

Living Cationic Copolymerization of Isobutyl Vinyl Ether with *p*-Methoxystyrene by Hydrogen Iodide/Iodine Initiating System

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ABSTRACT: Living cationic copolymerization of isobutyl vinyl ether with *p*-methoxystyrene was effected by an equimolar mixture of hydrogen iodide and iodine (HI/I₂ initiator) at -15°C in nonpolar solvents (carbon tetrachloride and toluene). Isobutyl vinyl ether reacted faster than *p*-methoxystyrene. The products were random copolymers with a nearly monodisperse molecular weight distribution (MWD) ($M_w/M_n=1.1-1.2$). Their number-average molecular weight (M_n) increased in proportion to total monomer conversion. The iodine-initiated copolymerization under similar conditions led to long-lived (but not perfectly living) copolymers with a narrow MWD ($M_w/M_n=1.2-1.3$). In contrast, boron trifluoride etherate induced a conventional transfer-dominant copolymerization. The M_n of the copolymers obtained with the HI/I₂ initiator was almost independent of the monomer feed ratio, but in the BF₃OEt₂-initiated non-living process, the polymer molecular weight decreased sharply with increasing isobutyl vinyl ether content in the feed. These findings show the living copolymerization by HI/I₂ to be free from the cross-transfer usually involved in the conventional cationic copolymerization of vinyl monomers.

KEY WORDS Cationic Copolymerization / Living Polymer / Monodisperse Polymer / Cross-Transfer / Isobutyl Vinyl Ether / *p*-Methoxystyrene / Hydrogen Iodide / Iodine / Narrow Molecular Weight Distribution /

In most cationic copolymerizations between vinyl compounds, the molecular weight of the product copolymers is much less than those of the respective homopolymers.¹ This molecular weight depression of copolymers is attributed to cross-transfer^{2,3} that occurs particularly when the monomers to be copolymerized differ considerably in reactivity and structure (*e.g.*, isobutene *vs.* styrene² and vinyl ethers *vs.* styrenes⁴). Accordingly, the synthesis of (random) copolymers with controlled molecular weight and narrow molecular weight distribution (MWD) has been difficult in cationic vinyl copolymerization.

Recently we have found nearly perfect

“living” polymerizations of vinyl ethers^{5,6} and related monomers^{7,8} initiated by a mixture of hydrogen iodide and iodine (HI/I₂ initiator). In view of the absence of chain transfer (and termination) in living polymerization, it is of interest to apply the HI/I₂ initiating system to cationic “copolymerizations” that may involve frequent cross-transfer reaction(s) when initiated by conventional acid initiators.

Thus, in this study, we copolymerized, using the HI/I₂ initiator, isobutyl vinyl ether (IBVE) and *p*-methoxystyrene (pMOS) which differ in structure and reactivity and undergo (cross)-transfer dominant cationic copolymerization under usual conditions.^{1,4} Our object was to

prevent cross-transfer and other chain-breaking reactions so as to control polymer molecular weight and MWD and thus be able to synthesize "living random" IBVE-pMOS copolymers with a monodisperse MWD, hitherto not yet prepared.

EXPERIMENTAL

Materials

IBVE (Tokyo Kasei) was washed with aqueous sodium hydroxide solution and then water, dried over potassium hydroxide pellets, and distilled twice before use over calcium hydride and then sodium metal. pMOS was prepared from *p*-methoxyacetophenone by the literature method⁹ and purified by double distillation over calcium hydride under reduced pressure. The two monomers were of gas chromatographic purity exceeding 99.8%.

Hydrogen iodide was obtained as an *n*-hexane solution (*ca.* 1 M) by dehydration of a commercial 57% aqueous solution as reported.^{5,6} Iodine was sublimed over potassium iodide. Boron trifluoride etherate (BF₃OEt₂) was purified by vacuum distillation. These initiators were stored under dry nitrogen in ampules in the dark. Solvents (carbon tetrachloride, toluene, and *n*-hexane) and tetrahydronaphthalene (internal standard for gas chromatography) were washed successively with sulfuric acid, aqueous sodium hydroxide, and water, and doubly distilled over calcium hydride before use.

Procedures

The copolymerization of IBVE with pMOS was carried out under dry nitrogen in a baked glass tube equipped with a three-way stopcock. The reaction was initiated by adding an initiator solution to a monomer solution *via* dry syringe and terminated with prechilled ammoniacal methanol. When HI/I₂ initiator was employed, hydrogen iodide and iodine solutions were added successively in this order. The concentration of hydrogen iodide stock

solutions was determined by titration as reported.⁶ Conversions of the two monomers were measured by gas chromatography on a Shimadzu temperature-programmed gas chromatograph GC-6A with tetrahydronaphthalene as internal standard (*ca.* 5 vol%): column, PEG 6000 (Shimadzu), 3 mm i.d. × 2 m; carrier gas, hydrogen, 1.0–1.5 kg cm⁻²; the column temperature was raised from 60 (for IBVE) to 180°C (for pMOS and tetrahydronaphthalene) at the rate of 10 deg min⁻¹.

The quenched reaction mixture was washed with aqueous sodium thiosulfate solution (*ca.* 10% w/v) and then water, evaporated to dryness under reduced pressure below 40°C, and vacuum-dried to give the product polymers. For runs with BF₃OEt₂, treatment with sodium thiosulfate was omitted. The MWD of the copolymers was measured by size exclusion chromatography (SEC) in chloroform on a JASCO Trirotar-II chromatograph equipped with three polystyrene gel columns (Shodex A-802, A-804, and A-806, 8.0 mm i.d. × 500 mm each) and refractive index (RI)/ultraviolet (UV) dual detectors. The number-average molecular weight (M_n) and polydispersity ratio (M_w/M_n) of the polymers were calculated from SEC eluograms on the basis of a polystyrene calibration. ¹H NMR spectra were recorded in CDCl₃ at 30°C on JEOL FX 90Q spectrometer.

RESULTS AND DISCUSSION

Living IBVE-pMOS Copolymerization by HI/I₂ Initiator

Our previous studies showed that nonpolar solvents are best suited for the living polymerization of IBVE by HI/I₂ initiator⁵ and the formation of long-lived polymers from pMOS by iodine.^{10,11} For this reason, IBVE and pMOS were copolymerized (IBVE/pMOS = 1/3 in feed) by an equimolar mixture of hydrogen iodide and iodine at -15°C in carbon tetrachloride, a good solvent for the homopolymers of the two monomers. Iodine was

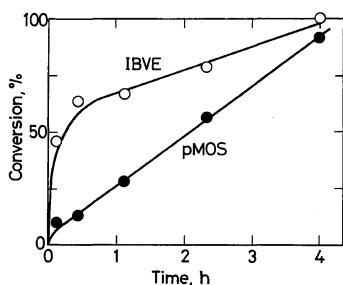


Figure 1. Time-conversion curves for IBVE-pMOS copolymerization by HI/I₂ at -15°C in CCl₄: [IBVE]₀ = 0.19 M; [pMOS]₀ = 0.57 M (IBVE/pMOS = 1/3); [HI]₀ = [I₂]₀ = 10 mM.

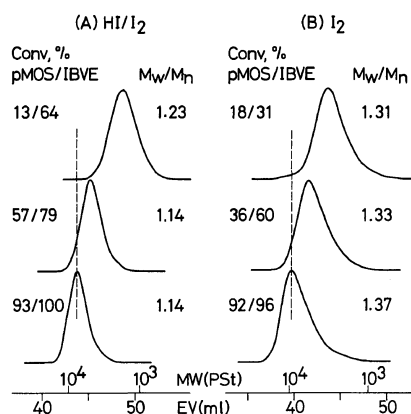


Figure 2. MWD of IBVE-pMOS copolymers obtained with HI/I₂ (A) and iodine (B) at -15°C in CCl₄: [IBVE]₀ = 0.19 M; [pMOS]₀ = 0.57 M (IBVE/pMOS = 1/3); (A) [HI]₀ = [I₂]₀ = 10 mM; (B) [I₂]₀ = 20 mM. Conversion and M_w/M_n as indicated.

also used as an initiator under the same conditions. Figures 1—3 summarize the results.

With both initiators, IBVE and pMOS were polymerized without an apparent induction phase up to 100% conversion; IBVE reacted faster than pMOS (Figure 1). The polymers obtained with HI/I₂ initiator exhibited a very narrow, nearly monodisperse MWD with the M_w/M_n ratio 1.1–1.2. Keeping their near monodispersity, they shifted progressively toward higher molecular weight with increasing monomer conversions (Figure 2A). The iodine-initiated copolymerization led to narrow but broader MWDs than those for HI/I₂ (Figure

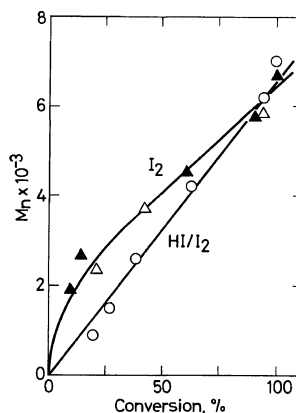


Figure 3. M_n of IBVE-pMOS copolymers obtained at -15°C as a function of total monomer conversion: [IBVE]₀ = 0.19 M; [pMOS]₀ = 0.57 M (IBVE/pMOS = 1/3). Initiator and solvent: (△) I₂ (20 mM), CCl₄; (▲) I₂ (20 mM), toluene; (○) HI/I₂ (10 mM each), CCl₄. Total monomer conversion (%) = 100 × (molar sum of IBVE and pMOS polymerized)/(molar sum of IBVE and pMOS in feed).

2B). A progressive increase in polymer molecular weight with conversion was also observed for iodine.

Extraction of the copolymerization products with 2-propanol [a good solvent for poly(IBVE) and a nonsolvent for poly(pMOS)¹¹] showed them true (random) copolymers free from the respective homopolymers. Thus, following their extraction, they gave 2-propanol-soluble and insoluble fractions, both consisting of IBVE and pMOS units of different composition (by ¹H NMR spectroscopy). The formation of true copolymers was further supported by the narrowness and unimodality of the MWDs coupled with almost superimposable RI and UV detector traces on SEC measurements. The latter fact indicates that UV-sensitive pMOS units are distributed uniformly in the copolymer over the entire molecular weight range.

Figure 3 (open circles and triangles) plots the M_n of the copolymers obtained with HI/I₂ and iodine in carbon tetrachloride, as a function of the total monomer conversion [100 × (molar sum of IBVE and pMOS polymerized)/

(molar sum of IBVE and pMOS in feed)]. The M_n was calculated from the MWD curve by assuming the uniform distribution of the two monomer units in the copolymer (see above).

The HI/I₂ initiating system led to a linear M_n -conversion plot passing through the origin, that is, the M_n was directly proportional to monomer conversion, which is a typical characteristic of "living" processes. The M_n of the iodine-initiated copolymers also increased progressively with conversion but the plot showed some curvature. These results show the HI/I₂ initiator to produce "living" copolymers of IBVE and pMOS with a nearly monodisperse MWD in carbon tetrachloride, whereas iodine forms long-lived polymers neither monodisperse nor perfectly living. The living IBVE-pMOS copolymers thus obtained are most likely "random" in nature.

Copolymerization in Toluene

The effects of solvents and initiators on living IBVE-pMOS copolymerization were further studied in toluene, another nonpolar solvent differing from carbon tetrachloride. This aromatic solvent is better suited than carbon tetrachloride or *n*-hexane for the formation of long-lived poly(IBVE) with iodine as the initiator.^{5,12,13}

Figure 4 compares the MWD of the IBVE-pMOS copolymers formed by HI/I₂, iodine, and BF₃OEt₂ in toluene at -15°C (total monomer conversion *ca.* 100%; IBVE/pMOS = 1/3 in feed). The HI/I₂ initiator led to nearly monodisperse living copolymers whose M_n 's were proportional to monomer conversion and nearly the same as those for carbon tetrachloride solvent. As expected, the copolymers produced by iodine showed an MWD narrower than that with carbon tetrachloride, but still broader than a monodisperse distribution. The M_n of these polymers (Figure 3, filled triangles) increased with conversion nearly in the same way as in carbon tetrachloride.

In contrast, BF₃OEt₂ resulted in copolymers having a broad MWD with M_w/M_n ratio

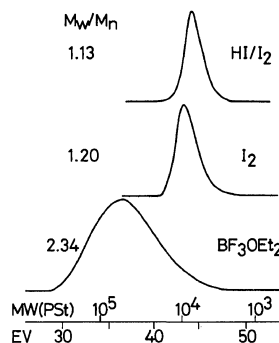


Figure 4. MWD of IBVE-pMOS copolymers obtained at -15°C in toluene: [IBVE]₀ = 0.19 M; [pMOS]₀ = 0.57 M (IBVE/pMOS = 1/3); total monomer conversion = 100%. Initiator concentration: HI/I₂, 10 mM each; I₂, 20 mM; BF₃OEt₂, 1.0 mM. M_w/M_n as indicated.

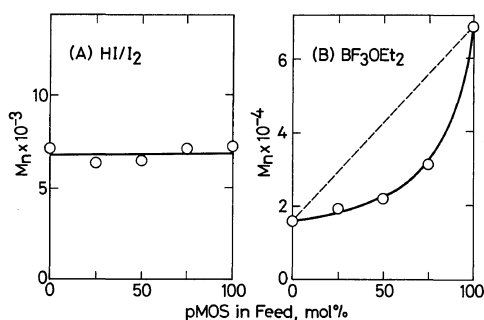


Figure 5. M_n of IBVE-pMOS copolymers obtained at -15°C as a function of IBVE/pMOS feed ratio ([IBVE]₀ + [pMOS]₀ = 0.76 M). Initiator and solvent: (A) HI/I₂ (10 mM each), CCl₄; (B) BF₃OEt₂ (1.0 mM), toluene. Total monomer conversion = 100%.

around 2, and their molecular weight remained almost unchanged with increasing conversion. Thus, the metal halide initiates transfer dominant, non-living copolymerization.

Effects of IBVE/pMOS Feed Ratio on Polymer Molecular Weight

The difference between the living (HI/I₂-CCl₄ or toluene) and non-living (BF₃OEt₂-toluene) copolymerizations became even clearer by the effects of the IBVE/pMOS feed ratio on the M_n of the product copolymers (Figure 5). In the non-living copolymerization by BF₃OEt₂, the M_n of the copolymers was much less than the arithmetic mean (Figure 5B,

broken line) of the M_n 's of the respective homopolymers formed under the same conditions. In particular, a small increase in IBVE, a more nucleophilic partner, in the feed sharply depressed the copolymer molecular weight. For example, the M_n of the product at the IBVE/pMOS feed ratio of 1/3 (75 mol% pMOS) was less than one half that of homopoly(pMOS). Such a molecular weight depression in the copolymers should be due to frequent cross-transfer typically occurring in conventional non-living cationic copolymerization.¹⁻⁴

In contrast, the living copolymers obtained with HI/I₂ had M_n values almost independent of the IBVE/pMOS feed ratio and very similar to those of the respective homopolymers (Figure 5A).¹⁴ This also shows the absence of (cross-)transfer and other chain-breaking reactions in the HI/I₂-initiated copolymerization.

To summarize, this study has shown the HI/I₂ initiating system to induce not only living "homopolymerization" of vinyl and propenyl ethers⁵⁻⁸ but living "random copolymerization" between IBVE and pMOS to yield monodisperse copolymers.

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- Since the formula weight of the pMOS repeat unit is greater than that of the IBVE repeat unit (134 vs. 100), the M_n of the pMOS-IBVE copolymers should increase with increasing pMOS content in the feed, if no chain-breaking reactions are involved in the copolymerization. The discrepancy between this expectation and the independence of the observed M_n values on the pMOS/IBVE feed ratio is probably due to that they were determined by SEC on the basis of a polystyrene calibration.