Novel SG1-Based Water-Soluble Alkoxyamine for Nitroxide-Mediated Controlled Free-Radical Polymerization of Styrene and *n*-Butyl Acrylate in Miniemulsion

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ABSTRACT: Nitroxide-mediated controlled free-radical polymerizations of *n*-butyl acrylate and styrene were performed in miniemulsion using, for the first time, a water-soluble SG1-based alkoxyamine as an initiator. For *n*-butyl acrylate, polymerizations exhibited all the features of a controlled system. In particular, the initiator efficiency was high, indicating an extensive entry in the monomer droplets of all of the oligoradicals generated in the aqueous phase. The efficiency, however, was not high for styrene homopolymerization, which was explained by a highly pronounced persistent radical effect, leading to a large proportion of dead oligomers, to a large concentration of free nitroxide, and thus to a too slow chain growth in the aqueous phase. Nevertheless, the addition of a very small amount of methyl acrylate strongly enhanced the entry rate, as a consequence of a favorable kinetic effect due to appropriate copolymerization conditions.

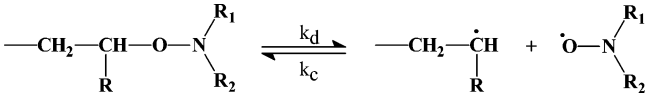
Introduction

Presently, controlled free-radical polymerization (CRP)[1−3] is a powerful tool for synthesizing tailor-made macromolecular architectures in varied media. During the past decade, the emergence of CRP with nitroxide-mediated free radical polymerization (NMP),[4−6] atom transfer radical polymerization (ATRP),[7,8] and reversible chain transfer (i.e., iodine transfer polymerization,[9,10] reversible addition−fragmentation chain transfer,[11−13] and organotellurium-mediated CRP[14]) has enabled a good control over polymer characteristics, especially under homogeneous polymerization conditions. Indeed, most of the studies were performed in bulk or in solution. However, with the increasing environmental constraints, academic and industrial laboratories have turned toward the application of CRP in aqueous dispersed systems,[15,16] such as suspension, emulsion, and especially miniemulsion.[17−19]

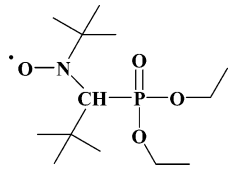
Among the various possible techniques, NMP, which is one of the oldest methods, remains increasingly interesting because the range of polymerizable monomers still broadens.[6,20] In addition, this method presents the advantage of being a purely thermal process (no catalyst, no bimolecular exchange), which facilitates its application in heterogeneous media. The basic key of nitroxide-mediated controlled free-radical polymerization is based on a reversible activation−deactivation equilibrium (Scheme 1) where the role of the nitroxide is to reversibly deactivate the growing radicals into alkoxyamine dormant functionality.

In the beginning, TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy), and its derivatives, were the most widely used and studied nitroxides for NMP in homogeneous[4−6] and aqueous dispersed systems[17−19] (suspension, seeded emulsion, batch emulsion, and miniemulsion polymerizations) at temperatures larger than 120 °C. However, the difficulties met in polymerizing monomers other than styrene and derivatives[21] recently gave rise to a new class of acyclic nitroxides.[22,23] One of them is the *N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (also called SG1)[23] (Scheme 2), which is particularly well-suited for the controlled polymerization of styrene,[24] acrylates such as *n*-butyl acrylate,[24] and quite recently dimethylacrylamide[25,26] and acrylic acid.[27]

Scheme 1. Activation−Deactivation Equilibrium in Nitroxide-Mediated Controlled Free-Radical Polymerization (Equilibrium Constant: $K = k_d/k_c$)



Scheme 2. Structure of the SG1 Nitroxide



NMP can be initiated in two different ways. The first one is the bicomponent initiating system, which uses a conventional radical initiator and free nitroxide.[5] However, it does not allow accurate control over the number of growing chains and the concentration of free SG1 because the initiator efficiency is ill-defined. It therefore has some repercussions on the kinetics and the control over the polymer characteristics. The second initiating system (monocomponent system) avoids this problem by using a preformed alkoxyamine initiator, the efficiency of which is theoretically close to 1.[28]

Difficulties and limitations encountered in nitroxide-mediated ab initio emulsion polymerization induced researchers to use the miniemulsion polymerization approach, which can be considered as a simplified model for emulsion polymerization as far as the nucleation step is regarded.[29−31] Indeed, in the miniemulsion case, only monomer droplet nucleation exists, and those droplets behave as individual reactors in which the different

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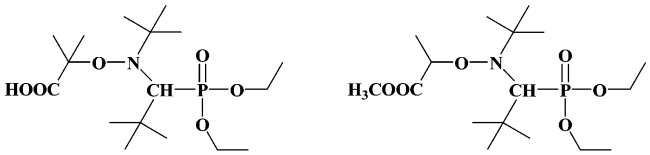
Table 1. Experimental Conditions for the SG1 Nitroxide-Mediated Bulk and Miniemulsion Polymerizations

					alkoxyamine initiator				
expt	process	monomer and additive[a]	additive over styrene molar ratio	T (°C)	type of alkoxyamine	mol L^{-1}_{org}[b]	mol L^{-1}_{aq}[c]	$[SG1]_0$ (mol L^{-1}_{org})[b]	r[d]
1	miniemulsion	BA		112	A-Na	2.73×10^{-2}	7.66×10^{-3}	0	0
2	miniemulsion	BA		112	A-Na	2.67×10^{-2}	7.53×10^{-3}	7.21×10^{-4}	0.027
3	miniemulsion	S		120	A-Na	2.71×10^{-2}	7.63×10^{-3}	0	0
4	miniemulsion	S		120	A-Na	2.72×10^{-2}	7.63×10^{-3}	7.32×10^{-4}	0.027
5	bulk	BA		112	A-H	2.71×10^{-2}		0	0
6	bulk	S		120	A-H	2.72×10^{-2}		0	0
7	miniemulsion	S		120	MONAMS	2.73×10^{-2}		0	0
8	miniemulsion	S		120	MONAMS	2.80×10^{-2}		7.52×10^{-4}	0.027
9	miniemulsion	S + MA[e]	0.008	120	A-Na	2.70×10^{-2}	7.47×10^{-3}	0	0
10	miniemulsion	S + MA[e]	0.016	120	A-Na	2.71×10^{-2}	7.46×10^{-3}	0	0
11	miniemulsion	S + MA[e]	0.031	120	A-Na	2.71×10^{-2}	7.40×10^{-3}	0	0
12	miniemulsion	S + AA[e]	0.031	120	A-Na	2.73×10^{-2}	7.34×10^{-3}	0	0
13	miniemulsion	S + MP[e]	0.031	120	A-Na	2.66×10^{-2}	7.31×10^{-3}	0	0
14	miniemulsion	S + PA[e]	0.031	120	A-Na	2.71×10^{-2}	7.44×10^{-3}	0	0

[a] Monomers = BA (*n*-butyl acrylate) and S (styrene); additives = MA (methyl acrylate), AA (acrylic acid), MP (methyl propionate), or PA (propionic acid). [b] With respect to the overall organic phase. [c] In the aqueous phase. [d] $r = [SG1]_0/[\text{alkoxyamine initiator}]_0$. [e] Experiments performed in the presence of a small concentration of an additive: expt 9 ($[MA]_0/[A\text{-}Na]_0 = 2.5$), expt 10 ($[MA]_0/[A\text{-}Na]_0 = 5.1$), expt 11 ($[MA]_0/[A\text{-}Na]_0 = 10.0$), expt 12 ($[AA]_0/[A\text{-}Na]_0 = 10.0$), expt 13 ($[MP]_0/[A\text{-}Na]_0 = 10.1$), expt 14 ($[PA]_0/[A\text{-}Na]_0 = 10.1$).

Scheme 3. Structure of the Alkoxyamine Initiators Used in This Work, i.e., A-H and MONAMS



A-H MONAMS

polymerization steps take place. Many previous NMP works have been devoted to miniemulsion polymerization initiated by either a bicomponent system (oil-soluble[32−36] or water-soluble[33−35,37−39] initiator) or a monocomponent one but strictly with an oil-soluble alkoxyamine.[21,33,40−47]

The purpose of this work was to investigate the effect of a novel SG1-based water-soluble alkoxyamine[48] (called A-H in the acidic form, see Scheme 3) on the CRP of *n*-butyl acrylate and styrene in a miniemulsion process. Special attention was given to the polymerization kinetics, the control over the homopolymer characteristics, and the colloidal properties of the final latexes. This study also focused on the nucleation step and the transport from the continuous phase to the organic one. The goal was to establish judicious comparison with the previously used SG1-based oil-soluble alkoxyamine (MONAMS, see Scheme 3) and especially to lay the foundation of a forthcoming study on true emulsion polymerization with the same water-soluble alkoxyamine. This work cannot be considered only as a new step toward true emulsion polymerization, but also as a way to create particles with controlled morphology. Indeed, as chains should remain attached to the particle surface by the charged initiator group (sodium salt of A-H), their growth is directed from the outer shell toward the core. Hence, block copolymers should lead to core−shell morphologies.[49] As far as we know, this present work is the first one using a water-soluble alkoxyamine as an initiator in miniemulsion polymerization.

Experimental Section

Materials. *n*-Butyl acrylate (BA, Aldrich, 99%), methyl acrylate (MA, Aldrich, 99%), and styrene (S, Aldrich, 99%) monomers were distilled under reduced pressure before use. Acrylic acid (AA, purest grade, Atofina) stabilized with 200 ppm of hydroquinone was stored at room temperature and used without further purification. Methyl propionate (MP, Aldrich, 99%) and propionic acid (PA, Acros, 99%) were used as received. The surfactant Dowfax 8390 (a mixture of mono- and dihexadecyl disulfonated diphenyl oxide disodium salt, supplied by Dow Chemical Co. as a 35 wt % aqueous solution) and the buffer sodium hydrogen carbonate ($NaHCO_3$, >99%, Prolabo) were used as received. Two kinds of alkoxyamine initiators, supplied by Atofina, were used in this work. The first one is the SG1-based oil-soluble alkoxyamine, MONAMS (98% purity) (see Scheme 3). The second one is the SG1-based alkoxyamine A-H (99% purity) also displayed in Scheme 3. Both initiators are soluble in styrene and in *n*-butyl acrylate, whereas the latter is water-soluble when converted to its sodium salt (A-Na). The *N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (SG1, 86%) was also supplied by Atofina.

Bulk Polymerization. In a typical experiment, a mixture of the A-H alkoxyamine (1.894 g, 4.97 mmol) and *n*-butyl acrylate (162.9 g, 1.27 mmol) was deoxygenated with nitrogen bubbling for 20 min at room temperature. The medium was poured into a 300 mL thermostated glass reactor heated at 112 °C and stirred at 300 rpm. A 1 bar pressure of nitrogen was then applied. Time zero of the reaction corresponded to the introduction of the mixture in the preheated reactor. Samples were periodically withdrawn to monitor the monomer conversion by gravimetry. For this purpose, the samples were dried in a ventilated oven thermostated at 70 °C until constant weight. After drying, the raw polymer from each sample was analyzed by size exclusion chromatography for molar mass and molar mass distribution measurement. The experimental conditions were the same for styrene except the polymerization temperature, which was 120 °C. Experimental conditions are summarized in Table 1.

Batch Miniemulsion Polymerization. A typical recipe for the miniemulsion (ME) polymerization of *n*-butyl acrylate using the A-Na alkoxyamine initiator is the following. An aqueous emulsion of BA was prepared by mixing the organic phase with the water phase containing deionized water (321.4 g), Dowfax 8390 (5.34 g of the aqueous solution, 2.20 wt % with respect to the monomer), and $NaHCO_3$ (0.319 g, 3.80 mmol, 12 mmol L^{-1}_{water}). The organic phase contained BA (84.9 g, 0.663 mol), high molar mass polystyrene (M_w = 330 000 g mol^{-1}, 0.085 g, 0.1 wt % with respect to BA), hexadecane (0.680 g, 0.8 wt % with respect to BA), and, for one experiment, free SG1 (20.0 mg, 0.068 mmol, 2.70 mol % with respect to the alkoxyamine). Polystyrene and hexadecane[50] were used as hydrophobes to stabilize the monomer droplets against Ostwald ripening.[29−31] The formed unstable emulsion was then subjected to ultrasonication (Branson 450 Sonifier; power 7; 10 min) in order to disperse the organic phase into submicronic droplets. This led to a stabilized emulsion, which was deoxygenated by nitrogen bubbling for 20 min at room temperature and then poured into a 600 mL glass thermostated reactor

heated at 112 °C and stirred at 300 rpm. The A-H alkoxyamine (0.963 g, 2.53 mmol) was first dissolved in an excess (1.6 equiv) of a 0.4 M sodium hydroxide solution and then poured into the reactor when the temperature reached 90 °C, triggering the beginning of the reaction. A 3 bar pressure of nitrogen was then applied. Samples of about 6 mL were periodically withdrawn to monitor the latex pH (pH meter from Tacussel), the average particle diameter by dynamic light scattering, and the particle size distribution by capillary hydrodynamic fractionation (see next section). Monomer conversion was followed by gravimetry. For this purpose, the latex samples were dried in a ventilated oven thermostated at 70 °C until constant weight. After complete drying, the raw polymer from each sample was analyzed by the various techniques described below. Conditions for the miniemulsion polymerizations of *n*-butyl acrylate are summarized in Table 1.

For styrene polymerization, the experimental conditions were almost the same. The respective amounts of high molar mass polystyrene and hexadecane were 1.0 and 5.0 wt % with respect to the monomer.[51] As in bulk, the reactor was heated at 120 °C. When the MONAMS initiator was used instead of the A-Na alkoxyamine, it was introduced in the organic phase at the beginning of the preparation, and time zero of the reaction corresponded to the time when temperature of the medium reached 90 °C. All of the other experimental conditions remained the same. When an additive was used (MA, MP, AA, or PA), it was introduced with styrene during the preparation of the organic phase. Conditions for the various styrene miniemulsion polymerizations are presented in Table 1.

Analytical Techniques. The average particle diameter (D) was measured by dynamic light scattering (DLS) at a temperature of 25 °C and an angle of 90°, with a Zetasizer4 from Malvern, using a 5 mW He−Ne laser at 633 nm. The particle size distributions were measured by capillary hydrodynamic fractionation (CHDF, MATEC Applied Sciences, model 2000).

Size exclusion chromatography (SEC) was performed at 40 °C with two columns (PL-gel 10μ mixed, 60 cm; Shodex KF 801L, 30 cm). The eluent was tetrahydrofuran (THF) 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. This technique allowed to determine M_n (the number-average molar mass), M_w (the weight-average molar mass), and M_w/M_n (the polydispersity index).[52] In all of the figures representing the experimental M_n as a function of monomer conversion, the displayed full straight line corresponds to the theoretical evolution of M_n calculated by

$$M_n = \mathrm{MW(initiator)} + \frac{[\mathrm{monomer}]_0}{[\mathrm{initiator}]_0} \times \mathrm{conversion} \times \mathrm{MW(monomer)}$$

When needed, the apparent initiator efficiency was calculated according to

$$f = \frac{\text{theoretical } M_n}{\text{experimental } M_n}$$

It corresponds to the proportion of polymer chains efficiently generated by the initiator molecules.

Surface tension measurements were performed with a drop tensiometer (ITC Concept) using the pendant drop method at 25 °C. The variations with time of interfacial tension between two fluids (in our case water solution against air) was determined by a digital processing of the shape of a drop of the first fluid formed within a quartz cell containing the second fluid. The drop was illuminated by a light source, and its profile was digitalized by a CCD camera driven by a microcomputer using the Windrop 1.1 software from ITC Concept. After a period of 30 min, the equilibrium was reached as the surface tension remained constant. The A-H alkoxyamine was first dissolved in a little excess (1.4 equiv) of a 0.04 M sodium hydroxide solution. Nine solutions at different concentrations (regularly ranging from 2.0×10^{-4} to 0.25 mol L^{-1}) were then prepared and analyzed following the procedure described above.

Results and Discussion

1. Characteristics of the A-Na Initiator. To initiate the miniemulsion polymerization in the water phase, the SG1-based A-H alkoxyamine initiator is particularly well-suited as its sodium carboxylate salt (A-Na) is water-soluble. For this reason all of the miniemulsion polymerizations using this initiator were started at alkaline pH. (For styrene polymerization, the pH remained close to 9 throughout the polymerization, whereas for *n*-butyl acrylate it was above 7 for the first 2 h and then decreased to approximately 6−5.5 for longer times, most probably due to partial hydrolysis of the butyl ester groups located near the particle surface.) Because of the hydrophobicity of the SG1 capping agent, A-Na exhibits surface activity in water solution. The critical micelle concentration measured by the pendant drop method (see experimental part) was 6.5×10^{-2} mol L^{-1} at 25 °C (after 30 min stabilization, the surface tension was $\gamma = 36.2$ mN m^{-1} for [A-Na] = 0.25 mol L^{-1}), which is much larger than the typical initial concentration used in this work (see Table 1). Thus, the alkoxyamine partitioned between the aqueous phase and the monomer−water interface, without forming micelles. Additionally, upon homolytic dissociation of the alkoxyamine, the initiating 2-(hydroxycarbonyl)prop-2-yl sodium salt radical is a highly water-soluble species. Therefore, although part of the alkoxyamine might be located at the monomer−water interface, initiation most likely took place in the water phase only.

2. Homopolymerization of *n*-Butyl Acrylate. We previously reported a complete kinetic study of the miniemulsion polymerization of *n*-butyl acrylate, using the MONAMS alkoxyamine as an initiator.[45] With such a monomer-soluble initiator, the transposition of a bulk process to a miniemulsion one was quite straightforward.[19] The average molar masses were controlled by the initial concentration of alkoxyamine and increased linearly with monomer conversion. Molar mass distributions were narrow, depending on the initial concentration of free nitroxide in the system. In particular, M_w/M_n significantly decreased when the initial $r = [\mathrm{SG1}]_0/[\mathrm{alkoxyamine}]_0$ molar ratio increased. In addition, this r parameter controlled the rate of polymerization: the larger r was, the slower the reaction. Indeed, as previously proposed in bulk,[53] a small fraction of free nitroxide was added at the beginning of the polymerization in order to better control the conversion rate and the molar mass distribution by compensating for the too low amount that is naturally released at the early stage of the polymerization. (With *n*-butyl acrylate, the fraction of SG1 released upon macroradical self-termination—the so-called persistent radical effect (PRE)[54]—remains usually quite small, indicating a very low fraction of dead chains.) Some of the experiments presented in the previous work[45] were performed under similar conditions as those reported here (except the nature of the initiator), which allows direct comparison.

Control of Molar Mass and Molar Mass Distribution with the A-Na Initiator. In all cases, whatever the process (i.e., bulk or miniemulsion; Table 1), the polymerizations exhibited controlled molar masses and narrow molar mass distribution (Figure 1). The M_n

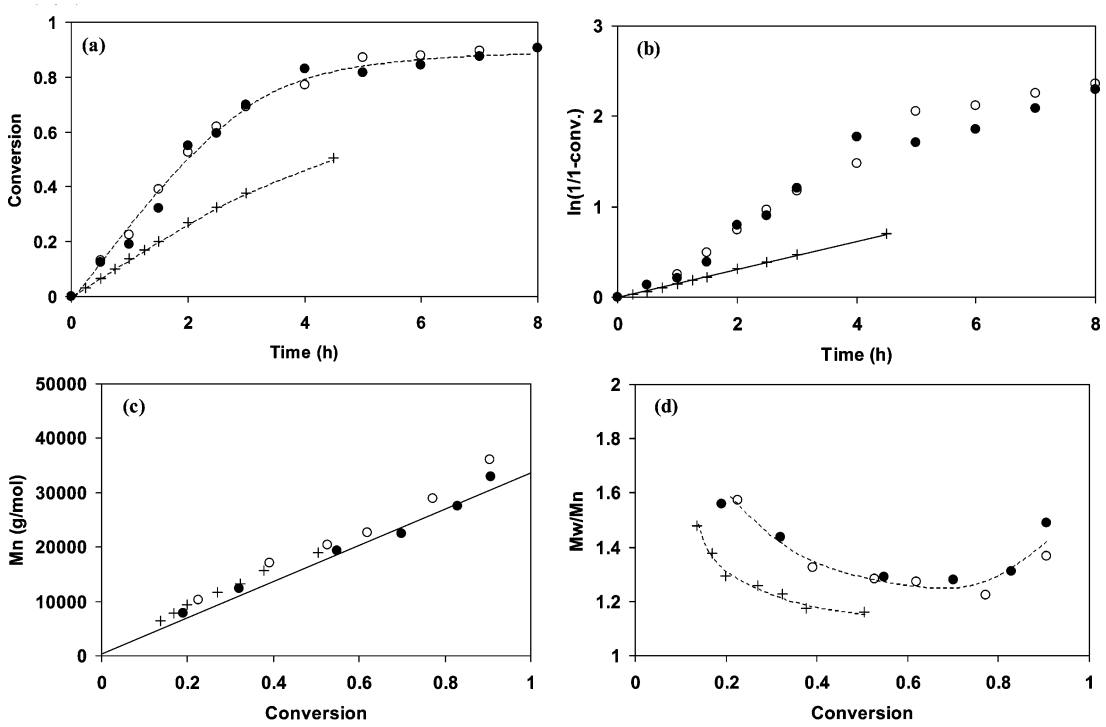


Figure 1. Bulk and miniemulsion (ME) polymerizations of *n*-butyl acrylate respectively initiated by the A-H and A-Na initiators: ○, expt 1 (ME, A-Na, $r = 0$); ●, expt 2 (ME, A-Na, $r = 0.027$); +, expt 5 (bulk, A-H, $r = 0$). See Table 1 for the experimental conditions.

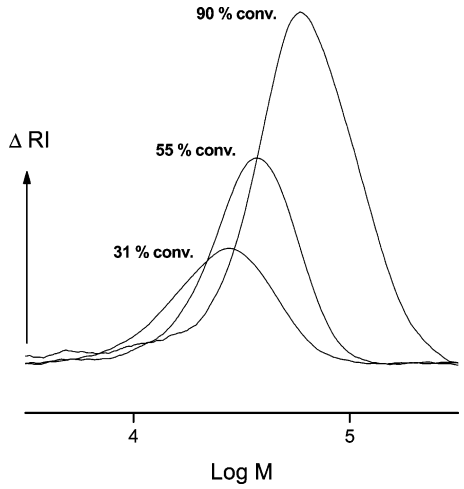


Figure 2. Size exclusion chromatograms recorded at various conversions for the miniemulsion polymerization of *n*-butyl acrylate initiated by A-Na (expt 2). See Table 1 for the experimental conditions.

values followed the theoretical line as a result of a high initiator efficiency. The molar mass distributions were, however, narrowest when the polymerization was performed in bulk (experiment 5). In this case, although no free SG1 was added at the beginning of the polymerization, the polydispersity index, M_w/M_n, which decreased with monomer conversion, was as low as 1.16 at 50% conversion. Differently, in miniemulsion, irrespective of the r value, M_w/M_n first decreased down to 1.3 with conversion but increased slightly up to 1.4−1.5 at 90% conversion (which is not surprising in the CRP of *n*-butyl acrylate at very high conversions due to side reactions such as chain transfer to polymer[46]). Nevertheless, the continuous shift of the size exclusion chromatograms shown in Figure 2 points out the controlled character of the polymerization.

In miniemulsion polymerization, such a good control of M_n with the water-soluble initiator, related to a very effective initiation, is a clear indication of the efficient entry in the monomer droplets of the oligomers formed in the aqueous solution. Consequently, the miniemulsion polymerization of BA can be easily carried out in the presence of a water-soluble initiator, without sacrificing the initiator efficiency and the control over M_n and M_w/M_n.

Polymerization Kinetics with the Water-Soluble A-Na Initiator. The kinetic features of BA miniemulsion polymerizations initiated with the water-soluble A-Na alkoxyamine slightly differed from those using the MONAMS as an oil-soluble initiator.[45] Whereas with the latter the rate of polymerization strongly depended upon the initial $r = [SG1]_0/[alkoxyamine]_0$ molar ratio, with the former this was not the case anymore. Both miniemulsion polymerizations (experiment 1 with $r = 0$ and experiment 2 with $r = 0.027$) exhibited exactly the same rate, which was larger than in the same polymerization performed in bulk, with $r = 0$ (experiment 5) (Figure 1). Additionally, those miniemulsion polymerizations were slower than that with MONAMS and $r = 0$, whereas they were only slightly faster than the corresponding miniemulsion polymerization performed with MONAMS and $r = 0.027$.[45]

These results show that with the A-Na alkoxyamine initiator there is no need to initially add free nitroxide as with MONAMS, to regulate the polymerization kinetics and enhance the control. Indeed, with a particularly high rate constant of dissociation ($k_d = 0.34$ s^{-1} at 120 °C in *tert*-butylbenzene, owing to its unique structure with tertiary carbon radical attached to the nitroxide),[48] a large concentration of transient radical was initially produced, hence favoring the irreversible termination and allowing the release of a sufficient amount of deactivator. Nevertheless, the extent of termination remained quite low as shown by the good

Table 2. Experimental and Calculated Characteristics for the SG1-Mediated Polymerizations of *n*-Butyl Acrylate[a]

expt	experimental conditions	$[P^\bullet]_{org}$[b] (mol L^{-1})	$[SG1]_{org.}/[initiator]_{0,org}$[c]	final average *D* (nm) from DLS	average *D* from CHDF (nm)	
					D_n (number average)	D_w (weight average)
1	ME[d]/A-Na/$r = 0$	1.4×10^{-9}	0.031	260	220	440
2	ME/A-Na/$r = 0.027$	1.8×10^{-9}	0.024	280	300	370
5	bulk/A−H/$r = 0$	5.3×10^{-10}	0.081			

[a] For simplicity, all concentrations are expressed per volume unit of organic phase. [b] Concentration of propagating macroradical in the organic phase, calculated from the slope of ln(1/(1 − conv)) vs time using $k_p = 82\,000$ L mol^{-1} s^{-1} for *n*-butyl acrylate at 120 °C (ref 56); the slope was taken between 1 and 4 h for the miniemulsions. [c] Calculated proportion of free SG1 based on the initial alkoxyamine: $[SG1]_{org}/[initiator]_{0,org} = K/[P^\bullet]_{org}$ with $K = 4.34 \times 10^{-11}$ mol L^{-1} (ref 53). It should be noted that these values cannot be considered as absolute, since neither k_p, nor *K* is accurately known. They can, however, be used to compare the various experiments. [d] ME = miniemulsion.

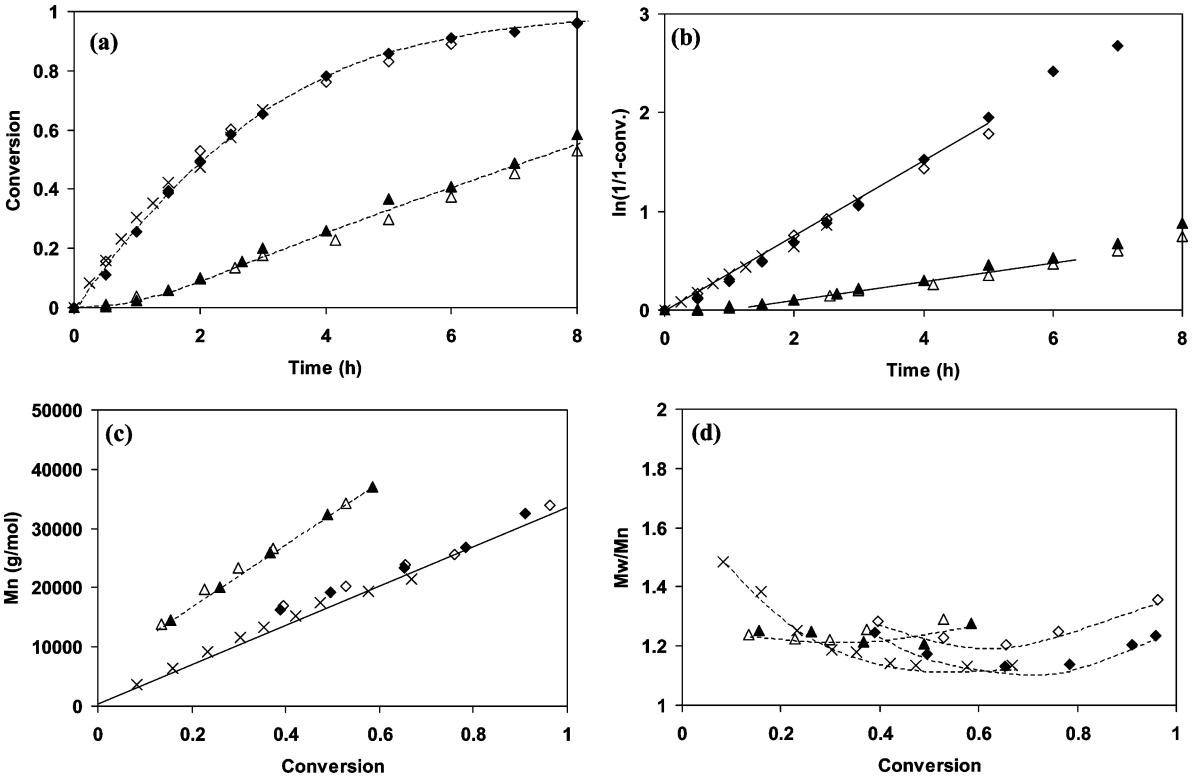


Figure 3. Bulk and miniemulsion (ME) polymerizations of styrene initiated by the A-H, MONAMS, and A-Na initiators: △, expt 3 (ME, A-Na, $r = 0$); ▲, expt 4 (ME, A-Na, $r = 0.027$); ×, expt 6 (bulk, A−H, $r = 0$); ◇, expt 7 (ME, MONAMS, $r = 0$); ◆, expt 8 (ME, MONAMS, $r = 0.027$). See Table 1 for the experimental conditions.

quality of control and the low amount of released free nitroxide (see Table 2). The faster polymerization observed in miniemulsion than in bulk was the consequence of a lower SG1 local concentration and might be explained in three different ways, without however any proof to draw definitive conclusion: (i) same amount of released SG1 but partition of the nitroxide between water and monomer; (ii) same amount of released SG1 but degradation of part of the free nitroxide; (iii) reduced termination, i.e., reduced amount of released SG1 (less pronounced PRE in miniemulsion than in bulk).

The fast entry rate and high initiator efficiency were the direct consequence of the water phase kinetics. Indeed, fast propagation rate of *n*-butyl acrylate and low SG1 concentration in water would allow the oligoradicals generated in the aqueous phase to undergo fast growth and to become sufficiently hydrophobic to directly enter the monomer droplets before being deactivated. Hence, first deactivation might essentially occur in the droplets (i.e., $(k_p[BA]_{aq})/(k_c[SG1]_{aq} \gg 1)$.[19] It is thus very unlikely that the activation−deactivation equilibrium was established in the aqueous phase.

3. Homopolymerization of Styrene. Various experiments were carried out either in bulk or in miniemulsion. In bulk, the A-H initiator was used whereas in miniemulsion, A-Na and MONAMS were both used, with or without added free SG1 (see Table 1).

Control of Molar Mass and Molar Mass Distribution. In bulk with the A-H initiator (experiment 6) as well as in miniemulsion with MONAMS (experiments 7 and 8), control of molar mass and molar mass distribution was good, demonstrating the easy transposition from bulk to miniemulsion as far as a monomer-soluble alkoxyamine initiator is used (Figure 3). Like for the polymerization of *n*-butyl acrylate, the A-H initiator exhibited an excellent ability to control the SG1-mediated homopolymerization of styrene in bulk, leading to polydispersity indexes below 1.2 (1.13 at 67% conversion). Quite differently, when used in miniemulsion, the water-soluble A-Na initiator was unable to yield polymers with the predicted M_n (experiments 3 and 4). Indeed, the experimental M_ns were twice as large as the theoretical ones, and thus, the apparent initiator efficiency was close to 50%, irrespective of the initial concentration of free nitroxide (see Table 3). Nevertheless, the formed polystyrene exhibited a controlled character with a continuous increase of M_n with mono-

Table 3. Experimental and Calculated Characteristics for the SG1-Mediated Polymerizations of Styrene[a]

expt	experimental conditions	$[P^\bullet]_{org}$ (mol L^{-1})[b]	apparent initiator efficiency	$[SG1]_{org.}/[initiator]_{0,org}$[c]	calcd $[SG1]_{PRE}/[initiator]_0$[d]	final average D from DLS (nm)
3	ME/A-Na/$r = 0$	1.2×10^{-8}	0.5 (final value)	0.26		275
4	ME/A-Na/$r = 0.027$	1.4×10^{-8}	0.5 (final value)	0.21		310
6	bulk/A−H/$r = 0$	4.8×10^{-8}	0.98	0.12	0.14	
7	ME/MONAMS/$r = 0$	5.0×10^{-8}	0.96	0.12	0.14	330
8	ME/MONAMS/$r = 0.027$	5.6×10^{-8}	0.92	0.10	0.14	355
9[e]	ME/A-Na/$r = 0/[MA]_0/[A\text{-}Na]_0 = 2.5$	2.4×10^{-8}	0.75 (final value)	0.19		340
10[e]	ME/A-Na/$r = 0/[MA]_0/[A\text{-}Na]_0 = 5.1$	3.3×10^{-8}	0.87	0.16		330
11[e]	ME/A-Na/$r = 0/[MA]_0/[A\text{-}Na]_0 = 10.0$	4.9×10^{-8}	0.93	0.11		340
12[e]	ME/A-Na/$r = 0/[AA]_0/[A\text{-}Na]_0 = 10.0$	5.8×10^{-8}	0.64	0.07		345
13	ME/A-Na/$r = 0/[MP]_0/[A\text{-}Na]_0 = 10.1$	2.6×10^{-8}	0.63	0.15		350
14	ME/A-Na/$r = 0/[PA]_0/[A\text{-}Na]_0 = 10.1$	5.5×10^{-8}	0.73	0.08		340

[a] For simplicity, all concentrations are expressed per volume unit of organic phase. [b] Concentration of propagating macroradical in the organic phase, calculated from the slope of $\ln(1/(1 - \text{conv}))$ vs time (taken after the induction period when present, i.e., after 1.5 h) using $k_p = 2036$ L mol^{-1} s^{-1} for styrene at 120 °C (ref 57). [c] Calculated proportion of free SG1 based on the initial alkoxyamine: $[SG1]_{org}/[initiator]_0 = (K \times \text{efficiency})/[P^\bullet]_{org}$ with $K = 6.0 \times 10^{-9}$ mol L^{-1} (ref 55). [d] Estimated proportion of SG1 released at $t = 1$ h according to Fischer's equation: $[SG1]_{PRE}/[initiator]_0 = (3k_tK^2[initiator]_0^2t)^{1/3}/[initiator]_0$ (ref 54). (The equation was only applied when initiation and propagation took place in the same phase.) For calculation, the rate constant of termination was $k_t = 2 \times 10^8$ L mol^{-1} s^{-1}. [e] When a copolymerizable additive was used, $[P^\bullet]_{org}$ was also calculated with $k_p = 2036$ L mol^{-1} s^{-1} for styrene alone.

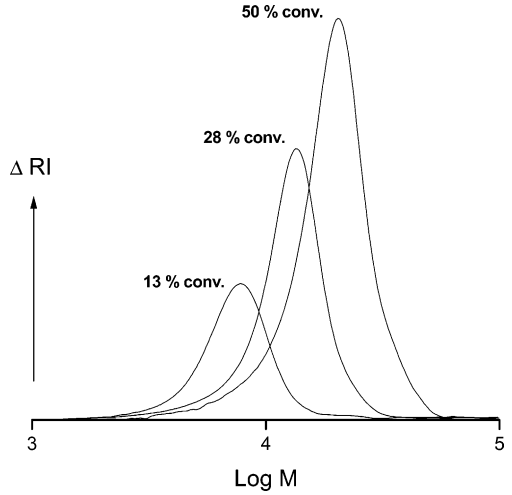


Figure 4. Size exclusion chromatograms recorded at various conversions for the miniemulsion polymerization of styrene initiated by A-Na (expt 3). See Table 1 for the experimental conditions.

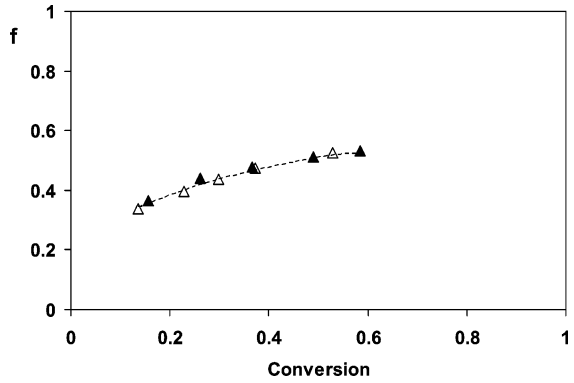


Figure 5. Apparent initiator efficiency, f, vs monomer conversion for the miniemulsion polymerizations of styrene for expt 3 (△, ME, A-Na, $r = 0$) and expt 4 (▲, ME, A-Na, $r = 0.027$). See Table 1 for the experimental conditions.

mer conversion and M_w/M_n remaining between 1.2 and 1.3 (see Figure 3); these features were accompanied by a shift of the size exclusion chromatograms with conversion (Figure 4).

Polymerization Kinetics. Whereas the polymerization rate was the same in bulk with the A-H initiator and in miniemulsion with MONAMS (whatever the r ratio), very slow polymerizations together with an induction period of about 1 h were observed when the water-soluble A-Na was applied as an initiator (see Figure 3). Again, the polymerization rate was not affected by the initial concentration of added free SG1. A slow polymerization reflects a high concentration of free nitroxide, hence leading to the conclusion that the persistent radical effect was strongly pronounced for those experiments (see experimental and calculated data in Table 3).

When A-H was used as an initiator in bulk, or when MONAMS was used in miniemulsion, the concentration of free SG1, calculated from the activation−deactivation equilibrium relationship, was of about 10−12 mol % with respect to the alkoxyamine initiator (Table 3). This large proportion explains why an initial $r = 2.7$ mol % ratio was quite insufficient to affect the polymerization rate. This situation is the direct consequence of the large equilibrium constant K for polystyrene,[55] leading to large concentrations of propagating radicals and hence to irreversible termination.

With the A-Na initiator in miniemulsion, the even larger proportion of released SG1 (21−26 mol %; see Table 3) was also the consequence of fast termination, occurring most probably in the aqueous phase at the early stage of the polymerization. The large dissociation rate constant of the alkoxyamine and the large equilibrium constant K of polystyryl-based alkoxyamine were responsible for this situation. In addition, with a rather large free SG1 concentration and a slow propagation, it can be inferred that, besides irreversible termination, reversible deactivation might also take place in water. (The kinetic chain length in the water solution $(k_p[S]_{aq})/(k_c[SG1]_{aq})$ would thus be very small.[19]) The activation−deactivation equilibrum might establish in the aqueous phase, and the consequence would be a slow and incomplete entry process (that is to say, a slow transport of the still living polystyryl oligoradicals/oligomers from the aqueous phase to the monomer droplets) as illustrated by the existence of an induction period. This can also be correlated with the continuous increase in the apparent initiator efficiency throughout the polymerization (see Figure 5). In conclusion, the high level of irreversible termination and the slow propagation in the aqueous phase at the beginning of the polymerization are the best explanations for the observed slow kinetics together with poor initiator efficiency.

4. Miniemulsion Polymerization of Styrene in the Presence of a Small Concentration of Addi-

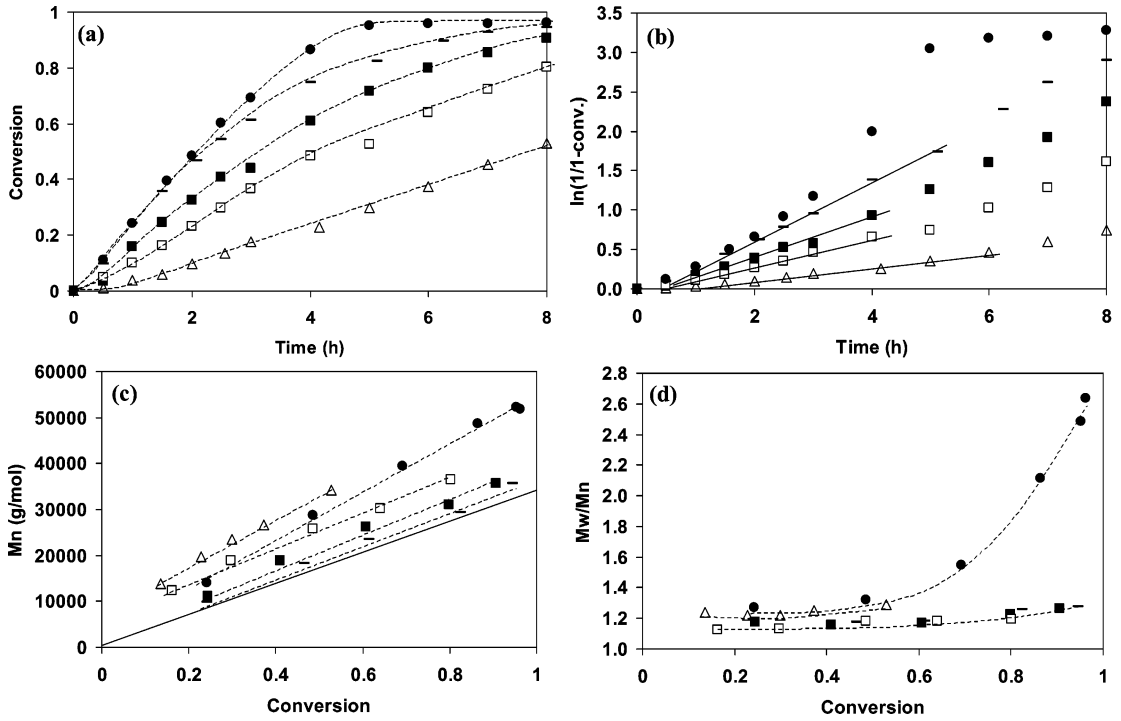


Figure 6. Miniemulsion polymerizations of styrene initiated by the A-Na initiator in the presence of various concentrations of methyl acrylate (MA) or acrylic acid (AA): △, expt 3 (no additive); □, expt 9 ($[MA]_0/[A\text{-}Na]_0 = 2.5$); ■, expt 10 ($[MA]_0/[A\text{-}Na]_0 = 5.1$); —, expt 11 ($[MA]_0/[A\text{-}Na]_0 = 10.0$); ●, expt 12 ($[AA]_0/[A\text{-}Na]_0 = 10.0$). See Table 1 for the experimental conditions.

tive. *Methyl Acrylate and Acrylic Acid Comonomers.* To enhance the rate of water phase propagation, and hence induce an efficient entry of the oligoradicals in the droplets, the addition of a monomer with larger water solubility than styrene, with larger rate constant of propagation, and with lower activation−deactivation equilibrium constant (to reduce the PRE) was searched. As the acrylics (esters and acid) exhibit large k_p[56−59] together with low K in SG1-mediated controlled free-radical polymerization,[27,53,55,60] methyl acrylate (MA) and acrylic acid (AA) were thus selected for their fairly high water solubility.

First, three experiments were carried out in the presence of increasing concentrations of MA (experiments 9, 10, and 11; $[MA]_0/[A\text{-}Na]_0 = 2.5$, 5.1, and 10.0, respectively; see Table 1). In all cases, polymerizations were performed in the absence of added free nitroxide. As shown in Figure 6, the polymerization rate increased with the increase in acrylate initial concentration. Parallel to this, the apparent initiator efficiency increased (M_ns got closer to the theoretical values) (Figure 7), and the polydispersity indexes were even lower (<1.2) than in the corresponding experiment 3 carried out in the absence of added acrylate. Consequently, the addition of a very small concentration of a fairly water-soluble acrylate considerably improved the control over the SG1-mediated miniemulsion polymerization of styrene initiated by the A-Na initiator. This was the result of a reduction of the irreversible termination reaction in the initial stage of the reaction (26 mol % of SG1 was released in experiment 3 and 11 mol % in experiment 11, i.e., the normal level in styrene polymerization (owing to lower K for the polyacrylate/SG1 system) and of faster propagation in the water phase (owing to the lower free SG1 concentration and to the large k_p of the acrylate). Therefore, as previously concluded,[19] the water-phase kinetics play a crucial role in those systems.

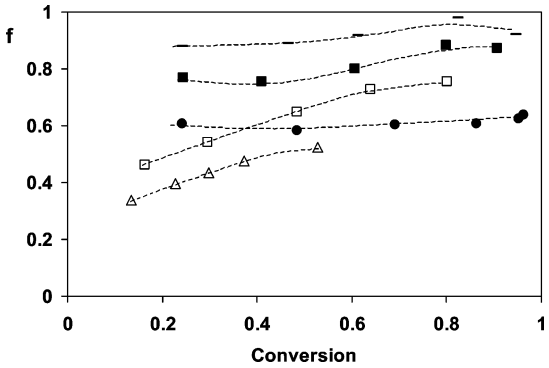


Figure 7. Apparent initiator efficiency, f, vs monomer conversion for the miniemulsion polymerizations of styrene in the presence of various concentrations of methyl acrylate (MA) or acrylic acid (AA): △, expt 3 (no additive); □, expt 9 ($[MA]_0/[A\text{-}Na]_0 = 2.5$); ■, expt 10 ($[MA]_0/[A\text{-}Na]_0 = 5.1$); —, expt 11 ($[MA]_0/[A\text{-}Na]_0 = 10.0$); ●, expt 12 ($[AA]_0/[A\text{-}Na]_0 = 10.0$). See Table 1 for the experimental conditions.

When MA was replaced by acrylic acid (experiment 12, with the same concentration as in experiment 11, i.e., $[AA]_0/[A\text{-}Na]_0 = 10.0$), the polymerization rate was initially the same, but an acceleration could be detected after 2 h (Figure 6). The increase in propagating macroradical concentration was particularly visible in the logarithmic conversion vs time plot (Figure 6). The apparent initiator efficiency was not really improved with respect to experiment 3 (Figure 7), and the molar mass distribution broadened very significantly above 50% conversion (i.e., 2 h). Such broadening was an evident signature of the loss of control, which could be related to the fast polymerization, itself related to a decrease in free SG1 concentration most likely due to degradation in the acidic aqueous system (pH was below 4 throughout the polymerization; Figure 8). Consequently, a too low pH deteriorated the quality of control

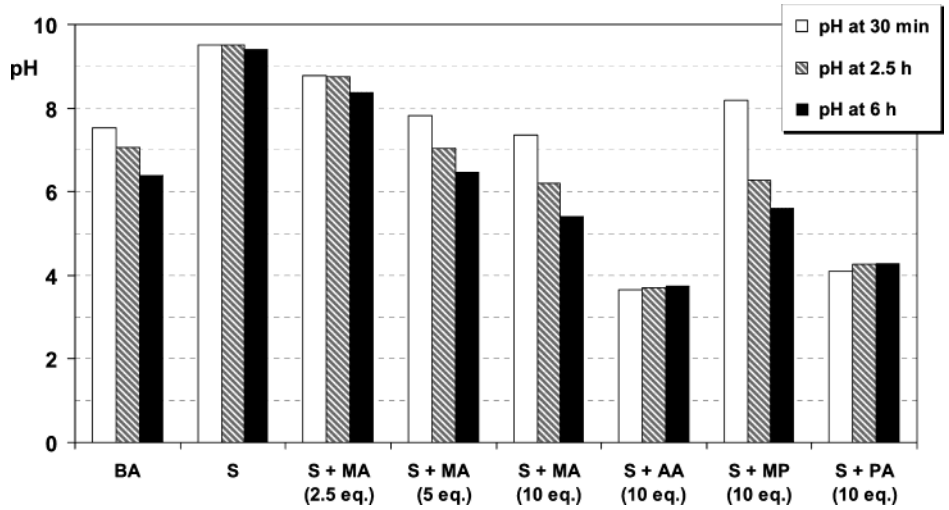


Figure 8. Latex pH at various polymerization times for expt 1 (BA), expt 3 (S), expt 9 (S + MA, $[MA]_0/[A\text{-}Na]_0 = 2.5$), expt 10 (S + MA, $[MA]_0/[A\text{-}Na]_0 = 5.1$), expt 11 (S + MA, $[MA]_0/[A\text{-}Na]_0 = 10.0$), expt 12 (S + AA, $[AA]_0/[A\text{-}Na]_0 = 10.0$), expt 13 (S + MP, $[MP]_0/[A\text{-}Na]_0 = 10.1$), and expt 14 (S + PA, $[PA]_0/[A\text{-}Na]_0 = 10.1$). Monomers = BA (*n*-butyl acrylate) and S (styrene); additives = MA (methyl acrylate), AA (acrylic acid), MP (methyl propionate), or PA (propionic acid). See Table 1 for the experimental conditions.

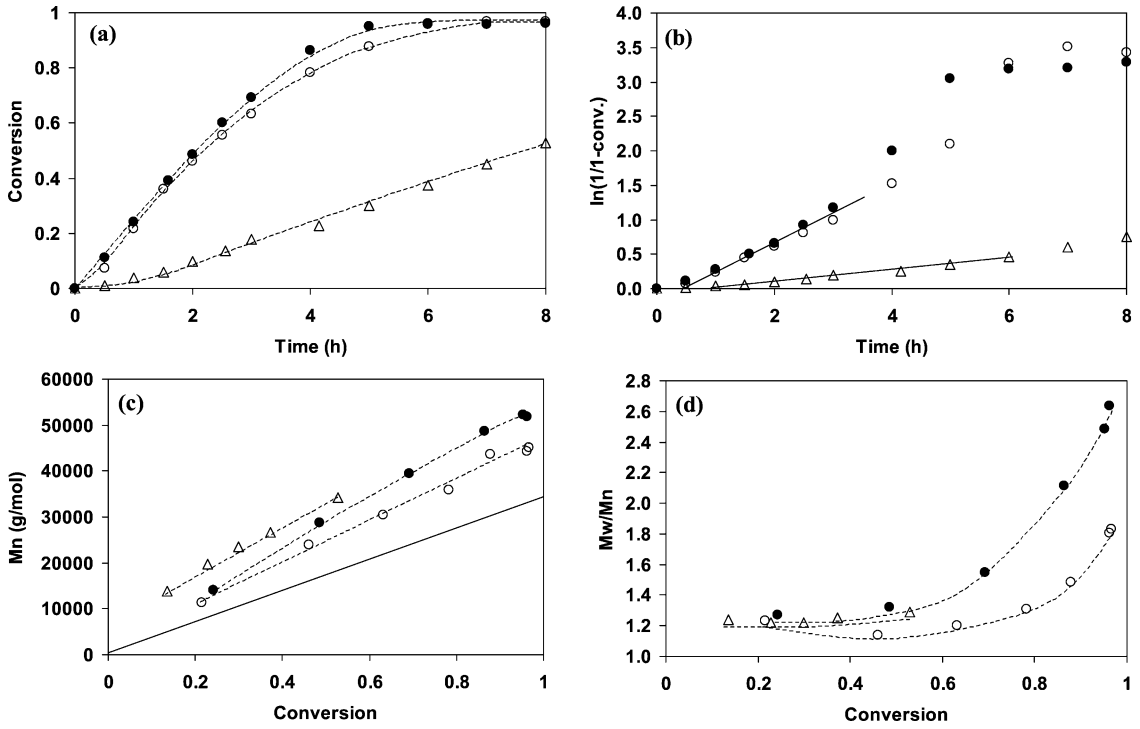


Figure 9. Miniemulsion polymerizations of styrene initiated by the A-Na initiator, in the absence of any additive (expt 3, △) or in the presence of acrylic acid, AA (expt 12, $[AA]_0/[A\text{-}Na]_0 = 10.0$, ●), or propionic acid, PA (expt 14, $[PA]_0/[A\text{-}Na]_0 = 10.1$, ○). See Table 1 for the experimental conditions.

in SG1-mediated miniemulsion polymerization as it was previously shown.[36,38]

Nonpolymerizable Ester or Acid. It was observed that the addition of an increasing concentration of MA led to a change in the water-phase pH, as illustrated in Figure 8. Indeed, with styrene alone, the pH remained above 8 throughout the polymerization reaction (whatever the iniator type, i.e., A-Na or MONAMS), whereas with the acrylate, not only the initial pH decreased with the increase in $[MA]_0$, but for a given experiment it slightly decreased with time, too. (It was true also for the homopolymerization of *n*-butyl acrylate and was assigned to ester hydrolysis.) So we had to address the issue of the effect of pH in the success of the polymerizations carried out in the presence of MA: (i) acidic conditions might improve the rate of entry by altering the degree of ionization of the initiating radicals and hence their hydrophilicity; (ii) a slight decrease in pH might contribute to reduce the free SG1 excess by acidic degradation and thus increase the polymerization rate, which might also enhance the entry rate (along with the production of dead chains, however).

To solve this question, we decided to replace MA and AA by nonpolymerizable counterparts, namely methyl propionate (MP; experiment 13) and propionic acid (PA; experiment 14), respectively. The results are presented in Figure 8 for the pH and in Figures 9−11 for the kinetics and molar mass evolutions. PA had an effect

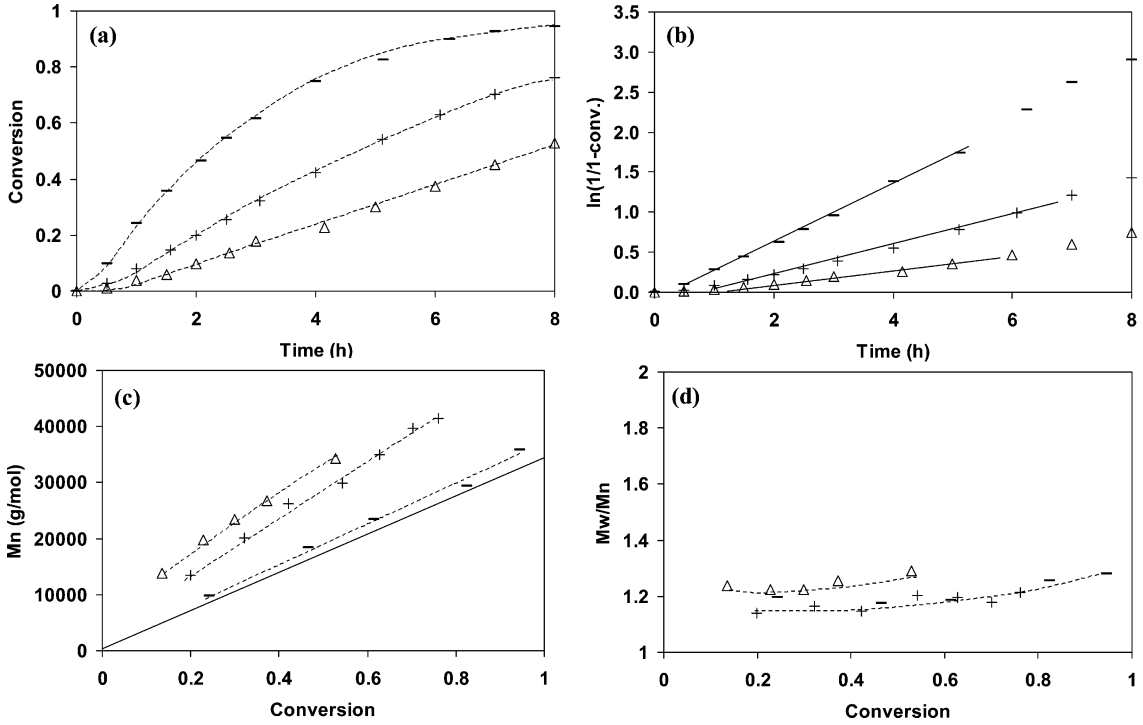


Figure 10. Miniemulsion polymerizations of styrene initiated by the A-Na initiator, in the absence of any additive (expt 3, △) or in the presence of methyl acrylate, MA (expt 11, $[MA]_0/[A\text{-}Na]_0 = 10.0$, —), or methyl propionate, MP (expt 13, $[MP]_0/[A\text{-}Na]_0 = 10.1$, +). See Table 1 for the experimental conditions.

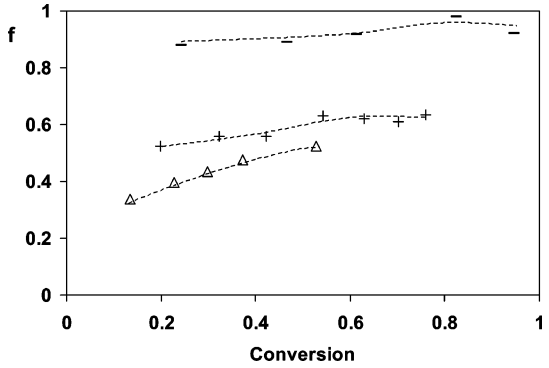


Figure 11. Apparent initiator efficiency, *f*, vs monomer conversion for the miniemulsion polymerizations of styrene in the absence of any additive (expt 3, △) or in the presence of methyl acrylate, MA (expt 11, $[MA]_0/[A\text{-}Na]_0 = 10.0$, —), or methyl propionate, MP (expt 13, $[MP]_0/[A\text{-}Na]_0 = 10.1$, +). See Table 1 for the experimental conditions.

very similar to that of acrylic acid on all of the investigated parameters (kinetics, M_n, apparent initiator efficiency, M_w/M_n; Figure 9), confirming the negative influence of a too low pH. However, when MA was replaced by MP (in the same concentration, $[MP]_0/[A\text{-}Na]_0 = 10$), several interesting features were observed. As expected, the pH followed exactly the same trend throughout the polymerization (Figure 8). Nevertheless, the polymerization rate was slower with MP than with MA, and the apparent initiator efficiency was much lower: 63% for experiment 13 with MP vs 93% for experiment 11 with MA (Figures 10 and 11; Table 3). As a conclusion, pH might only have a small indirect effect (actually more pronounced on the overall polymerization rate than on the apparent initiator efficiency as it was also the case in the presence of acrylic acid and propionic acid), but the major role was played by copolymerizable additives; that is to say, a major kinetic effect took place via appropriate copolymerization conditions.

The pK_a of pivalic acid, a carboxylic acid similar to A-H, is equal to 5.03.[61] This means that for BA homopolymerizations as well as for styrene homopolymerizations in the presence of a small amount of methyl acrylate, the water-phase pH was above the pK_a for the major part of the polymerization (particularly the entry step), indicating a high ionization degree. Consequently, no reduction in the ionization degree that would amplify the oligoradicals hydrophobicity is expected. The slight positive effect on polymerization rate of the decrease of pH observed in the presence of MP suggests that degradation of a small fraction of released free nitroxide took place. In conclusion, such A-Na-initiated miniemulsion polymerizations should be performed under controlled pH conditions. Typically, the pH should remain above 5.5; below pH = 4, as shown in the presence of an acid, stability of the SG1 nitroxide was strongly affected.

5. Colloidal Characteristics of the Latexes. Latexes were synthesized at 20 wt % solids content and were stabilized by a classical anionic surfactant at low concentration (2.2 wt % based on the monomer). All of them were very stable with neither coagulum nor destabilization over time. With the MONAMS alkoxyamine initiator, the average particle diameters were rather large, and the particle size distribution was very broad for BA[45] as well as for styrene miniemulsion polymerizations. With the water-soluble A-Na alkoxyamine used in the same conditions, the DLS number-average particle diameters were significantly lower. For *n*-butyl acrylate homopolymerization, they were systematically below 300 nm (Table 2), whereas with MONAMS, average *D* was in the 450−650 nm range.[45] Knowing, however, that DLS is inaccurate for broad particle size distribution, CHDF was used to visualize the whole particle size distribution of experiment 2 (see Table 2

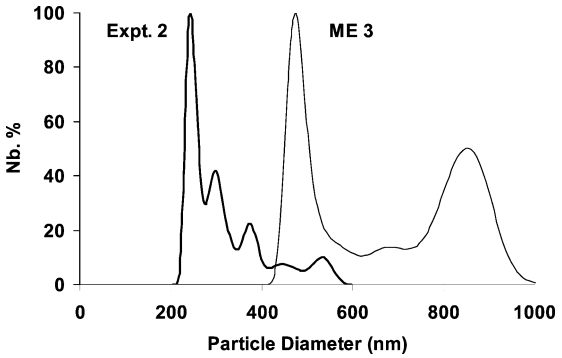


Figure 12. Number distribution of particle diameter from CHDF analysis of expt 2 and of expt ME3 in ref 45. See Table 1 for the experimental conditions.

and Figure 12) in comparison with the same miniemulsion polymerization initiated with MONAMS (experiment ME3**,** in ref 45). Indeed, changing from MONAMS to A-Na, all the other experimental conditions remaining the same, the particle size distribution narrowed and shifted toward the lower values. This trend can be directly assigned to the use of the water-soluble alkoxyamine. Indeed, as the A-H alkoxyamine was in the neutralized form, part of the end groups might remain located at the particle surface, hence leading to an increase in the surface charge density. Knowing precisely the respective concentrations of the Dowfax 8390 surfactant and of the A-Na alkoxyamine used in the miniemulsion recipe and assuming that all of the negative charges were located at the particle surface, it can be calculated that the charges coming from the A-Na alkoxyamine represented 30% of the whole amount.

Conclusion

SG1-mediated controlled free-radical polymerization of *n*-butyl acrylate and styrene was performed in miniemulsion using, for the first time, a water-soluble alkoxyamine as an initiator. Besides its water solubility, the novel alkoxyamine used exhibits a particularly high dissociation rate constant owing to its unique structure with tertiary carbon radical attached to the nitroxide. This has the advantage to better control the persistent radical effect in the case of acrylate polymerization and avoid the addition of free nitroxide at the onset of the polymerization. For *n*-butyl acrylate the miniemulsion polymerizations exhibited all the features of a controlled system. In particular, a high initiator efficiency was observed, indicating an extensive entry in the monomer droplets of all of the oligoradicals formed in the aqueous phase. Such high efficiency was however not observed for styrene homopolymerization, owing to a highly pronounced persistent radical effect (large concentration of dead oligomers and of free SG1; too slow chain growth in the aqueous phase and hence poor entry rate). Nevertheless, the addition of a small amount of methyl acrylate was shown to strongly enhance the entry rate. This was the consequence of a favorable kinetic effect due to appropriate copolymerization conditions permitting the reduction of the persistent radical effect along with an increase of the propagation rate in water. Moreover, the pH of the aqueous phase was shown to have a strong influence on the polymerization rate: it should remain above ~5 to avoid side reactions of SG1 degradation. Besides the high quality of molar mass and molar mass distribution control, the charged alkoxyamine that remained attached onto the polymer particle surface contributed in the reduction of the average particle diameter. The next step, which is under progress, will be devoted to true emulsion polymerization.

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(50) Since our first works on SG1-mediated miniemulsion polymerization,[38] we used polystyrene as a hydrophobe in addition to hexadecane because it was previously supposed to play the role of nucleation enhancer.[29] For this article, the recipe was not changed to allow the comparison.
(51) Polystyrene and hexadecane hydrophobes were used in lower amounts in the miniemulsion polymerizations of *n*-butyl acrylate than in those of styrene (for which the quantities corresponded to classical values), as we observed for the former that too large amounts led to latex destabilization after a few days storage [see ref 45 and Farcet, C. Ph.D. Thesis Dissertation, Paris, 2002]. The true reason for this phenomenon has not been explored yet.
(52) The polystyrene calibration is appropriate for poly(*n*-butyl acrylate) samples as shown by the Mark−Houwink−Sakurada parameters: actually, it leads to an error of about 3−5%, which is within the accepted range for SEC analysis. Indeed, the MHS parameters in THF at 30 °C are the following: $K_{PS} = 11.4\ 10^{-5}$ 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 Monographs* **1995**, *131*, 467]; $K_{PBA} = 12.2 \times 10^{-5}$ dL g^{-1} and $\alpha_{PBA} = 0.700$ for poly(*n*-butyl acrylate) [see: Beuermann, S.; Paquet, D. A., Jr.; McMinn, J. H.; Hutchinson, R. A. *Macromolecules* **1997**, *29*, 1918].
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