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Synthesis of Monodisperse Living Poly(vinyl ethers) and Block Copolymers by the Hydrogen Iodide/Iodine Initiating System

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ABSTRACT: Monodisperse living polymers ($\bar{M}_w/\bar{M}_n \lesssim 1.1$) of alkyl vinyl ethers ($CH_2{=}CH{-}OR$; R = CH_3, C_2H_5, i-C_3H_7, n-C_4H_9, n-$C_{16}H_{33}$) were synthesized by the hydrogen iodide/iodine initiating system in nonpolar solvents at −5 to −35 °C. The number-average molecular weight ($\bar{M}_n$) of the polymers was directly proportional to the ratio of initial monomer concentration to initial initiator concentration. These living polymers were able to initiate polymerization of other vinyl ethers or *p*-methoxystyrene to give various block copolymers with a narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n \lesssim 1.3$), e.g., poly(methyl vinyl ether-*b*-hexadecyl vinyl ether), poly(ethyl vinyl ether-*b*-hexadecyl vinyl ether), and poly(alkyl vinyl ether-*b*-*p*-methoxystyrene). These block copolymers were synthesized in high blocking efficiency.

Introduction

Living polymerization is very useful to synthesize tailor-made polymers such as monodisperse polymers and block copolymers. Almost all living processes so far utilized are anionic; well-defined living polymerizations of cationically polymerizable vinyl monomers have not been discovered yet. This limits the range of monomers and initiators for living polymerization and polymer synthesis thereby. Consequently, the synthesis of block copolymers of cationically polymerizable monomers (e.g., vinyl ethers) has been difficult, although some inefficient examples using long-lived propagating species have been reported.[1-5]

Recently we have shown[6] that an equimolar mixture of hydrogen iodide (HI) and iodine (I_2) as an initiating system leads to a living polymerization of isobutyl vinyl ether (IBVE) in *n*-hexane as −15 °C. The molecular weight distribution (MWD) of the product polymers was nearly monodisperse ($\bar{M}_w/\bar{M}_n \lesssim 1.1$) and their number-average molecular weight ($\bar{M}_n$) increased in direct proportion to monomer conversion and to the reciprocal of the initial HI concentration. Thus, in this reaction chain transfer and termination are absent while the initiation is quantitative and faster than the propagation.

This study aims (i) to examine whether the HI/I_2 initiator gives monodisperse living polymers from a series of vinyl ethers ($CH_2{=}CH{-}OR$; R = CH_3, C_2H_5, i-C_3H_7, n-C_4H_9, n-$C_{16}H_{33}$) independent of their alkyl groups and (ii) to synthesize block polymers of the vinyl ethers by the HI/I_2-initiated living processes.

Experimental Section

Procedures. Polymerization was carried out under dry nitrogen in a vessel equipped with a three-way stopcock at −5 to −35 °C. The concentration of adventitious water in the polymerization mixture was in the range 0.2–0.3 mM (by the Karl Fischer method). The reaction was initiated by adding, successively, a hydrogen iodide solution (kept at −78 °C) and an iodine solution to a monomer solution. The hydrogen iodide and iodine concentrations were equal in all experiments. The concentration of hydrogen iodide was determined by extracting the acid with deionized water and subsequently titrating the aqueous phase with a standard sodium hydroxide solution with the aid of a pH meter (Horiba Model M-7). After the complete consumption of the monomer, the reaction was terminated with prechilled ammoniacal methanol.

The quenched reaction mixture was washed with aqueous sodium thiosulfate solution and then water, evaporated to dryness under reduced pressure, and vacuum-dried to give the product polymers. Their MWDs were measured by gel permeation chromatography (GPC) in chloroform on a Jasco Trirotar high-performance liquid chromatograph equipped with polystyrene gel columns (Shodex A-802, A-803, and A-804, 8.0 mm i.d. × 500 mm each or 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 product polymers was measured by vapor pressure osmometry (VPO) in benzene at 30 °C on a Hitachi-117 molecular weight apparatus. The composition of block copolymers was determined by ^{1}H NMR spectroscopy (JEOL NMR FX 90-Q) in $CDCl_3$.

Materials. Commercial IBVE, *n*-butyl vinyl ether (nBVE), and ethyl vinyl ether (EVE) (all from Tokyo Kasei) were washed with aqueous sodium hydroxide solution and then water, dried overnight over potassium hydroxide, and distilled twice over calcium hydride and then sodium metal before use. Commercial methyl vinyl ether (MVE) (Tokyo Kasei; purity ≳ 99%) was dried by passing the gaseous monomer through columns packed with calcium chloride and calcium hydride. Isopropyl vinyl ether (IPVE) was synthesized by dealcoholation of the corresponding acetal with *p*-toluenesulfonic acid. The crude monomer was washed and distilled in the same way as described above for IBVE. The purities of these monomers (except for MVE) were better than 99.9% by gas chromatography. Hexadecyl vinyl ether (cetyl vinyl ether; CVE) was fractionated from a commercial product (Shin Nihon Rika) over calcium hydride; a middle cut boiling at 140–145 °C (3 mmHg) was used. This monomer contained about 2 wt % *n*-dodecyl and *n*-tetradecyl vinyl ethers but no other impurities. *p*-Methoxystyrene (pMOS) was synthesized from *p*-methoxyacetophenone[7] and distilled twice over calcium hydride under reduced pressure (purity ≳ 99%).

Hydrogen iodide was obtained from a 57% aqueous solution (Wako Chemicals) by dehydration with phosphorus pentoxide[6,8] and stored as an *n*-hexane solution (ca. 1 M) in ampules in a freezer in the dark. Solvents (*n*-hexane, toluene, methylcyclohexane (MCH), and carbon tetrachloride) were purified by the usual methods and distilled twice over calcium hydride before use.

Results and Discussion

Synthesis of Monodisperse Living Poly(vinyl ethers). Six alkyl vinyl ethers ($CH_2{=}CH{-}OR$; R = CH_3, C_2H_5, i-C_3H_7, n-C_4H_9, i-C_4H_9, n-$C_{16}H_{33}$) were polymerized at low temperatures (−5 to −35 °C) in nonpolar solvents (*n*-hexane, toluene, MCH, and carbon tetrachloride) by the HI/I_2 initiating system which induces the living polymerization of IBVE.[6] Depending on the solubility of product polymers, appropriate nonpolar solvents were used for each monomer (see Figure 1). The initial concentrations of hydrogen iodide and iodine ($[C]_0 = [HI]_0 = [I_2]_0$) were changed, while the initial monomer concentration was kept constant ($[M]_0 = 0.38$ M). The polymerizations were quantitative for all the monomers.

Figure 1 illustrates the MWDs of the polymers produced under these conditions. The MWDs were nearly monodisperse ($\bar{M}_w/\bar{M}_n = 1.04$–$1.10$) in all cases and shifted obviously toward higher molecular weight with an increase of the feed ratio of monomer to initiator ($[M]_0/[C]_0$).

Figure 2 shows the relationships between the ratio $[M]_0/[C]_0$ and the $\bar{M}_n$ of the formed polymers. The $\bar{M}_n$ was directly proportional to the ratio. The straight lines

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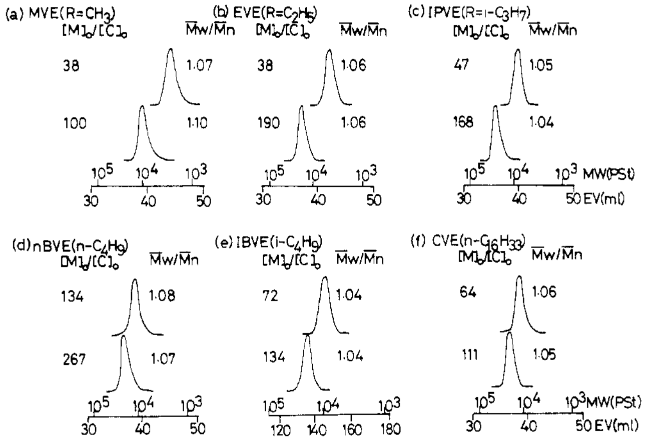

Figure 1. MWD of poly(alkyl vinyl ethers) obtained by HI/I$_2$: $[M]_0 = 0.38$ M; conversion ca. 100%. Polymerization solvent and temperature: (a) and (b) toluene, -35 °C; (c), (d), and (e) n-hexane, -15 °C; (f) MCH, -5 °C; $[C]_0 = [HI]_0 = [I_2]_0$. $[M]_0/[C]_0$ and $\bar{M}_w/\bar{M}_n$ ratios as indicated.

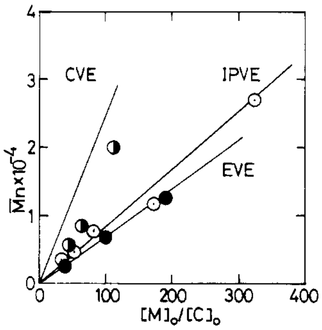

Figure 2. $\bar{M}_n$ vs. $[M]_0/[C]_0$ relationships for poly(CVE), poly(IPVE), and poly(EVE) obtained by HI/I$_2$: $[M]_0 = 0.38$ M; conversion ca. 100%. Polymerization solvent and temperature: poly(CVE) (◑) MCH, -5 °C; poly(IPVE) (◎) n-hexane, -15 °C; poly(EVE) (●) toluene, -35 °C. The straight lines indicate the $\bar{M}_n$ values for living polymerization, calculated by $\bar{M}_n$ = (wt of consumed monomer per L)/$[HI]_0$.

in Figure 2 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 satisfactory, indicating that the $\bar{M}_n$ of the poly(vinyl ethers) obtained by HI/I$_2$ is inversely proportional to the HI concentration. The $\bar{M}_n$ for other vinyl ethers showed similar relationships with the ratio $[M]_0/[C]_0$. Thus, not only IBVE[6] but also the five vinyl ethers, in conjunction with the HI/I$_2$ initiating system, gave monodisperse living polymers, irrespective of their alkyl side chains. The molecular weight ($\bar{M}_n$) of these living polymers can readily be controlled by simply regulating the $[M]_0/[C]_0$ ratio.

This 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.

Monomer-Addition Experiment. Living polymers are characterized by an increase of their molecular weight when additional monomer is supplied to the polymerization system. To obtain further evidence for the living nature of the polymerizations by HI/I$_2$ initiator, this characteristic was examined for poly(IBVE) prepared in n-hexane at -15 °C.[6] Thus IBVE was polymerized at two initiator concentrations ($[C]_0 = 5.0$ and 10 mM), and to these polymerizing mixtures (conversion 60–80%) was added an IBVE solution in n-hexane. Figure 3 compares the MWD of the products obtained before and after the monomer addition. After monomer addition the MWD (Figure 3b,d) obviously shifted toward higher molecular weight without tailing, while keeping its near monodispersity ($\bar{M}_w/\bar{M}_n \lesssim 1.1$). The $\bar{M}_n$ of the product polymers (b and d) was nearly doubled by halving the HI concentration. Therefore we can conclude that all the growing chains formed in the first-stage polymerization (Figure 3a,c) can resume their propagation when additional monomer is supplied.

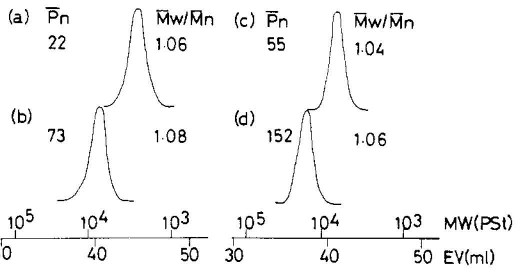

Figure 3. MWD of poly(IBVE) obtained in monomer-addition experiments in the polymerization by HI/I$_2$ in n-hexane at -15 °C: (a) $[M]_0 = 0.38$ M, $[HI]_0 = [I_2]_0 = 10$ mM, conversion 58%; (b) after addition of IBVE (1.9 mmol) to sample a, conversion 193% relative to the first IBVE feed; (c) $[M]_0 = 0.38$ M, $[HI]_0 = [I_2]_0 = 5.0$ mM, conversion 72%; (d) after addition of IBVE (1.9 mmol) to sample c, conversion 200% relative to the first IBVE feed.

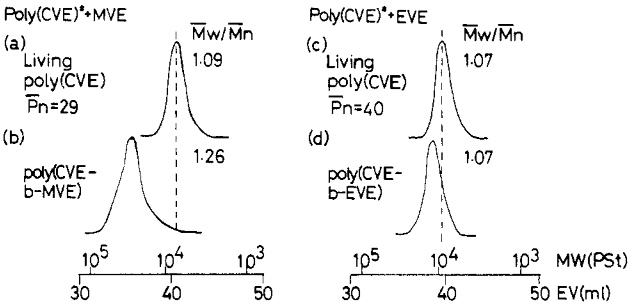

Figure 4. MWD of CVE–MVE and CVE–EVE block polymers obtained by blocking from living poly(CVE): (a) starting poly(CVE), $[M]_0 = 0.20$ M, $[HI]_0 = [I_2]_0 = 7.0$ mM; (b) poly(CVE-b-MVE) from polymer a, CVE/MVE = 1/3; (c) starting poly(CVE), $[M]_0 = 0.33$ M, $[HI]_0 = [I_2]_0 = 7.6$ mM; (d) poly(CVE-b-EVE) from polymer c, CVE/EVE = 1/0.7. Solvent and temperature: (a) and (c) MCH, -5 °C; (b) and (d) MCH/toluene (1/1, v/v), -15 °C. Conversion was 100% in each stage.

Block Copolymerization of Vinyl Ethers. The living polymerizations initiated by HI/I$_2$ were applied to the block copolymerization between a pair of vinyl ethers. As typical examples block copolymers of CVE and MVE or EVE were first synthesized. These block polymers appear interesting as amphiphilic materials in which a hydrophilic poly(MVE) or poly(EVE) chain is connected with a hydrophobic poly(CVE) segment having long alkyl pendants. CVE–MVE and CVE–EVE blocks were prepared either by blocking from living poly(CVE) or, vice versa, from living poly(MVE) and poly(EVE).

Blocking from Living Poly(CVE). CVE was polymerized quantitatively by HI/I$_2$ in MCH solvent at -5 °C to yield monodisperse living poly(CVE) (Figure 4a,c). To this solution of living polymer was added MVE in toluene or EVE in MCH, and the monomers were completely polymerized at -15 °C. The MWDs of the product polymers (Figure 4b,d) were narrow without tailing ($\bar{M}_w/\bar{M}_n \lesssim 1.3$) and shifted toward higher molecular weight than those of the starting poly(CVE).

The blocking products were extracted with methanol in which poly(MVE) and poly(EVE) are soluble whereas poly(CVE) is insoluble. A methanol-soluble part was completely absent. The absence of a methanol-soluble part

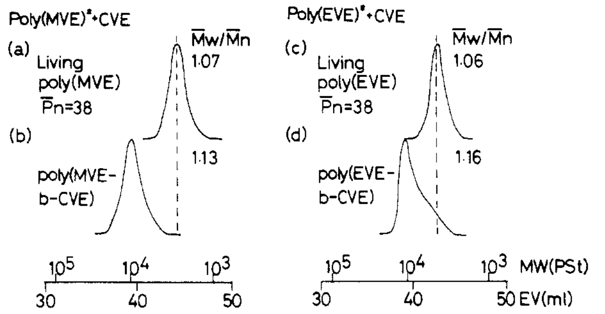

Figure 5. MWD of MVE–CVE and EVE–CVE block polymers obtained by blocking from living poly(MVE) and poly(EVE): (a) starting poly(MVE), $[M]_0 = 0.38$ M, $[HI]_0 = [I_2]_0 = 10$ mM; (b) poly(MVE-*b*-CVE) from polymer a, MVE/CVE = 1.9/1; (c) starting poly(EVE), $[M]_0 = 0.38$ M, $[HI]_0 = [I_2]_0 = 10$ mM; (d) poly(EVE-*b*-CVE) from polymer c, EVE/CVE = 1.9/1. Solvent and temperature: (a) and (c) toluene, −35 °C; (b) and (d) toluene/CCl_4 (1/1, v/v), −15 °C. Conversion was 100% in each stage.

indicates that the products are free from homopolymers of MVE or EVE. Therefore, all of the poly(CVE) living ends initiated the second-stage polymerizations of the added MVE and EVE, which were also living to give, respectively, CVE–MVE and CVE–EVE block polymers in a high blocking efficiency.

The CVE–MVE block copolymer, obtained from living poly(CVE) with $\bar{P}_n = 29$, contained 86 MVE units; the CVE–EVE block copolymer, from poly(CVE) with $\bar{P}_n = 40$, contained 28 EVE units, according to ^{1}H NMR analysis.

Blocking from Living Poly(MVE) and Poly(EVE). In this "reversed" block copolymerization, a solution of CVE in carbon tetrachloride was added to a solution of MVE or EVE living polymer in toluene at −35 °C. Then the reaction temperature was raised to −15 °C to complete the CVE polymerization. Figure 5 summarizes the results. The MWDs of the product polymers shifted toward higher molecular weight than those of the starting polymers without tailing. Extraction with methanol showed the absence of homopolymers of MVE or EVE in the products. This indicates that all of the poly(MVE) and poly(EVE) living ends initiated the living polymerization of CVE. The MVE–CVE block copolymer, obtained from living poly(MVE) with $\bar{P}_n = 38$, contained 20 CVE units; the EVE–CVE block copolymer, from poly(EVE) with $\bar{P}_n = 38$, contained 20 CVE units, according to ^{1}H NMR analysis.

Block Copolymerization between Vinyl Ethers and *p*-Methoxystyrene. Previously, pMOS–IBVE block polymers were synthesized via long-lived poly(pMOS) obtained with iodine,[4] but the blocking efficiency was unsatisfactory (40–50%). In order to synthesize block copolymers between a vinyl ether and *p*-methoxystyrene in high blocking efficiency, the living poly(vinyl ethers) prepared by HI/I_2 initiator were allowed to initiate polymerization of pMOS. pMOS–vinyl ether block copolymers are of interest because pMOS produces hard segments, whereas vinyl ethers give rubbery, soft segments. Thus, pMOS was polymerized by MVE, EVE, and IBVE living polymers produced by HI/I_2. A solution of pMOS in carbon tetrachloride was added to a completely polymerized solution of MVE, EVE, or IBVE. Figure 6 illustrates the MWDs of the product polymers.

All these MWDs (Figure 6b,d,f) are fairly narrow ($\bar{M}_w/\bar{M}_n \lesssim 1.3$) and obviously shifting toward higher molecular weight than those of the starting living polymers (Figure 6a,c,e). To check their homogeneity, blocking products 6b and 6d were dissolved in methanol, a good solvent for poly(MVE) and poly(EVE); product 6f was dissolved in 2-propanol, a good solvent for poly(IBVE).

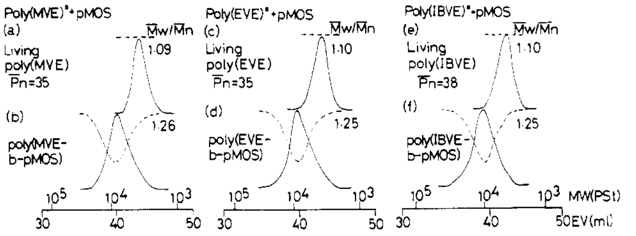

Figure 6. MWD of block polymers obtained by blocking pMOS from living poly(vinyl ethers) at −35 °C (feed, vinyl ether/pMOS = 1/1): (a) starting poly(MVE), $[M]_0 = 0.38$ M, $[HI]_0 = [I_2]_0 = 11$ mM; (b) poly(MVE-*b*-pMOS) from polymer a; (c) starting poly(EVE), $[M]_0 = 0.38$ M, $[HI]_0 = [I_2]_0 = 11$ mM; (d) poly(EVE-*b*-pMOS) from polymer c; (e) starting poly(IBVE), $[M]_0 = 0.38$ M, $[HI]_0 = [I_2]_0 = 10$ mM; (f) poly(IBVE-*b*-pMOS) from polymer e. Solvent: (a) and (c) toluene; (b) and (d) toluene/CCl_4 (1/1, v/v); (e) and (f) CCl_4. Conversion was 100% in each stage. (—) RI detection; (---) UV detection at 254 nm.

Both alcohols are nonsolvents for poly(pMOS). All alcohol solutions were slightly cloudy but free from precipitates at room temperature (∼+30 °C), indicating the absence of pMOS homopolymers in each blocking product. In addition, the products all showed a strong UV response at 254 nm [absent in the starting poly(vinyl ethers)] in dual-mode GPC measurement, and the UV traces (broken lines in Figure 6) were almost superimposable on the RI traces (solid lines).[9] This indicates the incorporation of pMOS units into each starting polymer chain.

Thus, all living chains of poly(MVE), poly(EVE), and poly(IBVE), produced by HI/I_2, are able to polymerize pMOS to give block polymers. According to ^{1}H NMR analysis, the degree of polymerization for each segment of the block polymers was as follows: 6b, MVE–pMOS = 35–35; 6d, EVE–pMOS = 35–35; 6f, IBVE–pMOS = 38–38.

In conclusion, this work has shown that monodisperse living poly(vinyl ethers) can be produced by the HI/I_2 initiating system and that they could initiate the polymerization of pMOS or other vinyl ethers to give block polymers in a high efficiency.

Registry No. MVE (homopolymer), 9003-09-2; EVE (homopolymer), 25104-37-4; IPVE (homopolymer), 25585-49-3; nBVE (homopolymer), 25232-87-5; IBVE (homopolymer), 9003-44-5; CVE (homopolymer), 9015-50-3; poly(CVE) + MVE (copolymer), 28964-00-3; poly(CVE) + EVE (copolymer), 92078-54-1; poly(MVE) + pMOS (copolymer), 92078-55-2; poly(EVE) + pMOS (copolymer), 92078-56-3; poly(IBVE) + pMOS (copolymer), 69644-35-5; HI, 10034-85-2; I_2, 7553-56-2.

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(9) Separate experiments showed that even a small amount (ca. 5 wt %) of homopoly(pMOS) present in a blocking product can readily be detected by GPC as a shoulder or a separate peak. For example, the GPC eluogram for a mixture of our IBVE–pMOS blocking product (Figure 6f; IBVE/pMOS = 38/38 by repeat unit) with 5 wt % of a poly(pMOS) sample ($\bar{P}_n$ = 38) exhibited a shoulder at the elution volume corresponding to the added homopoly(pMOS). The blocking product itself did not show such a shoulder but a unimodal narrow MWD as seen in Figure 6f.