Nitroxide-Mediated Miniemulsion Polymerization of *n*-Butyl Acrylate: Synthesis of Controlled Homopolymers and Gradient Copolymers with Styrene

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Summary: Controlled free-radical homopolymerization of n-butyl acrylate and its copolymerization with styrene have been studied in aqueous miniemulsion, using an acyclic β-phosphonylated nitroxide as a mediator, the N-*tert*-butyl-N-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide, also called SG1. Polymerization kinetics have been studied and characterization of the (co)polymers has been performed, demonstrating the successful synthesis of well-defined poly(n-butyl acrylate) homopolymers and poly(n-butyl acrylate-*co*-styrene) gradient copolymers.

Introduction

"Living"/controlled radical polymerization (CRP),[1] allows to synthesize polymers with predictable molar mass, narrow molar mass distribution, controlled topologies and compositions using the very versatile and robust radical chemistry. Various CRP systems have been described such as nitroxide-mediated polymerization (NMP),[2] atom transfer radical polymerization (ATRP)[3] and reversible transfer (iodine exchange[4] and reversible addition-fragmentation transfer (RAFT)[5]). Among those techniques, NMP, which was initially restricted to the high temperature polymerization of styrene, has witnessed an important advance with the recent development of a new generation of bulky acyclic nitroxides bearing an hydrogen atom on the α-carbon. Those novel nitroxides are able to control the polymerization of styrene at lower temperatures than the traditional nitroxides and

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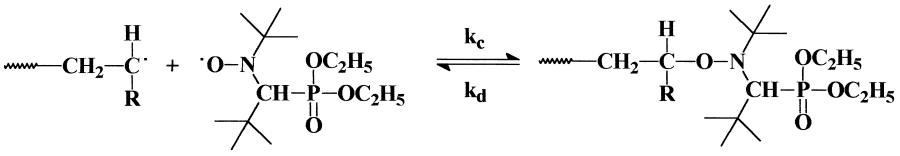
also to control the polymerization of other monomers such as alkyl acrylates, acrylamides, and dienes.[6,7] This feature has been successfully applied to the synthesis of well-defined copolymers of various structures in homogeneous systems such as bulk or solution.[7,8]



Scheme 1. Activation-deactivation equilibrium in SG1-mediated controlled free-radical polymerization (R = Ph, $COOC_4H_9$; $K = k_d/k_c$).

A substantial progress in controlled free-radical polymerization will now be achieved if this technique can be applied to aqueous dispersed systems. Indeed these processes are particularly used for industrial production, because of their numerous advantages such as the absence of organic solvent, the low viscosity even at high solids content, the fast kinetics... The final water suspension of stable polymer particles (also called latex) can be used directly for coating applications or as a dried polymer after removal of water. The early published results on nitroxide-mediated polymerization in aqueous dispersed systems concerned the use of TEMPO (2,2,6,6-tetramethyl piperidinyl-1-oxy) as a mediator in suspension,[9] dispersion,[10] seeded emulsion,[11] batch emulsion[12] and miniemulsion[13] polymerizations of styrene at temperatures above 120 °C. More recently, our group reported the use of an acyclic β-phosphonylated nitroxide of the new generation (the N-*tert*-butyl-N-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide, SG1) in the miniemulsion polymerization of styrene at 90 °C.[14] Using the same nitroxide, the miniemulsion process was also applied for the first time to the preparation of well-defined poly(n-butyl acrylate) homopolymers and poly(n-butyl acrylate-*b*-styrene) block copolymers at 115 °C.[15] The work presented here shows now the extension of the system to the synthesis of poly(n-butyl acrylate) and polystyrene based copolymers with a gradient composition. In this work, miniemulsion technique has been selected for various reasons. In miniemulsion polymerization,[16,17,18] the initial monomer in water emulsion is strongly sheared in order to divide the organic phase into very small droplets that are directly nucleated. In addition to classical surfactants, the use of ultra hydrophobes (such as hexadecane and/or polymer) was shown to enhance droplet stability via inhibition of Oswald ripening. This process leads to the same type of final latex as a

conventional emulsion polymerization, with the same properties but offers additional advantages. First, better latex stability was previously observed for nitroxide-mediated CRP.[14] Second, the complex nucleation step that exists in emulsion polymerization is avoided and, for this reason, the process allows the use of organic-soluble initiators, such as monomer- or polymer-based preformed alkoxyamines. This would not be possible in emulsion because undesirable polymerization would take place in the large non-stabilized monomer droplets.

Experimental part

Materials. Styrene (S) and n-butyl acrylate (BA) were distilled under reduced pressure before use. The surfactants, sodium dodecyl sulfate (SDS, 98 % Acros), Forafac ($C_8F_{17}CH_2CH_2COO^-K^+$, supplied by Atofina) and Dowfax 8390 (a mixture of mono- and di-hexadecyl disulfonated diphenyloxide disodium salt, supplied by Dow Chemical Company), the buffer, sodium hydrogen carbonate ($NaHCO_3$, Prolabo) were used as received. The alkoxyamine initiator (SG1-based alkoxyamine derived from methyl acrylate, CH_3-O(CO)-$CH(CH_3)$-SG1, MONAMS, 96 % purity) was supplied by Atofina and prepared using atom transfer radical addition from methyl-2-bromopropionate). The N-tert-butyl-N-(1-diethyl phosphono-2,2-dimethylpropyl) nitroxide (SG1, 86.5 % purity) was also supplied by Atofina.

Batch homopolymerization of n-butyl acrylate and copolymerization of n-butyl acrylate and styrene. A stable aqueous emulsion of the monomer(s) was prepared by mixing the organic phase (monomer(s), alkoxyamine, high molar mass polystyrene (M_w = 330000 $g.mol^{-1}$), hexadecane and, for some experiments, a small fraction of free SG1 with respect to the alkoxyamine) with the water phase containing the surfactant(s) and the buffer. This unstable emulsion was subjected to ultrasonication (Branson 450 Sonifier ; power 7 ; 10 min) in order to disperse the organic phase into submicron droplets and to improve their stability. The obtained stable emulsion was then poured into a 1 L stainless steel thermostated reactor. Deoxygenation was performed by three vacuum/nitrogen filling cycles. Afterward a 3 bar pressure of nitrogen was applied and the reactor was heated to 120 °C, which gave a temperature of 112 °C in the reaction medium for the n-butyl acrylate homopolymerizations ; for the copolymerizations, the reactor was heated to 125 °C to have 120 °C in the reaction

medium. The time when the temperature reached 90 °C corresponded to time zero of the reaction. Samples were periodically withdrawn to monitor the monomer conversion by gravimetry and the particle size by dynamic light scattering. After drying, the polymer from each sample was analyzed by the various techniques described below.

Table 1. Experimental conditions for the homopolymerization of n-butyl acrylate (T = 112 °C) and its random copolymerization with styrene (T = 120 °C) in miniemulsion.

Expt.	H_2O (g)	Surfactant (g)		BA (g)	S (g)	Molar fraction of S	wt% of monomer in water	$[MONAMS]_0$ (g ; $mol.L^{-1}_{org.}$)[a]	$[SG1]_0$ (g ; $mol.L^{-1}_{org.}$)[a]	r[b]
1	298	SDS : Forafac :	2.45 1.50	74.0	0	0	20.0	0.978 ; 0.032	0.021 ; $7.05\ 10^{-4}$	0.022
2	397	SDS : Forafac :	3.28 3.74	99.2	0	0	20.0	1.283 ; 0.027	0.028 ; $6.82\ 10^{-4}$	0.025
3	401	Dowfax8390 :	6.40	99.5	0	0	19.9	1.321 ; 0.028	0.029 ; $7.12\ 10^{-4}$	0.025
4	401	Dowfax8390 :	6.50	99.5	0	0	19.6	1.322 ; 0.028	0	0
5	398	SDS : Forafac :	3.28 3.87	120	65	0.40	31.7	1.293 ; 0.015	0.028 ; $4.08\ 10^{-4}$	0.027
6	400	Dowfax8390 :	6.50	140	49	0.30	32.0	1.319 ; 0.015	0.029 ; $3.82\ 10^{-4}$	0.026

Hexadecane : 0.8 wt% with respect to monomers ; High molar mass polystyrene (M_w = 330 000 $g.mol^{-1}$) : 0.1 wt% with respect to monomers ; $[NaHCO_3]$ = 12 mM_{aq}
a) with respect to the overall organic phase ; b) $[SG1]_0/[MONAMS]_0$

Analytical techniques. Dynamic light scattering measurements (DLS) of the latexes were performed using a Zetasizer4 from Malvern at an angle of 90° and a temperature of 24 °C. Size exclusion chromatography (SEC) was performed using a Waters apparatus equipped with three columns thermostated at 30 °C (Shodex KF 802.5, KF 804L, KF 805L). The eluent was tetrahydrofuran (THF) at a flow rate of 1 $mL.min^{-1}$. A differential refractive index detector and a UV detector operating at 254 nm were used and molar masses were derived from a calibration curve based on polystyrene standards. Proton NMR analyses of the polymers were carried out in $CDCl_3$ solution at room temperature using a Bruker AC200 apparatus, operating at a frequency of 200 MHz. The chemical shift scale was calibrated on the basis of the solvent peak (7.24 ppm) and composition was calculated by integrating the aromatic protons of the

styrene units (6.3–7.3 ppm, 5 H) and the CH_2 ester protons of the n-butyl acrylate units (3.4–4.2 ppm, 2 H). The liquid adsorption chromatography (LAC)[19] analyses were performed in the Groupement de Recherches de Lacq (Atofina). Separation was carried out on a grafted silica column with a gradient hexane/THF as eluent. The detection was performed using a UV detector (Waters 481) and an evaporative light scattering detector (DEDL 21, Eurosep). Details on the experimental conditions can be found in Ref. 19b. Glass transition temperature (T_g) was measured by differential scanning calorimetry (DSC7 from Perkin-Elmer) in a temperature range from –100 °C to +150 °C, at a scanning rate of 20 °C.min^{-1}.

Results and discussion

Kinetics of n-butyl acrylate homopolymerization and copolymerization with styrene.

Stable latexes with 20 wt% solids content for the poly(BA) homopolymers and 32 wt% for the poly(BA-*co*-S) copolymers were obtained with neither coagulation during synthesis nor destabilization over time. The particle average diameter was in the range 300 – 400 nm, with broad particle size distribution as commonly observed in controlled radical polymerizations performed in emulsion and miniemulsion.[12,13,14] In all experiments, the polymerization was fast (Figure 1) ; for instance conversion reached 92 % within 6 h in experiment **4**. As demonstrated for the BA homopolymerizations, the rate was governed by the initial concentration of added free nitroxide. Indeed, polymerization of BA in experiment **4** carried out without added SG1 was significantly faster than similar polymerizations (experiment **1, 2** and **3**) carried out in the presence of added free SG1. In contrast to what is usually observed in classical radical polymerization, rates of homopolymerization of n-butyl acrylate carried out in miniemulsion were not larger than those previously observed in bulk, with the same initiator.[20] Indeed, the compartmentalization effect that enhances the rate in classical emulsion and miniemulsion systems with respect to bulk or solution polymerizations, does not operate in nitroxide-mediated polymerization when particle diameter is sufficiently large, as it is the case here.[21] The rate of propagation should be the same for both processes, and for the homopolymerization of a given monomer M, it can be expressed as :

$$\frac{-d[M]}{dt} = k_p.[P^\bullet].[M] = k_p.K.([P\text{-}SG1]_0/[SG1]).[M] \qquad (1)$$

with k_p, K, $[P\text{-}SG1]_0$ and $[P^\bullet]$ the rate constant of propagation, the activation-deactivation equilibrium constant (Scheme 1), the alkoxyamine initial concentration and the concentration of propagating macroradicals in the organic phase, respectively. The variation of propagation rate with conversion depends not only on the initial nitroxide/alkoxyamine molar ratio but also on the build up of nitroxide concentration owing to the persistent radical effect.[22] An analytical expression of the evolution of nitroxide concentration with conversion was proposed in miniemulsion :[21]

$$[SG1] = -A + \sqrt{(A+[SG1]_0)^2 - B \cdot \ln(1-x)} \qquad (2)$$

with $[SG1]_0$, the initial concentration of free nitroxide in the system, x, the monomer conversion, and :

$$A = \frac{k_t}{N_A \cdot v_p \cdot k_c} \; ; \; B = \frac{4 \cdot K \cdot [P\text{-}SG1]_0 \cdot k_t}{k_p}$$

k_c being the rate constant of recombination between a propagating macroradical and a nitroxide molecule, k_t, the rate constant of irreversible termination between propagating radicals, N_A the Avogadro number, and v_p, the average particle volume. When v_p is very large, A is very small and becomes negligible. In this case, the expression giving [SG1] versus conversion is $[SG1] = \sqrt{[SG1]_0^2 - B \cdot \ln(1-x)}$, the same as in bulk. For the n-butyl acrylate/SG1 system, the equilibrium constant K is rather small (K_{BA} = 1.0 10^{-10} mol.L^{-1} at 112 °C)[20] and in contrast, k_p is very large ($k_{pBA} \approx$ 80000 L.mol^{-1}.s^{-1})[23]. Thus, the build up of free nitroxide with conversion should remain small with respect to the initial concentration. This can be calculated for experiment **3** for instance : A = 3.3 10^{-7} mol.L^{-1} using k_t = 2 10^8 L.mol^{-1}.s^{-1}, k_c = 3 10^7 L.mol^{-1}.s^{-1}[20] and a diameter of 400 nm ; after 6 hours, conversion x = 73 % and –B.ln(1–x) = 3.7 10^{-8} mol^2.L^{-2}. Then [SG1] = 7.38 10^{-4} mol.L^{-1} at this conversion while $[SG1]_0$ was 7.12 10^{-4} mol.L^{-1}. This confirms that kinetics of the experiments presented here is mainly governed by the initial concentration of free nitroxide, and more specifically by the initial nitroxide/alkoxyamine molar ratio.

The rates of both copolymerizations **5** and **6** were the same, irrespective of the composition of the mixture of monomers. In addition, they were similar to those of BA homopolymerizations, carried out with the same $[SG1]_0/[MONAMS]_0$ ratio, although the

temperature was different (120 instead of 112 °C) and the initiator concentration (0.015 instead of 0.028–0.032 mol.L^{-1}) was also different. In the case of copolymerization, analytical expression of the propagation rate becomes more complicated than for homopolymerization and depends on the respective rate constants of homo- and cross-propagation, on the various rate constants of termination, on both equilibrium constants, ...etc. Most of these constants are not known at 120 °C. However, as shown in equation (1), the $k_p.K$ product for both styrene and n-butyl acrylate can give rough indication on the kinetic behavior of these monomers. For styrene, k_{pS} = 2000 L.mol^{-1}.s^{-1}[24] at 120 °C, K_S = 6.0 10^{-9} mol.L^{-1} at 120 °C[20] and hence, $k_{pS}.K_S$ = 1.2 10^{-5} s^{-1}. For n-butyl acrylate, $k_{pBA} \approx$ 80000 L.mol^{-1}.s^{-1}[23] and K_{BA} = 2.0 10^{-10} mol.L^{-1} at 120 °C[20], which gives $k_{pBA}.K_{BA}$ = 1.6 10^{-5} s^{-1}, only slightly larger than the value found for styrene. The high rate constant of propagation of BA is compensated for by a low activation-deactivation equilibrium constant in SG1-mediated polymerization. Hence, the copolymerization with styrene should not strongly affect the rate.

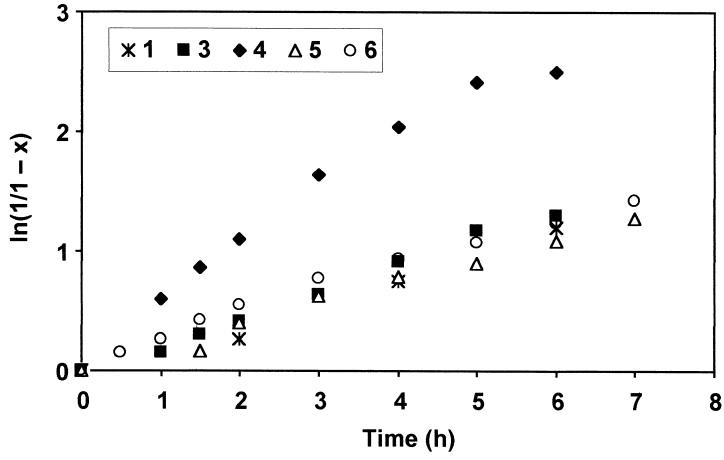


Figure 1. Semilogarithmic plot of monomer conversion versus time for the homopolymerization of n-butyl acrylate at 112 °C and its random copolymerization with styrene at 120 °C in miniemulsion.

In all the miniemulsion polymerizations carried out with added free nitroxide, the formed polymers were well controlled as molar masses linearly increased with monomer conversion and followed the predicted values (Figure 2, Table 2). Moreover, the polydispersity index was relatively low, typically in the range 1.1-1.4 particularly for the poly(BA) homopolymers.

When no free SG1 was initially added (experiment **4**), M_n followed the same trend, but because of faster polymerization, the polydispersity indexes were larger. For instance, the polymer recovered at 90 % conversion had M_n = 36400 g.mol^{-1} and M_w/M_n = 1.42.

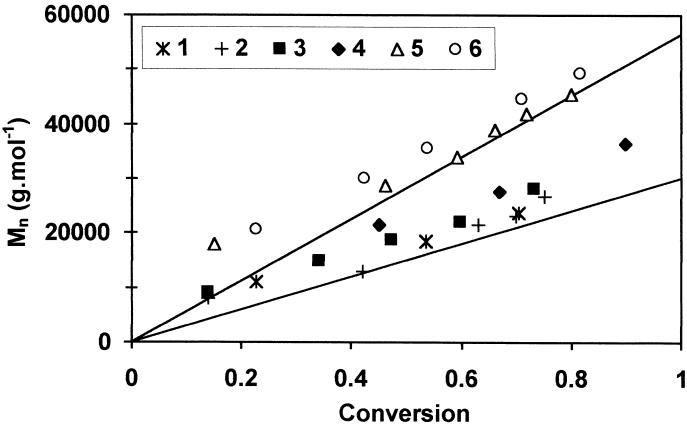


Figure 2. M_n as a function of monomer conversion for the homopolymerization of n-butyl acrylate (**1** to **4**) at 112 °C and its random copolymerization with styrene (**5** and **6**) at 120 °C in miniemulsion. The polydispersity indices, M_w/M_n, are given in Table 2 for experiments **5** and **6**. In the case of experiment **3** for instance, M_w/M_n decreased from 1.40 at 14 % conversion (M_n = 9030 g.mol^{-1}) down to 1.19 at 73 % conversion (M_n = 28100 g.mol^{-1}). (straight lines : theoretical values).

Characterization of the poly(n-butyl acrylate-co-styrene) gradient copolymers.

In addition to the good control over molar mass and molar mass distribution, the controlled radical copolymerization offers advantages concerning the structure of the random copolymers. Indeed, since the chain concentration remains constant throughout the reaction (as evidenced by the proportionality between M_n and conversion ; Figure 2), the composition drift due to difference in reactivity of the comonomers affects the distribution of the monomer units in each chain but not the composition distribution in the system, in contrast to conventional radical polymerization. As a consequence, a narrow composition distribution is expected and chains should exhibit a gradient composition. All the performed characterizations were undertaken to demonstrate those assumptions.

Table 2. Overall conversion (weight fraction) and molar masses versus time for the controlled radical copolymerizations of n-butyl acrylate (BA) and styrene (S) in miniemulsion at 120 °C (Experiments **5** and **6**).

Expt.	Time (h)	Conv.	Expt. M_n [a] ($g.mol^{-1}$)	M_w/M_n [a]	Molar fraction of S [b]	Theoretical M_n ($g.mol^{-1}$)	T_g (°C)
5	0	0	-	-	-	0	-
	1	0.15	17 900	1.89	-	8 340	-
	1.5	0.33	-		-	18 300	-
	2.5	0.46	28 600	1.36	0.53	25 600	+ 14.2
	3.5	0.55	-	-	-	30 600	-
	4.5	0.59	33 800	1.43	0.51	32 800	+ 11.7
	5.5	0.66	38 800	1.39	-	36 700	-
	6.5	0.72	41 800	1.40	0.50	40 000	+ 8.9
	8	0.80	45 400	1.38	0.48	44 500	+ 9.6
6	0	0	-	-	-	0	-
	0.5	0.14	-	-	-	7 970	-
	1	0.23	20600	1.33	0.45	13 100	+ 4.7
	1.5	0.34	-	-	-	19 400	-
	2	0.42	29900	1.23	-	23 900	-
	3	0.54	35600	1.23	0.43	30 800	– 1.5
	4	0.61	-	-	-	34 700	-
	5	0.66	-	-	-	37 600	-
	6	0.71	44700	1.25	0.38	40 400	– 6.8
	7	0.76	-	-	-	43 300	-
	8	0.78	-	-	-	44 400	-
	8.5	0.82	49400	1.34	0.36	46 700	– 11.3

a) from SEC ; b) in the copolymer, from ^1H NMR

Liquid adsorption chromatography displayed in Figure 3, is an analytical technique that gives information on the copolymer composition distribution ; conditions to get separation according to the composition independently of the molar mass were established.[19b] The composition distribution of the final copolymer of experiment **5** was much narrower than exhibited by an analogous non-controlled copolymer[25] (Figure 3A). Moreover, in the samples taken at intermediate conversions, the composition drift was evidenced, with a decrease in the proportion of styrene with monomer conversion (Figure 3B). The peaks remained narrow indicating a real change in the chain internal composition and not the superimposition of new chains with different composition. The composition drift could be

anticipated from the reactivity ratios reported by Chambard et al. (r_S = 0.81 and r_{BA} = 0.23 at 120 °C in bulk).[26] Furthermore, the experimental average compositions versus conversion, determined by proton NMR spectroscopy, also confirmed this trend and were in good agreement with the theoretical values calculated from those reactivity ratios (Figure 4). Finally, the DSC measurements showed a single T_g, which decreased with the progress of monomer conversion, indicating an augmentation of the proportion of n-butyl acrylate in the chains.

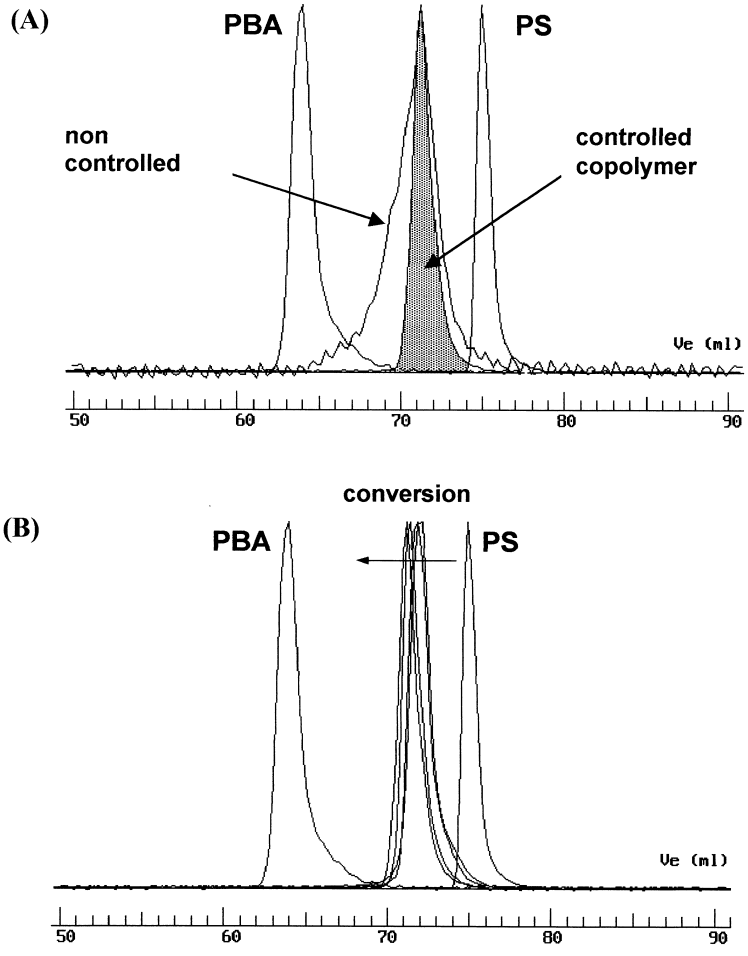


Figure 3. Liquid adsorption chromatograms ; (A) Final copolymer of experiment **5** and of a similar non controlled experiment ; (B) Copolymers of experiment **5** at various conversions.

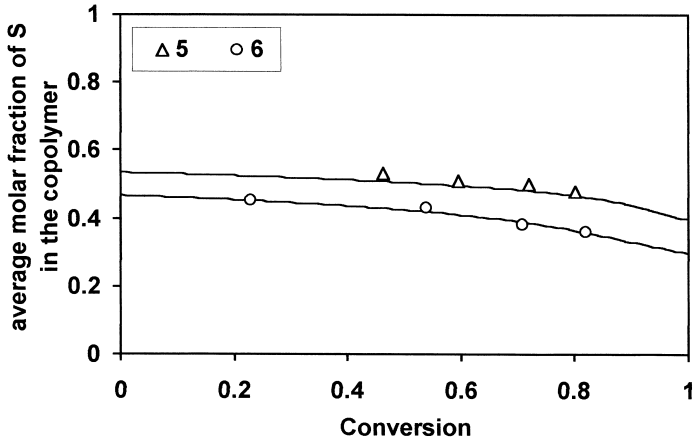


Figure 4. Comparison of the experimental and theoretical compositions versus conversion for the copolymers from experiments **5** and **6** (the theoretical curves were calculated using the reactivity ratios : $r_S = 0.81$ and $r_{BA} = 0.23$ determined in bulk at 120 °C).[26]

Conclusion

SG1-mediated CRP of n-butyl acrylate was performed in miniemulsion, leading to well-defined homopolymers, exhibiting the expected molar mass with a narrow molar mass distribution. Rate of polymerization and molar mass distribution can be fine tuned by the addition of free nitroxide at the beginning of the polymerization. Similar results were obtained when n-butyl acrylate was copolymerized with styrene, forming well-defined gradient copolymers with both a narrow molar mass distribution and a narrow composition distribution.

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