Intermediate Radical Termination in Reversible Addition-Fragmentation Chain Transfer-Mediated Polymerization: Identification of Termination Products

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Received December 14, 2006; Revised Manuscript Received March 20, 2007

ABSTRACT: Rate retardation in reversible addition-fragmentation chain transfer (RAFT)-mediated polymerizations is the topic of an ongoing debate. One of the main explanations for this rate retardation is termination of the intermediate radical. The use of a RAFT agent with a UV label in the leaving group acts as a means to identify products of intermediate radical termination (IRT). In the analysis of the polymeric samples with size exclusion chromatography (SEC), two different UV absorbance traces were compared (i.e., the UV absorbance of the label used and that of the thiocarbonyl thio moiety of the RAFT agent). Deviations in the ratio of the C═S of the RAFT moiety to the UV label indicate that IRT products could be formed. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry was used to identify these IRT products formed during a "normal" RAFT-mediated polymerization (not using forced conditions). These experimental findings support the postulated IRT model and therefore help to elucidate the fate of the intermediate radical during a RAFT mediated polymerization.

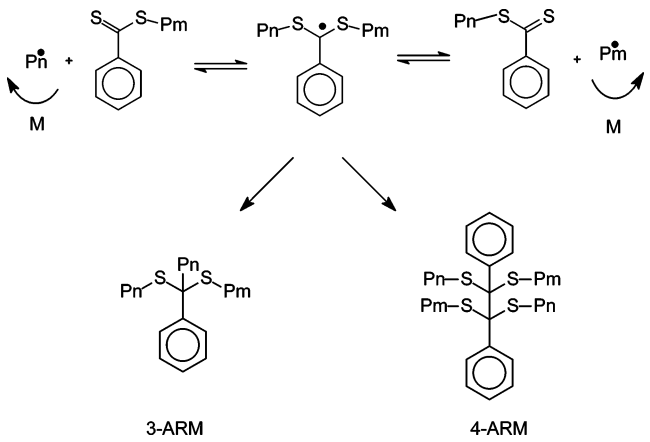
Introduction

In the field of living/controlled radical polymerizations, extensive research has been done on reversible addition-fragmentation chain transfer (RAFT)-mediated polymerization as a highly versatile method. Recently, an important focus has been on the elucidation of the reaction mechanism. Special interest has been given to the fate of the intermediate radical, as this is a potential source of side-reactions. These potential side-reactions of the intermediate radical could be the cause of rate retardation phenomena.

In the ongoing debate on the cause of rate retardation, there are two general schools of thought: (1) slow fragmentation of the intermediate radical or (2) termination reactions of the intermediate radical (Scheme 1). Many different techniques have been used to elucidate the RAFT mechanism such as NMR,[1,2] UV−vis, matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI−ToF−MS),[3] electron spin resonance (ESR) spectroscopy,[4,5,6] and size exclusion chromatography−elcetrospray ionization−mass spectrometry (SEC−ESI−MS).[7]

Barner-Kowollik et al. studied polymerizations mediated by a rate-retarding RAFT-agent (dithiobenzoate), and by a nonrate-retarding RAFT-agent (phenyl dithioacetate).[7] Predici was used to predict concentrations of the three-arm stars that would result from the termination of intermediate radicals. The theoretical predictions were compared with experimental concentration measurements of the termination products via SEC−ESI−MS. In their experimental work, they were unable to find evidence for termination products originating from the intermediate radical. Vana et al.[8] used Monte Carlo simulations to predict the concentrations of termination products resulting from intermediate radical termination and predicted several percents of terminated species at lower conversions (up to 25% monomer conversion).

Scheme 1. Proposed Mechanism for the RAFT Process with Intermediate Radical Termination



Other authors used model systems favoring the formation of intermediate radical termination products to show the chemical pathway that leads to these products. These model systems do not necessarily represent the mechanisms taking place in real polymerization systems because monomer was absent in these studies.[3,9]

Rate retardation almost exclusively occurs with RAFT-agents that carry a phenyl group as a radical stabilizing group (see Scheme 1) (i.e., dithiobenzoates). Elucidation of the origin of rate retardation is important to obtain a deeper understanding of the RAFT mechanism as has been reviewed recently by Vana et al.[10] It is tempting to relate the present study to ab initio quantum chemical calculations from Coote et al.[11,12] However, it needs to be stressed that these calculations are focused on the initialization process, or the so-called pre-equilibrium. The

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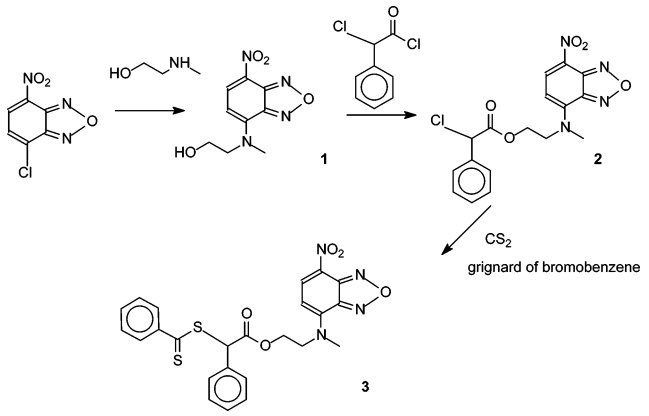
10.1021/ma0628634 CCC: $37.00
Published on Web 05/03/2007

Scheme 2. Synthesis of RAFT-Agent with 7-Nitro-1,2,3-Benzoxadiazole (NBD) Moiety



current study focuses on the post-initialization stages, often referred to as the main equilibrium.

On the basis of previous research, there are strong indications that intermediate radical termination products can occur in RAFT polymerizations. However, despite the many efforts in earlier research, the structure of possible termination products (three- and four-arm stars) has not been fully elucidated yet. Next to this, hardly any experimental proof was given of termination products in a real polymerization system, in the presence of monomer.[13] Barner-Kowollik et al.[14] discussed their results of a similar experiment as the one we will be discussing in this paper. They however were not able to detect any termination products. In a recent publication, Vana and Buback[15] point at the possibility that three- and four-arm stars in dithiobenzoate-mediated polymerization can undergo side reactions. These side reactions will lower the concentration of star-shaped polymers and will lead to the formation of chains that are potentially difficult to distinguish from products of conventional bimolecular termination.

In continuation of previous work in our group,[3] we polymerized *n*-butyl acrylate (BA) in the presence of a RAFT agent, 4-(1-methyl-amino ethanol)−7-nitro-1,2,3-benzoxadiazole (NBD−MAE) ester dithiobenzoate (see Scheme 2).

The use of the 7-nitro-1,2,3-benzoxadiazole (NBD)[16] moiety as part of the leaving group provides a UV absorbing group with a λ_{max} of 470 nm, which is present at virtually every polymer chain end. The C═S group of the RAFT agent has a λ_{max} of 305 nm. This means that the two different chromophores can be measured simultaneously during an SEC experiment, and therefore the ratio can be determined as a function of elution time. Because of the disappearance of the 305 nm chromophore upon (intermediate radical) termination (IRT), this ratio provides an entry into the study of IRT. We subsequently fractionated polymers by SEC and analyzed some relevant fractions by MALDI−ToF−MS.

Experimental Methods

Materials. All solvents and reagents were purchased from Aldrich Chemical Co. and used without further purification (unless mentioned otherwise). *n*-Butyl acrylate (BA, 99%) was filtered before use through a column packed with replacement packing for removing hydroquinone and monomethyl ether hydroquinone (Aldrich), to remove the radical inhibitor. 4-(*N*-methyl *N*-(2-hydroxy-ethylamine)−7-nitro-1,2,3-benzoxadiazole (NBD−MAE) (1) was prepared as described in the literature.[16]

Gas Chromatography (GC). GC was used to determine monomer conversion by determination of the residual monomer. The analysis was carried out on a Hewlett-Packard (HP 5890) GC, equipped with an AT-Wax capillary column (30 m × 0.53 mm × 10 μm); toluene was used as internal reference.

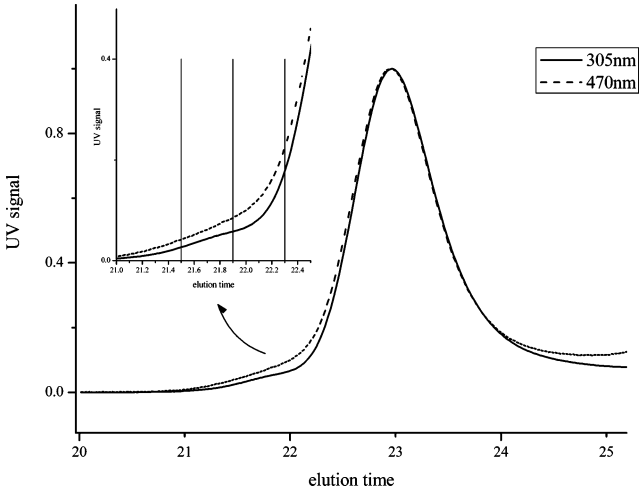


Figure 1. SEC chromatogram of a pBA sample at 62% conversion measured at wavelength of 470 and 305 nm (M_n = 4981 g/mol, PDI = 1.12). In the inset, an expansion of part of the SEC chromatogram is given. The straight vertical lines represent the positions of the collected SEC fractions that were analyzed with MALDI−ToF−MS. $[BA]_0/[RAFT]_0$ = 37.0, $[RAFT]_0/[AIBN]_0$ = 5.0, reaction temperature T = 70 °C.

Size Exclusion Chromatography (SEC). The polymer solution was diluted in tetrahydrofuran (THF, Biosolve) to a concentration of approximately 1 mg/mL. The solution was filtered over a 0.2 μm poly(tetrafluoroethylene) (PTFE) syringe filter. The analysis was carried out using a Waters 2695 Alliance pump and injector, a model 2996 photodiode array detector (at 305 and 470 nm) and a model 410 refractive index detector. The columns used were two PLgel Mixed-C (Polymer Laboratories, 5 μm particles) 300 × 7.5 mm followed by a PLgel Mixed-D (Polymer Laboratories, 5 μm particles) 300 × 7.5 mm in series (which were maintained at 40 °C for analysis). THF was used as an eluent (flow rate 1.0 mL/min). The fractionation of ATRP samples was performed on a different column set: a PLgel preGuard (Polymer Laboratories, 3 μm particles) 50 × 7.5 mm followed by two PLgel mixed-E (Polymer laboratories, 3 μm particles) 300 × 7.5 mm. Data acquisition was performed using Waters Empower 1 software. Calibration was carried out using narrow molecular weight distribution (MWD) (pSTY) standards ranging from 2450 to 16.5 × 10^4 g/mol. The molecular weights were calculated using the universal calibration principle and Mark−Houwink parameters [pBA: K = 1.22 × 10^{-4} dL/g, a = 0.700. pSTY: K = 1.14 × 10^{-4} dL/g, a = 0.716].[17] Molecular weights were calculated relative to the relevant homopolymer (in this case pBA).

In some instances, the obtained polymers were fractionated prior to MALDI−ToF−MS analysis using SEC. The SEC setup consisted of the same series of columns used for the determination of the molecular weights. The system also consisted of an isocratic pump (Waters 590, flow rate of 1.0 mL/min), UV detector (Linear Instruments Corporation UV−vis 200, 254 nm). THF was used as a solvent at a flow rate of 1.0 mL/min. A fraction collector (Millipore) was used to collect 40 fractions at equal volume intervals of 0.4 mL.

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) (Aldrich, ≥ 99%) was chosen as the matrix and recrystallized prior to use. Potassium trifluoroacetate (Aldrich, 98%) was added as the cationic ionization agent. The matrix was dissolved in THF at a concentration of 40 mg/mL. Potassium trifluoroacetate was added to THF at a concentration of 1 mg/mL. The dissolved polymer concentration in THF was 1 mg/mL. In a typical MALDI−ToF−

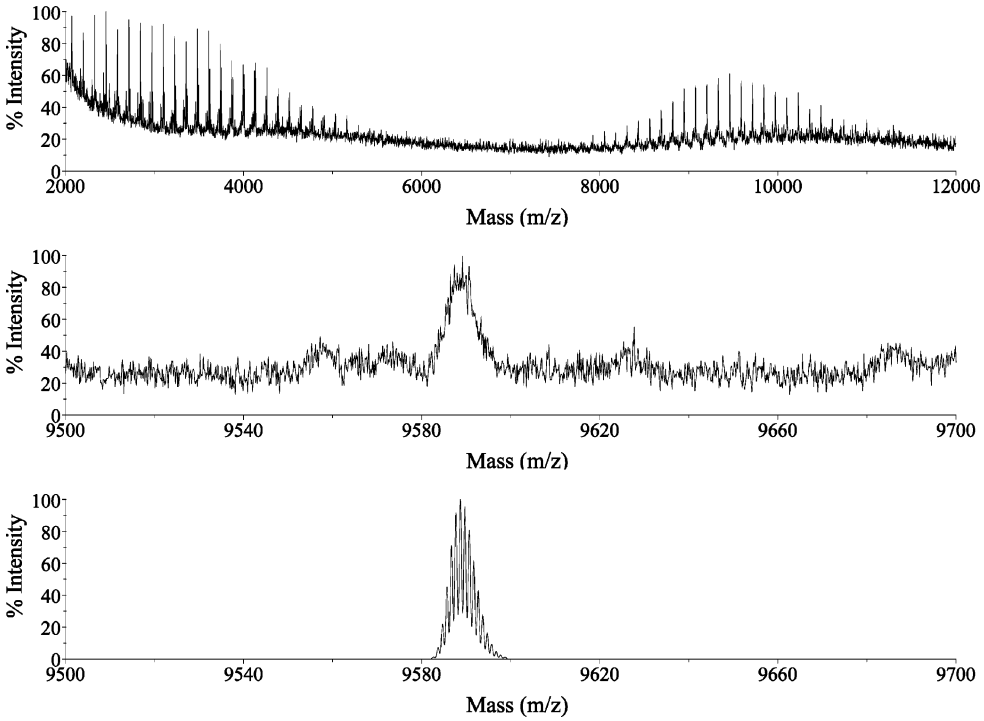


Figure 2. MALDI−ToF mass spectrum of fractionated pBA-RAFT sample (conversion of sample 62%) at SEC elution time 21.5 min together with an expansion between 9500 and 9700 g mol^{-1} and calculated isotopic patterns for poly(butyl acrylate) termination product between intermediate radical and propagating polymer chain (three-arm star in Scheme 1). $[BA]_0/[RAFT]_0 = 37.0$, $[RAFT]_0/[AIBN]_0 = 5.0$, reaction temperature $T = 70$ °C.

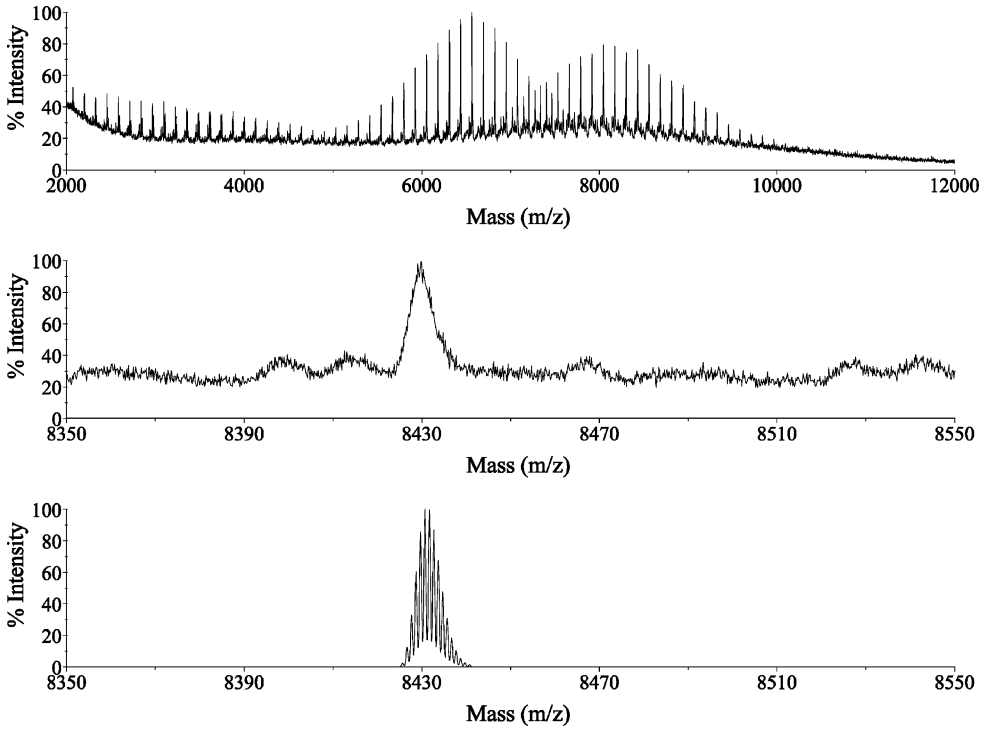


Figure 3. MALDI−ToF mass spectrum of fractionated pBA sample (conversion of sample 62%) at elution time 21.9 min together with an expansion between 8350 and 8550 g mol^{-1} and calculated isotopic pattern for poly(butyl acrylate) termination product between two intermediate radicals (four-arm star from Scheme 1). $[BA]_0/[RAFT]_0 = 37.0$, $[RAFT]_0/[AIBN]_0 = 5.0$, reaction temperature $T = 70$ °C.

MS experiment, the matrix, salt, and polymer solutions were premixed in the ratio 5 μL sample: 5 μL matrix:1 μL salt. Approximately 0.3 μL of the obtained mixture was hand-spotted on the target plate. For each spectrum, 1000 laser shots were accumulated.

Synthesis of Chlorophenyl Acetyl NBD−MAE Ester (2). A solution of chlorophenyl acetylchloride (6.08 g, 32.16 mmol) was added dropwise to a solution of NBD−MAE (**1**; 8.24 g, 34.6 mmol) and triethylamine (10.46 g, 103.4 mmol) in dry THF (300 mL). The reaction mixture was kept at 40 °C for 3 h and was left to react overnight at room temperature. The solvent was removed under reduced pressure and the residue was taken up into dichloromethane (300 mL). The solution was extracted twice with brine (300 mL). The organic phase was dried on anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. The product was isolated as a bright orange solid in 90% yield (11.30

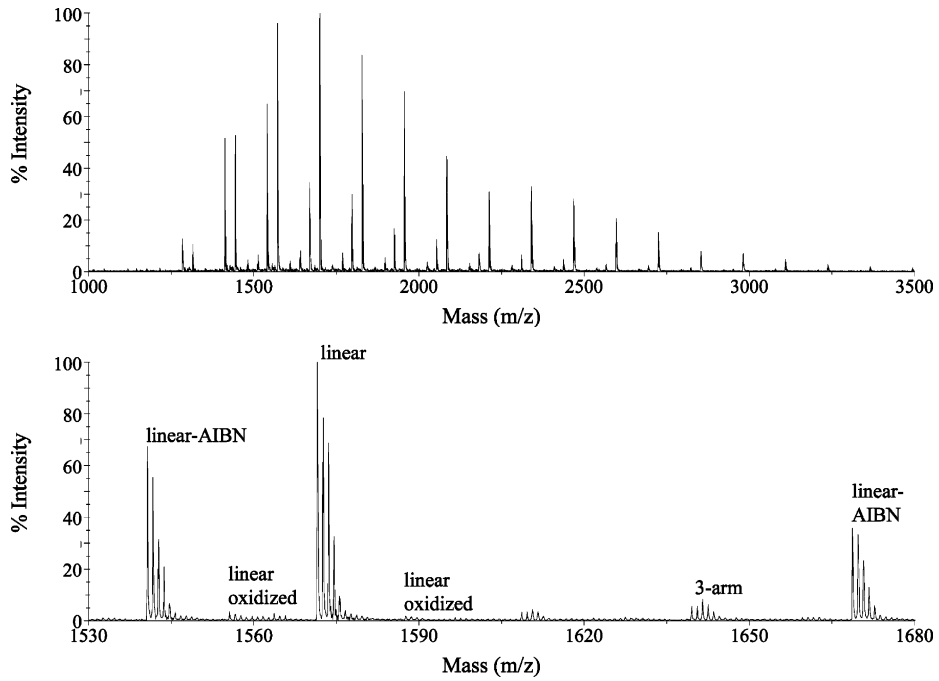


Figure 4. MALDI−ToF mass spectrum of fractionated pBA sample at elution time 23.1 min together with an expansion between 1530 and 1680 g mol^{-1}. The expansion shows the teminated product (three-arm star from Scheme 1) together with the linear pBA (conversion = 25%). $[BA]_0/[RAFT]_0 = 37.0$, $[RAFT]_0/[AIBN]_0 = 5.0$, reaction temperature $T = 70$ °C.

g, 28.9 mmol). ^{1}H NMR ($CDCl_3$, δ): 8.35 (d, 1H, Ph (*H*)), 7.30 (m, 5H, Ph (*H*)), 6.04 (d, 1H, Ph (*H*)), 5.25 (s, 1H, PhC*H*Cl), 4.66 (m, 2H, COCH_2CH$_2$), 4.47 (m, 2H, CH$_2$CH_2N), 3.27 (S, 3H, PhNC*Me*).

Synthesis of RAFT-Agent (3). Phenyl magnesium bromide was synthesized from bromobenzene (2.63 g, 16.7 mmol) and magnesium turnings (0.33 g, 13.4 mmol) in dry THF (10 mL). Carbon disulfide (0.99 g, 13.0 mmol) was added to the solution maintaining the reaction temperature below 35 °C.[18] Chlorophenylacetyl NBD−MAE ester (**2**, 4.99 g, 12.8 mmol) dissolved in THF (40 mL) was then added into the solution. The reaction temperature was raised to 75 °C and maintained for 72 h. Ice water was then added to the solution. After removal of THF, the water layer was extracted twice with dichloromethane. The combined organic layer was dried over anhydrous magnesium sulfate. After solvent removal a dark orange solid was obtained in 85% yield (5.5 g, 10.8 mmol), mp 118−120 °C. ^{1}H NMR ($CDCl_3$, δ): 8.23 (d, 1H, Ph (*H*)), 7.90 (m, 5H, Ph (*H*)), 7.5 (m, 5H, Ph (*H*)), 6.0 (d, 1H, NPh (*H*) NO$_2$), 5.52 (s, 1H, PhCS$_2$ (*H*) PhCO), 4.58 (m, 2H, OCOC (H_2) CH$_2$), 4.30 (m, 2H, OCOCH$_2$C (H_2)), 3.30 (s, 1H, NC (H_3)). Anal. Calcd for $C_{24}H_{20}N_4O_5S_2$: C, 56.68; H, 3.90; N, 11.02. Found: C, 56.73; H, 3.91; N, 10.81.

Polymerization Using RAFT-Agent (3). Butyl acrylate (9.5 g, 74 mmol), RAFT-agent (**3**, 1.02 g, 2.0 mmol) and α, α′-azobis-(isobutyronitrile) (AIBN) (0.066 g, 0.4 mmol) were added into a three-necked round-bottom flask together with toluene (8.5 mL). The flask was deoxygenated by flushing with argon for approximately 30 min, then the flask was placed in a preheated oil bath at 70 °C. During the polymerization, samples were taken at different times of conversion, which were further used for analysis. The reaction was stopped after 6 h by cooling the flask in an ice bath and the addition of a small portion of THF (2 mL) (Final conversion ≈ 65%, $M_n = 5500$ and PDI = 1.12).

Synthesis of NBD−MAE Initiator for ATRP. NBD-MAE (**1;** 4 g, 16.8 mmol) was dissolved in THF (30 mL) together with triethylamine (2.56 mL, 18.5 mmol). To this solution the bromo isobutyrylbromide slowly was added (2.3 mL, 18.6 mmol). Product precipitated from the solution. The product was filtered off and was stirred in petroleum ether to remove unreacted starting materials. The product isolated was a bright orange solid in 45% yield (2.95 g, 7.6 mmol), mp 120−122 °C. ^{1}H NMR ($CDCl_3$, δ): 8.46 (d, 1H, Ph (*H*)), 6.23 (d, 1H, Ph (*H*)), 4.56 (s, 4H, C (CH_2CH_2)O), 3.50 (s, 3H, C(CH_3)), 1.85 (s, 6H, COC$(CH_3)_2$Br). Anal. Calcd for $C_{13}H_{15}BrN_4O_5$: C, 40.33; H, 3.90; N, 14.47. Found: C, 40.27; H, 3.71; N, 14.42.

Polymerization using ATRP (Control Experiment). Butyl acrylate (9 g, 70.2 mmol), NBD−MAE initiator (0.73 g, 1.88 mmol) and Cu^{I}Br (0.2 g, 1.39 mmol) were added into a Schlenck tube together with toluene (10 mL) and THF (4 mL). The Schlenck tube was deoxygenated by flushing with argon for 45 min. The Schlenck tube was then immersed in a preheated oil bath at 70 °C, and PMDETA (0.32 mL, 1.43 mmol) was added to initiate the reaction. Samples were taken at different times of conversion and used for analysis purposes. The samples were analyzed with GPC. Some samples were fractionated prior to analysis with MALDI−ToF−MS. The polymerization was stopped after 3 h and 45 min (final conversion = 76%.)

Results and Discussion

Poly(butyl acrylate) synthesized in the presence of RAFT-agent (**3**) was analyzed by SEC ($M_n = 4980$ g/mol, $M_w/M_n = 1.12$). The polymerization showed a living character, as evidenced by a linear increase of molar mass with monomer conversion and a low polydispersity index throughout the whole reaction. It should be kept in mind that reactions were stopped at reasonably low conversions (65%) and that no bimodality was observed in the SEC trace.

To determine the presence and location of products from intermediate radical termination in the molar mass distribution, we carried out SEC with UV-detection. Detection at 305 nm allows the selective detection of the thiocarbonyl thio moiety of the RAFT-agent. Detection at 470 nm, on the other hand, shows the presence of the chromophore in the leaving group of the RAFT-agent (**3**). The ratio of UV_{470}/UV_{305} as a function of elution time in SEC will provide information on the possible location of products from intermediate radical termination.

The expected (i.e., linear) polymer is anticipated to include both UV chromophores in a 1:1 ratio. However, when termination occurs at the intermediate radical position, the polymer chain will lose its thiocarbonyl thio chromophore and a three- or four-arm star will be formed that contains three or four UV_{470}

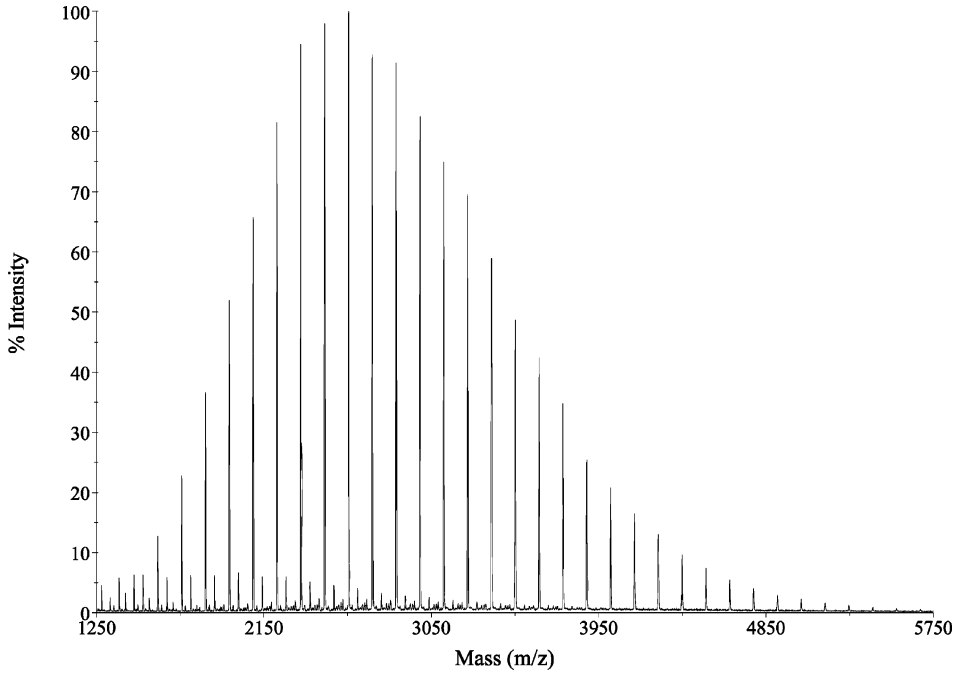


Figure 5. MALDI−ToF mass spectrum of pBA sample before fractionation at a conversion of 72% (M_n = 3551 g/mol, PDI = 1.11). $[M]_0/[I]_0$ = 37.3, $[I]_0/[Cu(I)]_0$ = 1.35, reaction temperature T = 70 °C.

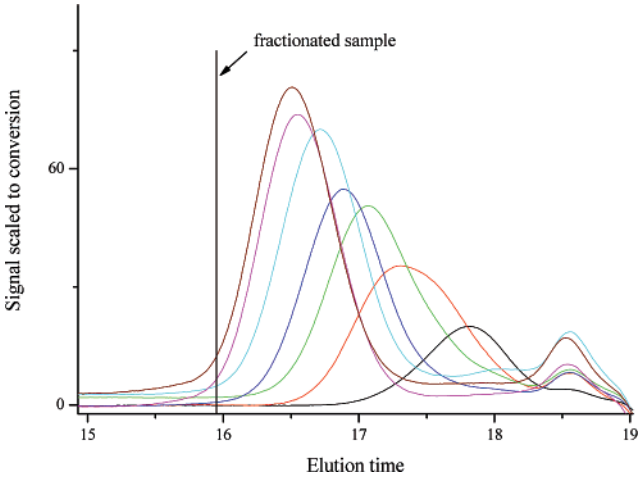


Figure 6. SEC traces of pBA samples taken during ATRP polymerization (the vertical line represents the position of the fractionated sample). $[M]_0/[I]_0$ = 37.3, $[I]_0/[Cu(I)]_0$ = 1.35, reaction temperature T = 70 °C.

chromophores, respectively. Therefore the UV_{470}/UV_{305} ratio will change and can be used to detect possible termination products. Note also that bimolecular termination of propagating polymer chains will lead to a decrease in the UV_{470}/UV_{305} ratio. It is therefore necessary to identify the nature of the chains that cause the decrease in UV_{470}/UV_{305} ratio.

The normalized SEC data measured at two different wavelengths is given in Figure 1. There is a significant difference in UV absorption noticed at both lower elution time (i.e., higher molar mass) and at higher elution time (i.e., lower molar mass).

The difference in UV absorption, present at both the higher and lower molar mass, is most likely caused by a disappearance of the thiocarbonyl thio moiety due to termination reactions of some of the chains. Fractionation was used to isolate samples at the higher molecular weight end of this material where the deviation between the two UV absorptions is the highest. Next to the difference in UV absorption it is important to measure at the higher molecular weight end of the distribution as around the peak maximum the concentration of linear chains is large and no termination products will be observed. The fractions from SEC were analyzed with MALDI−ToF−MS to identify possible termination products.

The first fraction is taken at an elution time of 21.5 min. Its mass spectrum is shown in Figure 2. Very clearly, two distributions are observed. The high molar mass distribution can be assigned to terminated chains carrying three UV_{470} chromophores. Next to that there is one thiocarbonyl thio moiety present. The molar mass of this distribution is in agreement with products resulting from intermediate radical termination with a propagating polymer chain. The agreement is shown in the comparison between experimental and theoretical isotope pattern in the bottom two graphs of Figure 2.

The first distribution at lower molar mass is linear pBA. The bimodal distribution observed can be explained by the hydrodynamic volume of the two different chain architectures. It is known that star polymers have a lower hydrodynamic volume compared to their linear equivalent having the same molecular weight. In our case, the stars produced by the intermediate radical termination having a higher molecular weight have the same hydrodynamic volume as the linear polymer of lower molecular weight. Therefore, the two distributions elute at the same elution time in the SEC chromatogram. It needs to be stressed that the origin of the seemingly narrow distributions in the MALDI spectra lies in the fractionation by SEC.

The second fraction at an elution time of 21.9 min also shows a bimodal distribution. The first distribution is assigned to linear poly(butyl acrylate), whereas the second distribution with higher molecular weight corresponds with the termination product carrying four UV_{470} chromophores and two thiocarbonyl thio moieties. This product is most likely formed via termination by combination between two intermediate radicals. The mass spectrum and a relevant expansion of the termination product is shown in Figure 3.

It is expected that intermediate radical termination occurs throughout the whole polymerization and therefore termination products should be found over the whole molecular weight range. This is also the case as we found in our study, even as

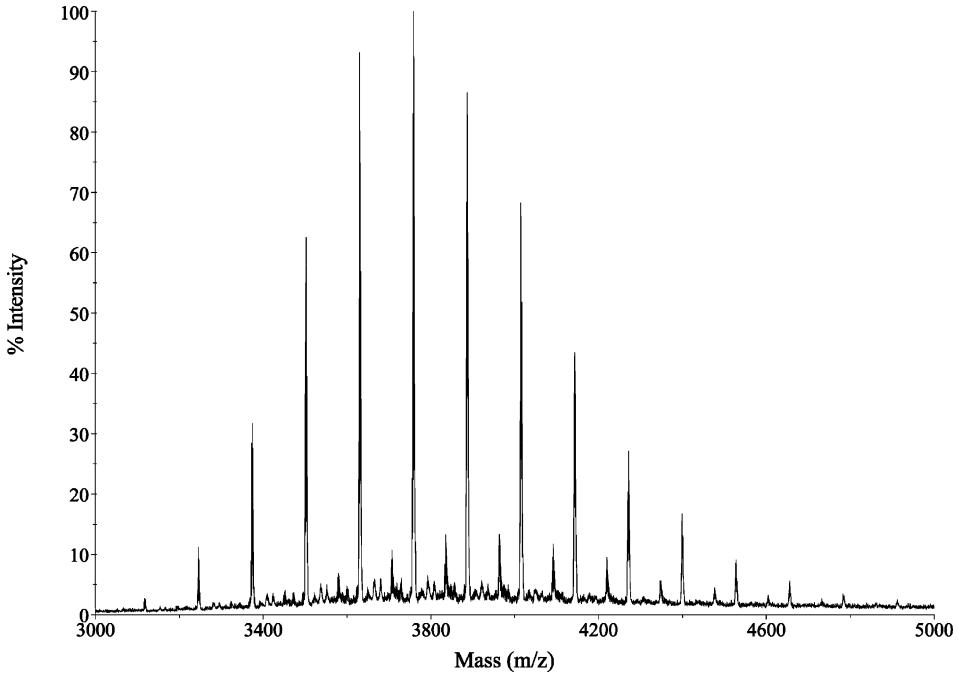


Figure 7. MALDI−ToF mass spectrum of fractionated pBA sample, taken at the end of the polymerization shown in Figure 6. $[M]_0/[I]_0 = 37.3$, $[I]_0/[Cu(I)]_0 = 1.35$, reaction temperature $T = 70$ °C.

early as the termination product of an intermediate radical bearing two monomer units and three leaving groups. These termination products are found in the different samples taken during the polymerization, having an increasing conversion, confirming that the termination products formed are irreversible. Unfortunately, the MALDI−ToF−MS analysis only provides information on the total molar mass and therefore an exact structural representation of the terminated product cannot be given.

A similar study by Ah Toy et al. employed SEC with online ESI-MS detection. In their sample, they identified a large number of polymer species carrying different types of end groups, and originating from various side reactions. In our spectra, there are some species that coincide with the observations of Ah Toy et al. (e.g., trace amounts of the oxidized RAFT agents can be identified in the low molar mass fraction) (see Figure 4). Other species that they find cannot be identified in the current spectra, such as the intermediate radical terminated with a hydrogen atom (their species 3b). However, in the present spectra there seems to be clear evidence for three- and four-arm stars that are absent in the Ah Toy study. It is difficult to pinpoint the origin of these discrepancies, but it could be due to mass spectrometry issues such as ionization method, sensitivity, and mass range of the different instruments.

As known from previous literature, a number of other explanations can be given for the formation of polymer chains bearing multiple leaving groups on one chain. One of the explanations is the often observed chain transfer to polymer of acrylates during a (living) radical polymerization. There are two possible pathways that lead to the introduction of multiple chain ends in a polymer chain. The first one is via intramolecular chain transfer to polymer or backbiting. This backbiting takes place at higher monomer conversion (≈80%) and higher temperature (≈80 °C) and results in bimodality observed in the SEC traces. At the higher temperatures, beta scission of the intermediate radical can occur, which leads to the formation of macromonomers. These macromonomers can subsequently copolymerize, which leads to the introduction of multiple end groups. The second one is via intermolecular chain transfer to polymer, which leads to a midchain radical.[19] This long-lived radical can undergo termination reactions with propagating chains, again leading to the introduction of multiple chain ends.

In our case, no bimodality can be observed in the SEC traces (only in the MALDI−ToF−MS analyses) and therefore we assume no significant chain transfer to polymer occurred in the system causing branching as observed by O'Shea et al.[20] (see also the discussion below).

To confirm that the products found are specific for the RAFT process, a control experiment is performed. ATRP is chosen as the technique for the control experiments because it is an alternative well-known living radical polymerization technique for acrylates. Therefore, the evolution of molar mass as a function of conversion is the same as in the case of RAFT-mediated polymerization. Also, polymerization conditions can be tuned in such a way that conversion versus time is comparable, which means that the propagating radical concentration is similar.

The ATRP polymerization was performed under the same conditions as the RAFT polymerization, and the samples taken during different times of conversion were handled in the same manner.

As expected the polymerization showed a living character having a low polydispersity index and having an increasing M_n with increasing conversion. In Figure 5 a typical MALDI−ToF−MS spectrum is given of a sample at 72% conversion. As shown in Figure 6 the corresponding SEC hardly shows any bimodality. The main distribution found corresponds to linear (dormant) polymer having the initiator fragment on the one side and a bromine chain end. The minor distribution is explained by the same linear chain end but where the bromine chain end is replaced by hydrogen. The latter distribution can be formed during the analysis or during the polymerization.

To come to a good comparison with the RAFT experiments, samples were fractionated at the higher molar mass end of the SEC distribution to find any possible termination products. A typical MALDI−ToF mass spectrum of a relevant fraction is given in Figure 7. The same pattern is found as in the unfractionated sample. The main distribution is the linear

(dormant) pBA. The minor distribution is explained by the linear chain having bromine replaced by hydrogen. Close inspection of the minor peaks in the spectra shows that there are no significant signals that point at the presence of chains carrying more than one initiator fragment. The tiny peaks that are seen among the two main distributions are most likely due to postsource fragmentation, as judged from the poor resolution. This confirms the earlier conclusion that under the conditions of the present experiments chain transfer to polymer and subsequent reactions[19,20] are insignificant.

Hence, the control experiment makes it clear that the termination products found in the RAFT polymerization are not caused by chain transfer to polymer and subsequent termination processes and are inherent to the RAFT process.

Conclusions

The present results provide additional proof of intermediate radical termination in a real polymerization system (i.e., in the presence of monomer). In addition, proof was found that termination products are being formed from the early stages of polymerization onward and remain unchanged throughout. This supports the argument of intermediate radical termination as a possible source for rate retardation and helps the further elucidation of the total RAFT mechanism. Furthermore, they support simulations predicting termination products of intermediate radicals and the terminated products found agree with model systems previously used to mimic intermediate-terminated products. The ATRP control experiment confirmed that the termination products found are inherent to the RAFT process and that these products were not formed by chain transfer to polymer processes.

Acknowledgment. This research forms part of the research program of the Dutch Polymer Institute (DPI), Project No. 494.

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MA0628634