

ORIGINAL ARTICLE

Predominant methyl radical initiation preceded by β -scission of alkoxy radicals in allyl polymerization with organic peroxide initiators at elevated temperatures

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Allyl monomers polymerize with difficulty and their polymerization yields polymers of medium molecular weight or oligomers. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry is a powerful tool for structural identification of oligomers; therefore, we aimed to use it to collect direct evidence for a full mechanistic discussion, including initiation and termination reactions. In the course of our investigation, which was concerned with the temperature dependence of the reinitiation reactivity of resonance-stabilized monomeric allyl radicals and was especially focused on polymerization behavior at elevated temperatures, we found by chance that any direct contribution of cumyloxy radicals to the initiation reaction was not observed in the polymerization of allyl benzoate with dicumyl peroxide (a typical peroxide initiator) at elevated temperatures. However, a methyl radical initiation preceded by β -scission of cumyloxy radicals predominantly occurred. This finding was extended to the generalization of an initiation reaction mechanism in allyl polymerization with organic peroxide initiators at elevated temperatures.

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INTRODUCTION

Allyl monomers polymerize with difficulty and their polymerization yields polymers of medium molecular weight or oligomers.^{1–4} This is attributable to ‘degradative monomer chain transfer’.^{5–7} The well-known allyl polymerization mechanism^{8–13} is based on kinetic data alone, without structural identification. In our preceding study,¹⁴ allyl acetate (AAc), a typical allyl monomer, 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) to reassess the AAc polymerization mechanism proposed by Litt and Eirich;¹³ their mechanism was based on results reported in the period 1940–1960. We propose a renewal of the well-known reaction scheme for the free-radical polymerization of AAc. On the basis of this renewed reaction mechanism, which yields oligomers, we investigated the fate of resonance-stabilized monomeric allyl radicals as follows. The coupling termination of monomeric allyl radicals with growing polymer radicals, leading to a shortening of the oligomeric poly(AAc) chain length, was significant under a common allyl polymerization condition, in which a remarkably large amount of initiator was used compared with common vinyl polymerization.

Under the completely opposite condition, in which polymerization was carried out at a low initiator concentration, the reinitiation reaction of monomeric allyl radicals occurred predominantly without any contribution from the monomeric allyl radical to the coupling termination reaction with growing polymer radicals. The latter reinitiation reaction of monomeric allyl radicals is significant because in allyl polymerization, it is conceivable that the resulting monomeric allyl radical is less active and/or less inclined to initiate a new polymer chain because of an ability to stabilize itself by resonance—the monomer chain transfer is essentially a termination reaction. Our investigation was concerned with the temperature dependence of the reinitiation reactivity of resonance-stabilized monomeric allyl radicals and was especially focused on polymerization behavior at elevated temperatures. We found by chance that any peak assignable to cumyloxy radical initiation was not observed in the MALDI-TOF-MS spectrum of the resulting oligomer in the free-radical polymerization of ABz, with DCPO as one of the typical peroxide initiators at 130 °C. However, initiation by methyl radical generation by β -scission of cumyloxy radicals predominantly occurred. This finding with DCPO was extended to other initiators such as *t*-butyl peroxybenzoate (BPOB)

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and di-*t*-butyl peroxide (DBPO) for generalization of this interesting initiation behavior of organic peroxides at elevated temperatures.

It is noteworthy that approximately 100 organic peroxide initiators are commercially produced throughout the world, primarily for polymer and resin industries. DCPO, BPOB and DBPO are typical organic peroxides used as initiators to generate radicals at elevated temperatures, being useful for vinyl monomer polymerizations, curing of unsaturated polyester and diallyl phthalate (DAP) resins, cross-linking of elastomers and polyolefins, and for reactive extrusion.^{15,16}

EXPERIMENTAL PROCEDURE

Materials

ABz (Daiso Co., Ltd., Osaka, Japan), as a monomer, was purified by vacuum distillation under nitrogen. DCPO, BPOB and DBPO (NOF Corp., Aichi, Japan), as initiators, were used without further purification.

2,5-Dihydroxybenzoic acid (DHBA; Sigma-Aldrich, Milwaukee, WI, USA), 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.) were purchased and used.

Polymerization

Polymerization was carried out in a glass ampule containing the required amounts of monomer 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 area at the 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, UK) with a pulsed N_2 laser (337 nm).^{14,17} The allyl polymer (2.0 mg ml^{-1}), DHBA matrix (20 mg ml^{-1}) and NaI cationizing agent (1.0 mg ml^{-1}) were dissolved in THF. Thereafter, $0.5\ \mu\text{l}$ from 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 and third, polymer solution. Analyte ions were accelerated at 20 kV under delayed extraction conditions. Sodiated ions of PEG ($M_w=2000$ Da) were used for calibration.

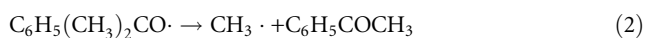
Size-exclusion chromatography (SEC) measurements were carried out at $40\ ^\circ\text{C}$ in THF using a two-column Shodex KF-802.5 and -803 (Showa Denko, Tokyo, Japan), at polymer concentrations of 0.1–0.5% (w/v) and at a flow rate of 1 ml min^{-1} . SEC curves monitored with a differential refractometer were analyzed using the calibration curve obtained with standard samples of monodispersed polystyrene to estimate the molecular weight.

^1H NMR spectra were recorded on a JEOL AL-400 (Jeol, Tokyo, Japan). NMR measurements were carried out at 400 MHz in CDCl_3 at $30\ ^\circ\text{C}$.

RESULTS AND DISCUSSION

Identification of oligomeric poly(ABz) with DCPO involving its end groups

For a long time, we have been concerned with the polymerization of multiallyl monomers, typically DAP;¹⁸ thus, ABz as a mono-ene counterpart of DAP was polymerized with DCPO as an initiator at elevated temperatures. DCPO underwent thermal decomposition to produce two primary cumyloxy radicals, as shown in Equation (1), subsequently followed by β -scission of a cumyloxy radical to yield a secondary methyl radical and acetophenone, as shown in Equation (2):^{15,16,19}

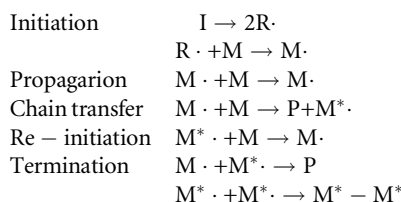


In general, the driving force for the β -scission reaction of the alkoxy radical is the reduced energy of the alkyl radical that is produced,

compared with that of the oxygen-centered radical. Thus, β -scission is less favored when a higher energy methyl radical is generated. Methyl and oxygen-centered radicals have higher energies than other alkyl radicals; therefore, the peroxides that produce them are generally preferred for use in applications requiring high-energy radicals for hydrogen abstraction reactions; for example, polyolefin cross-linking. However, in applications in which hydrogen abstraction is not desired, such as vinyl monomer polymerization and copolymerization, peroxides that generate alkyl radicals having lower energies than the methyl radical should be selected.¹⁵ We are interested in the elucidation of the initiation mechanism of ABz polymerization using DCPO as an initiator at elevated temperatures because DCPO is commercially important, being commonly used for curing DAP resins.²⁰

As the β -scission reaction of the alkoxy radical is, to the best of our knowledge, less favored, most work on alkoxy radicals as initiating species in polymerizations has concentrated on the chemistry of *t*-butoxy radicals.¹⁹ In a polymerization reaction, *t*-butoxy radicals may add to the double bond of a monomer to initiate polymerization, abstract a hydrogen from the monomer or another component to afford a new radical species and undergo β -scission to yield a methyl radical. The relative importance of these processes depends on the specified polymerization system. *t*-Butoxy radicals are slightly electrophilic.²¹ However, with allyl methacrylate²² and allyl acrylate,²³ the additional selectivity of *t*-butoxy radicals into two types of double bonds was markedly more favorable to the (meth)acrylic double bond than to the allylic double bond and, strikingly, allylic hydrogen abstraction predominated compared with addition.

Considering a renewed reaction mechanism that yields oligomers in the polymerization of AAC,¹⁴ the free-radical polymerization of ABz with DCPO could proceed as follows:



where I is DCPO, R \cdot the cumyloxy or methyl radical, M an ABz monomer, M \cdot the oligomeric growing polymer radical, P the oligomeric poly(ABz) produced and M $^*\cdot$ the monomeric allylic radical formed by the abstraction of an allylic hydrogen from the ABz monomer.

According to the above reaction scheme, 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 R or M * as the initial end group and H or M * as the terminal end group. For example, all possible molecular formulae of poly(ABz)s ($n=8$) could be depicted as follows: $\text{C}_9\text{H}_{11}\text{O}(\text{ABz})_8\text{H}$ (A) (1433.70); $\text{C}_9\text{H}_{11}\text{O}(\text{ABz})_8\text{CH}_2\text{CH}=\text{CHOCOC}_6\text{H}_5$ (B) (1593.87); $\text{CH}_3(\text{ABz})_8\text{H}$ (C) (1313.55); $\text{CH}_3(\text{ABz})_8\text{CH}_2\text{CH}=\text{CHOCOC}_6\text{H}_5$ (D) (1473.72); $\text{C}_6\text{H}_5\text{COOCH}=\text{CHCH}_2(\text{ABz})_8\text{H}$ (E) (1459.69) and $\text{C}_6\text{H}_5\text{COOCH}=\text{CHCH}_2(\text{ABz})_8\text{CH}_2\text{CH}=\text{CHOCOC}_6\text{H}_5$ (F) (1619.86) (figures in parentheses denote the corresponding molecular weight).

The bulk polymerization of ABz was carried out using 0.1 mol l^{-1} DCPO for 20 min at $130\ ^\circ\text{C}$, although the half-life of DCPO is about 120 min. Figure 1 shows the SEC curve of oligomeric poly(ABz) obtained at a conversion of 12.6% as a typical example. The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the resulting poly(ABz) were estimated to be 3770 and

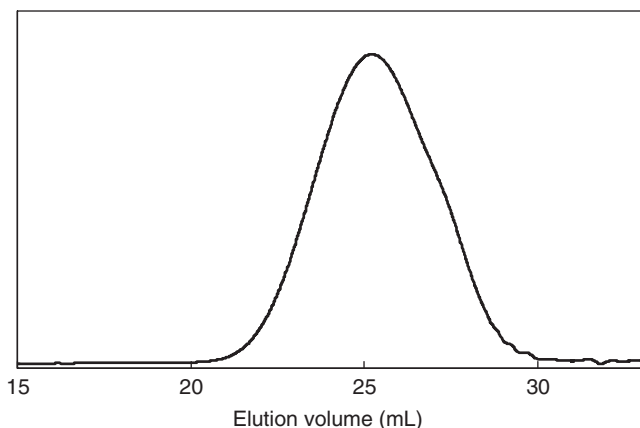


Figure 1 SEC curve of oligomeric poly(ABz) obtained at a conversion of 12.6% in the bulk polymerization of ABz using 0.1 mol l^{-1} DCPO for 20 min at 130°C .

1.51, respectively, by SEC. It should be noted that the polymerization result obtained with a remarkably large amount of initiator was required for discussing any contribution of primary cumyloxy or secondary methyl radicals to the initiation reaction for the following reason. At a low initiator concentration, the reinitiation reaction of monomeric allyl radicals would predominantly occur,⁴ and consequently, the A- or C-series peaks that are due to the cumyloxy or methyl radical initiation would be observed only weakly compared with the E-series peaks that are due to the reinitiation reaction of monomeric allyl radicals.

Figure 2 shows the MALDI-TOF-MS spectrum of poly(ABz) obtained at a conversion of 12.6%. Notably, both the addition to the double bond of a monomer and the abstraction reaction of an allylic hydrogen from monomers by primary cumyloxy radicals are bimolecular. However, the β -scission reaction of a cumyloxy radical to result in a secondary methyl radical and acetophenone, as shown in Equation (2) is unimolecular. Therefore, we carefully checked the influence of conversion on MALDI-TOF-MS spectra of oligomeric poly(ABz)s, but no significant difference was observed, although the polymerization was carried out in bulk. As can be seen in Figure 2, a simple spectrum was observed, as opposed to our expectation that a number of peaks (A- to F-series) could appear according to the above reaction scheme. Thus, the striking peaks in the mass spectrum of poly(ABz) corresponded only to C- and E-series peaks, although 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 the ABz repeat unit. Most strikingly, A-series peaks with cumyloxy $\text{C}_9\text{H}_{11}\text{O}$ as the initial end group did not appear at all.

The peaks with highest relative intensity (E-series) were assigned to the Na^+ adduct ions of poly(ABz)s, with degrees of polymerization from 7 to 9, along with M^+ . These were introduced by the reinitiation reaction of a monomeric allyl radical as the initial end group and H as the terminal end group ($161.18 + (162.19n + 22.98 (\text{Na}^+)) + 1.01$) (poly(ABz)s; $\text{C}_6\text{H}_5\text{COOCH}=\text{CHCH}_2-(\text{CH}_2-\text{CH}(\text{CH}_2\text{OCOC}_6\text{H}_5))_n-\text{H}$). This clearly supports the significance of monomer chain transfer as an allylic hydrogen abstraction in growing polymer radicals from monomers. In addition, the monomeric allyl radical could reinitiate to generate a new growing polymer radical at an elevated temperature.

The peaks with the second highest relative intensity (C-series) were assigned to the Na^+ adduct ions in the poly(ABz)s, with degrees of polymerization from 8 to 10, along with CH_3 . This was introduced by the initiation reaction of methyl radical generation through β -scission

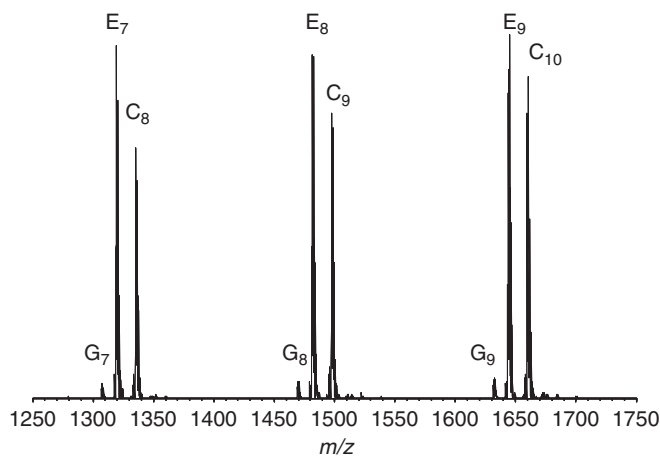


Figure 2 MALDI-TOF-MS spectrum of oligomeric poly(ABz) (see Figure 1).

of a cumyloxy radical as the initial end group and H as the terminal end group ($15.03 + (162.19n + 22.98 (\text{Na}^+)) + 1.01$) (poly(ABz)s; $\text{CH}_3-(\text{CH}_2-\text{CH}(\text{CH}_2\text{OCOC}_6\text{H}_5))_n-\text{H}$). This clearly shows the significance of β -scission of a cumyloxy radical in generating a methyl radical as shown by Equation (2).

Weak G-series peaks having a lower mass unit, 12, corresponding to one carbon atom, than E-series peaks, were also clearly observed. This will be discussed below in connection with the intramolecular (back-biting) hydrogen abstraction to form mid-chain radicals, which subsequently undergo β -scission of the main chain, resulting in oligomeric poly(ABz) with a terminal $=\text{CH}_2$ group and a new radical with a high reinitiation reactivity (see Equation 9).

Here it should be recalled that DCPO is one of the typical organic peroxides used as initiators to generate radicals at elevated temperatures and thus ABz polymerization with DCPO was accomplished at 130°C . Because fragmentation reactions are generally favored at elevated temperatures,¹⁹ β -scission of the resulting cumyloxy radical might be promoted. Accordingly, ABz polymerizations were conducted at 80, 90, 100, 110, 120 and 140°C . The spectra obtained at the lowest temperature (80°C) and the highest temperature (140°C) are shown in Figure 3. In both cases, C- and E-series peaks were observed strongly, although A-series peaks with cumyloxy $\text{C}_9\text{H}_{11}\text{O}$ as the initial end group appeared only slightly at 80°C . The peaks with the highest relative intensity changed from E-series to C-series at 140°C . In addition, new, small peaks (I- and J-series) appeared at 140°C . This will be discussed below in connection with the β -scission of growing polymer radicals through addition-fragmentation transfer, which leads to the formation of oligomers with a terminal allyl group.²⁴

Allylic hydrogen abstraction from the ABz monomer by cumyloxy radical

In the polymerization of ABz with DCPO, the cumyloxy radical generated may add to the double bond of ABz, abstract allylic hydrogen from ABz to afford monomeric allyl radical, and undergo β -scission to yield a methyl radical and acetophenone as shown in Equation (2). The aforementioned results show that the cumyloxy radical added little directly to the double bond. A-series peaks with cumyloxy $\text{C}_9\text{H}_{11}\text{O}$ as the initial end group were observed only slightly at 80°C (see Figure 3a), although their β -scission occurred significantly. We investigated the ability of cumyloxy radicals to abstract allylic hydrogen from ABz monomers. We did this because *t*-butoxy

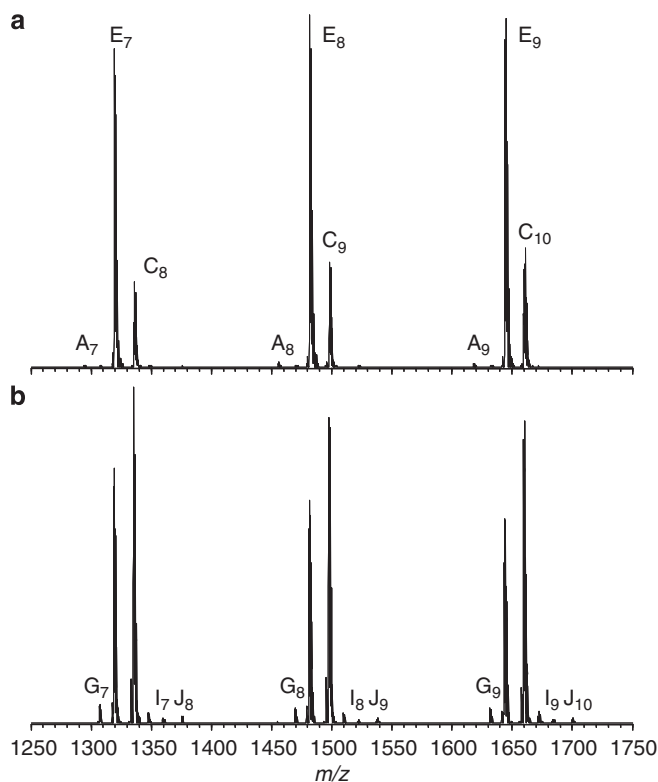


Figure 3 MALDI-TOF-MS spectra of oligomeric poly(ABz)s obtained in the bulk polymerizations of ABz: (DCPO), temperature, time, conversion, M_n ; (a) 0.4 mol l^{-1} , 80°C , 1260 min, 8.5%, 5090; (b) 0.1 mol l^{-1} , 140°C , 20 min, 31.9%, 3070.

radicals, as typical oxygen-centered radicals, easily abstracted allylic hydrogen from allyl methacrylate²² and allyl acrylate;²³ this allylic hydrogen abstraction predominated when compared with addition to the double bond of the allyl group. Moreover, Walling and Thaler²⁵ reported that allylic hydrogen abstraction, rather than addition, was the preferred reaction of *t*-butoxy radicals with many olefins.

The abstraction of a hydrogen from an ABz monomer by a cumyloxy radical should afford not only a monomeric allyl radical but also 2-phenyl-2-propanol. Thus, the generation of 2-phenyl-2-propanol was checked by ^1H NMR spectrometry. ABz polymerization was conducted in bulk using 0.1 mol l^{-1} DCPO at 140°C . As the half-life of DCPO at 140°C is about 37 min, we performed a dead-end polymerization²⁶ for 20 h to reach a conversion of 78%. The polymerization solution was then subjected to ^1H NMR measurements (see Figure 4a). Notably, an intense peak assignable to acetoxyl protons of acetophenone generated by β -scission was observed clearly at 2.61 p.p.m., whereas a weak peak assignable to methyl protons of 2-phenyl-2-propanol generated by allylic hydrogen abstraction appeared at 1.59 p.p.m. We estimated the molar ratio of acetophenone/2-phenyl-2-propanol to be 80:20 as follows. The polymerization solution was poured into a large excess of hexane containing a small amount of 4-*tert*-butylpyrocatechol as an inhibitor to precipitate poly(ABz). The supernatant solution was then evaporated to remove hexane, and the residue was subjected to ^1H NMR measurements (see Figure 4b). This is in line with the result that, at 140°C , the peaks with the highest relative intensity changed from E-series to C-series, with CH_3 as the initial end group, as introduced by the initiation reaction of methyl radicals generated by β -scission of cumyloxy radicals (see Figure 3b).

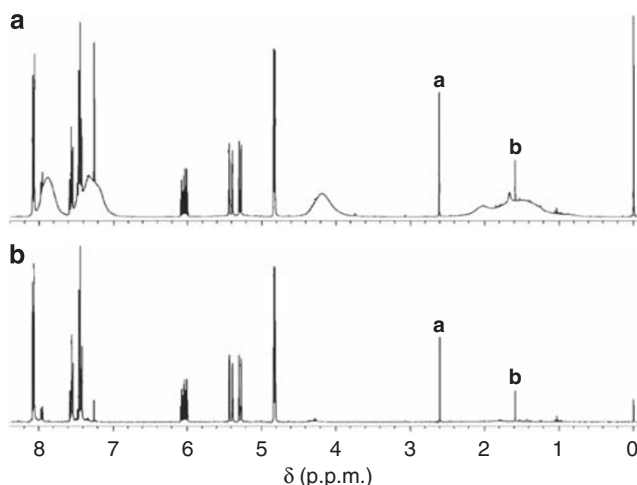


Figure 4 (a) ^1H NMR spectrum of the polymerization solution obtained at a conversion of 78% in the bulk polymerization of ABz using 0.1 mol l^{-1} DCPO for 20 h at 140°C . (b) ^1H NMR spectrum of the residue after removing poly(ABz) from the polymerization solution.

Because no A-series peaks with cumyloxy as the initial end group were observed in Figure 3b at 140°C , 20 mol% of cumyloxy radicals generated by the thermal decomposition of DCPO presumably preferentially abstracted allylic hydrogen from the ABz monomer because the allylic hydrogen abstraction was the preferred reaction of the *t*-butoxy radical with many olefins.²⁵ Related to this, Watanabe *et al.*²⁷ reported the temperature dependence of initiation reactions of oxygen-centered radicals using an α -methylstyrene dimer as a radical trapping agent; that is, the addition/ β -scission ratio of cumyloxy radicals was determined to be 40.8:59.2 at 140°C , although the α -methylstyrene dimer was assumed to be a model compound of styrene.

Generalization of the predominant methyl radical initiation preceded by β -scission of cumyloxy radicals to common alkoxy

As mentioned above, we found by chance that almost no direct contribution of cumyloxy radicals to the initiation reaction was observed in the polymerization of ABz with DCPO as one of the typical initiators at elevated temperatures. This prompted us to attempt the generalization of the specific initiation of cumyloxy radicals to common alkoxy radicals; that is, the predominant methyl radical initiation was preceded by β -scission of alkoxy radicals. Thus, ABz polymerizations were performed using BPOB and DBPO as initiators that afford *t*-butoxy radicals by their thermal decomposition.

Notably, BPOB undergoes thermal decomposition to produce two kinds of primary benzyloxy and *t*-butoxy radicals, as shown in Equation (3), which is subsequently followed by β -scission of both benzyloxy and *t*-butoxy radicals to yield secondary phenyl and methyl radicals, respectively, and carbon dioxide and acetone, as shown in Equations (4) and (5):

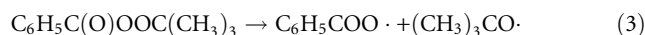


Figure 5 shows the MALDI-TOF-MS spectrum of poly(ABz) obtained in the bulk polymerization of ABz using 0.1 mol l^{-1} BPOB for 20 min at 130°C , although the half-life of BPOB is about 36 min. It should be

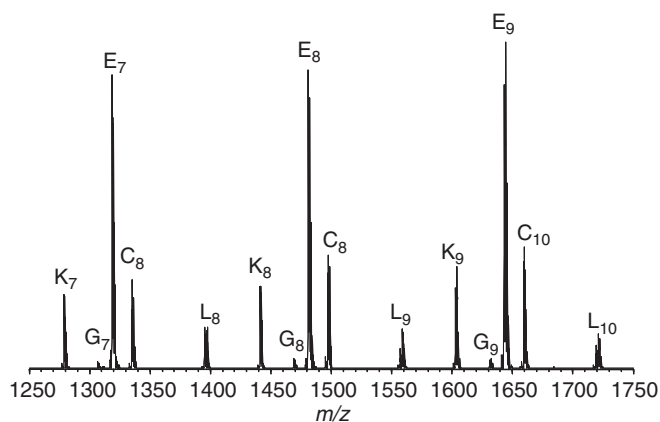


Figure 5 MALDI-TOF-MS spectrum of oligomeric poly(ABz) ($M_n=3420$) obtained at a conversion of 16.6% in the bulk polymerization of ABz using 0.1 mol l^{-1} BPOB for 20 min at 130°C .

noted that *t*-butoxy radicals could be generated as a counterpart of benzoyloxy radicals in the thermal decomposition of BPOB. Thus, K- and L-series peaks with benzoyloxy $\text{C}_7\text{H}_5\text{O}_2$ and phenyl C_6H_5 as the initial end groups, respectively, could newly appear. Clearly, both peaks were observed, although only weak L-series peaks appeared. Notably, any A-series peaks with *t*-butoxy $\text{C}_4\text{H}_9\text{O}$ as the initial end group did not appear.

As with DCPO, DBPO undergoes thermal decomposition to produce two primary *t*-butoxy radicals, as shown in Equation (6), subsequently followed by β -scission of a *t*-butoxy radical to result in a secondary methyl radical and acetone, as shown in Equation (7):



Figure 6 shows the MALDI-TOF-MS spectrum of poly(ABz) obtained in the bulk polymerization of ABz using 0.1 mol l^{-1} DBPO for 30 min at 130°C , although the half-life of DBPO is about 300 min. Any peaks with *t*-butoxy $\text{C}_4\text{H}_9\text{O}$ as the initial end group were not observed again at all, in accordance with our expectation.

It was conclusively confirmed that the initiation by methyl radical generated by β -scission of alkoxy radicals occurred predominantly in the polymerization of ABz with organic peroxide initiators at elevated temperatures.

Specific polymerization mechanism involving addition–fragmentation chain transfer and β -scission of mid-chain radicals

Addition–fragmentation chain transfer has been reported recently.²⁸ Even in allyl polymerization, the formation of oligomers with a terminal allyl group may be observed as a result of the occurrence of β -scission of growing polymer radicals, although Gaylord *et al.*²⁴ reported the β -scission of growing polymer radicals through addition–fragmentation transfer in the polymerization of AAc. Thus, a terminal allyl group characteristic of the I-series ($15.03 + (162.19n + 22.98 (\text{Na}^+) + 41.07)$ (poly(ABz)s; $\text{CH}_3-(\text{CH}_2-\text{CH}(\text{CH}_2\text{OCOC}_6\text{H}_5))_n-\text{CH}_2\text{CH}=\text{CH}_2$) and J-series ($161.18 + (162.19n + 22.98 (\text{Na}^+) + 41.07)$ (poly(ABz)s; $\text{C}_6\text{H}_5\text{COOCH}=\text{CHCH}_2-(\text{CH}_2-\text{CH}(\text{CH}_2\text{OCOC}_6\text{H}_5))_n-\text{CH}_2\text{CH}=\text{CH}_2$)) could be introduced by the following

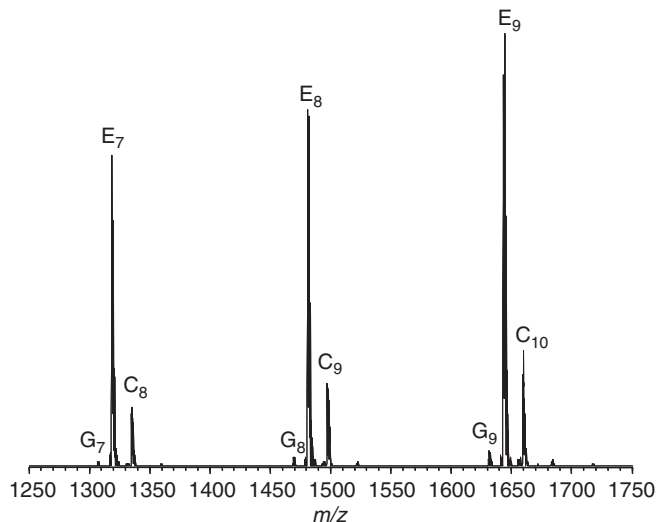
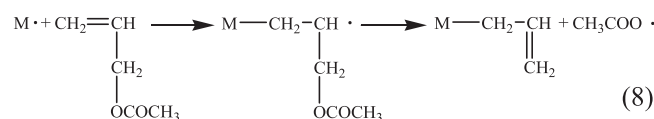


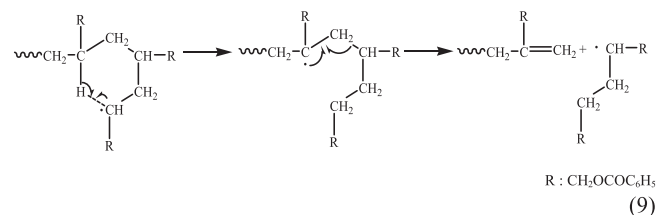
Figure 6 MALDI-TOF-MS spectrum of oligomeric poly(ABz) ($M_n=4120$) obtained at a conversion of 7.2% in the bulk polymerization of ABz using 0.1 mol l^{-1} DBPO for 30 min at 130°C .

chain termination involving β -scission of growing polymer radicals through addition–fragmentation transfer:



Notably, this kind of β -scission of growing polymer radicals was ruled out in the reaction scheme proposed by Litt and Eirich,¹³ although its significance has been shown in several reports.^{24,29–32} However, appreciable I- and J-series peaks were not observed in ABz polymerization at 80°C , although weak peaks were observed at 140°C (see Figure 2b). The result shown in Equation 8 could be enhanced at elevated temperatures and at a lower monomer concentration. A more detailed discussion of addition–fragmentation chain transfer will be given elsewhere.

Finally, we will briefly refer to the existence of the G-series ($149.17 + (162.19n + 22.98 (\text{Na}^+) + 1.01)$ (poly(ABz)s; $\text{C}_6\text{H}_5\text{COOCH}_2\text{CH}_2-(\text{CH}_2-\text{CH}(\text{CH}_2\text{OCOC}_6\text{H}_5))_n-\text{H}$). As discussed in our preceding article,¹⁴ the intramolecular (backbiting) hydrogen abstraction that forms mid-chain radicals, which subsequently undergo β -scission of the main chain, resulting in poly(ABz) with a terminal $=\text{CH}_2$ group, and a new radical $\text{C}_6\text{H}_5\text{COOCH}_2\text{CH}_2$ with high reinitiation reactivity, leads to the appearance of G-series peaks:



H-series peaks (15.03 or $\dots + (162.19n + 22.98 (\text{Na}^+) + 175.21)$ (poly(ABz)s; $\text{X}-(\text{CH}_2-\text{CH}(\text{CH}_2\text{OCOC}_6\text{H}_5))_n-\text{CH}_2-\text{C}(\text{CH}_2\text{OCOC}_6\text{H}_5)=\text{CH}_2$) (X = CH_3 , $\text{C}_6\text{H}_5\text{COOCH}=\text{CHCH}_2$, $\text{C}_6\text{H}_5\text{COO}$, C_6H_5 or

C₆H₅COOCH₂CH₂) could be observed as corresponding partners of the G-series, although they were quite weak.

CONCLUSIONS

In allyl polymerization, it is conceivable that allyl monomers polymerize only with difficulty and yield polymers of medium molecular weight or oligomers, because of 'degradative monomer chain transfer'. The resulting monomeric allyl radical is less active and/or less inclined to initiate a new polymer chain because of an ability to stabilize itself by resonance, the monomer chain transfer being essentially a termination reaction. Thus, the elucidation of reinitiation reactivity of monomeric allyl radicals is necessary for a deep understanding of allyl polymerization. In the course of our investigation, which was concerned with the temperature dependence of the reinitiation reactivity of resonance-stabilized monomeric allyl radicals and was especially focused on polymerization behavior at elevated temperatures, we found by chance that any direct contribution of cumyloxy radicals to the initiation reaction was not observed in the polymerization of ABz with DCPO at elevated temperatures. This prompted us to generalize the specific initiation of cumyloxy radicals to common alkoxy radicals. It was confirmed that initiation by methyl radicals, generated by β -scission of alkoxy radicals, occurred predominantly in the polymerization of ABz with organic peroxide initiators at elevated temperatures.

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- Odian, G. *Principles of Polymerization*. 4th edn. 263–264 (Wiley, New York, 2004).
- Schildknecht, C. E. *Allyl Compounds and their Polymers* (Wiley, New York, 1973).
- Laible, R. C. Allyl polymerizations. *Chem. Rev.* **58**, 807–843 (1958).
- Volodina, V. I., Tarasov, A. I. & Spasskii, S. Polymerisation of allyl compounds. *Russ. Chem. Rev.* **39**, 140–155 (1970).
- Bartlett, P. D. & Altschul, R. Polymerization of allyl compounds. I. Factors governing the acyl peroxide-induced polymerization of allyl acetate, and the fate of the peroxide. *J. Am. Chem. Soc.* **67**, 812–816 (1945).
- Bartlett, P. D. & Altschul, R. Polymerization of allyl compounds. II. Preliminary kinetic study of the peroxide-induced polymerization of allyl acetate. *J. Am. Chem. Soc.* **67**, 816–822 (1945).
- Bartlett, P. D. & Tate, F. A. The polymerization of allyl compounds. VI. The polymerization of allyl-1,1-d₂ acetate and the mechanism of its chain termination. *J. Am. Chem. Soc.* **75**, 91–95 (1953).
- Gaylord, N. G. & Eirich, F. R. Allyl polymerization. II. Decomposition of benzoyl peroxide in allyl esters. *J. Am. Chem. Soc.* **74**, 334–337 (1952).
- Gaylord, N. G. & Eirich, F. R. Allyl polymerization. III. Kinetics of polymerization of allyl esters. *J. Am. Chem. Soc.* **74**, 337–342 (1952).
- Sakurada, I. & Takahashi, G. Allyl polymerization. I. Polymerization of allyl acetate. *Kobunshi Kagaku* **11**, 255–260 (1954).
- Sakurada, I. & Takahashi, G. Allyl polymerization. II. Kinetics of polymerization of allyl acetate. *Kobunshi Kagaku* **11**, 260–265 (1954).
- Sakurada, I. & Takahashi, G. Allyl polymerization. III. Effective chain transfer. *Kobunshi Kagaku* **11**, 266–270 (1954).
- Litt, M. & Eirich, F. R. Polymerization of allyl acetate. *J. Polym. Sci.* **45**, 379–396 (1960).
- Matsumoto, A., Kumagai, T., Aota, H., Kawasaki, H. & Arakawa, R. Reassessment of free-radical polymerization mechanism of allyl acetate based on end-group determination of resulting oligomers by MALDI-TOF-MS spectrometry. *Polym. J.* **41**, 26–33 (2009).
- Sanchez, J. & Myers, T. N. *Polymeric Materials Encyclopedia*. Vol. 7, 4927–4938 (CRC Press, Boca Raton, 1996).
- Myers, T. N. *Encyclopedia of Chemical Technology*. Vol. 6, 563–600 (Wiley, New York, 2003).
- Kumagai, T., Kagawa, C., Aota, H., Takeda, Y., Kawasaki, H., Arakawa, R. & Matsumoto, A. Specific polymerization mechanism involving β -scission of mid-chain radical yielding oligomers in the free-radical polymerization of vinyl ethers. *Macromolecules* **41**, 7347–7351 (2008).
- Matsumoto, A. Polymerization of multiallyl monomers. *Prog. Polym. Sci.* **26**, 189–257 (2001).
- Moad, G. & Solomon, D. H. *The Chemistry of Radical Polymerization*. 2nd fully revised edn. 49–166 (Elsevier, Amsterdam, 2006).
- Laible, R. C. *Encyclopedia of Chemical Technology*. Vol. 1, 750 (Wiley, New York, 1964).
- Jones, M. J., Moad, G., Rizzardo, E. & Solomon, D. H. The philicity of *tert*-butoxy radicals. What factors are important in determining the rate and regioselectivity of *tert*-butoxy radical addition to olefins? *J. Org. Chem.* **54**, 1607–1611 (1989).
- Busfield, W. K., Jenkins, I. D., Thang, S. H., Rizzardo, E. & Solomon, D. H. Initiation mechanisms in radical polymerization: reaction of *tert*-butoxy radicals with allyl methacrylate. *Aust. J. Chem.* **38**, 689–698 (1985).
- Busfield, W. K., Jenkins, I. D., Thang, S. H., Rizzardo, E. & Solomon, D. H. Initiation mechanisms in radical polymerization: reaction of *tert*-butoxy radicals with allyl acrylate and with diallyl ether. *J. Chem. Soc. Perkin. Trans.* **1**, 485–490 (1988).
- Gaylord, N. G., Katz, M. & Mark, H. F. Radical displacement as a termination reaction in allyl ester polymerization. *J. Polym. Sci. Polym. Lett. Ed.* **2**, 151–155 (1964).
- Walling, C. & Thaler, W. Positive halogen compounds. III. Allylic chlorination with *tert*-butyl hypochlorite. The stereochemistry of allylic radicals. *J. Am. Chem. Soc.* **83**, 3877–3884 (1961).
- Odian, G. *Principles of Polymerization*. 4th edn. 234 (Wiley, New York, 2004).
- Watanabe, Y., Ishigaki, H., Okada, H. & Suyama, S. Temperature dependence of initiation reactions of oxygen-centered radicals. *Polym. J.* **29**, 693–696 (1997).
- Moad, G. & Solomon, D. H. *The Chemistry of Radical Polymerization*. 2nd fully revised edn. 296–309 (Elsevier, Amsterdam, 2006).
- Matsumoto, A., Tamura, I., Yamawaki, M. & OIwa, M. Studies of the polymerization of diallyl compounds. XXII. Polymerization of diallyl oxalate in the evolution of carbon dioxide at elevated temperatures. *J. Polym. Sci. Polym. Chem. Ed.* **17**, 1419–1429 (1979).
- Strumik, M. I., Krolikowski, W. & Jankowska, M. Polymerization of diallyl phthalate at high temperatures. *J. Appl. Polym. Sci.* **26**, 3537–3541 (1981).
- Kostanski, L. K. & Krolikowski, W. Bulk polymerization of diallyl benzene-dicarboxylates. I. Influence of temperature on allyl group reactivity. *J. Polym. Sci. Polym. Chem. Ed.* **23**, 605–614 (1985).
- Kostanski, L. K. & Krolikowski, W. Effect of temperature on the structure of prepolymers of diallyl benzenedicarboxylates. *Polymer* **27**, 403–408 (1986).