Macromolecules

NOTE

pubs.acs.org/Macromolecules

Addition−Fragmentation Chain Transfer in Allyl Polymerization at Elevated Temperatures

Satoshi Inoue,[†,‡] Hajime Tamezawa,[†] Hiroyuki Aota,[†] Akira Matsumoto,[*,†] Katsutoshi Yokoyama,[‡] Yasuo Matoba,[‡] and Michirou Shibano[‡]

[†]Department of Chemistry and Materials Engineering, Faculty of Chemistry, Materials and Bioengineering, Kansai University, 3-3-35 Yamate-cho, Suita-shi, Osaka 564-8680, Japan

[‡]Material Development Department, Research & Development Division, Daiso Company, Ltd., 9 Otakasu-cho, Amagasaki-shi, Hyogo 660-0842, Japan

INTRODUCTION

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] 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".[5] 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:

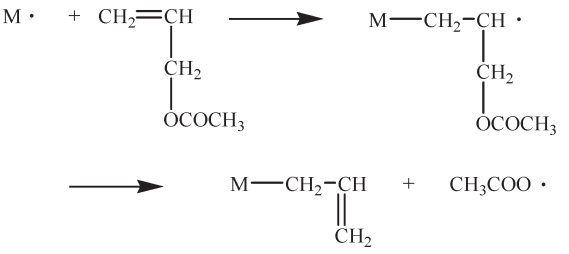
$$M^{\bullet} + CH_2{=}CH - CH_2 - R \rightarrow P + [CH_2 \cdots CH \cdots CH{-}R]$$

(monomeric allyl radical)

The resulting monomeric allyl radical is less active and/or has much less tendency to initiate a new polymer chain because of an ability to stabilize itself by resonance. The monomeric allyl radicals undergo termination by reaction with each other or with growing polymer radicals; therefore, in allyl polymerization this monomer chain transfer is considered to be essentially a termination reaction.

Here it is noteworthy that 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, commercially important multiallyl monomer were estimated to be 0.029 and 0.04, respectively, by the copolymerization of DAP with various vinyl monomers;[6] especially, 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 much less tendency to initiate a new polymer chain. On the contrary, the high reactivity of growing polymer radical formed from unconjugated monomer promotes the allylic hydrogen abstraction.

Recently, "addition−fragmentation chain transfer" is noted,[7] although the first reports of addition−fragmentation transfer agents in polymerization appeared in the late 1980s.[8−10] Allyl monomers could be very effective chain transfer agents,[11−13] although the main driving force for fragmentation is the weak single bond (CH_2−X) of CH_2=CH−CH_2X. Therefore, in addition to a well-known degradative monomer chain transfer[5] mentioned above, a following alternative chain termination involving β-scission of growing polymer radical through addition−fragmentation chain transfer is expected in the free-radical polymerization of allyl acetate (AAc) as a most typical allyl monomer (eq 1).



(1)

However, this kind of β-scission of growing polymer radical was ruled out in the AAc polymerization mechanism proposed by Litt and Eirich[14] as a summary of the results reported in the period of 1940−1960, although its significance has been demonstrated in several reports.[15−19]

The free-radical polymerization of various allyl monomers is specific as mentioned above but it may lack of direct evidence for a full mechanistic discussion, especially including initiation and termination reactions. That is, the well-known allyl polymerization mechanism[5,20,21] is based on only the kinetic data but any structural identification has not been given. In our previous article,[22] with the intention of a full understanding of allyl polymerization mechanism, AAc was polymerized radically and the resulting oligomeric poly(AAc)s were characterized using matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI−TOF−MS)[23] in order to reassess the AAc polymerization mechanism proposed by Litt and Eirich.[14] Conclusively, we have proposed a renewal of the well-known reaction scheme for the free-radical polymerization of AAc.[22] On the course of our investigation, we pursued an occurrence of addition−fragmentation chain transfer via eq 1. However, the

Received: December 24, 2010
Revised: March 15, 2011
Published: March 25, 2011

poly(AAc)s with a terminal allyl group were negligibly observed in the bulk polymerization of AAc at 80 °C as opposed to our expectation, although the oligomers with a terminal allyl group were clearly obtained in the solution polymerization of allyl benzoate (ABz) at 130 °C.

Here it is worthy to note that approximately 100 different organic peroxide initiators are commercially produced throughout the world, primarily for the polymer and resin industries. Practically, organic peroxides are used as initiators to generate radicals at elevated temperatures, being useful for vinyl monomer polymerizations, curing of unsaturated polyester and DAP resins, cross-linking of elastomers and polyolefins, and reactive extrusion.[24,25] Thus, the detailed experimental work of allyl polymerization at elevated temperatures is still required.

In this connection, our previous work was referred to the pursuit of reinitiation efficiency of resonance-stabilized monomeric allyl radical generated via degradative monomer chain transfer in allyl polymerizatin.[26] The reinitiation efficiencies of monomeric allyl radical at different temperatures were estimated by the dead-end polymerizations of ABz at 80, 105, and 130 °C. Conclusively, by extrapolating the temperature dependency of the reinitiation number/primary radical to a higher temperature, the enhanced reinitiation could bias the well-known degradative monomer chain transfer characteristic of allyl polymerization toward the chain transfer in common vinyl polymerization at an elevated temperature. On the course of our investigation, we found by chance that any direct contribution of cumyloxy radical to initiation reaction was not observed in the polymerization of ABz with dicumyl peroxide (DCPO) as a typical peroxide initiator at elevated temperatures but the methyl radical initiation preceded by β-scission of cumyloxy radical occurred predominantly. This finding with DCPO was then extended to the generalization of initiation reaction mechanism in allyl polymerization at elevated temperatures with other organic peroxide initiators such as di-*t*-butyl peroxide (DBPO) and *tert*-butyl peroxybenzoate.[27]

Thus, the present article deals with a more detailed discussion of allyl polymerization at elevated temperatures, especially focused on addition−fragmentation chain transfer. Notably, an alternative chain termination involving β-scission of growing polymer radical through addition−fragmentation chain transfer, in addition to a well-known degradative monomer chain transfer in allyl polymerization, could be significant only at elevated temperatures. Instead, it has been conceived that allyl monomers could be very effective chain transfer agents,[11−13] and, moreover, the significance of β-scission of growing polymer radical in allyl polymerization has been demonstrated in several reports.[15−19]

EXPERIMENTAL SECTION

Materials. ABz (Daiso Co., Ltd., Osaka, Japan) as a monomer and methyl benzoate (MBz) (Wako Pure Chemical Industries, Ltd., Osaka, Japan) as a solvent were purified by vacuum distillation under nitrogen. DBPO (NOF Corp., Aichi, Japan) as an initiator was used without further purification.

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

Polymerization. Polymerization was carried out in a glass ampule containing the required amounts of monomer, solvent, and initiator. 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 predetermined reaction time, the polymer was precipitated by pouring the reaction mixture into a large excess of hexane containing a small amount of 4-*tert*-butylpyrocatechol as an inhibitor.

Measurements. MALDI−TOF−MS spectra were acquired in positive linear mode using an Axima-CFR time-of-flight mass spectrometer (Shimadzu/Kratos, Manchester, U.K.) with a pulsed N_2 laser (337 nm). Poly(ABz) (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 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.

^{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

Negligibly Small Contribution of Addition−Fragmentation Chain Transfer to Renewed Allyl Polymerization Mechanism in Bulk. In our previous article,[22] based on the MALDI−TOF−MS spectroscopic data, we made a renewal of the well-known reaction scheme proposed by Litt and Eirich[14] for the free-radical polymerization of AAc with benzoyl peroxide (BPO) as follows:

$$\text{initiation}: \quad \mathrm{I} \rightarrow 2\mathrm{R}^{\bullet} \tag{2}$$

$$\mathrm{R}^{\bullet} + \mathrm{M} \rightarrow \mathrm{M}^{\bullet} \tag{3}$$

$$\text{propagation}: \quad \mathrm{M}^{\bullet} + \mathrm{M} \rightarrow \mathrm{M}^{\bullet} \tag{4}$$

$$\text{chain transfer}: \quad \mathrm{M}^{\bullet} + \mathrm{M} \rightarrow \mathrm{P} + \mathrm{M}^{*\bullet} \tag{5}$$

$$\text{re-initiation}: \quad \mathrm{M}^{*\bullet} + \mathrm{M} \rightarrow \mathrm{M}^{\bullet} \tag{6}$$

$$\text{termination}: \quad \mathrm{M}^{\bullet} + \mathrm{M}^{*\bullet} \rightarrow \mathrm{P} \tag{7}$$

$$\mathrm{M}^{*\bullet} + \mathrm{M}^{*\bullet} \rightarrow \mathrm{M}^{*} - \mathrm{M}^{*} \tag{8}$$

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 allyl radical formed by the abstraction of an allylic hydrogen from AAc monomer.

For a deeper understanding of allyl polymerization mechanism, a pursuit of the fate of resonance-stabilized monomeric allyl radical generated via eq 5 is inevitable because the resonance-stabilization would lead not only to much less active species $M^{*\bullet}$ but also to an increased concentration of $M^{*\bullet}$ induced by spontaneous accumulation compared to those of other active species $R^{\bullet}$ and $M^{\bullet}$. The monomeric allyl radical has a possibility not only of initiating a new polymer chain via eq 6 but also of terminating a growing polymer radical via eq 7 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 mentioned in the Introduction. This leads to the drastic enhancement of bimolecular termination by accumulated allyl radicals in allyl polymerization as compared with common vinyl polymerization. Therefore, the coupling termination of monomeric allyl radical with growing polymer radical via eq 7 should compete with the propagation reaction via eq 4 as the degree of polymerization (P_n) is given as follows:

$$P_n = k_p[M^\bullet][M]/\{k_{tr,m}[M^\bullet][M] + k_{t1}[M^\bullet][M^{*\bullet}]\} \quad (9)$$

where the common bimolecular termination reaction between growing polymer radicals could be omitted as described previously.[22] Thus, the following equation is derived from eq 9:

$$1/P_n = k_{tr,m}/k_p + (k_{t1}/k_p)[M^{*\bullet}]/[M] \quad (10)$$

Now, the P_n value should depend on initiator concentration or monomeric allyl radical one: the lower the initiator concentration, the higher the P_n value. This was confirmed by the bulk polymerizations of AAc[22] and ABz.[26]

In the above discussion of the renewed allyl polymerization mechanism, an alternative chain termination involving β-scission of growing polymer radical through addition−fragmentation chain transfer, in addition to a well-known degradative monomer chain transfer via eq 5, may be missing. If the addition−fragmentation chain transfer occurred significantly, the formation of poly(AAc)s with a terminal allyl group, e.g., C_6H_5COO-$(AAc)_nCH_2CH{=}CH_2$ should be observed. However, the peaks assigned to the poly(AAc)s with a terminal allyl group were confirmed to be negligibly small in the AAc polymerization with BPO at 80 °C by MALDI−TOF−MS spectrometry, although the peaks assigned to poly(ABz)s with a terminal allyl group were clearly observed in the solution polymerization of ABz in MBz at 130 °C.[22] Thus, the occurrence of addition−fragmentation chain transfer could be enhanced at elevated temperatures and at a lower monomer concentration as will be discussed below.

Enhanced Addition−Fragmentation Chain Transfer at an Elevated Temperature and a Lower Monomer Concentration. First, we tried to explore the dependence of addition−fragmentation chain transfer on temperature until a quite high temperature of 150 °C, though common for the curing of DAP resins,[24,25] is reached. Here it should be recalled that the resonance-stabilized monomeric allyl radical could contribute competitively to both initiation and termination reaction.[22] That is, the coupling termination reaction between the growing polymer radical and the monomeric allyl radical via eq 7 was significant under the common allyl polymerization condition where a large amount of initiator was used, whereas the reinitiation reaction of monomeric allyl radical via eq 6 could occur predominantly under the completely opposite condition of common vinyl polymerization where the polymerization would be carried out at a low initiator concentration. Thus, rather simple spectra would be observed for oligomeric poly(ABz)s obtained at a low initiator concentration, being suitable for the discussion of addition−fragmentation chain transfer.

ABz was polymerized in MBz at a dilution of 1/3 in a total volume 5 mL using a low initiator concentration of 0.001 mol/L DBPO at 130 and 150 °C for 24 h. Figure 1 shows the SEC curves of oligomeric poly(ABz)s obtained at 1.8 and 5.0%, respectively.

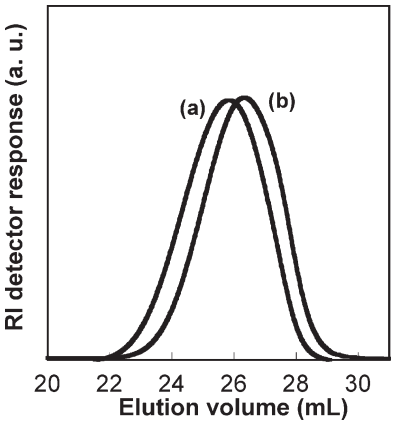


Figure 1. SEC curves of oligomeric poly(ABz)s obtained in the solution polymerizations of ABz in MBz at a dilution of 1/3 using 0.001 mol/L DBPO for 24 h at (a) 130 and (b) 150 °C.

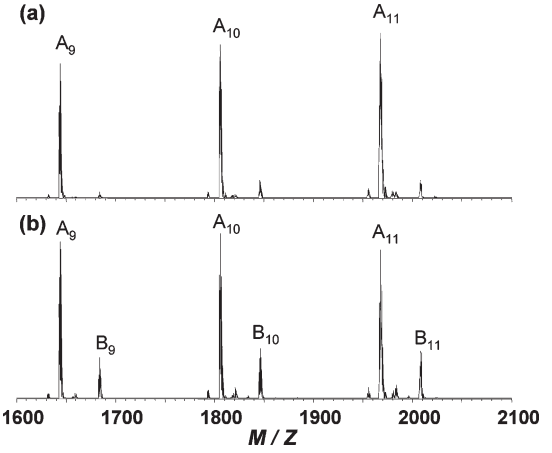


Figure 2. Comparison of MALDI−TOF−MS spectra of oligomeric poly(ABz)s obtained at (a) 130 and (b) 150 °C (see Figure 1).

Thus, the number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were estimated as follows: temperature (°C), M_n, M_w/M_n; 130, 3700, 1.28; 150, 3000, 1.25. The M_n value decreased with raised temperature as a reflection of enhanced monomer chain transfer and, probably, of concurrently enhanced addition−fragmentation chain transfer. The resulting poly(ABz)s were then subjected to MALDI−TOF−MS measurements to confirm an enhancement of the latter addition−fragmentation chain transfer at 150 °C because the oligomers with a terminal allyl group were clearly obtained in the solution polymerization of ABz at 130 °C as aforementioned but any spectrum was not given.[22] Figure 2 shows the comparison of MALDI−TOF−MS spectra of poly(ABz)s obtained at 130 and 150 °C. Simply, one kind of striking peaks were observed at 130 °C in Figure 2a, along with small peaks assignable to the addition−fragmentation chain transfer as will be discussed below. With raised temperature, the latter small peaks became more remarkable in the MALDI−TOF−MS spectrum of poly(ABz) obtained at 150 °C as shown in Figure 2b.

Based on the aforementioned discussion of addition−fragmentation chain transfer, we may need to add further the following two reactions to the renewed reaction scheme (eqs 2−8) as a reaction scheme of ABz polymerization at

dx.doi.org/10.1021/ma1029423 |Macromolecules 2011, 44, 3169–3173

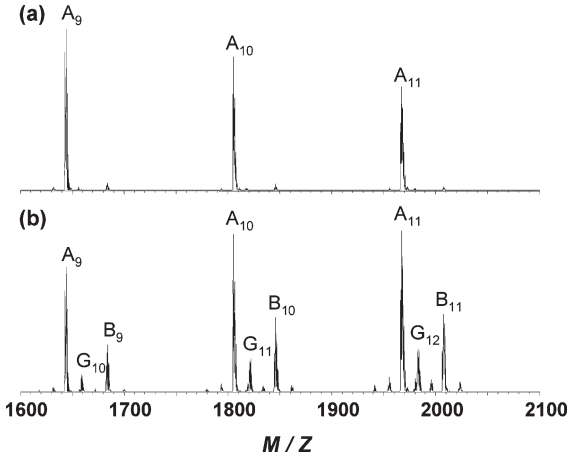


Figure 3. MALDI−TOF−MS spectra of oligomeric poly(ABz)s obtained at a conversion of 11.9 and 3.4%, respectively, in the (a) bulk and (b) solution polymerizations of ABz in MBz at a dilution of 1/5 using 0.001 mol/L DBPO for 24 h at 150 °C.

150 °C:

$$\beta\text{-scission}: \quad M^{\bullet} \rightarrow P - CH_2 - CH{=}CH_2 + C_6H_5COO^{\bullet} \tag{11}$$

$$\text{re-initiation}: C_6H_5COO^{\bullet} \quad (\text{or } C_6H_5{}^{\bullet}) + M \rightarrow M^{\bullet} \tag{12}$$

Thus, we should observe the specific MALDI−TOF−MS spectrum with a number of peaks assignable to oligomeric poly(ABz)s of different degrees of polymerization (n) with $C_6H_5COOCH{=}CHCH_2^{\bullet}$ ($M^{*\bullet}$), $C_6H_5COO^{\bullet}$, or $C_6H_5{}^{\bullet}$ as the initial end-group and H or $CH_2-CH{=}CH_2$ as the terminal end-group. For example, all possible molecular formulas of poly(ABz)s (n = 10) could be depicted as follows: $C_6H_5COOCH{=}CHCH_2(ABz)_{10}H$ (**A**) (1784.07); C_6H_5-$COOCH{=}CHCH_2(ABz)_{10}CH_2-CH{=}CH_2$ (**B**) (1824.13); $C_7H_5O_2(ABz)_{10}H$ (**C**) (1744.00); $C_7H_5O_2(ABz)_{10}CH_2-CH{=}CH_2$ (**D**) (1784.07); $C_6H_5(ABz)_{10}H$ (**E**) (1699.99); $C_6H_5(ABz)_{10}CH_2-CH{=}CH_2$ (**F**) (1740.06), where each figure in the parentheses denotes the corresponding molecular weight.

As is seen in Figure 2, the spectrum of the oligomeric poly(ABz) in the presence of NaI exhibited a series of ions repeating at an interval of 162.19 U corresponding to ABz repeat unit. The **A**-series peaks with highest relative intensity were assigned to the Na^+ adduct ions to the poly(ABz)s with the degree of polymerizations of 9 to 11, along with $C_6H_5COOCH{=}CHCH_2$ ($M^{*\bullet}$), introduced by reinitiation reaction of a monomeric allyl radical, as the initial end-group and H as the terminal end-group [161.18 + {162.19n + 22.98 (Na^+)} + 1.01] (poly(ABz)s; $C_6H_5COOCH{=}CHCH_2-(CH_2-CH(CH_2OCOC_6H_5))_n-H$). This clearly supports the significance of monomer chain transfer as an allylic hydrogen abstraction of growing polymer radical from monomer and also, the monomeric allyl radical could considerably reinitiate to generate a new growing polymer radical at elevated temperatures of 130 and 150 °C.

Notably, the **B**-series peaks with second highest relative intensity, remarkably appeared in Figure 2(b), were assigned to the Na^+ adduct ions to the poly(ABz)s with the degree of polymerizations of 9 to 11, along with $C_6H_5COOCH{=}CHCH_2$ ($M^{*\bullet}$) as the initial end-group and $CH_2-CH{=}CH_2$, introduced by addition−fragmentation chain transfer of growing polymer radical, as the terminal end-group [161.18 + {162.19n + 22.98 (Na^+)} + 41.07] (poly(ABz)s; $C_6H_5COOCH{=}CHCH_2-(CH_2-CH(CH_2OCOC_6H_5))_n-CH_2-CH{=}CH_2$). This clearly demonstrates the significant occurrence of β-scission of oligomeric growing polymer radical ($M^{\bullet}$) to generate a terminal allyl group via eq 1 or 11, especially at 150 °C. As a matter of course, the β-scission of growing polymer radical generates a benzoyloxy radical which may reinitiate to provide a new growing polymer radical via eq 12, although the benzoyloxy radical could decompose to give a phenyl radical and carbon dioxide. As a result, no **C**-, **D**-series peaks with C_6H_5COO or **E**-, **F**-series peaks with C_6H_5 as the initial end-groups appeared. This may be due to the fact that the benzoyloxy radical decomposed at 150 °C and, moreover, the resulting phenyl radical underwent easily allylic hydrogen abstraction from ABz monomer instead of reinitiation via eq 12.

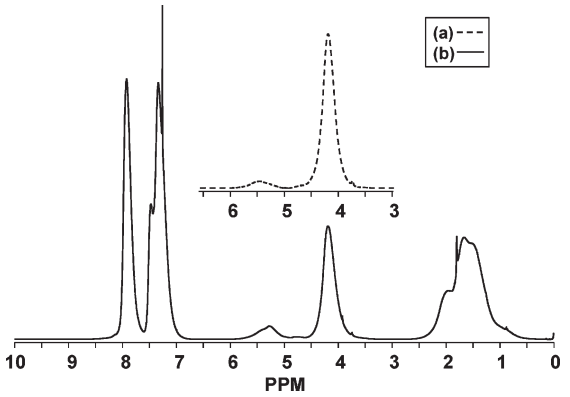


Figure 4. ^{1}H NMR spectra of oligomeric poly(ABz)s obtained in (a) bulk and (b) at a dilution of 1/5 (see Figure 3).

Second, we tried to explore the dependence of addition−fragmentation chain transfer on monomer concentration because the occurrence of unimolecular β-scission of oligomeric growing polymer radical could be enhanced at a lower monomer concentration. Figure 3 shows the MALDI−TOF−MS spectra of poly(ABz)s obtained in bulk and at a dilution of 1/5 at 150 °C. In the bulk polymerization (Figure 3(a)) almost no **B**-series peaks assignable to the addition−fragmentation chain transfer were observed but, to the contrary, they became more remarkable at a dilution of 1/5 (Figure 3(b)) as we expected. Furthermore, **G**-series peaks clearly appeared at a dilution of 1/5; they are assignable to the Na^+ adduct ions to the poly(ABz)s with the degree of polymerizations of 10 to 12, along with CH_3, introduced by initiation reaction of methyl radical generated via β-scission of *tert*-butoxy radical, as the initial end-group and H as the terminal end-group [15.03 + {162.19n + 22.98 (Na^+)} + 1.01] (poly(ABz)s; $[CH_3-(CH_2-CH(CH_2OCOC_6H_5))_n-H)$[27] because the feed molar ratio [DBPO]/[ABz] became five times higher at a dilution of 1/5.

Finally, the structure of resulting poly(ABz) was further checked by ^{1}H NMR spectroscopy because the structural identification of poly(ABz) was not performed directly from its mass spectrum. Figure 4 shows ^{1}H NMR spectra of poly(ABz)s obtained (a) in bulk and (b) at a dilution of 1/5 at 150 °C, corresponding to parts a and b of Figure 3, respectively. The existence of a terminal allyl end-group $CH_2-CH{=}CH_2$ was

dx.doi.org/10.1021/ma1029423 |*Macromolecules* 2011, 44, 3169–3173

confirmed as the absorption peaks assignable to vinyl methylene and methine protons of $CH_2-CH=CH_2$ group were clearly observed at 4.9−5.8 ppm, along with vinyl methine protons of an initial end-group $C_6H_5COOCH=CHCH_2$. Notably, an intensive peak assignable to vinyl methylene protons of the terminal allyl group generated by β-scission of growing polymer radical was observed clearly at 5.3 ppm in Figure 4b. Moreover, the ratio of the peak area corresponding to vinyl methylene and methine protons to the peak area of 3.7−4.6 ppm corresponding to methylene protons $-COOCH_2-$ of ABz units became about two times larger in Figure 4b than in Figure 4a as a reflection of β-scission of growing polymer radical leaving benzoyloxy group C_6H_5COO and a lower degree of polymerization at a dilution of 1/5 or a lowered monomer concentration.

CONCLUSION

As we discussed in our previous paper,[22] the poly(AAc)s with a terminal allyl group were negligibly observed in the bulk polymerization of AAc at 80 °C. This was opposed to our expectation because allyl monomers could be very effective chain transfer agents,[11−13] and, moreover, the significance of β-scission of growing polymer radical in allyl polymerization has been demonstrated in several reports.[15−19] Thus, an alternative chain termination involving β-scission of growing polymer radical through addition−fragmentation chain transfer, in addition to a well-known degradative monomer chain transfer in allyl polymerization, could be significant only at elevated temperatures. Thus, ABz was polymerized in MBz at a dilution of 1/3 using a low initiator concentration of 0.001 mol/L DBPO at 130 and 150 °C. The resulting poly (ABz)s were subjected to MALDI−TOF−MS measurements; the addition−fragmentation chain transfer was obviously enhanced at 150 °C. Then, the dependence of addition−fragmentation chain transfer on monomer concentration was explored because the occurrence of unimolecular β-scission of oligomeric growing polymer radical could be enhanced at a lower monomer concentration. The **B**-series peaks assignable to the addition−fragmentation chain transfer became more remarkable with dilution, although almost no **B**-series peaks were observed, notably, in the bulk polymerization even at 150 °C.

AUTHOR INFORMATION

Corresponding Author

*E-mail: amatsu@kansai-u.ac.jp. Fax +81-6-6339-4026.

ACKNOWLEDGMENT

We thank Prof. Ryuichi Arakawa of Kansai University for helpful discussions.

REFERENCES

(1) Odian, G. *Principles of Polymerization*, 4th ed.; Wiley: New York, 2004; pp 263−264.
(2) Schildknecht, C. E. *Allyl Compounds and Their Polymers*; Wiley: New York, 1973.
(3) Laible, R. C. *Chem. Rev.* **1958**, *58*, 807–843.
(4) Volodina, V. I.; Tarasov, A. I.; Spasskii, S. S. *Russ. Chem. Rev.* **1970**, *39*, 140–155.
(5) (a) Bartlett, P. D.; Altschul, R. *J. Am. Chem. Soc.* **1945**, *67*, 812–816. (b) Bartlett, P. D.; Altschul, R. *J. Am. Chem. Soc.* **1945**, *67*, 816–822. (c) Bartlett, P. D.; Tate, F. A. *J. Am. Chem. Soc.* **1953**, *75*, 91–95.
(6) (a) Oiwa, M.; Matsumoto, A. *Progress in Polymer Science Japan*; Kodansha: Tokyo, 1974; Vol. 4, pp 107−147. (b) Matsumoto, A. *Prog. Polym. Sci.* **2001**, *26*, 189–257.
(7) Moad, G.; Solomon, D. H. *The Chemistry of Radical Polymerization*, 2nd fully revised ed.; Elsevier: Amsterdam, 2006; pp 296−309.
(8) Cacioli, P.; Hawthorne, D. G.; Laslett, R. L.; Rizzardo, E.; Solomon, D. H. *J. Macromol. Sci., Chem.* **1986**, *A23*, 839–852.
(9) Meijs, G. F.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1988**, *21*, 3122–3124.
(10) Meijs, G. F.; Rizzardo, E.; Thang, S. H. *Makromol. Chem. Rapid Commun* **1988**, *9*, 547–551.
(11) Meijs, G. F.; Rizzardo, E.; Thang, S. H. *Polym. Bull.* **1990**, *24*, 501–505.
(12) Yamada, B.; Kobatake, S.; Aoki, S. *Polym. Bull.* **1993**, *31*, 263–270.
(13) Sato, T.; Seno, M.; Kobayashi, M.; Kohno, T.; Tanaka, H. *Eur. Polym. J.* **1995**, *31*, 29–34.
(14) Litt, M.; Eirich, F. R. *J. Polym. Sci.* **1960**, *45*, 379–396.
(15) Gaylord, N. G.; Katz, M.; Mark, H. F. *J. Polym. Sci., Polym. Lett. Ed.* **1964**, *2*, 151–155.
(16) Matsumoto, A.; Tamura, I.; Yamawaki, M.; Oiwa, M. *J. Polym. Sci. Polym. Chem. Ed.* **1979**, *17*, 1419–1429.
(17) Strumik, M. I.; Krolikowski, W.; Jankowska, M. *J. Appl. Polym. Sci.* **1981**, *26*, 3537–3541.
(18) Kostanski, L. K.; Krolikowski, W. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 605–614.
(19) Kostanski, L. K.; Krolikowski, W. *Polymer* **1986**, *27*, 403–408.
(20) (a) Sakurada, I.; Takahashi, G. *Kobunshi Kagaku* **1954**, *11*, 255–260. (b) Sakurada, I.; Takahashi, G. *Kobunshi Kagaku* **1954**, *11*, 260–265. (c) Sakurada, I.; Takahashi, G. *Kobunshi Kagaku* **1954**, *11*, 266–270.
(21) (a) Gaylord, N. G.; Eirich, F. R. *J. Am. Chem. Soc.* **1952**, *74*, 334–337. (b) Gaylord, N. G.; Eirich, F. R. *J. Am. Chem. Soc.* **1952**, *74*, 337–342. (c) Litt, M.; Eirich, F. R. *J. Polym. Sci.* **1960**, *45*, 379–396.
(22) Matsumoto, A.; Kumagai, T.; Aota, H.; Kawasaki, H.; Arakawa, R. *Polym. J.* **2009**, *41*, 26–33.
(23) (a) Saf, R.; Mirtl, C.; Hummel, K. *Acta Polym.* **1997**, *48*, 513–526. (b) Akakawa, R.; Watanabe, T.; Fukuo, T.; Endo, K. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4403–4406.
(24) Sanchez, J.; Myers, T. N. *Polym. Mater. Encycl.*, Vol. 7; CRC press: Boca Raton, 1996; pp 4927−4938.
(25) Myers, T. N. *Encycl. Polym. Sci. Tech.*, Vol. 6; Wiley: New York, 2003; pp 563−600.
(26) Inoue, S.; Kumagai, T.; Tamezawa, H.; Aota, H.; Matsumoto, A.; Yokoyama, K.; Matoba, Y.; Shibano, M. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 156–163.
(27) Inoue, S.; Kumagai, T.; Tamezawa, H.; Aota, H.; Matsumoto, A.; Yokoyama, K.; Matoba, Y.; Shibano, M. *Polym. J.* **2010**, *42*, 716–721.