Emulsifier-Free Controlled Free-Radical Emulsion Polymerization of Styrene via RAFT Using Dibenzyltrithiocarbonate as a Chain Transfer Agent and Acrylic Acid as an Ionogenic Comonomer: Batch and Spontaneous Phase Inversion Processes

Sébastien Fréal-Saison,†,‡ Maud Save,† Chuong Bui,† Bernadette Charleux,*,† and Serge Magnet‡

Laboratoire de Chimie des Polymères, Université Pierre et Marie Curie-Paris 6, CNRS-UMR 7610, 4, Place Jussieu, 75252 Paris Cedex 05, France, and Eliokem, 14, Avenue des Tropiques, 91955 Villejust Cedex, France

Received July 13, 2006; Revised Manuscript Received August 31, 2006

ABSTRACT: Surfactant-free, batch emulsion polymerization of styrene was carried out in the presence of sodium acrylate as a comonomer and dibenzyltrithiocarbonate (DBTTC) as a reversible addition−fragmentation chain transfer (RAFT) agent. Very stable latex was recovered with narrow particle size distribution. Because of the low water-solubility of DBTTC, diffusion of the RAFT agent from the monomer droplets toward the polymer particles was slow, which did not allow a linear increase of molar mass with monomer conversion. However, M_n eventually reached the expected value and the final polymer chains could be extended, when the latex was used as a seed for a second polymerization step. To overcome the slow diffusion of the RAFT agent, a new process was proposed, based on a spontaneous phase inversion mechanism. The method relies upon a first bulk copolymerization of styrene and acrylic acid, followed by neutralization of the carboxylic acid moieties by the addition of a sodium hydroxide solution under gentle stirring, leading to spontaneous phase inversion when a sufficient amount of water has been added. The method was applied to generate stable polymer nuclei, which were further used as a seed for chain extension upon monomer addition.

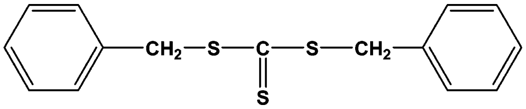
Introduction

Various ways of obtaining controlled polymers in free-radical polymerization are now available including ATRP[1,2] (atom transfer radical polymerization), SFRP or NMP[3] (stable free-radical or nitroxide-mediated polymerization), degenerative transfer (such as iodine transfer polymerization[4] and reverse iodine transfer polymerization[5]) and RAFT[6] (reversible addition−fragmentation chain transfer). Among them, the RAFT method usually requires little demanding conditions, the only change with respect to a noncontrolled system being the addition of a reversible chain transfer agent. The other polymerization variables, such as the temperature or the operating pressure are not changed, as long as polymerization in homogeneous media is concerned. The choice and design of the reversible chain transfer agent is an important parameter.[7−9]

The application of controlled free-radical polymerization via RAFT to heterogeneous media is a recurrent topic in the recent literature, including essentially aqueous miniemulsion[10−18] and emulsion[19−28] polymerizations.[29] The ability to obtain polymer chains with controlled features, such as composition, architecture and functionalities is now well-known. Nevertheless, the ability to form latexes or aqueous dispersions made of those polymers[30−34] is the key to industrialization, since it makes handling of the polymer very convenient, and is also necessary for applications such as paints and coatings.

When controlled polymerizations via RAFT in heterogeneous media were studied, difficulties were generally encountered:[35] the first polymerizations in miniemulsion have suffered from colloidal stability issues with formation of a colored, monomer-rich top layer in the polymerization medium. Different ways of avoiding these difficulties have progressively emerged,[20,23,36,37] but few of these processes yet matched the simplicity of batch ab initio emulsion polymerization process, where simple and affordable reactants can be loaded into the reactor at one time, before polymerization is started, and latex is retrieved at the end of the process.[20] Moreover most of them employ low molar mass surfactants to stabilize the latex particles during and after the polymerization. Only the work presented by Gilbert's group avoids the presence of added surfactant:[23,38] the stabilizer is a poly(sodium acrylate)-*b*-polyacrylate diblock copolymer created in situ from an amphipathic trithiocarbonate RAFT agent and the methodology is a multistep process with sequential and semicontinuous addition of the monomers.

Scheme 1. Structure of the Dibenzyltrithiocarbonate RAFT Agent (DBTTC)



The aim of this paper is to present an easy, reliable ab initio, emulsifier-free, controlled free-radical emulsion polymerization process via RAFT, in which sodium acrylate is used as a water-soluble, ionic comonomer, allowing the stabilizer to be created in situ by copolymerization with the main monomer. In this work, dibenzyltrithiocarbonate (DBTTC; Scheme 1) was used as a RAFT agent, as it is easy to synthesize[39] and, like other similar trithiocarbonates, has a reactivity adequate to polymerize styrene and acrylates in a living fashion.[40,41] Two main methods have been tested. The first one is a conventional, surfactant-free batch emulsion polymerization carried out in the presence of the ionic comonomer and DBTTC. In the second method,

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* Corresponding author: charleux@ccr.jussieu.fr.

† Laboratoire de Chimie des Polymères, Université Pierre et Marie Curie-Paris 6, CNRS-UMR 7610.

‡ Eliokem.

10.1021/ma061572s CCC: $33.50

Table 1. Summary of the Experimental Conditions for the Surfactant-Free, Batch Emulsion Polymerizations of Styrene in the Presence of Acrylic Acid at 60 °C

expt	process	RAFT agent	overall solids content, wt %	$f_{AA,0}$[a]	$[ACPA]_0$, mol $L_{aq.}^{-1}$	target M_n at 100% convn, g mol^{-1}
E1	batch	none	9.9	0.103	5.2×10^{-3}	
E2	batch	DBTTC	9.9	0.105	5.2×10^{-3}	20400
E3	chain extension of **E2**	poly(styrene-*co*-acrylic acid) from **E2**	23.0	0.034	6.8×10^{-3} [b]	62700

[a] $f_{AA,0}$ = molar fraction of AA in the monomer mixture (for **E3**, it corresponds to the overall value). [b] Added in the extension step.

we propose a new and original way to apply the RAFT technique in emulsion polymerization, based on a spontaneous phase inversion process. The latter is a process where water is added under stirring to a mixture of an organic phase in the presence of an emulsifier, resulting in a spontaneous phase inversion. This has been thoroughly studied at the University of Los Andes[42−46] and used to enable the handling and transportation of very viscous oils in south America. In this work, the technique has been modified to avoid the presence of the surfactant and a method used for the industrial production of polyurethane aqueous dispersions has been adapted.[47−50]

Experimental Part

Materials. Dibenzyltrithiocarbonate (DBTTC) was synthesized according to literature.[39,51] Monomers, styrene (St), *n*-butyl acrylate (BA), and acrylic acid (AA), were ordered from Aldrich and vacuum distilled prior to use. The initiators, AIBN (2,2′-azobis-(isobutyronitrile)) and ACPA (4,4′-azobis-4-cyanopentanoic acid), and all other reactants were ordered from Aldrich and used as received.

Polymerization and Mixing Setup. For the polymerizations, a Mettler RC-1 calorimeter equipped with a 1 L MP-10 reactor and connected to a pump was used. The temperature, the stirring speed and the flow rate of the continuously added solutions can be controlled throughout the polymerization. The impeller is made of 4 pitched blades. The stirring speed can be varied between 30 and 350 rpm. Nitrogen (Air Liquide; O_2 content below 5 ppm) was constantly kept flowing on top of the reactor.

Analytical Techniques. Monomer conversion was determined by gravimetry.

Size exclusion chromatography (SEC) was used to determine the number-average molar mass (M_n) and the polydispersity index (PDI = M_w/M_n, with M_w, the weight-average molar mass) of the polymers. For the polymer samples containing acrylic acid units, a reaction of methylation was performed before the SEC analyses, to turn the acrylic acid groups into methyl esters, using trimethylsilyldiazomethane, as described before.[52,53] The samples were injected (using a Viscotek VE 5200 injector) in two PSS linear M columns, thermostated at 40°C, with THF as an eluent (flow rate at 1 mL/min). Detection was made with a refractometer Refracto monitor IV (LDC analytical). The Viscotek TriSEC software was used for data analysis; calculation was based on a polystyrene calibration curve. All experimental M_n values based on methyl acrylate subunits have been recalculated for acrylic acid units.

Dynamic light scattering (DLS, Malvern HPPS) was used for the measurement of the *z*-average particle diameter, D_z, and the particle size distributions. The number of particles per L of latex was calculated using the expression: $N_p = 6\tau/\rho\pi D_z^3$ (the solids content τ is given in g·L^{-1}, the polystyrene density ρ is 1.05, and D_z is the *z*-average particle diameter in cm. The polydispersity of the particle size distribution, σ, given by the DLS ($\sigma > 0$), corresponds to the relative variance.

The NMR analyses were carried out at room temperature with a Bruker 250 MHz apparatus after dissolution of the samples in $CDCl_3$.

The surface tension of the latexes was measured using a Krüss Digital-Tensiometer K10, with a platinum Du Noüy ring.

The transmission electron microscopy (TEM) was performed using a JEOL JEM 100 cx II CHR microscope. The average particle diameters were calculated after manual measurement of 350 to 500 particles on the TEM pictures, using the following expressions: $D_n = \sum n_iD_i/\sum n_i$ for the number-average diameter and $D_w = \sum n_iD_i^4/\sum n_iD_i^3$ for the weight-average diameter. The particle-diameter dispersity was calculated as D_w/D_n.

Surfactant-Free Emulsion Polymerization. An aqueous solution of 7.0 g (0.097 mol) of acrylic acid and approximately 800 g of deionized water was neutralized by NaOH (1 molar equivalent based on acrylic acid), and bubbled with nitrogen. At the same time, the organic phase containing 87.8 g (0.84 mol) of styrene alone (experiment **E1**, Table 1) or 86.4 g (0.83 mol) of styrene and 1.35 g (0.00465 mol) of the dibenzyltrithiocarbonate RAFT agent (experiment **E2**, Table 1) was prepared and left under nitrogen bubbling. When both phases were exempt from oxygen, they were loaded into the MP-10 reactor of the RC-1 calorimeter, and heated to the polymerization temperature (60 °C). An aqueous solution (to reach an overall weight of water of 886 g for **E1** and 880 g for **E2**) containing the neutralized ACPA initiator (1.44 g; 0.0051 mol) was prepared and bubbled with nitrogen. When the medium reached the polymerization temperature, the initiator solution was introduced, which marked the beginning of the polymerization reaction. At that initial stage, the polymerization medium was not homogeneous, and both phases quickly separated from each other if stirring was stopped. The polymerization reaction was then carried out at a stirring speed of 350 rpm. At regular time intervals, samples were withdrawn from the reactor for analysis purposes.

For chain extension (experiment **E3**, Table 1), a first 20 g portion of styrene was added to 200 g of the latex **E2** (containing 16.3 g of polystyrene and 1.23 g of residual styrene) and the mixture was allowed to equilibrate for 24 h at room temperature, under gentle stirring to allow a good swelling of the polystyrene particles by the monomer. The mixture was then introduced into the reactor at 60 °C and a new 20 g portion of styrene was added, along with an aqueous solution of neutralized ACPA (0.50 g; 0.0018 mol in 16.5 g of water). The polymerization was allowed to proceed for 7 h at 60 °C, at a stirring speed of 350 rpm.

Spontaneous Phase Inversion. In this process, the polymerizations took place in two different steps, both carried out in the MP-10 reactor of the RC-1 calorimeter. The first step was a bulk copolymerization at 60 °C of styrene and acrylic acid with DBTTC as a RAFT agent and AIBN as an initiator. In the first experiment (**E4**), 62.5 g of styrene (0.601 mol) and 9.4 g of acrylic acid (0.131 mol; 0.179 molar fraction in the comonomer feed) with 0.28 g (1.7×10^{-3} mol) of AIBN initiator were placed in the reaction vessel with 2.0 g of the dibenzyltrithiocarbonate RAFT agent (6.9×10^{-3} mol; target M_n = 10 700 g mol^{-1} at full conversion). The whole system was heated to 60 °C for 3.5 h, to reach 55% conversion. In the second experiment (**E5**), 75.0 g of styrene (0.721 mol) and 25.0 g of acrylic acid (0.347 mol; 0.325 molar fraction in the comonomer feed) with 0.16 g (9.8×10^{-4} mol) of AIBN initiator were placed in the reaction vessel with 2.9 g of the dibenzyltrithiocarbonate RAFT agent (0.010 mol; target M_n = 10 300 g mol^{-1}). The whole system was heated to 60 °C for 6 h, to reach 54% conversion.

In the second step, the polymerization medium was cooled to room temperature and a concentrated aqueous solution containing the sodium hydroxide in equimolar amount with respect to the acid groups was slowly introduced. The system was left under stirring for a while to ensure its homogenization. Then, the remaining part of the water was added progressively (614 g of water for the experiment **E4**, i.e., 11.2 wt % targetted solids content and 755 g

Table 2. Emulsifier-free, Seeded Emulsion Polymerizations Using a Spontaneous Phase Inversion Process: Chain Extension with Styrene and *n*-butyl Acrylate of the Poly(styrene-*Co*-acrylic Acid) Dispersion E5 at 60 °C and Alkaline pH

expt	amt of dispersion **E5** (12 wt % solids), g	added monomer	amt of added monomer, g	$[\mathrm{ACPA}]_0$, mol $\mathrm{L_{aq.}}^{-1}$	target M_n at 100% convn, g mol^{-1}	target solids content, wt %
E6	200	St	40	8.4×10^{-3}	28000	25.8
E7	100	BA	30	1.36×10^{-2}	36700	30.4

Table 3. Characteristics of the Copolymers and Latexes

expt	time, h	final convn, %	D_z from DLS (σ), nm	$10^{-16} \times N_p$, L^{-1}	target M_n at the exptl convn, g mol^{-1}	exptl M_n, g mol^{-1}	PDI
E1	21	93	410 (0.01)	0.027			
E2	23	92	360 (0.05)	0.036	18800	19800	1.4
E3	7	38[a]	420 (0.04)	0.035	36400	25000	1.3
E4	3.5	55	20 (0.4)	300	6000	5500	1.4
E5	6+12[b]	94	23 (0.4)	200	9700	7500	1.4
E6	7	100	140 (0.2)	2	28000	22500	1.2
E7	1	100	180 (0.2)	1	36700	27500	1.2

[a] For the second step only. [b] See the experimental part. [c] Final latex pH is in the range 9.0−9.5 for the experiments **E1**−**E3** and in the range 8.5−9.0 for the experiments **E4**−**E7**.

for the experiment **E5**, i.e., 12.8 wt % targetted solids content). Initially the viscosity of the system built up and a gel was obtained. The rate of water addition was reduced to dilute the gel without too much heterogeneity in the flow, at a stirring speed of 30 rpm. In the end a transparent, yellow colored liquid was obtained. For the experiment **E5**, the system was heated again for 12 h at 60 °C until complete conversion (94%). Such final dispersion **E5** was used as a seed for further chain extension by styrene leading to 100% conversion within 7 h (**E6**) and by *n*-butyl acrylate leading to 100% conversion within 1 h (**E7**) (see Table 2).

All characteristics of the experiments **E1**−**E7** are given in Table 3.

Results and Discussion

1. Surfactant-Free, Batch Emulsion Polymerization. The surfactant-free emulsion polymerizations were carried out in batch conditions at 60 °C, with DBTTC as a RAFT agent (**E2**, Table 1) and without DBTTC (**E1**). Initially, in both cases, in the absence of any surfactant, the biphasic system was totally unstable. While, at the beginning of the reaction, the aqueous phase was perfectly transparent, it became more and more hazy with the progress of the polymerization, eventually leading to a stable latex. At final conversions, the colloidal properties of the latexes were not so different: without DBTTC the average diameter given by DLS was 410 nm, while with DBTTC it was 360 nm with a slightly broader particle size distribution (σ = 0.05 instead of 0.01) (see in Figure 1, the TEM image for the latex **E2**). In both cases, the surface tension was quickly decreasing to a minimum in the initial stage of the polymerization, and this effect was even more pronounced in the presence of DBTTC (Figure 2). Such result is the indication that there was the generation of surface-active species, which were not present initially, and were modifying the surface characteristics of the polymerization medium. Then, the surface tension increased again toward a value above 60 mN·m^{-1}. Such surface-active species were statistical copolymers of styrene and sodium acrylate (Scheme 2), the molar concentration of which was much larger in the presence of DBTTC, due to the reversible chain transfer reaction, which contributed to the creation of a large concentration of short chains.

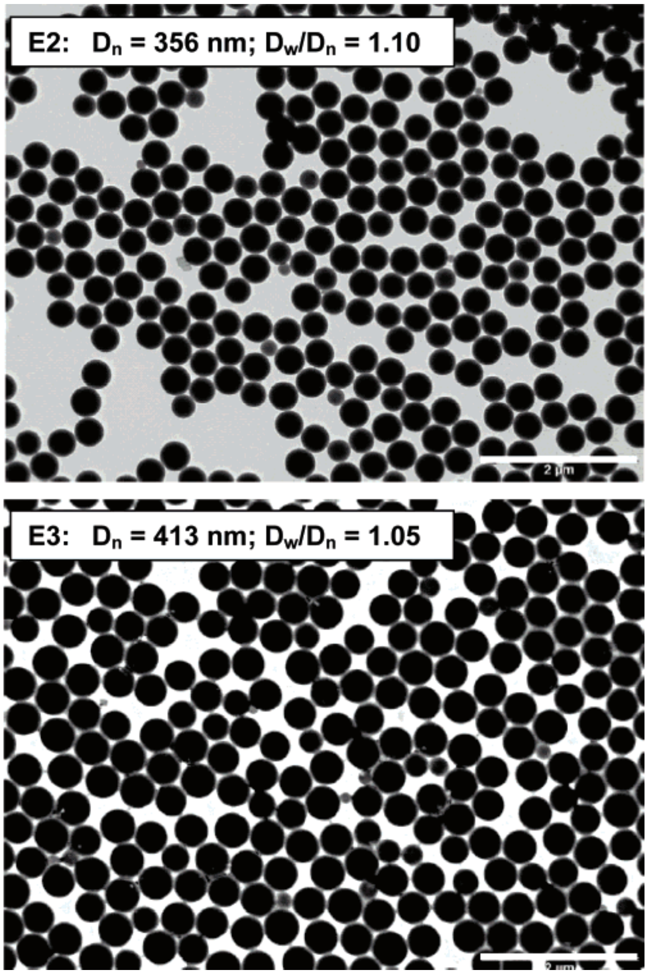


Figure 1. Transmission electron micrographs of the final latexes **E2** and **E3** (the white bar represents 2 μm).

In the presence of DBTTC, the polymerization was slightly slower than without any added RAFT agent (Figure 3), which is not an unexpected feature.[54,55] In Figure 4, one can see the evolution of the molar masses and polydispersity indexes as a function of monomer conversion. It is noteworthy that the average molar masses started much higher than the theoretical values expected in a controlled system. Above approximately 20% conversion, the PDI values were found below 2, which was an indication the polymerization has become controlled; the PDI continuously decreased, finally reaching a value of 1.4. At high conversion, the polymer showed a molar mass close to the predicted value. All those results are the indication of quite

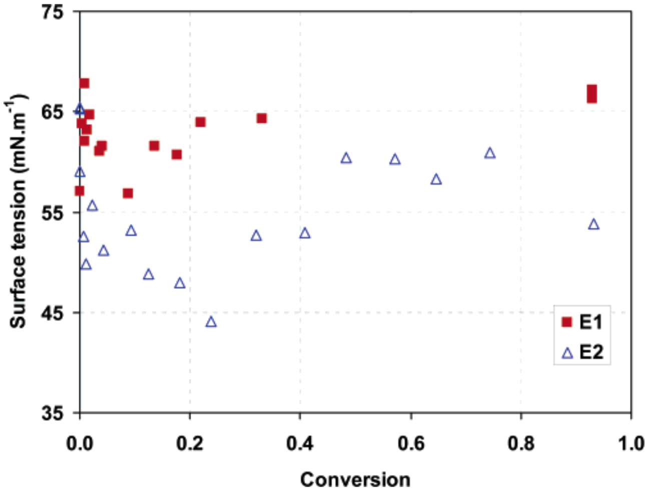


Figure 2. Surface-tension vs monomer conversion for the surfactant-free, batch emulsion polymerizations of styrene in the presence of acrylic acid at 60 °C: **E1**, without DBTTC; **E2**, with DBTTC.

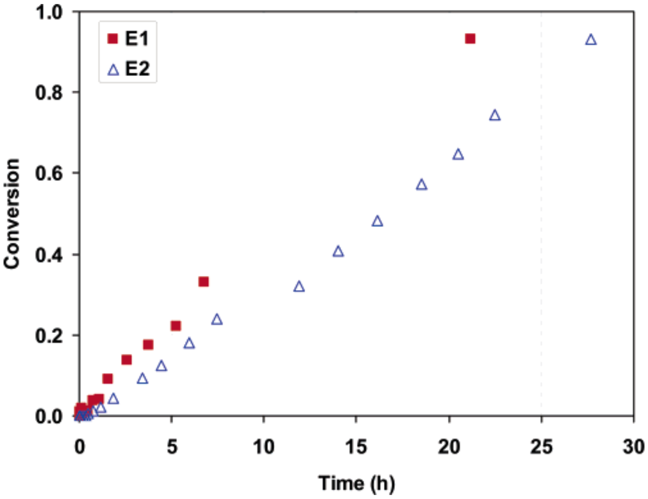


Figure 3. Conversion vs time plot for the surfactant-free, batch emulsion polymerizations of styrene in the presence of acrylic acid at 60 °C: **E1**, without DBTTC; **E2**, with DBTTC.

a low apparent chain transfer constant to DBTTC, not very different from 1,[56] which was quite surprising since the transfer constant in the polymerization of styrene was reported to be close to 20.[8,57] This raises the importance of the mass transport in the emulsion polymerization process. The low water-solubility of DBTTC may explain its limited ability to diffuse through water toward the polymerization loci, and hence its unexpectedly slow consumption rate. Such results have already been described in the past when for instance $C_6F_{13}I$, with an extremely low water-solubility, was used as a degenerative chain transfer agent in emulsion polymerization.[58]

To check that the latex was actually made of living chains, a new portion of styrene was added, the latex particles were swollen with this monomer for more than 24 h, and the polymerization was reinitiated (experiment **E3**, Table 1). The TEM picture in Figure 1 shows an increase in the average particle size along with a slight narrowing of the particle size distribution, when compared to the seed latex **E2**. No secondary nucleation could be observed (the N_p value given in Table 3 remained the same for **E2** and **E3**), which is a key point in seeded emulsion polymerization, in which a RAFT mechanism is involved, if one wants the formation of nonliving chains to be avoided. Chain extension actually occurred as shown by the shift of the size exclusion chromatogram (Figure 5), and the polymer exhibited a M_n of 25 000 g mol^{-1} at 38% conversion, with a PDI value reduced down to 1.3 (Table 3). Neither creation of new chains nor increased proportion of dead chains could be seen in the chromatograms, although the evolution of the molar masses showed a trend below the expected values (Table 3). The change from DBTTC with two benzyl leaving groups into a macromolecular chain transfer agent with two polystyrene-based leaving groups, during the first polymerization step, induced an increase in the chain transfer constant,[7] which

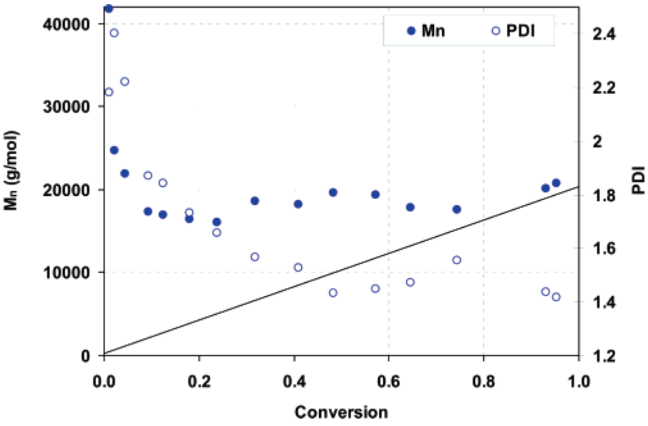


Figure 4. Number-average molar mass and polydispersity index vs conversion for the surfactant-free, batch emulsion polymerization of styrene, **E2**, carried out in the presence of acrylic acid and DBTTC at 60 °C.

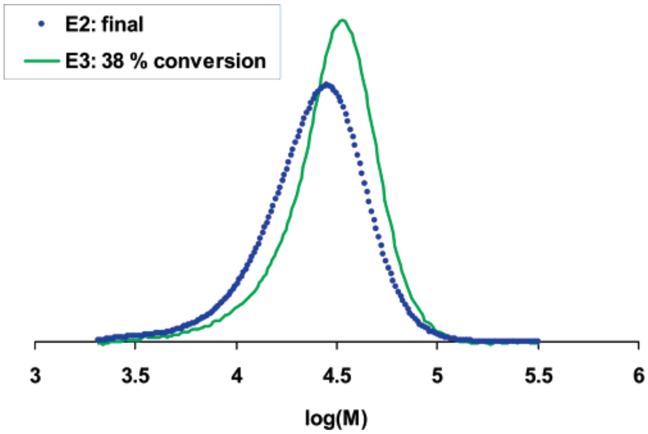
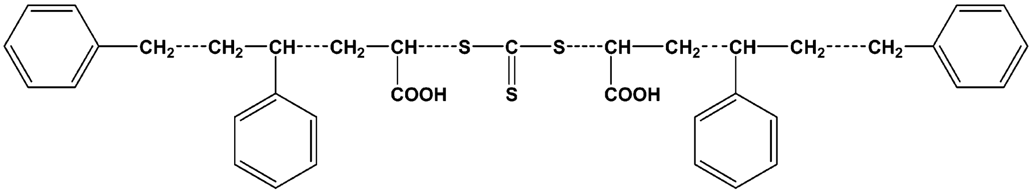


Figure 5. Size exclusion chromatograms of the polymer **E2** at final conversion and of the polymer **E3** after chain extension with styrene.

Scheme 2. Structure of the Poly(styrene-*co*-acrylic acid) Amphiphilic Random Copolymers Initially Formed in the Batch Emulsion Polymerization Processes and in the Preliminary Bulk Copolymerization Step



allowed the initial latex to be used as an efficient living seed for further chain extension.

The complex intertwined processes—nucleation in the continuous phase, monomer mass transfer and polymerization in the newly formed particles—have been studied in conventional emulsifier-free emulsion polymerization by Yamamoto et al.[59] In this case, it relied upon the use of a massive amount of initiator that was able to generate enough stabilizing moieties attached at the chain end and anchored to the particle surface, to ensure a good stability. In this work, a much lower initiator concentration was used, and we have added instead neutralized acrylic acid to improve the particles stabilization. In such conditions, polymerization starts in the aqueous phase with the formation of amphiphilic poly(sodium acrylate-*co*-styrene) copolymer chains. In the experiment **E2** with DBTTC, the chains had a higher molar mass than expected owing to the poor water-solubility of the RAFT agent, which affected the local monomer over chain transfer agent molar ratio. Such copolymers might form aggregates or stabilize small monomer droplets generated upon fission of the large ones, and consequently induce nucleation. The surface tension data described above indicate that, although DBTTC was not able to perfectly control the polymerization from the very beginning of the reaction, it nonetheless played an important role in the generation of surface-active species. After creation of the polymer particles stabilized by the carboxylate moieties, polymerization entered the interval II of a normal emulsion polymerization, with diffusion of the monomer and DBTTC from the droplets toward the particles. At that stage, consumption of DBTTC was diffusion-controlled, which explains the discrepancy between the apparent chain transfer constant and the one found in homogeneous polymerization conditions.[57] Nevertheless, a complete consumption of the RAFT agent was achieved, as supported by the convergence of the experimental M_n with the theoretical one at high monomer conversion. This result also indicates a good stability of the trithiocarbonate in the polymerization conditions.

Consequently the emulsifier-free, batch emulsion polymerization in the presence of sodium acrylate is a good method to achieve controlled free-radical polymerization via RAFT, using DBTTC as a reversible chain transfer agent. In particular it can be used to the production of a stable living seed latex, in which polymer chains can be extended upon addition of a new portion of monomer. The particle size still remains to be optimized according to the experimental parameters, such as the acrylic acid concentration in particular, to cover a broader range of accessible diameters.

2. Spontaneous Phase Inversion Process. To induce a fast consumption of the chain transfer agent according to the expected kinetics found in homogeneous conditions, a possibility might have been to use miniemulsion polymerization,[60] as we did before in the polymerization of styrene in the presence of $C_6F_{13}I$.[58] We decided, however, to propose a new process, avoiding both the mechanical shear or ultrasonication of the initial monomer-in-water emulsion, and the addition of a hydrophobe to prevent Ostwald ripening. The method is based on a first bulk copolymerization of styrene and acrylic acid (Scheme 2), with low target molar mass and incomplete monomer conversion to maintain a low viscosity, followed by neutralization of the carboxylic acid moieties by the addition of a sodium hydroxide solution under gentle stirring, leading to spontaneous phase inversion when a sufficient amount of water has been added. Such a process presents similarities with that used for the production of polyurethane aqueous dispersions.[47−50] The method, which allows a living, water-dispersed stabilizer to be created in situ, was applied to generate stable, submicron particles, that can be used as a seed for further chain extension upon monomer addition.

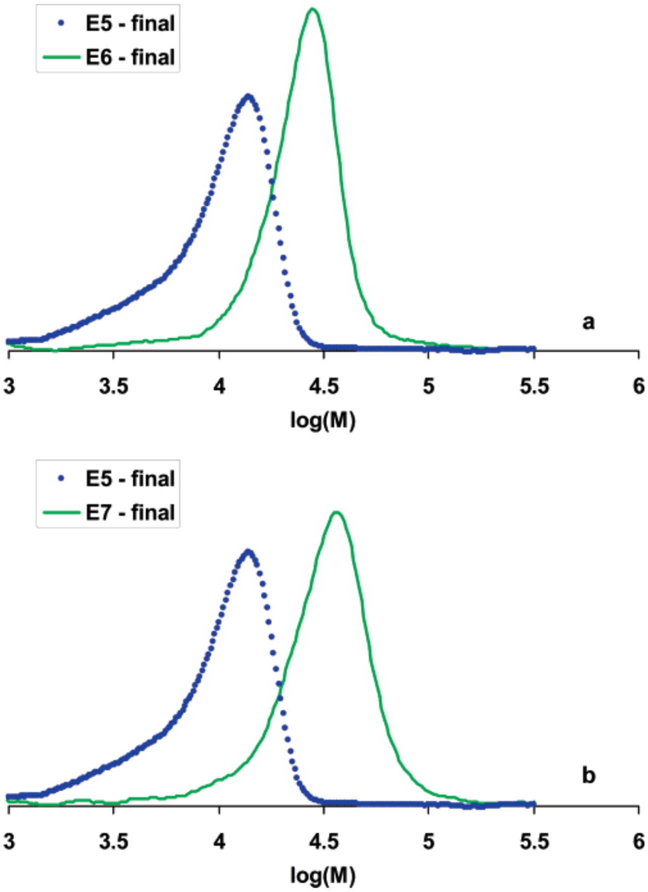


Figure 6. Size exclusion chromatograms of the polymer **E5** at final conversion and of the polymers **E6** (a) after chain extension with styrene and **E7** (b) after chain extension with *n*-butyl acrylate.

Two syntheses were performed with first a bulk copolymerization of styrene and acrylic acid, with DBTTC as a RAFT agent, and AIBN as an initiator at 60 °C (see the experiments **E4** and **E5** in the Experimental Part). The experimental results are summarized in Table 3. The formed copolymers exhibited a rather low acrylic acid content. The latter was indeed purposely chosen in order to get relatively hydrophobic amphiphilic copolymers, able to form aggregates in an alkaline aqueous phase instead of dissolving as unimers (Table 3).[61] For the experiment **E4** the overall fractional composition in acrylic acid was 0.179 whereas it was 0.325 for the experiment **E5**, and it remained about the same during the bulk copolymerization, with non significant composition drift. At 55% conversion, the target molar mass of the polymer from experiment **E4** was 6000 g mol^{-1} and the experimental molar mass was 5500 g mol^{-1}, with a polydispersity index of 1.4. For the copolymer **E5**, M_n was 7500 g mol^{-1} at 94% conversion (instead of the calculated 9700 g mol^{-1}; the error might come from the SEC analysis itself, owing to the tailing toward the lower molar mass in the chromatogram as shown in Figure 6) and PDI was 1.4.

After the addition of alkaline water inducing a spontaneous phase inversion, as described in the experimental part, a translucent sample was obtained in both cases. This transparency is a hint of the presence of very small particles: indeed, the determination of the particle size distribution by dynamic light scattering showed the diameter of the vast majority of particles

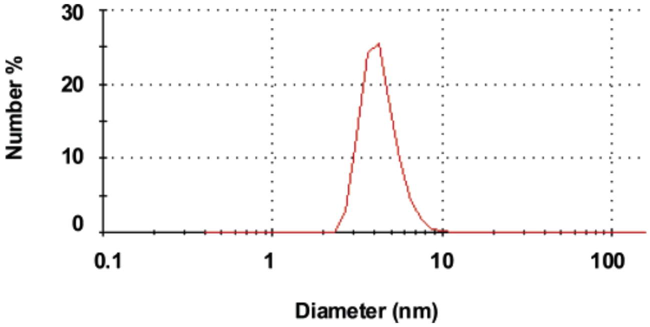


Figure 7. Number distribution of particle diameter (from the DLS analysis) for the aqueous dispersion **E4**.

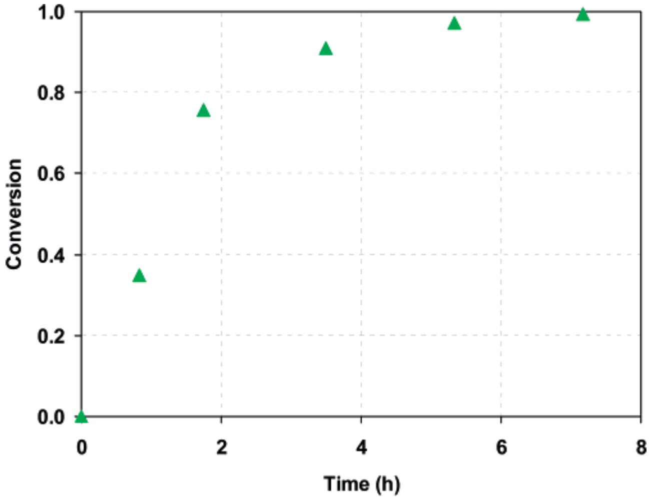


Figure 8. Conversion vs time plot for the seeded emulsion polymerization of styrene **E6** from the poly(styrene-*co*-acrylic acid) dispersion **E5** (see Tables 2 and 3).

was centered around 4 nm (Figure 7), but with a broad distribution (a fraction of the particles had larger diameter values, which is the reason the average particle diameter given in Table 3 is higher). This broad particle size distribution makes it difficult to have a reliable average diameter; conventional transmission electron microscopy was unable to access to the measurement of the diameter of the particles. We figured the average density of the polymer solution in the remaining monomer is around 1.02 (assuming the DBTTC moieties present in the polymer chains have a density equal to that of polystyrene). This enabled us to calculate the average number of polymer chains present in a single 4 nm diameter particle, around 2.5.

The final copolymer dispersion **E5** was later used as a seed for chain extension, as indicated in Table 2 and detailed in the experimental part. The second polymerization step proceeded quite rapidly, whatever the added monomer, styrene or *n*-butyl acrylate (Table 2; see also Figure 8, showing the conversion vs time in experiment **E6**). The molar masses were close to the expected values, and polymer chains were continuously growing as illustrated by the size exclusion chromatograms shift with conversion (Table 2; Figures 6 and 9). The experiments took thus advantage of the use of a polymeric RAFT agent, with a higher efficiency than DBTTC itself, as already shown above for the second step of the batch emulsion polymerization process. The possibility for the trithiocarbonate group to get hydrolyzed during the phase inversion process was not observed, which can be explained by (i) the fact that NaOH was just added in stoichiometric amount with respect to the acid groups, hence avoiding a too critical pH increase (hydrolysis of pure poly(acrylic acid) chains with a trithiocarbonate central group was shown to take place only after prolonged heating times when neutralized with 1 equiv. NaOH[62]), (ii) the phase inversion process was carried out at room temperature, and (iii) the trithiocarbonate group was in the core of already formed relatively hydrophobic macromolecules. The particle diameter and the number of particles per unit volume are shown in Table 3, for both the experiments **E5** and **E6**. It appears that during the seeded emulsion polymerization process, a stable latex was formed, with particle diameter in the 140−180 nm range, along with a very significant drop in the particle number with respect to the number of primary nuclei formed during the phase inversion process, as a sign of limited flocculation.

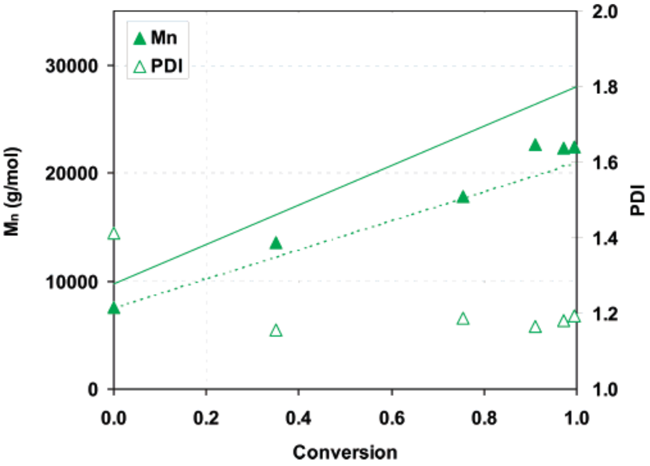


Figure 9. Number-average molar mass and polydispersity index vs conversion for the seeded emulsion polymerization of styrene **E6** from the poly(styrene-*co*-sodium acrylate) dispersion **E5** (see Tables 2 and 3). The full straight line represents the theoretical M_n vs conversion calculated from the initial concentration of DBTTC in the experiment **E5**. The dotted straight line represents the theoretical M_n vs conversion calculated from the final copolymer characteristics of experiment **E5**, used as a macro-RAFT agent for the chain extension process.

Consequently, the spontaneous phase inversion is a very convenient one-pot process for applying RAFT to surfactant-free aqueous emulsion polymerization. The method leads first to a seed latex containing the amphiphilic living chains as a dispersed phase. The emulsion polymerization following such an initial step allows stable, 30% solids latex to be produced with simultaneous chain extension. The particle size and particle size distribution still have to be optimized in agreement with the target application.

Conclusions

To overcome the difficulties usually arising with hydrophobic RAFT agents in emulsion polymerization and to avoid the presence of ionic surfactants, which led sometimes to colloidal unstabilities and which are not considered as environmentally benign, we proposed here a new, one-pot process starting with a bulk copolymerization of a hydrophobic monomer with an ionogenic comonomer. By the addition of water and simultaneous generation of charges in the living macromolecules inducing phase inversion, several goals can be simultaneously achieved: (i) A RAFT agent of low reactivity can be used; (ii) there is no need for transport of the RAFT agent in the biphasic system and its water-solubility is not an issue anymore; (iii) stable particles are formed, which contain living macromolecules able to be extended upon monomer addition; (iv) unlike miniemulsion polymerization using a macromolecular RAFT agent, the method does not require any high shear device and is therefore not energy consuming as it is based on a spontaneous phase inversion mechanism. It is simply driven by chemistry of polymerization and thermodynamics, and for this reason the process is expected to be fairly reproducible and upscalable. Consequently, it might be extended to the use of other RAFT agents as well as to other controlled free-radical polymerization techniques such as ATRP and NMP.

Acknowledgment. The authors thank Patricia Beaunier from UPMC for the TEM analyses.

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(51) Dibenzyltrithiocarbonate was synthesized by a two step process according to the ref 39. In the first step sodium trithiocarbonate was prepared in a 1 L reactor equipped with a stirrer and a thermometer and charged with 146.3 g of hydrated sodium sulfide (1.125 mol), 350 mL of water, 6 g of methyltributylammonium chloride in 6.7 g water, and 88.4 g carbon disulfide (1.15 mol). The reaction mixture was stirred for 60 min, and the solution turned bright red as sodium trithiocarbonate formed. In the second step, 255 g of benzyl chloride (2 mol) were added slowly over a period of 15 min. The reaction temperature rose to 50 °C. The stirring was maintained for 3 hours and then the mixture was heated to 70 °C for 30 additional minutes. To drive the reaction to completion a second catalyst charge containing 3.8 g of methyltributylammonium chloride in solution in 5.1 g water was added. The reactor was left overnight under stirring without heating. The organic phase was then isolated, and DBTTC was obtained therefrom by precipitation in 0.5 L of cold ethanol. The yellow crystals were filtered off, washed with 0.5 L of ethanol, and dried in a vacuum chamber. 211 g of DBTTC were obtained (72.6% yield). ^{1}H and ^{13}C NMR and mass spectrometry were used to analyze the product and no impurities were detected (purity > 99%). ^{1}H NMR (δ ppm, $CDCl_3$): 4.68 (CH_2), 7.38 (aromatic H).

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MA061572S