) toluene; (●) CH_2Cl_2.

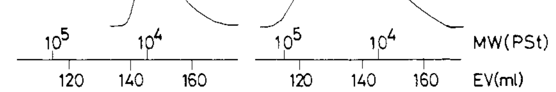

Figure 8. MWD of poly(IBVE) obtained in (A) toluene and (B) CH_2Cl_2 at -15 °C and $[M]_0 = 0.38$ M; conversions are ca. 100%. Initiators and $\bar{M}_w/\bar{M}_n$ as indicated. $[C]_0$ (mM): (a) 2.0 each; (b) 1.0; (c) 20; (d) 1.0 each; (e) 1.0; (f) 1.0.

The polymerization with HI/I_2 in toluene was much faster than in n-hexane (Figure 6), and the MWD of the produced polymers remained unchanged with conversion (Figure 8).

With iodine, on the other hand, the polymerization rate in toluene was intermediate between those for CH_2Cl_2 and n-hexane, and the time–conversion curve indicated an induction phase (Figure 7). The MWD of the produced polymers was narrower ($\bar{M}_w/\bar{M}_n \simeq 1.2$) than those obtained in CH_2Cl_2 and shifted toward higher molecular weight as the polymerization proceeded.[12] Accordingly, the $\bar{M}_n$ of the polymers increased with increasing conversion (Figure 5). The N values increased from ca. 0.5 to 1.0 as the polymerization proceeded (Figure 4b). The increase of polymer molecular weight with conversion shows that a long-lived propagating species is formed by iodine in toluene. However, this intermediate is not "living" in a strict sense, in view of the observed increase of N (Figure 4b), which is probably due to chain transfer occurring to some extent.

It is of interest that the polymerizations by iodine in toluene and in n-hexane differ considerably, though the solvents are both nonpolar. For instance, the N values for n-hexane (Figure 4c) do not exceed 0.5; those for toluene (Figure 4b) are already close to 0.5 at the beginning of the reaction and increase beyond this value with conversion. These facts indicate that initiation is faster in toluene than in n-hexane, whereas chain transfer is more frequent in the former solvent.

Although the polymerization by hydrogen iodide alone in n-hexane was very slow (Figure 1), in toluene this acid resulted in a rapid polymerization (ca. 100% conversion within 1 min), similar to that by HI/I_2. The MWD of the produced polymers was also similar to that with HI/I_2; no increase in polymer molecular weight with conversion was observed (Figure 8). Thus neither HI/I_2 nor HI alone could generate long-lived propagating species in toluene. Perhaps the π-electrons of this solvent may promote the ionic dissociation of the propagating species to give a less stable intermediate.

In conclusion, this work has shown that the HI/I_2 initiating system leads to an almost perfect living polymerization of IBVE in n-hexane, in which nearly monodisperse polymers are formed. To our knowledge, monodisperse polymers were obtained for the first time with an initiator for cationic polymerization. At present, the nature of the propagating species derived from the HI/I_2 system is unknown, and our current investigations concern this problem, which is important in understanding living cationic polymerization.

Registry No. Hydrogen iodide, 10034-85-2; iodine, 7553-56-2; poly(IBVE), 9003-44-5.

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Polyurethane Interpenetrating Polymer Networks (IPN's) Synthesized under High Pressure. 1. Morphology and T_g Behavior of Polyurethane–Poly(methyl methacrylate) IPN's

Doo Sung Lee and Sung Chul Kim*

Department of Chemical Engineering, Korea Advanced Institute of Science and Technology, Chongyangni, Seoul 131, South Korea. *Received March 18, 1983*

ABSTRACT: A series of simultaneous interpenetrating polymer networks of polyurethane–poly(methyl methacrylate) were synthesized under high pressure (up to 20 000 kg/cm^2). The morphology via transmission electron microscopy and the glass transition behavior via DMA and DSC measurements were studied, and the effect of the synthesis pressure was evaluated. The composition of the polyurethane and poly(methyl methacrylate) was fixed at 50/50% by weight. The polyurethane phase domain sizes decreased from about 300 to 30 Å with increasing synthesis pressure from 1250 to 20 000 kg/cm^2. The phase continuity changed also with pressure; the polyurethane phase became continuous at low pressure, while the poly(methyl methacrylate) phase showed continuity at high pressure. A very broad glass transition ranging from about 0 to about 100 °C was observed for IPN's synthesized under 20 000 kg/cm^2, and they were optically transparent.

Introduction

The chemical and physical combination methods and their properties of multipolymers have been of commercial and academic interest, since it provides a convenient route for the modification of properties to meet specific needs. Among these methods, considerable interest has been given to interpenetrating polymer networks (IPN's).[1,2] IPN's are defined as a mixture of two or more cross-linked polymer networks which have partial or total physical interlocking between them. They have been prepared in three different modes of synthesis: latex blending,[3] sequential polymerization,[4,5] and simultaneous polymerization.[6-11] The degree of physical interlocking is dependent on the degree of phase separation at the time of interlocking (cross-linking in the presence of already cross-linked network). Thus by considering the mixture components of the three different synthetic methods, polymer–polymer mix in latex blending, polymer–monomer mix in sequential polymerization, and monomer–monomer (or oligomer–oligomer) mix in simultaneous polymerization, the simultaneous polymerization method would yield a higher degree of interpenetration.

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