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COMMUNICATION TO THE EDITOR

Reducing the Degree of Branching in Polyacrylates via Midchain Radical Patching: A Quantitative Melt-State NMR Study

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Introduction. The radical polymerization of acrylates leads to polymers with a high degree of branching caused by the formation of so-called midchain radicals (MCRs).[1] Such midchain radicals are formed via intra- and intermolecular (chain) transfer to polymer reactions caused by the high reactivity of the propagating radical species (secondary propagating radicals (SPR)). The generated MCRs (which can represent up to 80% of the total radical population at temperatures exceeding 80 °C)[2,3] can subsequently react with monomer units (albeit at a reduced rate compared to SPRs),[4] participate in bimolecular termination events (either with themselves or with SPRs), or undergo β-scission reactions to yield macromonomer species and SPRs[5] (see Scheme 1).

Soft ionization mass spectrometry techniques allowed a detailed study of the product spectra that emerge from the radical polymerization of *n*-butyl acrylate (BA) in the presence of 1-octanethiol as a chain transfer agent (CTA).[6,7] The presence of the CTA, beside leading to a reduction in the molecular weight of the generated polymeric materials, greatly influences the product distribution of the obtained polymer. Specifically, with increasing concentrations of CTA the amount of unsaturated β-scission product was progressively reduced to levels where practically no β-scission product was detected at intermediate temperatures and only low levels at elevated temperatures (note that under such conditions the majority of material usually consists of β-scission products, quantitative data on what fraction of chains contain either the thiol-specific moiety or other end groups have been provided before).[8−11] The explanation for such an observation can be provided by a rapid transfer of a hydrogen from the transfer agent to the relatively long-lived MCR at a higher rate than the MCR can undergo β-scission (see Scheme 1). The hypothesis was also tendered that the degree of branching in the generated polymeric material would be significantly reduced by a similar amount as the formation of the β-scission product is suppressed.[7] However, branching is not observable via electrospray ionization mass spectrometry (ESI-MS) due to the isobaric nature of the branched and linear structures. The only method for directly accessing the degree of branching in polyacrylates is quantitative ^{13}C NMR spectroscopy.[12]

Quantitative ^{13}C NMR spectroscopy is no routine method. There have been several attempts to quantify the degree of branching in polyacrylates synthesized in various conditions, with various NMR methods.[12−14] Both resolution and sensitivity are required for a reliable quantification of the degree of branching. Initial attempts were carried out either on polymer solutions[13] or on swollen samples;[14] they exhibit high resolution (owing to high sample mobility) but suffer from limited sensitivity (and thus low precision) partly due to limited sample concentration. Moreover, polyacrylates often exhibit a significant gel fraction and only the soluble fraction (and thus a fraction that assumingly consists of polymer with fewer branches) of the sample is measured in some cases.[12] Recently, however, a method has been proposed and validated to estimate the precision of the determined degree of branching from the signal-to-noise ratio of the quaternary carbon at the branching point.[12,15] As for any experimentally determined quantity, taking the precision into account allows for a meaningful comparison of samples. In an earlier study of the possible patching of MCRs,[7] an attempt was made to determine the degree of branching via ^{13}C NMR in solution. Unfortunately, the low signal-to-noise ratio of the quaternary carbon (5.5) led to a rather limited precision on the measured degree of branching (27% according to eq 2 below). A degree of branching in the range of 1.0 to 1.8% of the monomer units at 140 °C at a 1-octanethiol concentration of 0.4 $\text{mol}\cdot\text{L}^{-1}$ was found. No literature data allowed for direct comparison in terms of effect of CTA, and the somewhat higher value of close to 2% found in some known systems with similarity (bulk) but at a far lower temperature (70 °C)[16] was not significantly different. A general increase of the degree of branching with reaction temperature is expected, thus the similar results led to the speculation that the CTA addition leads to lower number of branches in the polymer. The latter measurement was obtained by fast-pulsing NMR,[13,16] yielding a precise but inaccurate value; a calibration carried out with a longer measurement time was not shown[16] from which the precision could have been estimated. Therefore, although previous mass spectrometry results hinted at a MCR patcher (and thus branching suppression) effect, previous NMR results were not precise and accurate enough to confirm the effect.

We recently developed a reliable melt-state ^{13}C NMR method for the quantification of the degree of branching in polyacrylates.[12] Quantitative ^{13}C melt-state NMR is described in detail in the literature[12,15] and has also been used to quantify branching or chain ends in polyolefins.[15,17−19] Melt-state NMR (using solid-state NMR equipment) is more sensitive than solution- or gel-based methods as it measures the pure (undiluted) sample. It yields sufficient resolution for branching quantification through the high mobility of polymer chains in the melt combined with magic-angle spinning and dipolar decoupling. The

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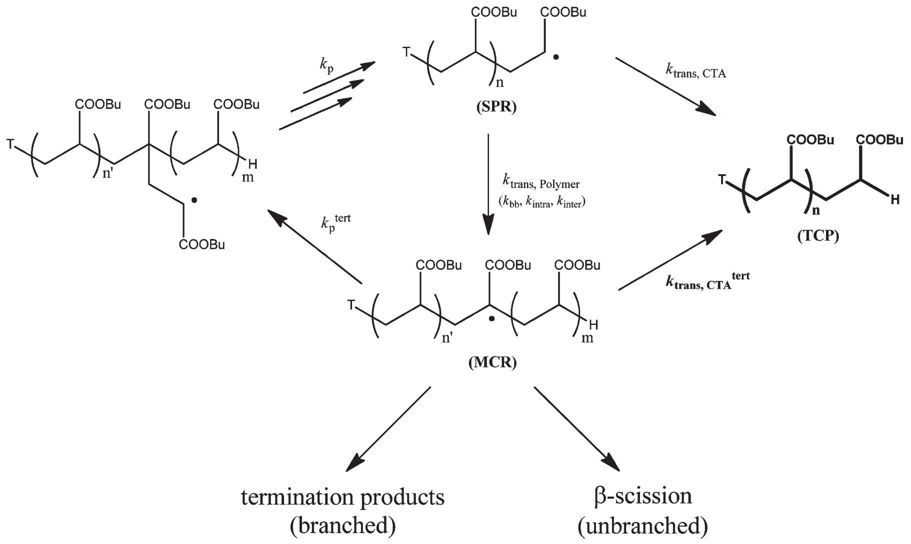
Scheme 1. Reaction Pathways of MCRs[a]



[a] In the presence of a CTA, the MCRs are transformed ("patched") into thiol-capped linear polyacrylate species (TCP). T is the initiating moiety arising from the initiator or the thiol.

accuracy of measured degrees of branching is ensured by full relaxation of the relevant signals between pulses.[12] In the current communication, we employ the melt-state ^{13}C NMR method to compare degrees of branching in polyBAs synthesized with and without CTA (at various temperatures) and investigate whether the inclusion of an efficient hydrogen donor in the polymerization actually leads to a strong reduction in the degrees of branching observed in polyacrylates in agreement with the hypothesis tendered from earlier mass spectrometry results on the same system.

Experimental Section. Materials and radical polymerization in bulk at various temperatures with or without 1-octanethiol were similar to those of previous works.[6,7] Long-chain branches can lead to a high level of band broadening in size-exclusion chromatography (SEC).[20] The molecular weights from SEC might thus be of limited accuracy.[21] The glass transition temperature (T_g) and decomposition temperature were measured for all samples using differential scanning calorimetry and thermogravimetric analysis. Details of materials, polymerization, SEC, and thermal analysis can be found in Supporting Information.

Quantitative ^{13}C melt-state NMR experiments followed variations of a published method[12] with single-pulse excitation under magic-angle spinning (SPE-MAS) at exactly $T_g + 150$ °C (77 to 104 °C, more than 200 °C below their decomposition temperature) and 75.47 MHz with 10 s relaxation delay. Nitrogen gas was used for all pneumatics. Samples synthesized with thiol were measured in 7 mm rotors at MAS rotational frequencies of 1.8 to 4.5 kHz, while samples synthesized without thiol were measured in 4 mm rotors at 9 kHz MAS (due to extensive cross-linking preventing their spinning in 7 mm rotors). Nitrogen gas was used for all pneumatics. More experimental NMR details are given in Supporting Information. The degree of branching (DB) was quantified in percents of the monomer units from the integrals I of the signals of the quaternary carbons (C_q) at 49 ppm and of the OCH_2 moiety at 63 ppm, following eq 1

$$\mathrm{DB}(\%) = \frac{I(\mathrm{C_q})100}{I(\mathrm{OCH_2})} \tag{1}$$

Note that due to a signal from 1-octanethiol overlapping with the backbone signal of polyBA, the latter could not be used for quantification. The full chemical shift assignment, known from literature,[14,22] is detailed in the Supporting Information. The relative standard deviation SD of DB was calculated from the signal-to-noise ratio of the quaternary carbon SNR using eq 2, established experimentally from branching measurements in polyethylene by ^{13}C melt-state NMR[15]

$$\mathrm{SD}(\%) = \frac{238}{\mathrm{SNR}^{1.28}} \tag{2}$$

Its deviation from the theoretically expected dependency of SD on 1/SNR (with only limited practical differences), and its wider applicability were discussed for branching measurements for poly(n-alkyl acrylates).[12]

Results and Discussion. The presence of 1-octanethiol during the polymerization has significant effects on its mechanism and on the obtained polymer, such as a significant reduction in terminal double bonds,[7] as well as a decrease in molecular weight as demonstrated by calorimetry and SEC (see Tables S3 and S1 in Supporting Information). As the chain length of the polymer is expected to influence the local chain dynamics, which may change the conditions for recording quantitative ^{13}C melt-state NMR spectra, all spectra were recorded at exactly 150 °C above the T_g. The ^{13}C melt-state NMR spectra of the samples exhibiting the lowest and the highest DB are shown in Figure 1. The DB values measured for all samples are shown in Figure 2 with their precision and listed in Table S3 (Supporting Information).

The degrees of branching obtained in the CTA-containing systems are significantly lower than the ones obtained in the conventional system for all temperatures as can be seen in Figure 2. The "patching" effect of tertiary midchain radicals by the CTA can thus be confirmed as operational. In addition, the degree of branching significantly increases with increasing temperature, for both the CTA and non-CTA systems. Such an observation is explicable by the increased frequency of the reactions that lead to the formation of MCRs, that is, intermolecular chain transfer as well as random intramolecular transfer and backbiting. Typical

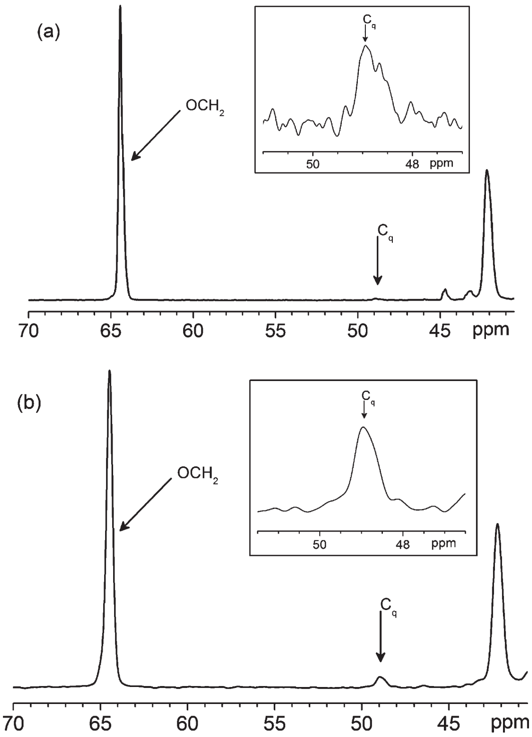


Figure 1. Melt-state ^{13}C SPE-MAS NMR spectra recorded at T_g + 150 °C for poly(n-butyl acrylate) samples synthesized at 60 °C with thiol (a) and at 140 °C without thiol (b).

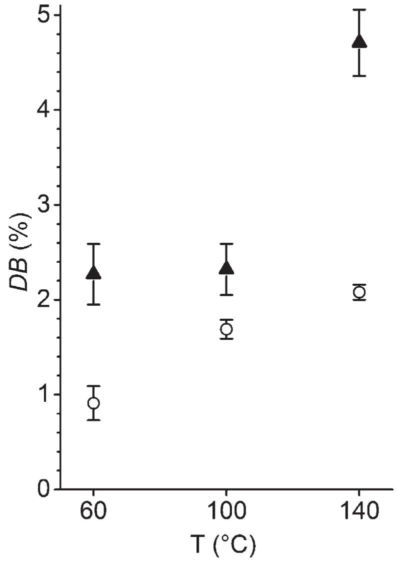


Figure 2. Degree of branching (in percent of monomers units) as a function of the reaction temperature for poly(n-butyl acrylates) polymerized in bulk in the absence (solid triangles ▲) or presence (empty circles ○) of 0.4 mol·L^{-1} 1-octanethiol as chain transfer agent. The error bars given for each measurement were calculated according to eq 2.

activation energies for the rate coefficients governing these reactions may be 20 to 25 kJ·mol^{-1} higher than that of propagation.[1] At the same time, the transfer rate of the CTA onto the MCR may be hypothesized to be similar to the one of propagation. Therefore, even though the CTA is capable of reducing the amount of branching significantly, its effectiveness decreases with increasing temperature. Generally, it should be noted that of course the CTA not only reduces the amount of branching, but also the average chain length of polymers. The reduction of chain length is however a separate effect that may influence the number of branches per chain (as expected in pulsed laser polymerization),[4,23] but it does not directly influence the number of branches per monomer unit (degree of branching). The conventional transfer to the CTA does not change the (macro-)radical concentration, hence the frequency at which transfer to polymer reactions occur is unchanged. As MCRs, once they are formed they are then either patched (which in fact is a conventional transfer to CTA reaction itself), undergo scission, or form a chain branch; the number of branches per chain units or the concentration of scission products is not affected by the chain-length reducing action of the CTA. Overall the NMR results confirm and support our previous mass spectrometric findings relating to the β-scission products[6,7] as the reduction in degree of branching and the reduction in the amount of β-scission product correspond well with each other. The degrees of branching obtained in this work moreover now allow for more detailed investigations into the kinetics of acrylate polymerizations. Both mass spectrometric and NMR spectroscopic data are highly complementary to each other. Together they provide a complete microstructural image of the obtained polymer product. Even though numerous studies have shown by ^{13}C NMR that branching plays an important role, only with the present work have reliable quantitative data become available for a systematic variation of reaction conditions that can be utilized for further kinetic and mechanistic studies that will help to find improved conditions for polyacrylate synthesis in numerous applications.

Conclusions. Degrees of branching were measured with ^{13}C melt-state NMR in poly(n-butyl acrylates) synthesized in both the presence and absence of 1-octanethiol at various temperatures, and their precision calculated based on the signal-to-noise ratio of the quaternary carbon at the branching point. A significant decrease of branching was observed in the presence of a thiol during the polymerization process, experimentally confirming the "patching" effect of midchain tertiary radicals by the thiol. Thus, the addition of a chain transfer agent not only controls the chain length of the polyacrylate, but also the complexity of its microstructure is significantly reduced. In addition, the current work illustrates the potential of melt-state NMR for the quantitative determination of the degrees of branching with precision for example, for kinetics studies.[24]

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Supporting Information Available: Experimental details and results for polymerization, size-exclusion chromatography, thermal analysis, and ^{13}C NMR. This material is available free of charge via the Internet at http://pubs.acs.org.

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