Mapping Poly(butyl acrylate) Product Distributions by Mass Spectrometry in a Wide Temperature Range: Suppression of Midchain Radical Side Reactions

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ABSTRACT: The polymer product spectra of poly(butyl acrylate), polyBA, samples obtained by full conversion bulk polymerization in the temperature range of 60−140 °C in presence of the chain transfer agent (CTA) octylthiol is analyzed via electrospray ionization−mass spectrometry (ESI−MS) and quantitative ^{13}C NMR. The combination of both these analytical techniques allows for very detailed information on the reaction products associated with the formation of midchain radicals to be obtained. At 60 °C, highly uniform polyBA is generated that consists of the structure alkyl−S−$(BA)_n$−H. With increasing temperature, several other peaks emerge that can be assigned to either conventional termination product or to the three different β-scission products of the so-called midchain radicals that are known to be formed in acrylate polymerization via transfer to polymer reactions. Because of the formation of β-scission products that were formed by scission to either side of the radical functionality, intermolecular transfer to polymer presumably plays an important role in the present system. For the 140 °C sample, 1.37 mol % of quaternary carbons on the polymer backbone are identified with only a small fraction of the chains carrying an unsaturated end group. As much higher levels of branching and unsaturation are expected under the same conditions from conventional free radical polymerization, it is concluded that the chain transfer agent is capable of suppressing the midchain radical side reactions to a large extent.

Introduction

The mechanism of acrylate polymerization differs significantly from the ideal free-radical polymerization (FRP) reaction scheme, which is reflected by the observation of reaction orders ω in monomer concentration larger than unity (where $R_P \sim c_M{}^{\omega} c_R$, with R_P being the overall polymerization rate, c_M the monomer concentration, and c_R the radical concentration).[1−3] In the past years it has become widely accepted that these differences originate from the presence of so-called midchain radicals (MCR) and that this type of radical is responsible for the failure of so-called pulsed laser polymerization−size exclusion chromatography (PLP−SEC) experiments for the determination of the propagation rate coefficient at temperatures above room temperature.[4,5] Moreover, a profound impact on the molecular weight distribution in controlled radical polymerization has also been identified.[6−8]

MCRs are formed via chain transfer to polymer reactions where the radical functionality of the secondary propagating radical (SPR) is transferred onto the polymer backbone via an H-shift reaction.[9−12] Such reactions may proceed via *intra*molecular pathways (so-called backbiting, favored to occur via an [1,5] H-shift or, less likely, to remote positions) as well as via *inter*molecular reactions, where a more stabilized tertiary radical is formed in both cases. This radical can subsequently undergo propagation at a significantly reduced rate (being mostly responsible for the observation of nonideal reaction orders), may terminate with any other radical or may undergo β-scission reactions forming unsaturated dead polymer and shortened propagating macroradicals.[10,13,14] As midchain radicals are increasingly formed from temperatures even as low as −40 °C onward,[15] the impact on the molecular weight distributions as well as uniformity of the polymer is high.

While the mechanistic reaction steps arising from the midchain radicals seem to be clear, kinetic coefficients are only partially known for these reactions and often associated with relatively high uncertainty, although the rate parameters for propagation (of the SPR) and termination are accurately known.[4,3] Various attempts have been used to determine individual rate coefficients. Examples for methods of investigation are electron spin resonance (ESR) detection of the midchain radical concentration,[16−18] determination of branching points in the residual polymer[9,11,19] and kinetic modeling of high-temperature polymerizations.[13,14,20] However, for precise determinations of the kinetic rate coefficients governing acrylate polymerizations, it is mandatory to separate the individual reaction steps to study their rate. In search for experimental conditions and methods of observation that allow for such separation, we will herein present a convenient route to (i) fully characterize the polymer product by means of soft-ionization mass spectrometry (MS) and to (ii) significantly reduce the concentration of midchain radicals during polymerization, whereby conditions can be achieved, where no reaction side products from transfer to polymer reactions are to be found in the polymer and thus formation of highly uniform polyacrylate with respect to the end group chemistry is possible.

Such suppression of MCR side reactions becomes feasible by adding a chain transfer agent to the polymerizable reaction mixture. The chain transfer agent (which is octylthiol in the present study) is able to transfer its proton from the thiol function to a growing radical site, which becomes the dominant chain terminating event. The sulfur-centered radical that is produced in the same instance subsequently reinitiates polymerization so that mainly polymer is formed that contains an alkyl−sulfur

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end group on one side and a proton on the other. As will be shown, this mechanism is also operational for the midchain radicals and hence the amount of reaction side products is significantly reduced. A second benefit from employing a CTA in the polymerization is that the average molecular weight is—depending on the CTA concentration—reduced and thus polymer is obtained that is easily analyzable via the so-called electrospray ionization−mass spectrometry (ESI−MS) technique as the resulting molecular weights lie in the mass range of below 2000 $g \cdot mol^{-1}$, which is the limit for the ESI setup used (see below).

While size exclusion chromatography (SEC) allows for easy access to the molecular weight distribution, it does not yield any information about the end groups of the polymer chains. Limited information about the end group composition can, however, be gathered by NMR spectroscopy, whose usage is rather time-consuming and widely hampered by the relative insensitivity and sometimes low solubility of branched polyacrylates. Also, no coupled information on end group chemistry and molecular weight can be obtained. The development of modern soft-ionization mass spectrometry techniques such as matrix assisted laser desorption ionization−time-of-flight (MALDI−TOF) spectrometry and especially ESI−MS gave rise to a convenient route for the unambiguous determination of the product spectrum and its change within the chain length distribution.[21−23] On one hand, those soft ionization techniques have a drawback in that they may not be fully quantitative and/or in that they are restricted to lower molecular weight material. On the other hand, they allow for imaging the product spectrum in great detail and with high accuracy. Hence they are able to provide information that cannot be obtained by other techniques, such as the exact composition of the polymeric chains. Although such knowledge is of advantage especially with respect to the still outstanding problems arising from midchain radical formation, only limited research efforts have been directed at this area. Charleux and co-workers used the MALDI−TOF technique to trace the number of nitroxide end groups in the SG1-mediated polymerization of BA and to detect the influence of intermolecular transfer to polymer (as this potentially leads to more than one active center on the polymer chain).[7] However, in their study, no more detailed information on the product spectrum could be assessed due to the reasonably high yet still limited spectra quality of MALDI−TOF MS. To the best of our knowledge, with a view to investigate the acrylate specific reactions, no other high-resolution MS study has been carried out with the exception of studies into the rather particular system of high-temperature polymerization of BA in xylene solution.[24,25] Because soft ionization mass spectrometry allows for very detailed characterization and mapping of what reactions take place during polymerization, it appears to be of high priority to carry out a systematic MS study directed toward elucidating MCR reactions. In the following, a complete assignment of the MCR derived products in butyl acrylate polymerization will be presented. Additionally, the influence of chain-transfer agents (e.g., thiols) that allow for efficient suppression of secondary reactions of MCRs is discussed as this appears to be an access route to structurally highly uniform polyacrylates.

Experimental Section

Materials. Butyl acrylate (BA, Fluka, 99%) was freed from the inhibitor by percolating over a column of activated basic alumina. Octylthiol (Aldrich, 98.5%) was used as received as was the initiator 1,1-azobis(cyanocyclohexane) (VAZO 88, DuPont). 2,2′-Azoisobutyronitrile (AIBN, DuPont) was recrystallized twice from ethanol prior to use.

Polymerizations. Bulk monomer solutions of BA, thiol and initiator, typically at $c_{octylthiol} = 0.4\ mol \cdot L^{-1}$ and $c_{AIBN} = 5 \times 10^{-3}\ mol \cdot L^{-1}$, were mixed and transferred into sample vials (containing about 2 mL of reactions solution each) and sealed with rubber septa. Oxygen was removed by purging the samples with nitrogen for 15−20 min. After polymerization in a constant temperature oil bath (Julabo HD-4), the samples were rapidly cooled down in either a liquid nitrogen or water bath to cease the reaction. Monomer conversion was subsequently determined by gravimetry. To allow for polymerization to maximum monomer conversion, several samples have been prepared for each reaction condition, and the reaction was stopped after different time periods. The polymer that was obtained after the shortest time interval without showing significant further increase in conversion was subjected to ESI−MS analysis. Nevertheless, as prolonged heating of the polymer and initiator in the absence of monomer may lead to the formation of unwanted products, it was tested whether this may occur on the time scale of the experiment by analyzing polymer samples obtained at 60 °C where heating was continued for an extended time interval (8 h instead of 4 h reaction time). No significant changes in the product spectrum were observed.

Molecular Weight Analysis. For the determination of molecular weight distributions (MWD), a Shimadzu modular system, comprising an auto injector, a Polymer Laboratories 5.0 μm bead-size guard column (50 × 7.5 mm), followed by three linear PL columns (10^5, 10^4, and 10^3 Å) and a differential refractive index detector using THF as the eluent at 40 °C with a flow rate of 1 $mL \cdot min^{-1}$ was used. The SEC system was calibrated using narrow polystyrene standards ranging from 540 to $2 \times 10^6\ g \cdot mol^{-1}$. The resulting molecular weight distributions have been recalibrated using Mark−Houwink parameters for poly(butyl acrylate) ($K = 12.2 \times 10^{-5}$ dL g^{-1}, $\alpha = 0.70$)[26] and for polystyrene ($K = 14.1 \times 10^{-5}\ dL \cdot g^{-1}$ and $\alpha = 0.70$).[27]

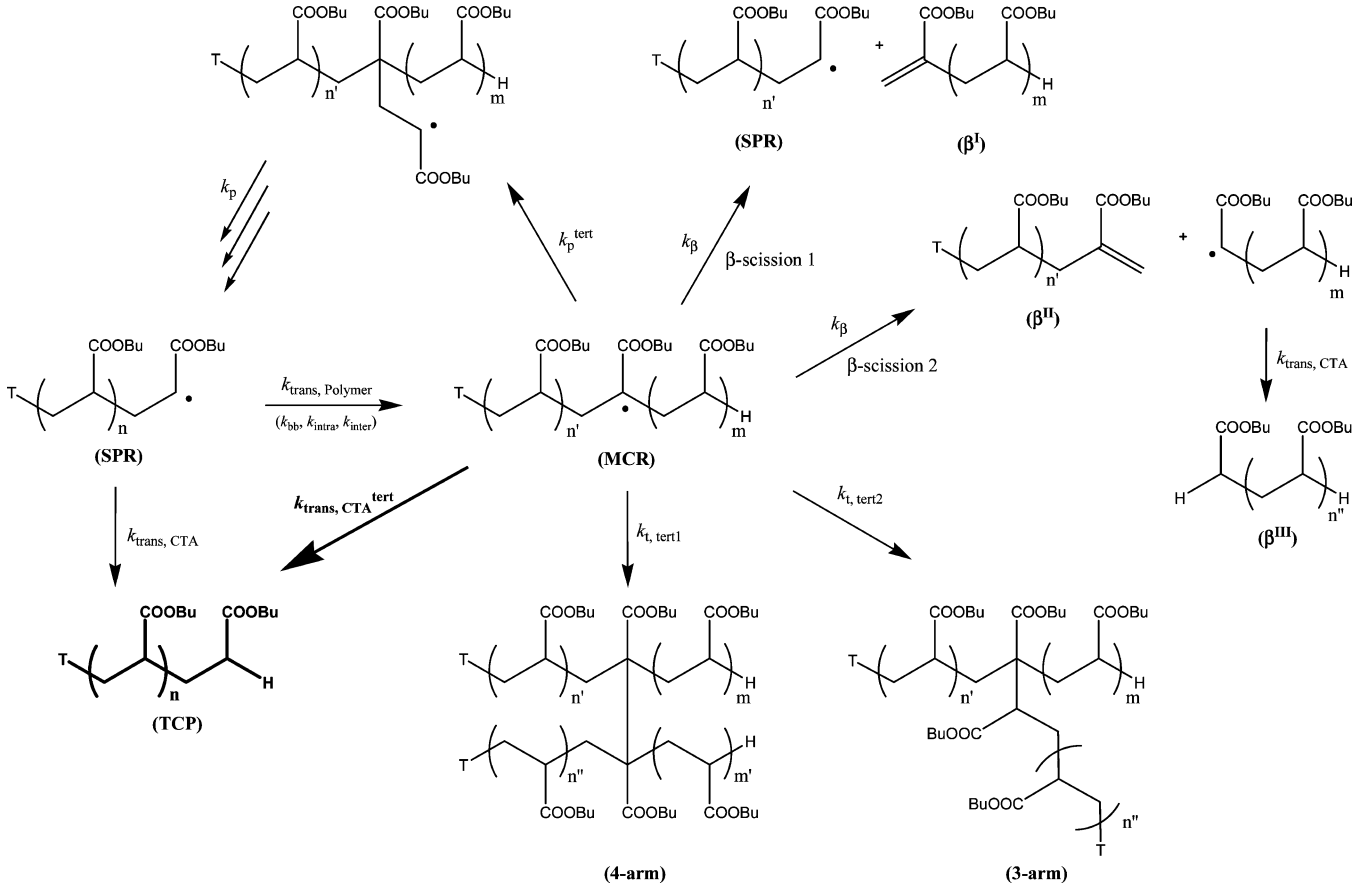
Electrospray Ionization—Mass Spectrometry. ESI−MS experiments were carried out using a Thermo Finnigan LCQ Deca quadrupole ion-trap mass spectrometer (Thermo Finnigan, San Jose, CA)in positive ion mode. The ESI−MS is equipped with an atmospheric pressure ionization source which operates in the nebulizer assisted electrospray mode. The instrument was calibrated with caffeine, MRFA, and Ultramark 1621 (all from Aldrich) in the mass range 195−1822 amu. All spectra were acquired over the mass to charge range (m/z) of 150−2000 Da with a spray voltage of 5 kV, a capillary voltage of 39 V and a capillary temperature of 275 °C. Nitrogen was used as sheath gas (flow: 40 of maximum) while helium was used as auxiliary gas (flow: 5% of maximum in all experiments). The eluent was a 6:4 v/v mixture of THF:methanol with polymer concentration being around 0.4 $mg \cdot mL^{-1}$. The instrumental resolution of the employed experimental setup is 0.1 amu.

NMR Analysis. Ambient temperature ^{13}C NMR spectra were obtained on a Bruker DMX-600 operated at 150.92 MHz of 10 wt % polymer solution in $CDCl_3$. To allow for satisfying signal-to-noise and to adjust for the yield of a quantitatively integrable spectrum, 30° pulses have been employed with 0.5 s recording time of the FID and additional 5 s delay until the next pulse was applied. A total of 10000 scans were coadded to yield one spectrum. To allow for faster longitudinal relaxation tris(acetylacetonato)chromium(III) ($Cr(acac)_3$) was added to the sample. It should be noted that if the delay time between two successive pulses is too short, relaxation is incomplete hence resulting in partial saturation of the spin transition. In consequence, no quantitative information may then be obtained from the spectrum as the various nuclei are subjected to different levels of saturation. For the present work, delay time and pulse angle have been chosen to meet the conditions that have been used before to assess the branching level of poly(butyl acrylate).[9,11,19]

Results and Discussion

As shown in Scheme 1, midchain radicals are generated via *inter*- or *intra*molecular transfer to polymer reactions from the

Scheme 1. Possible Reaction Pathways of Midchain Radicals (MCR) Formed upon Intra- or Intermolecular Transfer to Polymer Reactions in Presence of a Potent Chain-Transfer Agent (CTA)



SPR species. It goes without saying that *inter*molecular transfer is a bimolecular reaction and requires dead polymer to be present, which has not been included in the scheme in order not to overload the figure. Also *intra*molecular transfer might be seen as a bimolecular reaction that increases with the concentration of monomeric units in the polymer backbone available for transfer. What should be treated separately and is a truly unimolecular transfer reaction is the *intra*molecular transfer that occurs via a [1,5] H-shift reaction electronically favored by transition via a six-membered ring structure. This particular H-shift is in the following denoted as "backbiting" with m (number of monomer units as shown for the MCR species) being 2 and the rate coefficient being k_{bb} while all other transfer reactions to random positions on the backbone are assumed to occur with the general rate constant of k_{intra}. Other reactions that SPRs can undergo are chain propagation, termination via combination/disproportionation and transfer to a CTA. The scheme is shown for a thiol-type transfer agent that transfers a proton to the radical site leaving a radical fragment T that can reinitiate polymerization. As the majority of all chains will carry such a T end group, all structures in Scheme 1 originate from an SPR as depicted. In principle, a small portion of chains will carry an initiator fragment end group whose products are not shown in the scheme as they are mostly not identified in the resulting spectra.

In the present system, midchain radicals can follow four major reaction pathways of which three are typical for any acrylate polymerization system. MCRs can undergo chain propagation (associated with the reduced rate coefficient k_p^{tert}), by which the tertiary radical is transformed back into a SPR leading to some sort of equilibration between both species while forming short-chain or long-chain branches. Alternatively, the MCR can undergo β-scission, potentially resulting in four different products, of which one is again identical to the SPR. Two other fragments are dead polymer chains carrying an unsaturated end group (species β^{I} and β^{II}). The fourth fragment is a radical that may undergo transfer to CTA (β^{III}) or chain extension until it is either terminated, or—most likely in the presence of a CTA—its chain growth is ended by a transfer which results in a polymer chain that is mass-wise indistinguishable from β^{III}. The third reaction pathway for MCRs is termination forming either a 4-arm or a 3-arm star by combination. Considering the steric hindrance of an MCR, disproportionation may also be taking place yielding unbranched dead chains that can almost not be distinguished from conventional termination products. Because transfer to polymer always results in radicals coinciding in mass with the corresponding SPR, both termination products are fully indistinguishable from conventional termination products via MS. The only exception would, in principle, be stars that contain more than two end groups other than a proton which may only be produced by intermolecular transfer reactions. Species β^{I} is most probably congruent with the polymer that is formed after transfer to monomer has taken place. As no such peak is identified for polymer synthesized at lower temperature (and hence no production of β^{I} either), it is likely that this reaction plays no major role in the systems under investigation and hence was not included in the scheme.

The *fourth* possible pathway of the MCR shown is the potential abstraction of a proton from the CTA, hence forming a dead, linear chain, whose product is indistinguishable from the product formed upon H-abstraction to a SPR. The occurrence of H-abstractions by the MCR from the CTA (as aimed at in

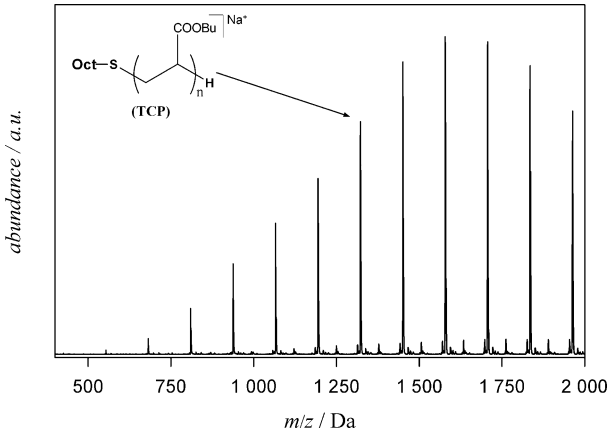


Figure 1. ESI−MS spectrum of polymer obtained from bulk polymerization of butyl acrylate at 60 °C in the presence of 0.4 mol·L^{-1} octylthiol initiated by 5·10^{-3} mol·L^{-1} AIBN. The polymerization was carried out for 4 h until almost full conversion of monomer was reached.

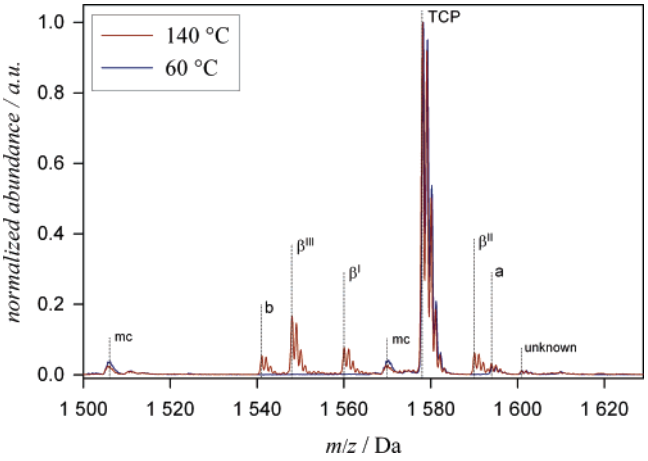


Figure 2. ESI−MS spectrum of polymer obtained from bulk polymerization of butyl acrylate at 60 and 140 °C, respectively, in the presence of 0.4 mol·L^{-1} octylthiol initiated by 5·10^{-3} mol·L^{-1} AIBN (60 °C) or Vazo-88 (140 °C). Each polymerization was carried out until almost full conversion of monomer was reached. The given labels correspond to Scheme 1 and 2 (where *T* stands for an octyl-S group) and the lines represent the theoretical *m*/*z*. mc denote peaks which are multiply charged.

the present study) may not be immediately apparent and its consequences on the end group chemistry and branching levels in acrylate polymerization have not yet been explored.

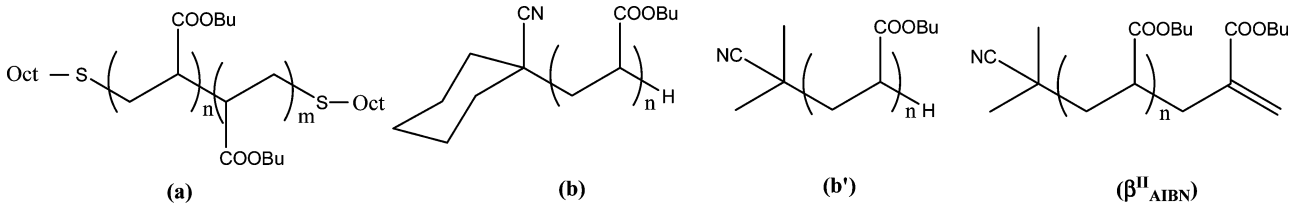
An ESI−MS spectrum of polyBA obtained from bulk polymerization at 60 °C to almost full monomer conversion in the presence of significant amounts of octylthiol (at a concentration of 0.4 mol·L^{-1} being chosen to allow for an average molecular weight of well below 2000 g·mol^{-1}) is depicted in Figure 1. As can be seen, the product spectrum indicates that almost none of the side products depicted in Scheme 1 are formed during the reaction and that the vast majority of chains consist of thiol-capped polymer (TCP, see Scheme 1). Most of the small peaks visible in Figure 1 are unambiguously identified to represent multiply charged species as the spacing between to isotopic peaks is smaller than one *m*/*z* unit (i.e., exactly 0.5 *m*/*z* for doubly charged species). Closer inspection into a single monomer repeat unit of the spectrum, as depicted in Figure 2, however, reveals the presence of a very small quantity of termination by combination product **a** (see Scheme 2). No mass peak according to a disproportionation product can be identified in the spectrum suggesting that combination is the primarily mode of termination in the system. This observation does not fully agree with our previous MS study on polyBA produced under pulse laser polymerization conditions at low temperatures.[28] However, the ratio between combination and disproportionation is known to change with temperature.[29,30] Additionally, the ratio could have been influenced in the previous study by the very high radical concentrations (and also other very different reaction conditions) occurring under laser irradiation. It should also been noted that **b** coincides in mass with the three and four arm stars as shown in Scheme 1. Unfortunately, mass spectrometry is unable to distinguish between the star/long chain branch structure and the normal combination product **b**, thus no clear conclusion can be drawn from the spectrum. Only star polymers that carry more than two nonproton end groups, formed after *inter*molecular transfer to polymer reactions would allow a clear detection of branched polymers. However, as the vast majority of polymer material consists of the TCP species, no such product may be formed in the present system.

Regardless of backbiting taking place or not, it is quite remarkable to generate such a clean spectrum of polyBA, where a multitude of products is usually expected. It is known from low conversion ESR experiments that at 60 °C the majority of radicals are—under normal reaction conditions, that is without addition of a CTA—of the MCR species.[15] It was also shown that the MCR concentration is likely to increase even further with ongoing polymerization as monomer becomes less available (decreasing the probability of chain propagation of the MCR) and the increasing polymer concentration favors *inter*molecular transfer.

As is shown in Scheme 1, MCRs can not only undergo chain propagation or termination forming long or short-chain branches, they can also undergo β-scission reactions yielding unsaturated polymer end groups, whose formation was reported for temperatures as low as 80 °C and whose presence is easy to establish via ^{1}H NMR.[10,20] However, no such macromonomeric species can be identified in the present example, neither in the ESI−MS spectrum, nor by NMR spectroscopy, although its formation is likely to occur at 60 °C under normal reaction conditions.[8]

It may hence be concluded that the presence of the CTA suppresses the secondary reactions of the MCR such as β-scission rather effectively under the given conditions. While the β-scission reactions are associated with a rather high activation energy and hence are not expected to be overly pronounced at 60 °C, measurable amounts of those side products would nevertheless be expected under the chosen conditions.[8] However, before any scission reaction may take place, the CTA

Scheme 2. Possible Reaction Products of Chain-Transfer Polymerization of BA with Octyl Thiol



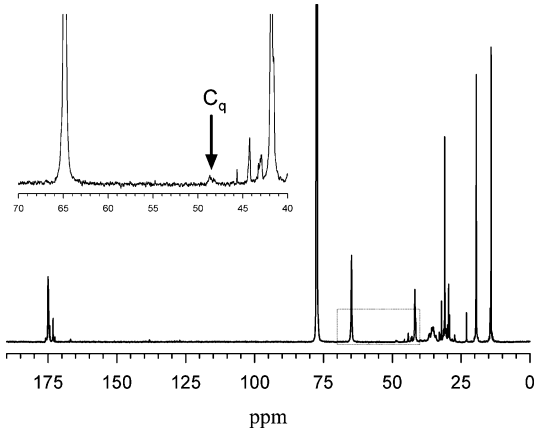


Figure 3. ^{13}C NMR of polymer obtained from full conversion BA bulk polymerization at 140 °C with $c_{AIBN} = 5 \cdot 10^{-3}$ mol·L^{-1} and $c_{SH} = 0.4$ mol·L^{-1} octylthiol carried out until almost full conversion. For an assignment of the relevant peaks in the spectrum the reader is referred to the literature.[9] The relevant peak of the quaternary backbone peak is marked in the inset.

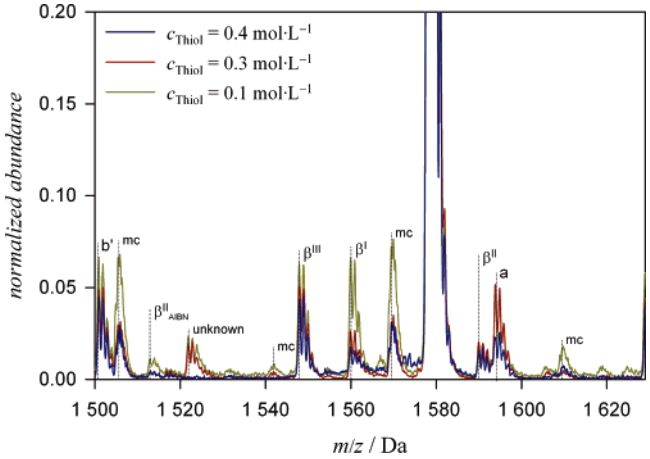


Figure 4. ESI−MS spectra of polyBA obtained from bulk polymerization at 80 °C in the presence of the amounts of octylthiol as indicated. Polymerization was initiated by $5 \cdot 10^{-3}$ mol·L^{-1} AIBN. The spectra have been normalized on the main product peak at 1578.1 Da to allow for comparability of the amounts of side products formed.

intervenes, acting as an effective repair device that mends the MCR, forming a linear dead chain.

Consequently, experiments at elevated temperatures were carried out to further confirm the hypothesis of a self-repairing acrylate system. Also shown in Figure 2 is the spectrum observed for the polymerization product obtained from bulk polymerization at 140 °C. Besides VAZO-88 being used as initiator (because AIBN would decay too fast to allow for an almost complete reaction) and besides change in reaction temperatures, no other experimental parameter was altered compared to the 60 °C sample.

Formation of four new products is clearly observed, three of which are products of the β-scission reaction. In principle, the scission reactions yield four different fragments. However, the fourth fragment is identical to a normal propagating chain and hence does not separately show up. The fourth fragment **b** coincides in mass with an azo-fragment initiated polymer chain whose appearance in the spectrum indicates the much higher average radical concentration at 140 °C compared to 60 °C even when a different initiator is used (a peak according to the mass of **b′** is also found in AIBN-initiated polymer when the reaction temperature and thus radical concentration is increased, see Figure 4). Only one peak remains unassigned, at an *m*/*z* ration of approximately 1601 Da. The same peak also appears (in the same quantity) in the 60 °C spectrum, but it is too low in abundance to allow for an unambiguous assignment and is not considered to be significant. However, all assigned species match the experimental data with an accuracy of 0.1 Da, which is the accepted accuracy limit of the quadrupole ion-trap ESI−MS. Theoretical and experimental *m*/*z* ratios for the monoisotopic peak are given in Table 1. Additionally, the isotopic patterns can be simulated based on the empirical formulas of the assigned products in good agreement with the experimental data.

That the fragments $\beta^{\mathbf{I-III}}$ appear in almost equal amounts indicates that the scission reaction is not favored to take place to one specific side, which is to be expected because the electronic nature is almost the same on either side. (It should be noted that in principle two different macromonomers plus two corresponding nonunsaturated fragments are formed. Probably because it is of no concern for rate-based investigations this is not always taken into account and therefore some literature studies only focus on the scission reaction forming $\beta^{\mathbf{II}}$).[14,24,25] More interestingly is, however, that the relative large quantities of $\beta^{\mathbf{I}}$ indicate that *inter*molecular transfer to polymer and *intra*molecular transfer to polymer to remote backbone positions take place to significant extents, as this fragment would only consist of two monomeric units and hence not show up in the displayed monomer repeat unit if backbiting via a six-membered ring was the only pathway.

Table 1. Theoretical and Experimental Mass of the Monoisotopic Peaks of Products Occurring in the Chain-Transfer Polymerization of BA with Octyl Thiol in the *m*/*z* Range between 1500 and 1629 Da[a]

species	theoretical *m*/z/Da	experimental *m*/z/Da
TCP	1578.02	1578.13
$\beta^{\mathbf{I}}$	1560.00	1560.07
$\beta^{\mathbf{II}}$	1590.02	1590.07
$\beta^{\mathbf{III}}$	1547.99	1548.07
a	1594.04	1593.93
b	1541.00	1541.07
b′	1500.97	1500.93
$\beta^{\mathbf{II}}{}_{AIBN}$	1512.96	1512.93

[a] All numbers refer to sodium adducts.

Also interesting is the amount of the unsaturated β-scission products relative to the main product peak. The most abundant β-scission peak ($\beta^{\mathbf{III}}$) shows less than 20% of the TCP signal strength and the peak of the second unsaturated product $\beta^{\mathbf{I}}$ shows slightly less than 10% abundance. While such amounts are quite significant, both are nevertheless minor products. Chiefari et al. reported formation of macromonomer in quantities above 90% at the same reaction temperature,[10] if yet at low monomer concentrations (which of course favors scission reactions over short-chain branching via MCR propagation). Also, for the BA polymerization in xylene at high temperatures, macromonomers have been identified to be the main product from NMR as well as from ESI−MS characterization.[24−26] Although scission products are clearly visible, their amount is widely reduced in the CTA system again demonstrating the repairing function of the CTA.

However, as ESI−MS is not a quantitative method, it cannot be excluded that slightly biased results are yielded due to suppression of ionization of the different end group functionalities. Although an almost complete suppression does not appear to be likely as very high ion counts could be achieved when analyzing the polyBA samples, the extent of ionization differences were tested by mixing a high-temperature octylthiol-mediated polyBA sample with macromonomer obtained by a

slightly modified procedure given by Chiefari et al.[10] by which an ESI−MS spectrum was obtained that satisfactorily reflected the mixing ratio in relative abundance of the peaks.[31] More detailed information on the quantification of the various species on the basis of the spectra can be found in the Supporting Information.

An alternative way to test for suppression of secondary MCR reactions is quantitative ^{13}C NMR spectroscopy. Such data are complementary to the ESI−MS data as they give access to the number of branchpoints in the polymer. Branchpoints are identified by observing the characteristic peak of the quaternary backbone carbon. By comparing the integral of such a peak (47.5−49.1 ppm) with the integral of one of the ester side chain peaks (e.g., the carbon closest to the ester function, 63.5−66.0 ppm) the mol-percentage of branchpoints in the sample is obtained. Multiplying this number by the average degree of polymerization yields the average number of branches per chain. It should be noted that due to the rather long relaxation time of quaternary carbons as well as due to the nuclear Overhauser effect such quantitative investigation are not easily done and must be treated with care. However, for the present study, NMR measuring parameters were chosen to match those used in the literature before (see experimental part) and are believed to yield adequately quantitative spectra. Regardless, the determination of the number of branches per chain via this method does not resolve whether the branching belongs to a short or a long chain branch and is therefore incapable to distinguish between *inter*- and *intra*molecular transfer. Despite this problem, ESI−MS in conjunction with ^{13}C NMR allows for an almost complete mapping of the secondary MCR reactions.

Shown in Figure 3 is the ^{13}C NMR spectrum of the sample obtained at 140 °C discussed above in conjunction with the ESI−MS data. Consistent with the observation of some β-scission products, small peaks in the double-bond region appear at 127 and 138 ppm. Accordingly, small signals indicating protons located at a double bond are also visible in the ^{1}H NMR spectrum (which are, however, not to be seen in the spectrum that was taken for the polyBA obtained at 60 °C).

Integration of the quaternary carbon peak and the ester side chain peak at 65 ppm yields a mol percentage of 1.37 of branched monomer units. With the number-average molecular weight of 1720 g·mol^{-1}, the number of branches per chain can be calculated to be close to 0.2. This level of branching is close to the level reported for 60 °C RAFT polymerization up to almost full conversion again indicating the MCR-suppressing ability of the CTA as much higher levels of branching are to be expected when the temperature is increased.[8] Even higher values, up to nearly 5%, were reported for 70 °C,[9] if only at lower monomer concentrations, which favors β-scission to some degree. Most other literature data deal with less converted systems and the numbers are thus hardly comparable. Nevertheless, mostly all literature data suggest much higher branching levels than identified for the octhylthiol-mediated sample of the present study.

If the CTA repairs the midchain radical functionality, decreasing the thiol concentration should increase the amount of side products as the absolute rate of transfer is reduced. As expected, when the thiol concentration is reduced from 0.4 to 0.1 mol·L^{-1}, the number-average molecular weight increases from 2230 to 4510 g·mol^{-1}. At the same time, as is evident from the mass spectra depicted in Figure 4, an increase in β-scission products as well as of termination product **a** is seen. However, although the total amount of side products increases, it should be noted that the total amount is yet much lower than in the sample taken at 140 °C indicating that even at reduced thiol concentrations, secondary MCR reactions are still considerably reduced. Again, no disproportionation product can be identified in the spectrum. In addition to the peaks identified above in the spectra shown in Figure 2, product peaks according to the structures **b′** and β^{II}_{AIBN} (see Scheme 2) appear. The presence of **b′** is a consequence of the increased radical concentration at 80 °C as compared to 60 °C. At the same time, as significant amounts of **b′** are present in the system, the β-scission product carrying an AIBN end group instead of a thiol group is also formed. However, one more peak appears at 1521.9 Da that is not present in the system at the highest thiol concentration. However, no structure, including macromonomer insertion into other chains, which was assumed to occur in some butyl acrylate polymerizations[8,25] could yet be assigned to this *m*/*z* ratio. Unfortunately, it could not be tested for any further increase of the side product peaks, as samples obtained at even lower thiol concentrations cannot yet be analyzed as the MWD shifts significantly to larger molecular weight and hence not enough material in the ESI mass range is available for ionization. The same effect is already evident from the present data, because absolute abundance is of course much smaller in the chosen mass range for the lower thiol concentrations. Hence multiple charged species appear more abundantly than they actually are as they reflect higher molecular weight species. Comparing the amounts of the other (single-charged) species nevertheless remains valid because β-scission and "normal" transfer should in principle occur to similar extents irrespective of chain length.

Conclusions

Electrospray ionization mass spectrometry allows for detailed mapping of the product spectrum in acrylate polymerization giving access to mechanistic information that are complementary to the data obtained by size exclusion chromatography (MWD) and ^{13}C NMR (branching level). The main product peak found in the ESI−MS spectra obtained from polymer made by octylthiol mediated polymerization could be assigned to the expected transfer to thiol product. At lower temperatures, this peak was almost exclusively found with slight traces of termination product being present. At elevated temperatures, additionally four β-scission products can be identified in the spectrum that arise from scission to both sides of the midchain radical indicating pronounced levels of intermolecular transfer to polymer taking place. Because the chain transfer agent is able to patch the midchain radical by transferring its proton to the backbone radical, mostly unbranched polymer chains are formed and the secondary reactions, such as β-scission are (partially) suppressed giving access to more uniform polyBA than would be obtained under the same conditions from conventional polymerization.

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Supporting Information Available: Text discussing the impact of the ionization ability of the polymer end groups on the identified ratio of abundances and a figure showing ESI-MS spectra of the

polyBA sample previously shown in Figure 2 for different optimizations of the instrument on the different peaks. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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(31) polyBA macromonomer has been synthesized by polymerization of BA in butyl acetate solution (5 *w*%) at a low initiator concentration. The polymerization was continued for 45 min at 140 °C. A complete characterization of the macromonomer obtained will be published in an upcoming study.

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