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Kinetics of in-Situ Formation of Poly(acrylic acid)-*b*-polystyrene Amphiphilic Block Copolymers via Nitroxide-Mediated Controlled Free-Radical Emulsion Polymerization. Discussion on the Effect of Compartmentalization on the Polymerization Rate

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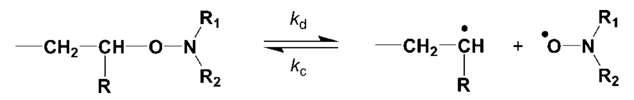
ABSTRACT: The kinetics of surfactant-free, ab initio, batch emulsion polymerization of styrene mediated by the nitroxide SG1 ((*N*-*tert*-butyl-*N*-1-diethylphosphono-(2,2-dimethylpropyl) nitroxide) in the presence of a poly(sodium acrylate) macroalkoxyamine playing the role of both the initiator and the stabilizer were studied, and the influence of the compartmentalization of the propagating radicals on the monomer conversion rate was discussed. It was pointed out that the local monomer concentration within very small particles has to be considered with great care. The results showed that free nitroxide was not compartmentalized and that the kinetics were not particularly affected by particle size, even for very small particles below 66 nm in diameter.

Introduction

In classical free-radical emulsion polymerization,[1–7] the radicals are generated in the aqueous solution, whereas the majority of propagation takes place in the monomer-swollen latex particles. Consequently, the polymerization kinetics are governed by multiple parameters such as aqueous-phase events, radical entry into a latex particle, radical exit following a chain transfer reaction, and fate of an exited radical. Some of those parameters directly depend on the particle size and particle number. The steady-state conditions are then determined by the termination reaction being rate-determining or not. In the latter case, when particles are small enough, two radicals present within the same particle at the same time undergo instantaneous termination. This situation corresponds to the zero-one model: particles contain either zero or one radical. The radicals can then be considered as compartmentalized, and the overall rate of termination is reduced with respect to that in a similar bulk process. The total concentration of propagating radicals calculated per unit volume of the organic phase and the polymerization rate are significantly larger than in bulk.

Besides classical free-radical polymerization, there is now the development of controlled/living free-radical polymerization (CRP) methods in aqueous dispersed systems such as emulsion and miniemulsion.[8–13] An important issue is then to understand whether or not the compartmentalization effect operates in such polymerizations. In other words, is there any influence of the particle size on the rate of the various reactions involved? This question concerns most particularly the CRP methods that obey a reversible termination mechanism such as nitroxide-mediated polymerization (NMP)[14–16] and atom transfer radical polymerization.[17,18] In homogeneous conditions, the kinetics of those CRP reactions are regulated by the activation−deactivation equilibrium (see Scheme 1 and eq 1 for NMP, in which $[\mathrm{P}^\bullet]$ is the concentration of propagating radicals, $K = k_d/k_c$ is the activation−deactivation equilibrium constant, the alkoxyamine is the dormant state of the polymer chains, and the free nitroxide is the deactivator of the propagating radicals) and by the persistent radical effect.[19,20] The concentration of deactivator continuously increases with time due to irreversible termination between propagating radicals, the concentration of which then continuously decreases. The large difference in concentration between the two species (usually 3−4 orders of magnitude) kinetically favors the reversible termination over the irreversible one.

Scheme 1. Activation−Deactivation Equilibrium in Nitroxide-Mediated Controlled Free-Radical Polymerization[a]



[a] $K = k_d/k_c$, with k_d the rate constant of alkoxyamine dissociation and k_c the recombination rate constant of a propagating radical and a nitroxide.

$$[\mathrm{P}^\bullet] = \frac{K[\text{alkoxyamine}]}{[\text{free nitroxide}]} \qquad (1)$$

The compartmentalization effect in nitroxide-mediated miniemulsion polymerization was studied on a theoretical basis for the first time by Butté et al. in 1998.[21] Several other papers followed,[22–25] all of which concluded that the kinetics in small particles should be affected. Butté et al.,[21] Zetterlund et al.,[23,24] and Tobita et al.[25] assumed that both propagating radicals and nitroxide were compartmentalized, and they calculated that in small particles the polymerization rate should decrease, providing that the initial nitroxide concentration is low enough for the effect to be observed. Zetterlund et al.[23,24] and Tobita et al.[25] explained the slower polymerization rate by a confined space effect whereby the rate of deactivation of a propagating radical by a nitroxide increased, the consequence being a reduced lifetime of the propagating radicals. In such systems, the free nitroxide does not accumulate within the particles, and the average number of both propagating radicals and free nitroxide should be below 1 (i.e., a major part of the particles should contain none of those radical species). Our group[22] considered differently that the free nitroxide was not compartmentalized (fast diffusion between the different phases of the system) and came to an opposite conclusion: when particles are small enough and the initial nitroxide concentration is low, because of the compartmentalization of the propagating radicals, the initial rate of irreversible termination is lower in miniemulsion than in bulk, hence leading to a slower production of free

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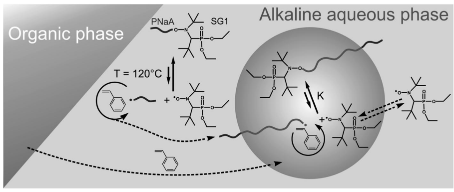
nitroxide and consequently to a higher total concentration of propagating radicals. We calculated that the average number of propagating radicals per particle, which depends on the particle number, should be far below 1, whereas the average number of free nitroxide per particle should be well above 1 (all particles contain free nitroxides molecules; only very few of them contain a propagating radical).

For the NMP of styrene at a temperature above 100 °C, many other side reactions may affect the polymerization kinetics. An important one is thermal autoinitiation.[20] The effect of this additional source of radicals depends on the type of nitroxide (due to the kinetic and thermodynamic parameters regulating the polymerization kinetics)[20] and on the particle size (in small particles one expects a fast geminate recombination of the radicals produced in pair).[21,26] The models proposed by Butté et al.,[21] Zetterlund et al.,[23,24] and Tobita et al.[25] accounted for that side reaction, which is actually of high importance in the kinetics of TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl)-mediated CRP of styrene,[20] but much less important in SG1 ((*N*-*tert*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide))-mediated CRP.[27] The partition coefficient of the nitroxide, possible degradation reactions, and fate of exited radicals may also affect the kinetics. Those features actually complicate the systems, leading to nonuniversal outcome.

All previous conclusions were based on theoretical models, but only one very recent article by Cunningham's group[28] reports experimental results. The study is based on TEMPO-mediated polymerization of styrene at 135 °C in miniemulsion, in which the particle diameter was varied from 180 to 50 nm, typically in the range where a compartmentalization effect was predicted. They found that decreasing the diameter resulted in lower conversion rates in the absence of hexadecane (only the TEMPO-terminated polystyrene macroinitiator played the role of the hydrophobe in the system). In the presence of hexadecane, however, the decreasing conversion rate in the small particles was not so pronounced. They also calculated that the average number of propagating radicals per particle was well below 1, dependent on the particle size, and that the average number of free nitroxides per particle was above 1 or close to 1 for the smallest particles. The very large difference in overall concentrations of propagating radicals (10^{-8}−10^{-7} mol L^{-1} in the particle phase) and free nitroxide (10^{-5}−10^{-4} mol L^{-1} in the particle phase) was an indication that the persistent radical effect operated. They considered a fast diffusion of TEMPO, as determined in a previous article,[29] and proposed that the decreased rate of polymerization was partially due to a rapid deactivation of the exited carbon-centered radicals by TEMPO present in the aqueous phase, with low probability of adding monomer and reentering a particle. They also concluded that the reduced rate of thermal initiation and the enhanced deactivation of propagating radicals by TEMPO due to the confined space effect within the particles both contributed to polymerization rate reduction. In addition, they carefully studied the effect of particle size on the polymer chain livingness (i.e., mole fraction of chains terminated with TEMPO-based alkoxyamine) and demonstrated that smaller particles exhibited superior livingness at equivalent conversion, in agreement with the reduced irreversible termination rate predicted by the confined space effect.

Scheme 2. Illustration of the SG1-Mediated Batch Emulsion Polymerization of Styrene Using a Water-Soluble SG1-Capped Poly(sodium acrylate) (PNaA) Alkoxyamine Macroinitiator



In this article, we show experimental results on the SG1-mediated batch emulsion polymerization of styrene at 120 °C, in which a water-soluble SG1-capped poly(sodium acrylate) alkoxyamine is used as a macroinitiator (Scheme 2). In such conditions, the system forms amphiphilic block copolymers, which self-assemble in very small, micelle-like particles (diameter was typically below 66 nm) simultaneously with the growth step. We focus exclusively here on the polymerization kinetics, and we address the important issue of the effect of compartmentalization of the propagating radicals on their total concentration and on the monomer conversion rate in emulsion NMP. Those results have never been presented and discussed before, whereas the evolution of molar mass, molar mass distribution, average number of block copolymers per particle and parameters that affect the particle size have been reported earlier.[30,31]

Experimental Part

Materials. Styrene (St, Aldrich, 99%) was distilled under reduced pressure before use. Sodium carbonate (Na_2CO_3, Prolabo, pure) was used as received. The *N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (SG1, 86%) was kindly supplied by Arkema.

Synthesis of the SG1-Capped Poly(acrylic acid) Macroinitiator. The synthesis and characterization of the SG1-capped poly(acrylic acid) macroinitiator (PAA-SG1) were already published.[32,33] For the purpose of using those homopolymers as macroinitiators, the polymerization conditions were defined in order to get the highest chain-end functionality (a precise description is given in the experimental part of ref 33). The macroinitiators were purified by precipitation in diethyl ether and dried under vacuum at room temperature. Three different samples with similar characteristics were used: number-average molar mass, $M_n = 1710$ g mol^{-1} (number-average degree of polymerization, $DP_n = 18.5$), for experiments 1, 2, and 3, $M_n = 1880$ g mol^{-1} ($DP_n = 20.8$) for experiments 4 and 5, and $M_n = 1820$ g mol^{-1} ($DP_n = 19.9$) for experiments 6 and 7. In all cases, the polydispersity index, M_w/M_n was below 1.2 and the chain-end functionality was close to 95%.[33]

Emulsion Polymerization of Styrene. The experimental conditions for the heterogeneous polymerization of styrene were already published.[30,31] The reactions were all carried out in batch, at 120 °C, under a 3 bar pressure of nitrogen, in a 300 mL thermostated glass reactor stirred at 300 rpm. In a typical recipe (experiment 1 in Table 1), 38.3 g of styrene (0.37 mol, 20.0 wt % based on water) was added at room temperature to a NaOH water solution (150 mL; 1 equiv of NaOH based on the carboxylic acid groups and 0.036 mol L_{aq}^{-1} of Na_2CO_3)) of the required amount (1.88 g; 1.1 × 10^{-3} mol; 7.33 × 10^{-3} mol L_{aq}^{-1}) of the SG1-capped poly(acrylic acid) macroinitiator. The obtained unstable biphasic system was introduced into the preheated and stirred reactor, after nitrogen bubbling for 20 min at room temperature. The polymerizations were allowed to proceed for 8 h. In all cases the pH remained close to 10 throughout the polymerization. During the polymerization course, 6 mL samples were taken at regular time intervals to follow the monomer conversion by gravimetry and to analyze the polymer and the particles by methods described below. The various experimental conditions are reported in Table 1.

Particle Size Analysis. The average particle diameter was measured by dynamic light scattering (DLS) of the diluted water suspensions at pH = 4, at a temperature of 25 °C and an angle of 90°, with a Zetasizer Nano S90 from Malvern, using a 4 mW He−Ne laser at 633 nm. By applying a multimodal analysis with the CONTIN routine, it was possible to extract a number-average particle diameter (D), which was further used for determination of the number of particles, N_p. Since the diameter was measured at low pH in diluted conditions, the poly(acrylic acid) shell was

Table 1. Experimental Conditions and Characteristics of the Emulsion Polymerizations of Styrene (St) at 120 °C, Initiated by an SG1-Terminated Poly(acrylic acid) Macroalkoxyamine (PAA-SG1) in Alkaline Conditions (Temperature = 120 °C; Pressure = 3 bar; $[Na_2CO_3]_0$ = 35 mM_{aq})

expt	$[PAA\text{-}SG1]_0$, mol L_{aq}^{-1}	$[PAA\text{-}SG1]_{org}$, mol L_{org}^{-1}	$[SG1]_0$, mol % based on PAA-SG1	St/water, wt %	dx/dt, s^{-1}	$10^8 \times [P^\bullet]_{org}$,[a] mol L_{org}^{-1}	final D, nm	$\bar{n}$[b]	$[SG1]_p/[PAA\text{-}SG1]_{org}$[c]
1	7.3×10^{-3}	0.023	0	20.0	5.6×10^{-5}	4.5	51	0.0024	0.134
2	7.2×10^{-3}	0.023	5.0	19.9	3.7×10^{-5}	2.9	52	0.0017	0.205
3	7.2×10^{-3}	0.023	10.4	19.9	2.7×10^{-5}	2.1	55	0.0014	0.287
4	1.2×10^{-2}	0.023	0	29.4	5.6×10^{-5}	4.5	50	0.0022	0.134
5	1.9×10^{-2}	0.023	0	39.1	6.0×10^{-5}	4.5	66	0.0052	0.134
6	3.6×10^{-3}	0.012	0	19.9	6.2×10^{-5}	4.6	63	0.0047	0.129
7	1.5×10^{-2}	0.047	0	20.0	6.3×10^{-5}	5.9	31	0.0007	0.102

[a] $[P^\bullet]_{org}$ is the total concentration of propagating radicals calculated per unit volume of the overall organic phase. [b] $\bar{n}$ = average number of propagating radicals per particle. [c] Ratio of the concentration of free SG1 in the particles over the overall initial alkoxyamine concentration (per unit volume of organic phase), calculated according to $[SG1]_p/[PAA\text{-}SG1]_{org} = K/[P^\bullet]_{org}$, with $K = 6 \times 10^{-9}$, the activation−deactivation equilibrium constant in the SG1-mediated polymerization of styrene at 120 °C.[27]

collapsed and the dissolved monomer was expelled; consequently, the hydrodynamic diameter was assumed to correspond to the unswollen polystyrene core diameter. The latexes have also been analyzed by transmission electron microscopy, and the number-average diameters are in good agreement with the DLS measurements (see ref 31 for the data).

Size Exclusion Chromatography. For analytical purposes, the acidic functions of the poly(acrylic acid) homopolymers and poly(acrylic acid)-*b*-polystyrene copolymers were turned into methyl esters. The poly(acrylic acid)-*b*-polystyrene block copolymers were recovered by drying of the aqueous suspensions. After acidification of the medium, they were methylated using trimethylsilyldiazomethane. The experimental conditions were the same as those described in ref 32. Size exclusion chromatography (SEC) of the methylated copolymers was performed at 40 °C with two columns (PSS SDV, linear M, 8 mm × 300 mm; bead diameter: 5 μm; separation limits: 400–2 × 10^6 g mol^{-1}). The eluent was tetrahydrofuran at a flow rate of 1 mL min^{-1}. A differential refractive index detector (LDC Analytical refractoMonitor IV) was used, and molar masses were derived from a calibration curve based on polystyrene standards from Polymer Standards Service. (For the poly(methyl acrylate) homopolymers this calibration is appropriate as discussed in ref 32: it leads to an error below 10%, which is within the accepted range for SEC analysis; for the copolymers, which contain a large weight fraction of polystyrene, this calibration is the most appropriate.) This technique allowed M_n, M_w (the weight-average molar mass), and PDI = M_w/M_n, the polydispersity index to be determined. All values were calculated from the copolymer peak, without taking into account the residual methylated macroinitiator.

Results and Discussion

In this work, surfactant-free, ab initio, batch emulsion polymerization conditions have been selected and were successful for the first time, in terms of latex stability, due to the polyelectrolyte nature of the initiator/stabilizer. They led to small particles with narrow particle size distribution.[30,31] In contrast, when a water-soluble, low molar mass alkoxyamine initiator was used, even in the presence of a surfactant, the latexes underwent complete coagulation above ∼50% conversion, most likely due to droplet nucleation (partition of the oligoalkoxyamines between the aqueous phase and the monomer phase). It was then necessary to work in two-step conditions, starting the polymerization with a low amount of monomer to avoid the presence of droplets.[34] In this work, the macroinitiator efficiency was not 100% as the experimental values of M_n of the formed block copolymers were above the theoretical line (see Figure 1). Initially, it was ascribed to extensive irreversible termination reactions taking place in the aqueous phase where initiation starts.[30,31] However, despite the existence of such reactions, the amount of released free nitroxide would be so large that the polymerization rate would be much slower than actually observed, like in previous miniemulsion polymerizations using a water-soluble alkoxyamine with a very large dissociation rate constant.[35] The low initiator efficiency is also related to a slow initiation and slow hydrophobic block growth in the aqueous solution in comparison with the particles due to the low concentration of styrene and lower activation−deactivation equilibrium constant of the poly(acrylic acid) macroinitiator with respect to that of the SG1-capped polystyrene.[27,32] Consequently,

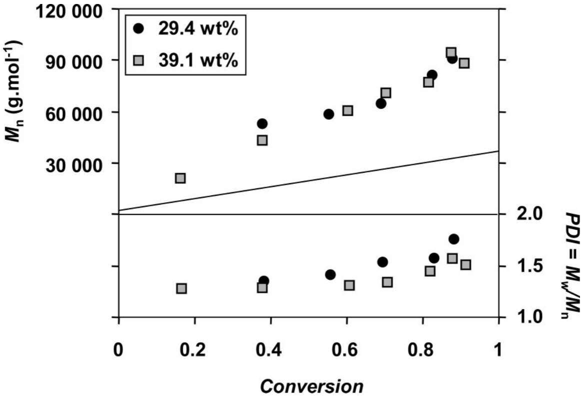


Figure 1. Typical number-average molar mass, M_n, and polydispersity index, M_w/M_n, vs monomer conversion for the emulsion polymerizations of styrene initiated by the water-soluble, SG1-capped, poly(sodium acrylate) macroinitiator at 120 °C and carried out at various solids content (see experiment 4 at 29.4 wt % and experiment 5 at 39.1 wt % in Table 1 for the experimental conditions). The straight line corresponds to the theoretical molar mass.

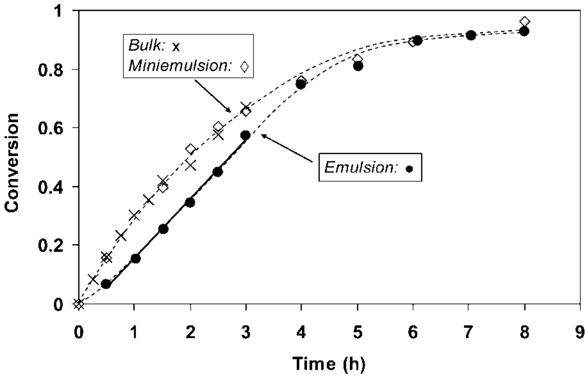
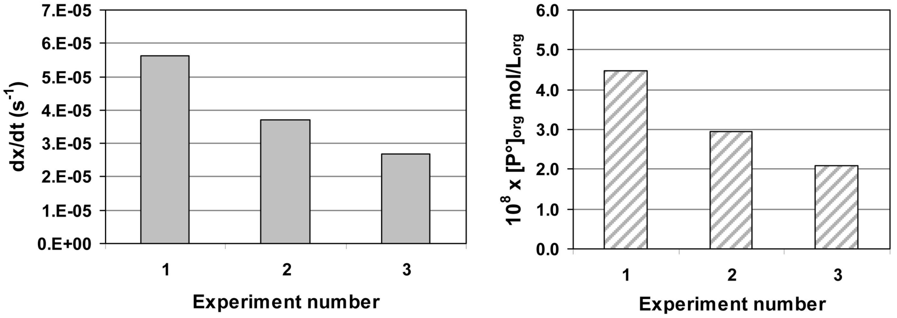


Figure 2. Typical conversion vs time plot (filled circles) for an emulsion polymerization of styrene initiated by the water-soluble, SG1-capped, poly(sodium acrylate) macroinitiator at 120 °C (experiment 1 in Table 1). The straight line corresponds to the linear part, from which the slope, dx/dt, was determined. For comparison, the crosses and open diamonds correspond to similar bulk and miniemulsion polymerizations (with D = 327 nm), respectively, from the experiments 6 and 7 in ref 35.

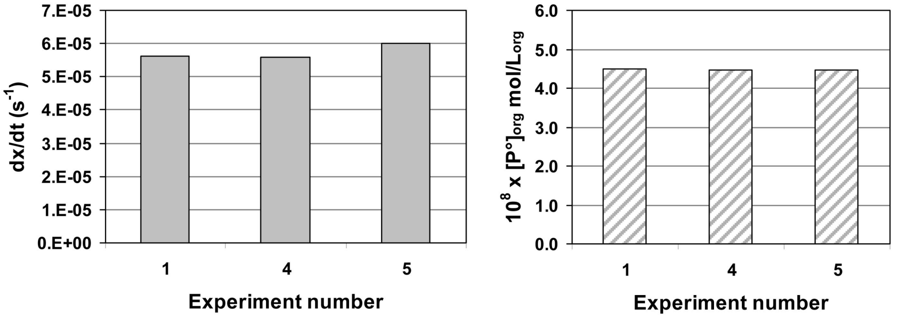
Influence of the initial concentration of free SG1

(1) 0 mol%; (2) 5.0 mol%; (3) 10.4 mol%



Influence of the solids content

(1) 20.0 wt%; (4) 29.4 wt%; (5) 39.1 wt%



Influence of the initial concentration of PAA-SG1

(6) 0.012 $M_{aq.}$; (1) 0.023 $M_{aq.}$; (7) 0.047 $M_{aq.}$

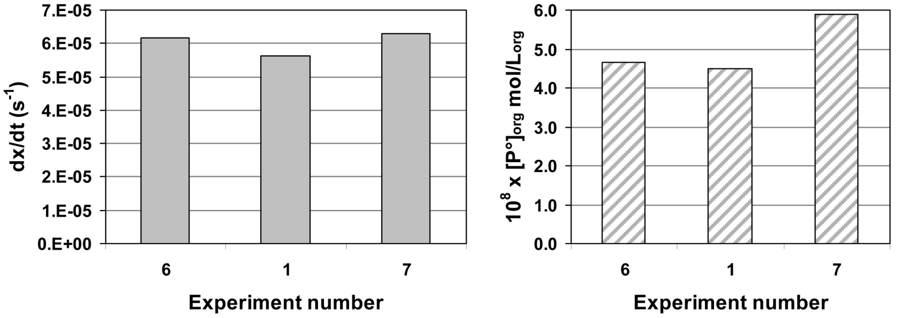


Figure 3. Conversion rate (d*x*/d*t*) and total concentration of propagating radicals calculated per unit volume of organic phase, $[\mathrm{P}^\bullet]_{\mathrm{org}}$, for the emulsion polymerization of styrene at 120 °C, initiated by the SG1-terminated poly(sodium acrylate) macroinitiator (experiments 1−7 in Table 1).

Table 2. Calculated Molar Concentration of Styrene in Polystyrene Particles at Saturation during Interval II of an Emulsion Polymerization, as a Function of the Particle Diameter[a]

unswollen *D*, nm	$[\mathrm{St}]_\mathrm{p}$, mol L^{-1}	unswollen *D*, nm	$[\mathrm{St}]_\mathrm{p}$, mol L^{-1}
31	4.11	55	4.92
50	4.80	63	5.10
51	4.82	66	5.16
52	4.85		

[a] The parameters used for calculation from eqs 3 and 4 are $\chi = 0.233$, $\Gamma = 30$ mN m^{-1}, and $\rho_{\mathrm{St}} = 817$ g L^{-1}, all of them taken at 120 °C, $\mathrm{MW}_{\mathrm{St}} = 104.15$ g mol^{-1}.

a major part of styrene consumption takes place in the latex particles, which form very early in the polymerization process.[31]

1. Determination of the Total Concentration of Propagating Radicals. In all experiments, the conversion (x) vs time plots exhibited a linear region below 50–60% conversion (Figure 2), which is a typical feature of classical free-radical emulsion polymerizations. This is the indication of zeroth-order kinetics with respect to monomer, corresponding to the interval II, when large monomer droplets are still present in the system and play the role of monomer reservoirs.[1−7] Monomer is supplied to the growing particles via molecular diffusion through the aqueous phase, and the monomer concentration in the particles, $[\mathrm{St}]_\mathrm{p}$, remains constant as a consequence of an equilibrium between opposing forces, i.e., the mixing of polymer and monomer and the reduction of the surface free energy.[1] The conversion rate, d*x*/d*t*, was determined experimentally in the linear part of the plot, from 10% to 50% conversion. The total concentration of propagating radicals expressed per unit volume of the overall organic phase (i.e., particles and monomer droplets), [P•]org, which remained approximately constant during that interval, was then calculated according to the equation

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_\mathrm{p}[\mathrm{P}^\bullet]_{\mathrm{org}}\frac{[\mathrm{St}]_\mathrm{p}}{[\mathrm{St}]_0} \tag{2}$$

in which k_p is the rate constant of propagation ($k_\mathrm{p} = 2040$ L mol^{-1} s^{-1} for styrene at 120 °C)[36] and $[\mathrm{St}]_0$ is the initial styrene concentration in bulk at 120 °C ($[\mathrm{St}]_0 = \rho_{\mathrm{St}}/\mathrm{MW}_{\mathrm{St}} = 7.85$ mol L^{-1}, with $\mathrm{MW}_{\mathrm{St}} = 104.15$ g mol^{-1}, the molar mass of styrene and $\rho_{\mathrm{St}} = 817$ g L^{-1}, its density at 120 °C[37]) (See the results in Table 1 and Figure 3; see the Supporting Information for presentation of the kinetic equations used in emulsion polymerization.)

During interval II, the monomer concentration in the particles, $[\mathrm{St}]_p$, depends on the particle size for very small particles and can be calculated from the Morton's equation (eq 3)[1,38] and from eq 4.

$$\ln(1-\varphi_p)+\varphi_p+\chi\varphi_p^{\ 2}+\frac{2\Gamma V_{\mathrm{St}}}{\frac{D}{2}RT}\varphi_p^{\ 1/3}=0 \tag{3}$$

$$[\mathrm{St}]_p=(1-\varphi_p)\frac{\rho_{\mathrm{St}}}{\mathrm{MW}_{\mathrm{St}}} \tag{4}$$

It was assumed to be independent of the polymer molar mass. In eq 3, φ_p is the volume fraction of polymer in the polymer solution constituting the latex particles, $\chi = 0.233$ is the Flory–Huggins interaction parameter of polystyrene and styrene at 133 °C,[39] Γ is the interfacial tension between the hairy polystyrene particles and the aqueous medium (arbitrarily taken at 30 mN m^{-1} for all experiments in the absence of clear experimental results in the literature for surfactant-free polystyrene particles with a poly(sodium acrylate) brush), $V_{\mathrm{St}} = \mathrm{MW}_{\mathrm{St}}/\rho_{\mathrm{St}}$ is the partial molar volume of styrene, and D is the unswollen diameter of latex particle. In our system, the average particle diameter is very small, and the variation of $[\mathrm{St}]_p$ with particle size cannot be neglected. The calculated $[\mathrm{St}]_p$ values are reported in Table 2 as a function of the particle diameter. Because the interfacial tension is not known with accuracy, the calculated data cannot be considered as absolute; they are however suitable enough for a comparison between the experiments, to analyze the influence of the experimental parameters on the concentration of propagating radicals. (It was checked that a variation of Γ does not change the relative values of $[\mathrm{P}^\bullet]_{\mathrm{org}}$: with $\Gamma = 10$ mN m^{-1}, $[\mathrm{P}^\bullet]_{\mathrm{org}}$ decreases by less than 20% with respect to the values calculated in Table 1.) It should also be added that the particle diameter increases during interval II, and consequently the local monomer concentration increases too. Using the final diameter for calculation leads then to a slight overestimate of $[\mathrm{St}]_p$ and to an underestimate of $[\mathrm{P}^\bullet]_{\mathrm{org}}$.

The conversion rate can also be calculated as a function of the number of particles per unit volume of organic phase, N_p, according to the equation

$$\frac{\mathrm{d}x}{\mathrm{d}t}=k_p\frac{\bar{n}N_p}{N_A}\frac{[\mathrm{St}]_p}{[\mathrm{St}]_0} \tag{5}$$

In eq 5, N_A is the Avogadro's number, $\bar{n} = [\mathrm{P}^\bullet]_{\mathrm{org}}N_A/N_p$ is the average number of radicals per particle, and N_p is calculated using eq 6 (see the Supporting Information), in which D is the final particle diameter, ρ_{St} is the density of styrene, and ρ_{PSt} is the density of polystyrene (it was shown earlier that N_p does not change with conversion[31]). The calculated ñ values, reported in Table 1, are all well below 1, in agreement with the theoretical predictions.[22–25]

$$N_p\,(\mathrm{L_{org}}^{-1})=\frac{6}{\pi D^3}\frac{\rho_{\mathrm{St}}}{\rho_{\mathrm{PSt}}} \tag{6}$$

2. Effect of the Initial Concentration of Free SG1 (Experiments 1−3). When the initial concentration of free nitroxide was increased (Figure 3 and Table 1, experiments 1−3), all other concentrations remaining the same, the concentration of propagating radicals in the overall organic phase decreased. This result is the indication that the polymerization rate is governed by the activation−deactivation equilibrium, like in a homogeneous polymerization. Because SG1 is produced either in the aqueous solution or in the particles via dissociation of the alkoxyamines or introduced into the monomer phase as a free component, the results indicate that free nitroxide is able to diffuse from water to monomer and from the monomer droplets to the particles. The SG1 concentration most probably equilibrates between the various phases of the system, which allows it to control the propagating radical concentration and hence the polymerization kinetics. Consequently, the proportion of free SG1 in the particles with respect to the alkoxyamine concentration can be roughly estimated using the equilibrium relationship, as reported in Table 1. It appears that this proportion remained very close for all experiments conducted in the absence of free SG1 (typically 13 mol %, in agreement with previous results obtained in miniemulsion and in good correspondence with the expectation based on the persistent radical effect in the SG1-mediated polymerization of styrene)[35] and increased when free SG1 was introduced initially.

3. Effect of the Solids Content (Experiments 1, 4, and 5). The batch emulsion polymerizations were carried out up to 39.1 wt % solids, leading to stable latexes without formation of coagulum. When the monomer/water content was increased and the macroinitiator/monomer molar ratio was maintained the same (increased concentration of macroinitiator in the aqueous phase), $[\mathrm{P}^\bullet]_{\mathrm{org}}$ was not affected (Figure 3 and Table 1). In some sense, those three experimental conditions might be regarded as a change in the amount of water in a similarly divided monomer phase. Those experiments point out the very good reproducibility of the polymerizations and show that the difference in the initial concentration of macroinitiator in the aqueous phase does not affect the kinetics. In other words, the system is essentially regulated by the reactions and equilibria that take place in the organic phase.

4. Effect of the Macroinitiator Concentration and Particle Size (Experiments 6, 1, and 7). At a given monomer/water ratio, when the macroinitiator concentration was increased, the particle size decreased from 63 nm (experiment 6) to 51 nm (experiment 1) and then to 31 nm (experiment 7), as discussed in our previous article.[31] In such a system, it is not possible to easily change the diameter without changing the macroinitiator concentration. It is expected that the propagating radical concentration increases accordingly as a result of a change in the equilibrium state. (On the basis of the persistent radical effect equations, $[\mathrm{P}^\bullet]_{\mathrm{org}}$ is expected to vary with $[\mathrm{alkoxyamine}]^{1/3}$ in a homogeneous system, but the experimental variation is not always so well-defined.[19,20]) Experiments 6 and 1 exhibit rather similar $[\mathrm{P}^\bullet]_{\mathrm{org}}$ values, whereas the increase is well observed for the experiment 7 with the highest alkoxyamine concentration (Figure 3 and Table 1). In conclusion, the overall concentration of propagating radicals does not seem to be affected in a significant way by the particle size.

5. Discussion on the Compartmentalization Effect. For bulk and miniemulsion polymerizations of styrene under conditions similar to those of experiments 1, 4 and 5,[35] i.e., $[\text{alkoxyamine initiator}]_0$[40] $= 0.024$ mol $\mathrm{L_{org}}^{-1}$ and $T = 120$ °C without free SG1 (see Figure 2), the concentration of propagating radicals was $[\mathrm{P}^\bullet] = 4.8 \times 10^{-8}$ mol L^{-1} and $[\mathrm{P}^\bullet] = 5.0 \times 10^{-8}$ mol L^{-1}, respectively, not very different from the results found here for the corresponding emulsion polymerizations.

In emulsion polymerization, a compartmentalization effect exists if $[\mathrm{P}^\bullet]_{\mathrm{org}}$ depends on the particle size under otherwise similar experimental conditions. The decrease of dx/dt when particle size was decreased in the TEMPO-mediated miniemulsion polymerizations reported by Cunningham's group in the absence of hexadecane[28] might not be simply related to a reduction of $[\mathrm{P}^\bullet]_{\mathrm{org}}$. Indeed, in systems with poor stabilization against Ostwald ripening as it can be the case in the absence of hexadecane, monomer might be expelled from the monomer droplets containing the polystyrene macroinitiator to form a pure monomer phase.[41] If it were the case, the local monomer concentration would be lower for smaller particles, and $[\mathrm{P}^\bullet]_{\mathrm{org}}$ should be calculated by eq 2 and not according to the traditional

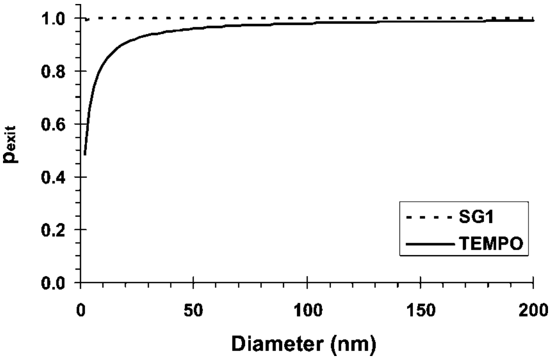


Figure 4. Probability (p_{exit} from eq 9) that the SG1 or TEMPO nitroxide desorbs from a particle rather than recombines with a polystyryl macroradical trapped inside the particle, as a function of the particle diameter. Partition coefficient of the nitroxide in the water and particle phases $[\text{nitroxide}]_{aq}/[\text{nitroxide}]_{org} = 0.01$ (M/M); diffusion coefficient in water, $D_{nitroxide}$, is 10^{-7} dm^2 s^{-1}; $k_c = 5.7 \times 10^5$ L mol^{-1} s^{-1} for SG1; $k_c = 8.0 \times 10^7$ L mol^{-1} s^{-1} for TEMPO.

pseudo-first-order kinetics usually applied in miniemulsion. Consequently, for the smallest particles, $[\text{P}^\bullet]_{org}$ may be slightly higher than actually calculated. The differences in shape of the conversion vs time plots as well as in dx/dt between bulk or miniemulsion polymerizations, on the one hand, and emulsion polymerization, on the other, whereas the overall radical concentration may be rather similar in all cases, is well illustrated in Figure 2.

As discussed above, the assumption that free SG1 diffuses rapidly from one phase to another one and that its concentration equilibrates between those various phases is perfectly reasonable and in agreement with previous conclusions drawn for TEMPO.[29] The fast diffusion of SG1 in our emulsion polymerization system may actually be supported by very simple calculation. Consider a spherical nanometric reactor with radius r_S (volume $v_p = \frac{4}{3}\pi r_S^3$) in a water phase. The nanoreactor contains styrene, a single polystyryl radical of sufficiently high molar mass (i.e., unable to exit), and a single free nitroxide able to exit. Such a situation is typical of a particle in which an alkoxyamine dissociates in the absence of free nitroxide (initial situation for instance). The free nitroxide radical has two possible fates: either it recombines with the carbon-centered radical to form back the alkoxyamine or it desorbs from the particle toward the aqueous phase and eventually re-enters another particle. The first-order rate coefficients associated with both events are k_{recomb} and k_{exit}, respectively, and can be calculated according to eqs 7 and 8. From those data, it is possible to estimate the probability of exit, p_{exit}, of the free nitroxide radical via eq 9. In eq 7, k_c is the rate constant of recombination of the nitroxide with the propagating radical: with SG1 at 120 °C, $k_c = 5.7 \times 10^5$ L mol^{-1} s^{-1},[27] whereas with TEMPO at 120 °C, $k_c = 8.0 \times 10^7$ L mol^{-1} s^{-1};[42] $1/(N_A v_p)$ corresponds to the concentration of a single propagating radical in the particle. In eq 8, it is assumed that the diffusion inside the particle is not rate determining and $D_{nitroxide}$ is the diffusion coefficient of the desorbing nitroxide in the water phase; a typical value of $D_{nitroxide}$ is 10^{-7} dm^2 s^{-1}.[1,29] The partition coefficient of TEMPO in the water and styrene phases has been determined by Ma et al.[29,43] in previous works: at 120 °C $[\text{TEMPO}]_{aq}/[\text{TEMPO}]_{org}$ is 0.01 (M/M). For calculation, it may be assumed that SG1 has similar water solubility and partition coefficient as TEMPO. In consequence, the only important difference in p_{exit} for SG1 and TEMPO comes from k_c. The values of p_{exit} have been calculated as a function of the particle diameter, $2r_S$, for both nitroxides and are shown in Figure 4. Whatever the particle size, p_{exit} is very close to 1 for SG1, whereas it may be lower for TEMPO in very small particles. In such conditions, the SG1 radical escapes from the particle within a much shorter time than that required for recombination. Therefore, it may deactivate any other compartmentalized propagating radical in the polymerization system after re-entry into another active particle. In other words, SG1 can never be considered as compartmentalized, whereas the conclusion may be different for TEMPO in very small particles. With more complete calculations, Ma et al.[29] concluded similarly that the characteristic time for recombination of TEMPO with a propagating radical was more than 10 times greater than the predicted equilibration time under typical miniemulsion NMP, even at high monomer conversion.

$$k_{recomb} = \frac{k_c}{N_A v_p} = \frac{k_c}{N_A \dfrac{4\pi r_S^{\,3}}{3}} \tag{7}$$

$$k_{exit} = 3\,\frac{D_{nitroxide}}{r_S^{\,2}}\,\frac{[\text{nitroxide}]_{aq}}{[\text{nitroxide}]_{org}} \tag{8}$$

$$p_{exit} = \frac{k_{exit}}{k_{recomb} + k_{exit}} \tag{9}$$

As SG1 is not considered as compartmentalized, the deactivation rate reads exactly like in a homogeneous system and has the same value (no confined space effect). The kinetic equations derived previously for an ideal miniemulsion polymerization[22] can be applied here (considering the total concentrations of propagating radicals and macroalkoxyamine calculated per unit volume of overall organic phase, $[\text{P}^\bullet]_{org}$ and $[\text{P-SG1}]_{org}$, respectively, and the concentration of free SG1 within the particles $[\text{SG1}]_p$). The evolution with time of the total concentration of propagating radicals in the organic phase reads then as in the equation (from ref 22)

$$\frac{d[\text{P}^\bullet]_{org}}{dt} = k_d[\text{P-SG1}]_{org} - k_c[\text{P}^\bullet]_{org}[\text{SG1}]_p - 2k_d[\text{P-SG1}]_{org}\bar{n}p_t \tag{10}$$

In eq 10, the last term corresponds to the termination rate, $R_t = 2k_d[\text{P-SG1}]_{org}\bar{n}p_t$, which depends on particle size (via $\bar{n}$ and p_t). It is expressed as the rate of dissociation of an alkoxyamine in an already active particle multiplied by p_t, the probability that the newly formed radical terminates irreversibly with the other active radical rather than reversibly with a nitroxide (see eq 11, in which k_t is the rate constant of irreversible termination between two propagating radicals).

$$p_t = \frac{k_t/(N_A v_p)}{k_t/(N_A v_p) + k_c[\text{SG1}]_p} \tag{11}$$

If one considers experiment 1 as a typical example, assuming $p_t = 1$ for a very small particle where irreversible termination should be close to instantaneous, one calculates $R_t = 2k_d[\text{P-SG1}]_{org}\bar{n} = 3.7 \times 10^{-7}$ mol L^{-1} s^{-1} with $k_d = 3.4 \times 10^{-3}$ s^{-1} for SG1-capped polystyrene at 120 °C,[27] $[\text{P-SG1}]_{org} = 0.023$ mol L_{org}^{-1} and $\bar{n} = 0.0024$ (see Table 1). In a homogeneous system with the same macroradical concentration, the irreversible termination rate would be $R_t = 2k_t([\text{P}^\bullet]_{org})^2 = 4.0 \times 10^{-7}$ mol L^{-1} s^{-1} with $k_t = 10^8$ L mol^{-1} s^{-1}.[44] One cannot thus conclude on significant difference between bulk and emulsion polymerizations once the SG1 concentration has reached its pseudo-steady-state value (here the average number of SG1 per particle is ~45 for the smallest particles and can reach values as high as 300 for larger particles).

In conclusion, the experimental results for the emulsion polymerizations of this work do not show the expected increase in polymerization rate predicted by our model for miniemulsion polymerization with very small particles but highlight the lack of a compartmentalization effect.[22]

Conclusion

The surfactant-free, ab-initio, batch emulsion polymerization of styrene initiated by a SG1-capped poly(sodium acrylate) macroalkoxyamine leads to stable particles with diameter below 100 nm. The polymerizations follow the typical zeroth-order kinetics with respect to monomer, and the conversion rate in the constant part allows the overall concentration of propagating radicals, $[\mathrm{P}^\bullet]_{\mathrm{org}}$, to be calculated. Several conclusions can be drawn from the experimental observations: (i) In heterogeneous polymerizations, calculating $[\mathrm{P}^\bullet]_{\mathrm{org}}$ requires a good knowledge of the local monomer concentration within the particles, which is not straightforward. (ii) SG1 cannot be considered as compartmentalized but diffuses rapidly between the various phases of the system. Only very hydrophobic nitroxides exhibiting very high k_c would be compartmentalized. (iii) In SG1-mediated emulsion polymerization under batch conditions, the polymerization rate is mainly regulated by the activation−deactivation equilibrium and by the persistent radical effect and the influence of particle size is not significant, even for very small particles. (iv) Finally, it is particularly difficult to draw accurate conclusions on small differences in polymerization rate; NMP in heterophase systems depends on many parameters, not always easy to identify and assess. Nevertheless, the difference in propagating radical concentration between emulsion and bulk will never be as pronounced in NMP as it is usually observed in a classical free-radical polymerization. A more complete conclusion of the advantage of emulsion over bulk NMP, as far as the kinetics are regarded, would require additional information on polymer chain livingness.

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Supporting Information Available: Kinetic equations of emulsion polymerization used in this work. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Gilbert, R. G. *Emulsion Polymerization: A Mechanistic Approach*; Academic Press: London, 1995.
(2) Daniels, E. S., Sudol, E. D., El-Aasser, M. S., Eds. Polymer Latexes. Preparation, Characterization and Applications. *ACS Symp. Ser.* **1992**, 492.
(3) Fitch, R. M. *Polymer Colloids: a Comprehensive Introduction*; Academic Press: London, 1997.
(4) Van Herk, A. M. *Chemistry and Technology of Emulsion Polymerization*; Blackwell Publishing: Oxford, 2005.
(5) Nomura, M.; Tobita, H.; Suzuki, K. *Adv. Polym. Sci.* **2005**, *175*, 1–128.
(6) Chern, C. S. *Prog. Polym. Sci.* **2006**, *31*, 443–486.
(7) Thickett, S. C.; Gilbert, R. G. *Polymer* **2007**, *48*, 6965–6991.
(8) Qiu, J.; Charleux, B.; Matyjaszewski, K. *Prog. Polym. Sci.* **2001**, *26*, 2083–2134.
(9) Cunningham, M. F. *Prog. Polym. Sci.* **2002**, *27*, 1039–1067.
(10) Cunningham, M. F. *C. R. Chim.* **2003**, *6*, 1351–1374.
(11) Monteiro, M.; Charleux, B. In *Chemistry and Technology of Emulsion Polymerisation*; van Herk, A., Ed.; Blackwell Publishing Ltd.: Oxford, 2005; Vol. 11, pp 1–139.
(12) Charleux, B.; Ganachaud, F. In *Macromolecular Engineering: From Precise Macromolecular Synthesis to Macroscopic Materials Properties and Application*; Matyjaszewski, K., Gnanou, Y., Leibler, L., Ed.; Wiley-VCH: New York, 2007.
(13) Charleux, B.; Nicolas, J. *Polymer* **2007**, *48*, 5813–5833.
(14) Solomon, D. H.; Rizzardo, E.; Cacioli, P. US 4581429, 1986.
(15) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987–2988.
(16) Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661–3688.
(17) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921–2990.
(18) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689–3746.
(19) Fischer, H. *Chem. Rev.* **2001**, *101*, 3581–3610.
(20) Goto, A.; Fukuda, T. *Prog. Polym. Sci.* **2004**, *29*, 329–385.
(21) Butté, A.; Storti, G.; Morbidelli, M. *DECHEMA Monogr.* **1998**, *134*, 497–507.
(22) Charleux, B. *Macromolecules* **2000**, *33*, 5358–5365.
(23) Zetterlund, P. B.; Okubo, M. *Macromolecules* **2006**, *39*, 8959–8967.
(24) Zetterlund, P. B.; Okubo, M. *Macromol. Theory Simul.* **2007**, *16*, 221–226.
(25) Tobita, H.; Yanase, F. *Macromol. Theory Simul.* **2007**, *16*, 476–488.
(26) Pan, G.; Sudol, E. D.; Dimonie, V. L.; El-Aasser, M. S. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 4921–4932.
(27) Benoit, D.; Grimaldi, S.; Robin, S.; Finet, J. P.; Tordo, P.; Gnanou, Y. *J. Am. Chem. Soc.* **2000**, *122*, 5929–5939.
(28) Maehata, H.; Buragina, C.; Cunningham, M.; Keoshkerian, B. *Macromolecules* **2007**, *40*, 7126–7131.
(29) Ma, J. W.; Cunningham, M. F.; McAuley, K. B.; Keoshkerian, B.; Georges, M. K. *Macromol. Theory Simul.* **2002**, *11*, 953–960.
(30) Delaittre, G.; Nicolas, J.; Lefay, C.; Save, M.; Charleux, B. *Chem. Commun.* **2005**, 614–616.
(31) Delaittre, G.; Nicolas, J.; Lefay, C.; Save, M.; Charleux, B. *Soft Matter* **2006**, *2*, 223–231.
(32) Couvreur, L.; Lefay, C.; Belleney, J.; Charleux, B.; Guerret, O.; Magnet, S. *Macromolecules* **2003**, *36*, 8260–8267.
(33) Lefay, C.; Belleney, J.; Charleux, B.; Guerret, O.; Magnet, S. *Macromol. Rapid Commun.* **2004**, *25*, 1215–1220.
(34) Nicolas, J.; Charleux, B.; Guerret, O.; Magnet, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 6186–6189.
(35) Nicolas, J.; Charleux, B.; Guerret, O.; Magnet, S. *Macromolecules* **2004**, *37*, 4453–4463.
(36) Buback, M.; Gilbert, R. G.; Hutchinson, R. A.; Klumperman, B.; Kuchta, F.-D.; Manders, B. G.; O'Driscoll, K. F.; Russell, G. T.; Schweer, J. *Macromol. Chem. Phys.* **1995**, *196*, 3267–3280.
(37) Manders, B. G.; Chambard, G.; Kingma, W. J.; Klumperman, B.; Van Herk, A. M.; German, A. L. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 2473–2479.
(38) Morton, M.; Kaizerman, S.; Altier, M. W. *J. Colloid Sci.* **1954**, *9*, 300–312.
(39) Covitz, F. H.; King, J. W. *J. Polym. Sci., Part A-1* **1972**, *10*, 689–699.
(40) Here the alkoxyamine concentration was recalculated using the correct density of styrene at 120 °C, which was not done in ref 35.
(41) Asua, J. M. *Prog. Polym. Sci.* **2002**, *27*, 1283–1346.
(42) Greszta, D.; Matyjaszewski, K. *Macromolecules* **1996**, *29*, 7661–7670.
(43) Ma, J. W.; Cunningham, M. F.; McAuley, K. B.; Keoshkerian, B.; Georges, M. K. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 1081–1089.
(44) Buback, M.; Kowollik, C.; Kurz, C.; Wahl, A. *Macromol. Chem. Phys.* **2000**, *201*, 464–469.

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