Structural Characterization of Nitroxide-Terminated Poly(*n*-butyl acrylate) Prepared in Bulk and Miniemulsion Polymerizations

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ABSTRACT: The structure of "living" poly(*n*-butyl acrylate) homopolymers prepared via nitroxide-mediated controlled radical polymerization in bulk and in miniemulsion at 112 °C was examined by SEC, NMR, and MALDI−TOF mass spectrometry in order to study the influence of chain transfer to polymer. The absence of detectable terminal unsaturation was confirmed by proton NMR. The branched structure was observed by ^{13}C NMR. MALDI−TOF MS demonstrated that the majority of chains, even at high conversion, had the ideal structure with one initiator fragment and one nitroxide end group. From these results, we concluded that intramolecular chain transfer occurred (presumably by backbiting) and was the predominant mechanism throughout the polymerization at 112 °C.

Introduction

Controlled radical polymerization (CRP)[1] offers the possibility to control the molar mass and molar mass distribution of polymers using the very versatile and robust radical chemistry. Stable free-radical polymerization (SFRP), using mainly nitroxides,[1−5] atom transfer radical polymerization (ATRP),[6−9] and reversible addition−fragmentation transfer (RAFT)[10,11] are currently the most common techniques used to achieve this goal. Concerning the former one, with the earlier use of TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy) and related cyclic nitroxides, the truly controlled polymerization was however essentially restricted to styrenic monomers. The design of new acyclic nitroxides, bearing a hydrogen atom on the carbon α to the N−O group made the controlled radical polymerization of acrylic monomers possible.[12,13] The so-called SG1 nitroxide is one of them (Scheme 1).[13] This enabled copolymers of styrene and acrylates to be synthesized with well-defined architectures, including diblock, triblock, star, and star−block copolymers.[5] For the preparation of macromolecules with a high degree of structural and compositional homogeneity, controlled radical polymerization can compete with the older ionic polymerizations with the additional advantage of being tolerant to water, hence allowing polymerization to be performed in aqueous dispersions.[14] Nevertheless, while anionic polymerization of acrylic monomers leads to linear and well-defined structures, the radical process suffers from several side reactions, mainly chain transfer reactions to monomer and to polymer. The former limits the achievable M_n and the latter leads to either branched structures or macromonomers. Branched structures have been well examined by ^{13}C NMR spectroscopy for poly(acrylate)s prepared via solution[15] and emulsion[16] polymerizations. This transfer reaction proceeds via abstraction of a hydrogen atom from a tertiary carbon of the polymer backbone, leading to a tertiary carbon radical that reinitiates the polymerization.[17−19] Another possible fate of this intermediate species is fragmentation, hence forming a new secondary carbon radical together with an unsaturated polymer (macromonomer with terminal 1,1-disubstituted alkene).[20] This reaction is enhanced at elevated temperatures (above 150 °C) and in dilute solutions. Branched polymer can also form in this case by copolymerization of the macromonomer. The real mechanism of the transfer reaction to polymer has not yet been fully elucidated, although an intramolecular hydrogen abstraction process (backbiting) was proposed by Plessis et al.[16] for emulsion polymerization. Ahmad et al. demonstrated that the extent of chain transfer to polymer depends on both the initial monomer concentration and the conversion.[15] For instance, at $[M]_0$ > 10 wt % and T = 70 °C, the mole percent of branches was independent of $[M]_0$ and increased (from 0.8 to approximately 2.2%) as conversion increased (from 35 to ∼95%), whereas, for more dilute solutions, the mole percent of branches increased as $[M]_0$ decreased. The dependence on monomer concentration was assigned to a change in the mechanism from intermolecular chain transfer at high concentration/high conversion, to intramolecular chain transfer for dilute solutions. Intermolecular chain transfer was supposed to be predominant over a broad conversion range when monomer concentration was above 10 wt %. In controlled free-radical polymerization, the chain transfer to polymer should also exist, although the extent has not been determined yet. For instance, from SEC results, Roos et al.[21] have shown that branched structures exist in poly(*n*-butyl acrylate)s of high molar mass (M_n > 50 000 g mol^{-1}) synthesized by ATRP in ethyl acetate solution at 80 °C, using a monomer concentration of 2.33 mol L^{-1}.

In this study, we have examined the structure of "living" poly(*n*-butyl acrylate) chains prepared via SG1-mediated CRP in bulk and in miniemulsion at 112 °C (Scheme 1; Table 1). Although the existence of branches was only demonstrated for high molar mass controlled polymers,[21] the mole percent of branches measured by Ahmad et al.[15] at 70 °C indicates that branched structures should also exist for low molar mass poly(*n*-butyl acrylate)s. The creation of new branches generates new

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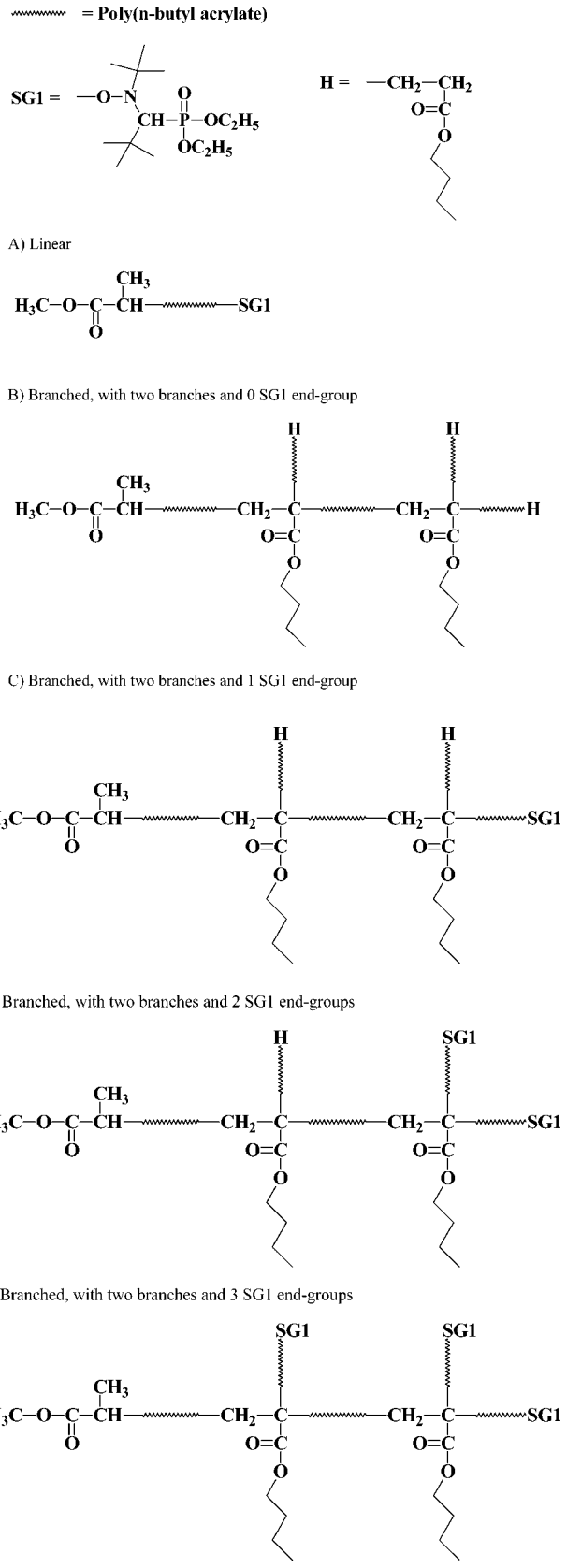
Scheme 1. Various Possible Structures of Poly(*n*-butyl acrylate) Synthesized via SG1-Mediated Controlled Free-Radical Polymerization



end groups of the type $-CH_2-CH_2(COOC_4H_9)$. Therefore, intra- and intermolecular mechanisms would have a completely different impact on the chain structure. Indeed, with intermolecular chain transfer, a statistical redistribution of the functional end groups (i.e., nitroxide in our case) among the chains is expected. In contrast, if intramolecular chain transfer predominates, all of the chains would bear one single nitroxide capping agent, with all of the other chain ends in the macromolecule being of the $-CH_2-CH_2(COOC_4H_9)$ type (identified as the H end group in the following) (Scheme 1). Hence, in the case of "living" chains, the mode of chain transfer to polymer might have a very strong influence on the structural quality of the final copolymer, especially if one tries to generate diblock or triblock copolymers. Only the intramolecular chain transfer mechanism is viable for macromolecular engineering.

Table 1. Experimental Conditions for the Miniemulsion and Bulk Homopolymerizations of *n*-Butyl Acrylate[e]

				M_n SEC, g mol^{-1} (M_w/M_n)	
expt	$[SG1]_0$ (g; mol L_{org}^{-1})[a]	r[b]	convn	PS calibration	poly(BA) calibration
ME1	0	0	0.45	22 600 (1.38)[c]	21 600 (1.43)
				20 400 (1.65)[d]	
			0.58	23 100 (1.61)[d]	–
			0.67	28 200 (1.31)[c]	27 500 (1.36)
				24 800 (1.55)[d]	
			0.81	27 500 (1.58)[d]	–
			0.90	36 900 (1.38)[c]	36 400 (1.42)
				33 900 (1.65)[d]	
ME2	0.029; 7.0×10^{-4}	0.026	0.14	10 550 (1.32)[c]	9600 (1.38)
				9030 (1.40)[d]	
			0.34	15 000 (1.24)[d]	
			0.47	19 800 (1.23)[c]	19 000 (1.26)
				18 800 (1.20)[d]	
			0.60	21 900 (1.21)[d]	–
			0.73	28 500 (1.21)[c]	27 950 (1.24)
				28 100 (1.19)[d]	
B1	0.012; 7.4×10^{-4}	0.025	0.42	14 800 (1.58)[d]	–
			0.71	24 050 (1.38)[d]	–
			0.83	29 550 (1.32)[d]	–
			0.87	30 550 (1.33)[d]	–

[a] With respect to the overall organic phase. [b] r = $[SG1]_0$/[alkoxyamine initiator]$_0$. [c] SEC Bayreuth. [d] SEC Paris. [e] Miniemulsion polymerizations (**ME1** and **ME2**): T = 112 °C; P = 3 bar; water = 400 g; BA = 100 g (final solid content: 20 wt %); $[NaHCO_3]$ = 12 mM_{aq} (0.40 g); initiator, MONAMS (1.323 g; 2.77 $\times 10^{-2}$ mol.L^{-1}_{org}); hexadecane = 0.77 g, 0.8 wt % with respect to monomer; high molar mass polystyrene (M_w = 330 000 g mol^{-1}) = 0.11 g, 0.1 wt % with respect to monomer. Bulk polymerization (**B1**): T = 112 °C; BA, 37.94 g; initiator, MONAMS (0.530 g; 2.91 $\times 10^{-2}$ mol L^{-1}); hexadecane = 0.32 g, 0.8 wt % with respect to monomer; high molar mass polystyrene (M_w = 330 000 g mol^{-1}) = 0.04 g, 0.1 wt % with respect to monomer.

Results and Discussion

To clearly identify their structure, the SG1-capped poly(*n*-butyl acrylate)s were analyzed by SEC (refractive index detector with polystyrene or poly(*n*-butyl acrylate) calibration), ^1H and ^{13}C NMR spectroscopy, and MALDI–TOF mass spectrometry.

Analysis by Size Exclusion Chromatography. Results from size exclusion chromatography are summarized in Table 1. The M_n values from experiment **ME2** are displayed in Figure 1 as a function of monomer conversion; they were calculated from a refractive index detector with polystyrene and/or poly(*n*-butyl acrylate) calibration (see experimental part). M_n increased linearly with conversion with both calibrations. The low initiator efficiency will be discussed in a forthcoming article.[22] When the polymerization was performed in the presence of added free nitroxide (2.5 mol % with respect to the alkoxyamine initiator; experiments **ME2** and **B1**), the polydispersity indexes were well below the 1.5 lower

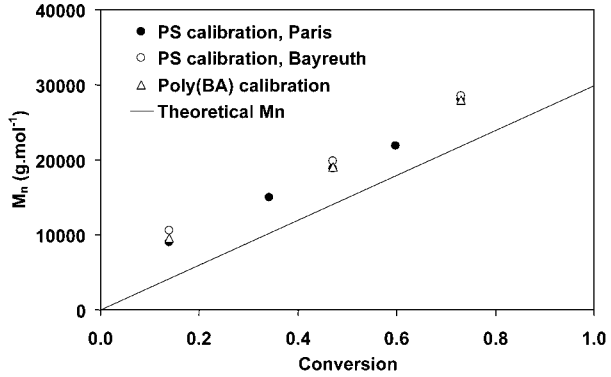


Figure 1. Number-average molar mass (M_n) vs conversion for poly(*n*-butyl acrylate)s prepared via SG1-mediated CRP in miniemulsion (experiment **ME2**, Table 1).

limit of classical radical polymerization. The downward curvature observed by Roos et al.[21] for molar masses larger than 50 000 g mol^{-1} was not detected, indicating that hydrodynamic volume did not contract significantly, as would be the case for long branched structures.

Analysis by NMR Spectrocopy. The structure of the chain end was first examined by ^{1}H NMR spectroscopy (Figure 2). None of the analyzed samples had detectable 1,1-disubstituted alkene end groups, which would be seen at δ 6.2 and 5.5 ppm, as observed by Chiefari et al.[20] This result indicates that the addition−fragmentation mechanism did not extensively operate in the SG1-mediated controlled radical polymerizations, although performed at 112 °C. Another explanation would be that the unsaturated species (macromonomers) might undergo complete copolymerization, which is quite unlikely and has never been previously described. In addition, no other proton from a terminal unsaturation could be seen, such as the two protons of a 1,2-disubstituted alkene, which would be the consequence of chain termination by alkoxyamine decomposition. However, the analysis was difficult because of the rather high molar mass of the polymers (M_n = 28 100 g mol^{-1} for the polymer, whose spectrum is shown in Figure 2). Nevertheless, a sharp peak at 3.6 ppm could be unambiguously assigned to the methyl ester of the alkoxyamine initiator. Thus, if present to a similar extent as that previously reported,[20] the terminal double bonds would also be seen quite clearly. Although the SG1 end group cannot be easily detected in the area of the aliphatic protons, broad peaks can still be observed between 1.0 and 1.1 ppm, which had previously been assigned to the *tert*-butyl groups of the nitroxide.[23]

^{13}C NMR spectra also confirmed the absence of terminal double bonds by the absence of resonances in the 90−130 ppm region. The expanded spectrum in Figure 3 shows the characteristic peaks, previously identified by Ahmad et al.[15] for branches, indicating that chain transfer to polymer actually occurred. The extent of branching was approximately 1 mol % for polymer **ME2** at 47% conversion, 1.5 mol % for polymer **ME2** at 73% conversion, and 1.8 mol % for polymer **ME1** at 90% conversion. More complete and accurate analyses are currently under investigation. These values are in the range of data reported by Ahmad et al.[15] for bulk polymerizations performed at 70 °C with large monomer

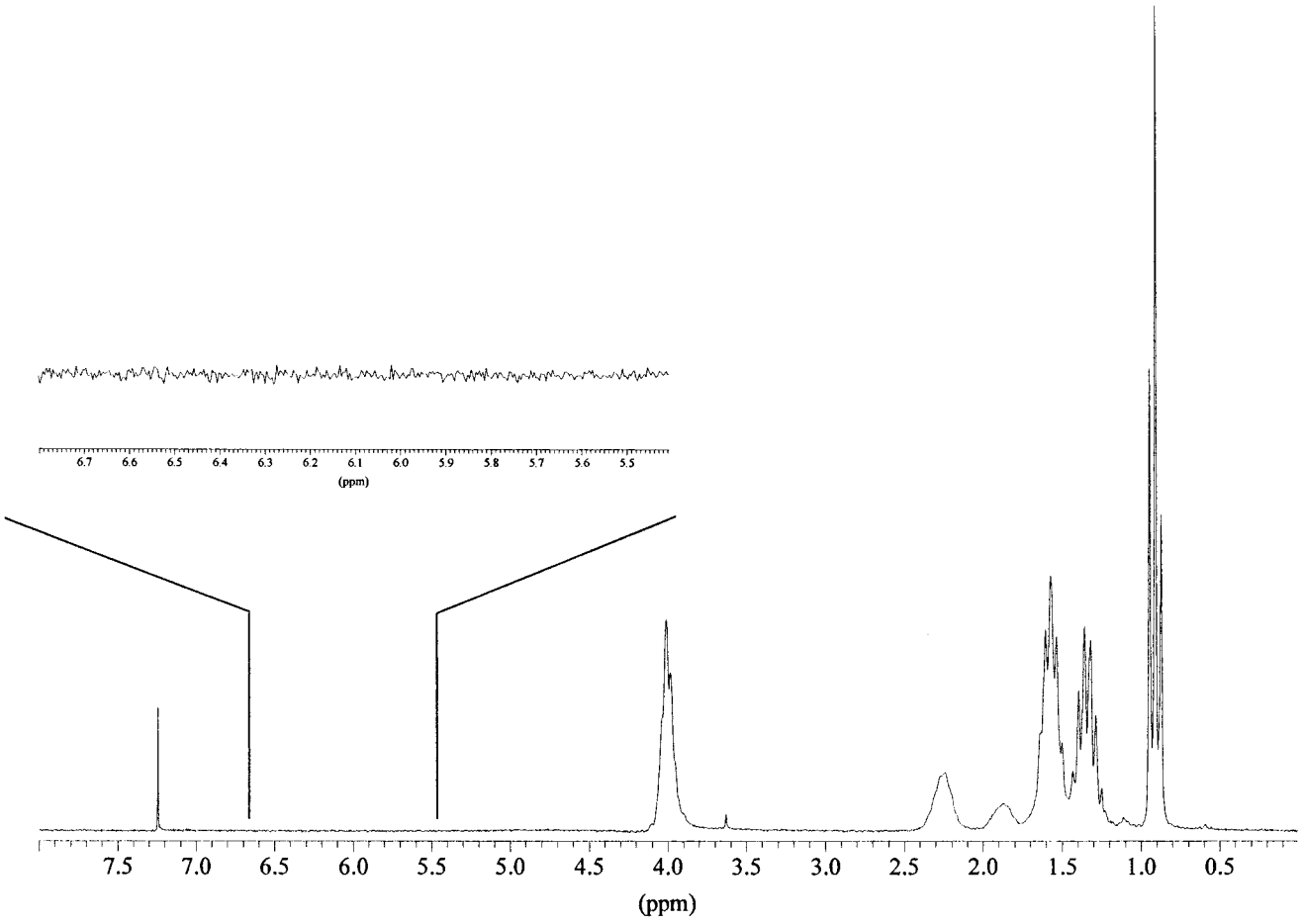


Figure 2. ^{1}H NMR spectrum of poly(*n*-butyl acrylate) from experiment **ME2** (Table 1) at 73% conversion.

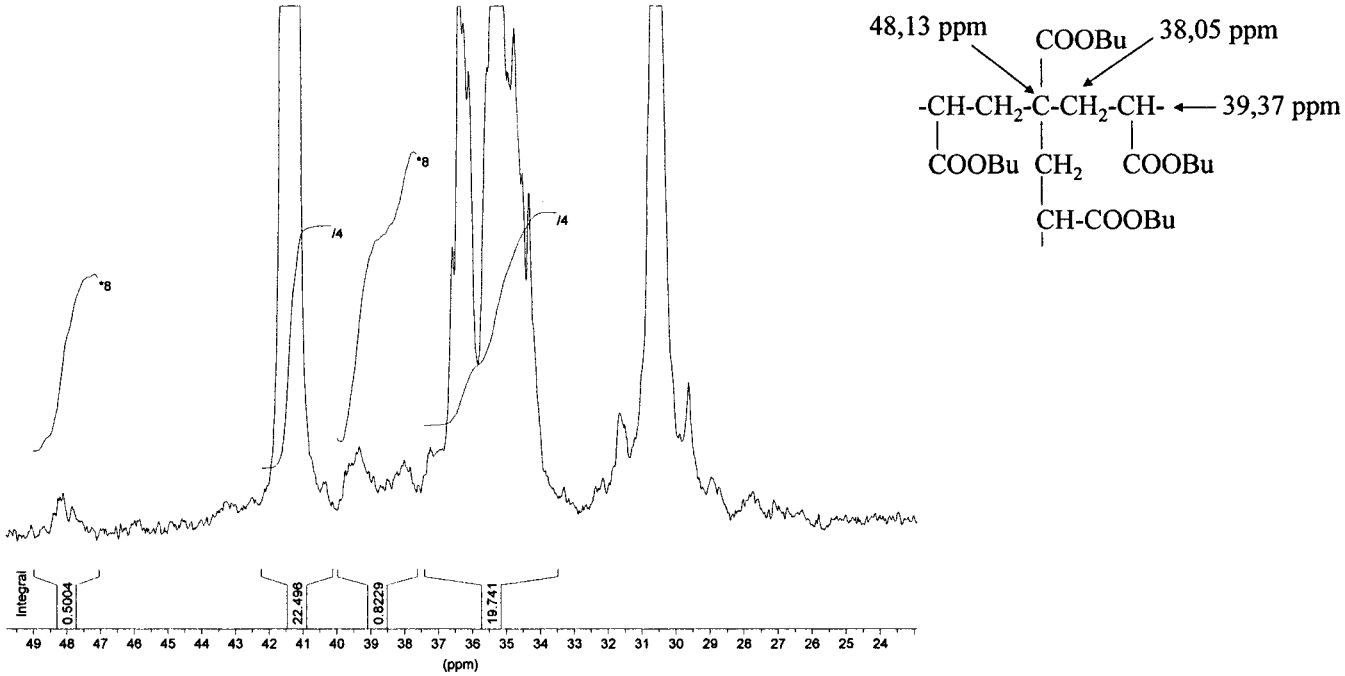


Figure 3. Carbon 13 NMR spectrum expanded between 23 and 50 ppm for **ME2** (Table 1) at 73% conversion.

concentrations (above 10 wt %, similar to the bulk and miniemulsion polymerizations presented in this work) and of data reported by Plessis et al. for emulsion polymerizations performed at 75 °C.[16]

Analysis by MALDI−TOF MS. If one considers a polymer with 1.5 mol % branching, chains with degree of polymerization below 67 (molar mass below 9000 g mol^{-1}) contain less than one branch on average; those with degree of polymerization between 67 and 133 (molar mass between 9000 and 17 500 g mol^{-1}) contain one or two branches, while those with degree of polymerization between 133 and 200 (molar mass between 17 500 and 26 000 g mol^{-1}) contain two or three branches on average. The macromolecules with two branches should possess four end groups: one (α end-group) from the initiating radical {$CH_3O(C{=}O)CH(CH_3)-$} and three other ones (ω end groups) terminated either with a SG1 or with a H (i.e., $-CH_2-CH_2-(COOC_4H_9)$). Assuming an intermolecular chain transfer process, and hence a statistical redistribution of the SG1 among all of the ω end groups of all the chains, the following molar proportion of the four different structures are expected, based on the probability of $^1/_3$ for SG1 and $^2/_3$ for H: 1/27 chain (3.7 mol %) with 3 SG1 end groups and no H; 6/27 chain (22.2 mol %) with 2 SG1 and 1 H; 12/27 chain (44.5 mol %) with 1 SG1 and 2 H; and finally, 8/27 chain (29.6 mol %) with no SG1 and 3 H. The chains with only one branch contain two ω end groups. The respective probabilities for a SG1 or a H end group are the same and equal to $^1/_2$. In the case of intermolecular chain transfer, three different structures would exist with the following proportions: $^1/_4$ (25 mol %) of chain with 2 SG1 end groups and no H; $^1/_2$ (50 mol %) of chain with 1 SG1 end group and 1 H; $^1/_4$ (25 mol %) of chain with no SG1 end group and 2 H. To summarize, polymer chains with degrees of polymerization between 67 and 166 (molar mass between 9000 and 22 000 g mol^{-1}) have most probably one or two branches; for these species, the respective proportion of chains with 0, 1, or 2 SG1 end groups should obey a ratio close to 1:2:1. If the desorption−ionization process

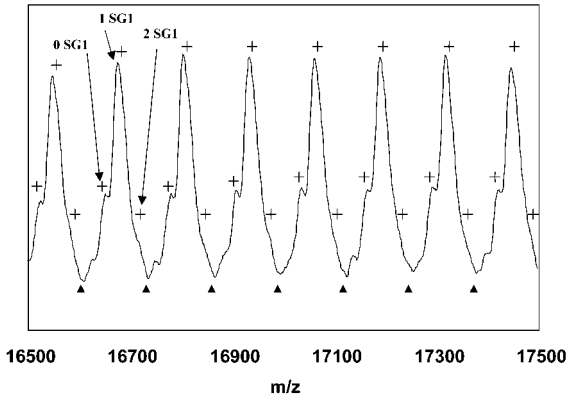


Figure 4. Expanded MALDI−TOF mass spectrum of a fraction centered at 17 000 g mol^{-1} of polymer obtained from experiment **ME1** (Table 1) at 90%: (+) theoretical *m*/*z* of the chains with 0, 1, or 2 SG1; (▲) theoretical *m*/*z* of the dead chains formed by coupling of two macroradicals (with 0 SG1).

is not strongly affected by the number of SG1 end groups in the chains, these different structures should be clearly seen in the MALDI−TOF mass spectra, in the expected proportions. In contrast, with intramolecular chain transfer dominating, one single structure should be identified, since this process does not change the chain composition and hence the molar mass (Scheme 1, structure C).

To properly characterize by MALDI−TOF-MS poly(*n*-butyl acrylate) samples with molar mass between 9000 and 22 000 g mol^{-1}, we fractionated the polymers. Various fractions were collected by semipreparative SEC and analyzed. Because the analyzed polymer samples had M_n either close to 22 000 g mol^{-1} or larger, only the fractions with molar mass close to this upper limit were considered to be sufficiently representative. Figures 4−6 show the expanded spectra of a selected fraction of various polymers, at intermediate and high conversion: **ME1** at 90% conversion; **ME2** at 47 and 73% conversion; **B1** at 87% conversion. In all cases, one major series was observed, with 128 mass units (the

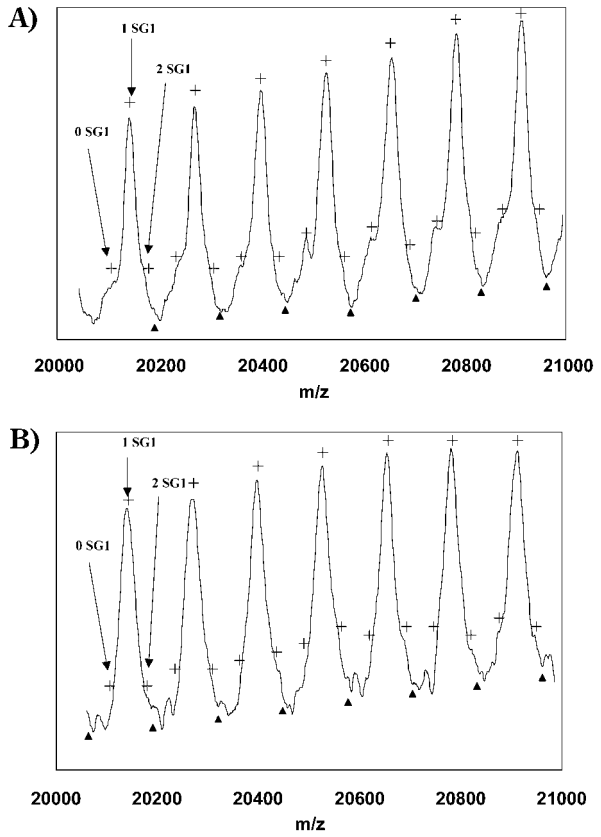


Figure 5. (A) Expanded MALDI−TOF mass spectrum of a fraction centered at 23 000 g mol^{-1} of polymer obtained from experiment **ME2** (Table 1) at 47% conversion. (B) Expanded MALDI−TOF mass spectrum of a fraction centered at 23 000 g mol^{-1} of polymer obtained from experiment **ME2** (Table 1) at 73% conversion. Key: (+) theoretical *m*/*z* of the chains with 0, 1, or 2 SG1; (▲) theoretical *m*/*z* of the dead chains formed by coupling of two macroradicals (with 0 SG1).

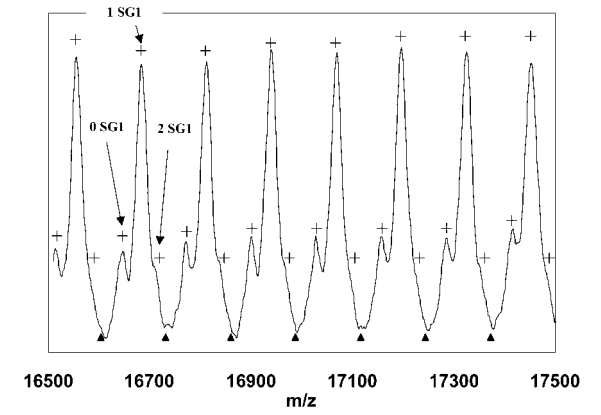


Figure 6. Expanded MALDI−TOF mass spectrum of a fraction centered at 17 000 g mol^{-1} of polymer obtained from experiment **B1** (Table 1) at 87% conversion: (+) theoretical *m*/*z* of the chains with 0, 1, or 2 SG1; (▲) theoretical *m*/*z* of the dead chains formed by coupling of two macroradicals (with 0 SG1).

molar mass of the monomer unit) separating the peaks. For a given peak, the molar mass corresponded to that of a chain with one methyl acrylate derivative, a given number of *n*-butyl acrylate units, one SG1 chain-end and the sodium cation. A second minor series could also be seen, corresponding to polymer chains with no attached SG1. In addition to being a possible product of intermolecular chain transfer to polymer, this type of chain can also form by (i) disproportionation termination between macroradicals without any SG1 in their structure or (ii) alkoxyamine decomposition, either occurring during synthesis (not unexepected at high conversion) or induced by the laser shot during analysis itself[24] (which would artificially increase the proportion of this byproduct). A third series corresponding to chains with 2 SG1 was also observed, but was significantly less intense than the latter. There were no peaks corresponding to chains produced by recombination termination (between two macroradicals without any SG1 in the structure), although this mode of termination is the most favored in radical polymerization of acrylates.[25] Therefore, the MALDI−TOF mass spectra did not exhibit the 1:2:1 proportion of chains with respectively 0, 1, and 2 SG1, that would be expected if intermolecular chain transfer to polymer was the dominant process throughout the polymerization.

Conclusions on Chain Structure and Mechanism of Transfer to Polymer. On the basis of the experimental results, one can conclude that the majority of the poly(*n*-butyl acrylate) chains had the ideal structure with one initiator fragment and one SG1 end group, even at high conversion. These results support the earlier reports of successful synthesis of di- and triblock copolymers (with very high crossover efficiency) from SG1-capped poly(*n*-butyl acrylate)s started from a mono- or a difunctional alkoxyamine initiator, respectively.[26−29] They confirm that poly(*n*-butyl acrylate) can be prepared with well-defined macromolecular architectures via SG1-mediated controlled radical polymerization in bulk and in miniemulsion. Branches, however, exist, but the chain transfer mechanism by which they are produced at 112 °C seems to be predominantly an intramolecular process (presumably backbiting). Undoubtedly, intermolecular chain transfer to polymer cannot be excluded, but this reaction remained comparatively slower under the applied experimental conditions, since only a very small proportion of chains contained 2 SG1 end groups. However, when targetting poly(*n*-butyl acrylate) of sufficiently high molar mass, the formation of at least one long branch per chain should eventually occur, which would strongly alter the polymer structure and end group integrity. These results agree well with Plessis's deduction,[16] but contradict somehow Ahmad's conclusions[15] of predominant intermolecular chain transfer process at large monomer concentration. Similarly to their observations, however, the mole percent of branches increased with monomer conversion, but this result is not in contradiction with an intramolecular chain transfer mechanism, since the probability that an active chain undergoes intramolecular hydrogen abstraction (the frequency of which remains constant) rather than propagation increases when conversion progresses. In our experiments, in addition to the use of a nitroxide, the temperature was 112 °C instead of 70 °C. Thus, is the intramolecular transfer to polymer enhanced with respect to intermolecular chain transfer when polymerization temperature is raised? Does the SG1 mediator (or the activation/deactivation equilibrium) have an effect on the chain transfer kinetics? Unfortunately, SG1-mediated CRP of *n*-butyl acrylate cannot be performed at low temperature. Only ATRP might help answer at least the first question since a broad temperature range can be employed for the polymerization of acrylates; moreover, like SG1, the terminal halogen atom might be used as a probe for end group characterization.

Experimental Part

Materials. *n*-Butyl acrylate (BA, Aldrich, 99+ % purity) was distilled under reduced pressure before use. The alkoxyamine initiator (SG1-based alkoxyamine derived from methyl acrylate, $CH_3-O(CO)-CH(CH_3)$-SG1, MONAMS, 96% purity) was supplied by Atofina and prepared using atom transfer radical addition from methyl-2-bromopropionate. The *N*-*tert*-butyl-*N*-(1-diethyl phosphono-2,2-dimethylpropyl) nitroxide (SG1, 86.5% purity) was also supplied by Atofina.

Batch Miniemulsion Polymerization of *n*-Butyl Acrylate. The batch miniemulsion polymerizations of *n*-butyl acrylate were performed at 112 °C, and the experimental procedure, the same as already described,[29] is presented in Table 1. Two experiments were performed with the same initiator concentration and different amounts of added free nitroxide, to optimize both the kinetics and the polydispersity index.[30] Samples were periodically withdrawn to monitor the monomer conversion by gravimetry and to analyze the dried polymers by SEC, ^{1}H and ^{13}C NMR, and MALDI−TOF MS.

Bulk Polymerization of *n*-Butyl Acrylate. *n*-Butyl acrylate was polymerized in bulk using the same components as the organic phase of a miniemulsion. *n*-Butyl acrylate, MONAMS alkoxyamine, high molar mass polystyrene (M_w = 330 000 g mol^{-1}), hexadecane, and a small fraction of free SG1 with respect to the alkoxyamine were mixed and poured into five Schlenk tubes. Experimental conditions are given in the caption of Table 1. The solutions were degassed by freeze−thaw cycles. Afterward, the tubes were immersed into an oil bath at 112 °C for different periods of time. The conversion was determined by gravimetry and the molar masses were analyzed by size exclusion chromatography.

Analytical Techniques. Analytical size exclusion chromatography (SEC) was performed using two different systems. The first one was a Waters apparatus equipped with two columns (PL-gel 10μ mixed, 60 cm; Shodex KF 801L, 30 cm, exclusion limit, 1.5×10^3). The eluent was tetrahydrofuran (THF) at a flow rate of 1 mL.min^{-1}. A LCD differential refractive index detector, thermostated at 30 °C, was used and molar masses were derived from a calibration curve based on polystyrene standards from PSS. The molar mass of selected samples of **ME1** and **ME2** were double checked in the group of Professor Axel Müller at the University of Bayreuth, Germany. SEC measurements were performed using a set of 30 cm SDV-gel columns of 5 μm particle size having 10^2, 10^3, 10^4, and 10^5 Å pore size and dual detectors (RI and UV [λ = 254 nm]). The solvent was THF at room temperature with an elution rate of 1 mL min^{-1}. Narrowly distributed polystyrene samples and linear poly(*n*-butyl acrylate) samples prepared via anionic polymerization were used as calibration standards.

Fractionation of the polymers was performed by semi-preparative SEC using a Waters apparatus equipped with three columns (UltraStyragel 500, 10^3, 10^4 Å). The eluent was tetrahydrofyran (THF) at a flow rate of 5 mL min^{-1}. A 200 μL portion of a polymer solution at 30 g L^{-1} was injected. Fractions were collected every 15 s, which allowed us to collect from 0.1 to 0.4 mg of polymer in each fraction. A differential refractive index detector was used, and molar masses were derived from a calibration curve based on polystyrene standards.

The polymers were analyzed by ^{1}H NMR in $CDCl_3$ solution at room temperature using a Bruker AC200 spectrometer operating at a frequency of 200 MHz, with the following conditions: spectral width 30 ppm with 16 K data points, flip angle of 15°, relaxation delay of 1.4 s, digital resolution of 0.36 Hz/pt. The chemical shift scale was calibrated on the basis of the solvent peak (7.24 ppm).

The polymers were analyzed by ^{13}C NMR in $CDCl_3$ solution at room temperature using a Bruker DRX 500 spectrometer, operating at a frequency of 125.7 MHz. Spectra were recorded using the following conditions, allowing quantitative analysis: spectral width 240 ppm with 64K data points, flip angle of 20°, relaxation delay of 20 s and the decoupler power switched off during the relaxation (no NOE). A zero filling (128K) was applied prior Fourier transform leading to a digital resolution of 18×10^{-4} ppm per point (0.23 Hz/pt). The chemical shift scale was calibrated on the basis of the solvent peak (77 ppm). The peak assignments were made according to Ahmad et al. (see Figure 3).[15] The mole percent of branches (number of branches per 100 monomer units in the polymer backbone) was estimated from integration of (i) the peak corresponding to the quaternary carbon at a branch junction (C_q; 48.13 ppm), (ii) the peak corresponding to the three CH and three CH_2 moieties adjacent to a branch junction (bCH + bCH_2; 39.37 and 38.05 ppm), (iii) the peak corresponding to the CH of the polymer backbone (41−42 ppm), and (iv) the peak corresponding to the CH_2 of the polymer backbone (33.5−37 ppm) (see Figure 3).

$$\text{mol \% branching} = \frac{\frac{1}{2}\,A(C_q) + A(\text{bCH} + \text{bCH}_2)/6}{\frac{1}{2}\,A(C_q) + A(\text{bCH} + \text{bCH}_2)/2 + A(\text{CH backbone})/2 + A(\text{CH}_2\text{ backbone})/2}$$

with $A(x)$ = area of the peak assigned to x.

Fractionated polymers were analyzed by MALDI−TOF MS performed using a PerSeptive Biosystems Voyager Elite (Framingham, MA) time-of-flight mass spectrometer. This instrument is equipped with a nitrogen laser (337 nm; 3 ns pulse), a delayed extraction, and a reflector. It was operated at an accelerating potential of 25 kV in linear mode. The MALDI mass spectra represent averages over 2048 consecutive laser shots (3 Hz repetition rate). The polymer solutions (2−5 g L^{-1}) were prepared in THF. The matrix, 1,8-dihydroxy-9[10*H*]-anthracenone (dithranol), was also dissolved in THF (25 g L^{-1}). A 10 μL portion of the polymer solution was mixed with 20 μL of the matrix solution. A sodium iodide solution (10 μL of a solution at 20 g L^{-1} in THF) was finally added to favor ionization by cation attachment. A 1 μL portion of the final solution was deposited onto the sample target and allowed to dry in air at room temperature. Standards (polystyrenes of known structure, M_n = 10 000 and 22 400 g mol^{-1} purchased from Polymer Standards Service) were used to calibrate the mass scale using the two point calibration software 3.07.1 from PerSeptive Biosystems. The theoretical molar mass (g mol^{-1}) of poly(*n*-butyl acrylate) chains was calculated according to the following formula, with n the number of *n*-butyl acrylate units: chains with 0 SG1 = 87.09902 + 128.1723 × n + 1.0079; chains with 1 SG1 = 87.09902 + 128.1723 × n + 294.3538; chains with 2 SG1 = 87.09902 + 128.1723 × n − 1.0079 + 2 × 294.3538. The theoretical molar mass (g mol^{-1}) of dead chains with 0 SG1, formed by coupling of two macroradicals without any SG1 in their structure, was calculated according to 87.09902 × 2 + 128.1723 × n. In all cases, to determine m/z, the molar mass of the sodium cation was added.

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