Experimental Study of the Spontaneous Thermal Homopolymerization of Methyl and *n*-Butyl Acrylate

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ABSTRACT: This article presents an experimental study of the spontaneous thermal homopolymerization of methyl acrylate (MA) and *n*-butyl acrylate (*n*BA) in the absence of any known added initiators at 120 and 140°C in a batch reactor. The effects of the solvent type, oxygen level, and reaction temperature on the monomer conversion and polymer average molecular weights were investigated. Three solvents, dimethyl sulfoxide (DMSO; polar, aprotic), cyclohexanone (polar, aprotic), and xylene (nonpolar) were used. The spontaneous thermal polymerization of MA and *n*BA in DMSO resulted in a lower conversion and higher average molecular weights in comparison to polymerization in cyclohexanone and xylene under the same conditions. The highest final conversion of both monomers was obtained in cyclohexanone. The high polymerization rate in cyclohexanone was most likely due to an additional initiation mechanism where cyclohexanone complexed with the monomer to generate free radicals. Bubbling air through the mixture led to a higher monomer conversion during the early stage of the polymerization and a lower polymer average molecular weight in xylene and cyclohexanone; this indicated the existence of a distinct behavior between the air- and nitrogen-purged systems. Matrix-assisted laser desorption/ionization time-of-flight analysis of the polymer samples taken from nitrogen-bubbled batches did not reveal fragments from initiating impurities. On the basis of the identified families of peaks, monomer self-initiation is suggested as the principal mode of initiation in the spontaneous thermal polymerization of MA and *n*BA at temperatures above 100°C. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 1898–1909, 2010

Key words: MALDI; spontaneous thermal polymerization; alkyl acrylates; methyl acrylate; butyl acrylate

INTRODUCTION

The high-temperature polymerization (above about 100°C) of acrylates has been used to produce high-solid, low-molecular-weight acrylic resins.[1–4] Commonly used initiators in moderate- to high-temperature polymerizations are azonitriles and organic peroxides.[5,6] The mechanism of the decomposition of peroxides at high temperatures has been studied extensively;[7,8] one-bond homolysis of the initiators species generates an acyloxy radical and an alkoxy radical. Each of these radicals decomposes further into carbon dioxide or a *tert*-butoxy radical and an alkyl radical by a concerted two-bond scission reaction. Chiefari et al.[9] reported that at high temperatures, trace quantities of initiators are sufficient to initiate free-r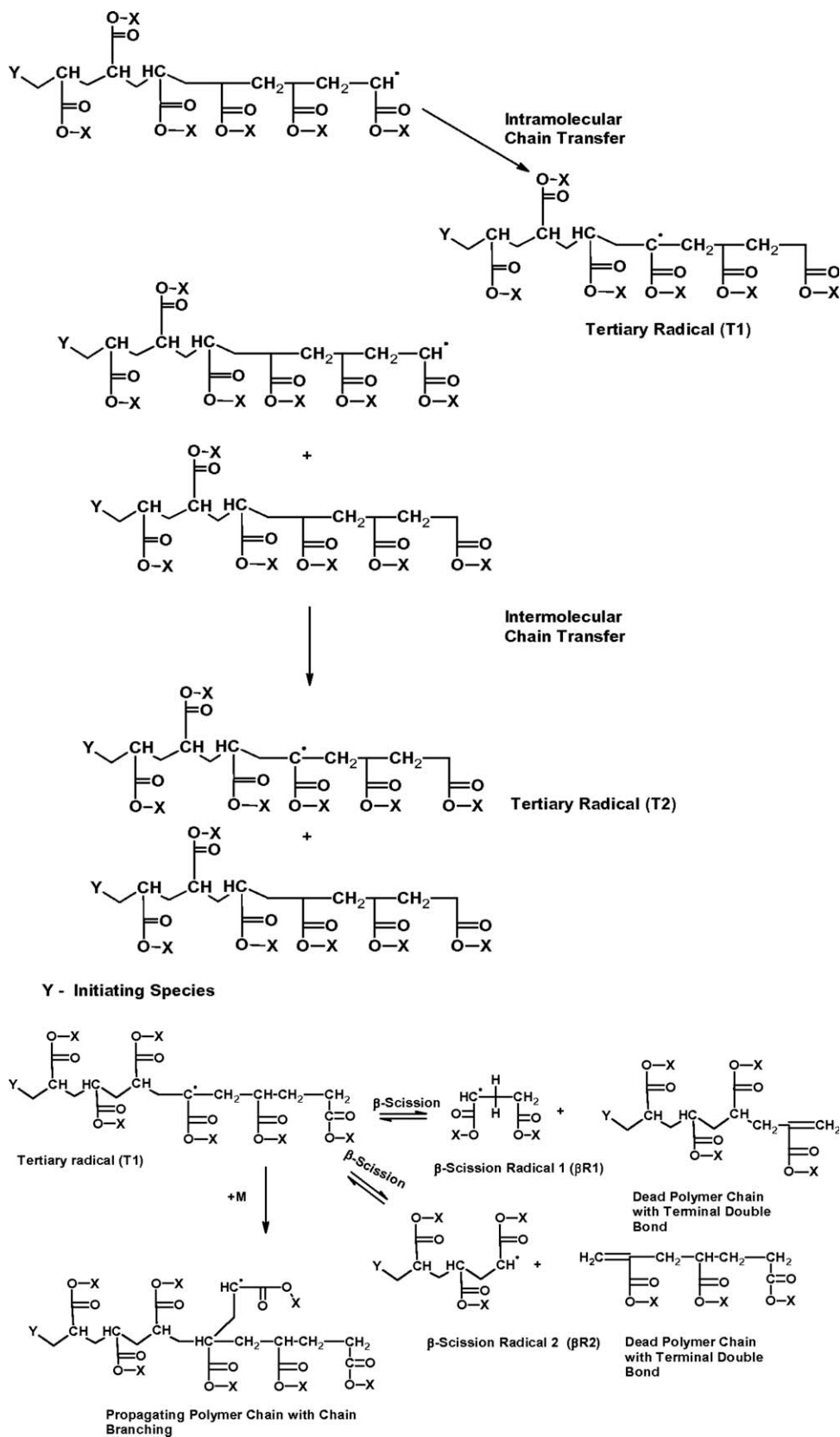adical polymerization in alkyl acrylates and to achieve substantial final conversions. Moreover, it was identified that secondary reactions, such as back-biting and β scission (Scheme 1), influence the structure of the polymer chains formed. Grady et al.[10] identified the occurrence of the sustained spontaneous thermal polymerization of alkyl acrylates in the absence of any known extraneous initiator at high temperatures. Although numerous studies with monomer concentrations ranging from 5 to 100% w/w in various solvents were performed to confirm the occurrence of the spontaneous thermal polymerization of alkyl acrylates,[11–13] the initiation mechanism remained unclear. Some believe that the decomposition of inherent monomer impurities, such as hydroperoxides and trace quantities of molecular oxygen, initiated the polymerization.[13,14] However, electron spray ionization (ESI)–Fourier transform mass spectrometry (FTMS) studies on the spontaneous polymerization of ethyl and *n*-butyl acrylates did not show the presence of polymer chains with end-group structures from such initiating species.[11]

The spontaneous thermal polymerization of styrene has been well studied, and the initiation has been shown to occur via Mayo's mechanism (Scheme 2).[15]

Intramolecular Chain Transfer

Tertiary Radical (T1)

Intermolecular Chain Transfer

Tertiary Radical (T2)

Y - Initiating Species

Tertiary radical (T1)

β-Scission

β-Scission

+M

β-Scission Radical 1 (βR1)

Dead Polymer Chain with Terminal Double Bond

β-Scission Radical 2 (βR2)

Dead Polymer Chain with Terminal Double Bond

Propagating Polymer Chain with Chain Branching

Scheme 1 Back-biting and β-scission reaction mechanisms (X = CH$_3$ or C$_4$H$_9$).

Pryor and Lasswell[16] postulated that spontaneous initiation in nonstyrenic monomers will occur via Flory's diradical mechanism[17] and the diradical will exist in a triplet state (Scheme 2). In nonstyrenic monomers, such as methyl methacrylate (MMA), Diels–Alder adducts lack the tendency to undergo hydrogen
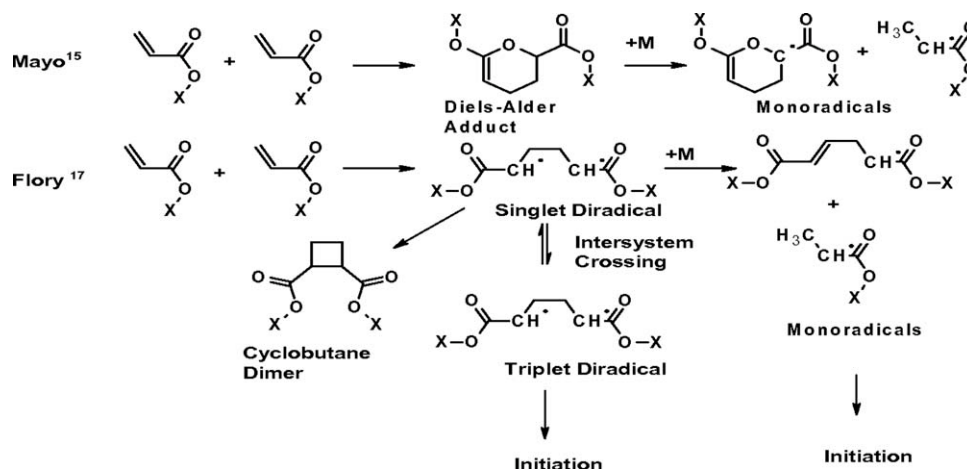
Scheme 2 Flory and Mayo mechanisms (X = CH_3 or C_4H_9; M = monomer).

abstraction to generate monoradicals. Stickler, Meyerhoff, and coworkers[18–25] studied the spontaneous thermal polymerization of MMA at high temperatures (100–130°C) and reported low-conversion ($\leq \sim 5\%$), high-average-molecular-weight polymers and the formation of a significant amount of dimers, trimers, and oligomers after 75 h of batch operation. The presence of diradical species and the initiation mechanism were identified from the predominant formation of a linear unsaturated dimer, dimethyl 1-hexene 2,5 carboxylate.[19–21]

Theoretical considerations lead to the conclusion that sustained polymer chain growth is not possible from diradical species.[23] The role of the solvent as a chain-transfer species was studied in the spontaneous thermal polymerization of MMA[23–25] and pentafluorostyrene.[26] Low rates of polymerization of MMA were found in nonpolar solvents,[23] and high rates of polymerization were found in halogenated solvents and polar, protic solvents, such as thiophenol. Halogenated solvents and thiophenol were reported to increase the rate of polymerization because of the rapid chain transfer and crossing of diradical species from an unstable singlet to a stable triplet state via collisions with the heavy halogen or sulfur atom.[23–25] However, the heavy atom effect in thiophenol was found to be less evident in comparison to halogenated solvents. The triplet diradical species were postulated to generate initiating species for the polymerization of MMA.[24] High rates of thermal spontaneous polymerization of alkyl acrylates accompanied with significant chain-transfer reactions, such as back-biting and β scission, in solvents of varying polarity, such as xylene, benzene, isopropyl alcohol, ethyl acetate, and methyl amyl ketone, have been reported.[10] This suggests that chain initiation and transfer reactions occur appreciably, regardless of the nature of the solvent. However, no study with a solvent with heavy atoms has

been conducted yet; it is not clear yet whether polar solvents influence the initiation and chain-transfer reactions.

Mass spectrometry has been used increasingly for the characterization of synthetic polymers.[27–29] Advances in instrument design and the discovery of ionization schemes such as ESI and matrix-assisted laser desorption/ionization (MALDI) have led to successful applications for the accurate mass analysis of synthetic polymers.[27,28] The advantage of ESI and MALDI mass spectrometry over other techniques such as IR spectroscopy and NMR spectroscopy is in their ability to provide chain length distribution and chemical composition with high accuracy.[28] It has been reported[29] that MALDI–time-of-flight (TOF) mass spectrometry is highly suited for studying polymer samples. This is mainly due to the simple nature of the mass spectra of MALDI–TOF, which mostly shows unfragmented, singly charged molecular ions, its capability to analyze high-molecular-weight polymers, and its high resolution, which allows the estimation of repeating monomer mass increment and the end groups plus known cation mass to an upper limit of 35 kDa. Indeed, the study presented in this article is the first reported study in which MALDI mass spectrometry was used for the analysis of polymethacrylate (poly-MA) generated by spontaneous thermal polymerization.

In this article, we present an investigation of the effects of three solvents with different dielectric constants (κ's): xylene (κ = 2.4), cyclohexanone (κ = 18.2), and dimethyl sulfoxide (DMSO; κ = 45) and nitrogen purge on the spontaneous thermal polymerization of MA and nBA at 120 and 140°C. MALDI results that point to initiation via monomer self-initiation and chain transfer via β scission are presented for the spontaneous thermal polymerization of MA and nBA at temperatures above 100°C.

EXPERIMENTAL

Methyl acrylate and n-butyl acrylate (both from BASF, Ludwigshafen, Germany, purity = 99.5%, boiling points = 80 and 146°C, respectively) were passed through an inhibitor-removal column before use. Xylene (ExxonMobil Chemical Company, Houston, TX, a mix of xylene isomers and ethylbenzene, boiling-point range = 137–143°C), cyclohexanone (Merck & Co, Rahway, NJ, boiling point = 155–156°C), DMSO (Merck & Co, Rahway, NJ, boiling point = 189°C), and 4-methoxyphenol (99% Acros, Fair Lawn, NJ, boiling point = 243°C) were used as received. The dielectric constants of the solvents were as follows: xylene, 2.4; cyclohexanone, 18.2; and DMSO, 45. Experiments were carried out in a 1-L RC1 calorimeter (Mettler-Toledo, GmBH, Schwerzenbach, Switzerland).

Nitrogen blanket

After the solvent and monomer were loaded into the reactor, the reaction mixture was purged with nitrogen gas for 25 min to reduce the residual oxygen level in the system. The reactor was then heated to the desired temperature (120 or 140°C) under a nitrogen blanket. Time $t = 0$ corresponded to the onset of heating. The reaction temperature was maintained at a constant level throughout the polymerization by adjustment of the jacket temperature. Samples were withdrawn from the reactor at 5, 10, 15, 20, 60, and 300 min from the time when the reactor temperature settled at the set point. The samples were then diluted to 50% v/v with a chilled solution of 1000 ppm of 4-methoxyphenol (inhibitor) in xylene.

Air blanket

After the solvent and monomer were loaded into the reactor, the reaction mixture was purged with air for 25 min to ensure the presence of dissolved oxygen in the solution. The reactor was then heated to the desired temperature (120 or 140°C) under an air blanket. Time $t = 0$ corresponded to the onset of heating. The reaction temperature was maintained at a constant level throughout the polymerization by adjustment of the jacket temperature. Samples were taken according to the same procedure described previously.

Monomer conversion and molecular weight measurements

Conversion was measured gravimetrically. The molecular weight distribution was measured with an HP 1090 high-performance liquid chromatography (HPLC) system (Hewlett-Packard, Palo Alto, CA) with a refractive-index detector and a four-column set configuration (10^5, 10^4, 10^3, and 10^2 Å, 30 cm ×

7.8 mm inside diameter microstyragel column). The instrument was calibrated against 16 polystyrene standards (Polymer Laboratories Ltd, Palo Alto, CA) in the range 1.03×10^6 to 580. Tetrahydrofuran (THF) was used as the mobile phase at a flow rate of 1 mL/min. The sample solutions were made by the dilution of the samples with THF to give a polymer concentration of 2%.

MALDI–TOF analysis

2,5-Dihydroxybenzoic acid (99%) and sodium iodide (NaI, purchased from Aldrich Chemical Co., Milwaukee, WI) were used without further purification. Stabilized THF, HPLC grade, was obtained from J. T. Baker (Phillipsburg, NJ). Solutions of the matrix (2,5-dihydroxybenzoic acid), polymer, and ionization salt were prepared in THF as follows: 100 mg/mL matrix solution, 2 mg/mL NaI solution, and 2 mg/mL polymer solution. Appropriate volumes of the three solutions were mixed to obtain a matrix/polymer/ionization salt ratio of 1 : 1 : 1. One microliter of the mixture was spotted on a stainless steel plate, and the solvent was allowed to evaporate. All of the MALDI spectra were acquired with a Waters Synapt High Definition Mass Spectrometry Instrument (Milford, MA) equipped with a 200-Hz Nd:YAG solid-state laser with a 355-nm wavelength and a 100-μJ pulse energy; the laser attenuator was set at 300. The MALDI spectra presented in this article were from samples taken from batches under nitrogen purging only.

RESULTS AND DISCUSSION

Effect of the solvent on polymerization

MA and nBA were found to have the highest final conversion ($\sim 80\%$) in cyclohexanone and the lowest final conversion ($\sim 30\%$) in DMSO, as shown in Figure 1. However, the polymerization of MA and nBA in DMSO generated a higher number-average molecular weight (M_n) polymer than the polymerizations in xylene and cyclohexanone, as shown in Figure 2. Spontaneous initiation was found to occur with MA and nBA in all three solvents, which suggested that initiation occurred regardless of the solvent type. The final conversion of MA and nBA in xylene (nonpolar, inert) at 140°C reached about 70%, which was significantly higher than the conversion ($\leq \sim 5\%$) reported[23] for MMA in benzene (nonpolar, inert) at 130°C. Furthermore, the MA and nBA polymers formed in xylene had a lower average molecular weight ($M_n \approx 10,000$ Da) than that of the MMA polymer ($M_n \geq \sim 20,000$ Da) formed in benzene.[21] The lower polymer average molecular weight and higher conversion of the MA and nBA polymers
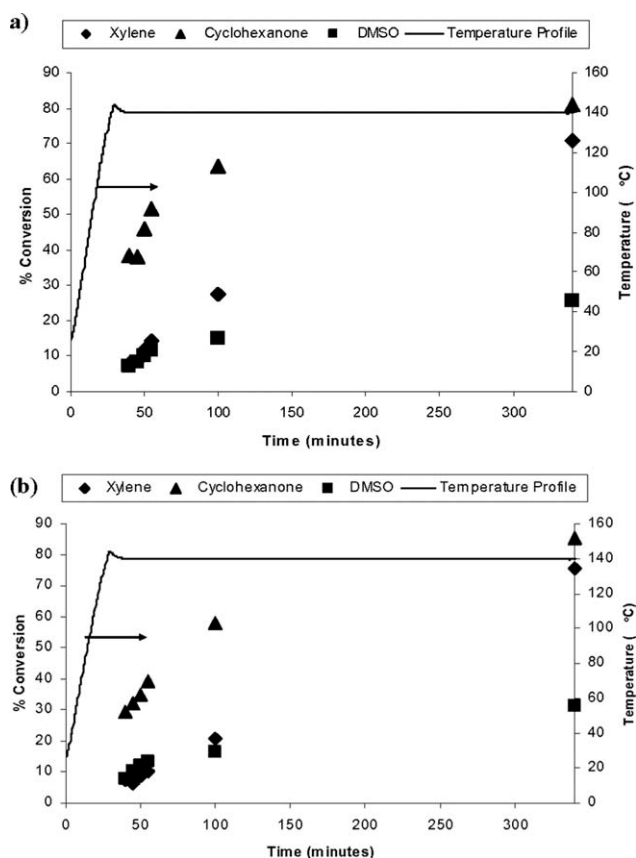
Figure 1 Monomer conversion in polymer samples from batch experiments (temperature = 140°C, monomer initial weight percentage = 40%; N$_2$ was bubbled before and during the reaction): (a) MA and (b) nBA.

were attributed to chain-transfer reactions, such as back-biting and subsequent β scission (Scheme 1), and chain transfer to the solvent. The back-biting reaction caused the formation of midchain radicals via an intramolecular hydrogen transfer reaction (which generally occurs under dilute monomer concentrations, as in this study) in the propagating chain. The midchain radical underwent cleavage to form a β-scission radical and dead polymer chain with a terminal double bond. This reduced the length of the polymer chain and, subsequently, the average molecular weight of the polymer. The formed β-scission radicals (βR1 and βR2) could act as initiating species and cause chain propagation. The chains with terminal double bonds could further propagate upon cleavage of the unsaturated bond in the presence of radical species. Furthermore, a propagating chain could abstract a hydrogen atom from xylene to form xylol radicals, which acted as an initiating species in the solution. We believe that the occurrence of these chain-transfer reactions contributed greatly to sustaining the spontaneous polymerization process. Experimental evidence of the occurrence of chain-transfer reactions in the spontaneous

thermal polymerization of ethyl acrylate and nBA has also been reported elsewhere.[11]

We found for the first time that spontaneous polymerization in DMSO (highly polar and aprotic solvent) yielded a lower conversion and significantly higher molecular weights in comparison to those in xylene and cyclohexanone. This indicated that chain-transfer reactions occurred more in the presence of xylene than DMSO, possibly because of the strong nucleophilicity of DMSO. The π bond (S=O) in DMSO was capable of accepting hydrogen atoms and solvating partially positive atoms in the solute (monomer or propagating polymer chain). The charge on the methine (CH) group on the propagating chain was weakly positive and formed the electrophilic center, with which the π bond could complex, as shown in Scheme 3. This may have caused stabilization of the chain, which reduced the rates of the back-biting and subsequent β-scission reactions. Because fewer β-scission radicals were formed in DMSO than in xylene, the higher monomer conversion observed in xylene was not seen in DMSO, and the average molecular weights were higher in DMSO. In addition, as DMSO was aprotic, it lacked the tendency to donate a proton. This eliminated the formation of DMSO radicals via hydrogen abstraction from the propagating chain. We believe that the overall reduction in chain-transfer reactions, back-biting, and transfer to solvent resulted in the lower conversions and higher average molecular weights. The polydispersity index of MA and nBA polymers formed in DMSO was about 1.8, which was not different from that of the polymers formed in xylene.

Figure 1 shows the higher conversion of MA and nBA in cyclohexanone than in xylene and DMSO during the early stage of polymerization. Previous studies showed that in the thermal polymerization of vinyl monomers, cyclohexanone-based initiating species positively contributed to the initiation step.[31,32] Two mechanisms were reported: (1) initiation via the formation of a cyclohexanone–monomer complex that dissociated to release monoradicals for initiation[31] and (2) the generation of initiating species via the radical thermal self-condensation of cyclohexanone.[32] We observed no self-condensation and believe that the ability of cyclohexanone to act as an initiator was via Scheme 4,[31] which caused the higher conversion. The results reported in ref. 31 were in agreement with our findings of higher conversion in the initial stages of MA polymerization in cyclohexanone. The higher final conversion and the lower average molecular weights of MA and nBA in cyclohexanone than in the other two solvents also pointed to a larger contribution of chain-transfer reactions (back-biting, β scission and transfer to solvent) in the presence of cyclohexanone. Cyclohexanone, which had a higher polarity (higher dielectric
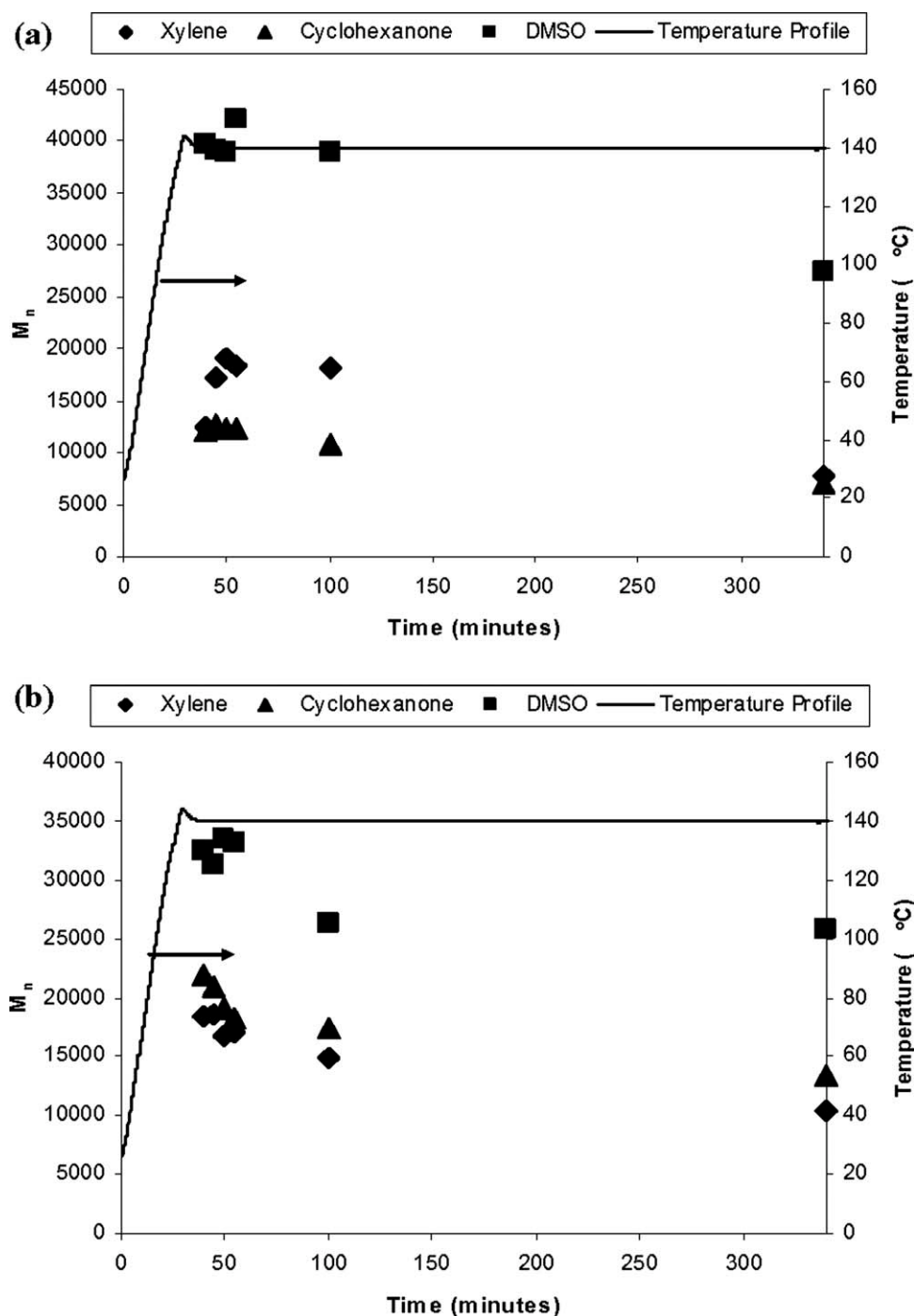
Figure 2 M_n in the polymer samples from the batch experiments (temperature = 140°C, monomer initial weight percentage = 40%; N_2 was bubbled before and during the reaction): (a) MA and (b) nBA.

constant) than xylene and a lower polarity than DMSO, provided a desirable solvent environment for the production of MA and nBA polymers. This showed that in the spontaneous thermal polymerization of alkyl acrylates, aprotic solvents such as DMSO and cyclohexanone can be used to tailor the structural characteristics of the polymer and adjust the polymerization rate. Previous studies[10] with methyl ethyl ketone, which is a solvent with a dielectric constant similar to cyclohexanone and

without any known ability to initiate polymerization, showed spontaneous thermal polymerization and a monomer conversion closer to xylene. More studies with various aprotic solvents with dielectric constants between 18.0 and 44.0 need to be carried out to verify the observed behavior further and develop correlations quantifying the dependence of the average molecular weights and monomer conversion on solvent properties such as the dielectric constant. In addition, experiments with purified solvents should
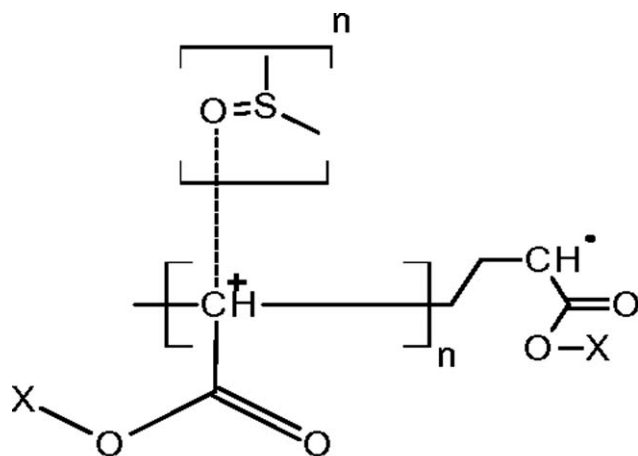
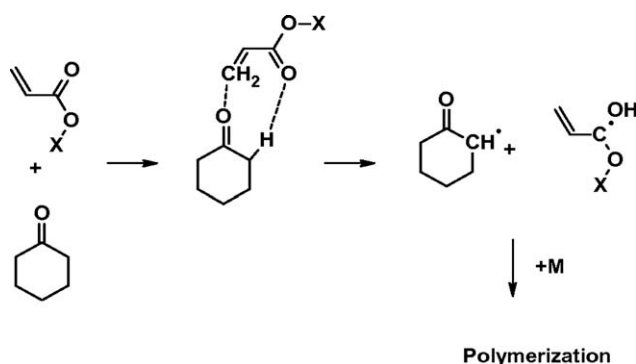**Scheme 3** MA or *n*BA polymer and DMSO solvate (X = CH$_3$ or C$_4$H$_9$).[30]

be conducted to evaluate the impact of solvent impurities (if any) on the polymerization.

Effect of purging

We studied the influence of the oxygen level on spontaneous initiation by conducting polymerizations at 120°C under air and nitrogen purging. The spontaneous polymerization of MA showed the highest monomer conversion and the lowest M_n in cyclohexanone purged with nitrogen and air, respectively, as shown in Figures 3 and 4.

The polymer average molecular weights measured throughout the batch were lower under purging with air than with nitrogen, as shown in Figure 4.

Figure 5 depicts the molar ratio of polymer formed to reacted monomer (inverse of the number-average chain length of the dead polymer chains) in xylene and cyclohexanone in the presence of nitrogen and air. In both solvents, this ratio was higher in the pres-
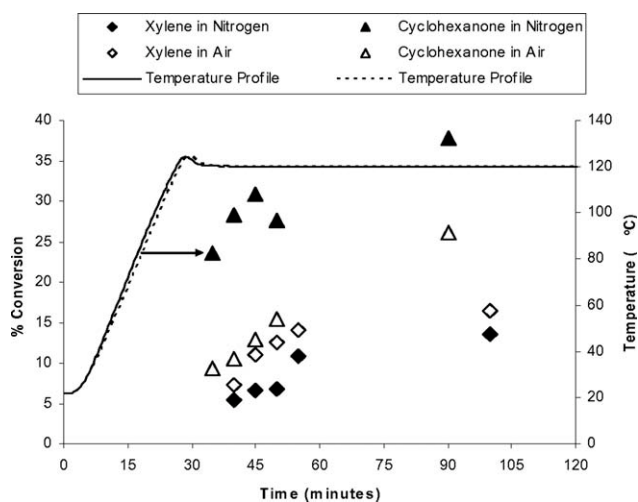

Figure 3 Percentage monomer conversion in the polymer samples from the MA polymerization in xylene and cyclohexanone (temperature = 120°C, monomer initial weight percentage = 40%) with air versus N$_2$ bubbling.

ence of air than in that of nitrogen. Also, the ratio was higher in cyclohexanone than xylene; this observation was in agreement with the reported[33] higher rate of chain transfer to cyclohexanone than that of chain transfer to xylene. As air was not purified of its impurities, such as nitrogen oxides and carbon monoxide, we could not conclusively state that molecular oxygen was solely responsible for the observed effects. However, as the concentration of molecular oxygen in air was significantly greater than those of the impurities ($\sim 20\%$ O$_2$ vs 2×10^{-6} % NO$_2$ and 3×10^{-5} % N$_2$O), we assumed that molecular oxygen should have had a stronger influence on the radical concentration in the solution. The mechanism of radical generation by molecular oxygen was speculated[34]
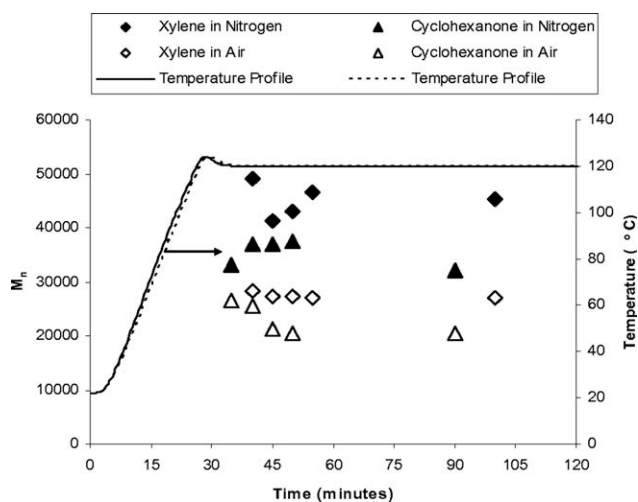

Scheme 4 Initiation (formation of monoradicals) via the dissociation of the cyclohexanone and monomer complex[31] (X = CH$_3$ or C$_4$H$_9$).

Figure 4 M_n values of the polymer samples from the MA polymerization in xylene and cyclohexanone (temperature = 120°C, monomer initial weight percentage = 40) with air versus N$_2$ bubbling.
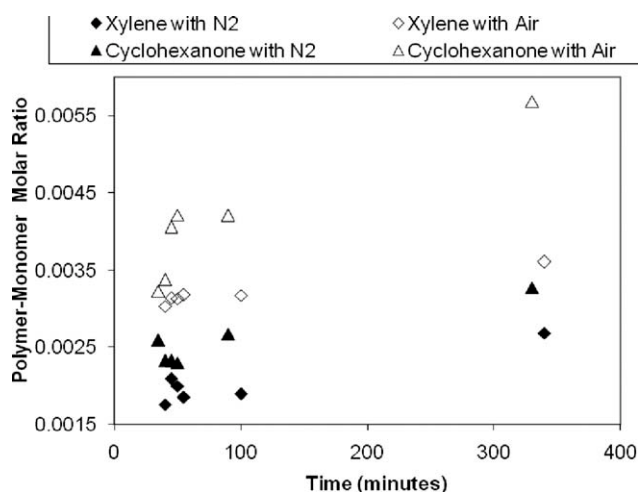
Figure 5 Molar ratio of poly-MA formed to reacted MA (inverse of the number-average chain length) at 120°C in xylene and cyclohexanone in the presence of nitrogen and air.

to be via a two-step process: (1) the reaction of molecular oxygen with monomer to form hydroperoxides and (2) the subsequent decomposition of these hydroperoxides to form peroxide-based initiating species. However, the tendency of the peroxide-based initiating species to terminate rapidly may have been the reason we observed a higher conversion only in the initial stage. The continuous involvement of chain transfer to molecular oxygen, which has been previously reported in high-temperature ethylene polymerization,[35] seemed to cause the formation of lower average polymer molecular weights in air than in nitrogen in both of the solvents.

Previous studies of acrylates and methyl methacrylate in cyclohexanone and xylene[10,36] have shown that the rate of spontaneous initiation in nitrogen increases with the initial monomer concentration. Moreover, the absence of impurity-based, end-group initiating species in ethyl acrylate and nBA polymer samples taken from batch operations under nitrogen bubbling and analyzed via ESI–FTMS has been reported.[11] These previous studies and the new results presented in this article point to the occurrence of an alternative initiation mechanism, that is, monomer self-initiation, in the spontaneous thermal polymerization of alkyl acrylates. In particular, monomer self-initiation via a diradical mechanism[17] is probably occurring in the spontaneous thermal polymerization of MA and nBA.

Mechanism of spontaneous initiation

We postulated that the diradical self-initiation shown later in Figure 7 occurred in the spontaneous thermal polymerization of MA.[37] To verify the proposed mechanism, low-average-molecular-weight MA polymer made in xylene via spontaneous initia-

tion at 140°C was analyzed with MALDI. The upper limit of M_n effectively analyzed by MALDI was found to be about 1700 Da. Figure 6 is the MALDI spectrum of poly-MA made at 140°C with an initial MA concentration of 40% w/w under nitrogen purging. This sample was removed from the reactor 5 min after the temperature set point was reached. The monomer conversion was about 8%, the M_n was about 8000, and the polydispersity index was about 1.8. The MALDI spectrum showed the following series of m/z peaks: 453, 539, 625, 711, 797, 883, 969, 1055, 1141, 1227, 1313, 1399, 1485, 1571, 1657, and 1743 Da. These peaks corresponded to sodiated ions of oligomeric species formed during the spontaneous thermal MA polymerization in the absence of any known external initiators. A gap of 86 Da between the peaks was consistent with the MA repeat unit of the polymer. Previous studies[4,11] of the spontaneous high-temperature polymerization of ethyl and nBA with ESI–FTMS showed four families of peaks that represented polymer chains: those initiated by β-scission radicals that propagated with the monomers formed midchain radicals and subsequently underwent β-scission reaction to form unsaturated macromonomers with terminal double bonds; those initiated by β-scission radicals that propagated and underwent termination via hydrogen abstraction; those initiated by xylol radicals (formed when a propagating chain abstracted a hydrogen atom from xylene), which grew and underwent intramolecular chain transfer to form tertiary radicals and subsequent β scission; and those initiated by xylol radicals that grew and terminated via hydrogen abstraction. No families of peaks were found to represent chains initiated from peroxide-based, end-group species.[4,11]

We found that the $m/z = 453, 539, 625, \ldots$ series of peaks represented the β-scission radical (βR1)-initiated chains that propagated with MA until they underwent intermolecular or intramolecular chain transfer and subsequent β scission to form terminally unsaturated macromonomers. The series of peaks $m/z = 527, 613, 699, 785, \ldots$ represented polymer chains initiated by the β-scission radical βR1 and terminated via hydrogen abstraction. The series of peaks $m/z = 465, 551, 637, 723, \ldots$ represented polymer chains initiated by xylol radical and terminated via hydrogen abstraction. The series of peaks $m/z = 1/4\ 743, 829, 915, \ldots$ represented polymer chains initiated by xylol radical and terminated via b-scission reactions. These families of peaks, listed in Table I, were found to be in good agreement with reported mechanisms for the spontaneous polymerization of alkyl acrylates.[4,11]

We found, for the first time, that the $m/z = 453$, 539, 625, $\ldots$ series of peaks represented chains that were initiated and terminated by monoradicals produced from a self-initiation mechanism (Fig. 7). As
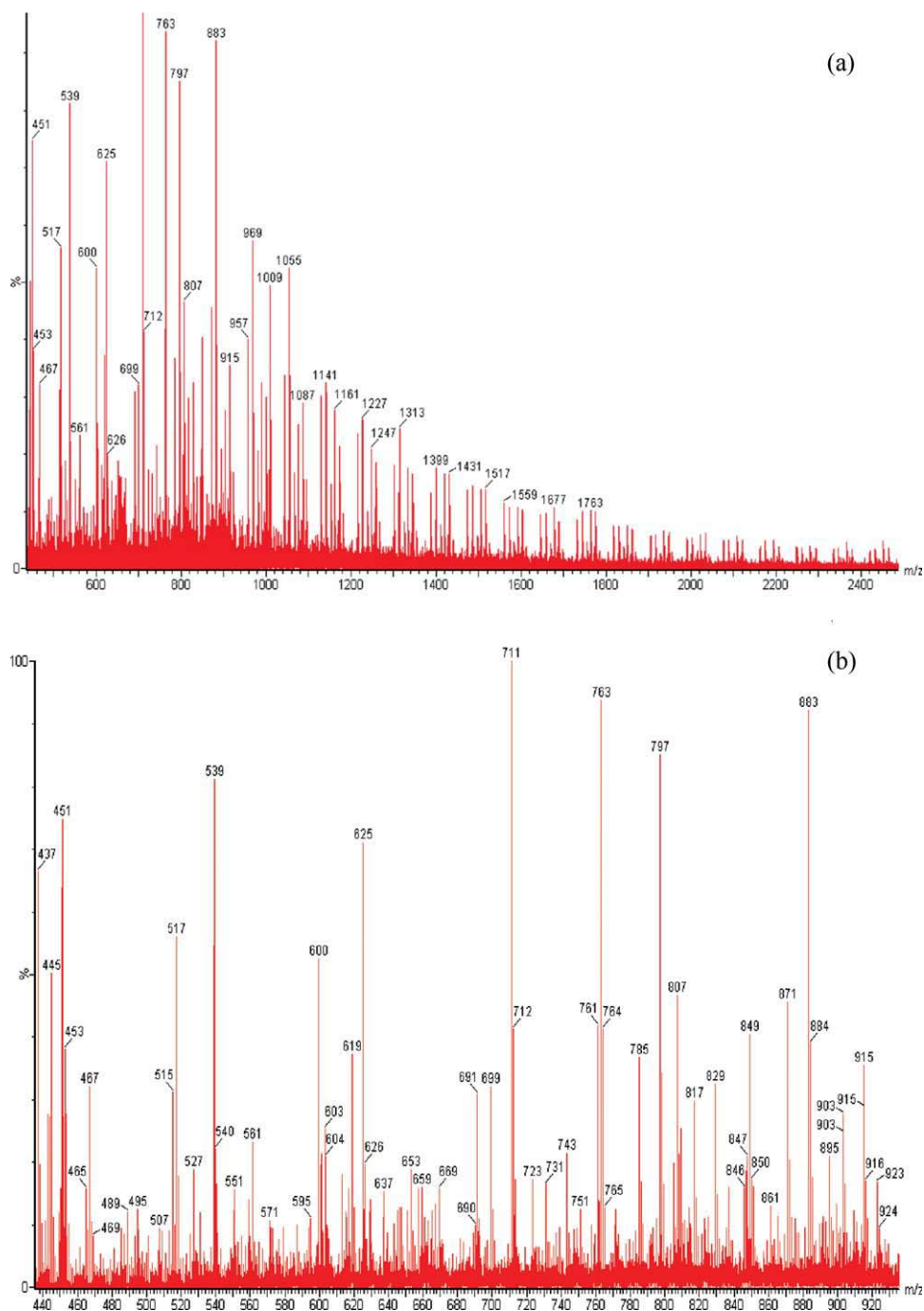
Figure 6 (a) 300–2500 Da MALDI spectra of the poly-MA sample taken after 5 min of reaction in xylene (temperature = 140°C, monomer initial weight percentage = 40; N$_2$ was bubbled before and during the reaction) and (b) magnification of the 440–930 Da range of the MALDI spectra shown in Figure 6(a). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

given in Table I, they consisted of polymer chains initiated by **1** and terminated by **2** or vice versa, initiated by **3** and terminated by **4** or vice versa, initiated by **1** and terminated by **3** or vice versa, initiated by **2** and terminated by **4** or vice versa, initiated by **1** and terminated via hydrogen abstraction from the monomer or solvent, and initiated by **4** and terminated via hydrogen abstraction from the monomer

or solvent. We identified that the m/z = 551, 637, 723, ... series of peaks represented chains initiated by **1** or **2** that propagated with MA monomers and formed a tertiary radical (**T1**; low monomer concentration), which subsequently underwent a β-scission reaction to form terminally unsaturated polymers. The m/z = 731, 817, 903, ... series of peaks also represented chains that were initiated by **2** and

TABLE I
Possible Molecular Weights of Single-Ion Species Generated from the MALDI–TOF Analysis of Poly-MA

Molecule [I-(MA)$_n$-T]		n							
		1	2	3	4	5	6	7	8
β-Scission-radical-initiated termination via TDB formation	$M_{MA} + Na^+$	453	539	625	711	797	883	969	1055
β-Scission-radical-initiated termination via hydrogen abstraction	$M_{MA} + Na^+$	527	613	699	785	871	957	1043	1129
Xylol-radical-initiated, termination via TDB formation	$M_{MA} + Na^+$	743	829	915	1001	1087	1173	1259	1347
Xylol-radical-initiated, termination via hydrogen abstraction	$M_{MA} + Na^+$	465	551	637	723	809	895	987	1073
Self-initiation by 1 and termination via 2 or vice versa	$M_{MA} + Na^+$	453	539	625	711	797	883	969	1055
Self-initiation by 3 and termination via 4 or vice versa	$M_{MA} + Na^+$	453	539	625	711	797	883	969	1055
Self-initiation by 1 and termination via 3 or vice versa	$M_{MA} + Na^+$	453	539	625	711	797	883	969	1055
Self-initiation by 2 and termination via 4 or vice versa	$M_{MA} + Na^+$	453	539	625	711	797	883	969	1055
Self-initiation by 1 or 4 and termination via hydrogen abstraction	$M_{MA} + Na^+$	453	539	625	711	797	883	969	1055
Self-initiation by 1 or 2 and termination via TDB formation	$M_{MA} + Na^+$	551	637	723	809	895	987	1073	1159
Self-initiation by 1 or 2 and termination via xylol radicals or vice versa	$M_{MA} + Na^+$	731	807	893	979	1065	1151	1237	1323
Self-initiation by βR1 and termination via 4 or 2 or vice versa	$M_{MA} + Na^+$	699	785	871	957	1043	1129	1215	1301

M_{MA} = molecular weight of MA; TDB = terminal double bond; n = number of monomer units; I = initiating group; T = terminating group.

terminated by xylol radicals or vice versa. The m/z = 699, 785, 849, . . . series of peaks were found to represent polymer chains that were initiated by β-scission radical βR1 and terminated by 4 or vice versa and polymer chains that were initiated by β-scission radical βR1 and terminated by 2 or vice versa. We believe that the unknown initiating species (Y) in the βR2 radical (minimum three monomer units + Y) could have been 1, 2, 3, 4, βR1, or xylol radicals. This indicated that the βR2-radical-initiated systems could be represented as a subset of all of the aforementioned series of peaks.

The molecular structures of a few species listed in Table I are shown in Figure 8. No series of peaks that represented end- group species generated from impurities or molecular oxygen were found. In addition, we were unable to identify chains that were initiated by species with the structural formula $C_4H_6O_3$; this was is analogous to that of the apparent initiating species suggested in the self-directed polymerization of nBA.[13] This is attributed to the possibility that these species formed in relatively less abundance than βR1, 1, 2, 3, and 4 and were undetected with MALDI. In view of these results, monoradicals generated via the diradical self-initiation mechanism and the β-scission radicals appeared to be the dominant initiating species. Self-initiation and β-scission reactions seemed to have a strong significant influence on the spontaneous thermal polymerization of MA and nBA.

CONCLUSIONS

The spontaneous initiation of MA and nBA in the absence of any extraneous initiators was observed in solvents (unpurified) with different polarities. A low
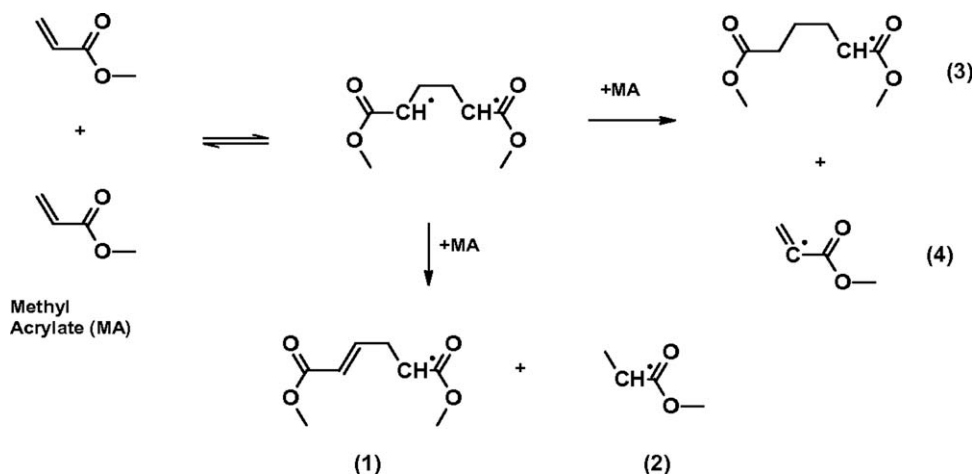

Figure 7 Mechanism for the generation of monoradicals from a diradical in the thermal polymerization of MA. 1 and 2 were monoradicals generated via hydrogen transfer from the diradical species, and 3 and 4 were monoradicals generated via hydrogen abstraction from the diradical species.
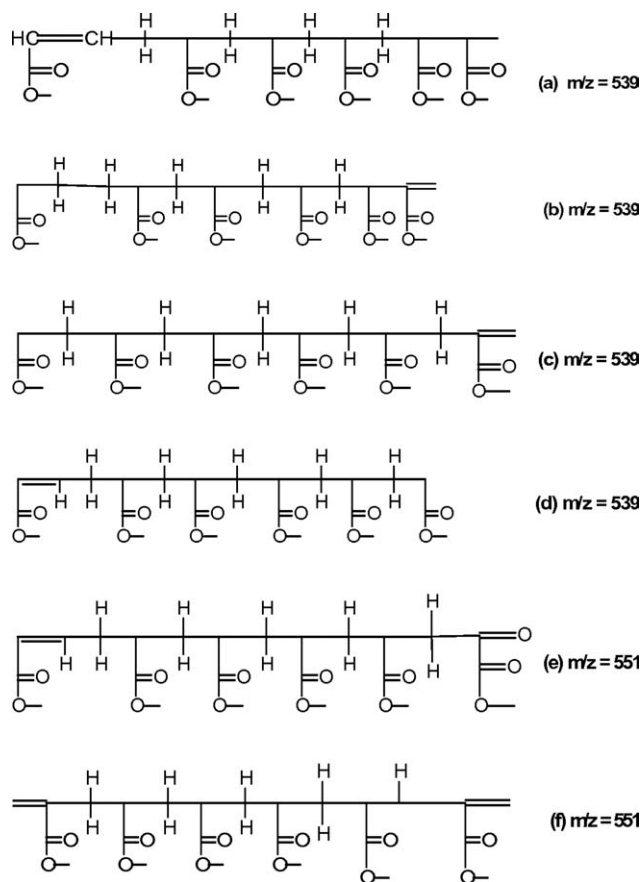
Figure 8 Representative structures of the (a) polymer chain initiated by **1** and terminated by **2** ($m/z = 539$); (b) polymer chain initiated by **3** and terminated by **4** ($m/z = 539$); (c) polymer chain initiated by the β-scission radical βR1 (defined in Scheme 1) that grew and underwent intramolecular hydrogen transfer and subsequent β scission ($m/z = 539$); (d) polymer chain initiated by **1** and terminated via hydrogen abstraction ($m/z = 539$); (e) polymer chain initiated by **1** and terminated by β scission, which led to the formation of a terminal double bond ($m/z = 551$); and (f) polymer chain initiated by **4** and terminated by β scission, which led to the formation of a terminal double bond ($m/z = 551$).

conversion and high-molecular-weight polymers of MA and nBA in polar, aprotic DMSO were found. The high conversion at the initial stages of polymerization of both monomers in polar, aprotic cyclohexanone was thought to be due to additional solvent-based initiating species in the solution. Considering the monomer conversion measurements in the initial stage of the polymerization and the M_n measurements, we found the behavior of air- and nitrogen-purged spontaneous polymerization systems of MA and nBA in xylene and cyclohexanone to be different. It was most likely that the initiation via peroxide-based radicals from molecular oxygen in air was limited. MALDI analyses of polymer samples from

polymerizations under a nitrogen blanket did not reveal fragments from initiating impurities. They pointed to the strong possibility for the occurrence of monomer self-initiation via the diradical mechanism and β-scission reactions.

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