First Nitroxide-Mediated Controlled Free-Radical Polymerization of Acrylic Acid

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ABSTRACT: Controlled poly(acrylic acid) homopolymers were synthesized for the first time by direct nitroxide-mediated polymerization of acrylic acid. The polymerizations were performed in 1,4-dioxane solution at 120 °C, using an alkoxyamine initiator based on the *N*-*tert*-butyl-*N*-(1-diethyl phosphono-2,2-dimethyl propyl) nitroxide, SG1. The kinetics were controlled by the addition of free nitroxide at the beginning of the polymerization and the optimal amount was 9 mol % with respect to the initiator. In this case, whatever the initiator concentration, all polymerizations exhibited the same rate and conversion reached 85−90% within 5 h. Although the rate constant of propagation of acrylic acid is very large, its reactivity is moderated by a low activation−deactivation equilibrium constant between active macroradicals and SG1-capped dormant chains. Various alkoxyamine concentrations were investigated to target different molar masses. At high initiator concentrations, the number-average molar mass, M_n, increased linearly with monomer conversion and followed the theoretical values; the polydispersity indexes ranged between 1.3 and 1.5. At low initiator concentration (high target M_n), a deviation from linearity was observed in the M_n vs conversion plot and was clearly assigned to chain transfer to 1,4-dioxane. From these results, the best experimental conditions to obtain well-defined homopolymers with the minimum amount of dead chains were identified.

Introduction

A wide variety of well-defined homopolymers and copolymers with complex architectures have become easily accessible since the advent of controlled free-radical polymerization (CRP).[1,2,3] Several methods are available such as nitroxide-mediated polymerization (NMP),[4] atom transfer radical polymerization (ATRP),[5,6] and reversible transfer techniques (reversible addition−fragmentation chain transfer, RAFT[7,8] and macromolecular design via the interchange of xanthates, MADIX[9]). Free-radical polymerization process is particularly attractive for industrial applications and this explains the great success of these techniques. For some monomers, they compete with the ionic polymerizations, whereas for others they are the only way to achieve controlled structures. This is particularly true for functional monomers that behave as poisons for propagating anionic and cationic chain ends.

Acrylic acid is one of these monomers that can only polymerize via a free-radical mechanism. However, even with the CRP techniques, difficulties were encountered to get well-defined homopolymers or copolymers from its direct (co)polymerization. Indeed, the early works on CRP of acrylic acid showed that actually ATRP and NMP were rather inappropriate methods.[10] With ATRP, some incompatibility with the transition metal complex catalyst was suspected[11] whereas with NMP, the acidic group was supposed to be involved in side reactions with the nitroxide, which was actually seen for strong organic acids.[12] Even though unwanted chemical reactions were usually invoked, it is worth noting that acrylic acid also exhibits a very high rate constant of propagation in free-radical polymerization[13] together with a propensity for self-initiation,[14] both beeing able to ruin the quality of control. Nevertheless, CRP of this monomer was still reported in a small number of papers[10] as briefly described below.

Cyanoxyl-mediated free-radical polymerization was shown to be appropriate to control sodium acrylate polymerization starting from polystyrene precursors with pendant arene-diazonium salts, hence leading to graft copolymers.[15]

Using the 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide, Benoit et al.[16] were able to copolymerize acrylic acid with *n*-butyl acrylate in bulk, up to 50 mol % of the acidic comonomer, in a controlled fashion, but no attempt of homopolymerization, either in bulk or in solution has been reported. Also using NMP, sodium acrylate was polymerized in water-solution, using poly(sodium 4-styrenesulfonate) macroinitiators end-capped with water-soluble nitroxides, but the controlled behavior was not demonstrated.[17]

ATRP was even less successful since neither copolymers, nor homopolymers based on acrylic acid were synthesized by this technique.[11] Only methacrylic acid gave satisfactorily results in aqueous solution, providing the pH was carefully adjusted.[18,19]

With RAFT, the first example of acrylic acid controlled homopolymerization was reported by Chiefari et al. in dimethylformamide solution at 60 °C,[20,21] but no detailed information was provided. Ladavière et al.[22] examined a series of RAFT agents to control the free-radical polymerization of acrylic acid in alcohol or water solution, and they came to the conclusion that phenoxyxanthates and trithiocarbonates were particularly well-suited. Recently, the same group completed this work with a thorough examination of the controlled character of the polymerization and its limitations.[23]

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Table 1. SG1-Mediated Homopolymerization of Acrylic Acid in 1,4-Dioxane Solution at 120 °C

expt	symbol	$[AA]_0$ (mol·L^{-1})	$[solvent]_0$ (mol·L^{-1})	$[Monams]_0$ (mol·L^{-1})	$[SG1]_0$ (mol·L^{-1})	r^a	$k_p[P^\bullet]$ (s^{-1})	k_pK (s^{-1})^b
1	●	3.0	9.3	0.0195	0.0009	0.044	2.5×10^{-4}	1.1×10^{-5}
2	▲	3.0	9.3	0.0200	0.0018	0.090	1.3×10^{-4}	1.2×10^{-5}
3	■	3.0	9.3	0.0387	0.0034	0.090	1.9×10^{-4}	1.8×10^{-5}
4	◆	3.0	9.3	0.0098	0.0009	0.090	1.4×10^{-4}	1.3×10^{-5}
5	◇	3.1	9.2	0	0		6.4×10^{-5}	

[a] $r = [SG1]_0/[Monams]_0$. [b] Calculated from eq 2 (see text).

They also described the application of RAFT to the synthesis of controlled poly(*n*-butyl acrylate)-*b*-poly(acrylic acid) block copolymers and their use as stabilizers in emulsion polymerization.[24] The controlled homopolymerization of acrylic acid was performed by another group in the presence of dibenzyl trithiocarbonate, under ^{60}Co irradiation at room temperature.[25] Similarly, the MADIX process was successfully used in aqueous solution to prepare well-defined poly(acrylic acid) homopolymer and hydrophilic copolymers based on acrylamide and acrylic acid.[26]

Although the previous conclusions concerning NMP of acrylic acid were rather pessimistic, it appeared to us that actually the invoked rationale were not strong enough. For this reason, the purpose of this work was to achieve a better and totally new understanding of the nitroxide-mediated homopolymerization of acrylic acid and to select the best conditions for control. The nitroxide used was the *N*-*tert*-butyl-*N*-(1-diethyl phosphono-2,2-dimethyl propyl) also called SG1, that proved to be better-suited than TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy) to control the polymerization of monomers other than styrene and derivatives, particularly acrylates.[4,27,28]

Experimental Part

Materials. Acrylic acid (AA, purest grade, Atofina, stabilized with 200 ppm of hydroquinone) was stored at room temperature and used without further purification. Styrene (S, Aldrich, 99% purity) was distilled under vacuum before use. The alkoxyamine initiator (SG1-based alkoxyamine, $CH_3-O-C(=O)-CH(CH_3)-SG1$, Monams, 96% purity) and the *N*-*tert*-butyl-*N*-(1-diethyl phosphono-2,2-dimethyl propyl) nitroxide (SG1, 86.5% purity) were kindly supplied by Atofina. The solvent 1,4-dioxane (from SDS, synthesis grade) was used as received. The methylation agent, trimethylsilyldiazomethane (2 M solution in hexanes) was supplied by Aldrich and used as received.

Solution Polymerizations of Acrylic Acid. The polymerization reactions were carried out in a Parr reactor of 300 mL, thermostated at 120 °C, under a 2 bar nitrogen atmosphere. The stirring rate was 300 rpm. In a typical recipe (experiment 2), Monams (1.400 g, 3.65×10^{-3} mol, 0.020 mol·L^{-1}) and SG1 (0.0965 g, 3.3×10^{-4} mol, 0.0018 mol·L^{-1}, 9 mol % with respect to Monams) were dissolved in the solvent (1,4-dioxane, 145 mL). Then, acrylic acid (40.0 g, 0.556 mol, 3.03 mol·L^{-1}) was added to the mixture. Deoxygenation was performed by nitrogen bubbling for 30 min. Afterward, the polymerization solution was transferred into the reactor (already heated at 120 °C) and a 2-bar pressure of nitrogen was applied. Time zero of the reaction was arbitrary set when the mixture reached 110 °C. Samples were periodically withdrawn (on the top of the reactor) and cooled in an iced water bath to stop the polymerization. Conversion was determined by ^{1}H NMR as described later in this experimental part. Polymers were recovered by drying into a ventilated oven at 35 °C for 2 days. After chemical modification they were analyzed by size exclusion chromatography (SEC) in THF solution. All performed experiments are collected in Table 1.

Synthesis of a Poly(acrylic acid)-*b*-poly(styrene-*co*-acrylic acid) Block Copolymer. Synthesis of the first poly(acrylic acid) block was carried out under the same conditions as in the previous section (Table 2). Monams (1.200 g, 3.1×10^{-3} mol, 0.020 mol·L^{-1}) and SG1 (0.0700 g, 2.4×10^{-4} mol, 1.5×10^{-3} mol·L^{-1}, 7.5 mol % with respect to Monams) were dissolved in the solvent (1,4-dioxane, 123 mL). Then, acrylic acid (34 g, 0.478 mol, 3.04 mol·L^{-1}) was added to the mixture and polymerization was performed at 120 °C and 2 bar. After 2 h, one sample was taken to check the conversion of acrylic acid (56% conversion) and temperature was decreased down to 80 °C. Then styrene (20 g, 0.192 mol, 1.08 mol·L^{-1}) was introduced into the polymerization solution, and another sample was immediatly withdrawn and used as the initial reference for proton NMR determination of the individual monomer conversions. Finally, temperature and pressure were respectively raised again to 120 °C and 2 bar to start the second polymerization step. Samples were periodically withdrawn (on the top of the reactor) and cooled in an iced water bath to stop the polymerization. They were analyzed by proton NMR for conversion measurement, and after modification, they were analyzed by SEC in THF solution.

Table 2. Synthesis of a Poly(acrylic acid)-*b*-poly(styrene-*co*-acrylic acid) Block Copolymer in 1,4-Dioxane Solution at 120 °C

First Block

expt	symbol	$[AA]_0$ (mol·L^{-1})	$[solvent]_0$ (mol·L^{-1})	$[Monams]_0$ (mol·L^{-1})	$[SG1]_0$ (mol·L^{-1})	r^a	convn
6	×	3.04	9.3	0.020	0.0015	0.075	0.56

Second Block

expt	symbol	$[AA]_0$ (mol·L^{-1})^b	$[S]_0$ (mol·L^{-1})	$f_{AA0}{}^b$
6	×	1.17	1.08	0.52

[a] $r = [SG1]_0/[Monams]_0$. [b] $[AA]_0$ and f_{AA0} are respectively the molar concentration and the molar fraction of AA in the polymerization medium at the beginning of the second polymerization step.

Chemical Modification of the Polymers. For size exclusion chromatography, the polymers were modified by methylation of the carboxylic acid groups using trimethylsilyldiazomethane. In this way, 50 mg of each sample was dissolved in a mixture of THF and water (to get solubilization at room temperature), overall volume 10 mL. The yellow solution of trimethylsilyldiazomethane was added dropwise at room temperature into the polymer solution. Upon addition, bubbles appeared and the solution became instantaneously colorless. Addition of the methylation agent was continued until the solution became yellow and stopped bubbling. Then, an excess of methylation agent was added and the solution was stirred for 3 h more at room temperature. As verified by ^{1}H NMR analysis of the polymers, the proportion of methyl ester was always quantitative.

Analytical Techniques. For the homopolymerizations, the raw polymerization media with added deuterated water were analyzed by proton NMR spectroscopy at regular time intervals. Analyses were performed in 5 mm tubes at room temperature using a Bruker AC200 apparatus, operating at a frequency of 200 MHz. The chemical shift scale was calibrated on the basis of the solvent peak (deuterated water at 4.65 ppm). The conversion, *x*, was determined by integrating the peaks corresponding to the vinyl protons of the monomer (5.5−6.3 ppm) on the one side and to the aliphatic protons of the polymer (0.6−2.3 ppm) on the other side.

For the copolymerization (second block of experiment 6), the same technique for sample preparation was used (except that D_2O was replaced by acetone-d_6; chemical shift = 2.04 ppm). The individual conversions (x_S for styrene and x_{AA} for acrylic acid) were determined by integrating the peaks corresponding to the vinyl protons of the considered monomer, using the broad peak between 6.5 and 7.5 ppm as an internal reference (five aromatic H for styrene and polystyrene, and one vinylic H for styrene monomer that was subtracted before calculation). The overall molar conversion was deduced from the integral of the peaks corresponding to all of the vinyl protons. The overall weight conversion (x_{wt}) was recalculated from the individual conversions and the initial weight fraction of each monomer (w_{AA0} and w_{S0}), according to $x_{wt} = x_{AA}w_{AA0} + x_S w_{S0}$.

The molar mass and molar mass distribution of the methylated (co)polymers were obtained by SEC in THF solution with a 1 mL·min^{-1} flow rate. The apparatus is composed of a degasser (Viscotek, VE7510 GPC), a Waters 515 HPLC pump, an auto-sampler (Viscotek,VE5200 GPC), three linear columns (3 PSS SDV linear) in an oven (Croco-cil) thermostated at 40 °C and two detectors: RI (LDC Analytical, refractoMonitor IV) and UV at 254 nm (Waters 484). The molar masses were derived from a calibration curve based on polystyrene standards (162−1090000 g·mol^{-1}) from Polymer Standards Service. This calibration remains appropriate for poly(methyl acrylate) samples as shown by the Mark−Houwink−Sakurada parameters: actually it leads to an error below 10%, which is within the accepted range for SEC analysis.[29]

The existence of branches resulting from chain transfer to polymer was investigated by carbon 13 NMR spectroscopy. The poly(acrylic acid)s were previously precipitated in dichloromethane and dried in an oven overnight. Then, they were dissolved in deuterated water. Analyses were performed in 10 mm tubes at room temperature using a Bruker DRX500 apparatus, operating at a frequency of 125.7 MHz for carbon 13. 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/point). The chemical shift scale was calibrated on the basis of added 1,4-dioxane (peak at 66.5 ppm).

Result and Discussion

1. Selection of Suitable Experimental Conditions. SG1-mediated polymerization of acrylic acid was carried out using a SG1-based unimolecular alkoxyamine initiator, $CH_3-O-C(=O)-CH(CH_3)-SG1$, also called Monams. Solution polymerization with 3 mol·L^{-1} acrylic acid (21 wt %) was the best choice because of too fast, exothermic reaction and poorly controlled behavior in concentrated media (typically above 5 mol·L^{-1}). Consequently, an important point was the choice of an appropriate solvent, different from water in which Monams is not fully soluble. Preliminary experiments were performed in *N*-methylpyrrolidone, but a too high chain transfer constant eliminated it ($C_{tr} = 3 \times 10^{-3}$, experimentally determined from our data). A solvent that actually met the required conditions was 1,4-dioxane, in which monomer, polymer, alkoxyamine, and nitroxide were all soluble. In this work, the initial monomer concentration was kept constant and equal to 3 mol·L^{-1}; only the initial concentrations of free SG1 and alkoxyamine were changed. The polymerization temperature was 120 °C, which is the optimal value for Monams decomposition[30] as well as for polymerization. Details on the experimental parameters can be found in Table 1.

2. Effect of the Initial Concentration of Free SG1. It has been previously shown for *n*-butyl acrylate, a monomer with high propagation rate constant k_p, that the best condition to get controlled SG1-mediated homopolymerization was to add a few percents of free nitroxide with respect to the alkoxyamine initiator, at the onset of the polymerization.[28] This excess of free nitroxide contributed to reduce the polymerization rate and to improve the quality of control. Because in the absence of added free nitroxide the rate of polymerization of AA initiated by Monams was too high, the same conclusion should also hold for acrylic acid. Consequently, with a constant initiator concentration ($[Monams]_0 \approx 0.02$ mol·L^{-1}) we varied the initial $r = [\text{free SG1}]_0/[Monams]_0$ molar ratio from 0.044 to 0.090, so as to determine the optimal value. The corresponding experimental conditions are reported in Table 1, entries 1 and 2. The first and important result is that the polymerization rate was strongly affected by the initial concentration of free nitroxide (Figure 1). Indeed, the slope of the logarithmic conversion vs time, taken in the linear region (which is actually $k_p[P^\bullet]$, with $[P^\bullet]$ the concentration of propagating macroradicals) was divided by a factor of 2 when the initial amount of free SG1 was multiplied by 2 (the initial S-shape might be due to the arbitrary selection of the time zero, when the reaction medium reached 110 °C, which might be too low a temperature for an efficient decomposition of the initiator; see experimental part).

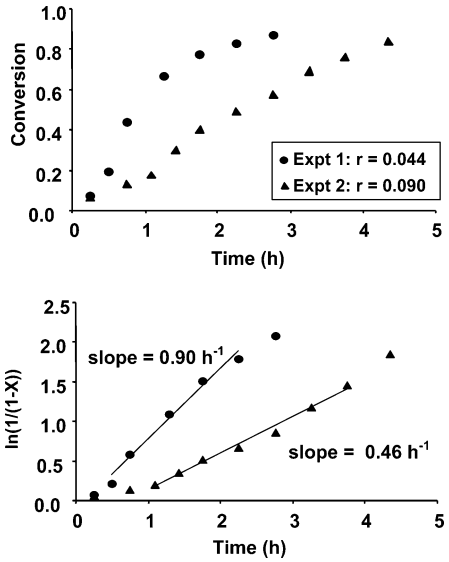


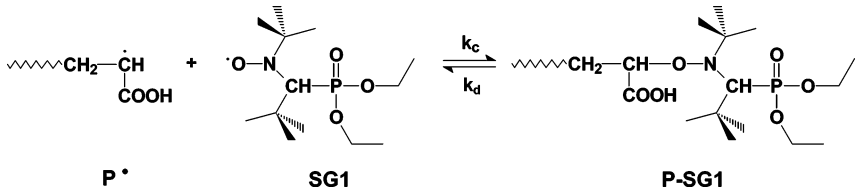
Figure 1. Conversion, x, and $\ln(1/(1-x))$ vs polymerization time for the experiments 1 and 2 (see Table 1 for experimental conditions).

This effect on $[P^\bullet]$ is in agreement with the participation of SG1 in the polymerization process, i.e., with the existence of an activation−deactivation equilibrium relationship that controls the polymerization kinetics[31] (eq 1) (see Scheme 1).

$$K = \frac{[P^\bullet][SG1]}{[P-SG1]} \quad (1)$$

K is the equilibrium constant, [SG1] is the concentration of free nitroxide and [P−SG1] is the concentration of poly(acrylic acid)-based alkoxyamine. With large initial concentration of free nitroxide, as it is the case here, [SG1] should remain close to the initial value, $[SG1]_0$. The effect of $[SG1]_0$ on the concentration of progagating radicals points out the possibility of a controlled behavior. This last point was confirmed by the analysis of the

Scheme 1. Activation−Deactivation Equilibrium in Nitroxide-Mediated Controlled Free-Radical Homopolymerization of Acrylic Acid ($K = k_d/k_c$ = [P•][SG1]/[P−SG1])



molar masses and molar mass distributions of the corresponding methylated polymers. Indeed, as shown in Figure 2 a linear increase in the number-average molar mass, M_n, with monomer conversion was observed, following the theoretical line, irrespective of the initial concentration of free SG1. Again, this feature is in agreement with a controlled behavior, disclosing that polymerization actually took place with fast initiation and a constant chain concentration corresponding to the alkoxyamine initial concentration ([P−SG1] = $[\text{Monams}]_0$). The effect of SG1 initial concentration was not only seen on the polymerization rate but also on the quality of molar mass distributions: in both experiments, the polydispersity indexes were below 1.6 but they were lower when $[\text{SG1}]_0$ was increased (below 1.4 for experiment 2). Consequently, all of the expected criteria of a controlled free-radical polymerization were met by the SG1-mediated polymerization of acrylic acid, initiated by Monams, in 1,4-dioxane at 120 °C. From these results, an excess of 9 mol % of free SG1 with respect to the alkoxyamine initiator seems to be the most appropriate amount: it corresponded to the best compromise between fast reaction (80% conversion within 4 h) and good quality of control. Thus, for all other experiments this same initial ratio was applied.

3. Effect of the Monams initial concentration. In this series of experiments (Table 1, experiments 2−4), the initial concentration of Monams was varied from 0.0098 (experiment 4) to 0.0387 mol·L^{-1} (experiment 3) and the initial concentration of free SG1 was adjusted so as to keep the r ratio constant and equal to 0.090.

Molar Mass and Molar Mass Distribution. For experiments 2 and 3, which corresponded to the highest Monams concentrations and hence to the lowest target molar masses, the M_n values of the methylated polymers followed the related theoretical lines and the final polydispersity indexes were in the 1.3−1.4 range (Figure 3). This result supports the previous observations that a controlled behavior operated in the investigated system. In contrast, for experiment 4, the experimental M_n values fitted the calculated ones until 30% conversion and then deviated from linearity (Figure 3). Simultaneously, the polydispersity indexes increased from 1.3 to 1.7. This downward curvature of M_n vs conversion, along with the broadening of the molar mass distribution, is characteristic of the creation of new chains (by chain transfer to solvent) and will be discussed later.

Polymerization Kinetics. The polymerization kinetics were followed by ^{1}H NMR for all of the experiments. The conversions are displayed vs time in Figure 4. All polymerizations achieved large conversions, typically 85−90 mol %, within 4 to 5 h. The slopes of ln(1/(1 − x)) vs time, giving $k_p[\text{P}^\bullet]$, were determined in the linear region and are reported in Table 1. It appears that $k_p[\text{P}^\bullet]$, and hence [P•], did not directly depend upon the initiator concentration, but upon the r ratio only.

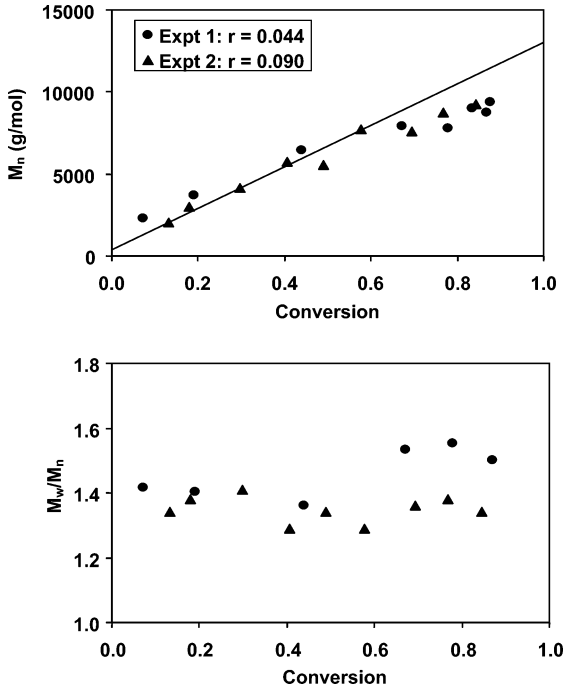


Figure 2. M_n and polydispersity indexes, M_w/M_n, (from SEC, polystyrene calibration) of the methylated polymers vs conversion x (from NMR) for the experiments 1 and 2 (see Table 1 for experimental conditions); the line refers to the corresponding theoretical curve $M_n = \text{MW}_{\text{Monams}} + x[\text{AA}]_0\text{MW}_{\text{methyl acrylate}}/[\text{Monams}]_0$.

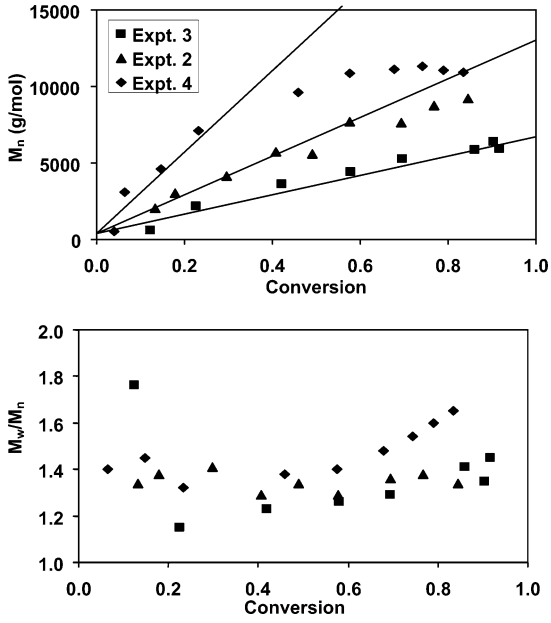


Figure 3. M_n and polydispersity indexes, M_w/M_n (from SEC, polystyrene calibration) of the methylated polymers vs conversion (from NMR) for experiments 2−4 (see Table 1 for experimental conditions); the lines refer to the corresponding theoretical curves $M_n = \text{MW}_{\text{Monams}} + x[\text{AA}]_0\text{MW}_{\text{methyl acrylate}}/[\text{Monams}]_0$.

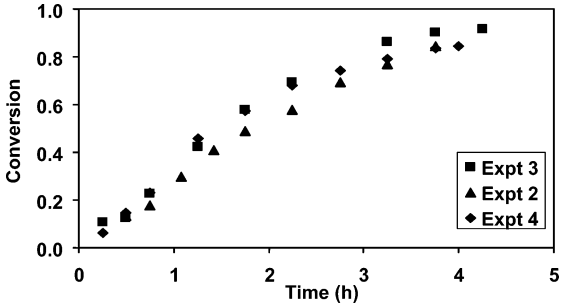


Figure 4. Conversion, x, vs polymerization time for experiments 2−4 (see Table 1 for experimental conditions).

From $k_p[P^\bullet]$, the k_pK value can be estimated (Table 1) according to eq 2 (because the initial concentration of free SG1 was large, the amount of this nitroxide released owing to the persistent radical effect[32] could be neglected, thus, eq 1 can be rewritten as $K = [P^\bullet][SG1]_0/[Monams]_0$ with $[P-SG1] = [Monams]_0$ as shown above).

$$k_pK = k_p \cdot \frac{[P^\bullet][SG1]_0}{[Monams]_0} = k_p[P^\bullet]r \qquad (2)$$

For all four experiments (experiments 1−4), as anticipated, the k_pK values were very close to each others, in the 1.1×10^{-5} to 1.8×10^{-5} s^{-1} range. With k_p larger than 10^5 $L \cdot mol^{-1} \cdot s^{-1}$,[13] K should be close to 10^{-10} or below. So even if acrylic acid exhibits a very large rate constant of propagation, its reactivity is moderated by quite a low activation−deactivation equilibrium constant (Scheme 1). As a comparison, the k_pK value for styrene at 120 °C is 4.8×10^{-6} s^{-1} and for *n*-butyl acrylate at 120 °C, it is 1.8×10^{-5} s^{-1}.[33] Consequently acrylic acid exhibits a behavior, in SG1-mediated CRP, that is not very different from that of *n*-butyl acrylate (large k_p, low K).

Because of the high initial concentration of free nitroxide, the autopolymerization of acrylic acid has no influence on the kinetics. Indeed, the consumption of excess free nitroxide by the radicals produced by autoinitiation remains extremely negligible: from $k_p[P^\bullet]$ of experiment 5 performed without initiator (see Table 1) and using the steady-state assumption with $k_t = 3 \times 10^8$ $L \cdot mol^{-1} \cdot s^{-1}$, the rate of autoinitiation can be determined, $R_i = 3 \times 10^{-11}$ $mol \cdot L^{-1} \cdot s^{-1}$. Therefore, the overall concentration of radicals produced over a period of 5 h (and hence of consumed nitroxide) is approximately 5×10^{-7} $mol \cdot L^{-1}$, much lower that the minimum $[SG1]_0 \approx 10^{-3}$ $mol \cdot L^{-1}$ used in this work. Thus, the concentration of propagating macroradicals is well described by eq 2, in which the initial concentration of free nitroxide is considered.

4. Chain Transfer to 1,4-Dioxane. The chain transfer constant to 1,4-dioxane ($C_{tr} = k_{tr}/k_p$, with k_{tr} the rate constant of transfer) was evaluated from experiment 5 (Table 1), assuming that in this experiment, performed in the absence of initiator, chain transfer to solvent was the main irreversible chain breaking event. On the basis of samples taken at various conversions, C_{tr} was calculated from eq 3.[34]

$$C_{tr} = \frac{\ln\left(1 - \frac{[\text{polymer chains}]}{[\text{solvent}]_0}\right)}{\ln(1-x)} \qquad (3)$$

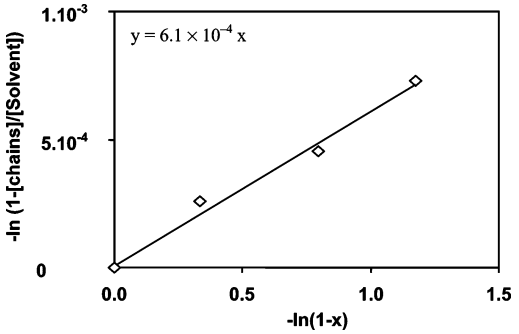


Figure 5. $-\ln(1 - [\text{polymer chains}]/[\text{solvent}])$ vs $-\ln(1-x)$ for experiment 5 (see Table 1 for experimental conditions). The slope gives C_{tr}, the chain transfer constant to 1,4-dioxane.

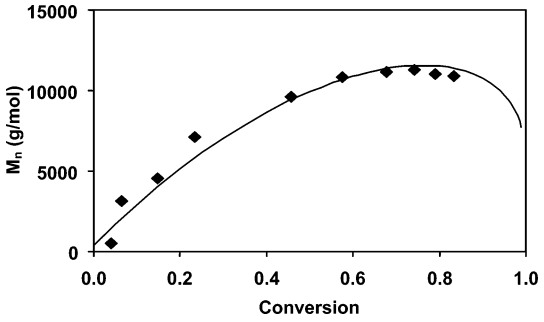


Figure 6. M_n (from SEC, polystyrene calibration) of the methylated polymers vs conversion (from NMR) for experiment 4 (see Table 1 for experimental conditions); the line refers to the theoretical curve including transfer to 1,4-dioxane and calculated according to eq 4.

In this equation, the concentration of polymer chains is calculated by $[\text{polymer chains}] = x[AA]_0/DP_n$, in which x is the monomer conversion and DP_n, the number-average degree of polymerization, is estimated from SEC analysis of the methylated polymers. The evolution of $-\ln(1 - [\text{polymer chains}]/[\text{solvent}]_0)$ as a function of $-\ln(1-x)$ gives a C_{tr} value of 6×10^{-4} (Figure 5), which is in good agreement with the $C_{tr} = 3.9 \times 10^{-4}$ calculated by Loiseau et al.[23] for the polymerization of acrylic acid in dioxane at 80 °C. This value fully explains the downward deviation of M_n with increasing conversion for experiment 4 as shown in Figure 6 with the comparison of the experimental data with the calculated ones; the latter were derived from eq 4, in which the concentration of new chains created by transfer to solvent was taken into account.[35]

$$DP_n = \frac{x[AA]_0}{[Monams]_0 + [solvent]_0(1 - (1-x)^{C_{tr}})}$$

$$M_n = MW_{Monams} + \frac{x[AA]_0}{[Monams]_0 + [solvent]_0 \cdot (1 - (1-x)^{C_{tr}})} \times MW_{Methyl\ Acrylate} \qquad (4)$$

Using $C_{tr} = 6 \times 10^{-4}$ and the following conditions ($[AA]_0 = 3$ $mol \cdot L^{-1}$ and $[1,4\text{-dioxane}] = 9$ $mol \cdot L^{-1}$), the evolution of DP_n with conversion was simulated (from eq 4) for different Monams concentrations (Figure 7). These theoretical results allow to determine the conversion range in which molar masses are mainly controlled by the alkoxyamine initiator concentration. For instance, with $[Monams]_0 = 10^{-2}$ $mol \cdot L^{-1}$, the polymerization can

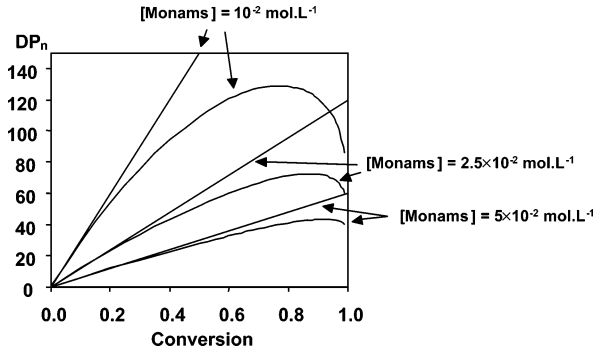


Figure 7. Calculated DP_n including chain transfer to 1,4-dioxane (according to eq 4) vs conversion and comparison with theoretical DP_n without transfer ($DP_n = x[AA]_0/[Monams]_0$). Data used for simulation: $[AA]_0 = 3$ mol·L^{-1}; [1,4-dioxane] = 9 mol·L^{-1}; $C_{tr} = 6 \times 10^{-4}$.

be considered controlled only below 20% conversion. Above this conversion, the proportion of dead chains cannot be neglected anymore. Only for larger Monams concentrations can the conversion proceed to acceptable value, while keeping a controlled system. This situation should be very carefully taken into account when block copolymers are designed.

Consequently, chain transfer to 1,4-dioxane is quite restraining for this system. The same conclusion was also drawn for the RAFT polymerization of acrylic acid.[23] To reduce the influence of solvent, we should stop the polymerization at low conversion or increase the initial monomer concentration. This last option is not flexible due to the highly exothermic reaction and poor control in concentrated media. However, for many applications related to dispersion stabilization (homopolymers for inorganic particles,[23] amphiphilic block copolymers for latex particles,[24,36] ...), low molar mass polymers with narrow molar mass distribution are usually targeted, and can thus be very simply achieved according to the proposed recipe.

5. Chain Transfer to Polymer. Structure of the polymer chains created by CRP is often depicted as linear. However with free-radical polymerization, some monomers are prone to chain transfer to polymer, which creates branched structures. This is the case for the family of acrylates[37] and, as recently demonstrated, for acrylic acid too.[23] Additionally, chain transfer to polymer is not eliminated when CRP is used, and the existence of branches has been clearly evidenced for SG1-capped poly(*n*-butyl acrylate)s prepared in bulk and in miniemulsion at 112 °C,[38] as well as for poly(acrylic acid) made from RAFT.[23] The best technique to quantitatively characterize the presence of branches is carbon 13 NMR, which allows to visualize the quaternary carbon at a branch junction, together with the three adjacent CH_2 and CH. Peak assignment has been presented by Loiseau et al. for poly(acrylic acid)s synthesized via the RAFT technique.[23] Figure 8 shows the ^{13}C NMR spectrum of the final polymer from experiment 2 and illustrates the existence of branches according to the previous assignments. The quantitative analysis for the final polymers at 85−90% conversion gives 4.7, 6.1, and 4.6 branches per 100 monomer units for experiments 3, 2, and 4, respectively (for calculation see ref 38). Depending on the target molar masses, this leads to an average of 3.2 branches per chain for experiment 3 (DP_n = 69), 6.5 for experiment 2 (DP_n = 107), and 5.8 for experiment 4 (DP_n = 127). Consequently, linear structures do not exist, even for short poly(acrylic acid)s. An

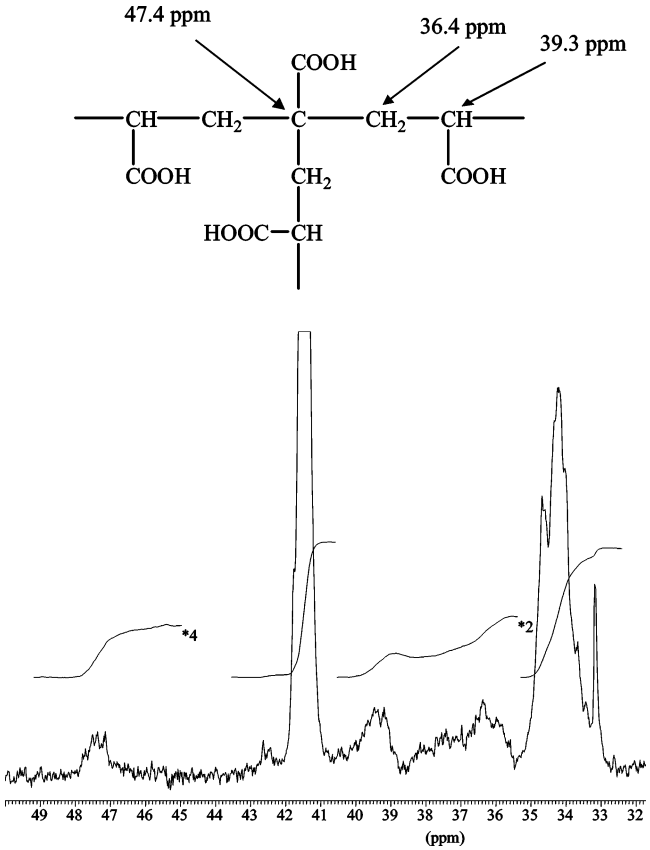


Figure 8. Carbon 13 NMR spectrum between 32 and 50 ppm for the final poly(acrylic acid) from experiment 2, isolated at 85% conversion.

important point that remains unsolved is the very mechanism by which chain transfer to polymer occurs, i.e., intermolecular or intramolecular (backbiting). This discussion is beyond the scope of this article but it should be reminded that it might have a strong impact on the chain structure.[38] From recent work on branching in *n*-butyl acrylate free-radical polymerization, the intramolecular mechanism is supposed to be the main pathway.[38,39]

6. Chain Extension: Synthesis of a Poly(acrylic acid)-*b*-poly(styrene-*co*-acrylic acid) Block Copolymer. A one-pot experiment was performed (see Table 2) to show the ability of SG1-capped poly(acrylic acid) to reinitiate a polymerization. In this way, acrylic acid was polymerized in the same conditions as previously used and styrene was added into the system after 56% conversion of acrylic acid (see experimental part). At this stage, the number-average molar mass of the methylated polymer was $M_n = 7100$ g·mol^{-1} with M_w/M_n = 1.32 (DP_n = 78, whereas theoretical DP_n was 85) and the calculated percentage of additional dead chains generated by chain transfer to solvent was 22 mol % (with respect to Monams). The second step corresponded to the copolymerization of acrylic acid and styrene with an acrylic acid initial molar proportion of $f_{AA0} = 0.52$. The overall molar conversion as estimated by ^1H NMR reached 90% within 8 h. The M_n values of the methylated polymers matched the theoretical ones (Figure 9) and the polydispersity indexes remained rather constant, around 1.3−1.4. Therefore, poly(acrylic acid) prepared via SG1-mediated CRP was perfectly able to reinitiate a polymerization in a controlled fashion, providing low molar masses are targetted for the first

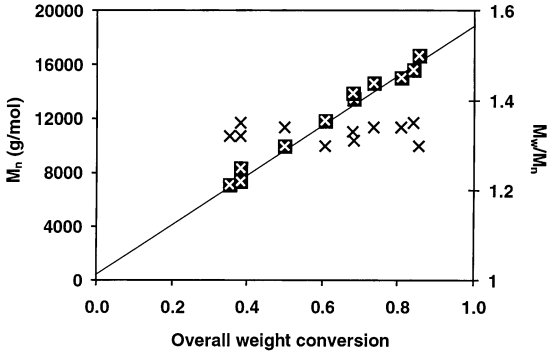


Figure 9. M_n and polydispersity indexes, M_w/M_n, (from SEC, polystyrene calibration) of the methylated copolymers vs the overall weight conversion (recalculated from ^{1}H NMR; see Experimental Part) for experiment 6 (see Table 2 for experimental conditions). The line refers to the corresponding theoretical curve.

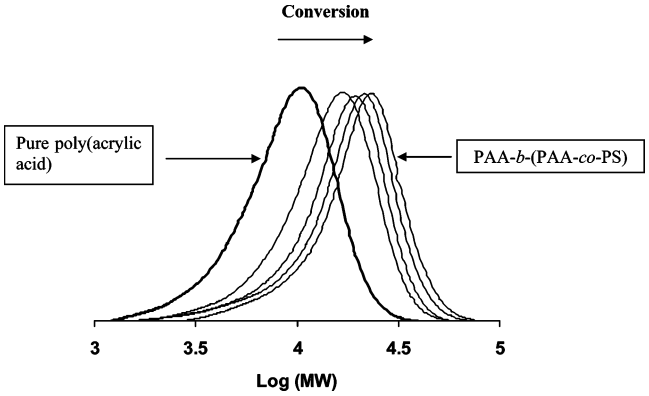


Figure 10. SEC curves (refractive index detector) for experiment 6 (see Table 2 for experimental conditions).

poly(acrylic acid) block. This behavior is illustrated in Figure 10, which displays the continuous shift of the SEC curves toward the higher molar masses, obtained for the methylated polymers of experiment 6. The tailing on the low molar mass side was the result of the aforementioned existence of short dead chains created by chain transfer to solvent.

Conclusion

Free-radical homopolymerization of acrylic acid was carried out in 1,4-dioxane solution at 120 °C and 2 bar, using an alkoxyamine initiator based on the *N*-*tert*-butyl-*N*-(1-diethyl phosphono-2,2-dimethyl propyl) nitroxide, SG1. The polymerization exhibited all the expected features of a controlled system based on both alkoxyamine thermal activation and macroradicals reversible deactivation by SG1 (the so-called activation−deactivation equilibrium). The kinetics were controlled by the addition of free nitroxide at the beginning of the polymerization and the optimal amount was 9 mol % with respect to the initiator. Consequently, the SG1 nitroxide was stable under the chosen experimental conditions and led to a good control of the polymerization. Although acrylic acid exhibits a very large rate constant of propagation, its reactivity was shown to be moderated by a low activation−deactivation equilibrium constant between active macroradicals and SG1-capped dormant chains. Chain transfer to 1,4-dioxane was the most restrictive event in the process and led to a drastic molar mass limitation. From these results, the best experimental conditions to obtain well-defined homopolymers with the minimum amount of dead chains were identified. Controlled character of the polymers was demonstrated by reinitiation of a styrene/acrylic acid mixture, to lead to a poly(acrylic acid)-*b*-poly(styrene-*co*-acrylic acid) block copolymer. In conclusion, the homopolymerization of acrylic acid can be controlled by a nitroxide, providing the most appropriate experimental conditions are selected.

References and Notes

(1) *Controlled Radical Polymerization*; Matyjaszewski, K., Ed.; ACS Symposium Series 685; American Chemical Society: Washington, DC, 1998.
(2) *Controlled/Living Radical Polymerization: Progress in ATRP, NMP, and RAFT*; Matyjaszewski, K., Ed.; ACS Symposium Series 768; American Chemical Society: Washington, DC, 2000.
(3) *Advances in Controlled/Living Radical Polymerization*; Matyjaszewski, K., Ed.; ACS Symposium Series 854; American Chemical Society: Washington, DC, 2003.
(4) Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661.
(5) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921.
(6) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689.
(7) Chong, Y. K.; Krstina, J.; Le, T. P. T.; Moad, G.; Postma, A.; Rizzardo, E.; Thang, S. H. *Macromolecules* **2003**, *36*, 2256.
(8) Chiefari, J.; Mayadunne, R. T. A.; Moad, C. L.; Moad, G.; Rizzardo, E.; Postma, A.; Skidmore, M. A.; Thang, S. H. *Macromolecules* **2003**, *36*, 2273.
(9) Charmot, D.; Corpart, P.; Adam, H.; Zard, S. Z.; Biadatti, T.; Bouhadir, G. *Macromol. Symp.* **2000**, *150*, 23.
(10) Qiu, J.; Charleux, B.; Matyjaszewski, K. *Prog. Polym. Sci.* **2001**, *26*, 2083.
(11) Patten, T. E.; Matyjaszewski, K. *Adv. Mater.* **1998**, *10*, 901.
(12) Odell, P. G.; Veregin, R. P. N.; Michalak, L. M.; Brousmiche, D.; Georges, M. K. *Macromolecules* **1995**, *28*, 8453.
(13) Lacik, I.; Beuermann, S.; Buback, M. *Macromolecules* **2001**, *34*, 6224.
(14) Ali-Miraftab, S.; Chapiro, A.; Mankowski, Z. *Eur. Polym. J.* **1981**, *17*, 1197.
(15) Gnanou, Y.; Grande, D.; Guerrero, R. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1999**, *40* (2), 99.
(16) Benoit, D.; Chaplinski, V.; Braslau, R.; Hawker, C. J. *J. Am. Chem. Soc.* **1999**, *121*, 3904.
(17) Huang, W.; Charleux, B.; Chiarelli, R.; Marx, L.; Rassat, A.; Vairon, J. P. *Macromol. Chem. Phys.* **2002**, *203*, 1715.
(18) Ashford, E. J.; Naldi, V.; O'Dell, R.; Billingham, N. C.; Armes, S. P. *Chem. Commun.* **1999**, 1285.
(19) Wang, X. S.; Jackson, R. A.; Armes, S. P. *Macromolecules* **2000**, *33*, 255.
(20) Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. G.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559.
(21) Chong, Y. K.; Le, T. P. T.; Moad, G.; Rizzardo, E.; Thang, S. H.; *Macromolecules* **1999**, *32*, 2071.
(22) Ladavière, C.; Dörr, N.; Claverie, J. P. *Macromolecules* **2001**, *34*, 5370.
(23) Loiseau, J.; Dörr, N.; Suau, J. M.; Egraz, J. B.; Llauro, M. F.; Ladavière, C.; Claverie, J. *Macromolecules* **2003**, *36*, 3066.
(24) Gaillard, N.; Guyot, A.; Claverie, J. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 684.
(25) Hong, C.-Y.; You, Y.-Z.; Bai, R.-K.; Pan, C.-Y.; Borjihan, G. *J. Polym. Sci., Part A, Polym. Chem.* **2001**, *39*, 3934.
(26) Taton, D.; Wilczewska, A.-Z.; Destarac, M. *Macromol. Rapid Commun.* **2001**, *22*, 1497.
(27) Grimaldi, S.; Finet, J. P.: Le Moigne, F.; Zeghdaoui, A.; Tordo. P.; Benoit, D.; Fontanille, M.; Gnanou, Y. *Macromolecules* **2000**, *33*, 1141.
(28) Lacroix-Desmazes, P.; Lutz, J. F.; Chauvin, F.; Severac, R.; Boutevin, B. *Macromolecules* **2001**, *34*, 8866.
(29) Mark-Houwink-Sakurada parameters in THF at 30 °C: $K_{PS} = 11.4\ 10^{-5}$ dL·g^{-1} and $\alpha_{PS} = 0.716$ for polystyrene [see Hutchinson, R. A.; Paquet, D. A., Jr.; McMinn, J. H.; Beuermann, S.; Fuller, R. E.; Jackson, C. *Dechema Monogr.* **1995**, *131*, 467]; $K_{PMeA} = 9.5\ 10^{-5}$ dL·g^{-1} and $\alpha_{PMeA} = 0.719$ for poly(methyl acrylate) [Piteau, G. Unpublished results; for experimental conditions, see: Couvreur, L.; Piteau, G.; Castignolles, P.; Tonge, M.; Coutin, B.; Charleux, B.; Vairon, J.

P. *Macromol. Symp.* **2001**, *174*, 197]. At 25 °C in THF, $K_{PMeA} = 10.0\ 10^{-5}$ dL·g^{-1} and $\alpha_{PMeA} = 0.730$ [see Penzel, E.; Goetz, N. *Angew. Makromol. Chem.* **1990**, *178*, 191]. The same conclusion was previously drawn for poly(*n*-butyl acrylate).[38]

(30) Marque, S.; Le Mercier, C.; Tordo, P.; Fischer, H. *Macromolecules* **2000**, *33*, 4403.

(31) Fukuda, T.; Goto, A.; Ohno, K. *Macromol. Rapid Commun.* **2000**, *21*, 151.

(32) Souaille, M.; Fischer, H. *Macromolecules* **2002**, *35*, 248.

(33) Benoit, D.; Grimaldi, S.; Robin, S.; Finet, J. P.; Tordo, P.; Gnanou, Y. *J. Am. Chem. Soc.* **2000**, *122*, 5929.

(34) Moad, G.; Solomon, D. H. *The chemistry of free-radical polymerization;* Pergamon, Elsevier Science Ltd.: Oxford, U.K., 1995.

(35) Equation 4 leads to similar results as the equation used by Loiseau et al.;[23] the difference is that we considered the consumption of solvent (which is actually a very small fraction) due to the chain transfer process; see Müller, A. H. E.; Zhuang, R.; Yan, D.; Litvinenko, G. *Macromolecules* **1995**, *28*, 4326.

(36) Burguière, C.; Pascual, S.; Bui, C.; Vairon, J. P.; Charleux, B.; Davis, K.; Matyjaszewski, K.; Bétremieux, I. *Macromolecules* **2001**, *34*, 4439.

(37) Ahmad, N. M.; Heatley, F.; Lovell, P. A. *Macromolecules* **1998**, *31*, 2822.

(38) Farcet, C.; Belleney, J.; Charleux, B.; Pirri, R. *Macromolecules* **2002**, *35*, 4912.

(39) Plessis, C.; Arzamendi, G.; Alberdi, J. M.; van Herk, A. M.; Leiza, J. R.; Asua, J. M. *Macromol. Rapid Commun.* **2003**, *24*, 173.

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