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Specific Polymerization Mechanism Involving β-Scission of Mid-Chain Radical Yielding Oligomers in the Free-Radical Polymerization of Vinyl Ethers

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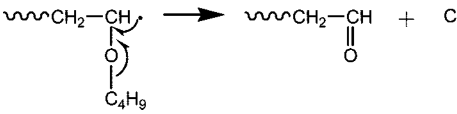
ABSTRACT: Butyl vinyl ether (BVE) was polymerized radically, and the resultant oligomeric poly(BVE)s were characterized mainly using MALDI-TOF-MS spectrometry. For a further structural identification, the poly(BVE) obtained in bulk was subsequently subjected to ^{1}H NMR measurement. Notably, an intensive peak assignable to $-CH_2C(=O)CH_2-$ protons was observed unexpectedly although a peak assignable to $-CHO$ proton as the terminal end-group generated via β-scission of growing polymer radical as a presumed chain-end forming reaction appeared only weakly. Thus, a plausible chain-end forming reaction would be the intramolecular (backbiting) hydrogen abstraction to form mid-chain radical which subsequently undergoes β-scission resulting in oligomeric poly(BVE) with carbonyl group in the polymer backbone. Then, the specific polymerization mechanism involving β-scission of mid-chain radical yielding oligomers is discussed. The hydrogen abstraction ability of growing poly(BVE) radical was checked by using toluene as a solvent having labile hydrogen. The dependence of the degree of polymerization on initiator concentration was examined because the occurrence of primary radical termination was remarkable, probably leading to reduced chain length. Finally, the reinitiation reaction by butyl group generated via β-scission of mid-chain radical was pursued.

Introduction

For a long time, it has been conceived that vinyl ethers undergo no radical but only cationic polymerization. In 1983, we found by chance that butyl vinyl ether (BVE) undergoes radical polymerization to yield an oligomer.[1] Thereafter, Kamachi et al.[2] performed ESR studies on the free-radical polymerization of vinyl ethers including ethyl vinyl ether, isopropyl vinyl ether, BVE, isobutyl vinyl ether, and *tert*-butyl vinyl ether from −50 °C to room temperature using di-*tert*-butylperoxide (DTBPO) as photoinitiator; they successfully observed ESR spectra of the growing polymer radicals using TM_{110} and TE_{011} cavities designed specially for photopolymerization.[3,4] The reason why high polymers are not obtained by the radical polymerization of vinyl ethers is discussed, probably being due to side reactions such as the transfer reaction as a reflection of higher reactivity of growing polymer radical. This is consistent with the result of *ab initio* calculation that suggests the deviation of the growing polymer radical from the planer sp^2 conformation.[5] Moreover, it is well-known that the vinyl ethers, typical electron-donating monomers, undergo readily alternating copolymerization with electron-accepting monomers; thus, vinyl ethers having a labile hydrogen and electron-accepting groups at a suitable position have been polymerized through a propagation mechanism involving intramolecular hydrogen abstraction, i.e., addition−abstraction mechanism.[6] In spite of the aforementioned results, however, it is still described in the textbook that vinyl ethers undergo no radical but cationic polymerization.[7]

Here it should be noted that the various chain transfer reactions are used for the well-known techniques of control of molecular weight, structure, and functionality of synthetic polymers.[8] Recently, addition−fragmentation chain transfer is noted,[9] although the first reports of addition−fragmentation transfer agents in polymerization appeared in the late 1980s.[10−12] Vinyl ethers can be very effective chain transfer agents.[12−15] The driving force for fragmentation is significantly provided by formation of a carbonyl double bond as a result of β-scission of growing polymer radical, being enhanced by the combined formation of a good leaving group. Thus, even in the radical polymerization of common vinyl ethers which do not contain any good leaving group, we can expect the formation of oligomeric poly(vinyl ether)s with a terminal aldehyde end-group since an essential chain-end forming reaction to give oligomer could be β-scission of growing polymer radical, being exemplified by BVE polymerization as follows:



$$\sim\!\sim CH_2-\underset{\underset{C_4H_9}{|}}{\underset{O}{|}}{CH}\cdot \longrightarrow \sim\!\sim CH_2-\underset{O}{\underset{\|}{CH}} + C_4H_9\cdot \qquad (1)$$

This prompted us to explore in more detail the characterization of resulting oligomers in the free-radical polymerization of BVE, mainly using matrix-assisted laser desorption/ionization time-of-flight mass (MALDI-TOF-MS) spectrometry[16,17] because recent advances in mass spectrometry could provide a powerful tool for structural identification of oligomer involving its end-groups.

Thus, we attempted to find out the reason why only oligomer is formed by the radical polymerization of BVE, based on the end-group determination of resultant oligomeric poly(BVE) by MALDI-TOF-MS spectrometry. As the structural identification of aldehyde as the terminal end-group of poly(BVE) was not performed directly from its mass spectrum, the resultant poly(BVE) was subsequently subjected to ^{1}H NMR measurement to confirm the existence of a terminal aldehyde end-group. Notably, the intensive peak assignable to $-CH_2C(=O)CH_2-$ protons was observed unexpectedly at 2.3−2.8 ppm although the peak assignable to $-CHO$ proton as the terminal end-group generated via β-scission of growing polymer radical appeared only slightly at 9.8 ppm. Conclusively, a plausible chain-end

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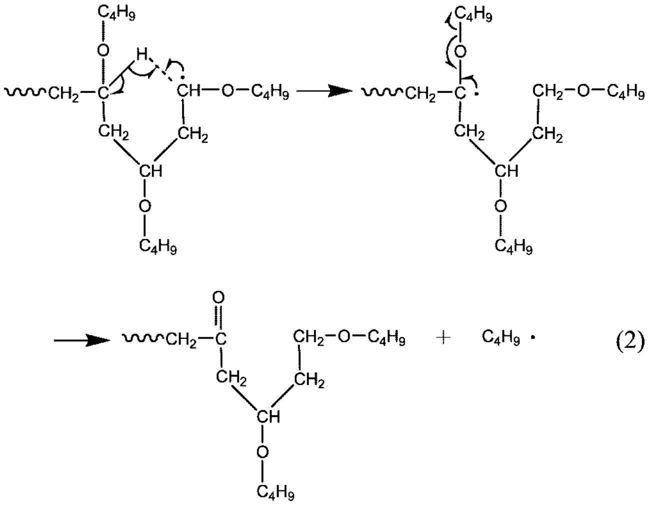
forming reaction, as an alternative to eq 1, would be the intramolecular (backbiting) hydrogen abstraction to form mid-chain radical which subsequently undergoes β-scission resulting in oligomeric poly(BVE) with carbonyl group in the polymer backbone as follows: In this connection, it is well-known that



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the free-radical polymerizations of ethylene,[18] vinyl chloride,[19] vinyl acetate,[20] acrylate esters,[21] and styrene[21a] are governed by the polymerization mechanism involving mid-chain radical formed through backbiting hydrogen abstraction of growing polymer radical, providing short-branched polymers.

Experimental Section

Materials. BVE (Tokyo Kasei Chemical Co., Ltd., Tokyo, Japan) as a monomer was purified by distillation. 2,2′-Azobis(isobutyronitrile) (AIBN) and dimethyl 2,2′-azobis(isobutyrate) (DMAIB) (azo initiators; Wako Pure Chemical Industries, Ltd., Osaka, Japan), and toluene (TOL) (Wako Pure Chemical Industries, Ltd., Osaka, Japan) as a solvent were purified by conventional methods.

2,5-Dihydroxybenzoic acid (DHBA) (Sigma-Aldrich, Milwaukee, WI) as a matrix, sodium iodide (NaI) (Wako Pure Chemical Industries, Ltd., Osaka, Japan) as a cationizing agent, and polyethylene glycol (PEG, M_w = 2000 Da) (Wako Pure Chemical Industries, Ltd., Osaka, Japan) were purchased.

Polymerization. Polymerization was carried out in a glass ampule containing the required amounts of monomer, initiator, and solvent. The ampule was degassed three times by the usual freezing and thawing technique under a vacuum and then sealed off. It was then placed in a thermostat regulated at a required temperature. After a definite reaction time, the reaction mixture was subjected to vacuum-evaporation at room temperature in order to remove unreacted monomer. It should be noted that only methanol soluble oligomers were obtained. On the other hand, methanol is a precipitant for poly(BVE) obtained cationically with boron trifluoride etherate.

Measurements. MALDI-TOF-MS spectra were acquired in positive reflection mode using an Axima-CFR time-of-flight mass spectrometer (Shimadzu/Kratos, Manchester, U.K.) with a pulsed N_2 laser (337 nm). Poly(BVE) (2.0 mg/mL), DHBA matrix (20 mg/mL), and NaI cationizing agent (1.0 mg/mL) were dissolved in THF. 0.5 μL of each of these solutions was deposited on a stainless sample target by the overlayer method as follows: first deposition, matrix solution; second, cationizing agent solution; third, polymer solution. The analyte ions were accelerated at 20 kV under delayed extraction conditions. Sodiated ions of PEG (M_w = 2000 Da) were used for calibration.

SEC measurements were carried out at 40 °C in THF using a two-column Shodex KF-802.5 and -803 at polymer concentrations of 0.1−0.5% (w/v) and at a flow rate of 1 mL/min. SEC curves monitored with a differential refractometer were analyzed using the calibration curve obtained with standard samples of monodisperse polystyrene to estimate the molecular weight.

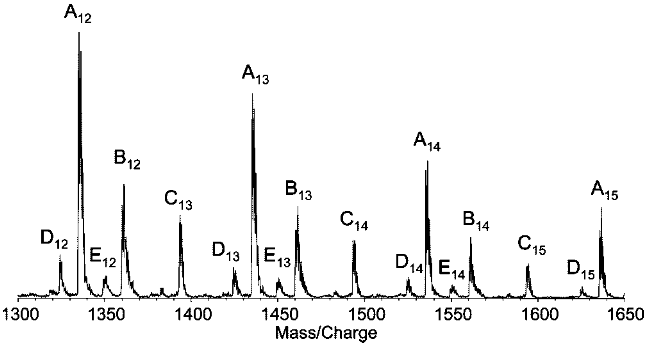

Figure 1. MALDI-TOF-MS spectrum of oligomeric poly(BVE) obtained at a conversion of 8.8% in the bulk polymerization of BVE using 0.1 mol/L of AIBN at 70 °C.

^{1}H NMR spectra were recorded on JEOL AL-400. NMR measurements were carried out at 400 MHz in $CDCl_3$ at 30 °C.

Results and Discussion

Structural Identification of Oligomeric Poly(BVE) Involving Its End-Groups by MALDI-TOF-MS Spectrometry. In our previous article,[1] the polymerization of BVE was conducted in bulk using typical radical initiators, i.e., AIBN and DTBPO, as compared with those of allyl acetate (AAc) and diethyl fumarate (DEF). Notably, the rate and degree of polymerization of resulting oligomer in BVE polymerization were in between AAc and DEF polymerizations. Then, the GPC curve and ^{1}H NMR spectrum of oligomeric poly(BVE) obtained radically with DTBPO were compared with those of poly(BVE) obtained cationically using boron trifluoride etherate as a typical cationic initiator. The results clearly demonstrated that BVE underwent radical polymerization to give an oligomer, but a detailed polymerization mechanism remained open in order to interpret the reason why only oligomer was obtained. Thereafter, the chain transfer reaction has been suggested as significant side reactions without any direct evidence.[4] On the other hand, recent advances in the radical polymerization[22] suggest that β-scission of growing polymer radical through addition−fragmentation transfer[10−15] could be an essential chain-end forming reaction to give oligomeric poly(BVE) with a terminal aldehyde end-group.

Figure 1 shows the MALDI-TOF-MS spectrum of poly(BVE) obtained at a conversion of 8.8% in the bulk polymerization using 0.1 mol/L of AIBN for 5 h at 70 °C as a typical example. The spectrum of the oligomeric poly(BVE) in the presence of NaI exhibited a series of ions repeating at an interval of 100.16 U corresponding to BVE repeat unit. A series of peaks with highest relative intensity (**A**-series) were assigned to the Na^+ adduct ions to the poly(BVE) with the degree of polymerization (n) of 12 to 15, along with $C(CH_3)_2CN$, an initiator fragment, as the initial end-group and, probably, CH_2CHO as the terminal end-group [68.10 + {100.16n + 22.98 (Na^+)} + 43.05] (poly(BVE); $(CH_3)_2C(CN)-(CH_2-CH(OC_4H_9))_n-CH_2-CHO$). Here it is worthy to note that the terminal aldehyde group of poly(BVE) will be generated only when an essential chain-end forming reaction to give oligomer is presumed to be β-scission of growing polymer radical via eq 1. However, a further structural identification of poly(BVE) by ^{1}H NMR spectroscopy demonstrated unexpectedly the existence of an intensive peak assignable to $-CH_2C(=O)CH_2-$ protons although a peak assignable to $-CHO$ proton appeared only weakly; this will be discussed later in detail.

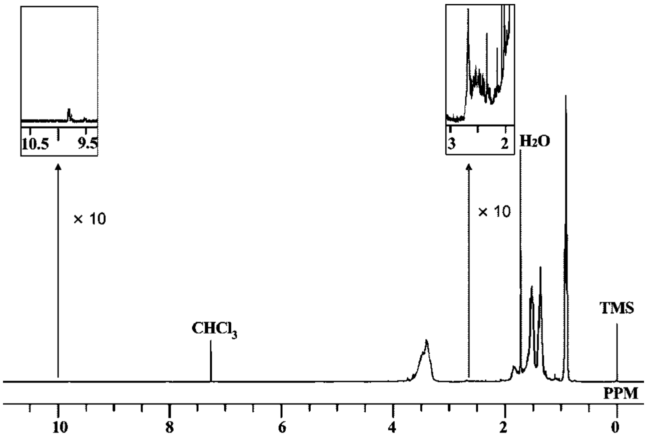

Figure 2. ^{1}H NMR spectrum of oligomeric poly(BVE) (see Figure 1).

The second intense peaks (**B**-series) corresponded to the Na$^+$ adduct poly(BVE) ions with $C(CH_3)_2CN$ as both initial and terminal end-groups [68.10 + {100.16n + 22.98 (Na$^+$)} + 68.10], due to a primary radical termination. The third intense peaks (**C**-series) corresponded to the Na$^+$ adduct poly(BVE) ions with $C(CH_3)_2CN$ as the initial end-group and H as the terminal end-group [68.10 + {100.16n + 22.98 (Na$^+$)} + 1.01]; this demonstrates the occurrence of hydrogen abstraction as the chain transfer reaction suggested by Kamachi et al.[4] and Sato et al.[6] The fourth intense peaks (**D**-series) corresponded to the Na$^+$ adduct poly(BVE) ions with C_4H_9 as the initial end-group and CH_2CHO as the terminal end-group [57.12 + {100.16n + 22.98 (Na$^+$)} + 43.05], due to a reinitiation reaction by the butyl group generated via β-scission of growing polymer radical. The fifth intense peaks (**E**-series) corresponded to the Na$^+$ adduct poly(BVE) ions with $C(CH_3)_2CN$ as the initial end group and C_4H_9 as the terminal end-group [68.10 + {100.16n + 22.98 (Na$^+$)} + 57.12], being ascribed to the occurrence of butyl radical termination. Similar results with DMAIB except that AIBN fragments are replaced by DMAIB ones were observed in the bulk polymerization of BVE using DMAIB at 70 °C.

Unexpected Observation of Mid-Chain $-CH_2C(=O)-$ in Place of Terminal $-CH_2CHO$ Group by ^{1}H NMR Spectrometry. The structural identification of aldehyde as the terminal end-group of poly(BVE) is not always performed from its mass spectrum, especially when other oligomers with the same molecular weight may be formed. Thus, the ^{1}H NMR spectrum of the poly(BVE) sample subjected to MALDI-TOF-MS measurement (see Figure 1) was measured as shown in Figure 2. Notably, an intensive peak assignable to $-CH_2C(=O)CH_2-$ protons was observed unexpectedly at 2.3−2.8 ppm although the peak assignable to the terminal −CHO end-group generated via β-scission of growing polymer radical as a presumed chain-end forming reaction appeared only weakly at 9.8 ppm. Now, we need to consider an alternative chain-end forming reaction to give oligomeric poly(BVE) with the same molecular weight. A plausible chain-end forming reaction, as an alternative to eq 1, is presumed to be the backbiting hydrogen abstraction to form mid-chain radical which subsequently undergoes β-scission resulting in oligomeric poly(BVE) with carbonyl group in the polymer backbone (see eq 2). Conclusively, **A**-series peaks with highest relative intensity in Figure 1 corresponded to the MALDI-TOF-MS spectrum of oligomeric poly(BVE) with $C(CH_3)_2CN$ as the initial end-group, $-CH_2C(=O)-$ as the mid-chain unit, and H as the terminal end-group [68.10 + {100.16n + 22.98 (Na$^+$)} + 42.04 + 1.01], as opposed to the Na$^+$ adduct ions to the presumed poly(BVE) with the degree of polymerization (n) of 12 to 15, along with $C(CH_3)_2CN$, an initiator fragment, as the initial end-group and CH_2CHO as the terminal end-group [68.10 + {100.16n + 22.98 (Na$^+$)} + 43.05].

Specific Polymerization Mechanism Involving β-Scission of Mid-Chain Radical. The MALDI-TOF-MS and ^{1}H NMR spectroscopic data (see Figures 1 and 2) clearly supported the preferential occurrence of the chain end-forming reaction mainly involving the backbiting hydrogen abstraction to form mid-chain radical which undergoes β-scission, leading to the formation of **A**- and **D**-series oligomeric poly(BVE) with carbonyl group in the polymer backbone. Thus, the kinetic scheme of free-radical polymerization of vinyl ethers with AIBN yielding oligomers, being typically exemplified by BVE polymerization, should be given as follows:

$$\text{initiation: } I \rightarrow 2R^\bullet + N_2$$

$$R^\bullet + M \rightarrow M^\bullet$$

$$\text{propagation: } M^\bullet + M \rightarrow M^\bullet$$

$$\text{backbiting: } M^\bullet \rightarrow P^\bullet$$

$$\beta\text{-scission: } P^\bullet \rightarrow P + C_4H_9^\bullet$$

$$\text{re-initiation: } C_4H_9^\bullet + M \rightarrow M^\bullet$$

$$\text{termination: } M^\bullet + M^\bullet \rightarrow P \text{ or } 2P$$

$$M^\bullet + R^\bullet \rightarrow P$$

$$M^\bullet + C_4H_9^\bullet \rightarrow P$$

$$\{R^\bullet + R^\bullet\},\{R^\bullet + C_4H_9^\bullet\},\{C_4H_9^\bullet + C_4H_9\}^\bullet \rightarrow \text{inactive products}$$

where I is AIBN, R$^\bullet$ is the $C(CH_3)_2CN$ radical, M is the BVE monomer, M$^\bullet$ is the growing poly(BVE) radical, P$^\bullet$ is the mid-chain radical, and P is the oligomeric poly(BVE) produced.

In this scheme, the reinitiation reaction of butyl radical generated via β-scission of mid-chain radical is overwhelmed because of the fact that a large amount of initiator was needed for the polymerization of BVE, corresponding to the case of AAc as a typical allyl monomer;[1] only weak peaks (**D**-series) due to a reinitiation reaction by the butyl group were observed for the oligomers (see Figure 1). On the other hand, the primary radical termination occurred remarkably, probably being due to a high initiator concentration of 0.1 mol/L, since the Na$^+$ adduct poly(BVE) ions with $C(CH_3)_2CN$ as both initial and terminal end-groups were detected clearly as the second intense **B**-series peaks as described above. The combination of the electron-donating growing polymer radical and the electron-accepting primary radical may cause the enhanced occurrence of the primary radical termination; this primary radical termination would compete with the backbiting hydrogen abstraction reaction. Here it may be worthy to note that the poly(BVE) with $C(CH_3)_2CN$ as both initial and terminal end-groups can be formed even via a coupling termination reaction of growing polymer radicals (M$^\bullet$ + M$^\bullet$ → P). In this connection, any peak, being due to a disproportionation termination reaction of growing polymer radicals (M$^\bullet$ + M$^\bullet$ → 2P), was not observed. Furthermore, the relative intensities of **B**-series peaks clearly became stronger with an increase in the initiator concentration, probably as an enhanced occurrence of primary radical termination. The more detailed primary radical termination will be discussed below.

Hydrogen Abstraction Ability of Growing Poly(BVE) Radical. As is described in the Introduction, Kamachi et al. suggested the importance of the chain transfer reaction as significant side reactions in the free-radical polymerization of vinyl ethers as a reflection of higher reactivity of growing polymer radical,[4] and then Sato et al. observed novel polym-

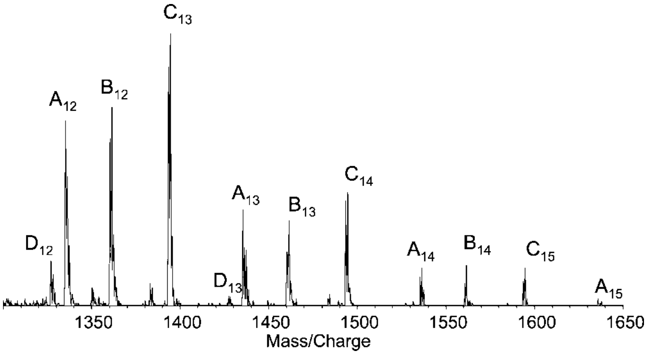

Figure 3. MALDI-TOF-MS spectrum of oligomeric poly(BVE) obtained at a conversion of 5.1% in the solution polymerization of BVE in TOL ([TOL]/[BVE] = 2/1 mol/mol) using 0.1 mol/L of AIBN at 70 °C.

erization behavior of vinyl ethers having a labile hydrogen and electron-accepting groups at a suitable position through a propagation mechanism involving intramolecular hydrogen abstraction, i.e., addition−abstraction mechanism.[6] In this connection, we tried to pursue the hydrogen abstraction ability of growing poly(BVE) radical from solvent, although the **C**-series peaks assignable to the Na^+ adduct poly(BVE) ions with $C(CH_3)_2CN$ as the initial end-group and H as the terminal end-group were observed in the MALDI-TOF-MS spectrum of poly(BVE) obtained by the bulk polymerization of BVE (see Figure 1).

Thus, the free-radical polymerization of BVE in the presence of a solvent having labile hydrogen, typically exemplified by TOL, was carried out. Figure 3 shows the MALDI-TOF-MS spectrum of poly(BVE) obtained at a conversion of 5.1% in the solution polymerization in TOL ([TOL]/[BVE] = 2/1 mol/mol) using 0.1 mol/L of AIBN at 70 °C. As a result of the hydrogen abstraction reaction of growing poly(BVE) radical from the CH_3 group of TOL to give a resonance-stabilized benzyl radical, the **C**-series peaks assignable to the Na^+ adduct poly(BVE) ions with $C(CH_3)_2CN$ as the initial end-group and H as the terminal one were detected with highest relative intensity, i.e., much stronger than those in the MALDI-TOF-MS spectrum of poly(BVE) obtained in bulk (see Figure 1). Also, it is worthy to note that the **B**-series peaks became rather intense as compared to the spectrum in Figure 1; this is ascribed to the enhanced occurrence of primary radical termination as a reflection of increased feed [AIBN]/[BVE] ratio.

Enhanced Reinitiation and Enlarged Chain Length by Reducing Primary Radical Termination. As is mentioned above, the occurrence of primary radical termination was remarkable, probably leading to reduced chain length. Thus, we tried to examine the dependence of the degree of polymerization (*n*) on initiator concentration [I]. Figure 4 shows SEC curves of the oligomeric poly(BVE)s obtained at conversions of 8.8, 7.4, 3.7, and 2.1% in the bulk polymerizations at [I] = 0.1, 0.05, 0.01, and 0.001 mol/L, respectively. The *n* values were estimated to be 21, 25, 34, and 40, respectively, at [I] = 0.1, 0.05, 0.01, and 0.001 mol/L. This increasing tendency of *n* with a decrease in the initiator concentration is in accordance with the above polymerization mechanism. Finally, Figure 5 shows the MALDI-TOF-MS spectrum of poly(BVE) obtained at a lowest initiator concentration [I] = 0.001 mol/L. The **B**-series peaks assignable to the Na^+ adduct poly(BVE) ions with $C(CH_3)_2CN$ as both initial and terminal end-groups due to the primary radical termination became quite weak. Instead, the prominent **D**-series peaks for the oligomers having C_4H_9 as the initial end-group, $-CH_2C(=O)-$ as the mid-chain unit, and H as the terminal end-group were observed; notably, they were much stronger than the **A**-series peaks for the oligomers having an initiator fragment $C(CH_3)_2CN$ as the initial end-group. This demonstrates strongly the repeated occurrence of reinitiation reaction by the butyl group generated via β-scission of growing polymer radical. As an extension, we tentatively tried to determine roughly the degree of polymerization of the resultant poly(BVE) to be 47 by comparing the peak area of 3.3−3.7 ppm assignable to the adjacent protons to ether oxygen with that of $-CH_2C(=O)CH_2-$ protons, although it was determined as 40 by SEC measurement (see Figure 4).

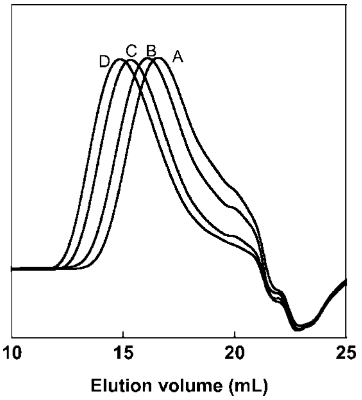

Figure 4. SEC curves of oligomeric poly(BVE)s obtained at conversions of (A) 8.8, (B) 7.4, (C) 3.7, and (D) 2.1% in the bulk polymerization of BVE using 0.1, 0.05, 0.01, and 0.001 mol/L of AIBN, respectively, at 70 °C.

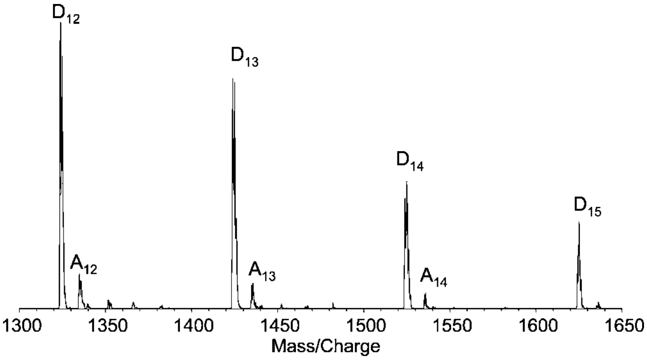

Figure 5. MALDI-TOF-MS spectrum of oligomeric poly(BVE) obtained at a conversion of 2.1% in the bulk polymerization of BVE using 0.001 mol/L of AIBN at 70 °C.

Conclusion

In 1983, we found by chance that BVE undergoes radical polymerization to yield an oligomer but a detailed polymerization mechanism remained open in order to interpret the reason why only oligomer was obtained. Thus, we attempted to explore in more detail the characterization of resulting oligomers in the free-radical polymerization of BVE, mainly using MALDI-TOF-MS spectrometry. As the structural identification of poly(BVE) was not performed directly from its mass spectrum, the resultant poly(BVE) was subsequently subjected to ^1H NMR measurement. Notably, an intensive peak assignable to $-CH_2C(=O)CH_2-$ protons was observed unexpectedly although a peak assignable to $-CHO$ proton as the terminal end-group generated via β-scission of growing polymer radical as a presumed chain-end forming reaction appeared only weakly. Conclusively, a plausible chain-end forming reaction, as an alternative to eq 1, would be the backbiting hydrogen abstraction to form mid-chain radical which subsequently undergoes β-scission via eq 2, resulting in oligomeric poly(BVE) with carbonyl group in the polymer backbone; this may be caused by the stabilization of mid-chain radical as compared with a rather unstable, highly reactive growing polymer radical deviated from the planer sp^2 conformation.[5]

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