Characterization of 3- and 4-Arm Stars from Reactions of Poly(butyl acrylate) RAFT and ATRP Precursors

Rajan Venkatesh,[†,§] **Bastiaan B. P. Staal,**[†] **Bert Klumperman,***[,†] **and Michael J. Monteiro***[,‡]

Dutch Polymer Institute, Department of Polymer Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands, and School of Molecular and Microbial Sciences, Australian Institute of Bioengineering and Nanotechnology, University of Queensland, Brisbane QLD 4072, Australia

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ABSTRACT: The mechanism of the reversible addition−fragmentation chain transfer (RAFT) process using cumyl dithiobenzoate has been the subject of intense debate. In an attempt to shed more light into the side reactions that affect the rate, it was decided to study the butyl acrylate (BA) system since its intermediate radical has a greater lifetime than for the styrene system and, as such, has the greatest opportunity to form intermediate radical terminated products. The approach taken was to elucidate the polymeric products made from the polymerization of BA in the presence of RAFT agent using a combination of size exclusion chromatography (SEC) and matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS). The approach was extended to analyze reactions of polyBA-Br (with the Br functionality at the polymer end group) with copper catalyst in the presence of polyBA-SC(Ph)═S (dormant RAFT species). Three- and four-arm stars are clearly observed when PBA-Br is reacted with Cu(I) and Cu(0) in the presence of polyBA-RAFT. This is the first example of the synthesis of 4-arm stars through intermediate−intermediate radical termination. We postulated that this is due to the much slower fragmentation rate in the BA system in comparison to the styrene system.

Introduction

Reversible addition−fragmentation chain transfer (RAFT) polymerization has become an important technique for producing polymers with controlled architectures, chain lengths, and chain length distributions.[1−3] The mechanism shown in Scheme 1 has been verified with the use of NMR, UV/vis, matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS), and electron spin resonance (ESR) spectrometry,[4,5] the latter showing the presence of the intermediate radical **4**. Although this mechanism is the case for many of the RAFT agents used, it does not strictly hold when Z, the activating group on the RAFT agent (see Scheme 1), is a phenyl group as suggested by significant retardation in the rate of polymerization.[2,6] There are currently two schools of thought to explain this observation: (1) the fragmentation of the intermediate radical is slow,[7] or (2) there are cross-termination reactions of the intermediate radical **4** with all other radicals[8−10] (Scheme 2) in the system, thus reducing the propagating radical population. Resolving this debate will lead to a deeper understanding of the RAFT mechanism and may allow the synthesis of as yet unpredictable and thus novel polymer architectures.

Up to now the debate has been directed toward the RAFT (with Z = phenyl) polymerization of styrene in bulk and solution. There is now proof from small radical reactions that intermediate termination does form a majority of 3-arm and a small amount of 4-arm stars[11] (see Scheme 2 for structures of 3- and 4-arm stars). However, in the polymeric systems only 3-arm stars have been observed through reactions involving the UV irradiation of dormant RAFT polymers in solvent[9] or copper catalysis with a polystyrene-Br compound in the presence of a dormant RAFT polymer.[10,12] Although small radical reactions provide information about the early stages of a “living” radical polymerization, they do not necessarily represent the mechanisms involved in polymeric systems due to the higher rate coefficients for propagation and termination of small radical reactions in comparison to polymeric radicals. (In some cases these are orders of magnitude greater.)

In an attempt to elucidate the mechanism and reaction pathways in polymeric systems, we polymerized butyl acrylate (BA) in the presence of the RAFT agent, cumyl dithobenzoate (CDB). The reason for using BA is that the PBA−SC$^\bullet$(Ph)−S−PBA intermediate radical has a much longer lifetime compared to that of PSTY−SC$^\bullet$(Ph)S−PSTY[5] and should promote detection of cross-termination products in a polymeric system. Mass spectrometry is a powerful technique to elucidate, with a high level of sensitivity and resolution, end groups of low molar mass polymers and has been successfully employed to study RAFT-derived polymers.[6,13,14] Recently, the CAMD group analyzed the SEC-ESI-MS (size exclusion chromatography coupled with electrospray mass spectrometry) of the polymer products from the polymerization of methyl acrylate in the presence of CDB.[15] They did not detect the termination products (i.e., 3- or 4-arm stars) and postulated that the intermediate radical itself was observed by this technique. We have taken a similar approach by using MALDI-TOF-MS coupled with size exclusion chromatography (SEC) to determine the structure of polymers made from the reaction of CDB with BA. We extended the analysis to reactions of PBA-Br with copper catalyst in the presence of PBA-SC(Ph)═S (dormant RAFT species).

[†] Eindhoven University of Technology.

[‡] University of Queensland.

[§] Current address: BASF AG, Global Polymer Research, 67056 Ludwigshafen, Germany.

[*] To whom correspondence should be addressed. E-mail: m.monteiro@uq.edu.au; l.klumperman@tue.nl.

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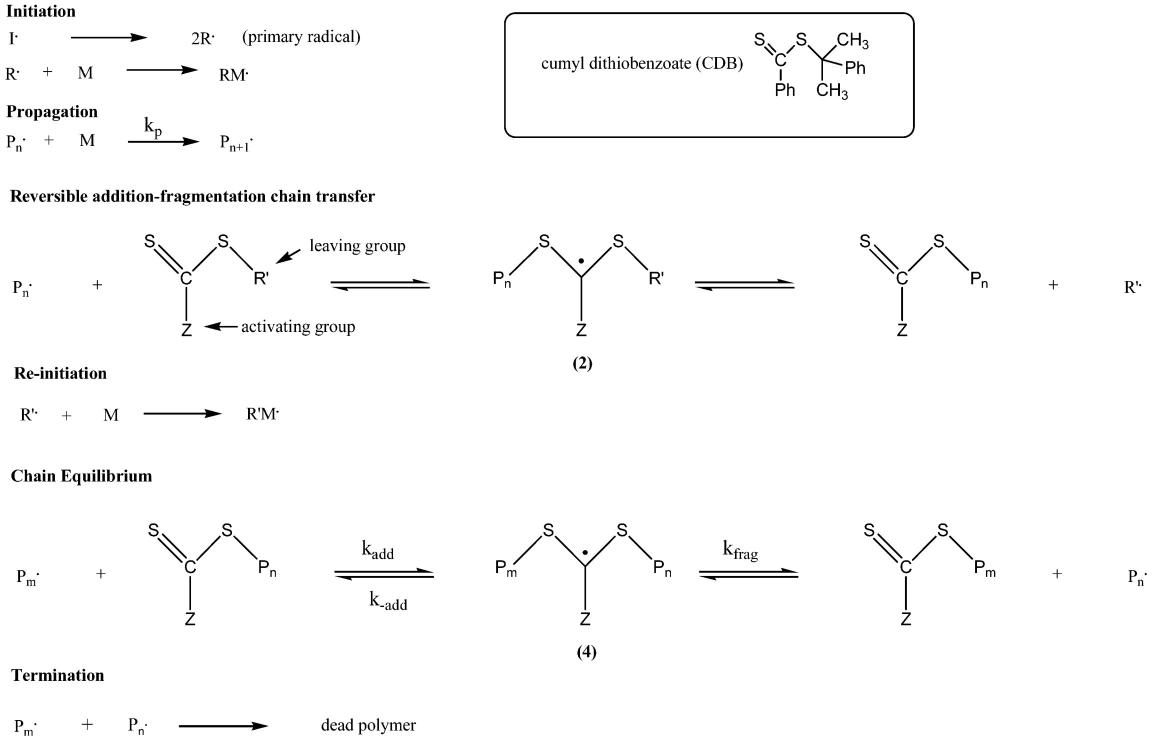
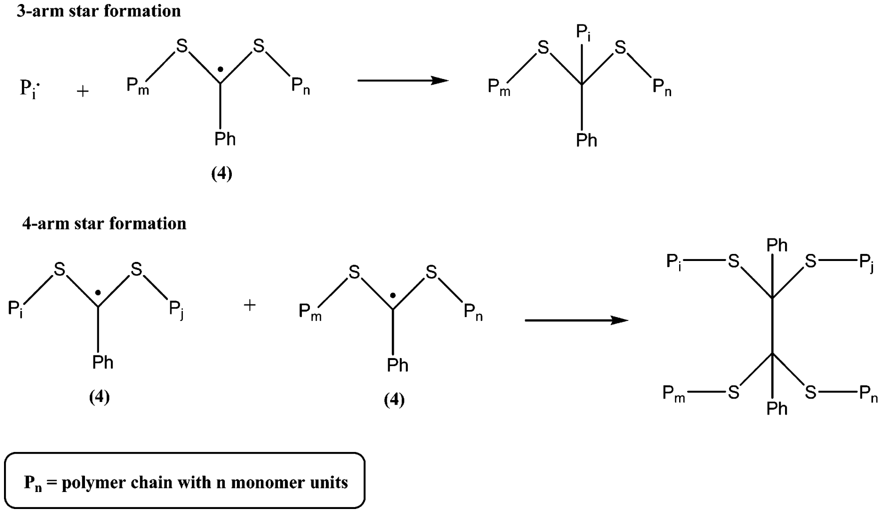
Scheme 1. Proposed Mechanism for the RAFT Process without Intermediate Radical Termination



Scheme 2. Termination Mechanism Used To Explain the Formation of 3- and 4-Arm Stars



Characterization of the polymers at each observed mass was also aided by comparing the experimental isotopic pattern to a simulated (theoretical) one.

Experimental Section

Materials. Butyl acrylate (BA, Merck, 99+%) was distilled under reduced pressure and stored over molecular sieves at −15 °C. Toluene (Aldrich, 99+% HPLC grade) and *tert*-butylbenzene (Aldrich, 99%) were stored over molecular sieves and used without further purification. The RAFT agent, cumyl dithiobenzoate (CDB, 2-phenylprop-2-yl dithiobenzoate), was synthesized as described in the literature.[2] *N,N,N′,N″,N″*-Pentamethyldiethylenetriamine (PMDETA, Aldrich, 98%), copper(I) bromide (CuBr, Aldrich, 99.98%), copper(II) bromide ($CuBr_2$, Aldrich, 99%), copper powder (Cu(0), Aldrich, 99%), ethyl 2-bromoisobutyrate (EBriB, Aldrich, 98%), aluminum oxide (activated, basic, for column chromatography, 50−200 μm), and tetrahydrofuran (THF, Aldrich, AR) were used as supplied. α,α′-Azobis(isobutyronitrile) (AIBN, Merck, >98%) was recrystallized twice from methanol before use.

PBA-RAFT (5). The RAFT agent, CDB (0.272 g, 1.0 mmol) and AIBN (0.033 g, 0.2 mmol) were transferred to a 25 mL three-neck round-bottom flask. Then a solution of toluene (4.6 g, 0.05 mol) and BA (4.73 g, 0.037 mol) was added. The reaction mixture was degassed by sparging with argon for 30 min. The flask was then immersed in an oil bath maintained at 70 °C for 5 h under argon. The monomer conversion determined using gas chromatography (GC) was 30%, with a number-average molecular weight (M_n) of 2025, a weight-average molecular weight (M_w) of 2344, and a polydispersity (PDI) of 1.15 according to SEC.

PBA-Br (6). In a typical polymerization, toluene (9.0 g, 0.08 mol), BA (4.67 g, 0.037 mol), CuBr (0.095 g, 0.66 mmol), and $CuBr_2$ (0.035 g, 0.15 mmol) were transferred to a 25 mL three-neck round-bottom flask. The ligand, PMDETA (0.14 g, 0.83 mmol), was then added. The reaction mixture was degassed by sparging with argon for 30 min. The flask was immersed in a thermostated oil bath maintained at 70 °C and stirred for 10 min. A light green, slightly heterogeneous system was obtained. The initiator, EBriB (0.33 g, 1.7 mmol), was then

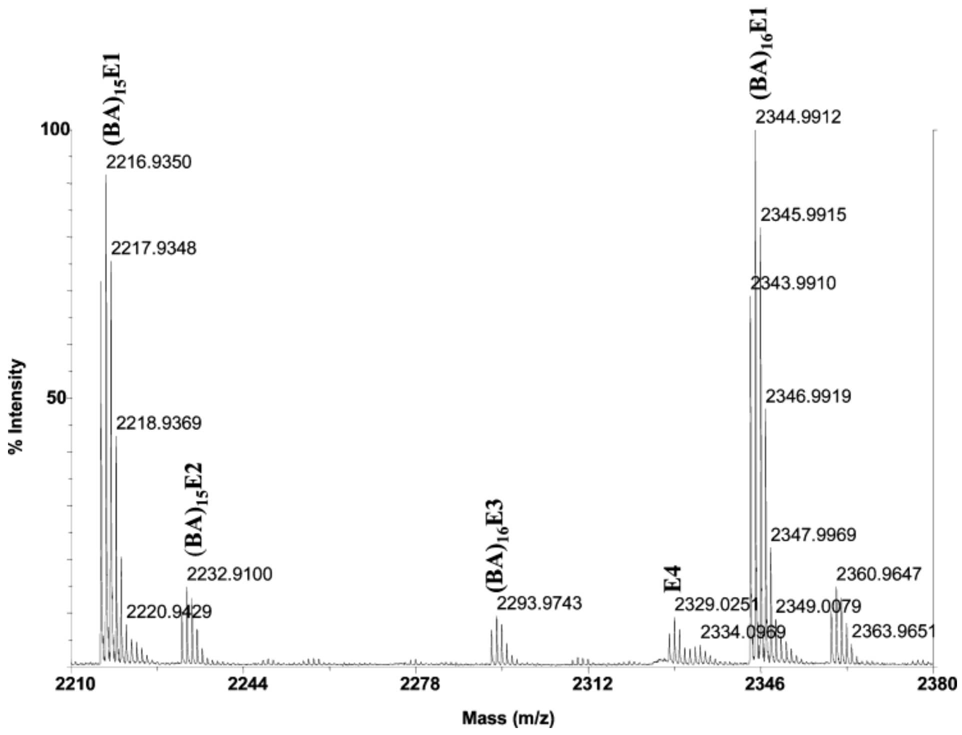


Figure 1. MALDI-TOF-MS spectrum for PBA-RAFT (**5**). Spectrum acquired in reflector mode; matrix: *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB). (BA)$_{15}$E1 denotes that the structure is **E1** from Figure 2 (Na salt attached), and it has 15 units of butyl acrylate (BA).

added slowly via a degassed syringe. The reaction was carried out for 4 h under a flow of argon. The final polymer was diluted with THF, passed through a column of aluminum oxide prior to SEC and MALDI−TOF-MS measurements. The final polymer consisted of a number-average molecular weight (M_n) of 2405, a weight-average molecular weight (M_w) of 2828, and a polydispersity (PDI) of 1.17 according to SEC.

PBA-RAFT (5) with AIBN. The PBA-RAFT (**5**) (0.052 g, 0.025 mmol) was added to *tert*-butylbenzene (1.6 g, 12 mmol) and stirred until a homogeneous mixture was obtained. AIBN (0.004 g, 0.025 mmol) was added, and the reaction mixture was degassed by sparging with argon for 30 min. The flask was immersed in an oil bath at 80 °C for 3 h under argon. The final polymer consisted of a number-average molecular weight (M_n) of 2131, a weight-average molecular weight (M_w) of 2530, and a polydispersity (PDI) of 1.18 according to SEC.

Model Reactions of PBA-Br (6) with PBA-RAFT (5). In a typical model reaction of PBA-Br [$M_n = 2405$, $M_w = 2828$, PDI = 1.17] (0.05 g, 0.02 mmol), PBA-RAFT [$M_n = 2025$, $M_w = 2344$, PDI = 1.15] (0.052 g, 0.02 mmol), CuBr (0.246 g, 1.7 mmol), Cu(0) (0.109 g, 1.7 mmol) and *tert*-butylbenzene (1.6 g, 12 mmol) was carried out in a 10 mL two-neck round-bottom flask. The ligand, PMDETA (0.433 g, 2.5 mmol), was then added. The reaction mixture was degassed by sparging with argon for 30 min. The flask was then immersed in a thermostated oil bath maintained at 80 °C. The reaction was carried out for 3 h under a flow of argon. The final polymer was diluted with THF and passed through a column of aluminum oxide prior to SEC and MALDI-TOF-MS measurements. SEC gave an M_n of 2131, M_w of 2530, and PDI of 1.18 for the final polymer.

Size Exclusion Chromatography (SEC). The dried polymer was dissolved in tetrahydrofuran (THF, Biosolve) to a concentration of 1 mg/mL. The solution was filtered over a 0.2 μm PTFE syringe filter. Analysis was carried out using a Waters model 510 pump, a Waters model WISP 712 autoinjector, a model 410 refractive index detector, and a model 486 UV detector (at 254 nm). The columns used were a PLgel guard (5 μm particles) 50 × 7.5 mm precolumn, followed by two PLgel mixed-C (5 μm particles) 300 × 7.5 mm columns in series (which were maintained at 40 °C for analysis). The columns used separate polymers in the molecular weight range between 500 and 2 million with high resolution. THF was used as an eluent (flow rate 1.0 mL/min). Data acquisition was performed using waters Millenium 32 (v3.05) software. Calibration was carried out using narrow molecular weight polystyrene (PSTY) standards ranging from 580 to 7×10^6 g/mol. The molecular weights were calculated using the universal calibration principle and Mark−Houwink parameters[16] [PBA: $K = 1.22 \times 10^{-4}$ dL/g, $a = 0.700$; PSTY: $K = 1.14 \times 10^{-4}$ dL/g, $a = 0.716$]. Molecular weights were calculated relative to the relevant homopolymer (in this case PBA).

In some instances, the obtained polymers after the model reactions were fractionated prior to MALDI-TOF-MS analysis, using a SEC apparatus, which constituted of a four-column set, PLgel Mixed-B (Polymer Laboratories, 10μ), PLgel Mixed-C (Polymer Laboratories, 5μ), two PLgel Mixed-D (Polymer Laboratories, 5μ), and a guard column (Plgel, Polymer Laboratories, 5μ). The system also consisted of an isocratic pump (Gyncotek P580, separations, flow rate of 1.0 mL/min), UV detector (Spectra Physics linear UV−vis 200, 254 nm), differential refractive index and viscosity detector (dual detector 250,Viscotek), and a light scattering detector (RALLS, Viscotek). THF was used as a solvent at a flow rate of 1.0 mL/min. A fraction collector (Millipore) was used to collect 120 fractions at equal volume intervals of 18 droplets. The system was calibrated using narrow MMD PSTY standards ranging from 580 to 2×10^6 g/mol.

MALDI-TOF-MS. Measurements were performed on a Voyager-DE STR (Applied Biosystems, Framingham, MA) instrument equipped with a 337 nm nitrogen laser. Positive-ion spectra were acquired in reflector mode. DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile) was chosen as the matrix. Sodium trifluoracetate (Aldrich, 98%) was added as the cationic ionization agent. The matrix was dissolved in THF at a concentration of 40 mg/mL. Sodium trifluoracetate was added to THF at a concentration of 1 mg/mL. The dissolved polymer concentration in THF was approximately 1 mg/mL. In a typical MALDI-TOF-MS experiment, the matrix, salt, and polymer solutions were premixed in the ratio 5 μL sample:5 μL matrix:0.5 μL salt. Approximately 0.5 μL of the obtained mixture was hand-spotted on the target plate. For each spectrum 1000 laser shots were accumulated.

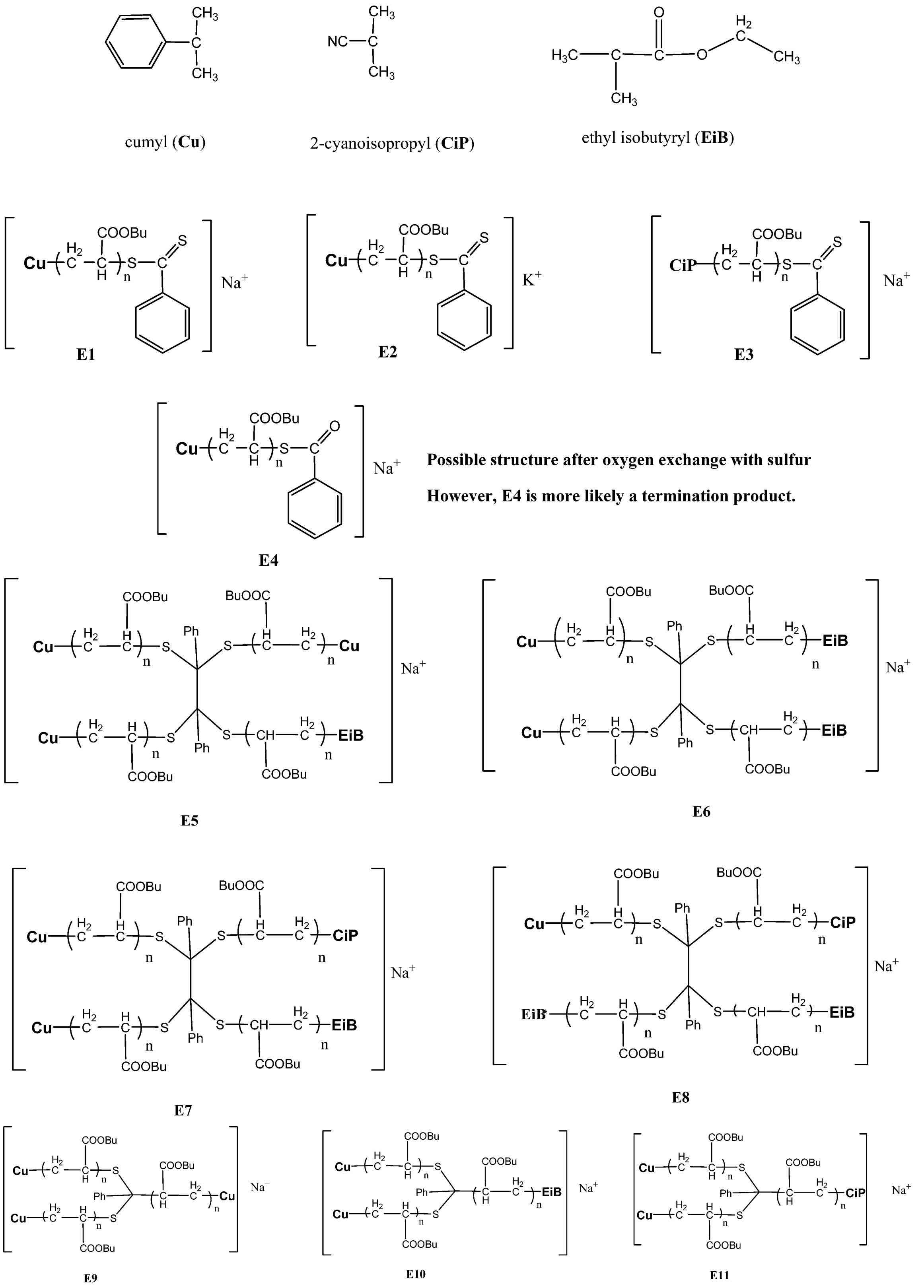


Figure 2. Structures derived from the MALDI-TOF-MS distributions for the reaction of poly(butyl acrylate)-S-C(Ph)=S (**5**) with poly(butyl acrylate)-Br (**6**) initiated with Cu(I) and Cu(0).

Results and Discussion

Analysis of Poly(butyl acrylate) (5) Made with CDB. The MALDI-TOF-MS spectrum of PBA-RAFT (**5**: $M_n = 2025$, $M_w = 2344$, PDI = 1.15) without SEC fractionation was first analyzed. Sodium trifluoracetate was added as a cationic ionization agent to the matrix, and hence, the majority of the polymer chains were cationized with sodium. This results in addition of 23 Da to the theoretically calculated mass. Figure 1 shows an expansion of a selected portion of the MALDI-TOF-MS spectrum, in which four distinct masses can be observed (**E1**, **E2**, **E3**, and **E4**).

The mass corresponding to **E1** in Figure 1 was assigned to 16 BA units, an end group consisting of a

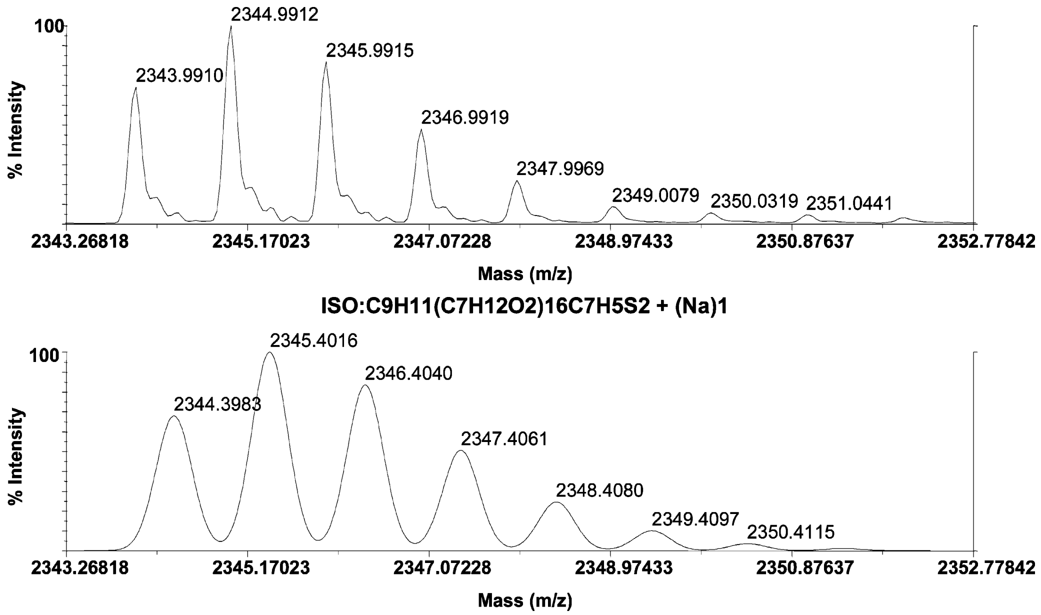


Figure 3. MALDI-TOF-MS spectrum of poly(butyl acrylate)-S-C(Ph)=S (PBA-RAFT) (**5**). On the basis of the isotopic mass distribution (observed (above) and theoretical (below)), the structure was assigned to **E1** from Figure 2.

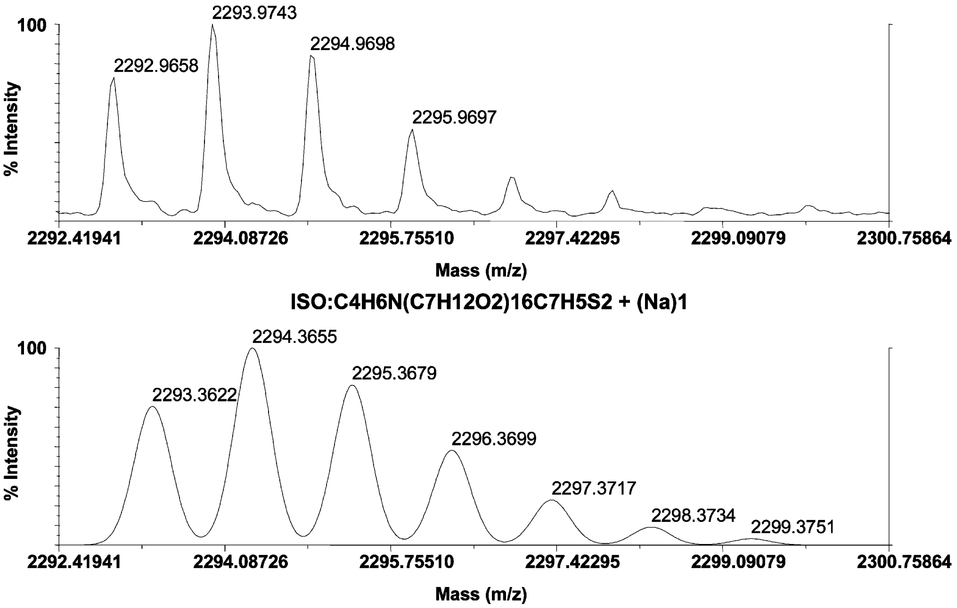


Figure 4. MALDI-TOF-MS spectrum of poly(butyl acrylate)-S-C(Ph)=S (PBA-RAFT) (**5**). On the basis of the isotopic mass distribution (observed (above) and theoretical (below)), the structure was assigned to **E3** from Figure 2.

cumyl group and a dithiobenzoate group (see Figure 2). This mass represents the pure PBA-RAFT species. Additional support for this structure is provided by the comparison of the theoretical and experimental isotopic mass distributions. Figure 3 clearly shows that there is an excellent agreement between experimental and theoretical masses. Equation 1 is based on the theoretical mass minus Na^+ and was used to confirm this structure of **E1** at different masses.

$$M_{\text{homo}} = 119.18 + (n \times 128.17) + 153.23 \qquad (1)$$

where 119.18 and 153.23 are the average masses of the end groups from the leaving group (cumyl fragment) and the dithiobenzoate chain transfer active group, respectively (derived from the CDB RAFT agent). The average mass of BA is 128.17, and n is the number of the monomer unit in the polymer chain.

A minor amount of polymer chains can also be cationized by potassium (K^+), a m/z value of 39 Da above the theoretically calculated mass. The theoretical mass for end group **E2** can be calculated using eq 1, where the only difference is that in end group **E2** the cation is now potassium.

The mass corresponding to **E3** was assigned to 16 BA units, a cyanoisopropyl fragment (from the AIBN initiator) and a dithiobenzoate (see Figure 2). The presence of this species is consistent with previous studies.[13–15] Once again, the theoretical and experimental isotopic patterns agree well (see Figure 4). The end group **E3** can be assigned by employing eq 2 with subtraction of the sodium cation.

$$M_{\text{homo}} = 68.09 + (n \times 128.17) + 153.23 \qquad (2)$$

Table 1. Peak Assignment of the MALDI-TOF-MS Spectrum Shown in Figure 1

peak	units of BA (n)[a]	obsd mass (Da)	theor mass (Da)	K^+	Na^+
E1	16	2344.9912	2345.4016		1
E2	15	2232.9100	2233.2918	1	
E3	16	2293.9743	2294.3655		1

[a] n is the number of butyl acrylate (BA) units for the structures **E1** to **E3** shown in Figure 2.

Table 2. Molecular Weight Averages for the Reaction of PBA-RAFT (5) with AIBN[a]

	[PBA-RAFT]:[AIBN][b]	M_n (g/mol)	M_w (g/mol)	PDI
1	no AIBN (PBA-RAFT)	2025	2344	1.15
2	6	2071	2421	1.16
3	1	2131	2530	1.18

[a] Reaction temperature = 80 °C, reaction time = 3 h, and solvent = *tert*-butylbenzene. [b] A decrease in the ratio of poly(butyl acrylate)-S-C(Ph)═S (PBA-RAFT) to α,α′-azobis(isobutyronitrile) (AIBN) results in an increase in both the number-average molecular weight (M_n) and the weight-average molecular weight (M_w), which leads to a slight increase in the polydispersity index (PDI).

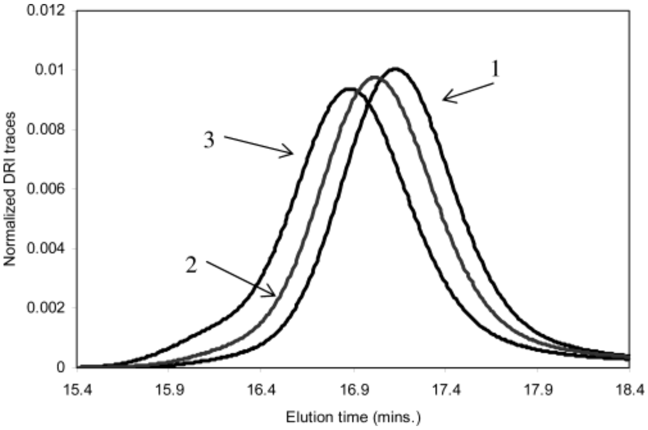


Figure 5. Plot of normalized differential refractive index (DRI) traces vs elution time for α,α′-azobis(isobutyronitrile) (AIBN) reactions with **5**: (1) molecular weight distribution of **5** before addition of AIBN, (2) 6:1 ratio of **5**:AIBN, (3) 1:1 ratio of **5**:AIBN.

where 68.09 is the average mass of the end groups from the cyanoisopropyl fragment.

End group **E4** could not be assigned to any of the possible structures, including 3- or 4-arm stars, other terminated products described by others, or even the intermediate radical. The closest match to end groups from all possible permutations and combinations of products in Schemes 1 and 2 was that of a 3-arm star, formed as a result of cross-termination of a propagating chain having a cumyl end group with an intermediate radical, having two polymeric chains each attached with a cumyl end group. However, for this structure the mass is 1.5 Da lower than the observed value, which is considered outside the error of the MALDI-TOF-MS measurements. The errors for the other assigned masses were within 0.5 Da. A recent publication[15] suggested that small amounts of peroxides present in stabilized THF (which is used as an eluent in SEC) aided in the exchange reaction of the double-bonded sulfur atom in the RAFT dithiobenzoate moiety by oxygen to form the structure given in Figure 2. This proposed structure corresponds within experimental error to the mass at **E4**. As will be shown below, the intensity of the mass at **E4** increased when **5** was reacted with excess AIBN, suggesting that this peak was due to a termination reaction and not the above exchange reaction.

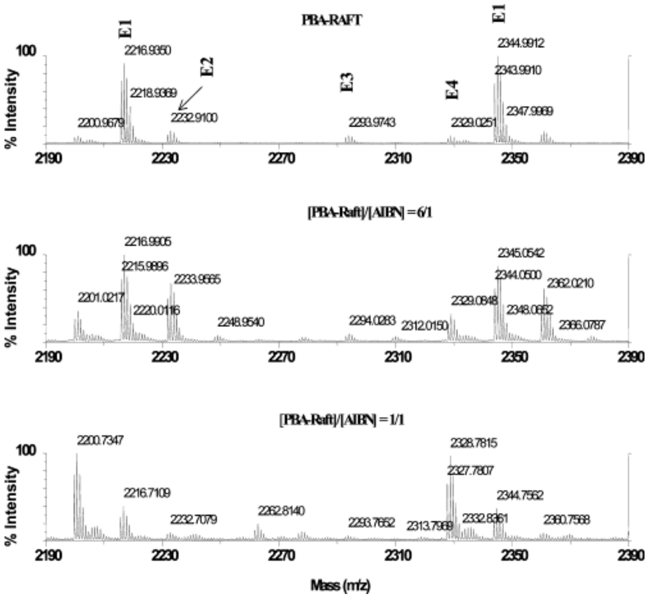


Figure 6. Comparison of the MALDI-TOF-MS spectra obtained from the poly(butyl acrylate)-S-C(Ph)═S (PBA-RAFT) and the α,α′-azobis(isobutyronitrile) (AIBN) termination experiments. Spectrum acquired in Reflector mode; matrix: *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB).

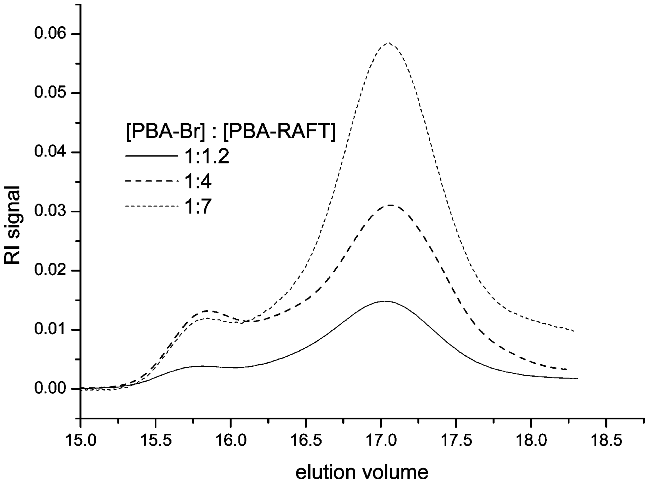


Figure 7. Normalized differential refractive index (DRI) traces vs elution volume obtained from size exclusion chromatography (SEC) measurements for the final polymers obtained after the termination reactions. For the termination reaction, [PBA-Br]:[PBA-RAFT]:[Cu(I)Br]:[Cu(0)]:[PMDETA] = 1:1.2/4/7:82:82:120. The reaction was carried out for 3 h at 80 °C.

Table 1 provides details of the observed and theoretical mass differences, and together with the good agreement between the isotopic patterns, the results strongly support the structure assignments.

Reaction of PBA-RAFT (5) with AIBN. Two reactions were carried out with different ratios of **5** to AIBN in *tert*-butylbenzene at 80 °C. Table 2 gives the resulting M_n, M_w, and PDI for these reactions. As the AIBN ratio is increased to 1, the M_n increased from 2025 to 2131 and M_w increased from 2344 to 2530. This can be more clearly seen from the SEC chromatograms (Figure 5). The data suggest that there must be termination reactions to produce polymer with molecular weight higher than that of the original **5**.

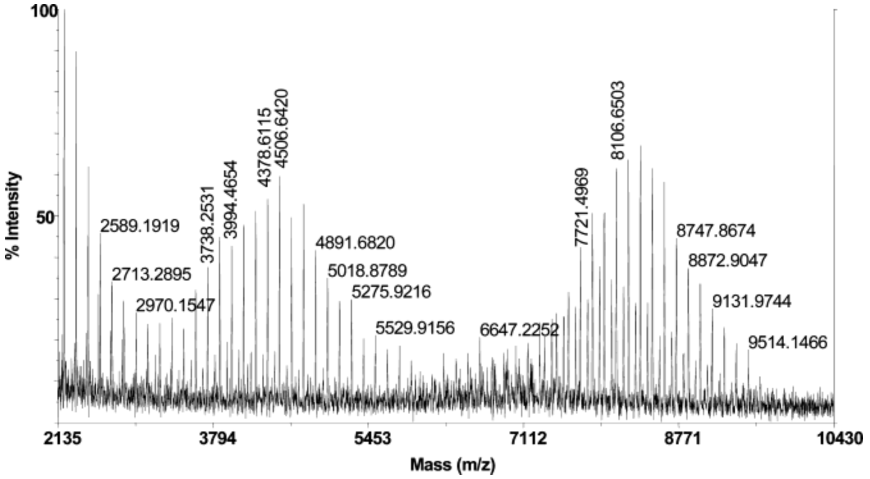


Figure 8. MALDI-TOF-MS spectrum for the fractionated polymer (details from SEC; $M_n = 6710$ g/mol, $M_w = 6830$ g/mol, and PDI = 1.018). Spectrum acquired in reflector mode; matrix: *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB).

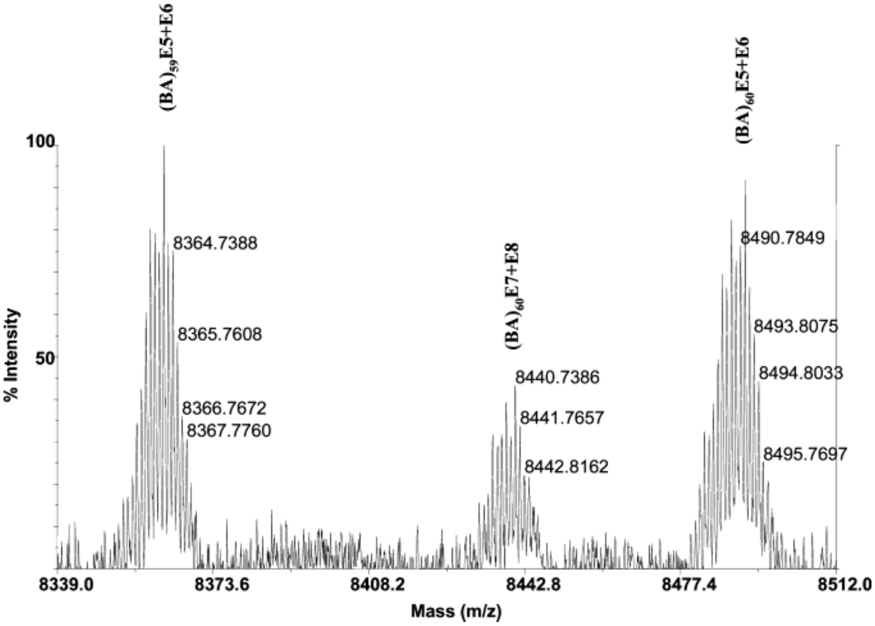


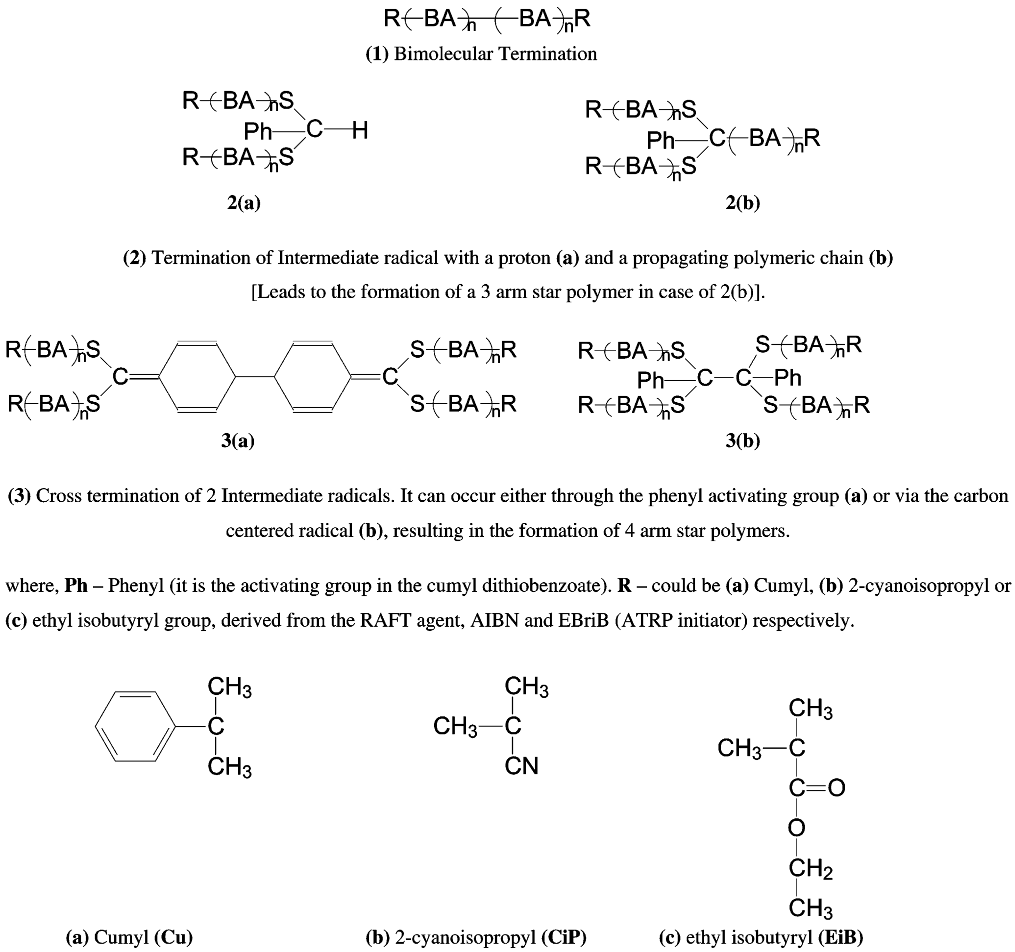
Figure 9. Expansion of the MALDI-TOF-MS spectrum from Figure 8, for the fractionated polymer in the high mass region. $(BA)_{59}E5+E6$ denotes that the structure is a combination of **E5** and **E6** from Figure 2 (Na salt attached), and it has 59 units of butyl acrylate (BA). Spectrum acquired in reflector mode; matrix: *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB).

On comparing the MALDI-TOF-MS spectra of the three polymers in Table 2 (see Figure 6), there are some interesting observations. The first is that the intensity of the peaks bearing the dithiobenzoate moiety as the terminal end group decreased as the ratio of AIBN to **5** was increased. This indicates that the PBA-RAFT does go through the equilibrium reaction in Scheme 1, terminating to produce a polymer of higher molecular weight. The second, and more interesting, is that the intensity of the polymer chain at **E4** also increased as the ratio of AIBN to **5** was increased. This suggests that either new chains were terminated to form **E4** or the amount of **E4** remained unchanged but increased relative to the loss of **E1** and **E3**. The MALDI-TOF-MS spectrum at an equal ratio of PBA-RAFT to AIBN showed that **E4** was the dominant peak, suggesting that **E4** is indeed a termination product and not the oxidation product shown in Figure 2.

To further explore cross-termination in polymeric systems, we used the Fukuda[12] model experiments for carrying out reactions of PBA-Br (**6**) with CuBr/PMDETA and Cu(0) in the presence of **5**. Should intermediate radical termination not participate in the RAFT mechanism, then 3- and 4-arm stars should, in principle, not be produced. Fukuda showed that 3-arm stars are found in styrene systems using this method.

Reaction of PBA-Br (6), CuBr/PMDETA, and PBA-RAFT (5). Compound **6** ($M_n = 2405$, $M_w = 2828$, PDI = 1.17) was activated by the CuBr/PMDETA complex and Cu(0) to form the PBA polymeric radical. Cu(0) was added to minimize the role of the Cu(II) species in the reaction.[17] The PBA radicals can terminate with each other or react with **5** to form an intermediate radical. The latter can fragment, terminate with other PBA radicals to form a 3-arm star, or self-terminate to form a 4-arm star.

These model reactions were carried out using varying ratios of **5** to **6**. The SEC traces of the final polymer distributions are given in Figure 7. It can be observed that a second and new peak appeared that increased at



(1) Bimolecular Termination

(2) Termination of Intermediate radical with a proton **(a)** and a propagating polymeric chain **(b)** [Leads to the formation of a 3 arm star polymer in case of 2(b)].

(3) Cross termination of 2 Intermediate radicals. It can occur either through the phenyl activating group **(a)** or via the carbon centered radical **(b)**, resulting in the formation of 4 arm star polymers.

where, **Ph** – Phenyl (it is the activating group in the cumyl dithiobenzoate). **R** – could be **(a)** Cumyl, **(b)** 2-cyanoisopropyl or **(c)** ethyl isobutyryl group, derived from the RAFT agent, AIBN and EBriB (ATRP initiator) respectively.

(a) Cumyl **(Cu)** **(b)** 2-cyanoisopropyl **(CiP)** **(c)** ethyl isobutyryl **(EiB)**

Figure 10. Overview of possible terminated polymeric products from the reaction of **5** and **6**.

a higher ratio of **5** to **6**. The new peak has an M_n of approximately 8000 based on PSTY standards and points to the presence of 3- or 4-arm stars or both. It is not easy to distinguish between either 3- or 4-arm stars solely on the basis of SEC since the hydrodynamic volume will decrease from linear to 3- to 4-arm stars, resulting in an overlap of the linear, 3- and 4-arm star distributions. Therefore, MALDI-TOF-MS was used, after SEC fractionation (described in the Experimental Section), to identify the products associated with this new peak. This is only a slice of the SEC chromatogram, and we do not expect to find all the possible species formed in the reaction. Therefore, the terminated products found in this slice are not representative of the whole SEC chromatogram.

Figure 8 gives the full MALDI-TOF-MS spectrum for the SEC fractionated polymer collected in the high molecular weight region for the reaction carried out at a 6:1 ratio of **5** to **6**. Analysis of this fraction by reinjection into the SEC showed a molecular weight distribution with an $M_n = 6710$, $M_w = 6830$, and PDI = 1.018. Despite the low PDI, the distribution is trimodal in the MALDI-TOF-MS spectrum. After an extensive analysis, the overall distributions were grouped into **(**i**)** the low mass region (mass range ~2000 Da), constituting terminated chains already present in the starting compounds of PBA-RAFT and PBA-Br, which do not participate in the reactions; **(**ii**)** middle mass range (mass range ~4000−6000 Da) which consisted of terminated products obtained from bimolecular or cross-termination during the reaction; and **(**iii**)** high mass range (mass range ~ 8000 Da) which comprised exclusively of cross-termination products. The observed trimodality in the MALDI-TOF-MS distribution clearly highlighted the pitfalls of the SEC and exposes its limitations in this particular case when analyzing branched polymers.

An expansion of the MALDI-TOF-MS spectrum in Figure 8 between mass points 8339 and 8512 shows two groups of peaks (Figure 9). This spectral region was selected since this is where 4-arm stars should be detected. The possible terminated products are given in Figure 10, consisting of 2-, 3-, and 4-arm stars with the various possible end groups. The individual distribution of peaks seems to be broad in comparison to the group of peaks denoted as **E1** in Figure 6. The width of the distribution could be due to the increased contribution from different carbon isotopes (e.g., ^{12}C and ^{13}C) with the increasing number of monomer units. However, it would seem more reasonable that the broadening is a result of an overlap between two isotopic distributions. The mass for the end groups cumyl (119.19 Da) and ethylisobutyryl (115.15 Da) only differ by 4.04 Da, as these end groups are the most predominant 4-arm species that form from intermediate termination (see Figure 2). This is based on the simple calculation that 4-arm stars will form at 4 times the original molecular weight of 2000 (i.e., 8000). The theoretical isotopic distributions of **E5** with **E6** (Figure 11) and **E7** with **E8** (Figure 12) were fitted to the observed distributions in Figure 9 by using a ratio of 2:1 (for **E5**:**E6** and **E7**:**E8**). The higher ratio of **E5** is not surprising since the ratio of **5** to **6** was 6:1, signifying that a greater percentage of end groups would be cumyl (Cu) originat-

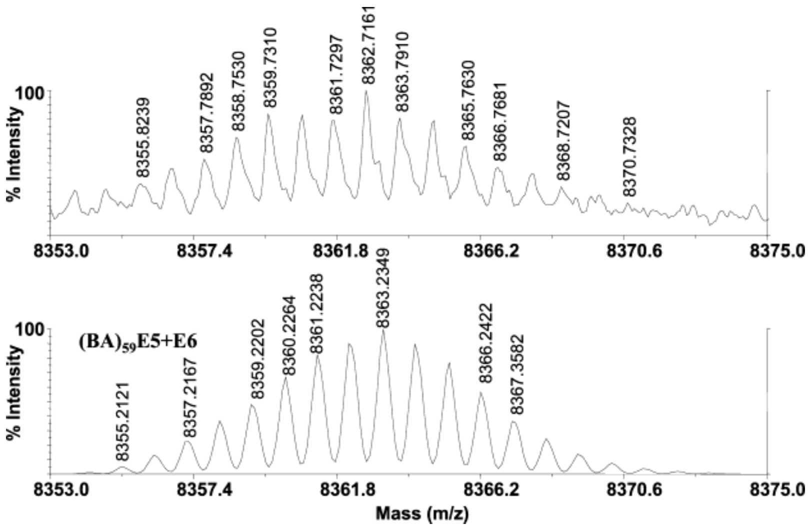


Figure 11. MALDI-TOF-MS spectrum of fractionated polymer in the high mass region. On the basis of the isotopic mass distribution (observed (above) and theoretical (below)), the structures were assigned to a combination of **E5** and **E6** from Figure 2. The ratio of the intensities for the distributions having end groups **E5** and **E6** is 2:1.

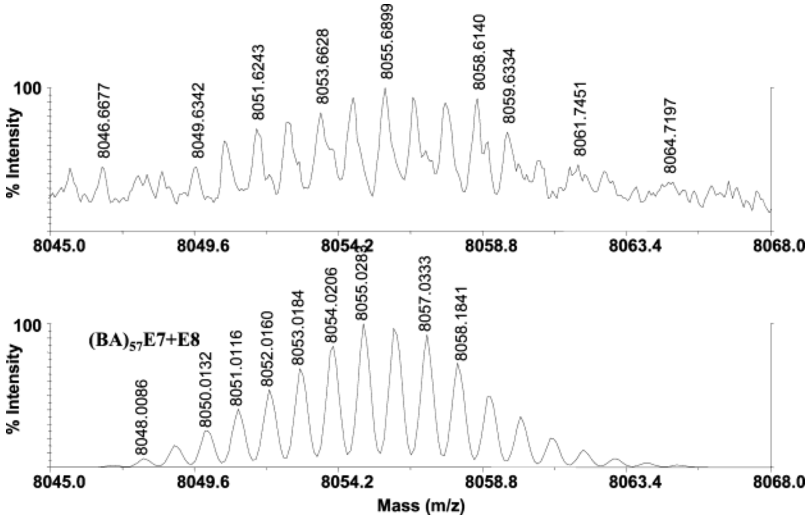


Figure 12. MALDI-TOF-MS spectrum of fractionated polymer in the high mass region. On the basis of the isotopic mass distribution (observed (above) and theoretical (below)), the structures were assigned to a combination of **E7** and **E8** from Figure 2. The ratio of the intensities for the distributions having end groups **E7** and **E8** is 2:1.

ing from **5** with a smaller amount consisting of the ethylisobutyryl (EiB) originating from **6**. The small amount of chains with 2-cyanoisopropyl (CiP**)** end groups is derived from the AIBN initiator to make **5** (i.e., **E3**). This translates to a lower amount of **E7** and **E8** compared to **E5**.

Figure 13 is an expansion of the spectrum in Figure 8 between 4479 and 4660 Da and shows two groups of peaks. It would appear, on the basis of the M_n's of the starting polymeric species **5** and **6**, this region would have terminated species from bimolecular termination between propagating radicals or from intermediate radical termination with a hydrogen atom or other low molar mass species (species **1** and **2a** given in Figure 10). However, it was not possible to assign the observed peaks using these species molecular weights. The masses could be ascribed to 3-arm star products (see Figure 2). Taking a simplistic view, 3-arm stars should form in the 6000 Da region and not be predominant at 4500 Da. This observation will be discussed below. The theoretical isotopic distributions of **E9** with **E10** (Figure 14) and **E11** (Figure 15) were fitted to the observed distributions in Figure 13 by using a ratio of 2:1 (for **E9**:**E10**). The intensities decrease in the order Cu > EiB > CiP, which is what should be expected from the quantities of the starting species.

The distribution in Figure 8 shows two peak maxima: one at 4506 Da and the other at 8106 Da. At first sight, it would be possible to reason that the 4506 Da peak is from species formed through bimolecular termination (2-arm stars) and that at 8106 Da is from 4-arm species. As suggested by the isotopic mass distributions, the 4506 Da peak corresponds to 3-arm star species. The question as to why this is not in the 6000 Da region needs to be addressed. Because of the differences in hydrodynamic volume of 3- and 4-arm stars, the SEC fraction may show the lower end of the 3-arm star molar mass distribution and the middle range of the 4-arm star. However, the fraction was taken on the basis of a linear calibration curve at $M_n = 6710$ and should actually show the higher molecular weight range of the 3-arm star distribution. This is supported by SEC fractions taken at higher M values, in which the distributions were in the same range as that given in Figure 8.

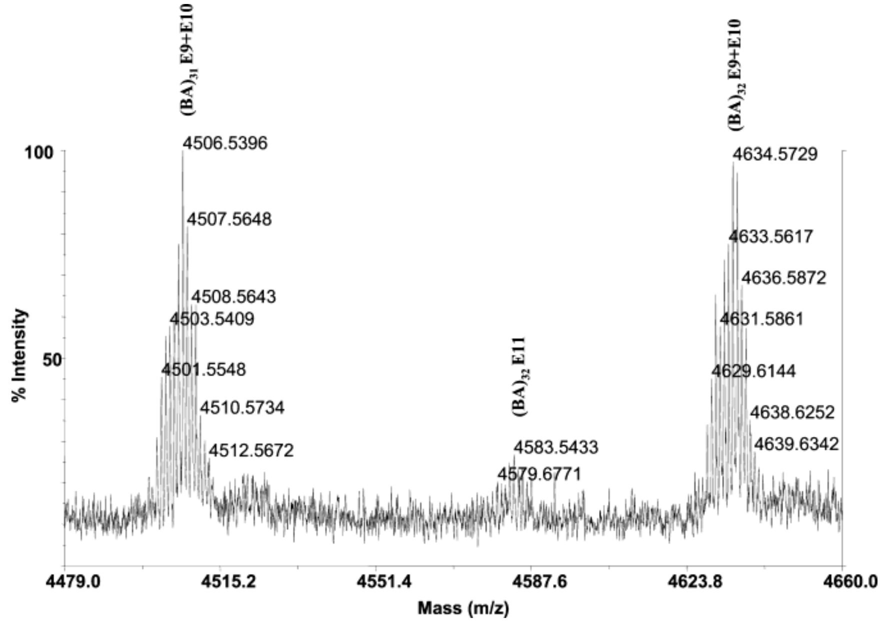


Figure 13. Expansion of the MALDI-TOF-MS spectrum from Figure 8 for the fractionated polymer in the middle mass region. Spectrum acquired in reflector mode; matrix: *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB).

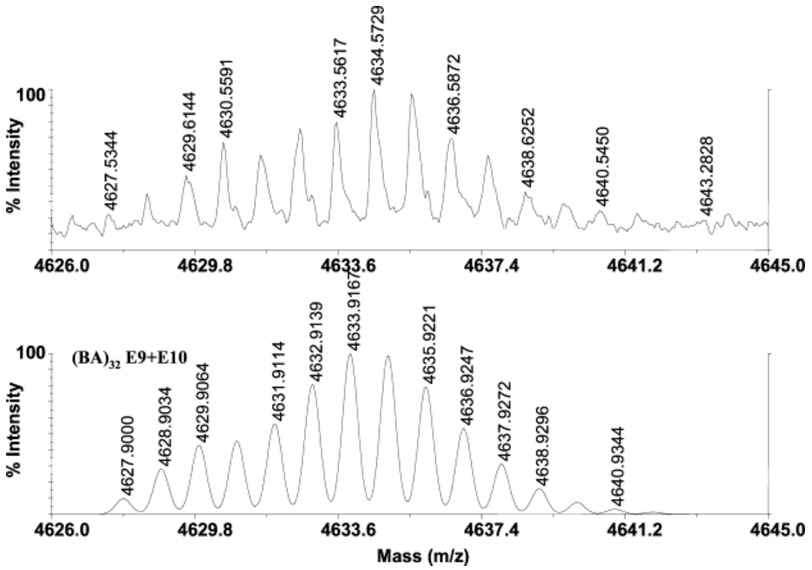


Figure 14. MALDI-TOF-MS spectrum of fractionated polymer in the middle mass region. On the basis of the isotopic mass distribution (observed (above) and theoretical (below)), the structures were assigned to a combination of **E9** and **E10** from Figure 2. The ratio of the intensities for the distributions having end groups **E9** and **E10** is 2:1.

To explore this further, the intensities of the various 3- and 4-arm stars as a function of mass are given in Figure 16. As it was difficult to provide data on all the individual species combinations (e.g., **E1** + **E2**, **E3** + **E4**, and **E5** + **E6**) taking into account the most prominent peak in that particular series was used. It is clear from the plot that the peak maximum for the 3-arm and 4-arm stars are close to 4000 and 8000, respectively. There is another species present between the mass range of 4000−6000. It has a low intensity, thus making identification using the theoretical isotopic distribution difficult. It is postulated simply on the basis of agreement between calculated and experimental mass that this species is a terminated product consisting of a 3-arm star with three EiB groups. The data show that 3-arm star products, regardless of the end group, can be found in the 4500 Da region of the MALDI-TOF-MS spectrum, and 4-arm star products are found in the 8000 Da region.

The results suggest that the termination processes of the intermediate radical to form 3- and 4-arm stars are different. Termination of the intermediate radical to form 3-arm stars appears to be controlled by chain length dependent termination, while self-termination of intermediate radicals to form 4-arm stars appears to be through random coupling. Before an explanation is given for the kinetic control in the formation of 3-arm stars, the majority of radicals in this polymerization consist mainly of the intermediate radical species. On the basis of this, we *tentatively* suggest that one way that 3-arm stars are observed in the 4500 Da mass range and not in the 6000 Da range is dependent on the addition−fragmentation process being under diffusion control. Although larger polymeric groups attached to the intermediate radicals are faster to fragment than small polymeric groups,[18] they are also slower to diffuse away from the site at which fragmentation took place. This results in a higher probability of reacting back with

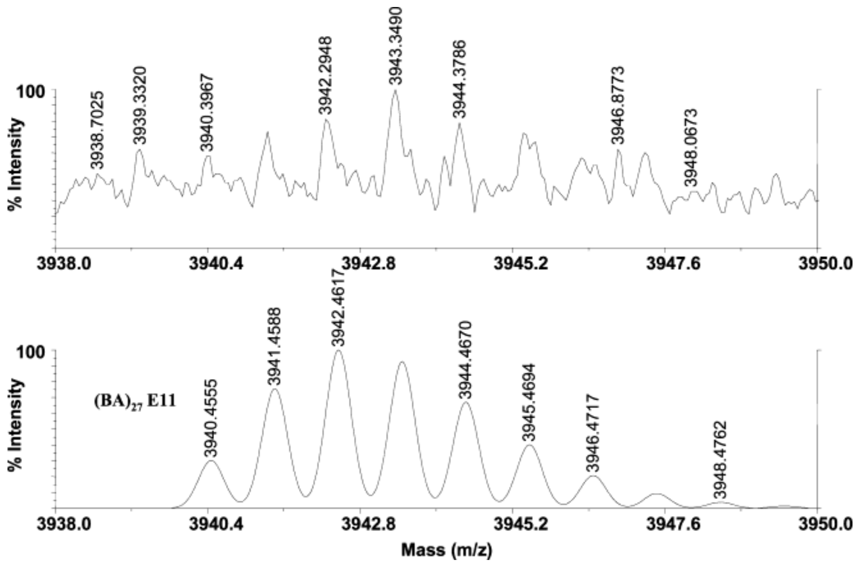


Figure 15. MALDI-TOF-MS spectrum of fractionated polymer in the middle mass region. On the basis of the isotopic mass distribution (observed (above) and theoretical (below)), the structure was assigned to a **E11** from Figure 2.

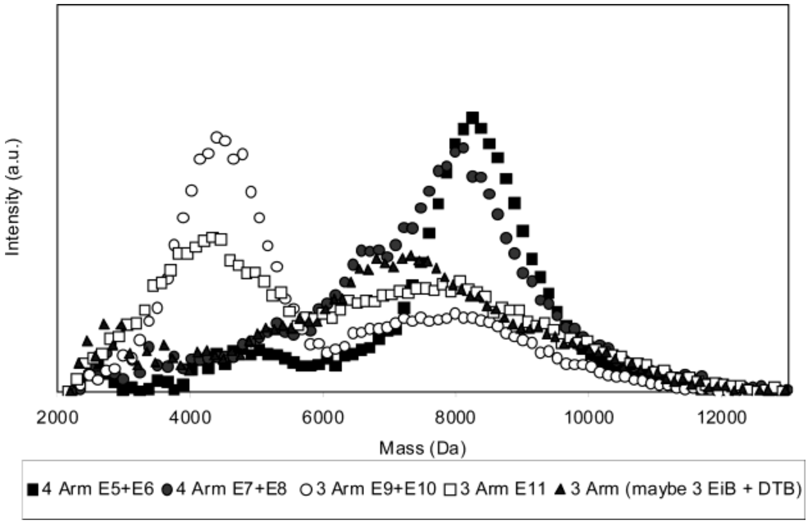


Figure 16. Plot of the intensities of the distributions for the observed terminated species, having the various end groups in the MALDI-TOF-MS spectrum (Figure 8).

dormant RAFT polymer (a type of cage effect). It is conceivable from the high addition rate constant k_{add} ($\sim 1 \times 10^6$ L mol^{-1} s^{-1} calculated from the k_{p} for BA and using a low value for $C_{\mathrm{tr,RAFT}}$ of 100) for polymeric radical addition to dormant RAFT species that this process becomes competitive with diffusion away from the "cage". Fragmentation to the small but faster diffusing polymeric radicals results in escape of these radicals from the cage and their termination with intermediate radicals in the system. The outcome of this postulate would suggest that termination of the intermediate radical would be by small oligomeric radicals to form 3-arm stars. The cage effect described above could be defined as the reaction radius and is similar to the dimensions for bimolecular termination that approximates to the van der Waals radii of a monomeric unit.[19,20]

Conclusion

The results described in this work have shown that SEC combined with MALDI-TOF-MS provides a powerful tool to elucidate the structures of polymeric species. Three- and four-arm stars are clearly observed when PBA-Br is reacted with Cu(I) and Cu(0) in the presence of PBA-RAFT. This is the first example of the synthesis of 4-arm stars through intermediate−intermediate radical termination. We postulated that this is due to the much slower fragmentation rate in the BA system in comparison to the styrene system. However, we cannot find clear evidence that 3- or 4-arm stars are formed in a pure RAFT experiment (i.e., in the production of PBA-RAFT, **5**). This is consistent with CAMD[15] findings, except that we could not observe the intermediate radical product by MALDI-TOF-MS. The possibility for the fragmentation of the RAFT moiety during MALDI-TOF-MS analysis was significantly reduced by using low laser intensity (1900−2000).

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