Synthesis by RAFT of Amphiphilic Block and Comblike Cationic Copolymers and Their Use in Emulsion Polymerization for the Electrosteric Stabilization of Latexes

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ABSTRACT: A series of diblock and comblike copolymers based on styrene and 4-vinylbenzyl chloride were synthesized by reversible addition fragmentation transfer (RAFT) using benzyl dithiobenzoate as a control agent. After quaternization of the well-defined hydrophobic precursors with triethylamine, the micellar aggregates, formed by the cationic amphiphilic diblock copolymer when dissolved in water, were investigated by static and dynamic light scattering. The spherical shape of the micelles was established in salted water. Then, the poly(styrene)-*b*-poly(vinylbenzyltriethylammonium chloride) cationic diblock copolymers were used as a stabilizer for the emulsion polymerization of styrene and appeared to display very good stabilization properties. The ratio between the initial number of micelles and the final number of latex particles was particularly high, as a characteristic of the high mobility of the copolymer chains. Finally, we underlined the strong influence of salt on the nucleation step of the emulsion polymerization. The influence of the architecture of the copolymers on the stabilization of latexes has also been established by using random copolymers quaternized with *N*,*N*-dimethyldodecylamine, which led to cationic comblike copolymers. They were used for the first time as stabilizers for the emulsion polymerization of styrene. These amphiphilic copolymers proved to be good stabilizers in very low proportions (0.5−1 wt% styrene), which makes them valuable due to their simple synthesis.

Introduction

Aqueous emulsion polymerization is a widely applied process for free-radical polymerization because it is environmentally safe and offers many synthetic and application advantages.[1] The required surfactant or stabilizer plays a key role in stabilizing the suspension of submicrometer particles. It participates in the nucleation step and contributes to the creation of stable particles which can further grow by monomer propagation. Therefore, it affects the polymerization kinetics, which are directly related to the number concentration of latex particles.[1] Polymeric surfactants, and especially diblock copolymers, exhibit interesting properties in emulsion polymerization, owing to their low critical micelle concentration and their lower diffusion coefficient with respect to low-molecular-weight surfactants.[2] The various architectures and block lengths are additional parameters which can be tuned to provide the best stabilization properties for emulsion polymerization.[3] The polyelectrolyte block copolymers impart good stability to the latex particles during polymerization and future storage due to the 'electrosteric' stabilization, which is the combination of the steric repulsion and electrostatic effect.[4] The good anchorage of the hydrophobic block to the latex particle limits the desorption events observed with molecular surfactants,[5] and the hydrophilic block length should control the thickness of the latex corona.

Controlled free-radical polymerizations[6,7,8] are efficient techniques for the synthesis of well-defined amphiphilic copolymers. They were applied to a large range of monomers[9,10,11,12] and allowed to produce macromolecules with various topologies.[13,14] However, the number of publications on block copolymers containing cationic or cationizable sequences is considerably lower than that concerning the corresponding anionic structures.[3] Most of the examples are diblock copolymers based on vinylpyridine[15,16,17,18] or 4-vinylbenzyl chloride (VBC).[19] Other block copolymers containing methacrylic units with a tertiary amine developed in the recent years by Armes and co-workers[20] offer interesting properties for stimuli-responsive micelles, as their solubility can be tuned by changing the pH, the temperature, and/or the electrolyte concentration. All of these diblock copolymers served as reactive precursors in the synthesis of cationic polyelectrolytes by simple protonation at low pH[15,21,22] or permanent quaternization with alkyl halide[3,23] or amine.[19]

In emulsion polymerization, the electrosteric stabilization of latex particles induced by cationic polyelectrolyte is much less described than that induced by the corresponding anionic structures.[3,24,25] In the present paper, we focus our attention on cationic amphiphilic copolymers containing both vinylbenzyltrialkylammonium chloride and styrene (S) units for the synthesis of latex with a cationic hydrophilic shell. First, we investigated the synthesis of the hydrophobic diblock and statistical copolymers based on styrene and 4-vinylbenzyl chloride units by RAFT (reversible addition fragmentation transfer) polymerization, which has not been

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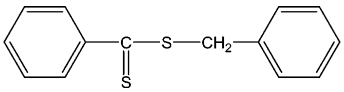
Scheme 1. Structure of *S*-(Benzyldithio)benzoate (BDB)



described previously for VBC. Derivatization of these copolymers using triethylamine for the diblock copolymer and long alkyl tertiary amines for the statistical copolymer led to cationic amphiphilic copolymers. Micellization of the poly(styrene)$_{12}$-*b*-poly(vinylbenzyltriethylammonium chloride)$_{62}$ [P(S)$_{12}$-b−P(VBTEAC)$_{62}$] cationic diblock copolymer in water was studied by static and dynamic light scattering. The cationic diblock copolymers served as stabilizers for the emulsion polymerization of styrene. The relationship between the final number of latex particles, N_p, and the amount of surfactant is discussed and compared to that previously established[26,27] for the analogous anionic poly(styrene)-*b*-poly(acrylic acid) [PS-*b*-PAA] block copolymers. Finally, the use of the cationic comblike amphiphilic copolymers poly(styrene-*co*-vinylbenzyldimethyldodecylammonium chloride) [P(S-*co*-VBDDAC)] and poly(styrene-*co*-vinylbenzyldimethylhexadecylammonium chloride) [P(S-*co*-VBDHAC)] derived from the statistical copolymers were used as stabilizers in emulsion polymerization of styrene.

Experimental Section

Materials. Styrene (S, Acros, 99%) was distilled under vacuum before use. 4-vinylbenzyl chloride (VBC, Aldrich, 90%), azobisisobutyronitrile (AIBN, Acros, 98%), 2,2′-azobis(2-amidinopropane)dihydrochloride (V50, Aldrich, 97%), *N*,*N*-dimethyldodecylamine (Aldrich, 98%), *N*,*N*-dimethylhexadecylamine (TCI), and triethylamine (Aldrich, 99%) were used as received. *S*-(Benzyldithio)benzoate, BDB (Scheme 1), was synthesized as previously described.[28]

Synthesis of the Precursor Copolymers. All the copolymers and homopolymers were prepared by controlled free-radical polymerization using the RAFT methodology in bulk. Experimental conditions are given in Table 1. For the synthesis of polystyrene (entry 3), the solution containing freshly distilled styrene (48 g, 0.461 mol), BDB (815 mg, 3.3×10^{-3} mol), and AIBN (60 mg, 3.7×10^{-4} mol) was poured into a tube, which was sealed after four freeze−pump−thaw cycles, and then immersed into an oil bath thermostated at 80°C for 2h. After polymerization, the reaction mixture was cooled and diluted with dichloromethane. The polystyrene (3.8 g) was recovered by precipitation in ethanol and dried under vacuum. Part of it (1.25 g, 8.2×10^{-4} mol) was used as a macro-RAFT agent for the synthesis of the PS$_{12}$-*b*-PVBC$_{62}$ block copolymer by mixing it with 4-vinylbenzyl chloride monomer (31 g, 0.205 mol) and AIBN (27 mg, 1.6×10^{-4} mol); then, the solution was poured into a tube, which was sealed after four freeze−pump−thaw cycles, and then immersed into an oil bath thermostated at 90°C for 48h. The block copolymer (10 g) was recovered by precipitation in ethanol and dried under vacuum.

In Table 1, the diblock copolymers 8, 9−10, and 11 were prepared using, respectively, polystyrene 1, 2, and 3 as macro-RAFT agents, and the diblock copolymer 7 was prepared using poly(4-vinylbenzyl chloride) 6 as macro-RAFT agent. The polymers 13 and 14 are statistical copolymers. Conversion were determined by ^{1}H NMR analysis of crude samples in CDCl$_3$.

Copolymer Quaternization. The precursor copolymers were quaternized by reaction with a tertiary amine (2-fold excess, amine/VBC = 2 mol/mol). In a typical recipe, the PS$_{12}$-*b*-PVBC$_{62}$ block copolymer (10 g, 9.2×10^{-4} mol, 5.7×10^{-2} mol of VBC units) was diluted in dichloromethane (140 mL); the appropriate amount of triethylamine (11.4 g, 0.113 mol) was then added, and the solution was stirred at room temperature for 48 h. The excess of dichloromethane was evaporated, and the resulting quaternized copolymer (15 g) was then precipitated twice in diethyl ether and dried under vacuum. The degree of quaternization was calculated from elemental analysis. It was found that 84% and 92% of VBC units were derivatized by triethylamine for the diblock copolymers PS$_{12}$-*b*-PVBC$_{62}$ and the homopolymer PVBC$_{40}$, respectively. The derivatization of the statistical copolymers P(S-*co*-VBC) was carried out according to the same procedure in chloroform, but the amine used was either *N*,*N*-dimethyldodecylamine or *N*,*N*-dimethylhexadecylamine and the derivatization was complete for all experiments.

Analytical Techniques. The average molar mass and molar mass distribution of the copolymers were obtained by size exclusion chromatography (SEC) in THF with a 1 mL/min flow rate. The apparatus was composed of three linear columns (3 PSS SDV 8 mm × 300 mm, 5μm) thermostated at 40°C and of two detectors: RI (LDC Analytical, refractorMonitor IV) and UV operating at 254 nm (Waters 484). The sample concentrations were 5 mg/mL. The molar masses were calculated from a calibration curve based on polystyrene standards. A triple detector system composed of a RI detector, a viscometer (intrinsic viscosity measured online), and a light scattering detector ($\lambda = 670$ nm, power = 3 mW, 90° scattering angle) in THF was used for some analyses. In this case, the concentration of the injected samples was 20 mg/mL.

^{1}H NMR (250 MHz) analyses of the hydrophobic precursor copolymers were performed in CDCl$_3$ in 5 mm tubes at room temperature using an AC250 Bruker spectrometer. The composition of the statistical copolymer was calculated on the basis of the integrals of the aromatic protons of both styrene and VBC units (6.3−7.3 ppm) and of the integrals of the protons corresponding to the chloromethylene group of the VBC units (4.5 ppm). The quaternized amphiphilic block copolymers were analyzed in d$_4$-methanol.

Light scattering. The analyzed P(S)$_{12}$-b−P(VBTEAC)$_{62}$ diblock copolymer was dissolved in pure deionized water, and a solution of NaCl was added into the vials (1 vol H$_2$O + 1 vol solution 20 mM or 100mM NaCl). The solutions at different concentrations of polymer (from 0.5 to 8 g/L) were stored for several days at room temperature. They were then filtered through 0.45 μm Millipore filters and directly used for the light scattering measurements performed at 25 °C. In all cases, the solutions were not difficult to filter and were perfectly clear. Light scattering measurements were performed with a Malvern goniometer in combination with a Spectra Physics laser operating at $\lambda = 514.5$ nm. The scattered photons were collected by an ALV photomultiplier and analyzed by an ALV-5000 multibit, multitau full digital correlator. This experimental setup allowed the measurements of the correlation functions ($g_2(t)$) and of the mean scattered intensity along an angular angle (θ) ranging from 30° to 140°. Since both the correlation functions and the scattered intensity were similar before and after filtration, we assumed that no significant amount of polymer was removed.[29] The experimental setup and the details concerning the treatment of the data have been previously published.[27] Briefly, one should emphasize that static light scattering (SLS) allows the measurement of structural parameters such as the weight average molar mass (M_w) and the radius of gyration (R_g) of the investigated particles after an extrapolation to zero angle and to zero concentration once the refractive index increment is known ($dn/dc = 0.14$ mL/g for our copolymers). This value of d*n*/d*c* has been measured with a Thermofinnigan RI-150 differential refractometer operating at 25°C with white light and without calibration. Moreover, thermodynamical parameters, such as the second virial coefficient (A_2), are also accessible by following the concentration dependence of the scattered intensity.[30]

In the same way, dynamic light scattering (DLS) measures the hydrodynamic radius of the particles (R_H), the mutual diffusion coefficient (D_0), and the dynamic virial coefficient (k_D) if the dynamics that are probed are diffusive, i.e., if the measured relaxation times are q^2 dependent, where q is the wave vector.[31] Along the angular and concentration ranges investigated, a single relaxation process was measured and

Table 1. Synthesis of Copolymers Based on Styrene (S) and Vinylbenzyl Chloride (VBC) by RAFT Polymerization

entry	polymer[a]	T °C	time h	conv	CTA	[AIBN] mol/L	[monomer] mol/L	[CTA] mol/L	[monomer] /[CTA]	$\bar{M}_n$ theo[b] g/mol	$\bar{M}_n$ SEC g/mol	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$ SEC[d] g/mol
1	$P(S)_{23}$	60	23	0.14	BDB	7.0×10^{-3}	8.7	6.5×10^{-2}	134	2200	2680	1.33	–
2	$P(S)_{17}$	60	16	0.11	BDB	7.0×10^{-3}	8.7	6.0×10^{-2}	145	1900	2020	1.21	–
3	$P(S)_{12}$	80	2	0.08	BDB	6.9×10^{-3}	8.7	6.3×10^{-2}	138	1390	1520	1.21	–
4	$P(VBC)_{40}$	130	5	0.26	BDB	1.0×10^{-2}	7.1	3.6×10^{-2}	200	8150	6290	1.32	7440
5	$P(VBC)_{47}$	60	60	0.26	BDB	1.0×10^{-2}	7.1	3.6×10^{-2}	200	8150	7440	1.35	8200
6	$P(VBC)_{20}$	80	2.5	0.15	BDB	1.0×10^{-2}	7.1	1.0×10^{-1}	71	1860	3340	1.30	–
7	$P(VBC)_{20}$-*b*-$P(S)_{67}$	90	24	0.47	$P(VBC)_{20}$	7.7×10^{-3}	8.7	5.8×10^{-2}	150	10600	10350	1.28	–
8	$P(S)_{23}$-*b*-$P(VBC)_{59}$	90	48	0.30	$P(S)_{23}$	5.6×10^{-3}	7.1	2.8×10^{-2}	250	14080	11600	1.25	13030
9	$P(S)_{17}$-*b*-$P(VBC)_{51}$	90	39	0.21	$P(S)_{17}$	4.0×10^{-3}	7.1	3.0×10^{-2}	237	9730	9840	1.15	
10	$P(S)_{17}$-*b*-$P(VBC)_{52}$	90	34	0.29	$P(S)_{17}$	6.0×10^{-3}	7.1	3.0×10^{-2}	237	12330	10000	1.27	
11	$P(S)_{12}$-*b*-$P(VBC)_{35}$	90	48	0.18	$P(S)_{12}$	6.6×10^{-3}	7.1	3.3×10^{-2}	212	7260	6850	1.27	–
12	$P(S)_{12}$-*b*-$P(VBC)_{62}$	90	48	0.30	$P(S)_{12}$	5.7×10^{-3}	7.1	2.8×10^{-2}	250	13680	10800	1.38	–
13	P(S-*co*-VBC)$_{102}$	90	8	0.25	BDB	4.5×10^{-3}	c	1.9×10^{-2}	425	14000	12400	1.16	–
14	P(S-*co*-VBC)$_{52}$	70	8	0.22	BDB	6.7×10^{-3}	c	3.3×10^{-2}	242	7050	6300	1.29	8250

[a] $P(S)_x$ or $P(VBC)_x$ with x equal to the number average degree of polymerization calculated from SEC. [b] M_n (theoretical) = M (CTA) + [Monomer]/[CTA] × conversion × $M_{monomer}$. [c] [VBC] = 3.2 mol/L, [S] = 4.8 mol/L; final composition of the copolymer: S/VBC = 55:45. [d] SEC with a triple detection.

always fulfilled the above condition. The relative error bar on the values for R_H is 8%.

Polymerization in Aqueous Dispersed Media. Emulsion polymerizations were performed at 70 °C under nitrogen in a conventional 0.25 L thermostated glass reactor equipped with a condenser. In a typical procedure, 0.68 g of the [$P(S)_{12}$-*b*-$P(VBTEAC)_{62}$] cationic block copolymer (4.2×10^{-5} mol, M_n = 16240 g/mol) and 134 g of deionized water were stirred for 15 min at room temperature, the solution was filled in the reactor and purged with nitrogen under stirring at 300 rpm for 45 min at 70 °C, and the styrene (34 g) was introduced and degassed for 20 min. The emulsion polymerization started by adding the aqueous solution of initiator (0.3 g V50, 1.1×10^{-3} mol, 4 g water), which corresponded to time zero. The polymerization time was 5 h to reach a complete conversion, and samples were withdrawn under a nitrogen flow every 30 mn in order to follow the monomer conversion and the latex particle diameter.

Latex Characterization. The monomer conversion was determined by gravimetry. The particle diameter was measured by DLS at 25 °C and an angle of 90° with a Zetasizer 4 from Malvern, using a 5 mW He–Ne laser at 633 nm, and by transmission electron microscopy (TEM, JEOL JEM 100 cx II CHR, 500 particles were counted). The diameter measured by DLS was a *z*-average diameter, and the diameter calculated by TEM was either a number (D_n)-, weight (D_w)-, or *z*-average diameter (D_z) (see Table 6).[32] The number concentration of latex particles, N_p, per liter of the suspension (particle + water) was calculated according to eq 1 (ref 1).

$$N_p = \frac{6\tau_p}{d_p \pi D_p^{\,3}}\,(\mathrm{L^{-1}}_{\mathrm{latex}}) \tag{1}$$

with D_p being the particle diameter expressed in cm, d_p being the polystyrene density (d_p = 1.05 g cm^{-3})[33] and τ_p is the polymer content (g/L$_{latex}$).

Results and Discussion

1. Synthesis. 1.1. Synthesis of the Precursor Hydrophobic Diblock Copolymers.

The controlled polymerization of VBC requires methods that do not interact with the chloromethyl group. Therefore, cationic, anionic, and atom transfer radical polymerizations (ATRP) are precluded, and only nitroxide-mediated polymerization using TEMPO as a mediator has actually been reported in the literature.[19,34,35,36]

We investigated the synthesis of poly(styrene)-*b*-poly(4-vinylbenzyl chloride) and poly(styrene-*co*-4-vinylbenzyl chloride) by RAFT polymerization expecting less side reactions compared to the nitroxide-mediated polymerization[19,36] and a good control over the copolymer structure. The 'reversible addition–fragmentation transfer' developed by Rizzardo et al.[37] and the MADIX[38] process are the most recent controlled radical polymerization methods. They are based on a rapid and reversible transfer of the growing radical-to-thiocarbonyl thio compounds. To our knowledge, no polymerization of VBC monomer by RAFT has been reported, although the method would be fully compatible with the chloromethyl group.

The polystyrene and poly(4-vinylbenzyl chloride) homopolymers were synthesized by RAFT polymerization between 60 and 130 °C using BDB, which proved to be a suitable chain transfer agent (CTA) for the controlled radical polymerization of styrene by RAFT.[39,40] The PS and PVBC macro-RAFT agents were used to carry out the P(S)-b–P(VBC) and P(VBC)-b–P(S) diblock copolymer syntheses at 90 °C, respectively (see Table 1). The retardation effect[41] described for styrene homopolymerization by RAFT was also observed here for the copolymerization of styrene and 4-vinylbenzyl chloride, as the conversions achieved after a given polymerization time (typically 48 h) were affected by the concentration of the chain transfer agent (Table 1, entries 11–12) and were lower than for a conventional free radical polymerization.[42] In addition, the use of AIBN with a rather short lifetime at 90 °C ($t_{1/2} \approx 20$ min) did not allow the reaction to reach a complete conversion in a reasonable polymerization time. As reported in Table 1, homopolymers, statistical polymers, and diblock copolymers displayed a narrow molar-mass distribution, and the experimental molar masses were close to the theoretical ones. The SEC chromatogram overlay (Figure 1) demonstrates that no residual polystyrene was present in the P(S)-*b*-P(VBC) diblock copolymer, in contrast with TEMPO-mediated polymerization.[19] By plotting the experimental molar masses of the diblock copolymer versus conversion, we observed a linear evolution of the degree of polymerization of the second block and polydispersity indexes below 1.3 (Figure 2). Comparison of the experimental molar masses with the theoretical ones indicated that 98% of the polystyrene chains were consumed[39] and were active as RAFT agents to control the synthesis of the diblock copolymer starting from the [macro-RAFT]/[AIBN] = 7.5 ratio.

In Figure 2, the theoretical molar masses were calculated according to eq 2 for the PS-*b*-PVBC block

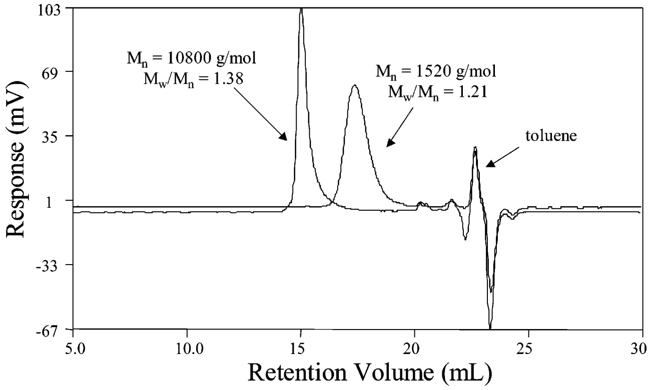


Figure 1. SEC chromatogram of the $P(S)_{12}$-*b*-$P(VBC)_{62}$ diblock copolymer synthesized by RAFT polymerization using BDB. First block: see Table 1, entry 3. Diblock copolymer: see Table 1, entry 12.

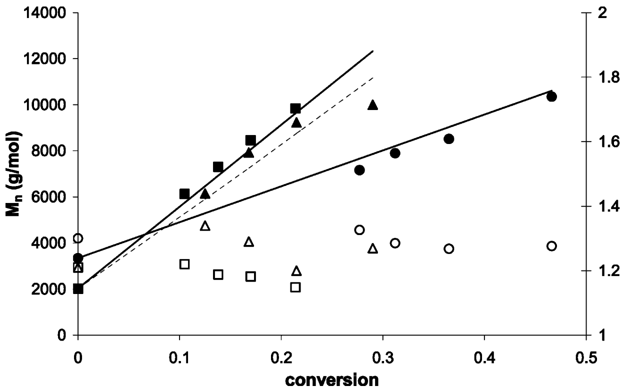


Figure 2. Synthesis of the diblock copolymers PS-*b*-PVBC and PVBC-*b*-PS by RAFT. Dependence of molar mass and polydispersity on monomer conversion for the second block. (A) PS first block (see entry 2 in Table 1); PVBC second block (see Table 1, entry 9 for *squared symbols* and Table 1, entry 10 for *triangular symbol*). (■)(▲) $\bar{M}_n$(SEC) of PS-*b*-PVBC; (□)-(△) $\bar{M}_w/\bar{M}_n$; (—) $\bar{M}_{n,\mathrm{theoretical}}$ (see eq 2); (- - -) $\bar{M}_{n,\mathrm{theoretical}}$ (taking into account the chains initiated by AIBN, see note 43). (B) PVBC first block (see Table 1, entry 6); PS second block (see Table 1, entry 7). (●) $\bar{M}_n$(SEC) of PVBC-*b*-PS; (○) $\bar{M}_w/\bar{M}_n$; — $\bar{M}_{n,\mathrm{theoretical}}$ (see eq 3).

copolymer and according to eq 3 for the PVBC-*b*-PS diblock copolymers.[43]

$$\bar{M}_{n,\mathrm{theoretical}} = 2020 + [\mathrm{VBC}]_0/[\mathrm{PS}]_0 \times 152 \times \mathrm{conversion} \quad (2)$$

$$\bar{M}_{n,\mathrm{theoretical}} = 3340 + [\mathrm{S}]_0/[\mathrm{PVBC}]_0 \times 104 \times \mathrm{conversion} \quad (3)$$

If we increased the initiator concentration and consequently decreased the [macro-RAFT]/[AIBN] ratio to 5, we observed higher polydispersity indexes and a loss of linearity of the M_n vs conversion plot beyond 22% conversion, which was not assigned to larger concentration of AIBN (Figure 2). This might be due to chain transfer reactions to the chloromethyl group of monomer or of polymer, which could produce branched structures and affect the hydrodynamic volume of the chains.[44] Some of the synthesized polymers were characterized by SEC with a triple detection system to get more-accurate molar masses (Table 1, entries 4, 5, 8, and 14). The absolute molar masses were slightly higher than the molar masses derived from a polystyrene calibration. Possible inaccuracy of the PS calibration for polymers containing a significant fraction of P(VBC) could be explained either by the presence of the halogenated functional group or by the existence of few branches.[45]

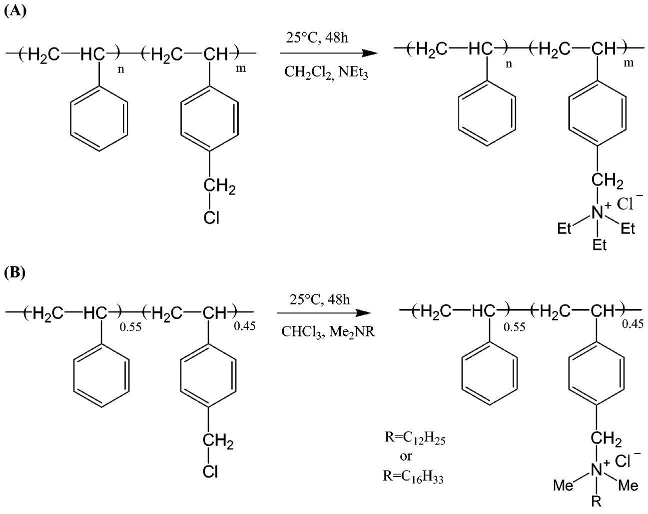


Figure 3. Quaternization of the hydrophobic precursor copolymers containing VBC units. (A) Diblock copolymers and (B) statistical copolymers.

When starting from a PVBC macro-RAFT agent, the experimental molar mass values of the P(VBC)-*b*-P(S) block copolymer were close to the theoretical ones (Table 1, entry 7) and a linear evolution of M_n with conversion was observed up to 45% conversion (Figure 2); the copolymerization exhibited a controlled character.

In conclusion, the block copolymerization of vinyl benzyl chloride and styrene monomers by RAFT was well controlled. Whatever the choice of the starting block, there was no residual homopolymer in the block copolymer.

1.2. Synthesis of the Precursor Hydrophobic Statistical Copolymers. The statistical copolymers synthesized by RAFT using BDB as a chain-transfer agent displayed narrow molar-mass distributions (Table 1, entries 13 and 14). The composition of the final copolymer (45:55 mol/mol VBC/S) was reached starting from a molar ratio of the monomer that was 40:60 mol/mol VBC/S. From the values of the reactivity ratios ($r_{\mathrm{VBC}} = 0.95$ and $r_{\mathrm{sty}} = 0.62$ at 70 °C [42]), both units are randomly distributed inside the copolymer with an homogeneous composition due to the simultaneous growth of the chains in a controlled radical polymerization mechanism.

1.3. Quaternization of the Hydrophobic Copolymers. The well-defined diblock copolymers described above can act as precursors for the synthesis of positively charged amphiphilic copolymers (Figure 3). The PVBC block of the P(S)-*b*-P(VBC) diblock copolymers was derivatized by triethylamine to form a water-soluble cationic polyelectrolyte block. After quaternization of the statistical copolymers with *N*,*N*-dimethyldodecylamine or *N*,*N*-dimethylhexadecylamine, the amphiphilic comblike copolymers exhibited a polystyrene backbone with amphiphilic and hydrophobic units. Similar water-soluble polymers based on dimethylhexadecylamine were previously synthesized using conventional radical polymerization,[46] and their aqueous solutions displayed gel characterictics at concentrations as low as 2 wt%/H_2O. We used these copolymers as stabilizers for polymerization in aqueous-dispersed media below the critical overlap concentration. The dithioester end-group

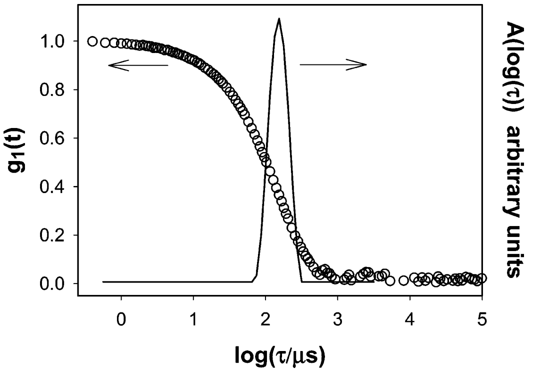


Figure 4. Normalized autocorrelation function measured for the $P(S)_{12}$-*b*-$(VBTEAC)_{62}$ copolymer at 1 g/L in pure water (angle of observation = 90°). The solid line corresponds to the calculated single-peak distribution of relaxation times.

of the copolymers remained stable during the quaternization step, as the polymer was still pink colored after precipitation and displayed a characteristic UV band at 480 nm in water ($\lambda_{BDB} = 500$ nm).

2. Aggregation of the $P(S)_{12}$-*b*-$P(VBTEAC)_{62}$ Cationic Diblock Copolymer in Water. For the system based on the $P(S)_{12}$-*b*-$P(VBTEAC)_{62}$ diblock copolymer, we did not detect any slow mode nor upturns in the angular dependence of the scattered light, even in the absence of salts, which can be correlated to the absence of 'polyelectrolyte effect'.[47] (Figure 4).

2.1. Determination of the Aggregation Number (N_{agg}). Table 2 reports the values of M_w, R_g, and A_2, which can be extracted from the SLS experiments. $M_{w,aggregate}$ is of particular interest because it allows us to get an estimate of the weight-average aggregation number according to eq 4 ($M_{w,copolymer}$ is calculated using the experimental value of M_w (SEC) of the $P(S)_{12}$-*b*-$P(VBC)_{62}$ hydrophobic copolymer and the degree of quaternization by triethylamine (85%)).

$$N_{agg} = \frac{M_{w,aggregates}}{M_{w,copolymer}} \tag{4}$$

The aggregation number for the $P(S)_{12}$-*b*-$P(VBTEAC)_{62}$ cationic block copolymer was between 12 and 47, depending on salt concentration (C_s: 0, 0.01, and 0.05 M NaCl) (Table 2). The values of N_{agg} were small compared to the values obtained for analogous anionic amphiphilic copolymers based on polystyrene and poly(potassium acrylate) blocks.[27,29] Nevertheless, they were in agreement with micelles formed by cationic diblock copolymers, such as poly(styrene)-*b*-poly(4-vinylpyridinium iodide), for which the aggregation numbers ranged from 37 in water to 42 in the presence of salts ([KI] = 7 mM).[2] It is interesting to note that the aggregation number was a function of the salt concentration (Table 2). As the copolymer was first dissolved in pure water before the addition of salt, the increase in N_{agg} with increasing the salt concentration was consistent with a dynamic exchange between the micelles and unimers. Moreover, according to O'Driscoll's data,[48] the T_g of the poly(styrene) block with a low degree of polymerization is only 23 °C (DP = 12). The micelles based on the $P(S)_{12}$-*b*-$P(VBTEAC)_{62}$ block copolymer appeared to have a *nonfrozen* structure.

In these systems, the parameter controlling the aggregation is the interchain distance, *b*, between corona copolymer segments. This distance can be calculated assuming b^2 is the surface area of one copolymer at the core/corona interface. The value of *b* can be calculated as follows (eq 5).

$$b^2 = \frac{4\pi R_c^{\ 2}}{N_{agg}} \tag{5}$$

R_c is the micellar core radius, which can be determined assuming a spherical geometry and the space filling conditions (eq 6)

$$\frac{4}{3}\pi R_c^{\ 3} = \frac{N_{sty}M_{sty}}{d_p N_A}N_{agg} = \nu_0 N_{agg} \tag{6}$$

where N_{sty} is the number of styrene repeat units, M_{sty} is the molar mass of styrene, N_A is the Avogadro number, d_P is the density of polystyrene, and ν_0 is the molar volume of a styrene monomer unit. The interchain distance, *b*, between corona and copolymer segment in the case of the cationic diblock copolymer $P(S)_{12}$-*b*-$P(VBTEAC)_{62}$ (1.5−1.6 nm, Table 2) was higher than the interchain distance, *b*, for the analogous anionic copolymer $P(S)_{10}$-*b*-$P(AK)_{56}$ (*b* = 1.14 nm, 20 mM salt).[27] This result is consistent with the chemical structure of the hydrophilic blocks since the volume of a potassium acrylate unit is smaller than the volume of a vinyl benzyl unit derivatized by a bulky triethylammonium chloride group.

2.2. Characterization by Dynamic Light Scattering. DLS enabled us to determine R_H, the hydrodynamic radius. By subtracting the contribution of the micellar core to R_H, the thickness of the hydrophilic corona, δ, can be estimated (Table 3). In our case, increasing the salt concentration induced a shrinkage of the corona, which was fully stretched in pure water (Table 3). This can be attributed to a screening effect and can be correlated to the decrease of the virial coefficients, A_2 and k_D (Table 2). The system was probably in a *"salted brush"* regime.[49]

Last, the ratio between the gyration radius (R_g) and the hydrodynamic radius (R_H) gave interesting information about the micellar structure. The values of R_g determined by static light scattering were in a low range (below 25 nm) for accurate measurements, but they were close to the R_H values measured by dynamic light scattering. A special attention can be focused on the experimental R_g/R_H value obtained in 0.05 mM NaCl solution ($R_g/R_H = 0.9$, Table 2) which is in favor of a spherical shape, as the theory predicts $R_g/R_H = 0.8$ for dense spherical micelles.[50]

3. Emulsion Polymerization of Styrene. The purpose of this work was to investigate the efficiency of the amphiphilic diblock and comblike copolymers based on styrene and vinylbenzyltrialkylammonium chloride units as stabilizers for the emulsion polymerization of styrene in water. Previous studies showed the ability of these permanent cationic copolymers to act as stabilizer for emulsion polymerization. Burguière et al.[24] presented only preliminary results and Jaeger and co-workers[25] used more-hydrophobic systems (≤50% of vinylbenzyltrimethylammonium chloride), which had to be heated for solubilization, and they focused their attention on the influence of the block length but not on the amount of copolymer.

Among the various possible criteria to compare the stabilization efficiency, the final diameter and then the final number of particles were considered as a function

Table 2. Characterization of the $P(S)_{12}$-*b*-$P(VBTEAC)_{62}$ Diblock Copolymer in Salted and Pure Water by Static Light Scattering (All Measurements Were Carried Out at 25 °C)

entry	solvent	M_w (g/mol) micelle	A_2 (mol mL/g^2)	N_{agg}	R_g (nm)	R_g/R_H[a]	b (nm)[b]
1	H_2O	469 500	3.8×10^{-5}	23	–	–	1.6
2	10 mM NaCl in H_2O	757 600	1.4×10^{-5}	38	17	1.1	1.5
3	50 mM NaCl in H_2O	862 000	-8.7×10^{-6}	43	14	0.9	1.5

[a] R_H from DLS, see Table 3. [b] According to eq 5.

Table 3. Characterization of the $P(S)_{12}$-*b*-$P(VBTEAC)_{62}$ Diblock Copolymer in Salted and Pure Water by Dynamic Light Scattering (All Measurements Were Carried Out at 25 °C)

entry	solvent	D_0 (m^2/s)	k_D (L/g)	R_H (nm)	V_{core} (nm^3)	R_c (nm)	$\delta_{corona} = R_H - R_c$ (nm)	% extension[a]
1	H_2O	$1.3\ 10^{-11}$	1.9×10^{-2}	19	45	2.2	16.8	>100
2	10 mM NaCl in H_2O	$1.5\ 10^{-11}$	-2.1×10^{-2}	16	74	2.6	13.4	86
3	50 mM NaCl in H_2O	$1.6\ 10^{-11}$	-2.4×10^{-2}	15	82	2.7	12.3	79

[a] % extension = $[\delta_{corona}(\exp)/\delta_{corona}(\text{theo})] \times 100$; $\delta_{corona}(\text{theo})$ is the theoretical upper limit calculated by $0.25N_{VBC}$, where 0.25 nm is the length of a fully extended monomer unit ($\delta_{corona}(\text{theo}) = 15.5$ nm).

Table 4. Emulsion Polymerization of Styrene with 2 wt% (Based on Monomer) of the P(S)-*b*-(VBTEAC) Amphiphilic Cationic Diblock Copolymers as Stabilizers. Final Characteristics of the Latex as a Function of the Degree of Polymerization of Each Block. 2 wt% of Copolymer Relative to the Amount of Monomer[a]

entry	DP (PS)	DP (VBTEAC)	% hydrophilic	[copolymer] 10^{-4} mol/L$_{latex}$	diameter nm	N$_p$ (final) 10^{16} L$_{latex}^{-1}$
1	12	62	83	2.3	280	1.60
2	12	35	74	3.9	310	1.26
3	23	59	72	2.2	330	0.99

[a] [V50] = 0.006 mol/L$_{latex}$, T = 70°C, solid content: 20 wt% Sty/H_2O, conversion = 100%.

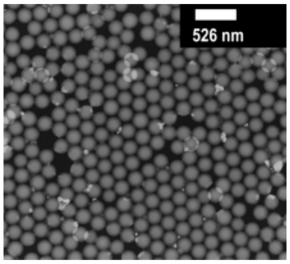


Figure 5. Transmission electron microscopy (TEM) of a latex synthesized with 1 wt% of $P(S)_{12}$-*b*-$(VBTEAC)_{62}$ stabilizer relative to the amount of monomer. See entry 2 in Table 6 for the experimental conditions.

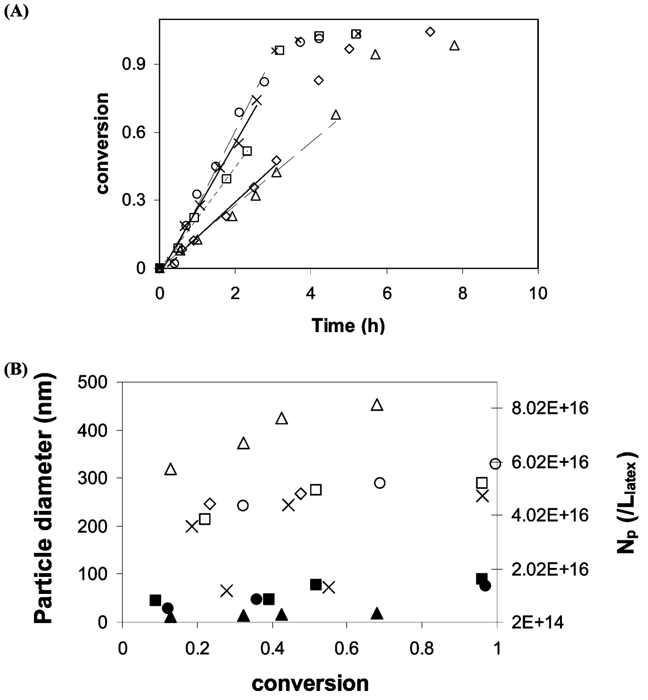


Figure 6. Emulsion polymerization of styrene with the $P(S)_{12}$-*b*-$(VBTEAC)_{62}$ diblock copolymer: (A) conversion (B) diameter (empty symbols) and number of particles N_p (filled symbols) versus time. See Table 6 for the experimental conditions. (△) 0.5 wt%/S; (◇) 1 wt%/S; (□) 2 wt%/S; (×) 3 wt%/S; (○) 4 wt%/S.

of the weight fraction of stabilizer with respect to the monomer in the emulsion. In fact, the efficiency of a stabilizer is related to the highest surface area stabilized per macromolecular chain, and consequently, for the same amount of stabilizer, the larger the final latex particle number, the better the efficiency.

3.1. Amphiphilic Diblock Copolymers. As reported in Table 4, the best stabilization properties were obtained with the most hydrophilic diblock copolymer (entries 1 and 3). For a given hydrophilicity (entries 2 and 3), the copolymer with the smaller block lengths exhibited a better efficiency, which could be explained by the higher molar concentration (entry 2). Nevertheless, the influence of the copolymer structure on the number of particle was weak and we can notice that the particle diameter was rather large ($D \approx 300$ nm). The recovered latex obtained using only 1 wt% of the $P(S)_{12}$-*b*-$P(VBTEAC)_{62}$ diblock copolymer as stabilizer displayed a very narrow particle size distribution, as shown by TEM (Figure 5). This implies a short nucleation period, as well as the absence of secondary nucleation during the emulsion polymerization process (Figure 6B). Several tests were carried out to get an idea of the stability of these hairy cationic latexes, and all the results are reported in Table 5. The latex was stable with time, and the steric effect of the copolymer is efficient since no flocculation was observed when freeze–thaw cycles were applied (entries 2–5). After one centrifugation cycle, the separation between the precipitated latex and the recovered clear serum was obvious. The latex was washed by five centrifugation cycles; the serum contained less than 10 wt% of the stabilizer that was desorbed from the latex particles

Table 5. Test of Stability for the Polystyrene Latex Synthesized by Emulsion Polymerization Using the $P(S)_{12}$-*b*-$(VBTEAC)_{62}$ Cationic Diblock Copolymer (Entries 1−10) and the Cationic Comblike Copolymer P(S-*co*-VBDDAC)$_{52}$ (Entries 11−14) as Stabilizers

entry	wt% copolym/ styrene	treatment	diameter[a] (nm) at 25 °C
1	1	initial latex	300
2	1	4 months after	390
3	1	16 h at −20°C, first cycle	370
4	1	16 h at −20°C, second cycle	320
5	1	16 h at −20°C, third cycle	330
6	1	centrifugation[b]	400
7	3	initial latex	260
8	3	4 months after	300
9[c]	3	$[NaCl]_{latex} = 10$ mM	310
10[c]	3	$[NaCl]_{latex} = 30$ mM	310
11	1	initial latex	200
12	1	4 months after	210
13[c]	1	$[NaCl]_{latex} = 10$ mM	200
14[c]	1	$[NaCl]_{latex} = 30$ mM	200

[a] From Malvern apparatus for the diluted latex (DLS). [b] The latex was cleaned by five centrifugation cycles and redispersed in water. [c] A solution of NaCl was added to the final latex to get the appropriate salt concentration, and the solid content of the latex was 15 wt%.

(estimated by gravimetry and ^{1}H NMR), and the precipitated latex was easily redispersed in water (entry 6). The elemental analysis of the cleaned latex confirmed the presence of the nitrogen and chlorine atoms coming from the copolymer with an experimental amount (0.07 mol% Cl, 0.1 mol% N) close to the theoretical one (0.05 mol% Cl, N). The resistance to addition of electrolyte was tested, and no destabilization occurred with addition of salt to the final latex (entries 8−10). In contrast, we will show later the strong influence of NaCl on the emulsion polymerization mechanism.

Because of its good stabilization properties, the $P(S)_{12}$-*b*-$P(VBTEAC)_{62}$ diblock copolymer was chosen to study the influence of the stabilizer concentration on the kinetics and N_p (Table 6). The variation of conversion versus time exhibited a short nucleation period (interval I), and the slope of the linear part (interval II) increased with an increase in the surfactant concentration (Figure 6A). This is a classical result in emulsion polymerization, as the rate of polymerization is proportional to N_p, which increases when the stabilizer concentration increases.[1] However, with a dithioester end-group, the cationic diblock copolymer might also act as chain-transfer agent and, hence, induce a rate retardation in emulsion polymerization. Indeed, the dithioester function at the hydrophilic extremity of the stabilizer copolymer was probably not hydrolyzed during the 3 h of the emulsion polymerization at 70 °C in acidic media (pH 5), as it was previously checked that the intensity of the dithioester UV band (480 nm) corresponding to the end-group was constant during 5 h in acidic water (pH 4) at 70 °C. This result was confirmed by a very recent study published by McCormick on the hydrolytic susceptibility of dithioester chain-transfer agents.[51] So, transfer reactions to the dithioester function could occur in the reaction medium, but the retardation effect was not predominant enough to reverse the classical trend of kinetic versus the stabilizer concentration (Figure 6A). The control of the molar mass was not the purpose of that work; moreover difficulties would be encountered in SEC analysis, owing to the poor solubility of the copolymer in THF, due to its permanent charges. When the emulsion polymerization of styrene was carried out in saline solution (Table 6, entry 5) with 3 wt% of the $P(S)_{12}$-*b*-$P(VBTEAC)_{62}$ diblock copolymer as stabilizer, a strong destabilization occurred, whereas no coagulation was observed when the polymerization were carried out in water, whatever the stabilizer concentration. On the other hand, the final latex was not sensitive to salt, as no destabilization was observed by adding 30 mM of NaCl (Table 5, entries 8−10). This results point out the important role of the amphiphilic block copolymer in the particle formation step. In particular, the experimental conditions should be such that a high particle coverage should be achieved from the onset of the reaction. By increasing the salt concentration, the exchange rate of the block copolymers between the non-nucleated micelles and the newly formed particles might be slowed,[52] and destabilization occurred because the latex particle coverage was not large enough to properly stabilize them. Additionally, by reducing the net charge and the extension of the hydrophilic corona, the salt would also contribute in destabilizing the early dispersion of deformable, sticky particles. In contrast, at the end of the polymerization, the coverage of the final latex particles was high enough to prevent destabilization in the presence of salt.

The theoretical relationship between N_p and the molar concentration of stabilizer, initially introduced by Smith and Ewart,[53] follows the power law $N_p \approx [S]^{\alpha}$. The theoretical predictions give $\alpha = 0.6$ for classical surfactants, which are able to exchange very rapidly between micelles, water, and the polymer/water interface. However, owing to their macromolecular structure, amphiphilic diblock copolymers do not behave similarly to molecular surfactants. For styrene emulsion polymerization in the presence of nonionic poly(styrene)−poly(ethylene oxide) di- and triblock copolymers[54] or poly(vinyl acetate)−poly(ethylene oxide) diblock copolymer,[55] the α exponent was, respectively, equal to 1.37 and in the range of 1.6−2.1. These higher values were attributed either to a homogeneous nucleation or to a nucleation process taking place throughout the polymerization course. In the case of anionic diblock copolymers, the polymerization of methyl methacrylate in the presence of a poly(methyl methacrylate)$_{120}$−poly(acrylic acid)$_{280}$ copolymer[3,56] led to the relationship: $N_p \approx [\text{Copolymer}]^{0.97}$. In a similar way, our group[26] demonstrated that the α coefficient was close to 1 for the emulsion polymerization of styrene in the presence of poly(styrene)-*b*-poly(potassium acrylate) [P(S)-*b*-P(AK)] copolymers with PAK contents lower than 75 mol%. In those examples, the monomer-swollen block copolymer micelles acted as seeds in the emulsion polymerization and the final particle concentration (N_p, L^{-1}) was equal to the initial micelle concentration (N_m, L^{-1}).[27]

In our system where the electrosteric stabilizer is a permanent cationic diblock copolymer [$P(S)_{12}$-*b*-$P(VBTEAC)_{62}$], the log(N_p) versus log([copolymer]) plot was not linear in the range of 0.5−4 wt% of copolymer, but it would rather display a maximum (Figure 7). The experimental data do not tend to follow the Smith−Ewart law. In contrast, the linearity was always observed by Burguière et al.[26] for all the anionic P(S)-*b*-P(AK) block copolymers in the range of 0.25−4 wt% of copolymer. However, care must be taken with measurements of the diameters, which allow the calculation of N_p (eq 1). Actually, the diameter of latex particles measured by DLS and TEM were comparable in the case of 1 wt% of the diblock copolymer (Table 6, entry

Table 6. Emulsion Polymerization of Styrene Using Various Amounts of the Amphiphilic Diblock Copolymer $P(S)_{12}$-*b*-$(VBTEAC)_{62}$ as Stabilizer[a]

	[copolymer]		particle diameter[b]	particle diameter TEM[c]			N_p		
entry	wt% vs S	10^{-4} mol/L_{latex}	DLS D_z (nm)	D_z (nm)	D_n (nm)	D_w/D_n[d] TEM	10^{16} L_{latex}^{-1} TEM[e]	N_m/N_p[f]	A_c (nm^2/copolymerchain)[g]
1	0.5	0.6	455	394	380	1.02	0.6	250	80
2	1	1.1	300	305	300	1.01	1.4	215	57
3	2	2.3	280	225	210	1.04	3.8	160	39
4	3	3.4	260	236	210	1.10	3.8	135	25
5[h]	3	3.4	coagulum	–	–		–	–	–
6	4	4.6	330	227	200	1.09	4.4	270	20
7	4	4.6	340	223	200	1.08	4.4	270	20

[a] Experimental conditions: [V50] = 0.006 mol/L_{latex}, $T = 70$ °C, solid content: 20 wt% Sty/H_2O, final conversion = 100%. [b] From Malvern apparatus: *z*-average diameter of the latex particle with the hydrophilic shell. [c] D_z is the *z*-average mean diameter and D_n is the number-average diameter of the polystyrene particles calculated from TEM with 500 particles. [d] D_w/D_n is the polydispersity. [e] Final number of particles, N_p, calculated from D_n (see eq 1). [f] N_m calculated from eq 7. [g] A_c = area per stabilizer chain (cationic amphiphilic copolymer): $4\pi(D_n/2)^2 = A_c N_{copolymer}$ with $N_{copolymer}$ = number of copolymer chain per particle = ([copolymer]N_A)/N_p; using D_n and N_p from TEM. [h] Emulsion polymerization carried out in saline solution: [NaCl] = 30 mM.

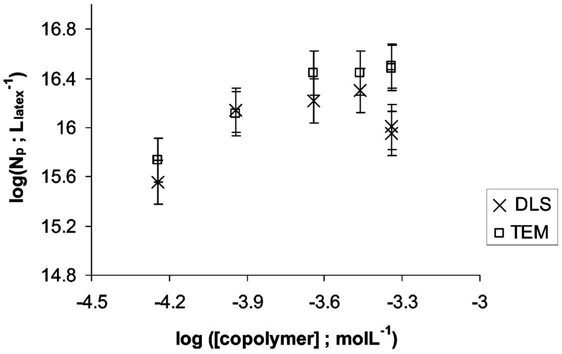


Figure 7. Influence of the amount of the $P(S)_{12}$-*b*-$(VBTEAC)_{62}$ diblock copolymer stabilizer on the final number concentration of latex particles. N_p calculated using the *z*-average diameter (TEM and DLS).

2). In contrast, in the case of 4 wt% of copolymer, the DLS *z*-average diameter of the latex particles was higher than the *z*-average diameter measured by TEM, and this emulsion polymerization experiment has been repeated twice to confirm this result (Table 6, entries 6 and 7). The diameter measured by TEM is close to the diameter of the polystyrene particle, as the hydrophilic corona should collapse onto the particle in the dry state. However, the difference with DLS cannot be explained only by the thickness of the hydrophilic cationic shell expanded in solution, which was in the range of 15 nm (Table 3). For this experiment (4 wt% copolymer/styrene), we probably overestimated the diameter measured by DLS because of a small amount of aggregates in solution.

From the aggregation number determined by static light scattering in the previous part, it was possible to calculate the number of micelles, N_m (eq 7), before the nucleation step and to compare it to the final latex particle number, N_p. Nevertheless, since light scattering measurements were carried out without styrene, which can affect the structure of the micelles, the ratio N_m/N_p is approximated.

$$N_m = \frac{[\text{copolymer}]N_A}{N_{agg}}\,(L_{latex}^{-1}) \tag{7}$$

The high value of N_m/N_p (135–270; Table 6) was characteristic of the very high mobility of the $P(S)_{12}$-*b*-$P(VBTEAC)_{62}$ macromolecular chains between micelles and the polymer/water interface and means that a large number of non-nucleated micelles was used to stabilize the latex particles. This behavior is different from that of the analogous anionic $P(S)_{16}$-*b*-$P(AK)_{55}$, as Burguière et al.[27] showed that the micelles formed by the anionic $P(S)_{16}$-*b*-$P(AK)_{55}$ served as a seed in the emulsion polymerization of styrene ($N_m/N_p = 1$–2).

The last interesting remark deals with the area stabilized by one copolymer chain, which was in the range of 20–80 nm^2 from 4 to 0.5 wt% of copolymer (Table 6). Actually, the polystyrene particles produced by emulsion polymerization using the anionic $P(S)_{10}$-*b*-$P(AK)_{56}$ diblock copolymer as stabilizer displayed a higher particle number ($N_p = 9 \times 10^{17}$ L_{latex}^{-1} for [$P(S)_{10}$-*b*-$P(AK)_{56}$] = 4.9×10^{-4} mol/L_{latex})[26] than the cationic latex stabilized by the $P(S)_{12}$-*b*-$P(VBTEAC)_{62}$ copolymer (Table 6, entries 6 and 7) for the same mole fraction of copolymer. If we focused on the area stabilized per copolymer chain, they were higher for the anionic than for the cationic copolymers (A_c was equal to 50 and 170 nm^2 for 4.9×10^{-4} and 1.1×10^{-4} mol/L_{latex} of the $P(S)_{10}$-*b*-$P(AK)_{56}$ copolymer, respectively).[57]

In conclusion, the major differences between the poly(styrene)-*b*-poly(vinylbenzyltriethylammonium chloride) cationic diblock copolymer composed of a hydrophobic backbone and the analogous poly(styrene)-*b*-poly(sodium acrylate) anionic diblock copolymer[26,27] were principally observed for the aggregation number in aqueous solutions and for the ratio between the number of initial micelles and the number of final latex particles. The other differences were the strong influence of the salt addition on the stability of the cationic latex during the emulsion polymerization and the trend of the bilogarithmic plot of the number of particles versus the stabilizer concentration, which was not linear in the range of 0.5–4 wt% of the cationic diblock copolymer.

3.2. Amphiphilic Comblike Copolymers. The comblike copolymers were composed of styrene units and amphiphilic units based on dodecyl (C_{12}) or hexadecyl (C_{16}) alkyl chains and a cationic quaternary ammonium group (Figure 3). The synthesis required only two steps, the one-pot copolymerization and the quaternization of the chloromethyl groups. The characteristics of the polystyrene latexes produced by emulsion polymerization are gathered in Table 7. The lower degree of polymerization of the backbone induced a slight stabilization improvement, but the aliphatic chain length appeared to be a key parameter. Indeed, a coagulum was always observed with the copolymer derivatized by the hexadecylamine, and it was not possible to increase

Table 7. Emulsion Polymerization of Styrene with the Amphiphilic Comblike Copolymers as Stabilizers

entry	cationic copolymer	[copolymer] wt% vs S	10^{-5} mol/L_{latex}	conversion %	particle diameter[a] DLS (nm)	N_p (final)[a] 10^{17} L^{-1}_{latex}	A_c (nm^2/copolymer chain)
1	P(S-*co*-VBDDAC)$_{102}$	0.25	2.4	10	845	0.006	–
2	P(S-*co*-VBDDAC)$_{102}$	0.5	4.5	100	140	1.4	318
3	P(S-*co*-VBDDAC)$_{102}$	1	9.5	100	200	0.4	88
4	P(S-*co*-VBDDAC)$_{52}$	0.5	10	100	115	2.4	165
5	P(S-*co*-VBDDAC)$_{52}$	1	20	100	160	0.9	60
6	P(S-*co*-VBDHAC)$_{102}$ [b]	0.5	4	44	coagulum	–	–
7	P(S-*co*-VBDHAC)$_{102}$ [b]	1	8	24	coagulum	–	–

[a] Experimental conditions: Initiator = [V50] = 0.006 mol/L_{latex}, $T = 70$ °C, solid content: 20 wt% Sty/H_2O. [b] From DLS. [c] The solution of the copolymer and deionized water was stirred for 1 h at room temperature.

the amount of stabilizer due to a high viscosity of the aqueous solution (entries 6 and 7). In contrast, the comblike cationic copolymers containing dodecyl aliphatic chains were able to play the role of stabilizer with a very low weight proportion, such as 0.5 wt% for instance (entries 2–5). The particle diameters were in the range of 115–200 nm depending on the copolymer type and concentration. The particle diameter increased when the copolymer concentration increased (Table 7, entries 2–5), and this behavior might be related to the aggregation of the cationic comblike copolymers in aqueous solution.[42] Further studies will be undertaken to better understand this mechanism. When using the cationic comblike copolymers as stabilizer, N_p was 1 order of magnitude higher compared to that of the cationic diblock copolymer (Tables 6 and 7). It is noteworthy that the area stabilized by one comblike copolymer chain was especially high (60–320 nm^2). These high values of A_c could be related to the hydrophobic character of these copolymers containing aliphatic side chains and a polystyrene backbone which might favor the adsorption on the hydrophobic polystyrene particles. In contrast to the cationic diblock copolymers, the comblike cationic copolymers do not display a segregated hydrophilic shell which was able to expand in water. The interesting point lied in the fact that the highly hydrophobic comblike copolymers displayed good stabilization properties for the emulsion polymerization of styrene providing stable latexes resistant to time and salt addition (Table 5, entries 12–14).

Conclusions

Well-defined diblock and comblike copolymers based on poly(styrene) and poly(4-vinylbenzyl chloride) were synthesized via the RAFT (reversible addition fragmentation transfer) method. Chemical modification of the methylene chloride side groups by a tertiary amine allowed us to obtain cationic amphiphilic copolymers containing quaternary ammonium units. The poly(styrene)-*b*-poly(vinylbenzyltriethylammonium chloride) diblock copolymers were highly hydrophilic with compositions ranging from 70% to 85% of VBTEAC units. The comblike copolymers were based on one backbone composition (55:45, S/VBC) and contained dodecyl or hexadecyl aliphatic side chains. The hydrophobic association of the P(S)$_{12}$-*b*-P(VBTEAC)$_{62}$ diblock copolymers in aqueous solution was studied by static and dynamic light scattering. As the aggregation number of the spherical micelles was salt dependent, we concluded that the system was nonfrozen. The efficiency of the cationic diblock copolymer as stabilizer for the emulsion polymerization of styrene has been proven, and stable latexes with narrow particle size distribution were produced. The high number of initial micelles compared to the number of final latex particles was attributed to a high mobility of the diblock copolymer and an initially low aggregation number of the micelles. A strong influence of the ionic strength on the stabilization of the latex was observed during the nucleation period, but the final latex was not sensitive to a subsequent addition of salt. The amphiphilic cationic copolymers presenting a comblike structure with dodecyl aliphatic side chains were able to act as stabilizer in the emulsion polymerization of styrene. A very low proportion (0.5–1 wt%/styrene) of these highly hydrophobic copolymers synthesized in only two steps was sufficient to recover stable polystyrene latexes.

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(43) The theoretical molar masses can be calculated by taking into account the number of chains initiated by AIBN using the following equation, but the trend was very close to the one calculated in Figure 2. M_n (theoretical) $= (1 - X_1) \times \{M_{\mathrm{CTA}} + \mathrm{conv} \times [M]_0 \times M_{\mathrm{monomer}}/[\mathrm{CTA}]_0 + 0.6 \times [\mathrm{AIBN}]_0 \times (1 - \mathrm{e}^{-k_d t})\} + X_1 \times \mathrm{conv} \times [M]_0 \times M_{\mathrm{monomer}}/[\mathrm{CTA}]_0 + 0.6 \times [\mathrm{AIBN}]_0 \times (1 - \mathrm{e}^{-k_d t})$ then, M_n (theoretical) $= (1 - X_1) \times M_{\mathrm{CTA}} + \mathrm{conv} \times [M]_0 \times M_{\mathrm{monomer}}/[\mathrm{CTA}]_0 + 0.6 \times [\mathrm{AIBN}]_0 \times (1 - \mathrm{e}^{-k_d t})$. X_1 is the molar fraction of chains initiated by AIBN.

(44) The chain-transfer constant to benzyl chloride molecule was measured in the conventional free-radical polymerization of styrene initiated with AIBN at 70 °C in order to model a possible transfer to the benzyl chloride function of the monomer and polymer chain. The experimental value of the transfer constant obtained using the Mayo equation was found to be $C_{tr} = k_{tr}/k_p = 4.4 \times 10^{-3}$. The conversion ($X$) of the ‘transfer agent’ (benzyl chloride functions) is only 0.15% for 30% monomer conversion (X_m) and 1% when X_m equals 90% according to $X = 1 - (1 - X_m)^{\mathrm{Ctr}}$. We can conclude from the calculation that, on average, the poly(4-vinylbenzyl chloride) contained less than one branch for 100 monomer units, but the length of the branches is still unknown.

(45) The Mark−Houwink-Sakurada (MHS) parameters of poly(vinyl benzyl chloride) have not been reported in the literature. Nevertheless, the slopes of the experimental plots log([η]) vs log(M) for the P(VBC)-containing polymers synthesized by RAFT were lower than that for a linear PS, suggesting lower MHS parameters for the P(VBC)-containing polymers. These data were not accurate enough to give MHS parameters values.

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