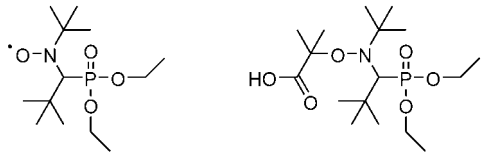
Polymerizations

Nitroxide-Mediated Controlled Free-Radical Emulsion Polymerization of Styrene and *n*-Butyl Acrylate with a Water-Soluble Alkoxyamine as Initiator

Julien Nicolas, Bernadette Charleux, Olivier Guerret, and Stéphanie Magnet*

Controlled free-radical polymerization (CRP) in water-based systems has been studied intensely during the last ten years as it combines the environmental and technical advantages of polymerization in aqueous dispersed media with the ability to synthesize tailor-made macromolecular architectures.[1–4] Most CRP methods, however, have not been applied in traditional macroemulsion polymerization processes (usually called simply emulsion polymerization),[5] but in miniemulsion polymerization,[1–4,6] as the latter process offers benefits from the mechanistic viewpoint and can be regarded as a simplified model of emulsion polymerization. Indeed, nucleation takes place directly in the monomer droplets, which become polymer particles upon initiation with either a hydrophobic or a hydrophilic initiator, and subsequent propagation. However, the formation of small, stable monomer droplets requires the application of high shear to the initial monomer-in-water emulsion and the addition of a highly hydrophobic molecule to the monomer phase.[6] Many authors have demonstrated the great success of this method for all CRP techniques.[1–4] However, industrial applications usually demand an easier process; in particular, the use of a high shear device in large-volume reactors is usually avoided, and furthermore, the introduction of a hydrophobic additive, which is sometimes a volatile organic compound, is not encouraged. Consequently, true emulsion polymerization is usually the technique of choice owing to its simplicity: this process does not require any special manipulation of the initial monomer-in-water emulsion, only the use of a water-soluble initiator,[5] and particles are generated in the aqueous phase, independently from the oil droplets, which only act as a monomer reservoir. Mainly due to the sensitivity of the nucleation step, CRP in emulsion systems often leads to unstable latexes, and is therefore still a challenge.[1–4] The formation of these unstable latexes has been explained by the very specific features of the chain growth in CRP with respect to a classical free-radical polymerization—a large number of oligomers undergo slow and simultaneous growth in the early stage of the polymerization, which completely modifies the particle-formation mechanism.

The goal of this work was to apply nitroxide-mediated polymerization in an emulsion process. This CRP method[7] takes advantage of the reversible deactivation of the propagating radicals by nitroxide, which gives alkoxyamine-terminated dormant chains and induces a controlled chain-growth. This method has recently been improved significantly with the discovery of very efficient acyclic nitroxides, such as SG1 (Scheme 1),[8] which can control the polymerization of a much broader range of monomers than cyclic nitroxides like TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy).[7] To perfectly control the chain growth and polymerization kinetics, a monocomponent alkoxyamine initiator should be selected rather than a normal bicomponent initiator system (classical radical initiator along with free nitroxide), because the latter suffers from poorly controlled initiator efficiency.[7] Consequently, the real challenge in nitroxide-mediated emulsion polymerization is first to select an appropriate water-soluble alkoxyamine initiator, and second to find the appropriate conditions to form a stable latex with sufficiently high solids content.[9] The very few reports on nitroxide-mediated ab initio emulsion polymerization have mainly concerned the application of a water-soluble radical initiator in conjunction with free nitroxide, either TEMPO[9–11] or SG1.[12] Marestin et al.[10] are the only group to report the use of a TEMPO-based water-soluble alkoxyamine in a diluted emulsion polymerization of styrene. However, the polymerization was rather slow and the use of TEMPO restricted its use to styrene.



Scheme 1. Structure of the nitroxide SG1 and of the SG1-based water-soluble alkoxyamine initiator (**A**-H for the displayed acidic form; **A**-Na for the corresponding sodium salt).

In this paper we present a new and simple way to perform nitroxide-mediated emulsion polymerization of both *n*-butyl acrylate (BA) and styrene (S), as well as the synthesis of a block copolymer, using a novel, water-soluble, SG1-based alkoxyamine (Scheme 1),[13] which can also be successfully applied in a miniemulsion.[14] The solubility in water is imparted by the sodium carboxylate group, providing the pH remains above about 6 ($pK_a = 4.98$),[15] at least during the nucleation step. Due to the hydrophobicity of the SG1 capping agent, **A**-Na exhibits surface activity in aqueous solution[14] but undergoes homolytic dissociation to the highly water-soluble 2-(hydroxycarbonyl)prop-2-yl sodium salt radical, which initiates the polymerization in the water phase.

[*] J. Nicolas, Prof. B. Charleux
Laboratoire de Chimie des Polymères
UMR 7610 Associée au CNRS
Université Pierre et Marie Curie, T44, E1
4, Place Jussieu, 75252 Paris, Cedex 05 (France)
Fax: (+33) -1-4427-7089
E-mail: charleux@ccr.jussieu.fr
Dr. O. Guerret, Dr. S. Magnet
ATOFINA
Groupement de Recherches de Lacq
B.P. no 34, 64170 Lacq (France)

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In a preliminary study, emulsion polymerizations initiated with the water-soluble **A**-Na alkoxyamine were performed in a single-batch step with 20 wt% monomer content and 2.2 wt% of various surfactants (see Supporting Information). In all cases the latexes underwent destabilization after about 50% monomer conversion, most probably due to the partition of the initially formed oligomeric alkoxyamines between the water phase and the oil phase, leading to unwanted droplet nucleation. Nevertheless, all polymers were well controlled, demonstrating the efficiency of the selected initiator. Consequently, improvement of the colloidal characteristics of the latexes was the main issue to address. This was done by making the process a multi-step polymerization.

The first polymerization step was the preparation of a living poly(*n*-butyl acrylate) seed latex, from a very dilute monomer-in-water emulsion (0.7 wt%; apparent concentration of 0.055 mol L^{-1}), with two different surfactant concentrations above the critical micelle concentration (experiments **1** and **2** in Table 1). The pH of the water phase was 7.4 and 6.9 for experiments **1** and **2**, respectively, that is, above the lower limit of 6 needed for a high ionization degree of the initiator. The majority of the *n*-butyl acrylate monomer was located either in the water solution[16] or in the swollen micelles. If present, the monomer droplets should therefore remain in only very small quantities. Indeed, with both the selected surfactant concentrations a clear solution was obtained at the polymerization temperature before the start of the reaction. The main purpose was to favor micellar nucleation over droplet nucleation. In both experiments the oligomers were obtained reproducibly with controlled molar masses in almost perfect agreement with the theoretical value (conversion at 8 h was close to 60% and theoretical $M_n =$ 1100 g mol^{-1}; experimental $M_n = 1060$ g mol^{-1} for experiment **1** with $M_w/M_n = 1.14$; experimental $M_n = 1080$ g mol^{-1} for experiment **1′**, with $M_w/M_n = 1.17$; experimental $M_n =$ 1120 g mol^{-1} for experiment **2**, with $M_w/M_n = 1.20$; experimental $M_n = 1110$ g mol^{-1} for experiment **2′**, with $M_w/M_n =$ 1.17). The molar masses indicate a high initiator efficiency, meaning that all **A**-Na molecules are consumed and turned into the hydrophobic polymer chains that form the particles.

Both seed latexes are stable, with an average particle diameter, given by dynamic light scattering (DLS), of 210 nm for the lowest amount of surfactant used (experiment **1**) and 150 nm when the amount of surfactant was multiplied by a factor of 2.3 (experiment **2**). As shown in Table 1, both experiments are also reproducible from the particle-size viewpoint, although the diameters are rather large and the particle-size distribution broad, in contrast to what is expected in a classical emulsion polymerization. Nucleation might lead to a change in the thermodynamic properties of the system, in close analogy with the theory of "superswelling" proposed for miniemulsions by Luo et al.[17] The presence of a large concentration of oligomers in the growing particles during the early stages of the reaction would lead to a lower chemical potential than in the non-nucleated micelles or droplets, which would enhance swelling of the former by the monomer. This would favor the formation of large particles with a broad particle-size distribution. The low amount of monomer, however, allowed us to limit the effects of this unwanted trend.

The low-solids-content poly(*n*-butyl acrylate) latexes produced in the first step were further used as a seed for the batch emulsion polymerization of *n*-butyl actylate and styrene (Table 1). As illustrated by the conversion versus time plots in Figure 1 and Figure 2, the dispersed oligomeric alkoxyamines initiate the polymerization and lead to fast and nearly complete polymerizations (85 to 95% conversion within 8 h), with very good reproducibility (see Table 1 and

Table 1: Experimental conditions for the living seed latex preparation and the seeded batch emulsion polymerization.[a]

Exp.	Seed Latex	Monomer(s)	Monomer content [wt%]	[Surfactant][b] [mol L^{-1}_{aq}] ([wt%])[c]	T [°C]	[**A**-Na]$_0$ [mol L^{-1}_{aq}]	Overall theoretical DP_n at 100% conv.[d]	Overall conversion after 8 h[e] [%]	Final average diameter from DLS [nm]
1	–	BA	0.7	6.89×10^{-3}	112	5.82×10^{-3}	10	55	210
1′	–	BA	0.7	6.89×10^{-3}	112	5.82×10^{-3}	10	60	230
2	–	BA	0.7	1.54×10^{-2}	112	5.71×10^{-3}	10	60	150
2′	–	BA	0.7	1.54×10^{-2}	112	5.71×10^{-3}	10	60	155
3	**1**	BA + BA	16.5	6.89×10^{-3} (2.2)	112	5.82×10^{-3}	267	95	660
3′	**1**	BA + BA	16.5	6.89×10^{-3} (2.2)	112	5.82×10^{-3}	267	95	650
4	**1**	BA + S	16.5	6.89×10^{-3} (2.2)	120	5.82×10^{-3}	327	87	530 (TEM: $D_n = 450$; $D_w = 830$)[f]
5	**2**	BA + BA	16.3	1.54×10^{-2} (5.1)	112	5.71×10^{-3}	266	92	270
6	**2**	BA + S	16.1	1.55×10^{-2} (5.1)	120	5.71×10^{-3}	328	85	260 (TEM: $D_n = 90$; $D_w = 350$)[f]
7[g]	**2**	BA + BA + S	26.4	1.55×10^{-2} (2.9)	112	5.71×10^{-3}	532	80	330
7′[g]	**2**	BA + BA + S	26.4	1.55×10^{-2} (2.9)	112	5.71×10^{-3}	532	85	310

[a] $[NaHCO_3] = 0.012$ mol L^{-1}; $p = 3$ bar N_2; **A**-H was dissolved in a 0.4 M sodium hydroxide solution (1.6 equiv.) to give **A**-Na, and was then added into the reactor at 90 °C, triggering the reaction. The experiments **1**, **2**, **3**, and **7** were duplicated, with the same experimental conditions. [b] Dowfax 8390; critical micelle concentration = 0.05 wt% at 25 °C, approximately 0.5–1 mM. [c] Based on the overall weight of monomer. [d] Theoretical $DP_n = [monomer]_0/[alkoxyamine]_0$. [e] Determined by gravimetry. [f] Determined by TEM, using $D_n = \sum n_i D_i / \sum n_i$ and $D_w = \sum n_i D_i^4 / \sum n_i D_i^3$ (see the full distribution in the supporting information). [g] Same initial molar amount of *n*-butyl acrylate and styrene (55 wt% of BA); composition of copolymer **7** at 80% conversion determined by ^{1}H NMR spectroscopy (200 MHz, $CDCl_3$) to be 47 mol% of BA.

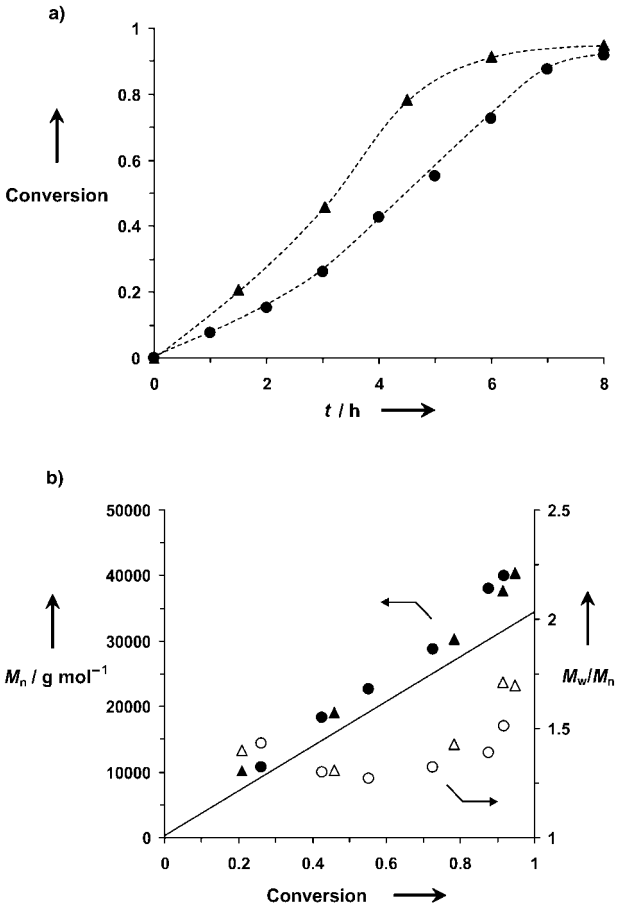

Figure 1. Seeded emulsion polymerizations of *n*-butyl acrylate (experiment **3**: ▲, △; experiment **5**: ●, ○): a) monomer conversion versus time; b) number-average molar mass and polydispersity index versus conversion. Straight line: theoretical evolution of M_n versus conversion.

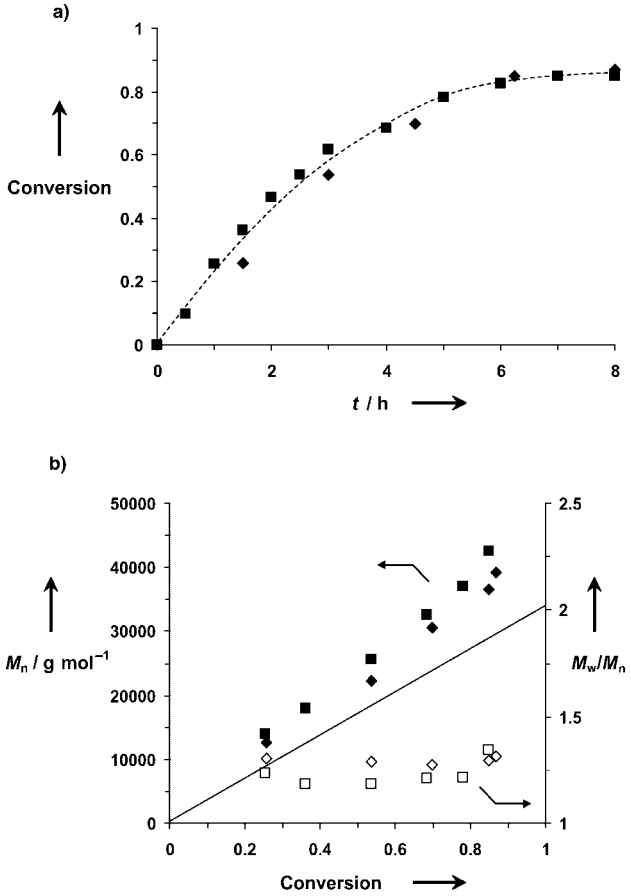

Figure 2. Seeded emulsion polymerizations of styrene (experiment **4**: ◆, ◇; experiment **6**: ■, □): a) monomer conversion versus time; b) number-average molar mass and polydispersity index versus conversion. Straight line: theoretical evolution of M_n versus conversion.

the Supporting Information for the comparison of experiments **3** and **3′**). Moreover, controlled molar masses and narrow molar-mass distributions were observed (Figure 1 and 2): the M_n values were close to the predicted ones, indicating a good reinitiation efficiency. For *n*-butyl acrylate polymerization, broadening of the molar-mass distribution was observed at the end of the reaction, possibly due to irreversible termination and/or to intermolecular chain transfer to the polymer, which are not unexpected at such large conversions.[18]

From the colloidal viewpoint, the important result is that the latexes are all stable for months. The final average diameters are given in Table 1. They are strongly dependent on the seed used (i.e. to the initial concentration of surfactant) and on the amount of polymer, but do not depend much on the type of monomer polymerized in the second step. DLS gave an average diameter of 660 nm for the poly(*n*-butyl acrylate) latex **3** and 530 nm for the polystyrene latex **4**, both extended from seed **1** (the calculated final diameter is 600 nm, on the basis of the DLS seed diameter and the amount of polymerized monomer). Moreover, the diameter increases with conversion in such a way that the total number of latex particles remains fairly constant throughout the polymerization. For latex **4**, transmission electron microscopy (TEM) was performed: $D_n = 450$ nm and $D_w = 830$ nm, indicating a broad particle-size distribution. For the latexes extended from seed **2**, DLS gave an average diameter of 270 nm for the poly(*n*-butyl acrylate) latex **5** and 260 nm for the polystyrene latex **6**, whereas the calculated diameter is 400 nm (TEM measurements on the latter gave $D_n = 90$ nm and $D_w = 350$ nm). The large discrepancy between DLS and TEM in those experiments comes from the existence of very small particles that are barely detectable by DLS. Although these results do not indicate a perfect control over the particle size and particle-size distribution, they are essentially the same as those currently obtained in analogous miniemulsion polymerizations.[1–4]

The process was also applied to the three-step synthesis of a block copolymer with a 1:1 molar composition. The first two steps were identical to those for the poly(*n*-butyl acrylate) latex **5**. Before the end of the second step (5.5 h, 55 % *n*-butyl acrylate conversion), the polymerization was stopped by cooling the reaction medium. The unreacted BA monomer was not removed, part of the styrene was added, and the mixture was stirred gently overnight at room temperature.

After addition of the remaining styrene, the temperature was raised again to 112 °C. All the features of a controlled polymerization were maintained, with the continuous increase of the average molar masses with monomer conversion, the low polydispersity indexes (Figure 3), and the shift of the size-exclusion chromatography (SEC) peaks toward larger molar masses (see Supporting Information). Again, a stable latex was recovered, with 26 % solids content.

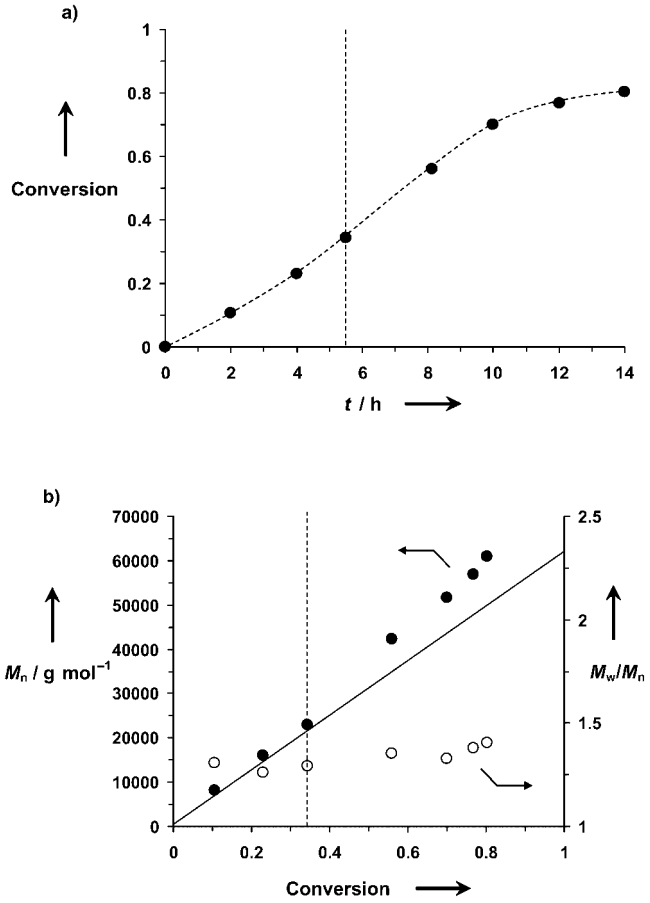

Figure 3. Synthesis of a poly(*n*-butyl acrylate)-*b*-poly(*n*-butyl acrylate-*co*-styrene) block copolymer in a three-step emulsion polymerization (experiment **7**): a) monomer conversion versus time; b) number-average molar mass and polydispersity index versus conversion. Vertical dotted line: time when styrene was added. Straight line: theoretical evolution of M_n versus conversion.

Nitroxide-mediated emulsion polymerization of *n*-butyl acrylate and styrene was successfully carried out in a multistep process in the presence of a novel water-soluble alkoxyamine initiator based on the nitroxide SG1. Fast reactions were observed, leading to polymers with controlled molar mass and narrow molar-mass distribution, which could be further extended by monomer addition. The process allowed us to form stable latexes with a solids content as high as 26 wt %. Such a true emulsion polymerization process in living conditions, which was previously a real challenge in the field of controlled free-radical polymerization, is of high academic and industrial relevance.

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[1] J. Qiu, B. Charleux, K. Matyjaszewski, *Prog. Polym. Sci.* **2001**, *26*, 2083 – 2134.
[2] M. F. Cunningham, *Prog. Polym. Sci.* **2002**, *27*, 1039 – 1067.
[3] B. Charleux, *ACS Symp. Ser.* **2003**, *854*, 438 – 451.
[4] M. F. Cunningham, *C. R. Chim.* **2003**, *6*, 1351 – 1374.
[5] R. G. Gilbert, *Emulsion Polymerization. A Mechanistic Approach*, Academic Press, London, **1995**.
[6] K. Landfester, *Macromol. Rapid Commun.* **2001**, *22*, 896 – 936.
[7] C. J. Hawker, A. W. Bosman, E. Harth, *Chem. Rev.* **2001**, *101*, 3661 – 3688.
[8] S. Grimaldi, J. P. Finet, F. Le Moigne, A. Zeghdaoui, P. Tordo, D. Benoit, M. Fontanille, Y. Gnanou, *Macromolecules* **2000**, *33*, 1141 – 1147.
[9] A. R. Szkurhan, M. K. Georges, *Macromolecules* **2004**, *37*, 4776 – 4782.
[10] C. Marestin, C. Noël, A. Guyot, J. Claverie, *Macromolecules* **1998**, *31*, 4041 – 4044.
[11] J. Cao, J. He, C. Li, Y. Yang, *Polym. J.* **2001**, *33*, 75 – 80.
[12] M. Lansalot, C. Farcet, B. Charleux, J. P. Vairon, R. Pirri, P. Tordo, *ACS Symp. Ser.* **2000**, *768*, 138 – 151.
[13] J. L. Couturier, O. Guerret, D. Bertin, D. Gigmes, S. Marque, P. Tordo, F. Chauvin, P. E. Dufils WO 2004/014926.
[14] J. Nicolas, B. Charleux, O. Guerret, S. Magnet, *Macromolecules* **2004**, *37*, 4453 – 4463.
[15] The pK_a of the acidic **A**-H alkoxyamine initiator was determined by titration in anhydrous ethanol against a 0.1M sodium hydroxide solution. The conversion between aqueous and alcoholic acidic scales was performed as described in the following reference: R. B. Bates, *Determination of pH, Theory and Practice*, Wiley, **1964**, Ch. 7.
[16] The saturated solution of *n*-butyl acrylate in water has concentration of 6.4×10^{-3} mol L^{-1} at 50 °C, according to ref. [5] and I. Capek, J. Barton, E. Orolinova, *Chem. Zvesti* **1984**, *38*, 803 – 822.
[17] Y. Luo, J. G. Tsavalas, F. J. Schork, *Macromolecules* **2001** *34*, 5501 – 5507.
[18] C. Farcet, J. Belleney, B. Charleux, R. Pirri, *Macromolecules* **2002**, *35*, 4912 – 4918.

