# Reassessment of Free-Radical Polymerization Mechanism of Allyl Acetate Based on End-Group Determination of Resulting Oligomers by MALDI-TOF-MS Spectrometry

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Allyl monomers polymerize only with difficulty and yield polymers of medium-molecular-weight or oligomers. This is attributable to "degradative monomer chain transfer." However, the well-known allyl polymerization mechanism is based on only the kinetic data but any structural identification is not given. Allyl acetate (AAc), a most typical allyl monomer, was polymerized radically and the resultant oligomeric poly(AAc)s were characterized using MALDI-TOF-MS spectrometry in order to reassess the AAc polymerization mechanism proposed by Litt and Eirich. The induced decomposition of benzoyl peroxide by both growing polymer radical and monomeric allyl radical was presumed but it was never of importance. Then, the fate of resonance-stabilized monomeric allyl radical generated *via* monomer chain transfer of growing polymer radical was pursued in terms of the competition between the initiation of a new polymer chain and the chain stopping reaction of a growing polymer radical providing monomeric allyl groups as the initial and terminal end-groups, respectively. The monomer chain transfer constant was estimated to be 3.73×10^{-2} from the P_n value of poly(AAc) obtained at a low initiator concentration where the coupling termination of growing polymer radical with monomeric allyl radical was negligible.
KEY WORDS: Allyl Acetate / Allyl Radical / Allyl Polymerization / Degradative Monomer Chain Transfer / MALDI-TOF-MS / End-Group Determination /

The free-radical polymerization of allyl monomers, generally referred to as "allyl polymerization," has received much less attention than the corresponding vinyl polymerization of common vinyl monomers.[1–4] Thus, the polymerization of allyl acetate (AAc) initiated by benzoyl peroxide (BPO), studied by Bartlett and Altschul[5] in the early 1940s, was the first topic of detailed investigations into allyl polymerization. The low tendency to polymerize and the obtainment of products with a low degree of polymerization were characteristic of allyl polymerization so that a large amount of initiator was required, *i.e.*, reaching up to almost 10^2 times when compared with common vinyl polymerization. These results are attributable to "degradative monomer chain transfer." That is, the hydrogen atoms attached to the carbon atom alpha to the double bond, *i.e.*, allylic hydrogens are responsible for this chain transfer:

$$M\bullet + CH_2{=}CH\text{-}CH_2\text{-}R \rightarrow P + [CH_2{\cdots}CH{\cdots}CH\text{-}R]$$
$$\text{(monomeric allyl radical)}$$
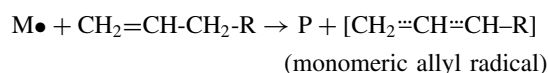
The resulting monomeric allyl radical is less active and/or has less tendency to initiate a new polymer chain because of an ability to stabilize itself by resonance. Therefore, the monomeric allyl radicals undergo termination by reaction with each other or with growing polymer radicals, the monomer chain transfer being essentially a termination reaction. This monomer chain transfer was further confirmed by Bartlett and Tate;[6] the polymerization of a deuterium-substituted AAc with allylic

deuteriums showed a rate more than twice that for normal AAc and yielded a proportionately higher molecular weight product, due to the stronger C-D bond than the C-H bond. Concurrently, a series of allyl monomers have been polymerized by Gaylord and Eirich.[7] Sakurada and Takahashi also made a detailed study of the polymerization of allyl monomers and proposed a kinetic mechanism for it.[8,9] As a summary of the results reported in the period of 1940'–1960, Litt and Eirich[10] developed a kinetic scheme that would account quantitatively for the facts of allyl polymerization, especially focused on "degradative monomer chain transfer."

Therefore, the most characteristic feature of the polymerization of allyl monomers is of the significance of monomer chain transfer which competes with normal propagation, yielding polymers of medium-molecular-weight or oligomers, not really low molecular weight, and produces resonance-stabilized monomeric allyl radical, causing the allyl monomers to retard polymerization. In this connection, another important aspect of the characteristics of allyl polymerization should be pointed out as follows: In the radical polymerization of allyl monomers, the research objectives would be oligomers or medium-molecular-weight molecules, the molecular weights of which are essentially intermediate between low- and high-molecular-weight molecules. Accordingly, allyl polymerization would provide useful information for finding out the inherent phenomena of polymers, not being of real low-

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molecular-weight molecules, by pursuing the molecular weight dependences of various properties of resulting medium-molecular-weight molecules. For example, anomalous head-to-head addition occurred remarkably[11,12] and its chain length dependency was observed due to the steric effect of side chains.[13]

Here it is worthy to note that other monomers such as methyl methacrylate and methacrylonitrile, which also contain allylic C-H bonds, do not undergo extensive monomer chain transfer, and thus form high-molecular-weight polymers. This is ascribed not only to lower reactivity of the growing polymer radical formed from these conjugated monomers but also to higher reactivity of their C=C double bonds.[1] In contrast to the above conjugated monomers, allyl monomers have typical unconjugated double bonds. In this connection, the Q and e values of one allyl group of diallyl phthalate (DAP) as a typical multiallyl monomer were estimated to be 0.029 and 0.04, respectively, by the copolymerization of DAP with various vinyl monomers;[14,15] the low Q value of 0.029 demonstrates that DAP is a typical unconjugated monomer. This unconjugation of allyl monomer is significant to understand the characteristics of allyl polymerization. That is, the low reactivity of C=C double bond in unconjugated monomer synergizes with the low reactivity of resonance-stabilized monomeric allyl radical to lead less tendency to initiate a new polymer chain and, on the contrary, the high reactivity of growing polymer radical formed from unconjugated monomer promotes the allylic hydrogen abstraction. On the other hand, Sakurada[8,9] and Gaylord[16] have pointed out that although the degradative monomer chain transfer is quite usual in allyl polymerization, monomeric allyl radicals also have an ability of adding monomer, and thus of continuing the chain reaction, referred to as "effective monomer chain transfer." Furthermore, Gaylord[17] reported the radical displacement as a chain-end forming reaction by effective monomer chain transfer, *i.e.*, β-scission of growing polymer radical through addition-fragmentation transfer as is discussed later, the product radical being active enough to initiate a new polymer chain.

Although the free-radical polymerization of various allyl monomers is specific as mentioned above, it may lack of direct evidence for a full mechanistic discussion, especially including initiation and termination reactions. Here it is worthy to note that matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS)[18,19] could provide a powerful tool for structural identification of oligomer. Thus, we felt strongly the necessity of a detailed characterization of oligomeric polymers obtained in the radical polymerization of allyl monomers using MALDI-TOF-MS, since for a long time we have been concerned with the polymerization of multiallyl monomers.[15] In the present article, we determined the end-groups of resulting oligomers by MALDI-TOF-MS spectrometry in the polymerizations of AAc as a most typical allyl monomer. On the basis of the results obtained, the characteristic of free-radical allyl polymerization mechanism is reassessed.

EXPERIMENTAL

Materials

AAc (Tokyo Chemical Industry Co., Ltd., Tokyo) as a monomer was purified by distillation. 2,2-Azobis(isobutyronitrile) (AIBN) and 1,1'-azobis(cyclohexane-1-carbonitrile) (ACHN) (azo initiators; Wako Pure Chemical Industries, Ltd., Osaka) and BPO (NOF Corp., Aichi) as initiators were purified by conventional methods.

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

Measurements

MALDI-TOF-MS spectra were acquired in positive reflection mode using an Axima-CFR time-of-flight mass spectrometer (Shimadzu/Kratos, Manchester, UK) with a pulsed N_2 laser (337 nm). Poly(AAc) (2.0 mg/mL), DHBA matrix (20 mg/mL), and NaI cationizing agent (1.0 mg/mL) were dissolved in THF. 0.5 μL 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 three Shodex KF-803L columns 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.

RESULTS AND DISCUSSION

Reassessment of AAc Polymerization Mechanism Proposed by Litt and Eirich

Litt and Eirich[10] proposed the following reaction scheme, *i.e.*, eqs 1–10, of AAc polymerization with BPO that would account quantitatively for the facts of allyl polymerization:
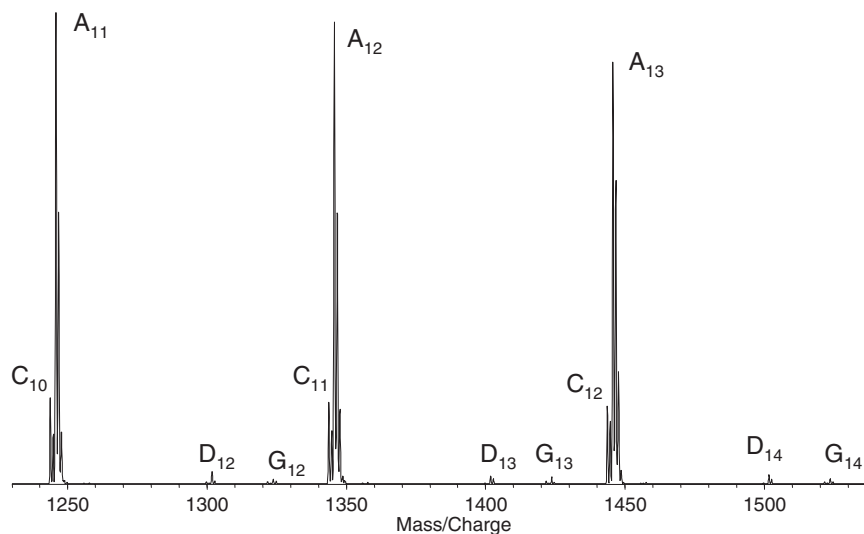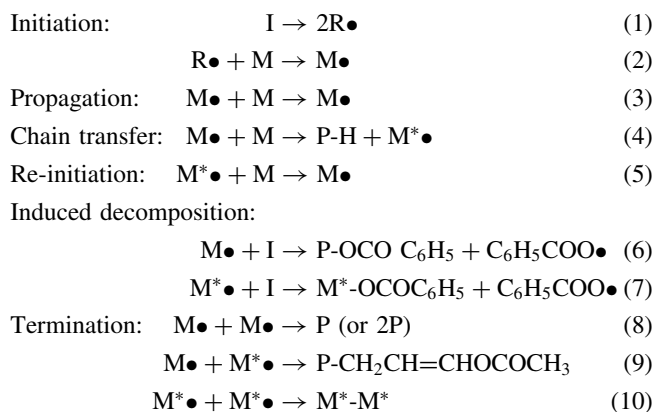
Figure 1. MALDI-TOF-MS spectrum of oligomeric poly(AAc) obtained at a conversion of 14.8% in the bulk polymerization of AAc using 0.1 mol/L of BPO at 80 °C.

Initiation: $I \rightarrow 2R\bullet$ (1)

$R\bullet + M \rightarrow M\bullet$ (2)

Propagation: $M\bullet + M \rightarrow M\bullet$ (3)

Chain transfer: $M\bullet + M \rightarrow P\text{-H} + M^*\bullet$ (4)

Re-initiation: $M^*\bullet + M \rightarrow M\bullet$ (5)

Induced decomposition:

$M\bullet + I \rightarrow P\text{-OCO } C_6H_5 + C_6H_5COO\bullet$ (6)

$M^*\bullet + I \rightarrow M^*\text{-OCOC}_6H_5 + C_6H_5COO\bullet$ (7)

Termination: $M\bullet + M\bullet \rightarrow P \text{ (or 2P)}$ (8)

$M\bullet + M^*\bullet \rightarrow P\text{-CH}_2CH\text{=}CHOCOCH_3$ (9)

$M^*\bullet + M^*\bullet \rightarrow M^*\text{-}M^*$ (10)

where I is BPO, $R\bullet$ is the benzoyloxy or phenyl radical, M is AAc monomer, $M\bullet$ is the oligomeric growing polymer radical, P is the oligomeric poly(AAc) produced, and $M^*\bullet$ is the monomeric allylic radical formed by the abstraction of an allylic hydrogen from AAc monomer. Here it is worthy to note that the hydrogen abstraction reaction by the benzoyloxy radical from AAc to form M* would be significant, especially at a high initiator concentration, although this allylic hydrogen abstraction is omitted in the reaction scheme proposed by Litt and Eirich.[10]

According to the above reaction scheme, we should observe the specific MALDI-TOF-MS spectrum with a number of peaks assignable to oligomeric poly(AAc)s of different degrees of polymerization (*n*) with R or M* as the initial end-group and H or C_6H_5COO or M* as the terminal end-group. For example, all possible molecular formulae of poly(AAc)s (*n* = 10) could be depicted as follows: $C_6H_5COO(AAc)_{10}H$ (**A**) (1123.30); $C_6H_5COO(AAc)_{10}OCOC_6H_5$ (**B**) (1243.40); $C_6H_5COO(AAc)_{10}CH_2CH\text{=}CHOCOCH_3$ (**C**) (1221.39); $C_6H_5(AAc)_{10}H$ (**D**) (1079.28); $C_6H_5(AAc)_{10}OCOC_6H_5$ (**E**) (1199.39); $C_6H_5(AAc)_{10}CH_2CH\text{=}CHOCOCH_3$ (**F**) (1177.38); $CH_3COOCH\text{=}CHCH_2(AAc)_{10}H$ (**G**) (1101.29);

$CH_3COOCH\text{=}CHCH_2(AAc)_{10}OCOC_6H_5$ (**H**) (1221.39); and $CH_3COOCH\text{=}CHCH_2(AAc)_{10}CH_2CH\text{=}CHOCOCH_3$ (**I**) (1199.39), where each figure in the parentheses denotes the corresponding molecular weight.

The bulk polymerization of AAc was carried out using 0.1 mol/L of BPO for 2 h at 80 °C. Here it should be noted that the polymerization conditions such as 0.1 mol/L of BPO at 80 °C in bulk are rather unusual in common vinyl polymerization, although in allyl polymerization, a remarkably large amount of initiator is usually required. Figure 1 shows the MALDI-TOF-MS spectrum of poly(AAc) obtained at a conversion of 14.8% as a typical example.

The spectrum of the oligomeric poly(AAc) in the presence of NaI exhibited a series of ions repeating at an interval of 100.12 U corresponding to AAc repeat unit. The peaks with highest relative intensity (**A**-series) were assigned to the Na$^+$ adduct ions to the poly(AAc)s with the degree of polymerizations of 11 to 13, along with C_6H_5COO, an initiator fragment, as the initial end-group and H as the terminal end-group $[121.12 + \{100.12n + 22.98(Na^+)\} + 1.01]$ (poly(AAc)s; $C_6H_5COO\text{-}(CH_2\text{-}CH(CH_2OCOCH_3))_n\text{-}H$). This clearly supports the significance of monomer chain transfer as an allylic hydrogen abstraction of growing polymer radical from monomer. In this connection, the intensities of **D**-series peaks with C_6H_5, an initiator fragment, as the initial end-group introduced by the decomposition of benzoyloxy radical to phenyl one were quite weak so that the benzoyloxy radical preferentially initiated the polymerization of AAc.

The monomer chain transfer inevitably leads to the generation of a monomeric allyl radical as a characteristic feature of allyl polymerization. Thus, to find out the fate of resonance-stabilized monomeric allyl radical would be a most significant subject for a full understanding of allyl polymerization mechanism but it is not clarified yet. According to the above mechanism proposed by Litt and Eirich,[10] the monomeric allyl radical could re-initiate to generate a new growing
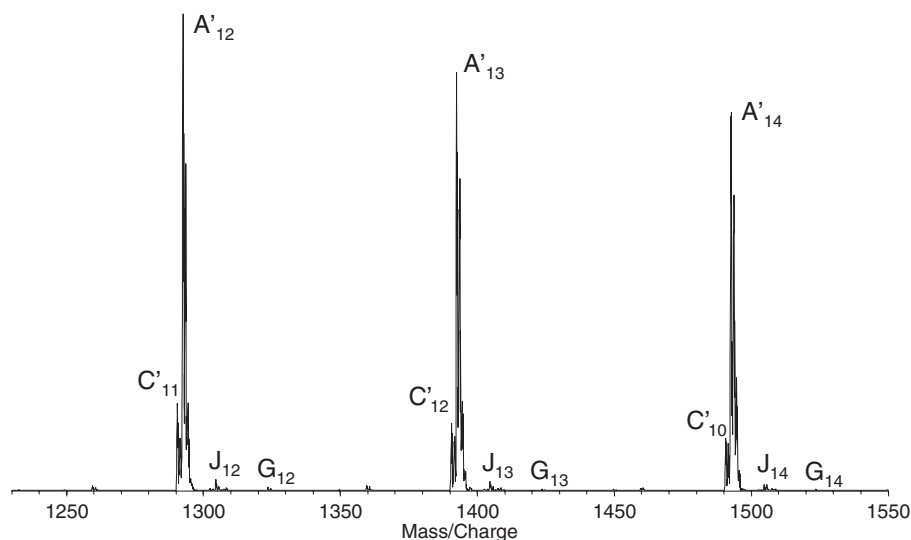
Figure 2. MALDI-TOF-MS spectrum of oligomeric poly(AAc) obtained at a conversion of 10.8% in the bulk polymerization of AAc using 0.1 mol/L of AIBN at 80 °C.

polymer radical (eq 5), induce the decomposition of BPO (eq 7), couple with a growing polymer radical (eq 9), and couple each other to form a dimer (eq 10). Firstly, we pursued the re-initiation reaction *via* eq 5 by checking the existence of the corresponding **G**-series peaks; it was clearly observed but their peak intensities were quite weak compared to those of **A**-series peaks corresponded to the initiation by benzoyloxy radical generated from the thermal decomposition of BPO. Secondly, we pursued the induced decomposition of BPO *via* eqs 6 and 7 by checking the existence of the **B**-, **E**-, and **H**-series peaks corresponded to the Na$^+$ adduct poly(AAc)s ions with benzoyloxy, phenyl, and monomeric allyl, respectively, as the initial end-group and benzoyloxy as the terminal end-group; they were not observed, implying that the induced decomposition of BPO by both growing polymer radical and monomeric allyl radical, proposed by Litt and Eirich,[10] is never of importance. Thirdly, the termination reaction *via* eq 9 was checked; the corresponding **C**-series peaks were clearly observed, suggesting the significance of the coupling termination of growing polymer radical with monomeric allyl radical. This monomeric allyl radical termination reaction will be discussed later in more detail in connection with the dependence of molecular weight of resultant poly(AAc) on initiator concentration.

For a reconfirmation of the specific MALDI-TOF-MS spectrum of the poly(AAc) obtained with BPO, we attempted to explore the polymerization of AAc using AIBN as another typical radical initiator. The simpler spectrum could be observed compared to the spectrum in Figure 1 because the initiating species changed from two kinds of benzoyloxy and phenyl radicals to single cyanoisopropyl radical $(CH_3)_2C(CN)\bullet$. Thus, Figure 2 shows the positive ion mass spectrum with the Na$^+$ adduct ions to oligomeric poly(AAc)s ($n = 12$–14) obtained at a conversion of 10.8% as a typical example.

Certainly, the simple spectrum was observed in conformity with our expectation. The striking peaks in the mass spectrum of poly(AAc) corresponded only to both $(CH_3)_2C(CN)$-$(AAc)_nH$ (**A′**) and $(CH_3)_2C(CN)(AAc)_nCH_2CH=CHOCOCH_3$ (**C′**). As a matter of course, **D**-series peaks with C_6H_5 as the initial end-group disappeared. In addition, **G**-series peaks were observed slightly, although the more intensive **G**-series peaks than **A′**-series ones were observed at a quite low AIBN concentration (see Figure 4) as this will be discussed below.

Fate of Resonance-Stabilized Monomeric Allyl Radical: Competitive Contribution to Both Initiation and Termination Reactions

For a full understanding of allyl polymerization mechanism, a pursuit of the fate of resonance-stabilized monomeric allyl radical, generated *via* well-known monomer chain transfer of growing polymer radical, is significant although the monomeric allyl radical has a possibility of both initiating a new polymer chain *via* eq 5 and terminating a growing polymer radical *via* eq 9 providing monomeric allyl groups as the initial and terminal end-groups, respectively. Notably, in allyl polymerization, a remarkably large amount of initiator is required as compared to the case of common vinyl polymerization, because of both the low tendency to polymerize and the obtainment of products with a low degree of polymerization. It reached almost 10^2 times. This leads to the drastic enhancement of bimolecular termination in allyl polymerization as compared with common vinyl polymerization. Therefore, the coupling termination of monomeric allyl radical with growing polymer radical *via* eq 9 should compete with the propagation reaction *via* eq 3, leading to a shortening of oligomeric poly(AAc) chain length, as the degree of polymerization (P_n) is given as follows:

$$P_n = k_p[M\bullet][M]/\{k_{tr,m}[M\bullet][M] + k_t[M\bullet][M^*\bullet]\} \quad (11)$$

where k_p, $k_{tr,m}$, and k_t denote the rate constants of propagation (eq 3), chain transfer (eq 4), and termination (eq 9) of growing polymer radical, respectively.

Here the common bimolecular termination reaction between growing polymer radicals *via* eq 8 could be omitted because the concentration of active growing polymer radical should be quite low compared to that of resonance-stabilized monomeric allyl radical. This is also evidenced in Figures 1 and 2 by the fact that any peak due to the occurrence of eq 8, *i.e.*, coupling or disproportionation termination giving the oligomers having the benzoyloxy or cyanoisopropyl groups as the initial and terminal end-groups or paired saturated and unsaturated end-groups, respectively, was not observed.

Thus, the following equation is derived from eq 11:

$$1/P_n = k_{tr,m}/k_p + (k_t/k_p)[M^* \bullet]/[M] \qquad (12)$$

Now, the P_n value should depend on initiator concentration or monomeric allyl radical one: the higher the initiator concentration, the lower the P_n value. To confirm the validity of eq 12, the polymerization of AAc was carried out by changing the initiator concentration. Figure 3 shows SEC curves of poly-(AAc)s obtained at conversions of 10.8, 4.0, 2.7, and 0.9% using 0.1, 0.01, 0.005, and 0.001 mol/L, respectively, of AIBN at 80 °C.

The P_n values were estimated to be 15.4, 23.4, 25.0, and 26.8, respectively, at $[I] = 0.1$, 0.01, 0.005, and 0.001 mol/L. Notably, the initiator concentration changed widely by a factor of 100 but the P_n value increased only from 15.4 to 26.8; this implies a remarkably significant contribution of the first term of monomer chain transfer in eq 12 to the end forming reaction of oligomeric polymer chain compared with the second term of coupling termination. Furthermore, eq 12 demonstrates that the P_n value of poly(AAc) obtained at a low initiator concentration, where the coupling termination of growing polymer radical
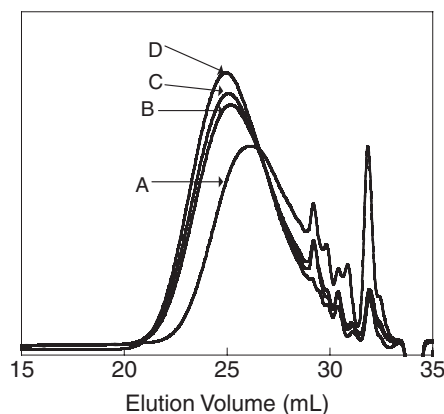

Figure 3. SEC curves of oligomeric poly(AAc)s obtained at conversions of 10.8, 4.0, 2.7, and 0.9% in the bulk polymerization of AAc using (A) 0.1, (B) 0.01, (C) 0.005, and (D) 0.001 mol/L, respectively, of AIBN at 80 °C.

with monomeric allyl radical is negligible, provides the monomer chain transfer constant ($C_m = k_{tr,m}/k_p$). Therefore, the P_n value of 26.8 at $[I] = 0.001$ mol/L was employed roughly to estimate the C_m value to be 3.73×10^{-2} because the coupling termination reaction was negligible from the MALDI-TOF-MS spectrum of the poly(AAc) obtained with 0.001 mol/L of AIBN (see Figure 4).

Here it should be recalled that the resonance-stabilized monomeric allyl radical could contribute competitively to both initiation and termination reaction. That is, the coupling termination reaction between the growing polymer radical and the monomeric allyl radical *via* eq 9 was significant under the polymerization condition where a large amount of initiator was used, whereas the re-initiation reaction of monomeric allyl radical *via* eq 5 could occur predominantly under the completely opposite condition where the polymerization would be
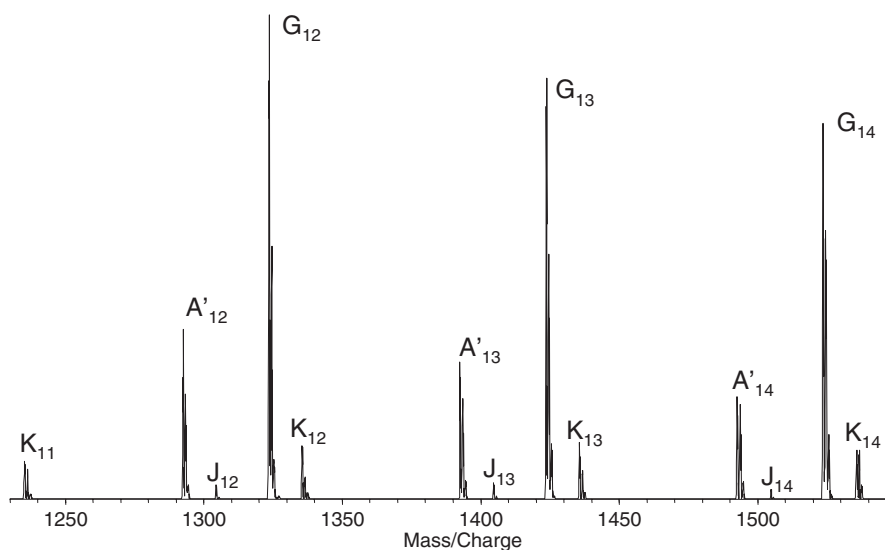

Figure 4. MALDI-TOF-MS spectrum of oligomeric poly(AAc) obtained at a conversion of 0.9% in the bulk polymerization of AAc using 0.001 mol/L of AIBN at 80 °C.

carried out at a low initiator concentration. Figure 4 shows the positive ion mass spectrum of oligomeric poly(AAc) ($n = 12$–14) obtained at a conversion of 0.9% in the bulk polymerization of AAc using 0.001 mol/L of AIBN for 8 h at 80 °C.

Clearly, the **G**-series peaks due to the re-initiation reaction of monomeric allyl radical were observed predominantly compared to those of **A$'$**-series due to the primary radical initiation. Furthermore, **C$'$**-series peaks disappeared, suggesting no contribution of the coupling termination reaction of growing polymer radical with monomeric allyl radical. These are in conformity with our expectation. In addition, weak **J**- and **K**-series peaks, having a higher mass unit of 12 corresponding to one carbon atom than **A$'$**- and **G**-series peaks, appeared newly; this will be discussed below in connection with addition-fragmentation chain transfer.

Does Addition-Fragmentation Chain Transfer Occur Significantly?

A variety of chain transfer reactions are used for the well-known techniques of control of molecular weight, structure, and functionality of synthetic polymers. In allyl polymerization, the hydrogen atoms attached to the carbon atom alpha to the double bond, *i.e.*, allylic hydrogens are responsible for facile chain transfer to monomer from reactive growing polymer radical to give resonance-stabilized monomeric allyl radical; it is well-known as "degradative monomer chain transfer."[5] Recently, addition-fragmentation chain transfer is noted,[20] although the first reports of addition-fragmentation transfer agents in polymerization appeared in the late 1980's.[21–23] Allyl monomers could be very effective chain transfer agents,[24–26] although the main driving force for fragmentation is the weak single bond (CH$_2$-X) of CH$_2$ = CH-CH$_2$X.
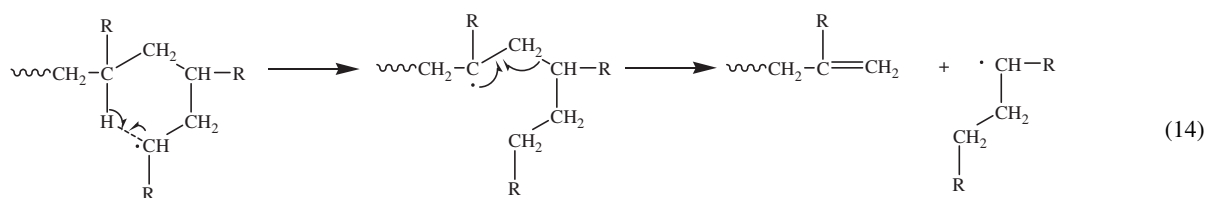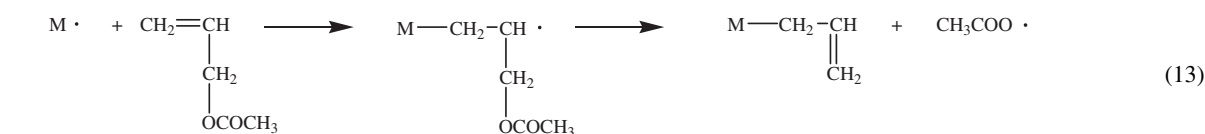
Therefore, even in the free-radical polymerization of AAc, the formation of oligomers with a terminal allyl group may be observed as a result of occurrence of β-scission of growing polymer radical *via* eq 13, although Gaylord reported the β-scission of growing polymer radical through addition-fragmentation transfer in the polymerization of AAc.[17] Thus, a terminal allyl group characteristic of **L**-series,

$C_6H_5COO(AAc)_nCH_2CH=CH_2$ [$121.12 + 100.12n + 41.07$], and **L$'$**-series, $(CH_3)_2C(CN)(AAc)_nCH_2CH=CH_2$ [$68.10 + 100.12n + 41.07$], could be introduced by a following alternative chain termination involving β-scission of growing polymer radical through addition-fragmentation transfer, in addition to a well-known degradative monomer chain transfer, although the benzoyloxy and cyanoisopropyl groups as the initial end-groups would be generated by the thermal decomposition of BPO and AIBN as the initiators.

Notably, this kind of β-scission of growing polymer radical was ruled out in the reaction scheme proposed by Litt and Eirich,[10] although its significance has been demonstrated in several reports.[27–31] However, any appreciable **L**- and **L$'$**-series peaks were not observed in AAc polymerization as is seen in Figures 1, 2, and 4. The occurrence of eq 13 could be enhanced at elevated temperatures; thus, the bulk polymerization of AAc was conducted at 100 °C using 0.1 mol/L of ACHN as an initiator. The peaks assigned to the poly(AAc)s with a terminal allyl group were still negligibly small as opposed to our expectation. A more detailed discussion of addition-fragmentation chain transfer will be done elsewhere, along with the polymerization results of other allyl monomers, since the peaks assigned to the oligomers with a terminal allyl group were clearly observed in the solution polymerization of allyl benzoate in methyl benzoate at 130 °C.
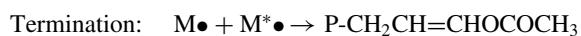
Finally, we will briefly refer to the existence of **J**- and **K**-series peaks in Figure 4, along with **J**-series peaks in Figure 2. As is described above, the new peaks having a higher mass unit of 12 than **G**- and **A$'$**-series peaks were observed unexpectedly. A plausible chain-end forming reaction *via* eq 14, as an alternative to eqs 4 (leading to **A$'$**-series peaks) and 9 (leading to **G**-series peaks), would be the intramolecular (backbiting) hydrogen abstraction to form mid-chain radical which subsequently undergoes β-scission of main chain resulting in oligomeric poly(AAc) with a terminal =CH$_2$ group.

In this connection, it is notably recalled that the free-radical polymerizations of ethylene,[32–37] vinyl chloride,[38,39] vinyl acetate,[40–43] and acrylate esters[44–49] are governed by the polymerization mechanism involving mid-chain radical formed through backbiting hydrogen abstraction of growing polymer radical.

(13)

(14)

(R : CH$_2$OCOCH$_3$)

CONCLUSIONS

As is evident from the above discussion based on the MALDI-TOF-MS spectroscopic data, we have to make a renewal of the well-known reaction scheme proposed by Litt and Eirich[10] for the free-radical polymerization of AAc with BPO as follows:

Initiation: $\qquad$ $I \rightarrow 2R\bullet$

$\qquad\qquad\qquad$ $R\bullet + M \rightarrow M\bullet$

Propagation: $\qquad$ $M\bullet + M \rightarrow M\bullet$

Chain transfer: $\qquad$ $M\bullet + M \rightarrow P\text{-}H + M^*\bullet$

Re-initiation: $\qquad$ $M^*\bullet + M \rightarrow M\bullet$

Termination: $\qquad$ $M\bullet + M^*\bullet \rightarrow P\text{-}CH_2CH{=}CHOCOCH_3$

$\qquad\qquad\qquad$ $M^*\bullet + M^*\bullet \rightarrow M^*\text{-}M^*$

where I is BPO, $R\bullet$ is the benzoyloxy or phenyl radical, M is AAc monomer, $M\bullet$ is the oligomeric growing polymer radical, P is the oligomeric poly(AAc) produced, and $M^*\bullet$ is the monomeric allylic radical formed by the abstraction of an allylic hydrogen from AAc monomer.

Based on a renewed reaction mechanism of free-radical polymerization of AAc yielding oligomer, the fate of resonance-stabilized monomeric allyl radical was pursued. The coupling termination of monomeric allyl radical with growing polymer radical leading to a shortening of oligomeric poly-(AAc) chain length was significant under a common allyl polymerization condition where a remarkably large amount of initiator was used as compared to the case of common vinyl polymerization. Under a completely opposite condition where the polymerization would be carried out at a low initiator concentration, the re-initiation reaction of monomeric allyl radical compared to the primary radical initiation occurred predominantly without any contribution of the coupling termination reaction of growing polymer radical with monomeric allyl radical.

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