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NOTE

Evidence of Scission Products from Peroxide-Initiated Higher Temperature Polymerization of Alkyl Methacrylates

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Introduction

Methacrylates are a principal component of acrylic binder resins used in automotive coatings; the low molecular weight polymers with reactive functionalities are made via high-temperature starved-feed free-radical solution semibatch copolymerization.[1] The initiator, *tert*-butyl peroxyacetate (TBPA), is often chosen for experiments conducted at 130−150 °C due to its short half-life relative to the monomer feeding time.[2] Scheme 1 illustrates the possible pathways for thermal decomposition of TBPA.[3,4] One-bond scission generates two oxygen-centered radicals while two-bond scission yields a methyl radical, an oxygen-centered radical, and carbon dioxide. Studies in Buback's group indicated that the methylcarbonyloxyl radical, if produced, undergoes fast decarboxylation before starting chain growth, as determined by the end-group analysis of the resultant polymers using electrospray ionization mass spectrometry (ESI-MS).[5]

As well as initiating a chain by adding to the double bond of a monomer, the *tert*-butoxy oxygen-centered radical can abstract hydrogen from monomer, solvent, and polymer and may also undergo β-scission to form carbon-centered radicals.[6,7] Thus, for the case of butyl methacrylate (BMA) homopolymerization initiated by TBPA in xylene at 138 °C, possible initiation pathways are summarized in Scheme 2.

Matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS) and ESI-MS, both soft ionization mass spectrometry techniques suitable for the imaging of nonfragmented synthetic polymer chains, have been applied for qualitative chain-end analyses of a number of polymers.[8−10] In this work, we use MALDI-MS to investigate the polymer species produced in BMA homopolymerization initiated by TBPA in xylene at 138 °C. While most of the species could be attributed to the initiation mechanisms in Scheme 2, an additional structure was found that we hypothesize originates from *tert*-butoxy attack on alkyl ester groups located on the polymer chains, followed by monomer addition, backbiting, and chain scission. The mechanistic pathway is further supported by one- and two-dimensional NMR spectra.

Experimental Section

Materials. Butyl methacrylate (99%, Sigma-Aldrich Co.), dodecyl methacrylate (96%, Sigma-Aldrich Co.), xylene (isomeric mixture with boiling point between 136 and 140 °C, Sigma-Aldrich Co.), and chloroform-*d* ($CDCl_3$, 99.96 atom % D, Sigma-Aldrich Co.) were used as received. *tert*-Butyl peroxyacetate (TBPA), provided as a solution of 75 wt % initiator in mineral spirits by Arkema, was used as received.

Sample Preparation. A starved-feed semibatch procedure[2] was used to produce the polymers in this study at 138 °C, with the final mixture (after 6 h feeding) containing 35% poly(BMA) in xylene; 1 wt % TBPA relative to monomer was used in the recipe. The resulting samples were precipitated in methanol, redissolved in tetrahydrofuran (THF) and reprecipitated twice, and dried in a vacuum oven at 60 °C before MALDI-MS and NMR analysis.

Polymer Characterization. Matrix-assisted laser desorption ionization (MALDI) mass spectra were acquired with an Applied Biosystems/MDS Sciex QStar XL quadrupole time-of-flight mass spectrometer equipped with an MALDI II source and a nitrogen laser operating at 337 nm. The matrix and cation used was 2,5-dihydroxybenzoic acid (Aldrich) and sodium cation, respectively. Polymer solutions in THF were made up at a concentration of 0.1 mg polymer/mL. The polymer solutions (0.5 μL) were mixed with the matrix, dried at room temperature, and then analyzed at positive ionization mode, with data recorded by Analyst QS 1.1 software.

^{1}H NMR and two-dimensional heteronuclear single quantum coherence (HSQC) were recorded at room temperature using a Bruker DPX-400 NMR spectrometer to analyze ~10% polymer solution in $CDCl_3$ solvent.

Results and Discussion

Figure 1 shows the MALDI mass spectrum of Na^+-ionized poly(butyl methacrylate) from polymerization in xylene at 138 °C with TBPA initiator; the inset expands the m/z axis to cover a range corresponding to one monomer repeat unit. Three main polymer species (**1**, **4**, **6**), as well as several minor ones, are observed and labeled in the expansion of Figure 1. The minor peaks labeled were chosen because their m/z values correspond to possible structures identified from the initiation pathways, as summarized in Table 1. Other small peaks seen in the spectrum were not identified. The number-average molecular weight of the sample determined by size exclusion chromatography was 2400 g/mol, slightly higher than that indicated by Figure 1. The difference may be due to different ionization efficiency for macromolecules with different chain end groups.[8]

Peak assignments are summarized in Table 1. The calculated theoretical polymer masses comprise a specific number of monomeric BMA units, one or two initiator fragments identified in Scheme 2, and a sodium cation originating from the MALDI ionization process. The differences between theoretical and experimental masses are less than 0.2 Da for all species listed, as also reported in other polymerization studies.[5,9] The one exception is peak 8, which has a difference of 0.6 Da; the reason for this larger deviation is not clear but does not impact the central focus of this paper. No detectable polymer species with *tert*-butoxy end groups indicates that, under the semibatch operating conditions, almost all *tert*-butoxy radicals abstract hydrogen instead of adding monomer to initiate a polymer chain.

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Minor peaks 3, 8, and 9 correspond to combination products, while peaks 1 and 6 are the products of xylol and methyl radical initiated macroradicals terminated by disproportionation. Disproportionation occurs via transfer of a hydrogen atom between two growing radicals to generate two dead polymeric chains with terminating end groups that differ in molecular weight by 2 Da, as seen for peaks 1 and 6. The second peak in each grouping is larger, not only because it overlaps with an isotopic satellite of the first but also from the contribution of radicals that are terminated by chain transfer.

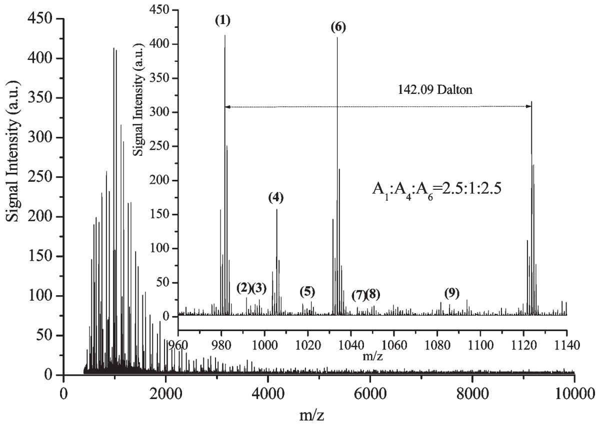
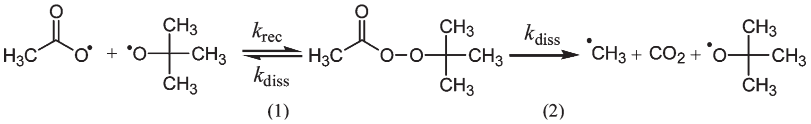


Figure 1. MALDI mass spectrum of Na^+-ionized poly(butyl methacrylate) generated by *tert*-butyl peroxyacetate-initiated butyl methacrylate polymerization in xylene at 138 °C with 65 wt % solvent content and expanded spectrum for *m*/*z* range corresponding to one monomer repeat unit. A_i represents the relative area of peak *i*. (See Table 1 for structures corresponding to labeled peaks.)

The significant signal, peak 4, as well as two small peaks (peaks 2 and 7), represents additional structures that cannot be matched by any of the chain-end structures shown in Scheme 2. The molecular weights of peaks 2 and 7 are larger than that of peaks 1 and 6, respectively, by 12 Da, and the molecular weight of peak 4 is less than that of peak 5 by 12 Da. These differences are characteristic of backbiting and scission mechanisms, as prevalent in acrylate systems.[1,11] One possible pathway to produce these structures during BMA polymerization is proposed in Scheme 3. The initiating reaction is attack of the butyl ester group on the polymer chain by a *tert*-butoxy radical to form radical **f**, which then adds two BMA monomers to form radical **g**. This species (or another *tert*-butoxy radical) abstracts hydrogen from the tertiary carbon to form radical **h**, which fragments into radical **j** and a macromonomer **i**. The radical **j** can propagate and terminate by disproportionation to form a polymer structure of peak **4**. Peaks **2** and **7** are macromonomers **i** with xylol and CH_3 as end groups, respectively.

Scheme 1. Reaction Scheme for the Thermal Decomposition of *tert*-Butyl Peroxyacetate by One-Bond Scission (1) or Concerted Two-Bond Scission (2)



Scheme 2. Possible Initiation Pathways for Butyl Methacrylate (BMA) Homopolymerization Initiated by *tert*-Butyl Peroxyacetate in Xylene at 138 °C

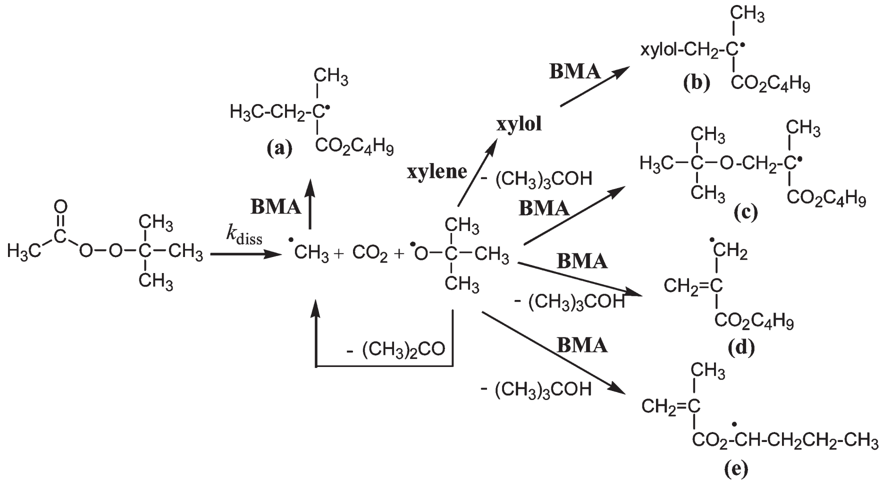


Table 1. Comparison of Experimental versus Theoretical Mass for Poly(BMA)[a]

peak	origin	theor mass (Da)	exptl mass (Da)
1	xylol-$(BMA)_6$-H + Na^+	981.66	981.68
2	**i** originated from xylol-$(BMA)_6$-H + Na^+	993.66	993.63
3	xylol-$(BMA)_6$-CH_3 + Na^+	995.68	995.76
4	**j**-$(BMA)_6$-H + Na^+	1005.69	1005.58
5	(**d** or **e**)-$(BMA)_6$-H + Na^+	1017.69	1017.53
6	CH_3-$(BMA)_7$-H + Na^+	1033.72	1033.70
7	**i** originated from CH_3-$(BMA)_7$-H + Na^+	1045.72	1045.92
8	CH_3-$(BMA)_7$-CH_3 + Na^+	1047.13	1047.73
9	xylol-$(BMA)_6$-xylol + Na^+	1085.73	1085.76

[a] BMA = butyl methacrylate; see Schemes 2 and 3 for end-group structures.

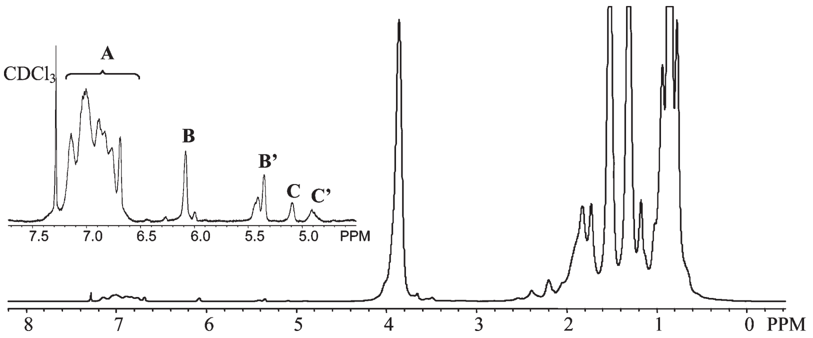
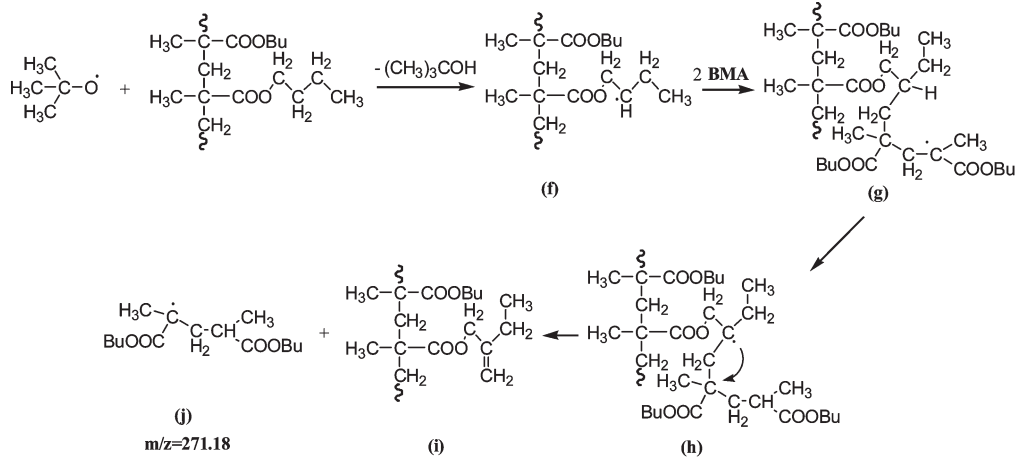


Figure 2. ^{1}H NMR spectra of poly(butyl methacrylate) generated by *tert*-butyl peroxyacetate initiated butyl methacrylate polymerization in xylene at 138 °C. Inset is an expansion of the region between 4.5 and 7.8 ppm (see text for further discussion).

Scheme 3. Proposed Backbiting and Scission Mechanisms after Chain Attack by *tert*-Butoxy Radicals during Butyl Methacrylate Homopolymerization Initiated by *tert*-Butyl Peroxyacetate in Xylene at 138 °C



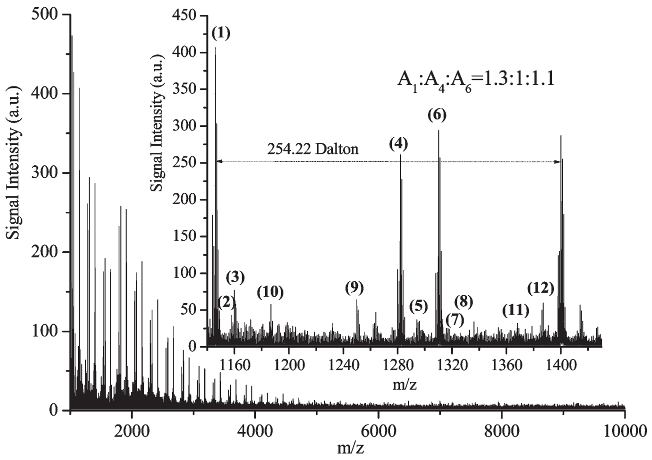


Figure 3. MALDI mass spectrum of Na$^+$-ionized poly(dodecyl methacrylate) generated by *tert*-butyl peroxyacetate-initiated dodecyl methacrylate polymerization in xylene at 138 °C and expanded spectrum for *m*/*z* range corresponding to one monomer repeat unit. A_i represents the relative area of peak *i*. (See Table 2 for structures corresponding to labeled peaks.)

The ^{1}H NMR spectrum of the same poly(BMA) sample is shown in Figure 2. The resonance signals between 6.5 and 7.2 ppm (A) can be ascribed to the hydrogen atoms of the xylol end group, and symmetric signals at 5.4 and 6.1 ppm (B, B′) are from the hydrogen atoms of double bonds conjugated with the carboxyl double bond of those macromonomers formed from termination by disproportionation or chain-initiating species **d** or **e** (Scheme 2). The additional resonance signals at 4.9 and 5.1 ppm (C, C′), with corresponding ^{13}C signals at 116.6 ppm (data not shown), indicate an alkene double bond that is not conjugated with carboxyl; the protons are more shielded and have chemical shifts at higher magnetic field relative to B and B′.[12] The positions of these sequences are consistent with structure **i** and support the mechanism proposed in Scheme 3.

According to Scheme 3, the additional peaks in Figure 1 originate from hydrogen abstraction by an oxygen-centered *tert*-butoxy radical. It is known that *tert*-amyl peroxyacetate (TAPA) is less likely to form oxygen-centered radicals, as β-scission of the alkoxyl radical to form acetone and an ethyl radical is favored.[5] A comparative BMA semibatch experiment using TAPA initiator was carried out, and MALDI-MS analysis of the resultant polymer showed that peak 4 was reduced in height relative to peaks 1 and 6 by greater than a factor of 2 compared to the TBPA initiated system.

It is also instructive to compare these poly(BMA) structures to other poly(alkyl methacrylates). For methyl methacrylate (MMA) polymerization initiated by TBPA in benzene at 130 °C, no peak corresponding to peak 4 was observed in the ESI-MS of the resultant poly(MMA).[5] The absence is reasonable according to the mechanism proposed in Scheme 3, as H-abstraction by *tert*-butoxy radical from a primary carbon is greatly reduced compared to abstraction from a secondary carbon. The possibility of H-abstraction and subsequent scission, however, should be higher for methacrylates with longer alkyl side chains. Poly(dodecyl methacrylate) (DMA) was synthesized at the same reaction conditions as those of poly(BMA), and its MALDI-MS and the assignments of the signals are shown in Figure 3 and Table 2. The ratio of peak 4 to peak 6 is 1:1.1 for poly(DMA) (Figure 3), which is higher than that of poly(BMA) (1:2.5 in Figure 1), as expected.

Table 2. Comparison of Experimental versus Theoretical Mass for Poly(DMA)[a]

peak	origin	theor mass (Da)	exptl mass (Da)
1	xylol-(DMA)$_4$-H + Na$^+$	1145.95	1145.86
2	**i** originated from xylol-(DMA)$_4$-H + Na$^+$	1157.95	1157.72
3	xylol-(DMA)$_4$-CH$_3$ + Na$^+$	1159.98	1159.80
4	**j**-(DMA)$_4$-H + Na$^+$	1282.11	1282.21
5	(**d** or **e**)-(DMA)$_4$-H + Na$^+$	1294.11	1294.08
6	CH$_3$-(DMA)$_5$-H + Na$^+$	1310.14	1310.08
7	**i** originated from CH$_3$-(DMA)$_5$-H + Na$^+$	1322.14	1321.95
8	CH$_3$-(DMA)$_5$-CH$_3$ + Na$^+$	1325.04	1324.80
9	xylol-(DMA)$_4$-xylol + Na$^+$	1250.73	1249.84
10	*tert*-butoxy-(DMA)$_4$-*t*-butoxy + Na$^+$	1186.02	1186.80
11	*tert*-butoxy-(DMA)$_5$-H + Na$^+$	1368.19	1368.25
12	**j**-(DMA)$_4$-xylol + Na$^+$	1386.18	1386.26

[a] DMA = dodecyl methacrylate; see Schemes 2 and 3 for end-group structures.

Conclusions

Matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS) was used to analyze a poly(BMA) sample generated by *tert*-butyl peroxyacetate-initiated polymerization in xylene at 138 °C with 65 wt % solvent content. In addition to the expected polymer species determined by MALDI-MS, one significant additional peak was found. A possible mechanism, methacrylate backbiting and scission with long alkyl side chain, was proposed in this work to explain its occurrence, with the structure confirmed by ^{1}H NMR and HSQC analysis. This work illustrates the importance of initiator choice for synthesis of poly(acrylics) under higher temperature conditions.

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