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# Synthesis of Telechelic Living Poly(vinyl ethers)

**Masaaki Miyamoto, Mitsuo Sawamoto, and Toshinobu Higashimura***

*Department of Polymer Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan. Received May 8, 1984*

ABSTRACT: Reaction of ethyl vinyl ether (EVE) with an equimolar amount of hydrogen iodide (HI) in nonpolar solvents at −30 °C gave an adduct $[CH_3CH(OEt)I]$ (1) in quantitative yield. Similarly to the $HI/I_2$ initiating system, 1, in conjunction with iodine, initiated living polymerization of a series of vinyl ethers in nonpolar media at −5 to −40 °C to give monodisperse polymers. Treatment of 1,4-bis(vinyloxy)butane with 2 equiv of HI led to a diadduct $[CH_3CH(I)O(CH_2)_4OCH(I)CH_3]$ (2) quantitatively, under the conditions similar to those for the EVE/HI system. In the presence of 2 equiv of iodine, 2 acted as an effective bifunctional initiator that generated monodisperse, telechelic living poly(vinyl ethers) in nonpolar solvents at −40 °C. These bifunctional living polymers were capable of polymerizing vinyl ethers to give ABA-type triblock copolymers with a narrow molecular weight distribution in a high blocking efficiency; e.g., poly(methyl vinyl ether-*b*-hexadecyl vinyl ether-*b*-methyl vinyl ether). Telechelic poly(EVE) having *sec*-amino termini was obtained by quenching the living ends with *n*-butylamine. Chain extension using hexamethylenediamine as coupling agent led to poly(EVE) with in-chain amino ether linkages and a broad molecular weight distribution extending from $10^4$ to $10^6$.

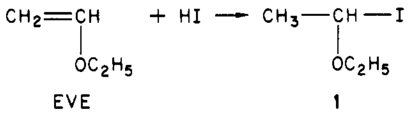
## Introduction

Telechelic living polymers are of use in the synthesis of ABA-type block copolymers and bifunctional prepolymers (telechelics) and in chain extension reactions. Although some bifunctional initiators are known in cationic polymerization of vinyl monomers,[1-3] well-characterized telechelic living polymers and ABA-type block copolymers have seldom been synthesized. Only recently, ABA-type block copolymers, e.g., poly($\alpha$-methylstyrene-*b*-isobutyl vinyl ether-*b*-$\alpha$-methylstyrene), were synthesized by the "quasi-living" method.[4]

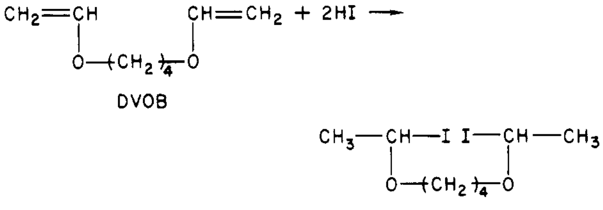
We have recently reported the synthesis of living poly(vinyl ethers) having monodisperse molecular weight distribution (MWD) ($\bar{M}_w/\bar{M}_n < 1.1$) by a mixture of hydrogen iodide (HI) and iodine ($I_2$) as an initiating system.[5,6] These living polymers were also applied to the synthesis of block copolymers between vinyl ethers or a vinyl ether and *p*-methoxystyrene (pMOS).[6]

In the course of this study, HI was found to add quantitatively to vinyl ethers in nonpolar solvents to produce $\alpha$-iodo ethers, e.g., (1-iodoethoxy)ethane (1) and 1,4-bis(1-iodoethoxy)butane (2) (eq 1 and 2). These HI–vinyl ether adducts seem to be involved in the initiation process in the $HI/I_2$-initiated living polymerization. In particular, adduct 2, obtained from 1,4-bis(vinyloxy)butane (BVOB) (eq 2), is of interest as a potential bifunctional initiator.

This study aims (i) to examine whether 1 and 2, when coupled with iodine, are capable of initiating living polymerization of vinyl ethers, (ii) to synthesize telechelic living polymers by the 2/iodine initiating system, and (iii) to apply these living polymers to chain extension and the synthesis of ABA-type block polymers.



$$\underset{\text{EVE}}{\underset{\displaystyle OC_2H_5}{\underset{|}{CH_2{=}CH}}} + HI \longrightarrow \underset{\mathbf{1}}{\underset{\displaystyle OC_2H_5}{CH_3{-}\underset{|}{CH}{-}I}} \qquad (1)$$



$$\underset{\text{DVOB}}{CH_2{=}CH{-}O{-}(CH_2)_4{-}O{-}CH{=}CH_2} + 2HI \longrightarrow \underset{\mathbf{2}}{CH_3{-}CH(I){-}O{-}(CH_2)_4{-}O{-}CH(I){-}CH_3} \qquad (2)$$

## Experimental Section

**Procedures.** Polymerization was carried out under dry nitrogen in a vessel equipped with a three-way stopcock at −5 to −40 °C. The reaction was initiated by adding, successively, an *n*-hexane solution of 1 or 2 (kept at −78 °C) and an iodine solution to a monomer solution. 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 three polystyrene gel columns (Shodex A-802 and A-804 (×2); 8.0 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

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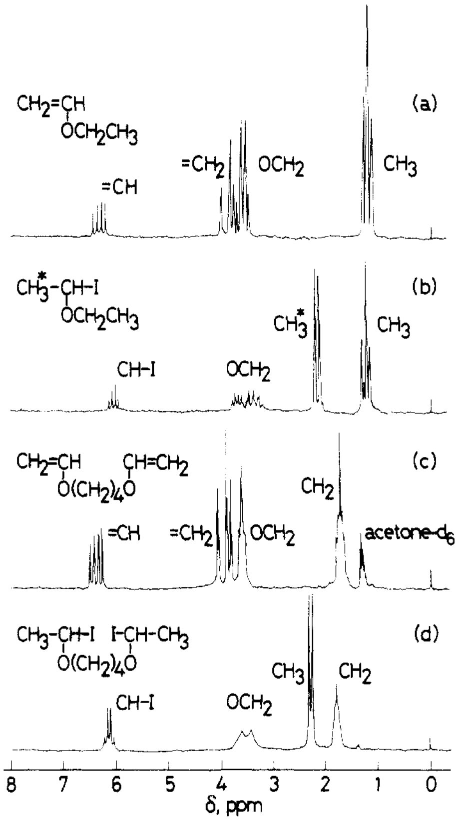

**Figure 1.** $^1H$ NMR spectra of (1-iodoethoxy)ethane (1), 1,4-bis(1-iodoethoxy)butane (2), and their precursors (EVE and BVOB) in $CCl_4$ at -25 °C: (a) EVE, 0.34 M; (b) 1, 0.17 M (EVE + HI); (c) BVOB, 0.34 M; (d) 2, 0.17 M (BVOB + 2HI).

polystyrene calibration. The number-average molecular weight ($\bar{M}_n$) of the produced polymers was measured by vapor pressure osmometry in benzene at 30 °C on a Hitachi-117 molecular weight apparatus. The composition of block copolymers was determined by $^1H$ NMR spectroscopy (JEOL NMR FX 90-Q) in $CDCl_3$ from the signal intensity ratio of the protons adjacent to the ether oxygen ($\delta$ 3.1–3.7) to the remaining alkyl protons ($\delta$ 0.7–2.1).

The cloud points of block copolymers were measured by heating and cooling their solutions (0.23 wt %) in methanol in a sealed tube gradually (1.0 °C/min) in the temperature range from 15 to 75 °C (precision ±0.1 °C).

**Materials.** Methyl, ethyl, isobutyl, and hexadecyl (cetyl) vinyl ethers (MVE, EVE, IBVE, and CVE, respectively) were purified as described previously.[5,6] Commercial BVOB (Polyscience) was distilled over calcium hydride under reduced pressure. The purities of these monomers were better than 99.8% by gas chromatography. Hydrogen iodide was obtained from a 57% aqueous solution (Wako Chemicals) by dehydration with phosphorus pentoxide.[5] Commercial iodine (Wako Chemicals) was sublimed over potassium iodide under reduced pressure and stored in ampules in a freezer in the dark. *n*-Butylamine (*n*-$BuNH_2$) and hexamethylenediamine (HMDA) (both from Wako Chemicals) were purified by distillation. Solvents [*n*-hexane, toluene, and carbon tetrachloride ($CCl_4$)] were purified by the usual methods and distilled twice over calcium hydride before use.

1,4-Bis(1-iodoethoxy)butane (2) was synthesized by treating BVOB with a double molar quantity of HI in *n*-hexane or $CCl_4$ at -30 °C. (1-Iodoethoxy)ethane (1) was synthesized from equimolar amounts of EVE and HI in a similar manner. Quantitative formation of 1 and 2 was confirmed by $^1H$ and $^{13}C$ NMR spectroscopy ($CCl_4$, acetone-$d_6$ capillary). These compounds were used immediately as prepared without isolation.

## Results and Discussion

**Formation of (1-Iodoethoxy)ethane and 1,4-Bis(1-iodoethoxy)butane.** EVE was allowed to react with an equimolar amount of HI in a nonpolar solvent (*n*-hexane or $CCl_4$) at -30 °C. Almost instantaneously an adduct, 1 (eq 1), was obtained in a quantitative yield; no polymers were formed according to $^1H$ NMR. Similarly, the reaction of BVOB with 2 equiv of HI produced 2 quantitatively under similar conditions (eq 2).

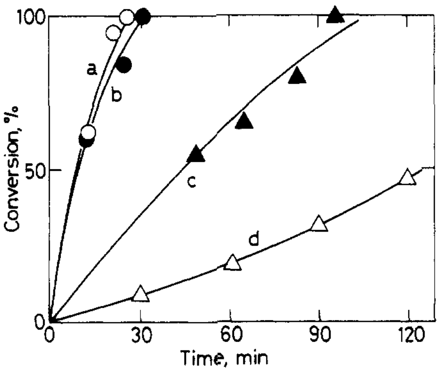

**Figure 2.** Time–conversion curves for the polymerization of EVE by $1/I_2$ or $2/I_2$ initiating system in toluene at -40 °C ($[M]_0$ = 0.38 M): (a) $[2]_0$ = 5.0 mM, $[I_2]_0$ = 10 mM; (b) $[1]_0$ = $[I_2]_0$ = 10 mM; (c) $[1]_0$ = $[I_2]_0$ = 5.0 mM; (d) $[I_2]_0$ = 10 mM.

The $^1H$ NMR spectra of these adducts, along with peak assignments, are shown in Figure 1. The addition of HI into a solution of EVE or BVOB in $CCl_4$ caused the disappearance of the vinyl protons of the monomers (3.5–4.0 and ~6.3 ppm) and in turn the appearance of a quartet (6.0–6.1 ppm) and a doublet (2.1–2.3 ppm). The former is assignable to the $-CH-I$ of 1 or 2; the latter is due to the methyl protons adjacent to the iodine atom. The splitting patterns and chemical shifts are all consistent with the adducts 1 and 2, and other peaks could not be observed.

Adducts 1 and 2 also gave $^{13}C$ NMR spectra that are consistent with the expected structures ($\delta$): 1, 13.92 ($\mathit{C}H_3CH_2$), 31.10 ($\mathit{C}H_3CH$), 69.41 ($CH_2$), and 78.18 ($\mathit{C}H-I$); 2, 24.98 ($OCH_2CH_2\mathit{C}H_2CH_2O$), 31.05 ($CH_3$), 72.98 ($O\mathit{C}H_2$), and 77.91 ($\mathit{C}H-I$).

These NMR spectral data show the quantitative formation of these adducts from the vinyl ethers and HI. It should be noted that the addition of iodine, instead of HI, to BVOB has been reported to occur only on one of its two vinyl groups and that the subsequent intramolecular rearrangement resulted in a cyclic diiodo compound.[7]

**Polymerization of Vinyl Ethers by 1 or 2 in the Presence of Iodine.** 1 and 2 were found to polymerize EVE in toluene at -40 °C in the presence of iodine. Figure 2 shows the time–conversion curves thus obtained. When 1 or 2 alone was added to an EVE solution, virtually no polymer formed in several hours, but the addition of iodine to this apparently quiescent mixture effected a polymerization. The conversion curves with these two initiators (Figure 2a–c) completely differed from that with iodine (Figure 2d). The polymerizations proceeded without an induction period and were faster than that by iodine;[5] the latter showed a clear acceleration phase. The polymerization rate by 2 (5.0 mM)/$I_2$ (10 mM) was in good agreement with that by 1 (10 mM)/$I_2$ (10 mM) (Figure 2, a and b). This indicates that 2 gives the same concentration of the active site as that by double the molar quantity of its monofunctional counterpart 1, and that both $CH_3CHI$ groups of 2 can independently initiate the EVE polymerization in the presence of iodine.

Figure 3 illustrates the MWD of the polymers thus produced. Both iodoethoxy compounds produced poly(EVE) with a nearly monodisperse MWD. The MWD obtained by $1/I_2$ (Figure 3a) was practically superimposable with that obtained by the same amount of $HI/I_2$[6] and shifted obviously toward higher molecular weight without

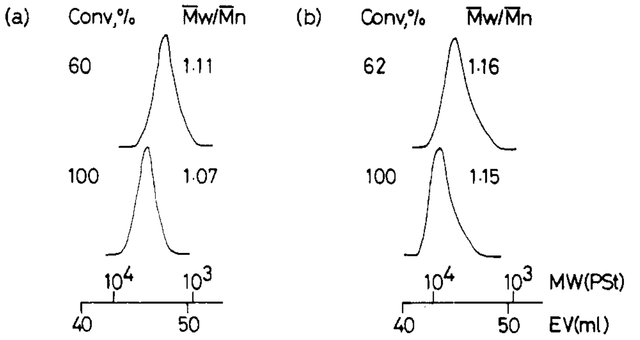

**Figure 3.** Effect of conversion on the MVD of poly(EVE) obtained by $1/I_2$ (a) and $2/I_2$ (b) in toluene at -40 °C ($[M]_0 = 0.38$ M): (a) $[1]_0 = [I_2]_0 = 5.0$ mM; (b) $[2]_0 = 5.0$ mM, $[I_2]_0 = 10$ mM.

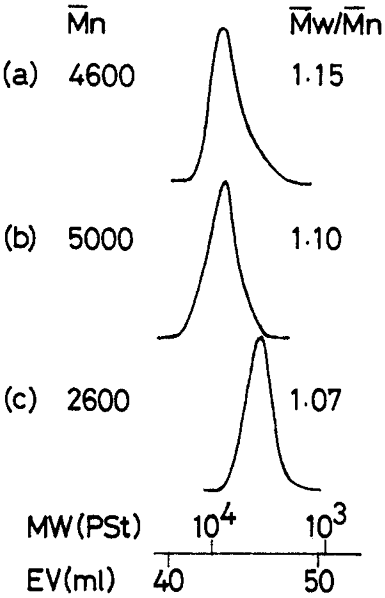

**Figure 4.** Effect of initiator concentration on the MWD of poly(EVE) obtained by $1/I_2$ and $2/I_2$ in toluene at -40 °C ($[M]_0 = 0.38$ M; conversion = 100%): (a) $[2]_0 = 5.0$ mM, $[I_2]_0 = 10$ mM; (b) $[1]_0 = [I_2]_0 = 5.0$ mM; (c) $[1]_0 = [I_2]_0 = 10$ mM.

tailing as the polymerization proceeded. Therefore, a nearly monodisperse living polymer was quantitatively produced by $1/I_2$, similarly to the polymerization by $HI/I_2$.[5,6]

The MWDs obtained by $2/I_2$ (Figure 3b) were nearly monodisperse and shifted obviously toward higher molecular weight with increasing conversion.

Figure 4 shows the effect of the initial concentrations of 1 and 2 on the $\bar{M}_n$ of poly(EVE) obtained at constant monomer concentration (0.38 M; conversion $\cong$ 100%). The $\bar{M}_n$ obtained by 5 mM of 2 ($[I_2]_0 = 10$ mM) (Figure 4a) was in good agreement with that by the same amount of 1 (5 mM; $[I_2]_0 = 5$ mM) (Figure 4b) and nearly twice as large as the $\bar{M}_n$ when the concentration of 1 was doubled ($[1]_0 = [I_2]_0 = 10$ mM) (Figure 4c).

All the $\bar{M}_n$ values of the polymers shown in Figures 3 and 4 were very close to the calculated values for living polymers which were assumed to be formed quantitatively from 1 and 2. These results show that 2, coupled with iodine, acts as a bifunctional initiator which quantitatively generates a bifunctional living poly(EVE).

The $1/I_2$ and $2/I_2$ initiating systems also led to nearly monodisperse living polymers of the other vinyl ethers (MVE, IBVE, and CVE).

**Reactions with Amines and Chain Extension.** To introduce an amino group to the chain end of the mono- and bifunctional living polymers thus obtained, their reactions with amines were examined. As an application of these reactions, the chain extension of the telechelic living polymer was also studied by using a diamine as coupling agent. Figure 5 summarizes the results.

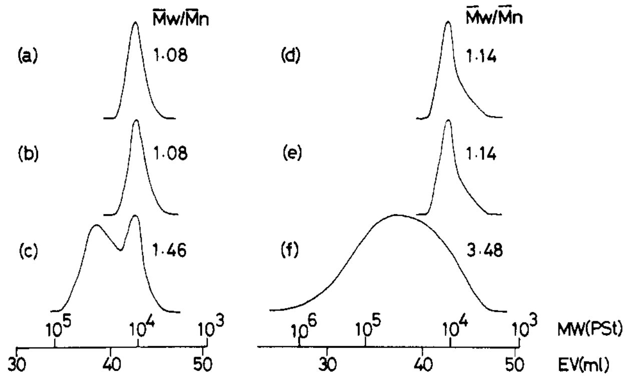

**Figure 5.** Reactions of $n$-butylamine ($n$-BuNH$_2$) and hexamethylenediamine (HMDA) with living poly(EVE) obtained by $1/I_2$ (a–c) and $2/I_2$ (d–f) in toluene at -40 °C: (a–c) $[1]_0 = [I_2]_0 = 5.0$ mM; (d–f) $[2]_0 = 5.0$ mM, $[I_2]_0 = 10$ mM; $[M]_0 = 0.38$ M; conversion = 100%. Reactions with (a) methanol (excess), (b) $n$-BuNH$_2$ (25 mM), (c) HMDA (1.25 mM), (d) methanol (excess), (e) $n$-BuNH$_2$ (25 mM), and (f) HMDA (2.5 mM).

The monofunctional living poly(EVE) produced by $1/I_2$ (Figure 5a) was treated with an excess amount of $n$-butylamine ($[-NH_2] = 5$[living end]). The resulting polymer (Figure 5b) exhibited virtually the same narrow MWD as that of the starting living polymer. The nitrogen content by elemental analysis of the product was 0.81 wt %, very close to 0.84 wt % expected for the quantitative reaction of the living end with the added amine. Thus, functionalized poly(EVE) having a *sec*-amino terminal was obtained (eq 3; the asterisk indicates the living end).

$$\sim\!\sim\!* + n\text{-BuNH}_2 \rightarrow \sim\!\sim\text{NH-}n\text{-Bu} \qquad (3)$$

The monofunctional living polymer was also allowed to react with a diamine, HMDA. When HMDA was in excess over the living polymer ($[-NH_2] = 20$[living end]), the 1:1 adduct ($\sim\!\sim NH(CH_2)_6NH_2$) was obtained. The MWD and its peak molecular weight remained practically unchanged after the addition of HMDA. On the other hand, the addition of a smaller amount of the diamine ($[-NH_2] = 0.5$[living end]) led to a product with a bimodal MWD (Figure 5c). The higher molecular weight peak is due to the reaction of HMDA with two living polymers (chain coupling); the lower molecular weight peak corresponds to 1:1 adduct (eq 4).

$$\sim\!\sim\!* + H_2N(CH_2)_6NH_2 \rightarrow \sim\!\sim NH(CH_2)_6NH_2 + \sim\!\sim NH(CH_2)_6NH\sim\!\sim \qquad (4)$$

The telechelic living poly(EVE) was also treated with the mono- and diamines (eq 5 and 6). When an excess amount of $n$-butylamine was added to the bifunctional living polymer ($[-NH_2] \cong 2.5$[living end]), the produced polymer showed an MWD (Figure 5e) almost identical with that of the starting living polymer (Figure 5d). The nitrogen content of the product was 0.63 wt % and close to the calculated value (0.50 wt %) assuming quantitative reaction of both living ends. These results indicate that the telechelic living poly(EVE) quantitatively reacts with $n$-butylamine to form a telechelic polymer with *sec*-amino groups (eq 5).

$$*\!\sim\!\sim\!* + 2n\text{-BuNH}_2 \rightarrow n\text{-Bu-NH}\sim\!\sim\text{NH-}n\text{-Bu} \qquad (5)$$

The reaction with bifunctional HMDA ($[-NH_2] = 0.5$[living end]) led to polymers with a broad MWD extending

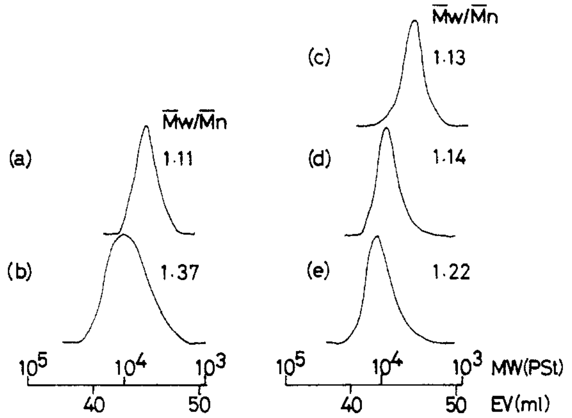

**Figure 6.** Synthesis of poly(MVE-*b*-CVE-*b*-MVE) triblock copolymers from (a,b) bifunctional living poly(CVE) and (c–e) monofunctional living poly(MVE): (a) starting poly(CVE) prepared in $CCl_4$ at −5 °C, $[CVE]_0$ = 0.10 M, $[\mathbf{2}]_0$ = 5.0 mM, $[I_2]_0$ = 10 mM, conversion = 100%; (b) triblock, $(MVE)_{60}$–$(CVE)_{20}$–$(MVE)_{60}$, by polymerizing MVE from polymer a in toluene/$CCl_4$ (1/1 v/v) at −15 °C; (c) starting living poly(MVE) prepared in toluene at −35 °C, $[MVE]_0$ = 0.60 M, $[HI]_0$ = $[I_2]_0$ = 10 mM, conversion = 100%; (d) living AB block, $(MVE)_{60}$–$(CVE)_{20}$, after the addition of CVE to polymer c; (e) ABA triblock, $(MVE)_{60}$–$(CVE)_{20}$–$(MVE)_{60}$, after the addition of MVE to polymer d.

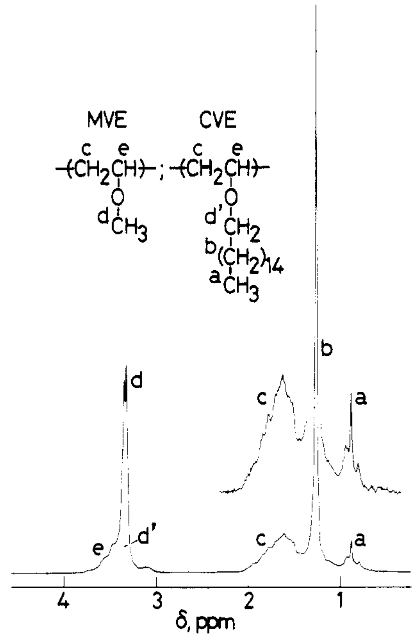

**Figure 7.** $^1$H NMR spectrum of triblock copolymer $(MVE)_{60}$–$(CVE)_{20}$–$(MVE)_{60}$ obtained from telechelic living poly(CVE). See Figure 6 (a and b) for synthesis conditions. Peak assignments as indicated.

**Table I**
**Cloud Points of MVE–CVE Tri- and Diblock Copolymers in Methanol**

| polymer | initiator | $\bar{M}_w/\bar{M}_n$ | cloud point, °C |
|---|---|---|---|
| triblock A<br>$(MVE)_{60}$-$(CVE)_{20}$-$(MVE)_{60}$ | $HI/I_2$ | 1.22 | 21 |
| triblock B<br>$(MVE)_{60}$–$(CVE)_{20}$–$(MVE)_{60}$ | $\mathbf{2}/I_2$ | 1.37 | 21 |
| diblock C<br>$(MVE)_{120}$–$(CVE)_{20}$ | $HI/I_2$ | 1.30 | >75[a] |
| diblock D<br>$(MVE)_{60}$–$(CVE)_{20}$ | $HI/I_2$ | 1.14 | >75[a] |

[a] Remained cloudy up to 75 °C.

from $10^4$ to $10^6$ and with a higher molecular weight than the starting living polymer ($\bar{M}_n \sim 5 \times 10^3$) (Figure 5f). Note the clear difference between Figure 5, c and f, where the same $[-NH_2]$/[living end] ratio was employed for the mono- and bifunctional living poly(EVE). These results indicate that the telechelic living polymer reacted with both ends of HMDA to induce a chain extension reaction (eq 6). The product is most likely poly(EVE) having

$$n{*}\!\sim\!\sim{*} + n\text{H}_2\text{N(CH}_2)_6\text{NH}_2 \rightarrow -[\sim\text{NH(CH}_2)_6\text{NH}\sim]_n- \quad (6)$$

in-chain amino ether units $-CH_2CH(OC_2H_5)-NH-(CH_2)_6NH-CH(OC_2H_5)CH_2-$.

These reactions with the amines further demonstrate that the $\mathbf{2}/I_2$ initiating system gives telechelic (bifunctional) living polymers.

**Synthesis of ABA Triblock Copolymers via the Telechelic Living Polymers.** ABA-type triblock copolymers were synthesized by using the telechelic living polymers obtained with $\mathbf{2}/I_2$. We were interested in amphiphilic polymers consisting of a hydrophilic center block and hydrophobic end blocks or vice versa. Thus, block polymerizations between CVE and MVE or EVE were studied; the former gives a hydrophobic segment, while the latter two lead to a hydrophilic block.

In a typical experiment, CVE was polymerized by $\mathbf{2}/I_2$ in carbon tetrachloride at −5 °C to yield telechelic living poly(CVE) (Figure 6a). To this solution was added MVE in toluene and the monomer was completely polymerized at −15 °C (Figure 6b). In another run, the reverse order of the polymer sequence was examined. Thus, a solution of CVE in carbon tetrachloride was added to a solution of telechelic living poly(MVE) in toluene at −35 °C. Then the reaction temperature was raised to −15 °C to complete the CVE polymerization.

In all experiments, the MWD of the product polymers shifted toward higher molecular weight than that of the starting polymer without tailing (e.g., Figure 6, a and b). This suggests that both active ends of the living poly(CVE) and poly(MVE) initiated the living polymerization of the added vinyl ether to produce ABA triblock copolymers in a high blocking efficiency. The compositions of the triblock polymers (by $^1$H NMR) were as follows: $(MVE)_{60}$–$(CVE)_{20}$–$(MVE)_{60}$ and $(CVE)_{10}$–$(MVE)_{120}$–$(CVE)_{10}$. Figure 7 shows the $^1$H NMR spectrum of the former triblock, indicating the existence of both MVE and CVE units.

Similarly, an ABA triblock copolymer between CVE and EVE [$(CVE)_{38}$–$(EVE)_{76}$–$(CVE)_{38}$, $\bar{M}_w/\bar{M}_n$ = 1.28] was obtained with $\mathbf{2}/I_2$ initiator.

For comparison, an ABA triblock copolymer, $(MVE)_{60}$–$(CVE)_{20}$–$(MVE)_{60}$, was synthesized by the successive addition of CVE and MVE to the monofunctional living poly(MVE) produced by $HI/I_2$ (Figure 6c–e). At all steps nearly monodisperse polymer was produced, indicating the production of triblock copolymer whose composition was the same as that obtained from the telechelic living polymer (Figure 6b).

It is known[8] that ABA-type triblock polymers differ in solubility characteristics from the corresponding AB diblock copolymers having the same A/B composition ratio. Thus, the cloud points of our MVE–CVE block polymerization products were compared to show the formation of triblocks from the telechelic living polymers (Table I). Measurements were done in methanol, a good solvent for the end block [poly(MVE)] and a nonsolvent for the center block [poly(CVE)]. Samples A and B are triblock copolymerization products having the same segment lengths;

A was obtained by the sequential polymerization starting from the monofunctional poly(MVE), and B was prepared from the telechelic living poly(CVE). Samples C and D are the corresponding AB diblocks; C has the same MVE/CVE unit ratio as A and B, whereas D is richer in CVE units.

The solutions of samples A and B (0.23 wt %) were cloudy at 15 °C and turned transparent at 21 °C on gradual heating. In contrast, the solutions of the diblock polymers C and D remained cloudy up to 75 °C. ABA triblock copolymers are known to exhibit a better solubility (lower cloud point) in a good solvent for end block than AB diblock copolymers having the same composition.[8] The results shown in Table I are consistent with this fact, demonstrating that the copolymer produced by the $2/I_2$ initiating system is an ABA-type triblock.

In conclusion, this work has shown that telechelic living poly(vinyl ethers) can be prouced by the $2/I_2$ initiating system in nonpolar media and that they could initiate the living polymerization of second vinyl ethers to give ABA triblock copolymers.

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# Degradable Polymers. Incorporating a Difunctional Azo Compound into a Polymer Network To Produce Thermally Degradable Polyurethanes

**Richard A. Kenley* and Gerald E. Manser†**

*Syntex Research, Palo Alto, California 94304.* *Received January 31, 1984*

ABSTRACT: We investigated polymers that feature useful structural or matrix properties at ambient temperature but that convert to soluble materials on heating. To do so we prepared the difunctional azo compound azobis[(3-hydroxypropyl)diisobutylmethane] (BHPA) and characterized its homolytic decomposition kinetics in solution and after incorporation into a cross-linked polyurethane. In poly(propylene glycol) solution, the BHPA first-order homolytic decomposition rate constant, $k_d$, adhered to the following Arrhenius expression: $k_d$ (s$^{-1}$) = $10^{(15.4\pm0.43)}$ exp[(−35400 ± 790)/$RT$]. At 140 °C, the half-life for BHPA thermolysis was 30 min. After chain extension of poly(propylene glycol) with BHPA, trimethylolpropane, and tolylene diisocyanate, BHPA segment thermolysis (as evidenced by $N_2$ evolution) obeyed the following expression: $k_d$ (s$^{-1}$) = $10^{(15.0\pm0.091)}$ exp[(−35100 $\bullet$ 170)/$RT$]. Thus, the BHPA homolysis rate was essentially unaffected by incorporation into the polymer. In the polyurethane network, BHPA decomposition paralleled polymer molecular weight reduction (as evidenced by size exclusion chromatography) and conversion of the polymer from an insoluble to a soluble material. BHPA and related compounds should have general application to preparation of polymers that can be deliberately degraded by heating at a predefined temperature.

## Introduction

Considerable polymer research focuses on materials that feature high strength and other useful structural properties under extreme environmental conditions (e.g., elevated temperature and high-intensity irradiation). This research area has an obverse, however, that has received considerably less attention. Polymers are frequently used not only as structural components but also as matrix materials, i.e., as carriers for other chemicals. Examples are polymer matrices for pigments (in paints and coatings), for high-energy compounds (in explosives and propellants), and for drugs (in controlled-release pharmaceuticals). For some applications it is desirable to have a matrix material that retains its physical properties under one set of environmental conditions, but that can be deliberately degraded in a controlled fashion by changing the conditions. Matrix degradation would thereby permit recovery of suspended materials or easy removal (including metabolism and excretion) of the polymer itself.

Several schemes for chemical degradation of polymer matrices (via hydrolysis, oxidation, photolysis, etc.) are possible in principle, but difficult to achieve in practice. As an alternative approach, we have considered thermally labile polymers that degrade simply upon heating. Specifically we have undertaken to prepare and evaluate a difunctional azo compound, azobis[(3-hydroxypropyl)diisobutylmethane] (BHPA), as a monomer suitable for incorporation, e.g., into polyurethanes.

$$\mathrm{HOCH_2CH_2CH_2C(\mathit{i}\text{-}C_4H_9)_2{-}N{=}N{-}C(\mathit{i}\text{-}C_4H_9)_2CH_2CH_2CH_2OH}$$

BHPA

As an azoalkane, BHPA should[1] undergo homolytic bond cleavage to yield molecular nitrogen and carbon radicals followed by radical disproportionation to saturated hydrocarbon and olefinic products (vide infra). Inducing these radical reactions in segments of a polymer chain would generate low-molecular-weight fragments and con-

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† Present address: Morton Thiokol Corp., Wasatch Division, Brighman City, UT 84302.

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