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Mechanistic Aspects of Nitroxide-Mediated Controlled Radical Polymerization of Styrene in Miniemulsion, Using a Water-Soluble Radical Initiator

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ABSTRACT: Nitroxide-mediated controlled free-radical polymerization of styrene was studied in a miniemulsion system. The use of an acyclic β-phosphonylated nitroxide enabled polymerization to be performed at a temperature below 100 °C, typically 90 °C. A bicomponent initiating system was chosen, i.e., a radical initiator in conjunction with added free nitroxide. This work focused on the mechanistic understanding of the polymerization. The parameters that affect both the kinetics of polymerization and the control of the molar mass and molar mass distribution have been examined and discussed, such as the nature and concentration of the pH buffer, the initiator concentration, the monomer/water ratio, and the process for chain extension.

Introduction

During the past 7 years, many academic and industrial laboratories have shown a tremendous activity in controlled free-radical polymerization (CRP). This is due to the possibility of applying versatile free-radical (co)-polymerization to the synthesis of (co)polymers with controlled molar mass, narrow molar mass distribution, and well-defined architecture.[1] Three different ways to achieve good control over the polymer characteristics are employed: the use of nitroxides,[2] atom transfer reaction catalyzed by a transition metal complex (ATRP),[3] and reversible chain transfer reaction (via either a direct exchange[4] or an addition−fragmentation step (RAFT)[5,6]). Until now, CRP has been predominantly studied in homogeneous systems, i.e., bulk or solution polymerizations. However, in industry, radical polymerization is widely performed in aqueous dispersed media and particularly as emulsion polymerization.[7,8] This technique has many advantages over homogeneous polymerizations such as the absence of organic volatile compounds (except the monomers) and the possibility of reaching high molecular weight polymers with high conversion and with higher rates of polymerization than in bulk or solution. This last point is the consequence of the compartmentalization of the propagating radicals, which reduces the rate of termination. Thus, it seems obvious that substantial progress in CRP will occur if this technique can be applied to aqueous dispersed systems. The first and main goal is to control the characteristics of the polymer in terms of molecular weight and architecture. It is likely that new types of latexes with new properties might arise, particularly for water-borne films. Until now, nitroxide-mediated CRP has been the most widely applied technique to control the polymerization of styrene under heterogeneous conditions such as suspension,[9] dispersion,[10] seeded emulsion,[11] batch emulsion,[12] and miniemulsion[13−15] polymerizations. In all cases, TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy) or a derivative was used as a mediator, and polymerization was performed at a temperature above 120 °C, which required high pressure. Furthermore, at such high temperatures, stabilization of the latexes was a challenge, and thermal self-initiation of styrene could not be avoided. ATRP and reverse ATRP were also successfully applied to emulsion and miniemulsion polymerizations, providing that the initiator and the surfactant were properly selected to avoid side reactions with the catalytic system.[16−21] Using the degenerative iodine transfer, studies on CRP of styrene in miniemulsion were recently published[22,23] and were followed by the synthesis of poly(styrene-*b*-*n*-butyl acrylate) block copolymers under the same experimental conditions.[24] Some examples of CRP using the RAFT process in emulsion with dithioester[5b,25] and with dithiocarbonate[6] chain transfer agents have also been reported. Although many attempts have been performed, CRP in a dispersed system is far from being fully understood. First of all, the nature of the control agent (nitroxide, transition metal complex, chain transfer agent, etc.) plays a key role in the process, and it should be carefully selected. In particular, the compatibility with water and with the other reagents, the water solubility and the partition coefficients between the various phases are all important factors. Moreover, the kinetics of polymerization cannot be directly compared with that in a homogeneous medium. When a reversible chain transfer technique is used, a conventional radical initiator is needed; the polymerization kinetics follows a stationary state[26] and thus should not differ from that of a classical radical polymerization. With a reversible termination technique (such as nitroxide-mediated CRP or ATRP), the kinetics is regulated by the persistent radical effect (PRE)[27] and is also affected by the heterogeneous nature of the system.[28]

In contrast to the other published works in the domain, we have carried out nitroxide-mediated CRP of styrene in aqueous dispersed systems at a temperature below 100 °C.[29,30] For this purpose, a stable acyclic phosphonylated nitroxide radical, the *N*-*tert*-butyl-*N*-

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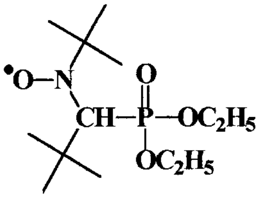
Scheme 1. Structure of SG1



(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (DEPN, also called SG1, Scheme 1), was used. It was reported to give excellent results in the controlled radical polymerization of styrene and acrylic esters in homogeneous systems.[31-36] Owing to a significantly higher equilibrium constant of activation−deactivation ($K = 1.9 \times 10^{-8}$ mol dm^{-3} at 125 °C)[35,36] than that of TEMPO for styrene polymerization ($K = 2 \times 10^{-11}$ mol dm^{-3} at 125 °C),[37] this stable radical can be used as a mediator at a lower temperature, i.e., from 90 to 130 °C.

Both batch miniemulsion and emulsion polymerization processes were applied for the SG1-mediated CRP of styrene in aqueous dispersed system at 90 °C.[29,30] We have shown that stable latexes with particles diameter in the range 100−300 nm could be obtained with the classical sodium dodecyl sulfate anionic surfactant. To keep the experimental conditions close to the usual ones, a bicomponent initiating system was chosen, i.e., a conventional radical initiator together with added free nitroxide. The miniemulsion system was initially selected in order to avoid the very complex nucleation step of classical emulsion polymerization. Moreover, the miniemulsion process is a good model for a polymerization in an aqueous dispersed medium because only two phases are present, i.e., water and small monomer droplets in which polymerization takes place. In contrast, in emulsion polymerization, propagation does not take place in the monomer droplets but in the particles which are created in the early stage of the polymerization from oligoradicals generated in the water phase. The monomer droplets act as monomer reservoirs and constitute a third phase in the system in which the nitroxide can preferentially dissolve initially and become inefficient for the deactivation. In the present work we have focused on the mechanistic understanding of the miniemulsion polymerization, under experimental conditions identical to previously.[29,30] The parameters that affect both the kinetics of polymerization and the control of the molar mass and molar mass distribution have been examined and discussed, such as the nature and concentration of the pH buffer, the initiator concentration, the monomer/water ratio, and the process for chain extension.

Experimental Part

Materials. Styrene (St) was distilled under vacuum before use. The initiating system potassium persulfate ($K_2S_2O_8$, 99% purity from Aldrich) and sodium metabisulfite ($Na_2S_2O_5$, 97% purity from Aldrich), the buffers sodium hydrogen carbonate ($NaHCO_3$, 99.5% purity from Prolabo) and potassium carbonate (K_2CO_3, 99% purity from Aldrich), the surfactant sodium dodecyl sulfate (SDS, 98% purity from Aldrich, cmc = 7.6×10^{-3} mol dm^{-3} at 20 °C), and the hydrophobe hexadecane (99% purity from Acros) were used without further purification. The *N-tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (SG1, 91% purity) was kindly supplied by ATOFINA.

Batch Miniemulsion Polymerizations. This polymerization technique leads to the same type of final latex as an emulsion polymerization but differs from the latter in the initial stage.[8,38,39] The initial monomer in water emulsion is strongly sheared in order to divide the organic phase into very small droplets (diameter < 1 μm). In addition to the classical surfactant, the use of a cosurfactant (e.g., hexadecanol) or of a hydrophobe (e.g., hexadecane) is required to stabilize the droplets from coalescence and from Ostwald ripening. Owing to their large surface area, the droplets can be directly nucleated and become polymer particles, providing that no micelles are present. Batch miniemulsion polymerizations were performed at 90 °C in a conventional 0.25 dm^3 thermostated glass reactor, under nitrogen atmosphere. Hexadecane was used as a hydrophobe (5 wt % with respect to styrene) and dissolved in the monomer together with a high molar mass polystyrene (M_w = 330 000 g mol^{-1}, 1 wt % with respect to styrene). Both additives were shown to improve monomer droplets stability.[38,39] The polystyrene is also supposed to have the additional role of nucleation enhancer.[38] The monomer with SG1, hexadecane, and polystyrene dissolved was then added to a water solution containing the buffer and the surfactant. This unstable initial emulsion was strongly sheared by ultrasonification (Branson 450 Sonifier; power 7) for 5 min in order to get a stable emulsion with submicronic monomer droplets (D = 150−180 nm). This emulsion was then poured into the preheated reactor and deoxygenated by nitrogen bubbling. After temperature stabilization, the initiators dissolved in deoxygenated water were added, $Na_2S_2O_5$ first, immediately followed by $K_2S_2O_8$. The redox couple was used because with potassium persulfate alone poor control of the polymerization was previously observed.[40] Such a result however is not clearly understood. This step corresponded to time zero of the polymerization reaction. Samples were withdrawn at various times in order to follow the evolution of monomer conversion, the latex pH (pH-meter from Tacussel), and the polymer molar mass and molar mass distribution. Monomer conversion was determined by gravimetry, after drying the samples overnight in an oven at 80 °C. Experimental conditions are summarized in Table 1.

Chain Extension Polymerizations. A first experiment was performed (expt 15) using the final latex 8 as a seed (see Table 1). A 60 g sample of this latex (solids content = 12.2 wt %, i.e., 7.3 g of polystyrene) was swollen overnight at room temperature with 3.0 g of styrene, under gentle stirring. Then, the suspension was deoxygenated with a flow of nitrogen and simultaneously heated to 90 °C. After temperature stabilization, 5.5 g of styrene was slowly added during 100 min. The polymerization was then continued for a further 3 h. For the other experiment (expt 16), a first step was performed using the experimental conditions of expt 5. After 4 h reaction time, corresponding to 50% conversion, a second charge of styrene was added continuously for 1 h. The polymerization was then stopped after 22 h. For both experiments, the latex and the polymer were characterized as usual (see Table 2).

Latex Characterization. The average particle diameter (D) was measured by dynamic light scattering (DLS) using a Zetasizer4 from Malvern. In some cases, transmission electron microscopy (TEM, JEOL, 100 Cx II, top entry) was used to observe the particles directly.

Polymer Characterization. Molar mass and molar mass distribution of the dried samples (washed with water to eliminate the water-soluble impurities) were measured by size exclusion chromatography (SEC) using a Waters apparatus equipped with three columns (Shodex KF 802.5, KF 804L, KF 805L) thermostated at 30 °C. The eluent was tetrahydrofuran (THF) at a flow rate of 1 mL min^{-1}. A differential refractive index detector was used, and molar masses were derived from a calibration curve based on polystyrene standards. Results are shown in Tables 3 and 4. In all the experiments the initial ratio $r = [SG1]_0/[K_2S_2O_8]_0$ was 1.2. This was previously shown to be the best compromise between a fast polymerization and a good control over the molar masses.[29,30] This means that the initial concentration of nitroxide is insufficient to deactivate all the radicals potentially produced by the initiating system. This fact together with the complex mechanism of radical formation makes the estimation of the theoretical molar mass quite difficult. In all cases it was calculated as following, taking

Table 1. Batch Miniemulsion Polymerizations of Styrene Using $K_2S_2O_8/Na_2S_2O_5$ as a Radical Initiating System at 90 °C and SG1 as a Mediator[a]

		$[K_2S_2O_8]_0$		buffer			
expt	St/water[b] (wt/wt)	(mol/dm^3_{water})	(mol/$dm^3_{styrene}$)	nature	(mol/dm^3_{water})	final pH	final *D* (nm)
1	1/9	0.0045	0.037	none		2.1	105
2	1/9	0.0045	0.037	NaCl	0.009	2.1	120
3	1/9	0.0011	0.009	$NaHCO_3$	0.009	8.4	157
4	1/9	0.0023	0.018	$NaHCO_3$	0.009	7.7	147
5	1/9	0.0045	0.037	$NaHCO_3$	0.009	6.6	180
6	1/9	0.0090	0.073	$NaHCO_3$	0.009	2.2	164
7	2/9	0.0023	0.009	$NaHCO_3$	0.009	7.8	207
8	2/9	0.0045	0.018	$NaHCO_3$	0.009	6.2	199
9	2/9	0.0090	0.037	$NaHCO_3$	0.009	1.6	180
10	1/9	0.0045	0.037	K_2CO_3	0.009	7.6	160
11	1/9	0.0045	0.037	K_2CO_3	0.0044	4.8	185
12	1/9	0.0045	0.037	K_2CO_3	0.003	2.9	198
13	2/9	0.0045	0.018	K_2CO_3	0.0044	5.9	205
14	3/9	0.0045	0.009	K_2CO_3	0.0046	6.5	259

[a] All experiments were carried out with 207 g of water; $r = [SG1]_0/[K_2S_2O_8]_0 = 1.2$; $[Na_2S_2O_5]_0 = [K_2S_2O_8]_0$; $[SDS]_0 = 0.015$ mol/dm^3_{water} (twice the critical micelle concentration at 20 °C). [b] The amount of water was kept constant (207 g), and only the amount of styrene was changed.

Table 2. Chain Extension Experiments with a Second Load of Styrene

	first step						second step						
expt	expt	conv in the first step (overall value)[a]	expt M_n (g/mol)	M_w/M_n	expt *D* (nm)	pH	overall conv	theor M_n (g/mol)	expt M_n (g/mol)	M_w/M_n	calcd D^b (nm)	expt *D* (nm)	pH
15	8	0.61 (0.36)	16900	1.53	199	6.2	0.57	26 200	24 800	1.41	232	225	6.8
16	5	0.50 (0.31)	8750	1.31	162	6.3	0.51	13 800	15 000	1.22			
							0.73	19 700	24 300	1.13	215	206	6.5

[a] Conversion in the first step: calculated according to the amount of styrene used in the first step. Overall conversion: calculated with respect to the total amount of styrene added in both the first and second steps. [b] The diameter in the second step was calculated according to the increase in overall conversion, assuming a constant number of particles: $D_2 = D_1(\text{conv}_2/\text{conv}_1)^{1/3}$ (where 1 refers to the first step and 2 to the second step).

into account both the "living" chains (with SG1-based alkoxyamine end group) and the dead chains coming from the possible terminations due to the excess of radical initiator (considering 100% of termination by coupling).

$$\text{theoretical concentration of chains} = [SG1]_0 + \frac{2[K_2S_2O_8]_0 - [SG1]_0}{2}$$

with the concentrations expressed as moles per unit volume of the monomer phase.

The fraction of dead chains represents theoretically 25 mol % of the total. However, it can be much less if irreversible terminations occur in the aqueous phase, because the formed species cannot be considered as polymer chains and are not taken into account in the SEC. Nevertheless, to use the same definition, the theoretical molar masses will always be calculated according to the following formula:

$$\text{theoretical } M_n = x d_{St}/(\text{theoretical concentration of chains})$$

where x is the styrene conversion and d_{St} the styrene density expressed in g dm^{-3} ($d_{St} = 906$ g dm^{-3} at 20 °C).

Results and Discussion

Stable latexes were always obtained without coagulum formation in all the experiments presented here. Mean diameters were generally between 150 and 250 nm, and the particle size distribution was relatively broad as evidenced by TEM. As the purpose of the present work was to gain a better understanding of the kinetics and of the control over the polymer characteristics, the parameters that would affect the particle size were not intentionally modified, and further colloidal characterization of the latexes was not performed.

1. Typical Behavior. a. Kinetics of Polymerization. Figure 1a–d shows the kinetics of a batch miniemulsion polymerization of styrene (expt 5) performed at 90 °C with a styrene/water ratio of 1/9 wt/wt and using a bicomponent initiating system as described in the Experimental Part and in Table 1.

From a kinetic viewpoint, this experiment provides a good example to describe the general behavior of this type of polymerization. The styrene conversion (x) and $\ln(1/1 - x)$ are plotted versus time in Figure 1a,b. It is worthwhile to mention here that the internal order with respect to monomer, which is zero in a conventional emulsion polymerization[7,8] owing to the presence of droplets acting as monomer reservoirs, should be one in a miniemulsion polymerization. This validates the use of a plot of $\ln(1/1 - x)$ as a function of polymerization time, and the slope at a given time then gives $k_p[P^\bullet]$ (with $[P^\bullet]$ the instantaneous concentration of propagating radicals expressed per volume unit of the whole organic phase). An induction period lasting about 45 min can be observed. At this stage, owing to the large concentration of free SG1, propagation is inhibited, and the dominating reaction is the trapping of the propagating radicals by the nitroxide. Actually, a first initiation step is required in order to turn the oxygen- or sulfur-centered radicals of the initiator into a styryl carbon-centered radical able to properly react with the nitroxide and to give an alkoxyamine C–O bond (Scheme 2). The duration of the induction period is a function of the initiator and nitroxide concentrations and of the rate of radicals formation.

For a styryl radical $X{-}St^\bullet$ produced in the water phase, the rate of monomer addition (R_p) can be compared with the rate of coupling with SG1 (R_c): $R_p =$

Table 3. Conversion and Molar Mass as a Function of Polymerization Time for the Batch Miniemulsion Polymerizations Described in Table 1, Using $NaHCO_3$ as a Buffer

expt	time (min)	conv	calcd M_n (g mol^{-1})	exptl M_n (g mol^{-1})	M_w/M_n
3	60	0.248	15 300	46 800	1.66
	120	0.554	34 200	49 300	1.94
	240	0.782	48 300	55 800	1.88
	480	0.936	57 800	63 000	1.79
4	90	0.177	5 460	9 670	2.03
	180	0.386	11 900	13 400	1.81
	300	0.490	15 100	14 200	1.75
	480	0.585	18 000	16 800	1.61
5	45	0.107	1 650	3 280	2.47
	75	0.284	4 390	6 220	2.06
	120	0.482	7 450	8 160	2.00
	240	0.735	11 400	11 300	1.82
	480	0.906	14 000	13 600	1.69
6	120	0.272	2 100	28 000	1.48
	180	0.590	4 600	30 200	1.62
	240	0.877	6 800	37 200	1.95
	480	1.00	7 700	40 400	2.36
7	90	0.149	9 200	12 200	2.06
	180	0.292	18 000	15 600	1.87
	240	0.355	21 900	18 700	1.82
	360	0.456	28 100	21 900	1.57
	480	0.531	32 700	23 600	1.54
8	90	0.163	5 000	7 220	2.09
	150	0.335	10 300	10 800	1.83
	180	0.405	12 400	11 300	1.85
	300	0.523	16 100	14 000	1.68
	480	0.612	18 800	16 900	1.53
9	90	0.111	1 710	18 700	1.52
	150	0.228	3 510	23 900	1.47
	250	0.361	5 560	29 400	1.49
	360	0.499	7 680	37 300	1.51
	480	0.700	10 800	47 700	1.61

Table 4. Conversion and Molar Mass as a Function of Polymerization Time for the Batch Miniemulsion Polymerizations Described in Table 1, Using K_2CO_3 as a Buffer

expt	time (min)	conv	calcd M_n (g mol^{-1})	exptl M_n (g mol^{-1})	M_w/M_n
10		[a]			
11	90	0.159	2 500	4 200	2.67
	120	0.289	4 500	7 100	1.90
	180	0.522	8 100	10 600	1.80
	240	0.704	11 000	13 800	1.71
	480	0.942	14 600	18 000	1.66
12	90	0.210	3 200	15 300	1.59
	120	0.433	6 700	22 100	1.56
	180	0.671	10 400	28 000	1.54
	240	0.818	12 600	31 900	1.64
	480	1.00	15 500	32 800	2.64
13	120	0.096	3 000	4 220	2.26
	180	0.175	5 400	6 540	1.94
	300	0.275	8 500	9 040	1.70
	420	0.369	11 400	10 000	1.76
	480	0.425	13 200	12 200	1.60
14	120	0.086	5 300	5 310	1.74
	240	0.190	11 700	8 740	1.52
	300	0.249	15 300	10 500	1.48
	360	0.309	19 000	13 600	1.29
	480	0.397	24 400	17 500	1.22

[a] No polymerization.

$k_p[X{-}St^\bullet]_{aq}[St]_{aq}$ and $R_c = k_c[X{-}St^\bullet]_{aq}[SG1]_{aq}$. The concentration of styrene in water can be roughly estimated at 0.01 mol dm^{-3} at 90 °C (it is 0.0043 mol dm^{-3} at 50 °C),[41] and the k_p value is 895 dm^3 mol^{-1} s^{-1} at this temperature[42] (the effect of solvent is neglected). The concentration of SG1 in water can be estimated according to preliminary ESR experiments:[43] $[SG1]_{aq} = 10^{-4}$–2.5×10^{-4} mol dm^{-3}. The rate constant k_c for the coupling of a styryl radical with SG1 equals 5.3×10^6 dm^3 mol^{-1} s^{-1} at 90 °C (see Table 5). The calculated ratio $R_p/R_c = k_p[St]_{aq}/k_c[SG1]_{aq} = 0.007$–$0.017$ is very small, which means that the propagation in water is strongly disfavored with respect to the coupling reaction. It can thus be concluded that the alkoxyamines that are formed during the initial stage of the polymerization have only one styrene unit (Scheme 3), and according to their structure, they are most probably water-soluble.

This situation lasts as long as $[SG1]_{aq}$ is larger than 1.7×10^{-6} mol dm$^{-3}{}_{aq}$ in the aqueous phase. Thus, at the end of the induction period, most of the radical initiator has been turned into the X−St−SG1 alkoxyamine, and the system behaves in a similar way as if the same preformed water-soluble alkoxyamine was introduced initially. Only when SG1 concentration gets smaller than 1.7×10^{-6} mol dm$^{-3}{}_{aq}$ does the propagation become favorable. This is the reason why, to avoid an excess of nitroxide, an initial $[SG1]_0/[\text{initiator}]_0$ ratio below 2 was used. Propagation leads to a reduction in the water solubility of the growing oligoradicals. Then, they can escape from the water phase and enter the monomer droplets to further propagate. If a deactivation occurs before the chain is totally water-insoluble, the formed alkoxyamine is partitioned between the aqueous and the monomer phases. As long as the alkoxyamines are not irreversibly located in the organic phase, their propagation remains slow, owing to the very low concentration of styrene in water. The situation is quite different in reverse ATRP when a very hydrophobic ligand is used. Actually, the Cu(II)/ligand deactivator is not water-soluble, and the deactivation step takes place in the organic phase only.[19,20] At the end of the induction period, the fast onset of the polymerization indicates that propagation has been transferred into the organic phase. After complete consumption of the radical initiator, the activation−deactivation process depicted in Scheme 4 governs the kinetics.

The concentration of propagating radicals in the monomer phase was calculated as a function of the polymerization time (Figure 1c) from the $\ln(1/1 - x)$ versus time slope (Figure 1b). From the activation−deactivation equilibrium relationship, the concentration of SG1 ($[SG1]_{org.}$) present in the organic phase and thus able to control the polymerization can be deduced.

$$[SG1]_{org} = \frac{K[P{-}SG1]_{org}}{[P^\bullet]_{org}} \tag{1a}$$

or

$$\frac{[SG1]_{org}}{[P{-}SG1]_{org}} = \frac{K}{[P^\bullet]_{org}} \tag{1b}$$

The activation−deactivation equilibrium constant K is approximately 7×10^{-10} mol dm^{-3} at 90 °C (Table 5); $[P{-}SG1]_{org}$ represents the concentration of “living” chains in the particles, which theoretically equals the initial concentration of SG1 with respect to the organic phase ($[P{-}SG1]_{org}$ is assumed to remain constant throughout the polymerization). As can be seen in Figure 1c, immediately after the induction period a maximum concentration of propagating radicals is observed, which is correlated with a small concentration of free SG1 in the particles (Figure 1d). Then $[P^\bullet]_{org}$

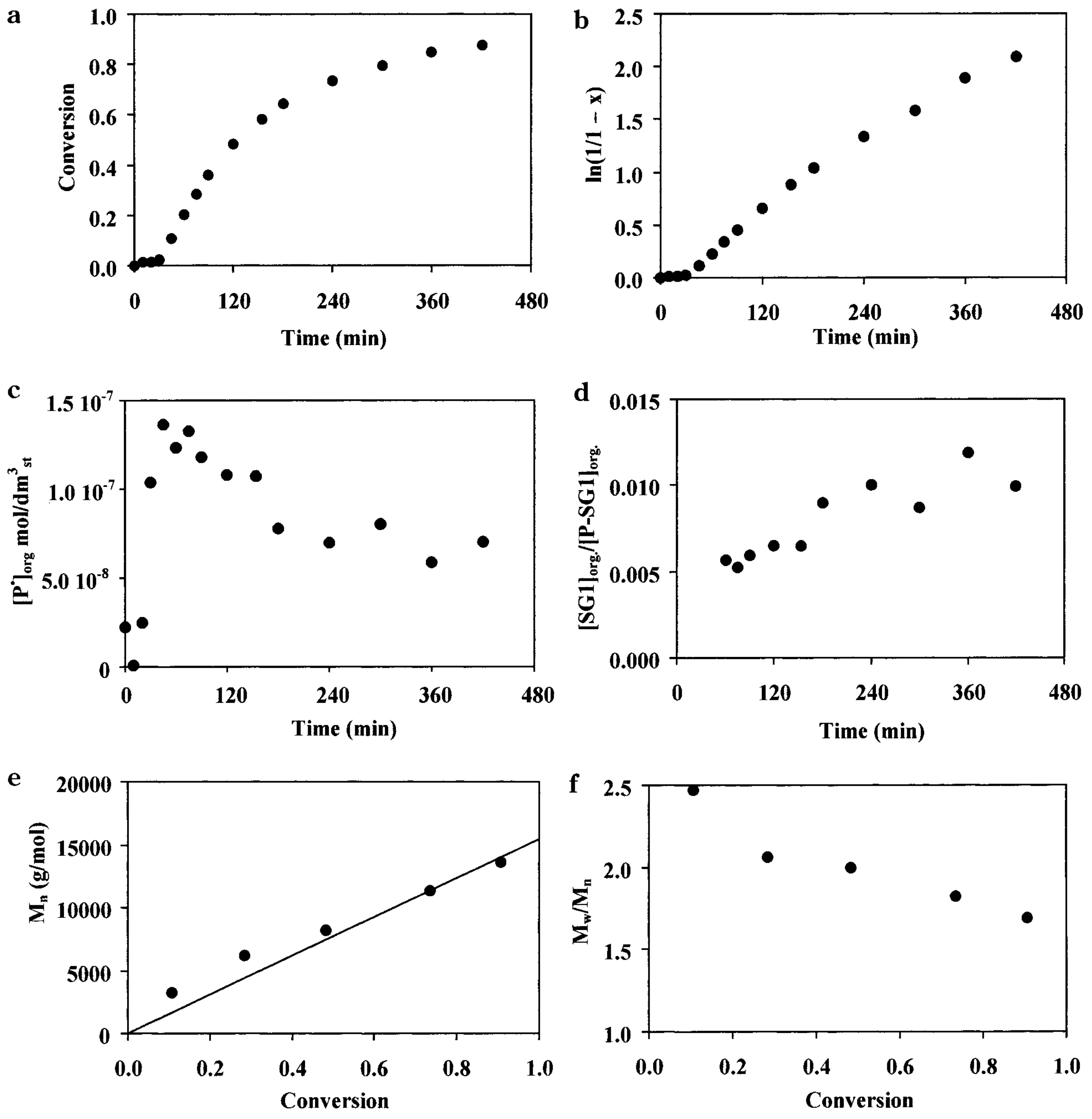


Figure 1. Results for expt 5 (see the experimental conditions in Table 1): (a) conversion; (b) ln(1/1 − *x*); (c) instantaneous concentration of propagating radicals in the organic phase, $[\mathrm{P}^\bullet]_{\mathrm{org.}}$, calculated from the slope of ln(1/1 − *x*) versus time given in (c); (d) ratio of the concentration of free nitroxide to the total concentration of "living" chains, calculated from eq 1b; (e) number-average molar mass (straight line = theoretical M_n); (f) polydispersity index.

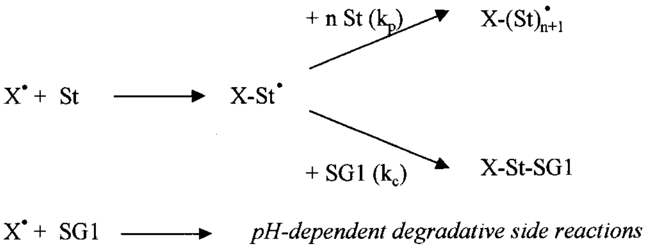
slowly decreases and $[\mathrm{SG1}]_{\mathrm{org}}$ continuously increases, which is typical of the persistent radical effect.[26-28] Knowing the particle size (D = 180 nm) and therefore the number of particles per volume unit, it is also possible to calculate the average number of propagating radicals per particle, $\tilde{n}$, the average number of SG1 molecules per particle, and the average number of macromolecular chains per particle. In the last period when the kinetics is governed by the activation–deactivation equilibrium, $\tilde{n}$ varies from 0.23 to 0.13 when $[\mathrm{P}^\bullet]_{\mathrm{org}}$ decreases from 1.2×10^{-7} to 7×10^{-8} mol dm^{-3}. During that same period, the average number of SG1 molecules per particle increases from approximately 500 to 900 ($[\mathrm{SG1}]_{\mathrm{org}}$ increases from 2.6×10^{-4} to 4.5×10^{-4} mol dm^{-3}). The average number of chains per particle is approximately 10^5. The value of $\tilde{n}$ below 1 indicates that the particles contain either one or zero radical. It means that the formation of a second radical by activation of an alkoxyamine in a particle which already contains one propagating radical is immediately followed by a termination reaction, which can be either irreversible (radical–radical coupling) or reversible (deactivation by SG1).[28]

The most interesting characteristic of the system is the fast polymerization: for expt 5, conversion reached 90% within 8 h. This is the consequence of a low concentration of SG1 in the polymerization locus. Indeed, the rate of propagation is

$$R_{\mathrm{p}} = k_{\mathrm{p}}[\mathrm{M}][\mathrm{P}^\bullet] = k_{\mathrm{p}}[\mathrm{M}]\frac{K[\mathrm{P{-}SG1}]_{\mathrm{org}}}{[\mathrm{SG1}]_{\mathrm{org}}} \qquad (2)$$

with k_{p} and [M] the rate constant of propagation and

Scheme 2



with $X^• = SO_4^{-•}, HSO_3^•, (HO^•)$

St = styrene in aqueous solution

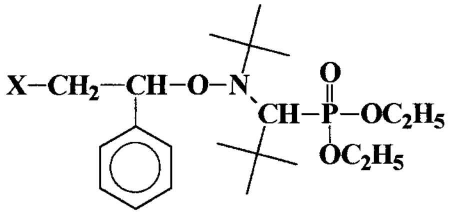
k_p = *rate constant of propagation in water*

k_c = *rate constant of coupling with the nitroxide*

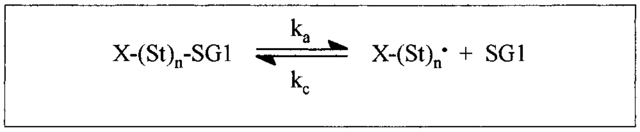
Table 5. Rate Constants of Activation and Deactivation and Equilibrium Constants for the Styryl- and Polystyryl SG1-Based Alkoxyamines at 90 °C

alkoxyamine	k_a (s^{-1})	k_c (dm^3 mol^{-1} s^{-1})	K (mol dm^{-3})	ref
St-SG1	2.3×10^{-4}	5.3×10^6	4.3×10^{-11}	34
PS-SG1	4×10^{-4}	6×10^5	7×10^{-10}	35 36

Scheme 3. Alkoxyamine X−St−SG1



Scheme 4



k_a *: rate constant of reversible decomposition (activation)*

k_c *: rate constant of deactivation (coupling with SG1)*

$K = k_a/k_c$ *: activation/deactivation equilibrium constant*

the concentration of monomer in the particles, respectively. R_p is thus inversely proportional to $[SG1]_{org}$. In Figure 1d, the ratio $[SG1]_{org}/[P-SG1]_{org}$ is plotted. It shows that the proportion of free nitroxide inside the particles does not exceed 2% of the "living" chains. This proportion is significantly lower than the 10% observed in bulk.[36] It can be explained by the partition of the nitroxide between the organic and the aqueous phases. Thus, this suggests that actually more than 2% of the chains are dead and have released their SG1 capping agent upon irreversible termination. The exact proportion of dead chains is not known, however, but might be deduced from an accurate measurement of the overall concentration of free nitroxide. Work is currently in progress to monitor by ESR the concentration of SG1 in each phase during the course of a miniemulsion polymerization. Interestingly, preliminary experiments with a more hydrophobic nitroxide, namely SG1 with two butyl instead of the two ethyl groups, exhibited a slower propagation than with SG1 under the same experimental conditions. Such result corroborates the effect of partition of the nitroxide on the polymerization kinetics.

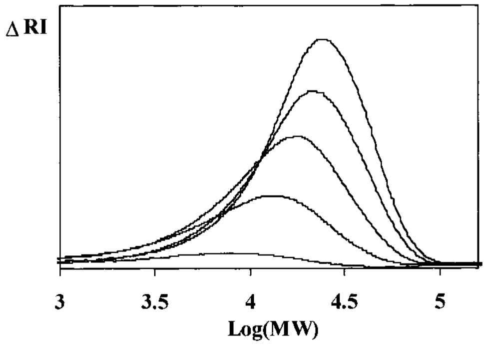


Figure 2. SEC chromatograms of expt 5. Conversions, M_n, and M_w/M_n values are given in Table 3.

b. Molar Mass and Molar Mass Distribution. The M_n versus conversion plot is represented in Figure 1e. As expected for a controlled polymerization, M_n increases linearly with monomer conversion and matches the theoretical value. However, at the beginning the values are slightly larger than the theoretical ones and display a broad distribution. This feature, which is typical of a slow initiation, can be related to the water-soluble character of the initially formed alkoxyamines and to their slow entry into the organic phase. This was already mentioned in the case of CRP in miniemulsion using AIBN as a radical initiator.[29,30] It is also visible on the size exclusion chromatograms (Figure 2) with the tailing on the low molar mass side. The molar mass distribution is not as narrow as it is usually in bulk.[31−36] The value of M_w/M_n starts above 2 at low conversion because of the very low concentration of free nitroxide deactivator but continuously decreases as conversion progresses to reach a value close to 1.5 (Figure 1f). The relatively high values of M_w/M_n can be related to the fast polymerization and to the low nitroxide concentration in the particles, which is a consequence of the partition of the nitroxide between the two phases.

2. Effect of the pH. When dissolved in water, $Na_2S_2O_5$ hydrolyzes into an acidic species, namely $NaHSO_3$. The pK_a of the HSO_3^-/SO_3^{2-} couple is 6.91 at 18 °C.[44] With the initial concentration $[NaHSO_3] = 0.0090$ mol dm$^{-3}{}_{aq}$, the calculated pH is 4.5, which value was experimentally observed when no buffer was used (expts 1 and 2; Figure 3b). In addition, reaction of the two partners of the initiating system leads to a simultaneous decrease in pH as observed during the induction period for the nonbuffered experiments 1 and 2 (Figure 3b). One of the possible processes that produces acidic species is the reaction of the sulfate radical with H_2O leading to the formation of HSO_4^- and $HO^•$.[45] Other side reactions might also exist owing to the use of a redox initiator, for which the reactions involved in the production of radicals are not completely identified.[46]

We have previously reported that the pH of the water phase was affecting the polymerization rate and the control over the molar masses.[30] It was also evidenced that the pH had a significant effect on the nitroxide stability in water in the presence of the initiating system.[30] Indeed, in the absence of styrene, the SG1 nitroxide was unstable at 90 °C in water solutions containing either the two partners of the initiating system or each of them individually. The SG1 stability was however improved when using a pH buffer, particularly K_2CO_3 rather than $NaHCO_3$ (Table 6).

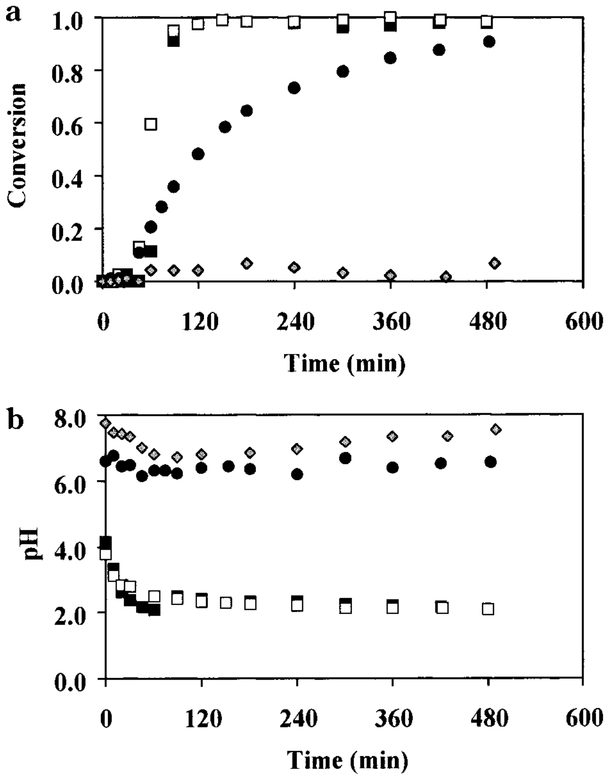


Figure 3. Effect of the added electrolyte on polymerization kinetics and on control of the pH when the initiator concentration is $[K_2S_2O_8] = [Na_2S_2O_5] = 0.0045$ mol $dm^{-3}{}_{aq}$ (see the experimental conditions in Table 1): (a) conversion; (b) pH Experiments: 1, ■ (no electrolyte); 2, □ (NaCl); 5, ● ($NaHCO_3$); 10, ◆ (K_2CO_3).

Table 6. Half-Lifetime of SG1 in Water Solution under Various Experimental Conditions As Measured by ESR[43,a]

reagent	buffer	pH	$t_{1/2}$ (min)
$Na_2S_2O_5$	no	<4	5[b]
	$NaHCO_3$	6	153
	K_2CO_3	8	stable
$K_2S_2O_8$	no	<4	1[b]
	$NaHCO_3$	6	6
	K_2CO_3	8	15
$Na_2S_2O_5/K_2S_2O_8$	no	<4	too fast
	$NaHCO_3$	6	1.7
	K_2CO_3	8	2.5

[a] $T = 90$ °C; [buffer] $= 9 \times 10^{-3}$ mol dm^{-3}; $[Na_2S_2O_5] = [K_2S_2O_8] = 4.5 \times 10^{-3}$ mol dm^{-3}; $[SG1] = 5 \times 10^{-3}$ mol dm^{-3}. [b] $[SG1] = 10^{-4}$ mol dm^{-3}.

Redox reactions (with pH-dependent rate and/or nature) between SG1, on one hand, and the O-centered or S-centered primary radicals or the strong reductors $Na_2S_2O_5$ or $NaHSO_3$, on the other, leading to a degradation of both the nitroxide and the initiating system were suspected to occur. In the water phase of a miniemulsion polymerization medium, those side reactions compete with the regular reactions of initiation and trapping of the styryl radicals by SG1 (Scheme 2). At neutral pH, however, these degradative side reactions are expected to remain negligible compared with the formation of alkoxyamines that are able to properly initiate the polymerization. As a first study, effect of the nature of the added electrolyte was investigated. A series of experiments were performed with a styrene/water ratio of 1/9 wt/wt. The initiator concentration was $[K_2S_2O_8] = [Na_2S_2O_5] = 0.0045$ mol $dm^{-3}{}_{aq}$ and the $[SG1]_0/[K_2S_2O_8]_0$ initial ratio was 1.2 in all cases. The added electrolyte was NaCl (expt 2), $NaHCO_3$ (expt 5), or K_2CO_3 (expt 10), all of them at a concentration of 0.009 mol $dm^{-3}{}_{aq}$. In a blank experiment (expt 1) no electrolyte was used. The results of monomer conversion and variation of pH with time can be viewed in Figure 3a,b, which illustrates the strong effect of the added electrolyte on the polymerization kinetics. When either no salt or the inert NaCl was added, the polymerization was extremely fast, and the pH simultaneously decreased from about 4 to 2 during the induction period. The polymerization was obviously not controlled. The molar masses were much larger than expected (above 50 000 g mol^{-1}); they did not vary with conversion and displayed a broad distribution (M_w/M_n increased from 2 to 3 with conversion). The fast polymerization after the induction period indicates the absence of free nitroxide in the polymerization locus. The added SG1 acted as a radical inhibitor only. After its complete consumption (most probably by the above-mentioned side reactions), polymerization could start owing to the presence of a slight excess of initiating radicals. In contrast, when $NaHCO_3$ was used, the pH value was stable at around 6.5, and the kinetics followed the typical trend as described previously. When the K_2CO_3 buffer was added instead, the pH remained above 7, but no polymerization occurred. This result is slightly different from that presented in our previous article.[30] In the presence of K_2CO_3 the polymerization started but was much slower than with $NaHCO_3$. The comparison is actually difficult to make because purity of the nitroxide used at that time was lower and the impurities were acidic (such as *m*-chlorobenzoic acid; SG1 was prepared according to a different procedure[47]). In the present work, an excess of free nitroxide is the best explanation to account for the absence of polymerization. Indeed, in the presence of K_2CO_3, the nitroxide remains quite stable, and thus, the concentration at the end of the induction period is larger than with $NaHCO_3$. It has been shown in the first paragraph that the concentration of SG1 should be lower than 1.7×10^{-6} mol $dm^{-3}{}_{aq}$ in water in order to favor the propagation. If $[SG1]_{aq}$ remains always larger, propagation is then very slow and becomes slower and slower owing to the establishment of the PRE upon irreversible radical−radical terminations in the aqueous phase. Thus, to promote the transfer of the alkoxyamines from the water phase to the monomer droplets, a very low concentration of free nitroxide in water is required at the end of the induction period.

A second study was undertaken with various concentrations of K_2CO_3. Like previously, the initiator concentration was $[K_2S_2O_8] = [Na_2S_2O_5] = 0.0045$ mol $dm^{-3}{}_{aq}$, and the $[SG1]_0/[K_2S_2O_8]_0$ initial ratio was 1.2. The initial concentration of K_2CO_3 was decreased from 0.009 mol $dm^{-3}{}_{aq}$ (expt 10) to 0.0044 mol $dm^{-3}{}_{aq}$ (expt 11), 0.003 mol $dm^{-3}{}_{aq}$ (expt 12), and finally to 0 (expt 1). Results are shown in Figure 4a−c. With $[K_2CO_3]_0 = 0.009$ mol $dm^{-3}{}_{aq}$, polymerization did not start. When $[K_2CO_3]_0$ was changed to 0.0044 mol $dm^{-3}{}_{aq}$, the polymerization started and followed a kinetics very close to that observed for the expt 5 performed with $NaHCO_3$ ($[NaHCO_3] = 0.009$ mol $dm^{-3}{}_{aq}$). The only difference is that the pH did not remain stable but decreased from 7 to 4.8 during the induction period. The molar masses were slightly above the theoretical values, increased with monomer conversion, and exhibited a relatively narrow distribution with M_w/M_n decreasing with conversion (Table 4). When the concentration of K_2CO_3 was

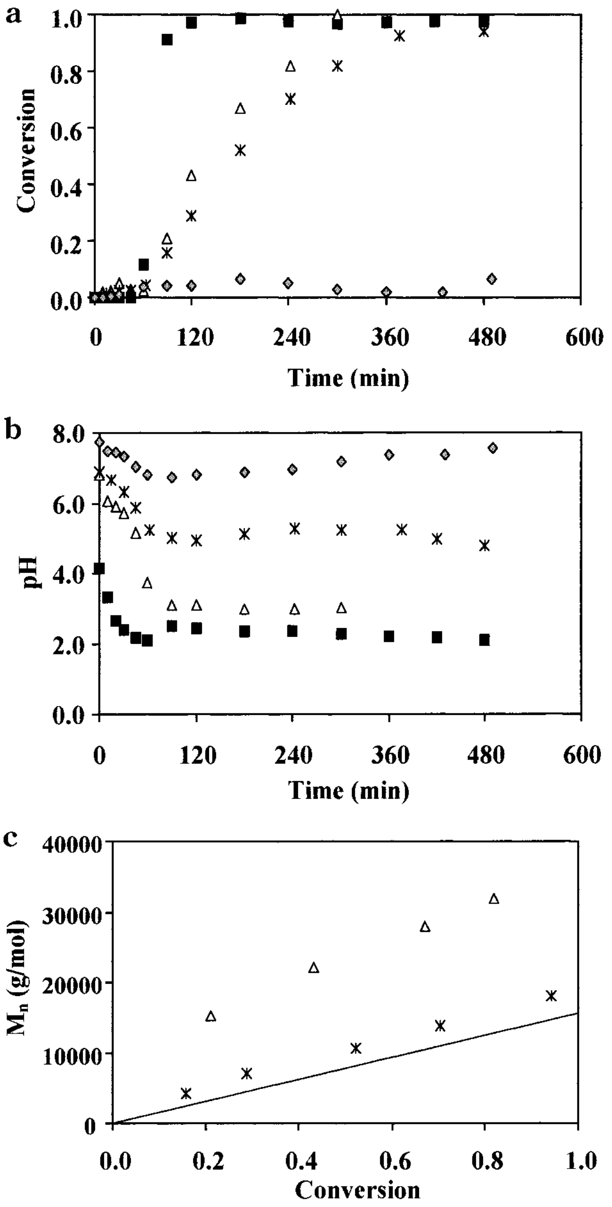


Figure 4. Effect of the initial concentration of K_2CO_3 on polymerization kinetics and on control of the pH when the initiator concentration is $[K_2S_2O_8] = [Na_2S_2O_5] = 0.0045$ mol $dm^{-3}{}_{aq}$ (see the experimental conditions in Table 1): (a) conversion; (b) pH; (c) number-average molar mass (straight line = theoretical M_n). Experiments: 1, ■ (0 mol $dm^{-3}{}_{aq}$); 12, △ (0.003 mol $dm^{-3}{}_{aq}$); 11, * (0.0044 mol $dm^{-3}{}_{aq}$); 10, ◆ (0.009 mol $dm^{-3}{}_{aq}$).

reduced again to 0.003 mol $dm^{-3}{}_{aq}$, the polymerization was slightly faster, but the molar masses were far above theoretical. The polydispersity index remained low ($1.5 < M_w/M_n < 1.6$) except at final conversion. The low initiator efficiency (molar masses higher than expected) together with a low SG1 concentration (fast polymerization) can be directly related to the decrease in pH to a value of 3 during the induction period. This result indicates that the concentration of initially formed X–St–SG1 alkoxyamines was below the theoretical value. It corroborates the existence of competitive side reactions between the initiator and the nitroxide under acidic conditions. It can be seen in Tables 1, 3, and 4 and in figures that the effect of pH corresponds to a general trend: the more acidic the pH at the end of the induction period, the larger the molar masses with respect to the theoretical values and the faster the polymerization.

3. Effect of the Initiator Concentration. In a controlled polymerization, the molar mass at a given conversion can be predicted by the simple knowledge of the monomer and the initiator initial concentrations. When a monocomponent initiating system is chosen (i.e., preformed alkoxyamine in nitroxide-mediated CRP), the calculation is straightforward, and the predicted molar mass is usually observed (in a given range of concentration). This is not so simple with a bicomponent initiating system. Although it is very convenient from a practical viewpoint, the use of a conventional radical initiator in conjunction with free nitroxide leads to a more complicated situation when prediction of the molar mass is desired. Indeed, the initiator efficiency is not always 1 and strongly depends on the initial concentration. Moreover, as seen above, the pH of the water phase, which affects the formation of alkoxyamines, can strongly affect the concentration of "living" chains together with the concentration of free nitroxide. There are also additional complications when working in a biphasic system with decomposition of the initiator and initiation in the water phase while propagation takes place in the organic phase.

In two different series, the initiator concentration was varied, and the effect was studied. In all cases, the initial molar ratio of SG1 to persulfate was kept equal to 1.2. In Table 1, the initiator concentrations are given in the water phase and are also calculated with respect to the organic phase. The series are displayed in Figure 5a–c (expts 3–6; styrene/water = 1/9 wt/wt) and in Figure 6a–c (expts 7–9; styrene/water = 2/9 wt/wt).

The effect of initiator concentration on the polymerization kinetics is not clear although it is expected that an increase of the initiator concentration would lead to an increased polymerization rate as it was previously observed in bulk.[35,36] According to eq 2, the rate of propagation (R_p) is proportional to the concentration of chains $[P{-}SG1]_{org}$ and inversely proportional to $[SG1]_{org}$. $[P{-}SG1]_{org}$ depends directly on the initiator concentration while $[SG1]_{org}$ is a complex function of monomer conversion, of the activation–deactivation equilibrium constant, of the rate constant of irreversible termination (owing to PRE[26–28]) of $[P{-}SG1]_{org}$ and of the partition coefficient. The additional effect of pH on the concentration of formed alkoxyamines and thus on $[P{-}SG1]_{org}$ and on R_p complicates the situation. This is why the system is much more complex than in bulk and also more complex than in the ideal case considered previously for theoretical description.[28] This explains that no general trend could be noted concerning the correlation of the rate of polymerization with the initiator concentration. A more systematic trend could be observed for the evolution of pH with time (Figures 5b and 6b) and for the evolution of molar masses with conversion (Figures 5c and 6c). Indeed, the variation of pH during the induction period could be directly related to the initiator concentration. For given experimental conditions with constant concentration of buffer, when the initiator concentration was increased, the pH significantly decreased. As a consequence, for the largest initiator concentration ($[K_2S_2O_8] = [Na_2S_2O_5] = 0.0090$ mol $dm^{-3}{}_{aq}$ in the aqueous phase; expts 6 and 9) the molar masses, although increasing with monomer conversion, were much larger than the predicted values. However, even though the true concentration of "living" chains

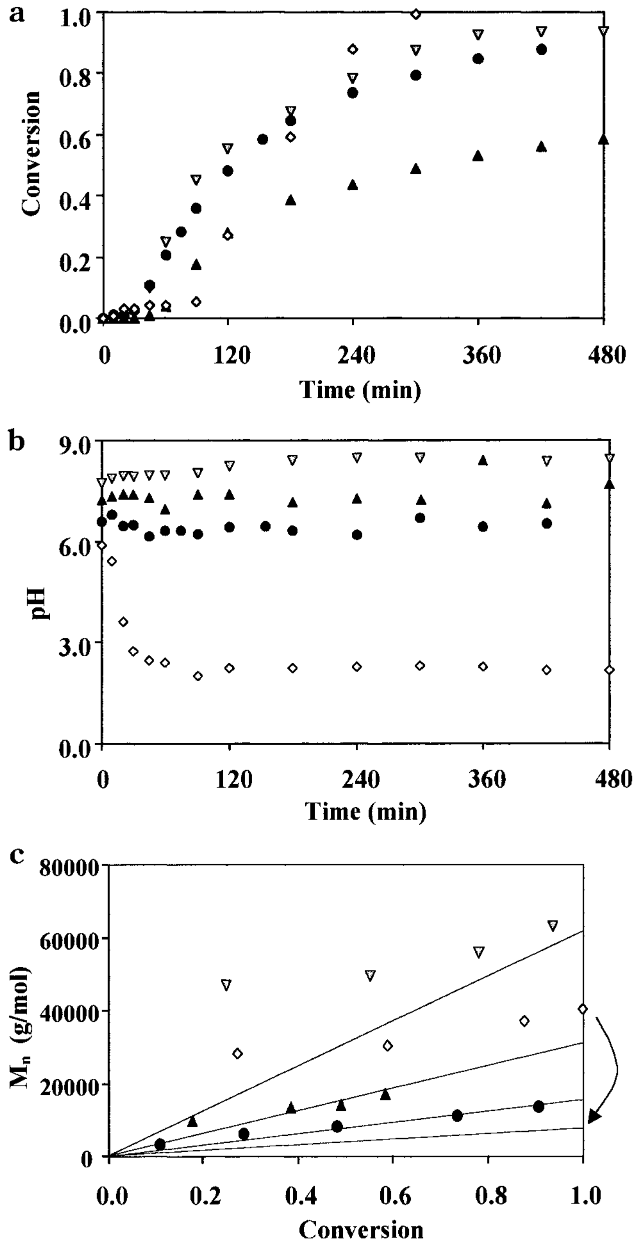


Figure 5. Effect of the initiator concentration for miniemulsion polymerizations with a St/water ratio of 1/9 wt/wt and with $NaHCO_3$ buffer (0.009 mol $dm^{-3}{}_{aq}$): (a) conversion; (b) pH; (c) number-average molar mass (straight lines = theoretical M_n). Experiments: 3, ▽ (0.0011 mol $dm^{-3}{}_{aq}$); 4, ▲ (0.0023 mol $dm^{-3}{}_{aq}$); 5, ● (0.0045 mol $dm^{-3}{}_{aq}$); 6, ◇ (0.0090 mol $dm^{-3}{}_{aq}$).

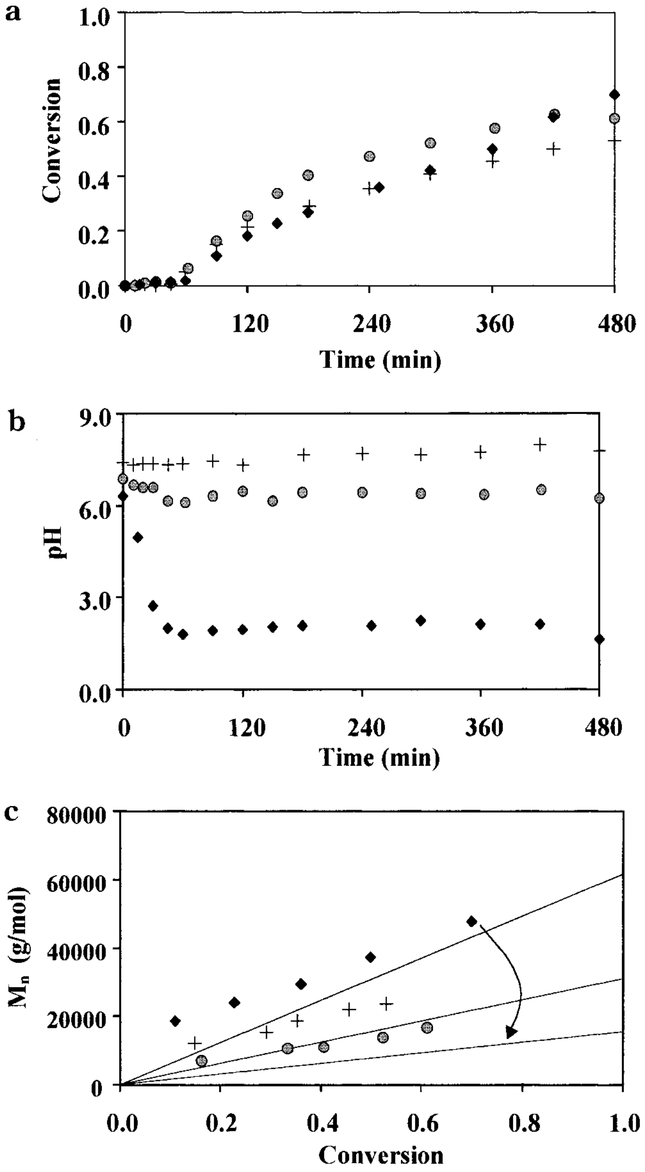


Figure 6. Effect of the initiator concentration for miniemulsion polymerizations with a St/water ratio of 2/9 wt/wt and with $NaHCO_3$ buffer (0.009 mol $dm^{-3}{}_{aq}$): (a) conversion; (b) pH; (c) number-average molar mass (straight lines = theoretical M_n): Experiments: 7, + (0.0023 mol $dm^{-3}{}_{aq}$); 8, ● (0.0045 mol $dm^{-3}{}_{aq}$); 9, ◆ (0.0090 mol $dm^{-3}{}_{aq}$).

$[P{-}SG1]_{org}$ was thus unexpectedly low, the polymerization was quite fast. Both effects are clearly the consequence of the side reactions that take place under acidic conditions, as described in the previous paragraph.

For intermediate initiator concentrations ($[K_2S_2O_8]$ = $[Na_2S_2O_5]$ = 0.0045 mol $dm^{-3}{}_{aq}$ for expts 5 and 8; $[K_2S_2O_8]$ = $[Na_2S_2O_5]$ = 0.0023 mol $dm^{-3}{}_{aq}$ for expts 4 and 7), the final pH was never below 6 and the molar masses exhibited the expected values. In this situation only, if one compares expts 4 and 5, on one hand, and expts 7 and 8, on the other, the polymerization was faster when the initiator concentration was larger.

When very low initiator concentrations were used, unusual effects occurred (expt 3 and to a lesser extent expt 7). For expt 3, the initial concentrations of potassium persulfate and sodium metabisulfite were 0.0011 mol $dm^{-3}{}_{aq}$ in water. The molar mass increased with monomer conversion, and at final conversion the target molar mass (62 000 g mol^{-1}) was reached (Figure 5c). However at low conversion, the M_n value was quite above the theoretical line. This initially fast chain growth can be explained by the small overall concentration of free nitroxide (an initial nitroxide/initiator molar ratio of 1.2 was used), leading to a slow deactivation together with a fast propagation. To this experiment with low initiator concentration, one can compare the previously presented experiments for which the concentration of formed alkoxyamines was too low owing to the acid-induced side reactions. The same features of fast propagation together with a nonlinear increase of M_n with monomer conversion were also observed. For expt 7 the same molar mass as for expt 3 was targeted, but owing to a higher styrene/water ratio (2/9 wt/wt instead of 1/9 for expt 3), the aqueous initiator concentration was twice as high (0.0023 mol $dm^{-3}{}_{aq}$), and the

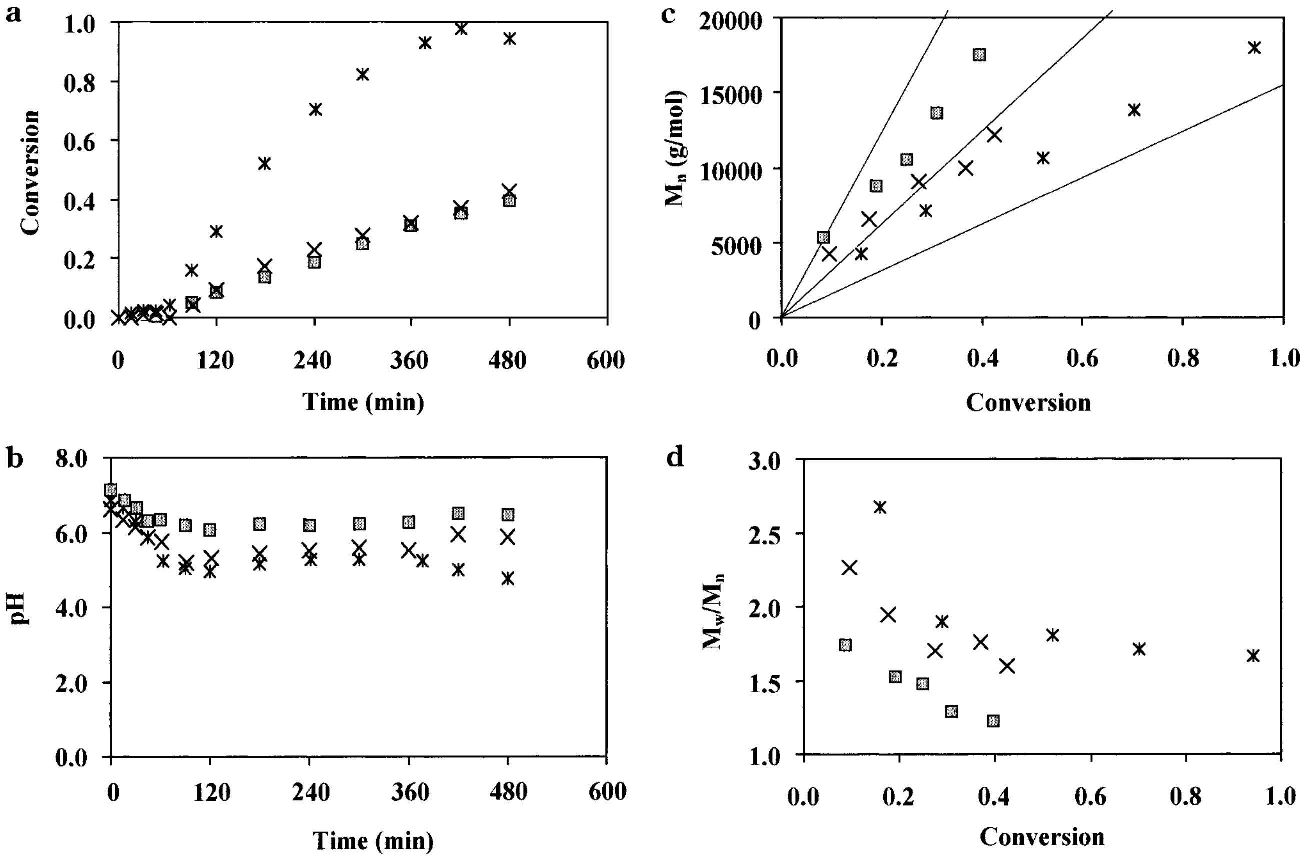


Figure 7. Effect of the initial styrene/water weight ratio. [$K_2S_2O_8$] = [$Na_2S_2O_5$] = 0.0045 mol dm^{-3}_{aq}; [K_2CO_3] = 0.0044 mol dm^{-3}_{aq}. (a) Conversion; (b) pH; (c) number-average molar mass (straight lines = theoretical M_n); (d) polydispersity index. Experiments: 11, $*$ (1/9); 13, × (2/9); 14, ■ (3/9).

effect on the molar masses at low conversion was not observed anymore (Figure 6c). At higher conversions, however, the experimental M_n's were found to be lower than the predicted values, indicating the interference of side reactions that produce new chains such as transfer reactions.

From these results it might seem that only a narrow range of molar masses can be successfully targeted. However, other parameters could be modified in order to overcome the encountered difficulties: change in the nature of the pH buffer and/or increase of its concentration for high initiator concentration; increase of the initial concentration of SG1 for low initiator concentration, etc. This actually means that the experimental conditions need to be carefully adjusted to suit the purpose.

4. Effect of the Monomer/Water Ratio. Influence of the ratio of styrene to water was examined for two different sets of experimental conditions. In all the experiments, the initial nitroxide/initiator molar ratio was the same and equal to 1.2. In the first case, the experiments of the following pairs were compared: expt 3 (St/water = 1/9 wt/wt) and expt 7 (St/water = 2/9 wt/wt); expt 4 (1/9) and expt 8 (2/9); expt 5 (1/9) and expt 9 (2/9). For each pair of experiments the amount of initiator with respect to styrene was kept constant, and thus the target molar mass was the same. However, the concentration of initiator in the aqueous phase was different, and this considerably affected the kinetics and control over the molar masses as shown before. In fact, it probably dominated over the effect of the monomer content. Therefore, the exact contribution of the monomer/water ratio cannot be easily deduced. Nevertheless, as reported in Table 3, the molar mass distribution was always found to be narrower when the monomer content was higher. For the second series, the aqueous concentration of initiator was kept the same. The following three experiments were compared: expt 11 (St/water = 1/9 wt/wt), expt 13 (St/water = 2/9 wt/wt), and expt 14 (St/water = 3/9 wt/wt). Since the amount of styrene was changed, the target molar mass was also changed (see Table 1 and Figure 7a–d). The pH was slightly affected by the proportion of styrene and decreased to a lower value when this proportion was smaller. A faster polymerization was observed for the largest amount of initiator with respect to styrene. For the other two cases, the rate was almost the same. The molar mass evolutions were typical of the effect of the initiator concentration, as discussed before. Again, the most important change concerned the molar mass distribution, which became much narrower when the styrene content was increased (for instance, $M_w/M_n = 1.22$ at 39.7% conversion for expt 14 with St/water = 3/9 wt/wt; see Table 4). This feature can be related to the change in partition of the nitroxide between the two phases. For a given concentration of SG1, the fraction that remains in the organic phase is larger when the volume of styrene is also larger, leading to a better control. The polymerization characteristics are then closer to those observed in bulk.

5. Chain Extension in Miniemulsion. The ability of the polymer chains prepared via SG1-mediated CRP in miniemulsion to reinitiate the controlled polymerization of a new charge of monomer was checked in situ according to two different procedures as described in the experimental part. The results are shown in Table 2 and in Figures 8 and 9. The polymer of expt 8, although

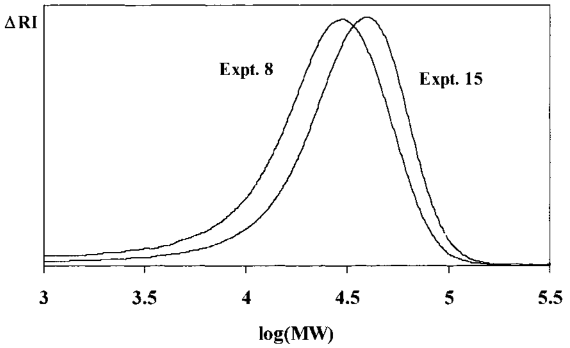


Figure 8. Size exclusion chromatograms of expt 8 and of expt 15 after chain extension (ΔRI as a function of log(MW)). Conversions, M_n, and M_w/M_n values are given in Table 2.

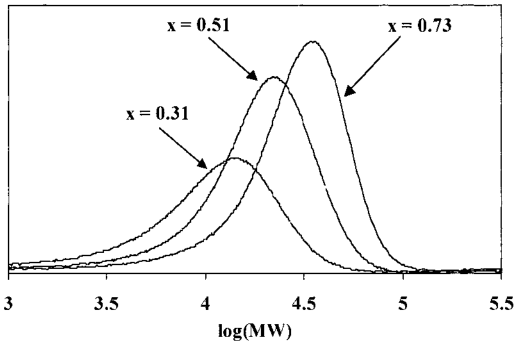


Figure 9. Chain extension from an experiment similar to expt 5: SEC of expt 16 (ΔRI as a function of log(MW)). Conversions, M_n, and M_w/M_n values are given in Table 2.

stored for $1^1/_2$ months as a latex, proved to be still “living” since chain extension could be performed, and a controlled polymer was obtained with the expected molar mass and a narrower molar mass distribution (Figure 8). In the second experiment (expt 16), a sequential procedure was implemented. The first step was performed under the same experimental conditions as expt 5. After 50% conversion, a new charge of monomer was fed into the reactor. Like previously, the polymer prepared under such heterogeneous conditions proved to be still “living” since chain extension occurred together with a narrowing of the molar mass distribution. In both cases, the average particle size increased between the two steps, and the final diameter was in good agreement with the expected value, which indicates that the new monomer was polymerized within the existing particles.

Conclusion

Nitroxide-mediated controlled free-radical polymerization of styrene was studied in a miniemulsion system, using sodium dodecyl sulfate as an anionic surfactant and hexadecane as a hydrophobe. This process produced stable latex particles with diameter between 150 and 250 nm but with a broad particle size distribution. The use of an acyclic β-phosphonylated nitroxide, the *N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (SG1), enabled polymerization to be performed at 90 °C. A bicomponent initiating system was chosen, i.e., a radical initiator in conjunction with added free nitroxide. The initiator was the conventional $K_2S_2O_8$/$Na_2S_2O_5$ redox system. Both the conversion versus time and M_n versus conversion were monitored. It was demonstrated that water-soluble alkoxyamines were initially formed during the induction period and were progressively transferred into the organic phase to continue the propagation. Fast polymerizations were usually observed owing to the partition of the nitroxide between the two phases and therefore to its small local concentration within the particles. The effect of pH was studied. When insufficiently buffered, the water phase became acidic during the initiation period. The decrease in pH was accompanied by an increased rate of polymerization together with a low “initiator efficiency”. These features were due to side reactions between SG1 and the two components of the initiating system leading to a decrease in the concentration of produced alkoxyamines. At neutral pH, these side reactions were unimportant, which ensured a better control over the polymer characteristics. Indeed, the molar masses increased with monomer conversion, matched the theoretical values, and displayed a narrow distribution. However, as a consequence of the partition of the nitroxide resulting in faster propagation, the molar mass distribution was generally broader than in bulk. It was however significantly improved when the monomer/water ratio in the miniemulsion was increased from 10% to 30%. The effect of initiator concentration was also examined. At too high a concentration, the pH decreased dramatically, and the above-mentioned features were observed. At very low concentration, a poor control was achieved initially owing to the low nitroxide concentration. Finally, “livingness” of the polymer chains was demonstrated by in situ chain extension. As a conclusion, the use of a bicomponent initiating system with addition of a radical initiator together with free nitroxide is a very simple way to achieve CRP in miniemulsion. From a practical viewpoint very few parameters have to be changed with respect to a classical polymerization. Nevertheless, because kinetics and control of molar mass are very sensitive to small changes in nitroxide concentration, it makes control fairly difficult to achieve because the concentrations of each component have to be very carefully adjusted.

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