Block Copolymers of Poly(styrene) and Poly(acrylic acid) of Various Molar Masses, Topologies, and Compositions Prepared via Controlled/Living Radical Polymerization. Application as Stabilizers in Emulsion Polymerization

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ABSTRACT: A series of well-defined diblock, triblock, and star-block copolymers composed of polystyrene and poly(acrylic acid) were synthesized by controlled/living radical polymerization and used as stabilizers in emulsion polymerization under alkaline conditions. The structure of the copolymers, the size of the blocks, and the composition were varied and their efficiency as stabilizers was correlated with their structural characteristics. The block length was varied from 10 to 30 units for the polystyrene block and from 13 to 266 units for the poly(acrylic acid) block. The copolymers appeared to be efficient stabilizers down to a block copolymer-to-monomer ratio of less than 0.5 wt %. From the comparison of the effect of the different structures and compositions, it was shown that the diblock copolymers were particularly efficient and that the optimal composition was about 10 styrene units and a maximum of 50 acrylic acid units. The triblock and star-block copolymers with external hydrophilic blocks did not behave much differently than diblock copolymers. In contrast, for the triblock copolymers with an internal hydrophilic segment, the efficiency strongly depended on the respective length of both blocks. The evolution of the number of latex particles, N_p, with the concentration of surfactant was also studied and N_p was shown to be proportional to $[\text{surfactant}]^{\alpha}$ over a wide range of surfactant concentrations. The value of α was a function of the block copolymer composition irrespective of the individual block lengths: it was 1 for block copolymers with a poly(acrylic acid) content lower than 75 mol % and decreased to 0.4 when the hydrophilic content was increased. This trend was correlated with the exchange dynamics of the stabilizer. The results obtained with various initiator concentrations, temperatures, and ionic strengths corroborated the previous observation that the important point to explain the evolution of α with the copolymer composition was the competition between nucleation of the micelles and exchange of the block copolymers between the micelles and the continuously created polymer /water interfaces in the system. The time scale of this exchange (which is very fast for small-molecule surfactants) was on the same order of magnitude as the nucleation step for emulsion polymerizations carried out in the presence of block copolymers.

Introduction

Emulsion polymerization is a widespread industrial technique used to perform radical polymerizations. It represents an easy route for preparing stable aqueous suspensions of polymeric particles of submicronic size and offers many advantages concerning the synthesis and application viewpoints. Theoretical backgrounds and practical applications of this polymerization process have been extensively discussed in several books, some of which have been published quite recently.[1,2] Among the components used in a classical emulsion polymerization recipe, the surfactant or stabilizer plays a key role. First, it participates in the nucleation step and contributes to the creation of stable mature particles which can further grow by monomer propagation. The final number of latex particles (N_p) is directly related to the initial concentration of the surfactant. The second role of the surfactant is to impart good stability to the latex particles during polymerization as well as during storage. With classical surfactants composed of a lipophilic hydrocarbon tail and a charged hydrophilic head, the particles' stability is ensured by electrostatic repulsion. When nonionic stabilizers with a hydrophilic block (such as poly(ethylene oxide) for instance) instead of the ionic head are used, a steric effect operates and is particularly efficient against electrolyte, high shear, and/or freeze−thaw induced destabilizations.[3] Usually, a mixture of an ionic and a nonionic surfactant is used to guarantee both proper nucleation and good stability. Finally, as the rate of polymerization is usually proportional to N_p, the surfactant also affects the overall polymerization kinetics.

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Besides the classical ionic and nonionic surfactants, a unique class of stabilizers can be used in emulsion polymerization, namely, the amphiphilic copolymers. Owing to the wide and powerful possibilities of macromolecular synthesis, they offer an almost unlimited diversity if one considers their nature, their structure, their composition, their molar mass, and so forth. A variety of nonionic amphiphilic block and graft copolymers have been used in emulsion polymerization and the structure/property relationship has been extensively studied, mainly for poly(ethylene oxide)-based copolymers.[4,5] Amphiphilic polyelectrolytes with various architectures and chemical compositions have already been used as stabilizers in aqueous emulsion polymerization (for review see ref 6). They operate via the electrostatic and steric stabilization modes. The combination of both effects is known as electrosteric stabilization.[7] Random copolymers can be easily prepared via conventional free-radical polymerization but their structure is usually ill-defined because they suffer from the heterogeneity in composition and in molar mass imparted by the polymerization technique. In contrast, amphiphilic block copolymers exhibit a well-defined structure. Unlike random and graft copolymers, amphiphilic diblock copolymers can be considered as the macromolecular counterparts of small-molecule surfactants. Particularly, they can form micellar aggregates in selected solvents.[8] In aqueous emulsion polymerization, the hydrophobic block can anchor on the particle surface while the hydrophilic blocks extend into the water phase and create a well-defined hydrophilic shell. They are mainly synthesized using "living" polymerization techniques, which ensure the formation of macromolecules with predictable molar mass, narrow molar mass distribution, and well-defined structure. Diblock copolymers with a polyelectrolyte segment are usually prepared via anionic polymerization, either using a protected precursor of the charged monomer or performing selective chemical modification of one of the blocks. Numerous examples can be found in the literature. Surprisingly, however, very few of them have been applied as stabilizers in emulsion polymerization.[5,9−13] More recently, controlled/living radical polymerization (CRP)[14] proved to be a valuable technique for the preparation of analogous copolymers. This method has the advantage of requiring a lower level of reagent purification than anionic polymerization. Moreover, a wider variety of functional monomers can be polymerized. For instance, nitroxide-mediated radical polymerization enabled us to directly polymerize sodium styrene sulfonate in a controlled manner and the resulting polymer was used as a macroinitiator for the polymerization of styrene to provide the corresponding polyelectrolyte amphiphilic block copolymer.[15] Similarly, block copolymers of quaternized poly(chloromethylstyrene) and polystyrene were prepared.[16] Both of them were efficient electrosteric stabilizers in styrene emulsion polymerization. Block copolymers of polystyrene and poly(acrylic acid) with various structures, molar masses, and compositions were made via CRP involving the *tert*-butyl acrylate hydrophobic precursor and were quite recently reported.[16−18]

As emulsion polymerization stabilizers, amphiphilic block copolymers can be used in lower concentrations than classical surfactants or than the analogous random copolymers.[10,13,15−17] Moreover, their reduced mobility is an advantage in the coating industry because mobile emulsifiers may weaken the polymer film properties, specifically with regard to adhesion. Finally, it was very recently demonstrated that the block copolymer micellar aggregates offer the unique property of acting as a seed for the creation of particles, provided that they are stable over long periods of time (frozen structures).[13] The study was carried out with poly(methyl methacrylate-*b*-acrylic acid) diblock copolymers. The length of the hydrophobic poly(methyl methacrylate) block was considered to be the key parameter for the long-term stability of the micelles. In the emulsion polymerization of acrylic or methacrylic esters, the final number of particles stabilized with a diblock copolymer with 35 methyl methacrylate units or more was found to be identical to the initial number of micelles, indicating that the micelles act mostly as a seed.

The purpose of the present work was to establish a relationship between the macromolecular structure of amphiphilic block copolymers composed of polystyrene and of ionized poly(acrylic acid) and their efficiency as stabilizers in emulsion polymerization. The criterion selected to evaluate the efficiency was the ability to create and stabilize new particles in model styrene emulsion polymerization. Therefore, the relationship between final N_p and the amount of surfactant was established and discussed. The effect of other parameters of the emulsion polymerization medium such as ionic strength, initiator concentration, temperature, and nature of the polymerized monomer was also investigated.

Experimental Section

Materials. Styrene (S, Acros, 99%), *tert*-butyl acrylate (*t*BA, Aldrich, 98%), and *n*-butyl acrylate (*n*BA) were vacuum distilled before use. Azobisisobutyronitrile (AIBN, Fluka, 98+%), trifluoroacetic acid (TFA, Aldrich, 99%), potassium carbonate (K_2CO_3, Aldrich, 99+%), and potassium persulfate ($K_2S_2O_8$, Aldrich, 99+%) were used without further purification. The *N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (SG1) was kindly supplied by ATOFINA (Centre de Recherche Rhône-Alpes, Lyon, France) and used as received. For the emulsion polymerizations, deionized water was used (USF Regeneration).

Analytical Techniques. Molar masses and molar mass distributions were measured by size exclusion chromatography (SEC) in stabilized tetrahydrofuran eluent with a set of 10^4, 10^3, 500, and 100 Å microstyragel columns and a refractometric detector using polystyrene standards for the calibration. Proton NMR analyses of the copolymers were performed in 5-mm-diameter tubes at room temperature using a 200-MHz AC200 Bruker spectrometer. The chemical shift scale was calibrated on the basis of the solvent peak. The poly(styrene-*b*-*tert*-butyl acrylate) precursor block copolymers were analyzed in $CDCl_3$ solution ($\delta = 7.24$ ppm). The amphiphilic poly(styrene-*b*-acrylic acid) block copolymers were analyzed in DMSO-d_6 ($\delta = 2.49$ ppm). The composition was calculated by integrating the aromatic protons of the styrene units (6.3−7.3 ppm) and the aliphatic protons of the *tert*-butyl group of the *tert*-butyl acrylate units together with those of the backbone (1.0−2.5 ppm). For emulsion polymerization, the particles average diameter was measured by dynamic light scattering (DLS) using the Zetasizer4 from Malvern at an angle of 90° and at 24 °C. Transmission electron microscopy (TEM) was performed using a LEO920 apparatus, with an accelerating potential of 80 kV. The latex diluted in 2 wt % of phosphotungstic acid was deposited onto a copper grid covered with a carbon membrane. After drying, the grid was quickly plunged into liquid ethane and analysis was performed at low temperature (−150 °C). This procedure was applied to avoid degradation of the particles in the electron beam.

Table 1. Experimental Conditions for the Synthesis of the Poly(styrene-*b*-*tert*-butyl acrylate) Diblock Copolymers Using SG1-Mediated CRP

A. Synthesis of the Polystyrene (PS) Macroinitiator

	[AIBN] (mol L^{-1})	[SG1] (mol L^{-1})	T (°C)	time (h)	styrene conversion (%)	M_n (g mol^{-1})	M_w/M_n
S10	3.1×10^{-2}	6.0×10^{-2}	120	1	20	3400	1.15
S17	6.0×10^{-2}	1.2×10^{-1}	95	19	20	1900	1.09

B. Synthesis of the Poly(styrene-*b*-*tert*-butyl acrylate) Diblock Copolymers

						$x_{(tBA)}$[a]	
	PS	[PS] (mol L^{-1})	*t*BA conversion (%)	M_n (g mol^{-1})	M_w/M_n	SEC	NMR (CDCl$_3$)
D8	S10	3.1×10^{-2}	20	9800	1.25	0.56	0.55
D7	S17	3.4×10^{-2}	24	7900	1.32	0.69	0.66

[a] Molar fraction of *t*BA units in the copolymer.

Scheme 1. Structure of the Diblock (D), Triblock (TA and TS), and Star-Block (S) Copolymers Prepared via ATRP

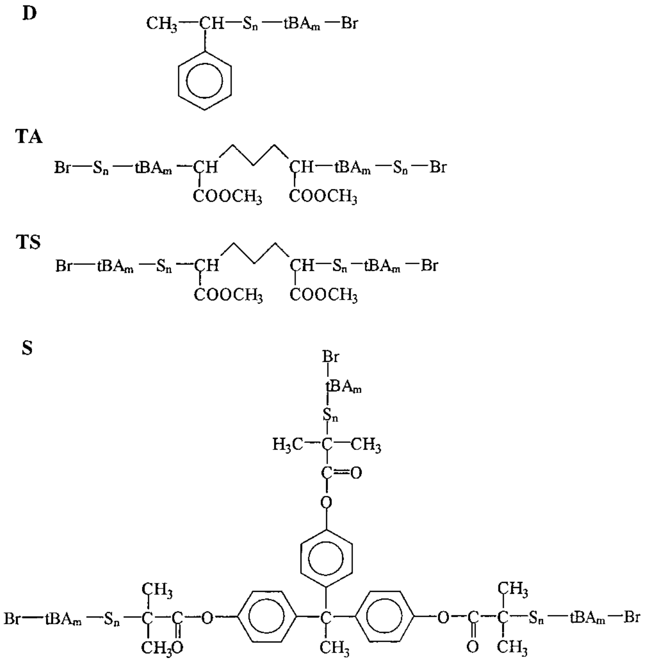

Table 2. Structure and Composition of the Amphiphilic Block Copolymers Based on Polystyrene and Poly(acrylic acid)[a]

copolymer	structure	M_n (M_w/M_n)[b]	composition (mol % of acrylic acid units)[c]
D1	$S_{10}-A_{21}$	2540 (1.20)	0.66
D2	$S_{10}-A_{56}$	5070 (1.14)	0.84
D3	$S_{10}-A_{100}$	8230 (1.44)	0.91
D4	$S_{10}-A_{139}$	11090 (1.28)	0.93
D5	$S_{16}-A_{55}$	5640 (1.29)	0.76
D6[d]	$S_{17}-A_{266}$	20900 (1.33)	0.94
D7[e]	$S_{15}-(A_{45}$-*co*-$S_6)$	5420 (1.32)	0.66
D8[e]	$S_{30}-(A_{47}$-*co*-$S_7)$	7230 (1.25)	0.55
TA1	$S_{16}-A_{49}-S_{16}$	6800 (1.14)	0.61
TA2	$S_4-A_{50}-S_4$	4500 (1.24)	0.85
TS1	$A_{39}-S_{11}-A_{39}$	6760 (1.16)	0.88
TS2	$A_{51}-S_{11}-A_{51}$	8500 (1.17)	0.91
TS3	$A_{75}-S_{11}-A_{75}$	11930 (1.17)	0.93
TS4	$A_{50}-S_{17}-A_{50}$	8930 (1.16)	0.85
S1	$(S_5-A_{13})_3$	4210 (1.14)	0.72
S2	$(S_5-A_{21})_3$	5950 (1.14)	0.81

[a] S: styrene; A: acrylic acid; S−A: diblock copolymer; S−A−S: triblock copolymer with poly(acrylic acid) as the central block; A−S−A: triblock copolymer with polystyrene as the central block; (S−A)$_3$: triarmed star-block copolymer with the polystyrene segments in the core. [b] From SEC of the precursor block copolymers of polystyrene and poly(*tert*-butyl acrylate), recalculated after hydrolysis. [c] From ^{1}H NMR. [d] Prepared by ATRP, starting from a poly(*tert*-butyl acrylate) macroinitiator. [e] Prepared by SG1-mediated controlled radical polymerization.

Synthesis and Characterization of the Block Copolymers. The synthesis of poly(styrene-*b*-*tert*-butyl acrylate) block copolymers (diblock, triblock, and star-block copolymers, see Scheme 1) via atom transfer radical polymerization (ATRP) and their characterization have been described in a previous article.[18] When using nitroxide-mediated CRP, the procedure was as follows. Polymerizations were performed in bulk in a three-neck round-bottom flask immersed in a thermostated oil bath and equipped with a reflux condenser. Styrene was polymerized first. A mixture of styrene, AIBN, and SG1 was bubbled with nitrogen before heating. After reaction, the polystyrene was recovered by precipitation into methanol and analyzed by SEC to determine M_n (the number average molar mass) and M_w/M_n (the polydispersity index). Polymerization of the second monomer, *t*BA, was carried out at 120 °C and was initiated by the previously prepared polystyrene macroinitiator in the presence of small amounts of free nitroxide ([nitroxide] = 0.025 [PS]) and of added styrene ([S] = 0.05 [*t*BA]) to decrease the propagation rate. Because of the experimental conditions for preparation of the second block when nitroxide-mediated CRP is used, several styrene units are incorporated into the acrylic acid block. This second block is expected to exhibit a tapered structure with a decreasing styrene molar fraction toward the ω-end of the chain. After 1 h of reaction, the block copolymers were recovered by precipitation into a water/methanol (1/3 v/v) mixture and analyzed by SEC and proton NMR. To remove the nitroxide capping agent that might affect the polymerization kinetics, the block copolymers were heated above 70 °C for 24 h; moreover, elimination of the end group was also very likely during the hydrolysis reaction, described below. Accurate experimental conditions are summarized in Table 1. Structure and composition of all the amphiphilic block copolymers used are reported in Table 2.

Hydrolysis of the Poly(*tert*-butyl acrylate) Block. The block copolymers were dissolved in dichloromethane and a 5-fold molar excess of TFA was added (with respect to the ester groups). The mixture was stirred at room temperature for 24 h. When hydrolyzed, the copolymers precipitate in dichloromethane. They were separated by filtration, washed with dichloromethane, thoroughly dried at 50 °C, and characterized using proton NMR in DMSO-d_6 solution. Complete hydrolysis was always observed.

Preparation of the Micellar Solutions. The copolymers in the acidic form did not dissolve directly in water. They needed to be ionized and heated to obtain clear solutions. The block copolymers and K$_2$CO$_3$ were introduced into 18 mL of deionized water. The samples were heated for 45 min at 70 °C for complete solubilization. At that stage, all the acrylic acid units were in the potassium salt form. For **D8** (Table 2) containing only 54 mol % of acid acrylic units, this procedure was not appropriate because it did not lead to polymer solubilization. Therefore, the block copolymer (1.5 g) was first dissolved in a THF/H_2O mixture (20 mL/10 mL). The solution was then dialyzed in cellulose acetate tubing (Spectra/Por, molecular weight cutoff 1000 Da) against an aqueous NaOH solution (pH = 9) for 4 days.

Emulsion Polymerization Procedure. Batch emulsion polymerizations were performed in a 100-mL three-neck round-bottom flask immersed in a thermostated oil bath and equipped with a reflux condenser, a nitrogen inlet, and a thermometer. A typical procedure was as follows. The micellar solution (18 mL), prepared in situ according to the former description, was bubbled with nitrogen. Then, 2 g of styrene (or *n*-butyl acrylate for some experiments) was introduced, and after 15 min an aqueous solution of initiator ($K_2S_2O_8$, 0.026 g, dissolved in 2 mL of deionized water) was added, which corresponded to time zero of the reaction. The pH of the polymerization medium was always between 8 and 9 for full ionization of the carboxylic acid units. The reactions were stopped after 4 h to ensure complete conversion.

Characterization of the Latexes. The final latexes were characterized by their polymer content τ (g L^{-1}) obtained by gravimetry and including the weight of polystyrene and of the block copolymer and by the particles diameter D (nm) measured by DLS in HCl aqueous solution (pH = 3) or TEM:

The final density of particles N_p (L^{-1}) was calculated according to

$$N_p = \frac{6\tau}{\pi d_p D^3} \quad (1)$$

with D the particle diameter expressed in cm and d_p the polystyrene density ($d_p = 1.05$ g cm^{-3}).

Results and Discussion

1. Accurate Measurement of the Particle Size. Determining the final number of latex particles is a key point in this work. As N_p was not directly measured, but calculated from the particle diameter D via eq 1, accurately determining the average value of D is of particular importance. When operating in an aqueous dispersed medium, the hydrodynamic diameter is measured and does not properly reflect the true size of the polystyrene core when an extended hydrophilic shell exists. As DLS was mainly applied in this study, it was essential to find out the conditions to perform an accurate measurement of D. The effect of pH on the measured diameter is of particular concern. For polystyrene particles stabilized with the diblock copolymer **D3** ($S_{10}-A_{100}$, 0.58 wt % vs styrene; Table 3), which contained a block of 100 acrylic acid monomer units, the hydrodynamic diameter increased when the pH was increased, that is, when the degree of ionization was increased (pK_a = 6.15 for the poly(acrylic acid)[19]). The smallest measurable value was obtained at pH = 3 (D = 95 nm, while it was 145 nm in pure deionized water). For a pH lower than 3, aggregation of the particles was observed. The value of D measured at pH = 3 was considered to be the closest estimation of the particle diameter (including the hydrophobic core and the collapsed hydrophilic shell). This was confirmed by TEM analysis that gave a number average diameter of 94 nm for the same latex (70 particles counted; polydispersity index = 1.03). Thus, in this work, particles diameter were systematically measured by DLS at pH = 3 and N_p was derived.

2. Efficiency of the Block Copolymer Stabilizers: Effect of Structure and Composition on N_p. Many possible criteria can be applied to compare the stabilizing efficiency of amphiphilic copolymers in an emulsion polymerization. The first is the possibility of obtaining stable latexes. In addition, the stabilizing efficiency can be evaluated according to either the number of stabilized particles or the stabilized surface area per macromolecular chain, which are obviously related parameters. Moreover, the comparison between various copolymers can be done on the basis of either the molar concentration or the weight fraction with respect to the monomer in the emulsion. The former provides more accurate information on the behavior of a given chain while the latter is the criterion that has the highest relevance for industrial applications. In this study, for fundamental understanding purposes, N_p was considered a function of the molar concentration of the copolymer and the effect of composition and structure of the stabilizers was examined.

As shown in Table 2, a large variety of amphiphilic block copolymers was tested in styrene emulsion polymerization, namely, diblocks, triblocks, with either the hydrophobic or the hydrophilic segment in the middle, and finally tri-armed star-block copolymers with the polystyrene segments in the core. The blocks length and the composition were also varied. All of them (except **D8**) contained more than 60 mol % of acrylic acid units to ensure proper water solubility in the ionized form at 70 °C. The diblock, the triblock with PS segment in the middle, and the star-block copolymers led to stable polystyrene latexes as evidenced by the results reported in Tables 3−5. Even very small weight fractions of stabilizer with respect to monomer (less than 1 wt %) led to stable latexes with relatively small diameters and a large number of particles. These amphiphilic block copolymers have structures that enable them to properly adsorb or anchor onto the particle surface, while the charged hydrophilic segments are well extended in the water phase and ensure electrosteric stabilization. The triblock copolymers with the hydrophilic segment in the middle should behave quite differently. When short enough, each chain is expected to adsorb onto the surface of a single particle with both external hydrophobic parts (no bridging effect) and to form a hydrophilic loop. Therefore, the effect of structure and composition on the ability to stabilize particles should be critical. For instance, **TA1** ($S_{16}-A_{49}-S_{16}$) proved to be a poor stabilizer because large particles were obtained together with partial flocculation during the emulsion polymerization, while **TA2** with shorter PS blocks ($S_4-A_{50}-S_4$) exhibited much better efficiency. The effect of blocks length and composition of the other copolymers was also examined in detail.

Effect of the PA Block Length. Figure 1a−d shows the effect of the poly(acrylic acid) block length for a constant number of styrene units in the copolymers with different structures.

Considering the diblock copolymers, the first series **D1**−**D4** represents a set of species with the same PS block (10 S units) and increasing PA block length. As seen in Figure 1a, in the range of studied concentrations, the highest number of particles was obtained for **D2** (56 A units). For the series **D5**−**D6**, the hydrophobic block of which contains 16/17 S units, owing to slope differences, **D5** with 55 A exhibited better efficiency than **D6** (with 266 A units) at high concentrations (>10^{-4} mol L^{-1}) while it was the reverse at lower concentrations (Figure 1b). The values of N_p remained lower, however, than those observed for **D2** in the same concentration range (Table 3). In addition, the diblock copolymers **D5** ($S_{16}-A_{55}$) and **D7** ($S_{15}-(A_{45}$-*co*-$S_6)$), which have the same PS block length, but a different

Table 3. Emulsion Polymerizations of Styrene at 70 °C Using the Amphiphilic Diblock Copolymers as Stabilizers: Final Characteristics of the Latexes[a,b]

	concentration				solid content of the latex (τ)	
copolymer	wt % vs S	10^{-4} mol L^{-1}	$[K_2CO_3]$ (mol L^{-1})	D (DLS) (nm)	(g L^{-1})	N_p (10^{17} L^{-1})
D1	0.78	3.11	0.020	70	81.9	4.3
	1.12	4.04	0.020	62	78.5	6.0
	1.63	6.53	0.020	54	78.6	9.1
	2.23	8.97	0.020	52	85.1	11.0
	2.45	8.82	0.020	46	72.3	13.5
D2	0.25	0.50	0.020	102	90.6	1.6
	0.56	1.11	0.020	79	90.5	3.3
	1.96	3.94	0.020	62	90.4	6.9
	2.41	4.87	0.020	57	90.4	8.9
	3.80	7.80	0.020	48	90.2	15
D2[c]	1.01	2.01	0.020	71	90.5	4.6
D2[d]	0.58	1.15	0.020	84	82.6	2.5
	0.97	1.93	0.020	73	84.1	3.9
	1.49	2.99	0.020	64	73.9	5.1
	2.52	5.09	0.020	54	78.2	9.0
D3	0.50	0.61	0.020	95	73.8	1.6
	0.82	1.00	0.020	93	86.5	2.0
	1.06	1.30	0.020	79	53.3	2.0
	1.62	2.00	0.020	85	85.8	2.5
	2.38	2.96	0.020	61	53.4	4.3
	2.41	3.00	0.020	64	59.2	4.1
	2.43	3.03	0.020	60	49.0	4.1
	3.00	3.76	0.020	63	57.5	4.2
	3.86	4.88	0.020	62	70.7	5.4
D3[e]	0.58	0.70	0.020	95	67.2	1.4
	1.52	1.88	0.020	76	66.2	2.7
	2.51	3.13	0.020	68	64.9	3.8
D4	0.53	0.48	0.020	97	73.8	1.5
	0.73	0.67	0.020	89	70.6	1.8
	0.99	0.90	0.020	80	72.4	2.6
	1.47	1.35	0.020	69	50.9	2.8
	2.19	2.02	0.020	74	74.3	3.3
	2.90	2.70	0.020	65	61.6	4.1
D4[f]	1.45	1.33	0.020	78	76.0	2.9
D5	0.26	0.46	0.020	119	67.1	0.7
	0.52	0.93	0.020	100	90.5	1.6
	1.13	2.03	0.020	80	90.5	3.2
	1.98	3.57	0.020	63	90.4	6.6
D6	0.25	0.24	0.020	122	90.6	0.9
	0.86	0.81	0.020	101	90.5	1.6
	2.07	1.98	0.020	90	90.4	2.3
	4.76	4.70	0.020	78	90.2	3.5
D6	0.47	0.44	0.040	110	68.1	0.9
	1.52	1.45	0.040	87	67.1	1.9
	2.03	1.95	0.040	86	67.2	1.9
	4.48	4.41	0.040	81	71.1	2.4
D7	0.24	0.49	0.023	129	99.6	0.8
	0.50	1.02	0.023	100	99.5	1.8
	1.01	2.10	0.023	82	99.5	3.3
	1.96	4.10	0.023	67	99.4	6.0
	2.42	5.08	0.023	61	99.3	8.0
D7	0.26	0.53	0.040	155	99.3	0.5
	0.53	1.09	0.040	130	99.3	0.8
	1.00	2.07	0.040	108	99.3	1.4
	1.96	4.10	0.040	82	99.2	3.3
	2.42	5.09	0.040	72	99.1	4.8
D8	0.44	0.55	0.005	117	91.7	1.0
	0.87	1.07	0.005	94	91.7	2.0
	1.30	1.61	0.005	82	91.6	3.0
	4.19	5.36	0.005	57	91.4	8.9

[a] $[K_2S_20_8\ ] = 0.005$ mol L^{-1}. [b] When nonspecified, the micellar solutions were prepared according to the procedure described in the Experimental Section. [c] The micellar solution was heated at 70 °C for 24 h before the emulsion polymerization was started. [d] The micellar solution was heated at 70 °C for 70 h before the emulsion polymerization was started. [e] The micellar solution was heated at 70 °C for 93 h before the emulsion polymerization was started. [f] The micellar solution was heated at 70 °C for 20 h before the emulsion polymerization was started.

structure of the hydrophilic block (owing to a difference in the synthesis; i.e., ATRP versus nitroxide-mediated polymerization), did not exhibit different behavior, indicating that the styrene units in the hydrophilic block of **D7** did not play any significant role in the adsorption mechanism. In the series of triblock copolymers **TS1**–

Table 4. Emulsion Polymerizations of Styrene at 70 °C Using the Amphiphilic Triblock Copolymers as Stabilizers: Final Characteristics of the Latexes[a−c]

copolymer	concentration wt % vs S	 10^{-4} mol L^{-1}	D (DLS) (nm)	solid content of the latex (τ) (g L^{-1})	N_p (10^{17} L^{-1})
TA1	1.25	1.87	320	90.5	0.05
TA2	0.94	2.11	114	90.5	1.1
TS1	0.60	0.89	107	90.5	1.3
	0.86	1.29	97	90.5	1.8
	5.43	8.49	67	90.1	5.4
TS2	0.24	0.28	110	90.6	1.2
	0.84	0.99	94	90.5	2.0
	1.71	2.04	86	90.4	2.6
	1.96	2.49	88	90.4	2.4
TS3	0.79	0.67	128	90.5	0.78
	2.16	1.85	102	90.4	1.5
TS4	1.42	1.61	84	90.5	2.8
	2.60	2.99	78	90.4	3.5

[a] $[K_2CO_3] = 0.020$ mol L^{-1}. [b] $[K_2S_2O_8] = 0.005$ mol L^{-1}. [c] The micellar solutions were prepared according to the procedure described in the Experimental Section.

Table 5. Emulsion Polymerizations of Styrene at 70 °C Using the Amphiphilic Star-Block Copolymers as Stabilizers: Final Characteristics of the Latexes[a−c]

copolymer	concentration wt % vs S	 10^{-4} mol L^{-1}	D (DLS) (nm)	solid content of the latex (τ) (g L^{-1})	N_p (10^{17} L^{-1})
S1	0.30	0.71	102	90.5	1.6
	1.00	2.37	88	90.5	2.4
	2.97	7.12	64	90.3	6.3
S2	0.31	0.51	109	90.5	1.3
	1.22	2.06	93	90.5	2.1
	3.03	5.16	73	90.3	4.3

[a] $[K_2CO_3] = 0.020$ mol L^{-1}. [b] $[K_2S_2O_8] = 0.005$ mol L^{-1}. [c] The micellar solutions were prepared according to the procedure described in the Experimental Section.

TS3 with 11 S units in the middle and increasing hydrophilic blocks on both sides, the best efficiency was observed for **TS2**, which contains 51 A units in each PA block (at least at the lowest concentrations) (Figure 1c). It was thus clearly evidenced that, for a given hydrophobic block, the length of the hydrophilic one(s) is of importance as far as N_p is regarded. A value of approximately 50−55 A units seemed to be optimal when the hydrophobic block contains 11 S units for the diblock copolymers and 16 S units for the triblock copolymers. In other words, for a given initial molar concentration of amphiphilic copolymer, the final stabilized area per macromolecule (which increases when N_p increases) does not continuously increase with the size of the hydrophilic block(s) but goes through a maximum for approximately 50−55 A units; additional A units do not contribute to efficiency enhancement of the stabilizer. These results, which concern the **D** and **TS** copolymers, have not been verified for the star-block copolymers tested because their PA blocks were significantly shorter. In the examined star-block copolymers, **S1** ($(S_5{-}A_{13})_3$) and **S2** ($(S_5{-}A_{21})_3$), the experimental results showed that changing the number of A units in each block from 13 to 21 did not considerably change N_p, for a given concentration (Figure 1d).

Effect of the PS Block Length. Figure 2a,b shows the effect of the polystyrene block length for a given number of A units in the copolymers. For the diblock copolymers, the highest value of N_p was obtained for the shortest PS block (10 S units, **D2** = $S_{10}{-}A_{56}$ and **D4** = $S_{10}{-}A_{139}$). In the case of the triblock copolymers **TS2** ($A_{51}{-}S_{11}{-}A_{51}$) and **TS4** ($A_{50}{-}S_{17}{-}A_{50}$), better efficiency was exhibited by **TS4** with the longest PS block (17 S units) (see Table 4). These results illustrate a tendency only because the number of S units has not been varied over a sufficiently broad range.

Optimal Structure and Composition for High Values of N_p. According to the previous sets of data, a trend can be highlighted regarding the structure and composition of the block copolymers. The most favorable composition of the diblock copolymers would be $S_{10}{-}A_{50}$ (**D2**), while it would rather be $A_{50}{-}S_{17}{-}A_{50}$ (**TS4**) for the triblock copolymers. Interestingly, when **D2** and **TS4** are compared (Tables 3 and 4), it appears that the diblock copolymer is slightly more efficient. When compared with a diblock copolymer of similar composition (**D5**, $S_{16}{-}A_{55}$), the star-block copolymers did not exhibit different behavior. Thus, among the various structures studied in this work, the diblock copolymers are preferred because they combine the advantages of easy preparation with an efficient stabilization of the latex particles. In Figure 3, the efficiency of the diblock copolymers is compared according to the concentration of A units in the emulsion polymerization (which reflects also the weight fraction with respect to styrene). It appears here that the most efficient becomes **D1** ($S_{10}{-}A_{21}$). Then come **D2**, **D7**, and **D5**, which contain between 45 and 55 A units in the hydrophilic segment. Finally, the least efficient copolymers were those with more than 100 A units. This result confirms the previous observation that increasing the length of the hydrophilic blocks beyond 50−55 A units did not improve the efficiency. In addition, if one aims at reducing the amount of incorporated ionic groups in the latex, the acrylic acid units should be distributed among a large number of block copolymers (small hydrophilic brush) rather than among fewer macromolecules with a longer hydrophilic block. Obviously, these conclusions might change if very different experimental conditions were used (for instance, ionic strength, as shown in paragraph 4). Concerning the amount of stabilizer, it should be mentioned, however, that the range of studied concentrations was between 0.5 and 5 wt % with respect to styrene, which corresponds to very typical conditions.

3. Effect of the Block Copolymer Concentration on N_p. In addition to the effect of structural factors on N_p, the relationship between N_p and the molar concentration of stabilizer can give more complete information. For a given monomer, the proportionality between N_p and $[\text{surfactant}]^{\alpha}$ initially set up by Smith and Ewart[20] for small-molecule surfactants is valid over a wide range of surfactant concentrations above the critical micelle concentration (cmc), with a constant value of α.[21] Theoretically, N_p should be proportional to $[\text{surfactant}]^{0.6}$, which applies well for styrene emulsion polymerization at surfactant concentrations above the cmc. In this study, the cmc has not been experimentally verified, but according to Eisenberg et al. who studied similar copolymers, it is below 10^{-5} mol L^{-1} at room temperature.[8c] Thus, all the emulsion polymerizations in the present work were conducted at a surfactant concentration above the cmc (Tables 3−5). The concentration of the amphiphilic block copolymer was varied, with all other experimental conditions remaining the same, and the final particle density was calculated from

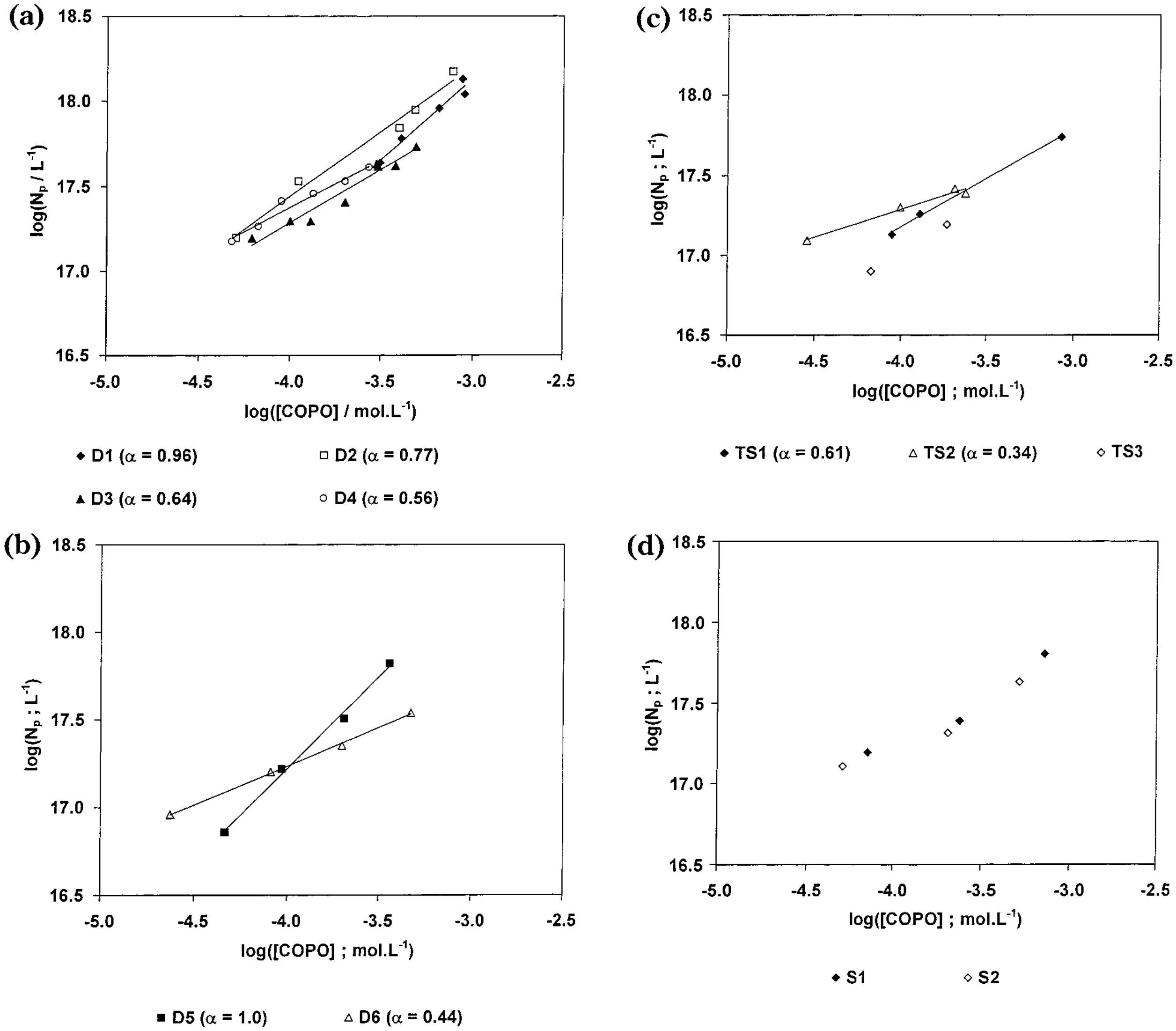

Figure 1. Logarithmic plot of the density of particles, N_p, versus the concentration of block copolymer: effect on N_p and on α of the length of the poly(acrylic acid) block. Micellar solutions prepared at 70 °C for 45 min; polymerization temperature = 70 °C; styrene/water = 10 wt %; $[K_2S_2O_8] = 0.005$ mol L^{-1}; $[K_2CO_3] = 0.020$ mol L^{-1}. (a) Diblock copolymers **D1** (S_{10}–A_{21}), **D2** (S_{10}–A_{56}), **D3** (S_{10}–A_{100}), and **D4** (S_{10}–A_{139}). (b) Diblock copolymers **D5** (S_{16}–A_{55}) and **D6** (S_{17}–A_{266}). (c) Triblock copolymers **TS1** (A_{39}–S_{11}–A_{39}), **TS2** (A_{51}–S_{11}–A_{51}), and **TS3** (A_{75}–S_{11}–A_{75}). (d) Star-block copolymers **S1** ($(S_5\text{–}A_{13})_3$) and **S2** ($(S_5\text{–}A_{21})_3$).

eq 1. Figures 1 and 2 display the logarithmic plot of N_p versus the copolymer molar concentration. Interestingly, linear relationships were always observed, indicating that the data followed the same type of power law as described above. As particularly studied for the diblock copolymers and for one triblock copolymer (**TS1**), the exponent α (i.e., the slope of the straight lines) depended mainly upon the copolymer composition, irrespective of the individual block lengths and of the structure. This trend is illustrated by Figure 4, which shows α as a function of the block copolymer composition. When the proportion of A units was small (between 50 and 75 mol %), α was close to 1. It decreased when the hydrophilic content increased and reached values close to 0.4–0.6 for proportions larger than 90 mol %. Thus, the theoretical prediction which gives α = 0.6 was not followed.

Actually, the Smith and Ewart's power law is based on several assumptions.[20] One of them is that the creation of new particles stops when the total surface area of the latex particles has increased sufficiently to adsorb all the micellar surfactant in a saturated monolayer. The non-nucleated micelles act as surfactant reservoirs. This hypothesis implies that the surfactant molecules organized in micelles are instantaneously available to stabilize the newly created interfaces that are formed either by particle growth or by the nucleation of new particles. In other words, the dynamics of exchange of the molecules between micelles, water, and the polymer/water interface is very fast with respect to the increasing surface area in the system. However, owing to their macromolecular structure, amphiphilic block copolymers should not behave similarly to small molecule surfactants.[11,13,22,23] Thus, it is not surprising that the theoretical prediction does not fully apply and that the exponent α is affected. The observed dependence of α on the copolymer composition might indicate that this exponent is directly related to the stabilizer mobility. Copolymers with a high A content showed a behavior close to that of the small-molecule surfactants. When the hydrophobicity of the macromolecules was increased, their dynamics of exchange was slowed and led to an increase of α. At the limit, when no exchange exists (such as for the so-called "frozen micelles" which act as a seed), the value of α should be 1, as each micelle is turned into a latex particle.[13] As an illustration, a series of styrene emulsion polymerizations were carried

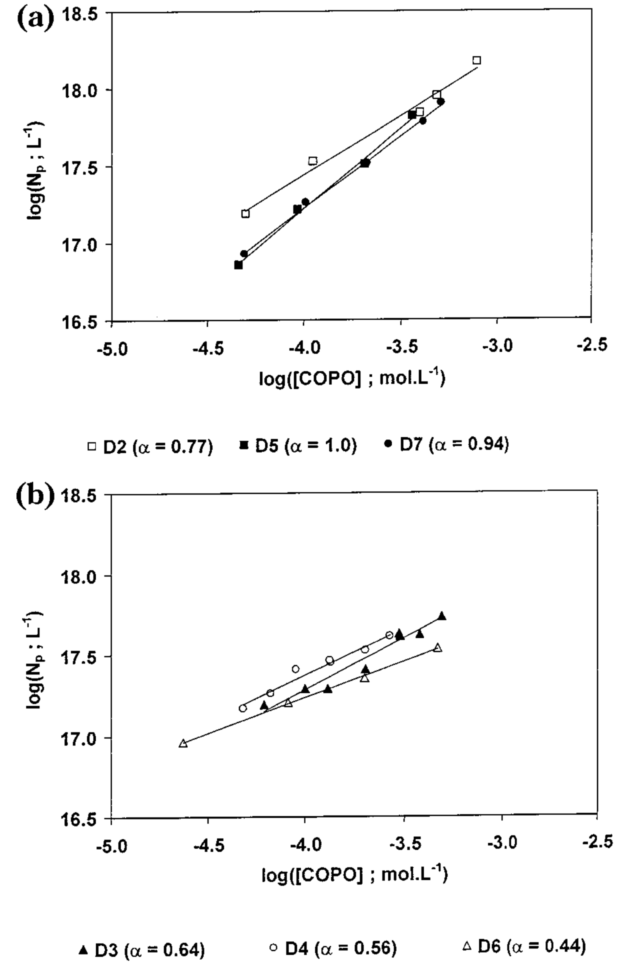

Figure 2. Logarithmic plot of the density of particles, N_p, versus the concentration of block copolymer: effect on N_p and on α of the length of the polystyrene block. Micellar solutions prepared at 70 °C for 45 min; polymerization temperature = 70 °C; styrene/water = 10 wt %; $[K_2S_2O_8]$ = 0.005 mol L^{-1}; $[K_2CO_3]$ = 0.020 mol L^{-1}. (a) Diblock copolymers **D2** (S_{10}–A_{56}), **D5** (S_{16}–A_{55}), and **D7** (S_{15}–(A_{45}-*co*-S_6)). (b) Diblock copolymers **D3** (S_{10}–A_{100}), **D4** (S_{10}–A_{139}), and **D6** (S_{17}–A_{266}).

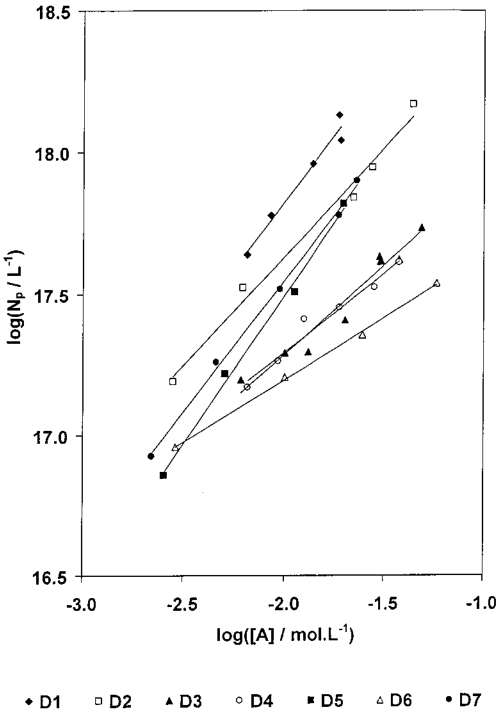

Figure 3. Logarithmic plot of the density of particles, N_p, versus the overall concentration of A units, for the diblock copolymers **D1** (S_{10}–A_{21}), **D2** (S_{10}–A_{56}), **D3** (S_{10}–A_{100}), **D4** (S_{10}–A_{139}), **D5** (S_{16}–A_{55}), **D6** (S_{17}–A_{266}), and **D7** (S_{15}–(A_{45}-*co*-S_6)). Micellar solutions prepared at 70 °C for 45 min; polymerization temperature = 70 °C; styrene/water = 10 wt %; $[K_2S_2O_8]$ = 0.005 mol L^{-1}; $[K_2CO_3]$ = 0.020 mol L^{-1}.

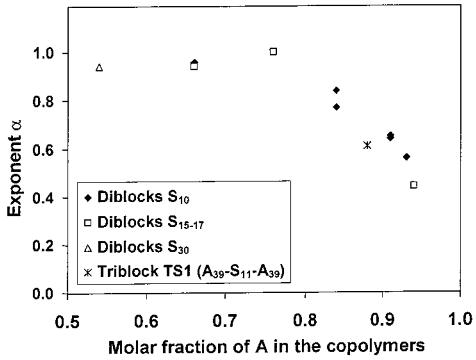

Figure 4. Effect of the molar composition of the block copolymers on the value of the exponent α.

out using a solution of the most hydrophobic block copolymer **D8** (S_{30}–(A_{47}-*co*-S_7); it was non-water-soluble and was thus solubilized with a cosolvent; see Experimental Section, Tables 2 and 3). This block copolymer was expected to exhibit very slow exchange dynamics in the micellar solution, as already observed for other systems.[22,23] The values of N_p, plotted in Figure 5, were perfectly proportional to $[\mathbf{D8}]^{0.94}$. The exponent value close to 1 confirms the relationship between α and the exchange dynamics of unimers in the system. In this case, all the micelles were stable enough to be nucleated and to become a latex particle.

Because of their higher hydrophilicity with respect to that of **D8**, the other ionized block copolymers were directly solubilized in water at 70 °C. However, the real structure of the formed micelles is unknown and is currently under investigation by static and dynamic light scattering. Nevertheless, to check the efficiency of the solubilization procedure, different experiments were performed. For the copolymers **D2** (S_{10}–A_{56}) and **D3** (S_{10}–A_{100}), a second series of emulsion polymerizations was carried out after heating the micellar solutions for more than 24 h at 70 °C in sealed tubes instead of the usual 45 min. The polymerization was then started using the normal procedure. As demonstrated in Table 3, this change affected neither N_p significantly nor the exponent α (Figure 6a). For the most hydrophobic water-soluble block copolymer **D7** (S_{15}–(A_{45}-*co*-S_6)), the same method of micelle formation as the one used for **D8** was also applied (solubilization in THF/water mixture followed by dialysis; see Experimental Section). Here again, as illustrated in Figure 6b, the technique of micelle formation had no effect on N_p (and consequently no effect on the exponent α).

Thus, the simple solubilization in hot water seemed to be efficient enough, even after only 45 min. Consequently, the formed micelles were not in a frozen state. Actually, the PS blocks were always short enough to have a low T_g. Indeed, the T_g, which depends on the molar mass, can be calculated according to the relationship proposed for polystyrene by O'Driscoll and Sanayei:[24] $T_g = T_{g,\max} - 404/(DP_n)^{2/3}$. The obtained value is T_g = 13 °C for DP_n = 10 and T_g = 39 °C for DP_n = 17. Thus, at 70 °C, the PS segments were not in a glassy

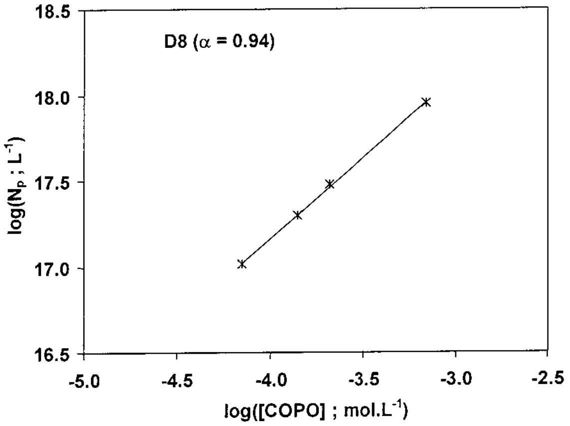

Figure 5. Logarithmic plot of N_p versus the molar concentration of copolymer **D8** (S_{30}–(A_{47}-*co*-S_7)). Micellar solutions prepared with THF as a cosolvent; polymerization temperature = 70 °C; styrene/water = 10 wt %; [$K_2S_2O_8$] = 0.005 mol L^{-1}; [K_2CO_3] = 0.005 mol L^{-1}.

state. In addition, the added monomer acted as a plasticizer, but it is not clear in the literature whether it favors the exchange as stated by van Stam et al.[22] or it promotes the association, as proposed by Rager et al.[23] Therefore, depending mostly on the overall hydrophobicity of the block copolymer rather than on the length of the polystyrene block, the exchange dynamics may be slow with respect to nucleation and polymerization time,[22] allowing sufficient time for the direct nucleation of all the micelles.

4. Effect on N_p of the Experimental Conditions of the Emulsion Polymerization of Styrene. Initiator Concentration. The complete power law developed by Smith and Ewart[20] includes the rate of radical generation, R_i, which is related to the initiator concentration and to the temperature,

$$N_p = k\left(\frac{R_i}{\mu}\right)^{0.4}(a_s S)^{0.6}$$

with μ, the rate of particle volume growth, a_s, the area occupied by a surfactant molecule, and S, the surfactant concentration (micellar surfactant only). The effect of the initiator concentration was investigated for **D6** (S_{17}–A_{266}), **D7** (S_{15}–(A_{45}-*co*-S_6)), and **D8** (S_{30}–(A_{47}-*co*-S_7)) (see Table 6). The number of particles was not significantly affected by the initiator concentration for any of these block copolymers. Such a situation was expected for the most hydrophobic species **D8** and to a lesser extent for **D7** because for those block copolymers, N_p equals the initial number of colloidal species as it is the case for a seeded emulsion polymerization. It was more surprising, however, to observe the same behavior for **D6**. This unexpected result might be explained by the fact that the generation of radicals is not the rate-determining step in the nucleation, but the rate of entry of the charged oligoradicals through the polyelectrolyte shell. This situation has already been observed for emulsion polymerizations performed in the presence of a seed latex with a dense neutralized poly(acrylic acid) shell.[25] It has also been observed with particles covered with a polyelectrolyte block copolymer.[26]

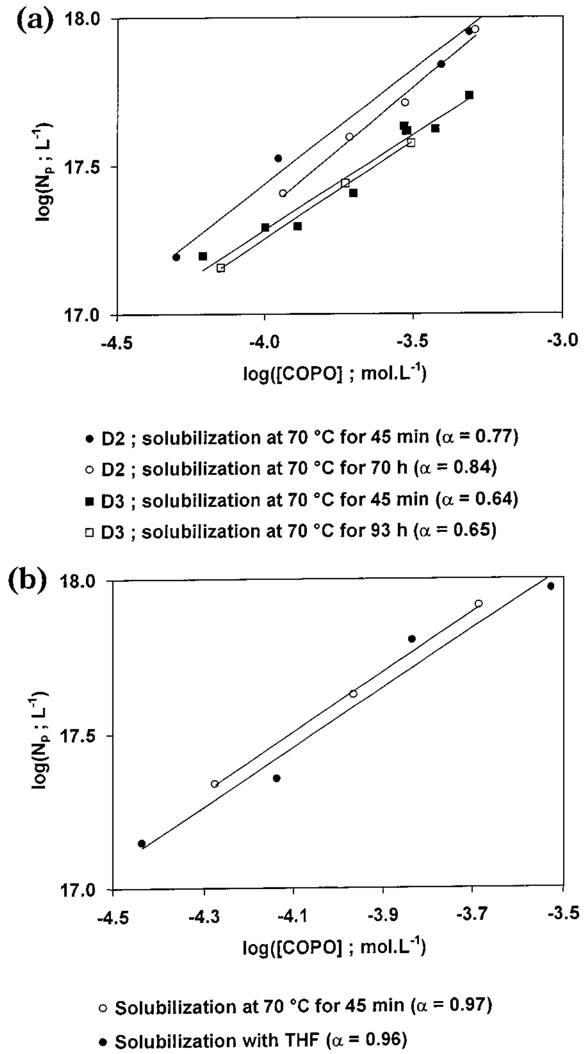

Figure 6. Logarithmic plot of the density of particles, N_p, versus the concentration of block copolymer: effect on N_p and on α of the mode of preparation of the micellar solutions. Polymerization temperature = 70 °C; styrene/water = 10 wt %; [$K_2S_2O_8$] = 0.005 mol L^{-1}. (a) Diblock copolymers **D2** (S_{10}–A_{56}) and **D3** (S_{10}–A_{100}): effect of preparation time at 70 °C; [K_2CO_3] = 0.020 mol L^{-1}. (b) Diblock copolymer **D7** (S_{15}–(A_{45}-*co*-S_6)): effect of the use of a cosolvent for the preparation of the micellar solution; [K_2CO_3] = 0.005 mol L^{-1}.

Temperature. When the temperature was raised from 70 to 90 °C, N_p slightly increased but the exponent α remained unchanged (as determined for **D7** = S_{15}–(A_{45}-*co*-S_6); Figure 7). For **D7**, the polystyrene block had 15 units and the calculated T_g of this block is 34 °C (according to the law mentioned above).[24] Both temperatures used for the emulsion polymerizations were above the T_g of the hydrophobic block. Therefore, increasing the temperature by 20 °C did not significantly affect either the mobility of the block copolymers or the structure of the micelles. Moreover, the same concentration of initiator was used for both polymerizations. Because the 20 °C temperature increase strongly affects the decomposition rate of $K_2S_2O_8$ (rate constant of decomposition k_d = 2.33 10^{-5} s^{-1} at 70 °C; activation energy, E_a = 140 kJ mol^{-1}),[27] and the change in N_p from 70 to 90 °C was small, this supports the above conclusion that the rate of radicals generation in the water phase did not affect significantly the final number of particles.

Concentration of K_2CO_3. The concentration of K_2CO_3 in the emulsion polymerization was varied for the diblock copolymers **D6** (S_{17}–A_{266}) and **D7** ((S_{15}–(A_{45}-*co*-S_6)) and the effect on N_p was examined (Figure 8). Interestingly, the two copolymers behaved quite differently. Actually, the concentration of K_2CO_3 did not

Table 6. Emulsion Polymerizations of Styrene Using the Amphiphilic Diblock Copolymers D6, D7, and D8 as Stabilizers: Final N_p as a Function of Temperature and Initiator Concentration[a]

copolymer	concentration		$[K_2S_2O_8]$ (mol L^{-1})	*T* (°C)	*D* (DLS) (nm)	solid content of the latex (τ) (g L^{-1})	N_p (10^{17} L^{-1})
	wt % vs S	10^{-4} mol L^{-1}					
D6[b]	0.90	0.86	0.005	70	110	70.2	0.96
	0.91	0.87	0.0025	70	107	66.7	0.99
	0.92	0.87	0.016	70	101	64.3	1.1
	0.89	0.84	0.005	90	89	72.8	1.9
D7[c]	1.01	2.10	0.005	70	82	99.5	3.3
	0.43	0.89	0.005	90	102	99.5	1.7
	0.67	1.38	0.005	90	85	99.5	2.9
	1.09	2.25	0.005	90	77	99.5	4.0
	1.55	3.23	0.005	90	68	99.4	5.8
	2.37	4.98	0.005	90	60	99.4	8.4
D7[b]	1.00	2.07	0.005	70	108	99.3	1.4
	0.98	2.06	0.016	70	107	99.0	1.5
	1.00	2.05	0.005	80	96	99.3	2.1
	0.99	2.05	0.005	90	80	99.3	3.6
D8[b]	0.87	1.07	0.005	50	102	91.7	1.6
	0.87	1.07	0.00025	70	100	91.8	1.7
	0.87	1.07	0.0025	70	94	91.7	2.0
	0.87	1.07	0.005	70	94	91.7	2.0
	0.87	1.07	0.02	70	94	91.3	2.0
	0.87	1.07	0.005	90	96	91.7	1.9

[a] The micellar solutions were prepared according to the procedure described in the Experimental Section. [b] $[K_2CO_3] = 0.040$ mol L^{-1}. [c] $[K_2CO_3] = 0.020$ mol L^{-1}.

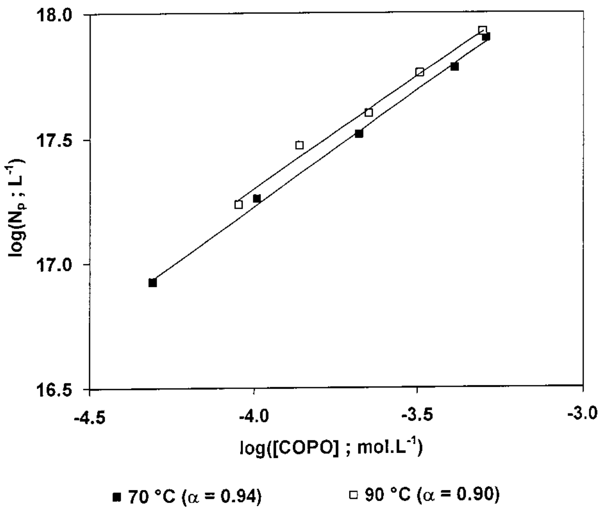

Figure 7. Effect on N_p and on α of the polymerization temperature for the diblock copolymer **D7** (S_{15}–(A_{45}-*co*-S_6)). Micellar solutions prepared at the polymerization temperature for 45 min; styrene/water = 10 wt %; $[K_2S_2O_8] = 0.005$ mol L^{-1}; $[K_2CO_3] = 0.020$ mol L^{-1}.

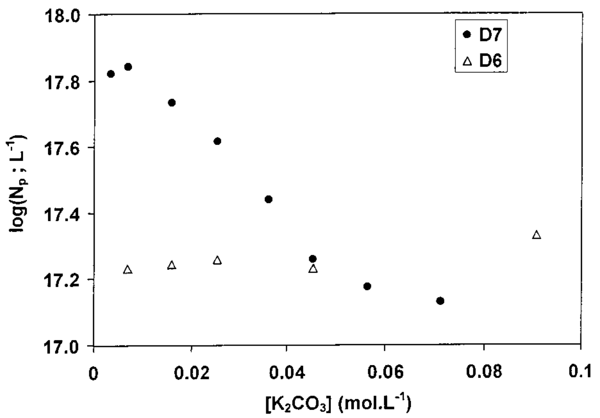

Figure 8. Effect of the concentration of K_2CO_3 on N_p for the diblock copolymers **D6** (S_{17}–A_{266}) and **D7** (S_{15}–(A_{45}-*co*-S_6)). Micellar solutions prepared at 70 °C for 45 min; polymerization temperature = 70 °C; styrene/water = 10 wt %; $[K_2S_2O_8] = 0.005$ mol L^{-1}; 1 wt % of copolymer with respect to styrene (**D6**: 0.5×10^{-4} mol L^{-1}; **D7**: 2.1×10^{-4} mol L^{-1}). (For a comparaison on the basis of the same molar concentration, a constant value of α log(2.1/0.5) = 0.27 with α = 0.44 should be added to the log(N_p) values obtained with **D6).**

significantly affect N_p for the copolymer **D6,** while an increase in the salt concentration led to a continuous decrease in the number of latex particles for **D7**. At low salt concentration, **D7** with the shortest PA block length exhibited the best efficiency, but the discrepancy diminished when the salt concentration was increased.

For both block copolymers, the value of the exponent α was unaffected by the concentration of salt (Figure 9). This last point means that the mobility of the block copolymers did not depend on the salt concentration. That the final number of particles was strongly affected for **D7** would be a consequence of a change in the aggregation number of the micelles as a function of the salt concentration. Indeed, it was shown by Eisenberg that, at low salt concentrations (<0.1 mol L^{-1}), the aggregation number of similar block copolymer micelles increased with the concentration of added salt, indicating a decrease in the number of micelles.[8d] Because the same result was obtained for N_p, it means that the final number of particles was strongly related to the initial number of micelles and corroborates the previously drawn conclusion that the nucleation step was fast with respect to the exchange dynamics of unimers between the micelles and the newly created interfaces. In contrast, for **D6**, the salt concentration had almost no effect on N_p, even though it most probably affected the aggregation number of the micelles. For this stabilizer, N_p did not result directly from the initial number of micelles but from kinetics parameters including the fast covering of the created interface by the more mobile surfactant.

5. Emulsion Polymerization of *n*-Butyl Acrylate. Changing styrene to *n*-butyl acrylate in emulsion polymerizations stabilized with **D7** did not affect the value of N_p (Figure 10), indicating that the nucleation mechanism was the same for both monomers. This result is

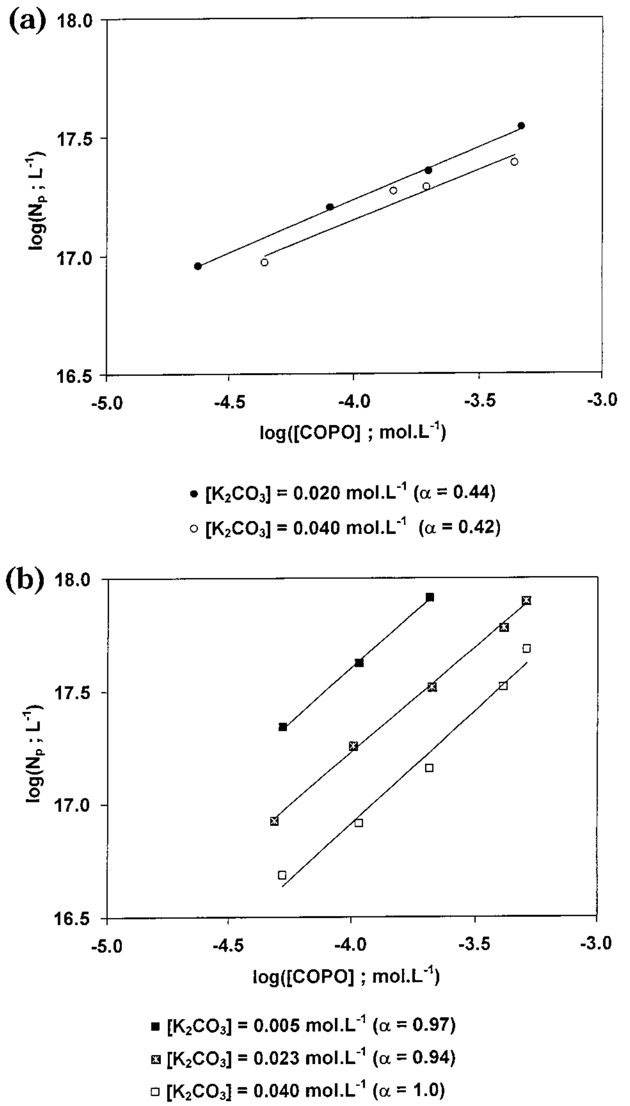

Figure 9. Effect of the concentration of K_2CO_3 on the value of α for the diblock copolymers **D6** (S_{17}–A_{266}) and **D7** (S_{15}–(A_{45}-*co*-S_6)). Micellar solutions prepared at 70 °C for 45 min; polymerization temperature = 70 °C; styrene/water = 10 wt %; $[K_2S_2O_8]$ = 0.005 mol L^{-1}. (a) Diblock copolymer **D6**. (b) Diblock copolymer **D7**.

particularly interesting because it means that it is not necessary to adjust the nature of the hydrophobic block to the polymerized monomer, even when the polymers are not truly compatible.

Conclusions

Amphiphilic block copolymers of polystyrene and poly(acrylic acid) were prepared via controlled/living radical polymerizations, namely, atom transfer radical polymerization and nitroxide-mediated polymerization, using *tert*-butyl acrylate as the precursor monomer to acrylic acid. Numerous diblock, triblock (with either the hydrophilic block or the hydrophobic one in the middle), and tri-armed star-block copolymers were synthesized with compositions ranging from 54 to 94 mol % of A units. Their stabilizing efficiencies for styrene emulsion polymerization were compared based on the final number of stable latex particles produced, N_p. It was shown that the structure and the composition of the copolymers had a strong effect on N_p. Indeed, in the range of studied copolymer concentrations (from 5×10^{-5} to 2×10^{-3} mol L^{-1}), the diblock copolymers with 10 S units and a maximum of 50 A units were the most efficient stabilizers, particularly at low salt concentration. An increase in the size of the hydrophilic segment did not lead to any improvement of the efficiency. The triblock and star-block copolymers with external hydrophilic blocks did not behave any differently than the diblock copolymers. In contrast, for the triblock copolymers with an internal hydrophilic segment, the efficiency strongly depended on the respective length of both blocks. The overall composition of the block copolymers was also an important parameter and affected the exponent α in the relationship $N_p = [\text{copolymer}]^{\alpha}$. This value was close to 1 when the proportion of A units was below 75 mol % and decreased to 0.4 when this content was increased, irrespective of the blocks length and of the structure. The value of α can be correlated with the exchange dynamics of the stabilizer in the system, indicating that there is a competition between micelle nucleation and exchange of the stabilizer between the micelles and the continuously created polymer/water interfaces. The time scale of this exchange for block copolymers is on the same order of magnitude as the nucleation step, while for small molecule surfactants it is much faster.

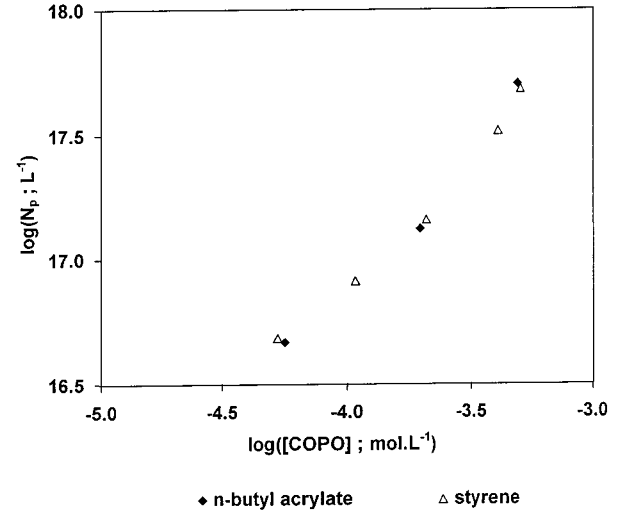

Figure 10. Emulsion polymerization of *n*-butyl acrylate using **D7** (S_{15}–(A_{45}-*co*-S_6)) as a stabilizer; comparison with styrene. Micellar solutions prepared at 70 °C for 45 min; polymerization temperature = 70 °C; monomer/water = 10 wt %; $[K_2S_2O_8]$ = 0.005 mol L^{-1}; $[K_2CO_3]$ = 0.040 mol L^{-1}.

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