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Kinetic Study of the Nitroxide-Mediated Controlled Free-Radical Polymerization of *n*-Butyl Acrylate in Aqueous Miniemulsions

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ABSTRACT: The controlled free-radical homopolymerization of *n*-butyl acrylate was studied in aqueous miniemulsions at 112 and 125 °C with a low molar mass alkoxyamine unimolecular initiator and an acyclic β -phosphonylated nitroxide mediator, *N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide, also called SG1. The polymerizations led to stable latices with 20 wt % solids and were obtained with neither coagulation during synthesis nor destabilization over time. However, in contrast to latices obtained via classical free-radical polymerization, the average particle size of the final latices was large, with broad particle size distributions. The initial $[SG1]_0/[alkoxyamine]_0$ molar ratio was shown to control the rate of polymerization. The fraction of SG1 released upon macroradical self-termination was small with respect to the initial alkoxyamine concentration, indicating a very low fraction of dead chains. Average molar masses were controlled by the initial concentration of alkoxyamine and increased linearly with monomer conversion. The molar mass distribution was narrow, depending on the initial concentration of free nitroxide in the system. The initiator efficiency was lower than 1 at 112 °C but was very significantly improved when either a macroinitiator was used at 112 °C or the polymerization temperature was raised to 125 °C. © 2002 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 40: 4410–4420, 2002

Keywords: radical polymerization; living polymerization; emulsion polymerization

INTRODUCTION

Free-radical polymerization offers the invaluable advantage of being tolerant of water, allowing the reaction to be carried out in aqueous solutions or aqueous dispersed systems. With the various types of radical polymerizations in aqueous dispersions, such as suspension, emulsion, miniemulsion, and microemulsion polymerizations, combined with multistep processes, it is possible to fine-tune the size, morphology, functionaliza-

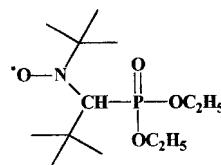
tion, and surface characteristics of polymer particles.^{1,2} However, because of the features of radical chemistry, the polymer composing those particles is generally ill defined. With the emergence of controlled/living radical polymerization (CRP),^{3–6} including, among other techniques, nitroxide-mediated polymerization,^{7–9} (Scheme 1) there is the possibility of additional control over the polymer characteristics. So far, it has successfully been applied to bulk and solution polymerizations. It has also been demonstrated that the transfer to aqueous dispersed systems is quite possible, although not straightforward.^{10,11} The early published results on nitroxide-mediated polymerization in aqueous dispersed systems concerned the use of 2,2,6,6-tetramethylpiperidinyl-

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1-oxy (TEMPO) as a mediator in suspension, seeded emulsion, batch emulsion, and miniemulsion polymerizations of styrene at temperatures greater than 120 °C.^{10,11} More recently, the polymerization of *n*-butyl acrylate (BA) was also controlled, with TEMPO in a miniemulsion system, but no kinetic data were provided.¹²

With the use of the acyclic SG1 nitroxide [*N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide; Scheme 2] as a mediator in the bulk,¹³ faster kinetics than those with TEMPO were observed for styrene; more importantly, this nitroxide was shown to be particularly well suited for the controlled polymerization of acrylic esters such as BA.^{13–15} We previously reported a complete kinetic study of the SG1-mediated CRP of styrene in a miniemulsion with a water-soluble radical initiator, and we highlighted the differences with bulk polymerization.^{16,17} Later, the miniemulsion process associated with an oil-soluble SG1-based alkoxyamine initiator was also shown to be very successful for synthesizing well-defined poly(*n*-butyl acrylate) (PBA) homopolymers as well as block and gradient copolymers with styrene.^{18,19} A miniemulsion performed with an oil-soluble alkoxyamine initiator is actually the direct adaptation of a classical bulk polymerization recipe. As in suspension polymerization, the monomer droplets behave as individual reactors in which the different polymerization steps take place. However, in contrast to suspension polymerization, submicrometer particles are formed, and the final polymer dispersion exhibits all the characteristics of a classical latex. Indeed, the miniemulsion process^{20–23} can be regarded as a simple model for emulsion polymerization. In miniemulsion polymerization, the initial monomer in water emulsion is strongly sheared to divide the organic phase into small droplets that are directly nucleated. In addition to classical surfactants, the use of a hydrophobe (e.g., hexadecane and/or a polymer) has been shown to enhance droplet stability via the inhibition of Oswald ripening. For nitroxide-mediated polymerization, the advantages over conventional emulsion polymerization are the following. The



Scheme 2. Structure of the SG1 nitroxide.

complex nucleation step that exists in emulsion polymerization is avoided and replaced by droplet nucleation; for this reason, the process allows the use of oil-soluble initiators, such as monomer-based preformed alkoxyamines. This would not be possible in emulsions because undesirable polymerization would take place in the large, nonstabilized monomer droplets.

The purpose of this work was to investigate the effects of the dispersed state of a miniemulsion polymerization on the polymerization kinetics and on the control over the homopolymer characteristics for the SG1-mediated CRP of BA initiated with an oil-soluble alkoxyamine.

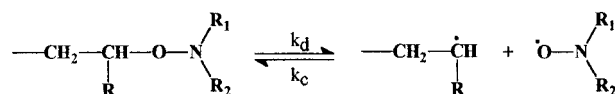
EXPERIMENTAL

Materials

BA was distilled under reduced pressure before use. The surfactant Dowfax 8390 (a mixture of mono- and dihexadecyl disulfonated diphenyloxide disodium salts, supplied by Dow Chemical Co.; an aqueous solution at 35 wt %; critical micelle concentration = 0.05 wt % at 25 °C; ca. 0.5–1 mM) and the buffer sodium hydrogen carbonate (NaHCO₃; Prolabo) were used as received. The alkoxyamine initiator [an SG1-based alkoxyamine derived from methyl acrylate, CH₃—O(CO)—CH(CH₃)—SG1 (MONAMS); 96% purity] was supplied by Atofina and prepared with atom transfer radical addition from methyl-2-bromopropionate. This alkoxyamine contains two diastereoisomers in proportions that are usually similar, with different rate constants of dissociation (*k_d*).²⁴ The (*R,R*) and (*S,S*) diastereoisomers have *k_d* = 2.6 × 10¹⁴ exp(−130.9 kJ mol^{−1}/RT), whereas the (*R,S*) ones exhibit *k_d* = 3.5 × 10¹⁴ exp(−128.4 kJ mol^{−1}/RT). SG1 (86.5% purity) was also supplied by Atofina.

Batch Miniemulsion Polymerization of BA

A stable aqueous emulsion of the monomer was prepared by the mixing of the organic phase



Scheme 1. Activation–deactivation equilibrium in nitroxide-mediated controlled free-radical polymerization ($K = k_d/k_c$).

{monomer, MONAMS alkoxyamine, high molar mass polystyrene [PS; weight-average molecular weight (M_w) = 330,000 g mol⁻¹], hexadecane, and, for some experiments, a small fraction of free SG1 with respect to the alkoxyamine} with the water phase containing the surfactant and the buffer. PS and hexadecane were used as hydrophobes to stabilize the monomer droplets against Oswald ripening. This unstable emulsion was subjected to ultrasonication (Branson 450 Sonifier; power = 7; 10 min) to disperse the organic phase into submicrometer droplets and to improve their stability. The obtained stable emulsion was then poured into a 1-L, stainless steel thermostated reactor and was stirred at 150 rpm. Deoxygenation was performed with three vacuum/nitrogen filling cycles. Afterward, a 3-bar pressure of nitrogen was applied, and the reactor was heated to 112 or 125 °C. The time when the temperature reached 90 °C was arbitrarily chosen as time zero of the reaction. Samples were periodically withdrawn to monitor the monomer conversion (x) by gravimetry. For this purpose, the latex samples were dried in a ventilated oven thermostated at 80 °C, until a constant weight was obtained. The particle diameter (D) was measured by dynamic light scattering (DLS). After drying, the polymer from each sample was analyzed by the various techniques described later.

For one experiment, MONAMS was replaced by an SG1-capped PBA macroinitiator, PBA-SG1, prepared by the nitroxide-mediated bulk polymerization of BA. The monomer, MONAMS (2.76×10^{-2} mol L⁻¹), additional free SG1 (2.5 mol % with respect to MONAMS), and hexadecane were poured into a 1-L, stainless steel thermostated reactor. Deoxygenation was performed by nitrogen bubbling for 30 min. Afterward, a 0.5-bar pressure of nitrogen was applied, and the reactor was heated to 112 °C. The reaction was stopped after 1 h at a 28% conversion, and the obtained polymer had a number-average molecular mass (M_n) of 9550 g mol⁻¹ with the polydispersity index $I_p = M_w/M_n$ 1.76 (theoretical M_n = 8800 g mol⁻¹; initiator efficiency = 92%). The polymer/monomer solution was further polymerized in a miniemulsion at 112 °C with the same recipe described previously.

Analytical Techniques

The average particle diameters were measured by DLS of the latices, with a Zetasizer4 from

Malvern at an angle of 90° and at a temperature of 25 °C.

Size exclusion chromatography (SEC) was performed with two different systems. The first one was a Waters apparatus equipped with four columns (PL-gel 10 μ , 10², 5 \times 10², 10³, and 10⁴ Å) for the PBA macroinitiator obtained in bulk and with two columns (PL-gel 10 μ mixed, 60 cm; Shodex KF 801L, 30 cm; exclusion limit, 1.5 \times 10³) for the other polymers (from miniemulsions). The eluent was tetrahydrofuran (THF) at a flow rate of 1 mL min⁻¹. A differential refractive-index (RI) detector was used, and the molar masses were derived from a calibration curve based on PS standards from Polymer Standards Service. The molar masses of selected samples of ME1 and ME3 were double-checked by the group of Professor Axel Müller at the University of Bayreuth (Germany). SEC measurements were performed with a set of 30-cm SDV-gel columns (5- μ m particle size) with 10⁵-, 10⁴-, 10³-, and 10²-Å pore sizes and with 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 PS samples and linear PBA samples prepared via anionic polymerization were used as calibration standards.

RESULTS AND DISCUSSION

The performed living miniemulsion polymerizations of BA led to stable latices with 20 wt % solids and were obtained with neither coagulation during synthesis nor destabilization over time. The kinetics of these miniemulsion polymerizations were studied at 112 and 125 °C as a function of the initial $r = [\text{SG1}]_0/[\text{alkoxyamine}]_0$ molar ratio for a given alkoxyamine concentration and as a function of the alkoxyamine initial concentration for a given r value (Table 1).

Effect of the Initial Concentration of Free Nitroxide at 112 and 125 °C

A series of three experiments (ME1, ME2, and ME3; Table 1) were performed at 112 °C with the same alkoxyamine initial concentration and various concentrations of the free nitroxide, that is, various $r = [\text{SG1}]_0/[\text{alkoxyamine}]_0$ molar ratios. The alkoxyamine was the low molar mass MONAMS, and the proportion of added free nitroxide with respect to this alkoxyamine was varied from 0 to 0.026. The logarithmic conversion

Table 1. Experimental Conditions for the Miniemulsion Homopolymerizations of BA^a

Experiment	Symbol	<i>T</i> (°C)	[Alkoxyamine] ₀ (mol L ⁻¹ _{org}) ^b	[SG1] ₀ (mol L ⁻¹ _{org}) ^a	<i>r</i> ^c
ME1	▲	112	MONAMS 2.77 × 10 ⁻²	0	0
ME2	○	112	MONAMS 2.77 × 10 ⁻²	3.5 × 10 ⁻⁴	0.013
ME3	△	112	MONAMS 2.77 × 10 ⁻²	7.0 × 10 ⁻⁴	0.026
ME4	+	112	PBA-SG1 3.38 × 10 ⁻²	9.7 × 10 ⁻⁴	0.029
ME5	□	112	MONAMS 1.38 × 10 ⁻²	3.6 × 10 ⁻⁴	0.026
ME6	◇	112	MONAMS 5.51 × 10 ⁻²	1.4 × 10 ⁻³	0.025
ME7	●	125	MONAMS 3.05 × 10 ⁻²	7.8 × 10 ⁻⁴	0.026
ME8	◆	125	MONAMS 3.05 × 10 ⁻²	1.6 × 10 ⁻³	0.051
ME9	■	125	MONAMS 3.07 × 10 ⁻²	3.1 × 10 ⁻³	0.101

^a The experimental conditions were as follows: BA, 100 g; water, 400 g; weight fraction of BA in the miniemulsion, 20 wt %; surfactant, Dowfax 8390, 2.2 wt % with respect to BA; hexadecane, 0.8 wt % with respect to the monomer; high molar mass, PS (*M_w* = 330,000 g mol⁻¹), 0.1 wt % with respect to the monomer; and [NaHCO₃], 12 mM_{aq}.

^b With respect to the overall organic phase.

^c [SG1]₀/[alkoxyamine initiator]₀.

versus time and the evolution of *M_n* with conversion are displayed in Figure 1. The *M_n* values were not affected, whereas the polydispersity indices and the rates of polymerization depended on *r*. The larger *r* was, the slower the polymerization was and the narrower the molar mass distribution (MMD) was. The values of *M_n* increased linearly with monomer conversion, indicating a constant chain concentration throughout the polymerization (see Fig. 1). As an illustration, the shift of the SEC peaks with the monomer conversion is displayed in Figure 2 for experiment ME3. The *M_n* values remained, however, above the theoretical line for experiments performed at 112 °C as a result of an initiator efficiency below 1 (see Table 2). When a polymerization was started in bulk (PBA-SG1 macroinitiator; experiment ME4; temperature = 112 °C; see Table 1), with all of the other experimental conditions being the same as those in experiment ME3, the initiator efficiency was substantially improved (see Table 2), but the rate remained unchanged (Fig. 1).

A similar series of experiments was performed at 125 °C with the same alkoxyamine initial concentration (ME7–ME9; see Table 1). Because the polymerization rate was much greater than that observed at 112 °C (see the *k_p*[P·] values in Table 2), higher initial concentrations of free nitroxide were used to slow it down, with *r* ranging from 0.026 to 0.101. For all three experiments, the final conversion was very high: 96% within 3 h for ME7, 94% within 6 h for ME8, and 91% within 7 h for ME9. Again, the same influence of *r* was observed on both the polymerization rates (Table 2)

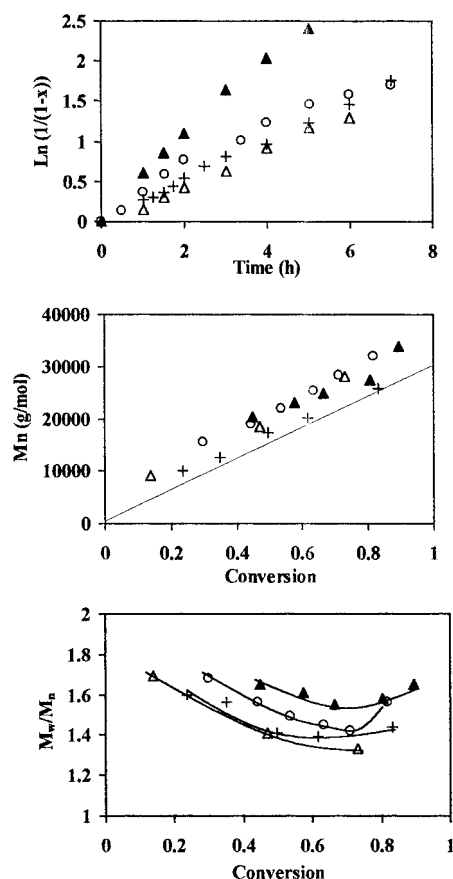


Figure 1. Logarithmic conversion (*x*) versus time, *M_n* versus conversion, and *M_w*/*M_n* (the polydispersity index) versus conversion for the miniemulsion polymerizations of BA carried out at 112 °C with the same initiator concentration and various SG1 initial concentrations (ME1–ME4; see Table 1 for the experimental conditions and symbols; the straight line indicates the theoretical *M_n*).

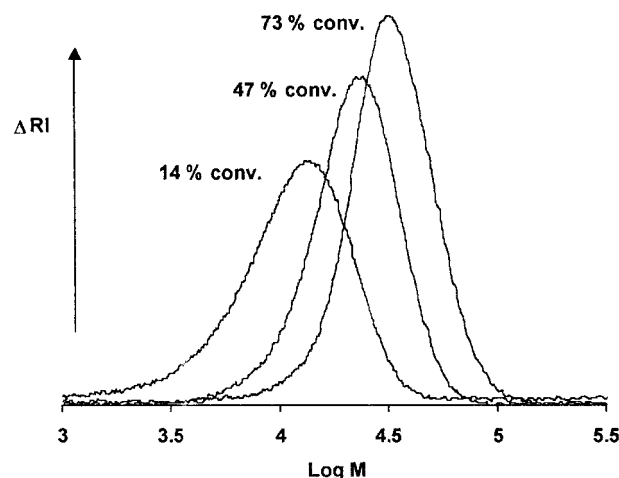


Figure 2. MMDs from the SEC analyses of selected polymer samples of experiment ME3.

and MMDs (Fig. 3), whereas the values of M_n were not affected. They increased linearly with monomer conversion, and in contrast to the previous experiments performed at 112 °C, 100% initiator efficiency was always observed at 125 °C (Fig. 3). With $r = 0.026$ (ME7), the MMD was quite broad, with I_p remaining above 1.5. With $r = 0.051$ (ME8) and $r = 0.101$ (ME9), the polydispersity indices continuously decreased to reach a minimum of 1.2–1.3 for approximately 70–80% conversions and then increased to 1.4–1.5 for conversions above 90%, indicating the occurrence of side reactions affecting the MMD. A possible side reaction could be chain transfer to the polymer, as discussed later.

In homogeneous nitroxide-mediated controlled radical polymerizations, the concentration of the

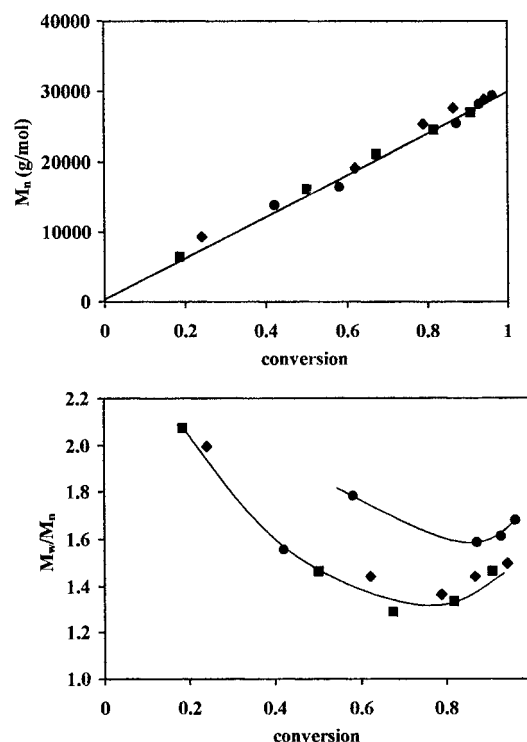


Figure 3. M_n and M_w/M_n (the polydispersity index) versus conversion for the miniemulsion polymerizations of BA carried out at 125 °C with the same initiator concentration and various SG1 initial concentrations (ME7–ME9; see Table 1 for the experimental conditions and symbols; the straight line indicates the theoretical M_n).

propagating radical, $[P\cdot]$, was shown to be inversely proportional to the concentration of the free nitroxide, $[SG1]$, when the activation–deactivation equilibrium was established (Scheme

Table 2. Some Kinetic and Colloidal Characteristics of the Miniemulsion Homopolymerizations of BA Presented in Table 1

Experiment	$k_p[P]_{org}$ (s^{-1})	Initiator Efficiency	Final Average D (nm) from DLS ^a
ME1	1.3×10^{-4}	0.80	460
ME2	8.5×10^{-5}	0.80	550
ME3	7.0×10^{-5}	0.80	640
ME4	7.0×10^{-5}	0.98	550
ME5	7.5×10^{-5}	Expt. $M_n < \text{theor. } M_n$	550
ME6	6.8×10^{-5}	1.0	540
ME7	5.0×10^{-4}	1.0	440
ME8	2.9×10^{-4}	1.0	410
ME9	2.3×10^{-4}	1.0	650

^a Simply given for information (inaccurate for a broad particle size distribution).

1).^{14,15,25} Therefore, the decrease in the polymerization rate with the increase in r indicated that the expected equilibrium also existed in the miniemulsion. In this context, the narrowing of the MMD with the increase in the free nitroxide concentration was an expected feature that was predicted for bulk^{26–28} and miniemulsion polymerizations.²⁹ Therefore, for a given temperature, a good balance between a fast polymerization and a narrow MMD had to be found, via the addition of a given amount of free nitroxide into the system, at the beginning of the polymerization.

Effect of the Initiator Concentration at 112 °C

The polymerization rates were the same for the reactions carried out at 112 °C in which the initiator concentration was varied but r was kept constant (0.025; experiments ME3, ME5, and ME6; see Table 1 and Fig. 4). As in the previous set of experiments, it appears that the important parameter for controlling the kinetics was not directly the initiator concentration but instead was the initial $[\text{SG1}]_0/[\text{alkoxyamine}]_0$ molar ratio. The average molar masses grew linearly with monomer conversion and were larger when the initiator concentration was lower. As a result, for a BA homopolymerization at a given temperature, the molar masses and kinetics can be adjusted independently by a judicious choice of the initial concentrations of both the alkoxyamine initiator and free SG1. For the experiments with intermediate and large initiator concentrations (ME3 and ME6), the MMD was narrow as I_p decreased down to 1.2–1.3 with the monomer conversion. When the alkoxyamine concentration was reduced to $1.38 \times 10^{-2} \text{ mol L}^{-1}$ (ME5, theoretical $M_n = 60,400 \text{ g mol}^{-1}$ at a complete conversion), the MMD was broader, with $I_p \approx 1.5$ at an 80% conversion (Fig. 4). This trend can possibly be assigned to the occurrence of intermolecular chain transfer to the polymer leading to branched structures and, therefore, MMD broadening, particularly visible for the larger M_n values and for high conversions.^{30,31} It could also explain the results obtained for experiments ME7–ME9, performed at 125 °C, exhibiting an increase in I_p when the conversion exceeded 80%. The effect of chain transfer to the polymer on the structure of the SG1-terminated PBA chains was discussed in a previous article.³²

Polymerization Kinetics

As demonstrated previously, very similarly to bulk systems,^{14,15} the polymerization rate was

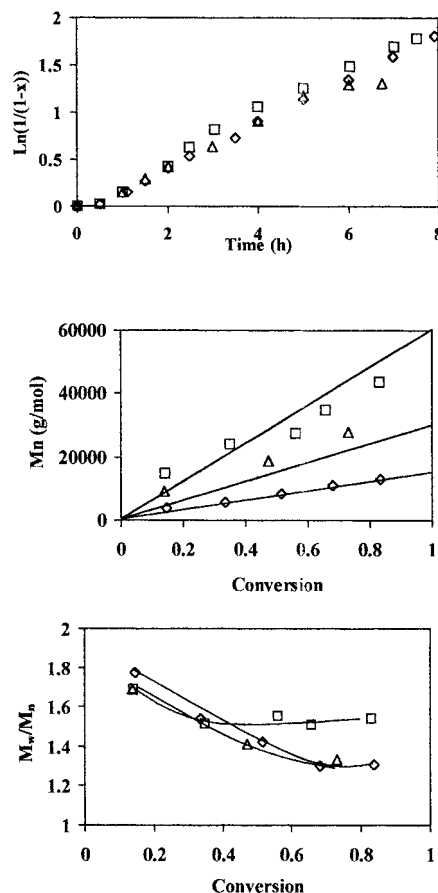


Figure 4. Logarithmic conversion (x) versus time, M_n versus conversion, and M_w/M_n (the polydispersity index) versus conversion for the miniemulsion polymerizations of BA carried out at 112 °C with the same SG1 initial concentration and various initiator concentrations (ME3, ME5, and ME6; see Table 1 for the experimental conditions and symbols; the straight lines indicate the theoretical M_n 's).

governed by the initial concentration of added free nitroxide and, particularly, by the initial $[\text{SG1}]_0/[\text{alkoxyamine}]_0$ molar ratio. In nitroxide-mediated controlled free-radical polymerizations, the concentration of active macroradicals is inversely proportional to the concentration of free nitroxide according to eq 1, with K , $[\text{P-SG1}]_{\text{org}}$, and $[\text{SG1}]_{\text{org}}$ the activation–deactivation equilibrium constant (Scheme 1), the alkoxyamine initial concentration in the organic phase, and the concentration of free SG1 in the organic phase, respectively:

$$[\text{P}^*]_{\text{org}} = \frac{K[\text{P-SG1}]_{\text{org}}}{[\text{SG1}]_{\text{org}}} \quad (1)$$

Therefore, with the polymerization following a first internal order with respect to the monomer, the slope of the logarithmic conversion, $\ln[1/(1-x)]$ versus time, that is, $k_p[P\cdot]_{\text{org}}$ (where k_p is the rate constant of propagation), should also vary inversely with the concentration of free SG1. The latter depends not only on the initial concentration but also on the concentration that is released upon early radical–radical terminations according to the persistent radical effect.^{27,28,33} In a miniemulsion system, the size of the droplets also has to be taken into account, and the overall concentration of free SG1 can be written as follows:²⁹

$$[\text{SG1}]_{\text{org}} = -A + \sqrt{(A + [\text{SG1}]_0)^2 - B \ln(1-x)} \quad (2)$$

where $[\text{SG1}]_0$ represents the initial concentration of free nitroxide in the system, x is the monomer conversion, A is $k_t/(N_A v_p k_c)$, and B is $(4K[P\cdot\text{SG1}]_0 k_t)/k_p$. The constant k_c is the rate constant of recombination between a propagating macroradical and a nitroxide molecule, k_t is the apparent rate constant of irreversible termination between propagating radicals (considered chain-length-independent), N_A is Avogadro's number, and v_p is the average particle volume. When v_p is very large, as is the case in this work (Table 2), A is very small and becomes negligible. In this case, the expression giving $[\text{SG1}]_{\text{org}}$ versus conversion is $[\text{SG1}]_{\text{org}} = \sqrt{[\text{SG1}]_0^2 - B \ln(1-x)}$, the same as in bulk. So-called pseudobulk kinetics should then operate, as actually observed, because no significant difference in the polymerization rate could be detected with similar bulk polymerizations.^{14,15}

If one considers, to simplify, that the concentration of macromolecular alkoxyamine (i.e., dormant chains) matches the initial concentration of MONAMS, this equation can then be written as eqs 4–6, where

$$[\text{SG1}]_x = \sqrt{[\text{SG1}]_0^2 - B \ln(1-x)} - [\text{SG1}]_0 \quad (3)$$

is the concentration of free SG1 released in the system at conversion x :

$$[P\cdot]_{\text{org}} = \frac{K[\text{MONAMS}]_0}{[\text{SG1}]_0 + [\text{SG1}]_x} \quad (4)$$

$$\frac{1}{k_p[P\cdot]_{\text{org}}} = \frac{[\text{SG1}]_0 + [\text{SG1}]_x}{k_p K[\text{MONAMS}]_0} \quad (5)$$

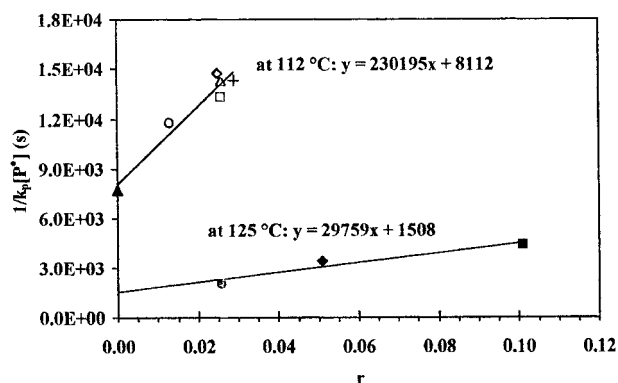


Figure 5. Effect of the initial r value on the rate of polymerization at 112 and 125 °C (see Table 1 for the experimental conditions and symbols and see Table 2 for the $k_p[P\cdot]_{\text{org}}$ values).

$$\frac{1}{k_p[P\cdot]_{\text{org}}} = \frac{r}{k_p K} + \frac{[\text{SG1}]_x}{k_p K[\text{MONAMS}]_0} \quad (6)$$

For experiment ME1 performed at 112 °C with $r = 0$, $[\text{MONAMS}]_0 = 0.0277 \text{ mol L}^{-1}$, $K = 4.34 \times 10^{-11} \text{ mol L}^{-1}$,¹⁵ $k_t = 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$, and $k_p \approx 82,000 \text{ L mol}^{-1} \text{ s}^{-1}$ (this value, extrapolated from the Arrhenius plot given in ref. 34, should not be considered accurate but a rough estimation), one has at a 90% conversion $-B \ln(1-x) = 1.3 \times 10^{-8} \text{ mol}^2 \text{ L}^{-2}$, which gives $[\text{SG1}]_x = 1.2 \times 10^{-4} \text{ mol L}^{-1}$ and $[\text{SG1}]_x/[\text{MONAMS}]_0 = 0.004$ ($[\text{SG1}]_x/k_p K[\text{MONAMS}]_0 \approx 1000 \text{ s}$). For a similar experiment performed at 125 °C with $k_p \approx 94,000 \text{ L mol}^{-1} \text{ s}^{-1}$ (see the previous remark on k_p) and $K = 2.0 \times 10^{-10} \text{ mol L}^{-1}$,¹⁴ one can calculate $[\text{SG1}]_x/[\text{MONAMS}]_0 = 0.008$ ($[\text{SG1}]_x/k_p K[\text{MONAMS}]_0 \approx 400 \text{ s}$). At a given temperature, when r is increased, the calculated $[\text{SG1}]_x/[\text{MONAMS}]_0$ value becomes negligible with respect to r . However, when r is sufficiently small, it is expected that $(k_p[P\cdot]_{\text{org}})^{-1}$ versus r will be a straight line with an intercept close to $[\text{SG1}]_x/k_p K[\text{MONAMS}]_0$ ($\approx 1000 \text{ s}$ at 112 °C and $\approx 400 \text{ s}$ at 125 °C). The values of $k_p[P\cdot]_{\text{org}}$, obtained from the initial slope of plots of the logarithmic conversion versus time, are given in Table 2. As illustrated in Figure 5, the evolution of $(k_p[P\cdot]_{\text{org}})^{-1}$ with r was indeed linear for both temperatures, but the intercept was larger than expected. Therefore, the contribution of early terminations was larger than supposed from the theoretical estimations. This might come from erroneous rate constants of termination and propagation, which are not known with accuracy for BA. At 112 °C,

Table 3. Average Molar Masses and Polydispersity Indices for ME1 and ME3 with PS and PBA Calibrations (See the Experimental Section)

Experiment	Conversion	SEC M_n (M_w/M_n)	
		PS Calibration (g mol ⁻¹)	PBA Calibration (g mol ⁻¹) ^a
ME1	0.45	22,600 (1.38) ^a 20,400 (1.65) ^b	21,600 (1.43)
	0.58	23,100 (1.61) ^b	—
	0.67	28,200 (1.31) ^a 24,800 (1.55) ^b	27,500 (1.36)
	0.81	27,500 (1.58) ^b	—
	0.90	36,900 (1.38) ^a 33,900 (1.65) ^b	36,400 (1.42)
ME3	0.14	10,550 (1.32) ^a 9,030 (1.40) ^b	9,600 (1.38)
	0.34	15,000 (1.24) ^b	—
	0.47	19,800 (1.23) ^a 18,800 (1.20) ^b	19,000 (1.26)
	0.60	21,900 (1.21) ^b	—
	0.73	28,500 (1.21) ^a 28,100 (1.19) ^b	27,950 (1.24)

^a SEC Bayreuth.
^b SEC Paris.

the intercept was 8112 s, whereas the slope, that is, $(k_p K)^{-1}$, was 2.3×10^5 s. From these values, one can calculate $k_p K = 4.3 \times 10^{-6}$ s⁻¹ and $[SG1]_x/[MONAMS]_0 = 0.035$. The value of $k_p K$ is similar to that reported by Lacroix-Desmazes et al.¹⁵ for the same system studied in bulk at 115 °C ($K = 4.34 \times 10^{-11}$ mol L⁻¹ and $k_p K = 3.6 \times 10^{-6}$ s⁻¹ with $k_p = 82,000$ L mol⁻¹ s⁻¹).³⁴ At 125 °C, the intercept was 1508 s, whereas the slope, that is, $(k_p K)^{-1}$, was 3.0×10^4 s; from these values, one can calculate $k_p K = 3.4 \times 10^{-5}$ s⁻¹ and $[SG1]_x/[MONAMS]_0 = 0.051$. At 125 °C, with $k_p \sim 94,000$ L mol⁻¹ s⁻¹,³⁴ $K = 3.6 \times 10^{-10}$ mol L⁻¹. For all of the experiments, the proportion of released SG1 remained, however, very small because it did not exceed 3.5% at 112 °C and 5% at 125 °C with respect to the initial concentration of alkoxyamine. This result means that the proportion of dead chains formed by macroradical self-termination remained quite low. This information is in agreement with data obtained in bulk¹⁴ and with the good reinitiation efficiency usually exhibited by the SG1-terminated PBA macroinitiators in bulk¹⁴ and in miniemulsions.¹⁸ The result of the small $[SG1]_x/[MONAMS]_0$ ratio is that a small concentration of added free nitroxide (a low *r* ra-

tio) is sufficient to accurately control the polymerization kinetics. However, it needs to be adjusted according to the temperature.

Initiator Efficiency

A feature of the reported miniemulsion polymerizations was that the initiator efficiency was usually lower than 1 for experiments performed at 112 °C. This trend was evidenced by the experimental molar masses being larger than the theoretical ones (Figs. 1 and 4; Table 2). So that the quality of the SEC analyses could be ascertained, some samples were analyzed with a second SEC apparatus, and molar masses were derived from a calibration curve based on PBA standards (see the Experimental section). As shown in Table 3, the agreement between the various data was very good, and this means that the conclusion on initiator efficiency was not driven by erroneous M_n values. No clear trend associated with the experimental conditions at 112 °C could, however, be found.

Kinetic data indicated that a low initiator efficiency could not be assigned to the extensive self-termination of primary radicals. Indeed, if early

radical–radical termination was responsible for the low initiator efficiency, a strong effect on the rate would have been evidenced simultaneously, as a result of the persistent radical effect, because of the release of the corresponding concentration of the nitroxide deactivator. For instance, the 20% loss in macromolecular chains of experiments ME1–ME3 did not match the calculated 3.5% of released SG1 derived from the kinetic analysis. Furthermore, experiments ME3, ME5, and ME6 with the same initial r value but different initiator efficiencies exhibited the same polymerization rate, indicating the same excess of free nitroxide throughout the polymerization.

The initiator efficiency was strongly improved mainly with two techniques: first by increasing the polymerization temperature and second by starting the polymerization in bulk with the obtained polymer as a macroinitiator (see Table 2 and Fig. 1). The first method is a way to enhance the rate of the MONAMS alkoxyamine dissociation and, therefore, the rate of initiation. This is particularly important for the diastereoisomer with the lower k_d value. Indeed, at 112 °C, $k_d = 4.5 \times 10^{-4} \text{ s}^{-1}$ for (*R,R*) or (*S,S*), and $k_d = 1.3 \times 10^{-3} \text{ s}^{-1}$ for (*R,S*); at 125 °C, $k_d = 1.7 \times 10^{-3} \text{ s}^{-1}$ for (*R,R*) or (*S,S*), and $k_d = 4.9 \times 10^{-3} \text{ s}^{-1}$ for (*R,S*). The second method has the same effect as the first one because k_d of the polymeric macroinitiator ($3.8 \times 10^{-3} \text{ s}^{-1}$ at 112 °C)¹⁴ is larger than k_d of the monomeric MONAMS alkoxyamine. This second method can also offer an additional advantage associated with the dispersed state of the system: it would prevent the exit of the alkoxyamine or the initiating radical from the monomer droplets. Actually, a small fraction of the monomeric alkoxyamine might not take part in the initiation step because of either its initial partitioning in the water phase or the exit of the 1-(methoxycarbonyl)eth-1-yl primary radical formed upon homolytic cleavage. Indeed, 1-(methoxycarbonyl)eth-1-yl is known to be quite hydrophilic. For instance, the water solubility of methyl acrylate at saturation at 50 °C is 0.6 mol L⁻¹, and the partition coefficient, that is, the ratio of the concentration in water to the concentration in the organic phase, is 0.05.³⁵ The desorption of primary radicals from latex particles was earlier thought to occur in a styrene miniemulsion polymerization performed in the presence of an oil-soluble radical initiator.³⁶ After exit, depending on the balance between the monomer and free nitroxide concentrations in water, deactivation of the 1-(methoxycarbonyl)eth-1-yl radical would oc-

cur either immediately or after the addition of a few monomer units. To explain their complete exclusion from the polymerization, one has to assume that the reentry of these short oligomers (with, most likely, a very low water solubility) into the particles would be greatly slowed down or even inhibited. Very similar conclusions had already been drawn for emulsion polymerizations with a reversible addition–fragmentation transfer agent producing 2-(ethoxycarbonyl)prop-2-yl primary radicals.³⁷ Therefore, a very hydrophobic initiator or a macromolecular one would prevent the exit of the initiating radicals and enhance the initiator efficiency.

In conclusion, the initiator efficiency was enhanced by an increase in the initiation rate and/or a reduction in the ability of the primary radicals to exit from the monomer droplets. With a macroinitiator, both approaches operate simultaneously. With the low molar mass MONAMS, an increase in the polymerization temperature enhances the dissociation rate and, therefore, favors the initiation.

Colloidal Characteristics of the Latices

With 20 wt % monomer with respect to water and with a classical anionic surfactant in a low amount (2 wt % with respect to the monomer), the latices were always very stable with no coagulum. Nevertheless, the average particle size of the final latices was rather large (Table 2), and the particle size distribution was very broad. Such a feature has often been described for controlled radical polymerizations in emulsions³⁸ and miniemulsions.^{17–19,39} As a hydrophobic initiator was used, exhibiting fast initiation, the droplet nucleation was necessarily a fast process, too. Therefore, slow nucleation could not be the cause of the broad particle size distribution. In addition, all droplets exhibited the same overall concentrations of the initiator and free SG1. As a result, the kinetics of propagation in the particles cannot be different, precluding extensive monomer transportation and differences in particle growth. Therefore, a broad particle size distribution can be the result of the broad initial size distribution of the monomer droplets, the coalescence of the soft monomer swollen particles during polymerization, or both. Actually, droplet growth by collision and coalescence cannot be totally avoided in miniemulsions until Laplace and osmotic pressures are equilibrated.²³ This process does not extensively take place in classical radical poly-

merizations because it is usually slower than the polymerization rate.²³ However, this is not the case any more in CRP because of the strongly reduced polymerization rate.

CONCLUSIONS

Stable PBA latices were successfully obtained by CRP carried out in aqueous miniemulsions at 112 and 125 °C with an oil-soluble alkoxyamine initiator and the SG1 nitroxide as a mediator. From kinetic and molar mass perspectives, the selected miniemulsion process did not differ from similar bulk polymerizations. It is, therefore, a very simple and direct way to perform CRP in an aqueous dispersed system. The molar masses and kinetics were controlled by the addition of chosen initial concentrations of alkoxyamine and free nitroxide, respectively. The fraction of SG1 released upon macroradical self-termination was small with respect to the alkoxyamine initial concentration, indicating a very low fraction of dead chains. The average molar mass was well controlled with a narrow MMD. The initiator efficiency was lower than 1 at 112 °C but was very significantly improved when either a macroinitiator was used at 112 °C or the polymerization temperature was raised to 125 °C.

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