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ORIGINAL CONTRIBUTION

Maggy Manguian
Maud Save
Christophe Chassenieux
Bernadette Charleux

Miniemulsion polymerization of styrene using well-defined cationic amphiphilic comblike copolymers as the sole stabilizer

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M. Manguian · M. Save (✉) · B. Charleux
Laboratoire de Chimie des Polymères,
UMR 7610 associée au CNRS,
Université Pierre et Marie Curie,
tour 44, 1er étage, case 185, 4 place Jussieu,
75252 Paris Cedex 05, France
E-mail: save@ccr.jussieu.fr

C. Chassenieux
Physicochimie des Polymères
et des Milieux Dispersés,
UMR7615, ESPCI-CNRS-UPMC,
10 rue Vauquelin, 75231 Paris cedex 05,
France

Abstract Well-defined, positively charged, amphiphilic copolymers containing long alkyl side chains were used as stabilizers in the miniemulsion polymerization of styrene. The copolymers were prepared by controlled free-radical copolymerization of styrene and vinyl benzyl chloride using either the reversible addition-fragmentation chain transfer method or TEMPO-mediated polymerization. The benzyl chloride moities were modified by two different long alkyl chain tertiary amines (*N*,*N*-dimethyldodecyl amine and *N*,*N*-dimethylhexadecyl amine) to yield the amphiphilic copolymers with vinylbenzyl dimethyl alkyl ammonium chloride units. Owing to their high structural quality, only a small amount of these copolymers was required to stabilize the latex particles (0.5–2 wt% vs styrene). Moreover, in the absence of any hydrophobic agent, the amphiphilic comblike copolymer preserved the colloidal stability of both the initial liquid miniemulsion and the final latex. Ill-defined, analogous copolymers were synthesized by conventional free-radical polymerization and in comparison, exhibited poor stabilization properties.

Keywords Radical polymerization · Miniemulsion · Amphiphilic copolymer · Polyelectrolyte · Reversible addition–fragmentation chain transfer · Nitroxide

Introduction

Miniemulsion polymerization [1–6] has become quite an important process in recent years, offering for instance the possibility to create hybrid particles by encapsulation of inorganic materials, [3, 7–9] also allowing to develop controlled free-radical polymerization [10, 11] and other polymerization chemistries [3, 12–15] in aqueous dispersed systems. The advantage of the process resides in the fact that the initial monomer-in-water emulsion is strongly sheared to produce small monomer droplets (100–500 nm), which can be directly nucleated and serve as microreactors for the polymerization. As in emulsion polymerization, the monomer droplets and polymer particles are stabilized against coalescence by the surfactant molecules. However, this is not sufficient to maintain constant initial droplet size, as Ostwald ripening is another cause of emulsion degradation [16]. This phenomenon could be avoided by the addition of a very hydrophobic agent in the dispersed phase, which counteracts the Laplace pressure of the droplet [2]. Various hydrophobes have been employed in miniemulsion polymerization and the most common one is certainly hexadecane [3, 5]. Nevertheless, to avoid the presence of an undesirable organic molecule in the final polymer, several alternatives were proposed. One of them consists in using a long alkyl chain comonomer (such as an acrylate or a methacrylate) [17, 18], which eventually incorporates itself in the polymer chains during the polymerization course. In principle, it has no detrimental effect on the polymer properties as far as it remains in fairly low amount. In other studies, a very hydrophobic initiator was used, such as lauroyl peroxide [19]. Another possibility was to replace the long alkyl chain comonomer by the corresponding copolymer, but for instance, Chern et al. [18] showed that stearyl methacrylate was a more efficient hydrophobe against Ostwald ripening than the corresponding poly(stearyl methacrylate-co-2-hydroxyethyl methacrylate) copolymer. A quite elegant, though different, solution was proposed by Landfester's group [20] with the use of very hydrophobic, charged copolymers, based on randomly distributed octadecyl methacrylate and acrylic or methacrylic acid monomer units (from 11 mol.% to 24 mol.%). With such a stabilizer, used in alkaline conditions, they showed that it was possible to obtain stable polystyrene latexes with particle diameters in the range of 100–250 nm by miniemulsion polymerization, without a hydrophobic agent or an additional surfactant. The stabilizer was initially mixed with monomer and water, and presumably reorganized itself at the monomer–water interface after mixing. However, large concentrations of the stabilizer were used, since the weight fraction of copolymer with respect to the monomer ranged between 1.7 wt% and 10 wt%.

In the present work, we applied well-defined, positively charged, amphiphilic copolymers containing long alkyl side chains as stabilizers for the miniemulsion polymerization of styrene. The copolymers were prepared by controlled free-radical copolymerization [21–23] of styrene and vinyl benzyl chloride using either the reversible addition-fragmentation chain transfer (RAFT) method [24–26] or TEMPO-mediated polymerization [27, 28]. The benzyl chloride moities were then modified by two different long alkyl chain tertiary amines (*N*,*N*-dimethyldodecyl amine and *N*,*N*-dimethylhexadecyl amine) to yield the amphiphilic copolymers with vinylbenzyl dimethyl alkyl ammonium chloride units. Our purpose was to test the efficiency of small concentrations of those macromolecular stabilizers, in the presence or in the absence of hexadecane as a hydrophobe. We also decided to compare them with an analogous copolymer prepared via conventional free-radical polymerization.

Experimental section

Materials

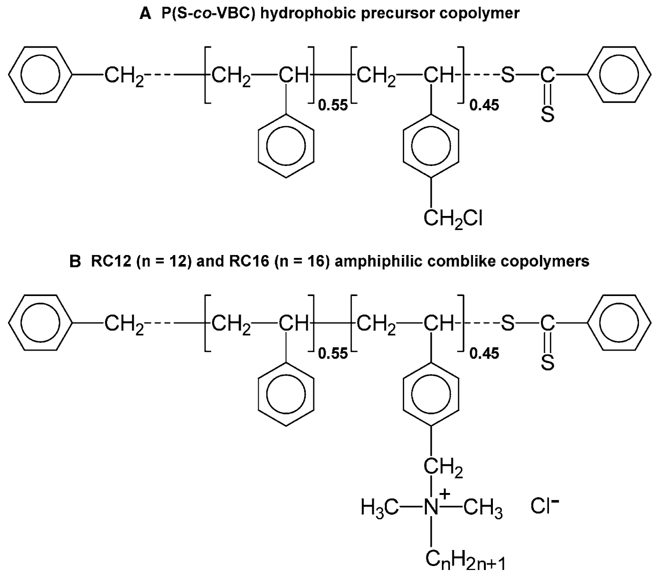
Styrene (S, Acros, 99% purity) was distilled under vacuum before use. 4-Vinylbenzyl chloride (VBC, Aldrich, 90% purity), hexadecane (HD, Aldrich, 99% purity), 2,2′-azobis(isobutyronitrile) (AIBN, Acros, 98% purity), 2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPO, Acros, 98% purity), 2,2′azobis(2-amidinopropane) dihydrochloride (V50, Aldrich, 97% purity), cetyltrimethylammonium chloride (CTACl) (Aldrich, 25% solution in water), *N*,*N*-dimethyldodecylamine (Aldrich, 98% purity), and *N*,*N*-dimethylhexadecylamine (TCI) were used as received. Benzyl dithiobenzoate (BDB) was synthesized and purified according to a protocol already described in Ladavière et al. [29].

Synthesis of the hydrophobic precursor copolymer

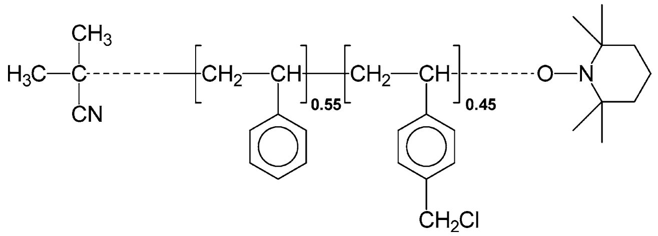
The P(S_{53}-*co*-VBC_{43}) copolymer was prepared by the controlled free-radical polymerization using the RAFT method, with benzyl dithiobenzoate as a reversible chain transfer agent. The polymerization was carried out in bulk at 90°C for 8 h, with the following concentrations: [S] = 4.8 mol L^{1}; [VBC] = 3.2 mol L^{1}; [BDB] = 0.019 mol L^{1} ; [AIBN] = 4.5×10^{-3} mol L^{1}; the molar proportion of VBC in the initial comonomer mixture was $f_{VBC,0} = 0.40$. Description of the polymerization procedure is given in Save et al. [30]. The overall monomer conversion, determined by ^{1}H NMR of the crude sample in $CDCl_3$, was 25%. The copolymer was then purified by two successive precipitations in ethanol and dried under vacuum, to completely remove the residual monomers. The number average molar mass was $M_n = 12{,}400$ g mol^{-1} (number average degree of polymerization: $DP_n = 96$) as measured by size exclusion chromatography (SEC) in THF, with a polydispersity index of 1.16 (theoretical $M_n = 14{,}000$ g mol^{-1}). The overall molar composition in VBC units was $F_{VBC} = 0.45$, based on the ^{1} H NMR analysis of the purified copolymer in $CDCl_3$ solution. General structure of the copolymer can thus be depicted as P(S_{53}-*co*-VBC_{43}), with the number of monomer units in the copolymer chains (see Scheme 1).

The P(S_{85}-*co*-VBC_{67}) copolymer was synthesized by controlled free-radical copolymerization in the presence of a stable nitroxide radical (TEMPO) (see Scheme 2). The polymerization was carried out in bulk at 130°C for 8 h and nearly complete conversion in monomer (> 90%) was reached. The reagent initial concentrations were [S] = 4.3 mol L^{-1}; [VBC] = 3.6 mol L^{-1}; [TEMPO] = 0.062 mol L^{-1}; [AIBN] = 0.031 mol L^{-1}. The final composition of the copolymer was $F_{VBC} = 0.45$ starting from $f_{VBC,0} = 0.45$. The number average molar mass of the purified polymer was 19,530 g mol^{-1} ($DP_n = 152$) with a polydispersity index of 1.38.

The P(S_{61}-*co*-VBC_{50}) statistical copolymer was synthesized by conventional free-radical polymerization using AIBN as an initiator at 70°C in bulk, as described in Chassenieux et al. [32]. The overall monomer conversion was 80%. The final molar composition was $F_{VBC} = 0.45$ starting from $f_{VBC,0} = 0.45$ and the average molar mass was 14,100 g mol^{-1} with a polydispersity index of 2.0.



Scheme 1 **a** Structure of the poly(styrene-co-vinyl benzyl chloride) copolymers prepared via controlled free-radical polymerization using the RAFT method and **b** structure of the quaternized conterparts



Scheme 2 Structure of the poly(styrene-co-vinyl benzyl chloride) copolymer prepared via TEMPO-mediated controlled free-radical polymerization

Synthesis of the cationic comblike copolymers

The copolymers were quaternized with *N*,*N*-dimethyldodecylamine or *N*,*N*-dimethylhexadecylamine in chloroform at room temperature for 48 h (amine/VBC = 2 mol/mol) to yield amphiphilic comblike copolymers (**RC12**, **RC16**, **NC12**, **CC12**), with respectively C_{12} or C_{16} alkyl side chains attached to the quaternary ammonium subunits (see Scheme 1 and Table 1). The resulting quaternized copolymers were then precipitated twice in diethylether, filtered, and dried under vacuum. The quaternization was complete for all experiments, based on the elemental analysis. The dithioester end-group of the copolymers prepared via RAFT remained stable during the quaternization step as the copolymers were still pink colored after precipitation and displayed a characteristic UV band with the maximum at 480 nm in water ($\lambda_{\mathrm{max,BDB}} = 500$ nm). It is thus possible that the copolymers played the role of a reversible chain transfer agent during the miniemulsion polymerization, hence favoring the anchoring of the stabilizer via chain extension. This role was however not assessed in this work, mainly for analytical reasons (the SEC analyses of quaternized amphiphilic copolymers is very difficult). In addition, the initial molar concentration of the copolymer was so low that the effect of control over the molar mass of the formed polystyrene would be difficult to detect. The TEMPO-based alkoxyamine end-group of one of the copolymers remained stable during the miniemulsion polymerizations carried out at 70°C, since it is far below the dissociation temperature of the C–ON bond. Table 1 summarizes the structure and composition of the copolymers used in this work.

Test of stability of the miniemulsions

The droplet size of the initial liquid miniemulsions stabilized by the cationic amphiphilic copolymer was assessed by dynamic light scattering (DLS). The miniemulsion was diluted with an aqueous solution saturated in styrene, and the droplet size was measured within 5 min of its preparation. For comparison, CTACl was used as a monomeric surfactant. The liquid miniemulsions were prepared by mixing 9 g of water with 2.3 g of styrene and 0.024 g of the stabilizer (4.8×10^{-5} mol of ammonium units for **RC12** and 8.2×10^{-5} mol of CTACl) under stirring for 15 min at room temperature. Then the miniemulsions were obtained by ultrasonication for 10 min in an iced water bath using a Branson Sonifier 450 (power 7). After the ultrasonication step, a part of the liquid miniemulsion was withdrawn for analysis at various time intervals between 2 min and 24 h.

Miniemulsion polymerizations of styrene

In a preliminary step, the oil-in-water unstable emulsions (20 wt% of styrene) were prepared by mixing the monomer phase with deionized water and the required amount of amphiphilic copolymer, under gentle stirring for 10 min at room temperature. The stable miniemulsions were then obtained by applying ultrasonication for 10 min in an iced water bath using a Branson Sonifier 450 (power 7). Depending on the experiment, the monomer phase was either pure styrene or a mixture of styrene and hexadecane (5 wt% based on S). The precise experimental procedure depended on the type of initiator (AIBN or V50). (1) When AIBN was used as an oil-soluble initiator it was also dissolved in styrene before sonication. Afterward, the sonicated, stable miniemulsion was subjected to nitrogen bubbling for 20 min, at 0°C and was then poured into a 0.25 L thermostated glass reactor, preheated at 70°C. Time 0 of the reaction

Table 1 Characteristics of the copolymers used in this work

Hydrophobic precursor copolymer	$f^{a}_{VBC,0}$	Final conv.%	F^{b}_{VBC}	Polymerization method and copolymer characteristics	Length of the alkyl chain	Quaternized copolymer
P(S_{53}-*co*-VBC_{43})	0.40	25	0.45	RAFT Narrow molar mass distribution Narrow composition distribution Uniform distribution along the chain	C_{12} C_{16}	**RC12** **RC16**
P(S_{85}-*co*-VBC_{67})	0.45	90	0.45	Nitroxide-mediated Narrow molar mass distribution Narrow composition distribution *Gradient composition along the chain*	C_{12}	**NC12**
P(S_{61}-*co*-VBC_{50})	0.45	80	0.45	Conventional free-radical *Broad molar mass distribution* *Broad composition distribution*	C_{12}	**CC12**

[a] $f_{VBC,0}$ = molar proportion of VBC in the initial comonomer mixture
[b] F_{VBC} = average molar proportion of VBC units in the copolymer

Table 2 Miniemulsion polymerizations of styrene using the **RC12** and the **RC16** amphiphilic comblike cationic copolymers as stabilizers

Entry	Copolymer		Hexadecane (wt% vs S)	Initiator	Conv. at 3 h (%)	D_z (nm) DLS	σ
	Structure	wt% vs S					
1	**RC12**	0.45	5	V50	98	130	0.02
2	**RC12**	0.45	0	V50	96	159	0.06
3	**RC12**	0.49	0	AIBN	86	124	0.17
4	**RC12**	0.95	5	V50	87	135	0.07
5	**RC12**	0.98	0	V50	97	113	0.13
6	**RC12**	0.98	0	AIBN	86	109	0.20
7	**RC12**	2.05	5	V50	91	127	0.07
8	**RC12**	1.78	0	V50	100	125	0.32
9	**RC12**	1.98	0	AIBN	92	116	0.20
10	**RC16**	0.44	5	V50	88	230	0.05
11	**RC16**	0.45	0	V50	91	330	0.10
12	**RC16**	1.94	5	V50	100	170	0.12
13	**RC16**	1.98	0	V50	93	180	0.03

Solids content = 20 wt%; initiator: 2,2′-azobis(2-amidinopropane)dihydrochloride (V50) or azobis(isobutyronitrile) (AIBN); initiator concentration = 0.007 mol L^{-1} $_{latex}$; T = 70°C

was arbitrarily taken when the temperature of the reaction medium reached 50°C. (2) When V50 was used as a water-soluble initiator, the sonicated stable miniemulsion was poured into the same type of preheated reactor and bubbled with nitrogen for approximately 20–30 min. At that stage, V50 was introduced into the medium, as a water solution, marking the time 0.

Polymerizations were allowed to proceed for 3 h or 6 h at 70°C and 300 rpm stirring speed, under a nitrogen atmosphere. Samples were taken at regular time intervals to follow the monomer conversion by gravimetry and analyze the particle size by dynamic light scattering. Tables 2 and 3 summarize the presented miniemulsion polymerizations.

Analytical techniques

The average molar mass and molar mass distribution of the P(S-co-VBC) precursor copolymer were obtained by size exclusion chromatography (SEC) in THF solution with a 1 mL mn^{-1} flow rate. The apparatus is composed of two linear columns (PSS SDV linear M 5 µm) thermostated at 40°C and two detectors: RI (LDC Analytical, refractorMonitor IV) and UV at 254 nm (Waters 484). The average molar masses were calculated from a calibration curve based on polystyrene standards (162–1090,000 g mol^{1}) from Polymer Standards Service.

Proton NMR analysis of the P(S-co-VBC) copolymer in $CDCl_3$ solution was performed in a 5 mm tube at room temperature using an AC250 Bruker sprectrometer, operating at a frequency of 250 MHz. The composition was calculated by integrating the aromatic protons of the styrene and VBC units (6.3–7.3 ppm) and the protons of the chloromethyl group of the VBC (4.5 ppm).

The average latex particle diameter (D_z) and polydispersity (σ; the lower σ, the narrower the particle size distribution) were measured by dynamic light scattering (DLS) using a Zetasizer 4 from Malvern. The droplet

Table 3 Miniemulsion polymerizations of styrene using the **CC12** and **NC12** amphiphilic comblike cationic copolymers as stabilizers

Entry	Copolymer		Hexadecane wt% vs S	Initiator	Conv. at 6 h (%)	D_z *(nm) DLS*	*σ*
	Structure	(wt% vs S)					
1	**CC12**	0.92	5	V50	70	310	0.13
2	**CC12**	0.92	0	V50	52	385	1.00
3	**CC12**	10	0	V50	100	185	0.18
4	**CC12**	0.92	0	AIBN	52	Coagulum	-
5	**CC12**	2.6	0	AIBN	56	Coagulum	-
6	**CC12**	10	0	AIBN	100	150	0.31
7	**NC12**	1.03	0	V50	92	177	0.05

Solids content = 20 wt%; initiator: 2,2′-azobis(2-amidinopropane)dihydrochloride (V50) or 2,2′-azobis(isobutyronitrile) (AIBN); initiator concentration = 0.007 mol $L^{-1}{}_{latex}$; $T = 70$°C

size measurements were performed with a Zetasizer Nano Series (S90) from Malvern Instrument. All diameters measured by DLS correspond to *Z*-average values. Transmission electron microscopy (TEM, JEOL JEM 100 cx II CHR) was also used to calculate the number-average particle diameter (D_n) and the particle size distribution (D_w/D_n) (500 particles were counted).

Results and discussion

1-Structure and properties of the amphiphilic copolymers

Composition microstructure of the P(S-*co*-VBC) precursor copolymers can be depicted on the basis of the terminal copolymerization model when the reactivity ratios are known. They were previously determined at 70°C: $r_{VBC} = 0.95$ and $r_S = 0.62$ [31]. We decided to use those values for the calculations, even though the copolymerizations were performed at different temperatures, assuming little temperature effect.

For the $P(S_{53}\text{-}co\text{-}VBC_{43})$ copolymer prepared by RAFT from an initial comonomer mixture of composition $f_{VBC,0} = 0.40$, one calculates that the theoretical average copolymer composition at 25% conversion is $F_{VBC} = 0.45$, as actually observed experimentally. At such a low conversion, the copolymer exhibits a negligible composition drift (1.6% of the overall composition) (see Fig. 1a). The average length of the polystyrene sequences is 1.96 units, and it is 1.61 for the P(VBC) sequences. These data give quite a good picture of the derived **RC12** and **RC16** amphiphilic comblike copolymers (see Table 1). They present indeed a very hydrophobic structure, from both the backbone and the alkyl side chains. However, at this composition, they are readily water-soluble and their aqueous solutions displayed gel characteristics, at concentrations as low as 0.7 wt% (7 g/L) for the C_{16} substituted copolymer and 9 wt% (90 g/L) for the C_{12} [32]. In both cases however, the copolymers were used in this study at concentrations remaining well below the gelation concentration. To summarize, the amphiphilic **RC12** and **RC16** copolymers exhibit a particularly well-defined structure, with homogeneous chain length, homogeneous composition and uniform distribution of the monomer subunits along the chain. Consequently, all chains have the same hydrophilic–lipophilic balance and the copolymers can be considered as model compounds.

Similarly to the copolymer prepared by RAFT, the $P(S_{85}\text{-}co\text{-}VBC_{67})$ copolymer prepared via TEMPO-mediated controlled free-radical polymerization exhibited a narrow molar mass distribution. However, because the polymerization was maintained up to large conversions (with RAFT the process was too slow to achieve the same goal within a reasonable time), it displayed a composition drift (Fig. 1b). Since in this controlled polymerization system the initiation was fast, all chains were created simultaneously in the early polymerization stage, and consequently exhibited the same composition with a gradient between both chain ends (they enriched in styrene with the conversion progress) [28].

In contrast to the other two precursor copolymers, the $P(S_{61}\text{-}co\text{-}VBC_{50})$ copolymer prepared via conventional free-radical polymerization exhibited a broad molar mass distribution, as well as a broad composition distribution. The composition drift is illustrated in Fig. 1b, which shows both the average and the instantaneous composition of the copolymer chains. In this type of synthesis, where chains are created continuously, a mixture of chains of different composition is obtained at the end of the copolymerization. In the selected system, those created initially from a comonomer mixture with $f_{VBC,0} = 0.45$ have a theoretical VBC molar fraction of 0.50, whereas it is 0.42 for those formed at 80% conversion.

The derived amphiphilic copolymers with C_{12} alkyl side chains (**CC12** for conventional radical polymerization and **NC12** for nitroxide-mediated polymerization) had thus the same average composition as **RC12**, along with a close average molar mass. They however differed,

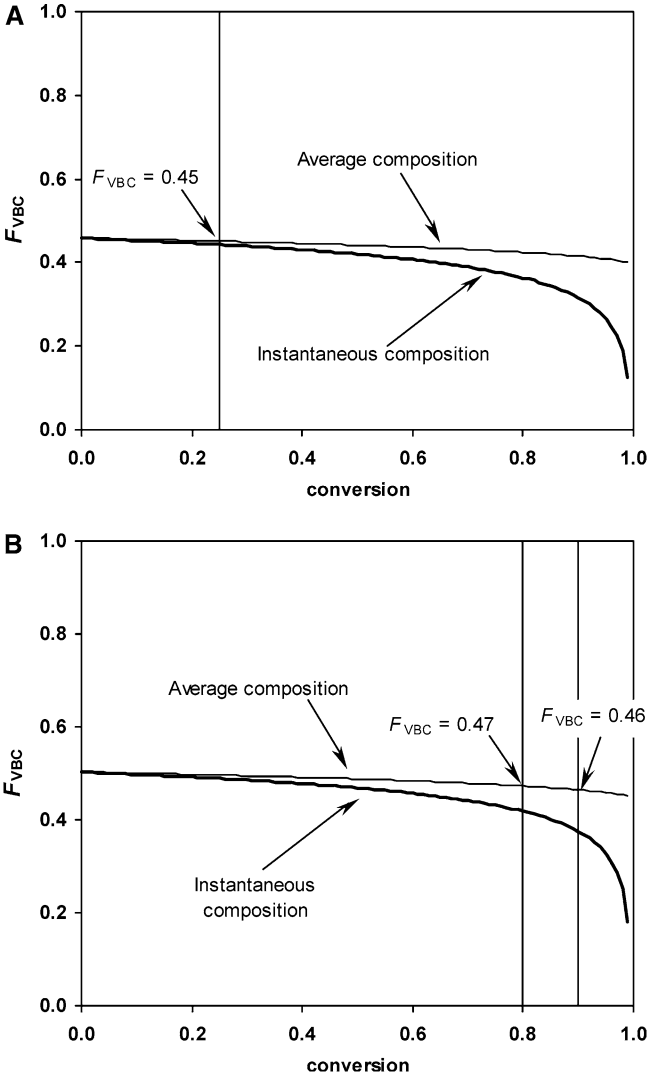


Fig. 1 Theoretical average and instantaneous compositions of the copolymers as a function of the overall molar conversion for two distinct compositions in the initial comonomer mixture. **a** Initial composition of the comonomer mixture: $f_{VBC,0}=0.40$ (polymerization via RAFT: final conversion = 25%) **b** Initial composition of the comonomer mixture: $f_{VBC,0}=0.45$ (TEMPO-mediated polymerization: final conversion = 90%; conventional free-radical polymerization: final conversion = 80%)

either in the composition microstructure only (**NC12**, gradient instead of uniform composition along the chain) or in both the composition distribution and the chain length distribution (**CC12**) (see Table 1).

2-Miniemulsion polymerizations

With both the **RC12** and **RC16** amphiphilic copolymers synthesized by RAFT, stable latexes were produced via a miniemulsion polymerization route, for copolymer concentrations as low as 0.5–2 wt%, based on the monomer (Table 2). It appeared, as illustrated in Table 2, that hexadecane was not really needed, in conjunction with the V50 initiator, to produce stable latexes via a miniemulsion process, whatever the structure of the stabilizer. Indeed, when this hydrophobe was removed, no significant change in the final particle size was observed. Additionally, to enhance droplet nucleation, a hydrophobic initiator, AIBN, was tested. As shown in Table 2, AIBN allowed production of stable latexes in the absence of hexadecane, irrespective of the initial concentration of stabilizer. With this neutral initiator, the final stability is the direct consequence of the charges provided by the copolymer stabilizer. Interestingly, the smallest diameters were observed with AIBN and ranged from 109 nm to 124 nm, quite independently of the amount of the **RC12** stabilizer. To obtain such good results without hexadecane, one has to assume that the amphiphilic comblike copolymers contribute to preserve the monomer droplet size at least during the nucleation period. This important point was assessed on the initial monomer-in-water sonicated miniemulsions.

In the absence of hexadecane, the sonicated miniemulsions were much more stable with the **RC12** amphiphilic copolymer than with cetyltrimethyl ammonium chloride (CTACl) as a surfactant. Indeed, as illustrated in Fig. 2, phase separation was clearly observed after 18 h for the miniemulsion stabilized with CTACl, whereas a styrene phase started to form at the top of the system only after 2 days with the quaternized copolymer. This result indicates that the latter has a significant effect on the stability of the initial monomer-in-water emulsion. When hexadecane was removed, the size of the droplets stabilized by the **RC12** copolymer increased respectively from 250 ± 20 nm (at 5 wt% HD) to 360 ± 20 nm (without HD). The polydispersity was higher in the absence of hexadecane, but in both cases, the liquid emulsion remained stable for 24 h after ultrasonication. When using the same weight percent of CTACl to stabilize the miniemulsion in the absence of hexadecane, the droplet size dramatically increased from 400 ± 20 nm just after the sonication step to 1,130 ± 20 nm at 24 h.

As shown in Table 2, concentrations of **RC12** and **RC16** as low as 0.5–2 wt% based on the monomer were sufficient to stabilize the miniemulsion polymerizations. Such a low efficient amount is supposed to be the direct consequence of the homogeneity in molar mass, in composition and hence in property of the copolymers prepared via RAFT, which was not the case for those used by Landfester et al. [20]. To test this hypothesis and confirm the usefulness of a controlled synthesis process, we decided to compare the efficiency of **CC12** (non-controlled polymerization) and **NC12** (controlled polymerization, but different composition microstructure) as stabilizers with that of **RC12**.

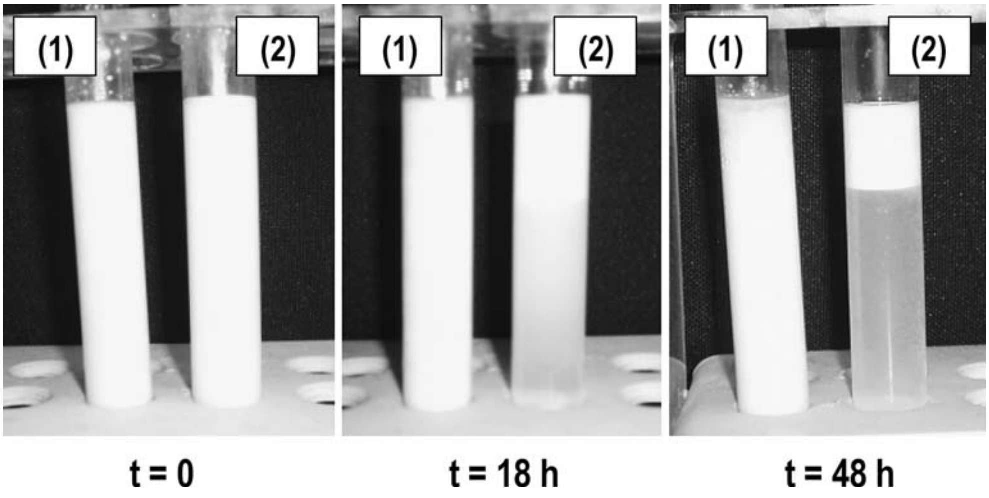


Fig. 2 Study of the stability of ultrasonicated miniemulsions with 20 wt% styrene in water, prepared without hexadecane. (*1*) 1.06 wt% of **RC12** based on styrene, (*2*) 0.92 wt% of cetyl trimethyl ammonium chloride based on styrene

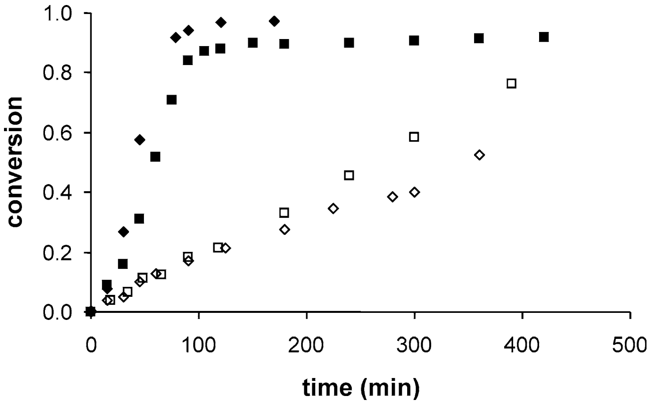


Fig. 3 Conversion vs time plots for the miniemulsion polymerization of styrene initiated by V50 and stabilized by the **RC12** and **CC12** amphiphilic copolymers. (*filled square*) 1 wt% **RC12**, 5 wt% hexadecane (Table 2, entry 4) (*filled diamond*) 1 wt% **RC12**, 0 wt% hexadecane (Table 2, entry 5) (*open square*) 1 wt% **CC12**, 5 wt% hexadecane (Table 3, entry 1) (*open diamond*) 1 wt% **CC12**, 0 wt% hexadecane (Table 3, entry 2)

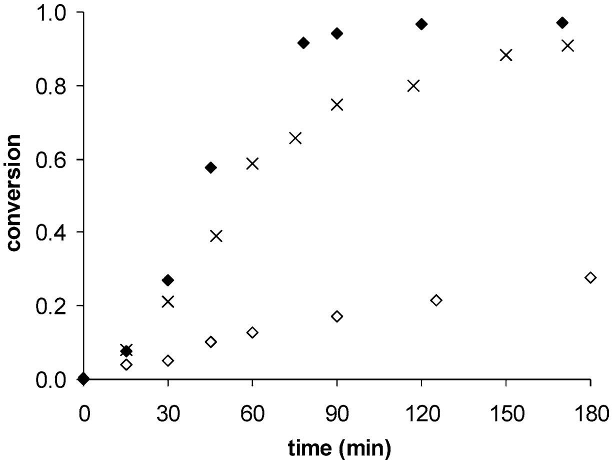


Fig. 4 Conversion versus time plots for the miniemulsion polymerization of styrene initiated by V50 and stabilized by the cationic amphiphilic copolymers, without hexadecane. (*filled diamond*) 1 wt% **RC12** (Table 2, entry 5), (*cross*) 1 wt% **NC12** (Table 3, entry 7), (*open diamond*) 1 wt% **CC12** (Table 3, entry 2)

For the experiments carried out with the hydrophilic initiator (V50) and whatever the hexadecane content, it is noteworthy that the polymerizations were slower when using the **CC12** copolymer instead of the **RC12** one (Fig. 3). In both cases, hexadecane had no influence on the kinetic plots (Fig. 3). In parallel, the particle diameters were much larger with the **CC12** stabilizer (Table 2, entries 4 and 5; Table 3, entries 1 and 2). Only when 10 wt% of **CC12** were used, the particle size was comparable (Table 3, entry 3). When a more hydrophobic initiator (AIBN) was selected to enhance the droplet nucleation, the absence of coagulum was observed only for a large amount of the **CC12** copolymer (10 wt% vs monomer, Table 3, entries 4–6), whereas the latexes were always very stable with **RC12**, even when it was used in very small amount. At this point, the drastic difference between the stabilization properties of both copolymers confirmed the previous assertion that a controlled polymerization method led to more efficient macromolecular stabilizers. To assess the effect of the composition drift, the stabilization properties of the **NC12** amphiphilic copolymer were also tested. Interestingly, they appeared to be quite close to those displayed by the **RC12** copolymer (see Fig. 4 for the kinetics and Table 3, entry 7 for the diameter). In consequence, it seems necessary to have amphiphilic copolymers with a narrow molar mass distribution together with a narrow composition distribution, but it is not necessary to have a uniform composition all along the chain. The important point seems that all chains exhibit the same composition, which is an important parameter for the amphiphilic properties. When using

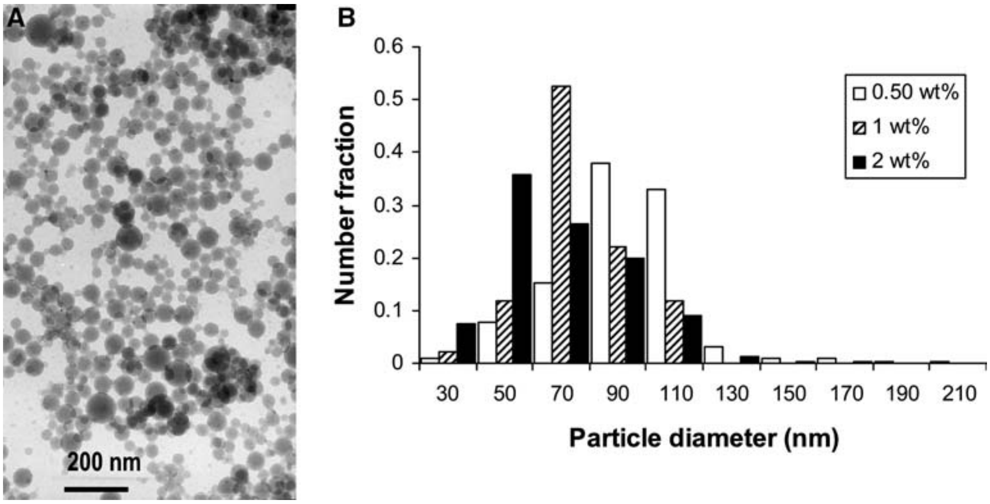


Fig. 5 Miniemulsion polymerization of styrene initiated by AIBN in the absence of hexadecane and stabilized by the **RC12** copolymer. **a** TEM of the final latex with 2 wt% of **RC12** (Table 2, entry 9); **b** Particle size distribution; *black bars*: 2 wt% of **RC12** (Table 2, entry 9), D_n = 70 nm, D_w/D_n = 1.30, D_z = 105 nm; *striped bars*: 1 wt% of **RC12** (Table 2, entry 6), D_n = 80 nm, D_w/D_n = 1.14, D_z = 95; *empty bars*: 0.5 wt% of **RC12** (Table 2, entry 3), D_n = 93 nm, D_w/D_n = 1.24, D_z = 124 nm

copolymers with a broad composition distribution, a fraction of the chains is useless, because they are either too hydrophobic or too hydrophilic, and do not contribute to the stabilization of the interface. The **NC12** copolymer with a gradient composition exhibits a good efficiency, although it seems a bit inferior to the model copolymer **RC12** with high composition uniformity (see Fig. 4; Table 3 entry 7 and comparison with Table 2 entry 5).

With the C_{16}-based copolymer, the final particle diameters were systematically larger than those obtained with the C_{12} counterpart (Table 2). Nevertheless, one should emphasize that, in contrast to **RC12**, the **RC16** copolymer was unable to produce stable latexes via conventional emulsion polymerization, in the same experimental conditions, whatever the copolymer content [30]. The high shear energy provided by the ultrasounds might favor the initial location of the copolymer at the monomer–water interface, whereas it certainly remained as inactive aggregates in the simple emulsion polymerization procedure.

The final diameters measured by DLS did not change very significantly with the **RC12** amphiphilic copolymer content, and only slightly decreased with the increase in **RC16** weight percent. The amphiphilic comblike copolymers used by Landfester et al. [20] did not behave very differently indeed, as only a slight decrease in diameter was noted when the copolymer content was raised from 1.7 wt% to 10 wt%, i.e over a much wider concentration range than that used in this work. However, the final latexes exhibited a rather broad particle size distribution, as illustrated by the TEM picture (Fig. 5), which makes the comparison of the DLS diameters given in Table 2 poorly meaningful. Nevertheless, the slight decrease of the number average diameters (D_n) with the increase in **RC12** stabilizer content, as calculated from the TEM analyses (Fig. 5), confirms the trend.

Conclusion

The cationic amphiphilic statistical copolymers based on styrene and vinylbenzylalkyl ammonium units proved to be efficient stabilizers for the styrene miniemulsion polymerization. The copolymers synthesized by controlled free-radical polymerization (either RAFT or TEMPO-mediated polymerization) displayed a narrow molar mass distribution and a homogeneous composition distribution. Owing to their high structural quality, only a small amount of these copolymers was required to stabilize the latex particles (0.5–2 wt% vs styrene) even in the absence of any hydrophobic agent. By opposition ill-defined homologue copolymers were synthesized by conventional free-radical polymerization and appeared to be far less efficient stabilizers.

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