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Dispersion Polymerization of Styrene in Ethanol−Water Mixture Using Polystyrene-*b*-poly(ethylene oxide) Macromonomers as Stabilizers

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ABSTRACT: The dispersion polymerization of styrene in an ethanol−water mixture using polystyrene-*b*-poly(ethylene oxide) macromonomers as stabilizers has been investigated. The influence of parameters such as the nature of the polymerizable group, the hydrophilic/hydrophobic balance, the overall molar mass, and the molecular architecture of the macromonomers on the colloidal dispersion has indeed been studied. Macromonomers of rather low molar mass and exhibiting high critical micellar concentration were best suited to produce stable particles. Latex particles of rather narrow size distribution could be obtained in the range of 300−350 nm with styrenyl or maleate ended PS-*b*-PEO macromonomers.

Introduction

Amphiphilic block copolymers self-organize in aqueous media[1] and form micelles, which provides an opportunity to use them as steric stabilizers for the latex particles produced in emulsion polymerization. However, because such surfactants are only physically adsorbed to the particle surface, they can migrate and destabilize the latex.[2] The colloidal stability may be improved by using reactive surfactants. The latter are bound covalently to the polymer particles to prevent desorption or migration from particle surfaces. However, substitution of macromolecular reactive dispersants for classical surfactants affects the polymerization process. In particular, exchange rates between surfactants in solution and those involved in micelles depend critically on both the size of the hydrophobic block[3−6] and the presence of unsaturation at chain ends.

In contrast to emulsion polymerization which involves micelles from its onset, dispersion polymerization begins homogeneous before turning heterogeneous as the conversion in monomer builds up. Such polymerizations also require dispersing agents to prevent the particles formed from coalescing. Amphiphilic block copolymers or some other amphiphilic species, including graft copolymers generated in situ by grafting reactions or via the macromonomer technique, can stabilize the polymer particles by physical adsorption or covalent bonding, the latter being the most efficient.

In a previous study,[7] ω-styrenyl (PEO-*b*-PS)-type macromonomers were successfully used in a two-step synthesis of core−shell PS latex particles. As an extension of that work, the ability of the same macromonomers to serve as reactive surfactants in a batch emulsion polymerization of styrene was also investigated.[8] The self-organization of such macromonomers in water resulted in a rapid consumption of the styrenyl entity and in an early depletion of these reactive surfactants from the reactive medium. Being immobilized in the particles formed in the early stages, they could not fully stabilize the latex throughout the polymerization process. To decrease the rapid consumption of such reactive dispersants and thus prevent coalescence of the latex, a less reactive unsaturation was substituted for the styrenyl one in these macromonomers.

The present study investigates the ability of PS-*b*-PEO-based macromonomers to serve as reactive dispersants in the dispersion polymerization of styrene. Most studies devoted to the stabilization of colloidal particles by macromonomers have used poly(ethylene oxide) chains functionalized with either methacryloyl,[9,12] styryl,[9,12] maleate,[10,12] or thiol[11] reactive groups. The mechanism of particle stabilization is well-established; copolymer chains resulting from the copolymerization of macromonomer with the hydrophobic monomer grow until reaching a critical size, above which they are no longer soluble in the medium and then coagulate with other insoluble polymer or are captured by existing particles. The latex becomes sterically stabilized whenever a sufficient amount of stabilizing copolymer can anchor to the particle surface. The macromonomer characteristics, such as the nature of its polymerizable entity,[13] its size,[13] and its hydrophilic/hydrophobic balance,[14] have been investigated in order to improve the colloidal stabilization of the dispersion.

Recently, several authors[15−18] have even contemplated using amphiphilic macromonomers in dispersion polymerization. These studies examined the influence of the amphiphilic nature of the macromonomers on the particle size and their size distribution. The adsorption of the hydrophobic block onto the formed latex particles not only increased the local concentration of macromonomers but also increased the grafting yield and thus stabilized the particle. The concentration of dispersing agents in the serum can be reduced in this way and minimize the formation of soluble "polysoaps" that waste stabilizer. These results prompted us to examine the potential of PS-*b*-PEO-based macromonomers to serve as stabilizers in the dispersion polymerization of styrene.

In this work, we varied the nature of the polymerizable group, the hydrophilic/hydrophobic balance, the molar mass, and the molecular structure of our mac-

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Table 1. Characteristics of PS-*b*-PEO Macromonomers

name	polymerizable group	av no. of styrene units m^a	av no. of EO units n^b	$\bar{M}_n$ global^c (g/mol)	wt % PEO (*Y*)	CMC^d) (mg/L) in water	$\bar{M}_w/\bar{M}_n$ SEC
A	styrenyl	13	112	6636	74.3	1.98	1.05
B	styrenyl	38	307	17816	75.8	2.69	1.02
C	no	13	109	6300	76.7	1.65	1.05
D	styrenyl	34	352	19607	79.0	6.84	1.08
F	maleate	16	167	9472	77.5	50.0	1.02
H	styrenyl	13	900	41308	95.9	nd^e	1.02

[a] Determined by ^{1}H NMR and SEC. [b] Determined by ^{1}H NMR. [c] $\bar{M}_{n,global} = \bar{M}_{n,PS} + \bar{M}_{n,PEO}$ + extremity of the chains, with $\bar{M}_{n,PS} = 104m$ and $\bar{M}_{n,PEO} = 44n$. [d] Determined by surface tension measurements. [e] Not detedcted.

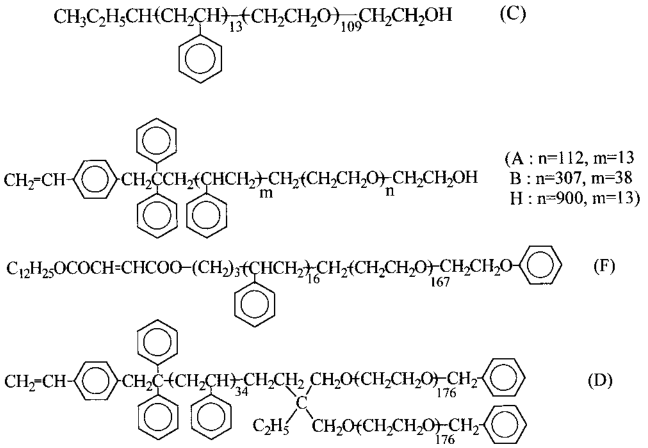

Figure 1. Structure of the macromonomers.

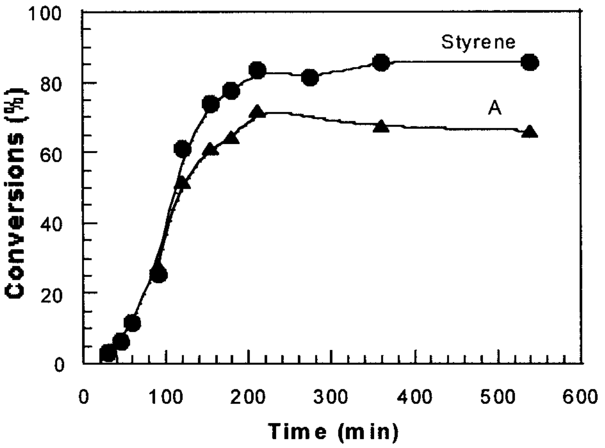

Figure 2. Conversions of styrene (●) and styrenyl-ended PS-*b*-PEO macromonomer (A, ▲) as a function of time.

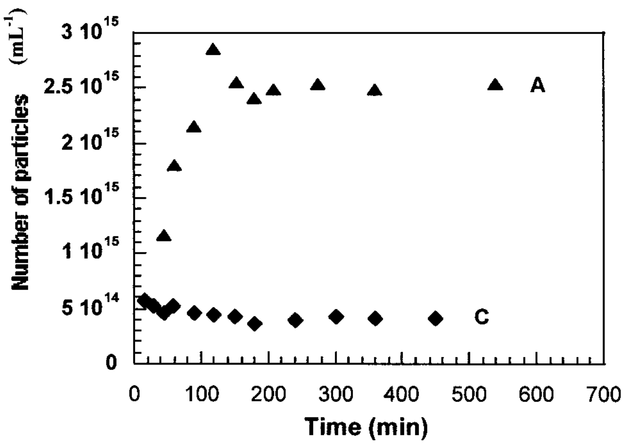

Figure 3. Evolution of the number of particles during the styrene polymerization with C (◆) and A (▲) as surfactants.

Table 2. Influence of the Type of Macromonomer on the Outcome of the Dispersion Polymerization

stabilizer	H	A	F	B	D
coagulum^a (%)	0	0	0	1	0.1
% PEO^b (*X*) NMR	1.22	1.93	2.10	2.97	2.2
macromonomer grafted^c (%)	30.6	61	67	70	62
$D_n{}^d$ (nm)	309	156	314	51	73
$D_w/D_n{}^e$	1.02	1.13	1.00	1.10	1.08

[a] m_c 100/($m_{st} + m_{macrom.}$) with m_c = weight of dry coagulum, m_{st} = weight of styrene introduced, and m_{macrom} = weight of macromonomer introduced. [b] *X* = weight percent of PEO in the cleaned samples. Determined from the oxirane protons of poly(ethylene oxide) (I_1, $\delta(CH_2O) = 3.6$ ppm) and aromatic protons of polystyrene (I_2, $\delta = 6.2-7.2$ ppm); $X = 100(44I_1/4)/((104I_2/5) + (44I_1/4))$. [c] Determined by the ratio ($X \times (m_{st} \times$ conversion St)/$(100 - X))/(m_{macrom.} \times Y)$, with *Y* = weight fraction of PEO in the macromonomer. [d] The number-average diameter is determined by TEM. [e] Determined by TEM on 200 particles.

romonomers and evaluated their impact on the kinetics of polymerization and the colloidal stability.

Results and Discussion

The dispersion polymerization of styrene was carried out in an ethanol−water mixture using as dispersing agents PS-*b*-PEO macromonomers functionalized with either styrenyl or maleate unsaturations (Figure 1). The characteristics of these macromonomers are reported in Table 1; they all tend to self-organize in micelles in water for a given concentration except for the hydrophilic copolymer H. Their behavior as surfactant was described in more detail in a previous article.[19]

The macromonomer incorporation was determined by ^{1}H NMR (Table 2) on cleaned latex. The grafting yield apparently depends on the amphiphilic feature of the macromonomer: the greatest grafting was obtained from those macromonomers that were amphiphilic enough to adsorb on the particles. In contrast, the grafting of macromonomer H, which was completely soluble in water, was limited to 30%. The molar mass and type of unsaturation do not appear to affect the grafting yield.

The amount of coagulum at the end of the reaction was always close to zero using either macromonomer. These results show that the macromonomers did stabilize the polystyrene particles.

The rate of conversion of both styrene and the styrenyl PS-*b*-PEO macromonomer (A) was followed by removing aliquots from the reaction medium at various polymerization times (Figure 2). The shapes of the two curves are very similar, and the incorporation of macromonomer into the particle is good.

Effect of the Presence of Polymerizable Group. The ability of ω-styrenyl PS-*b*-PEO macromonomer (A) to stabilize was compared to that of the nonpolymerizable parent copolymer (C) (same composition and molar mass), which can only weakly adsorb onto the particles

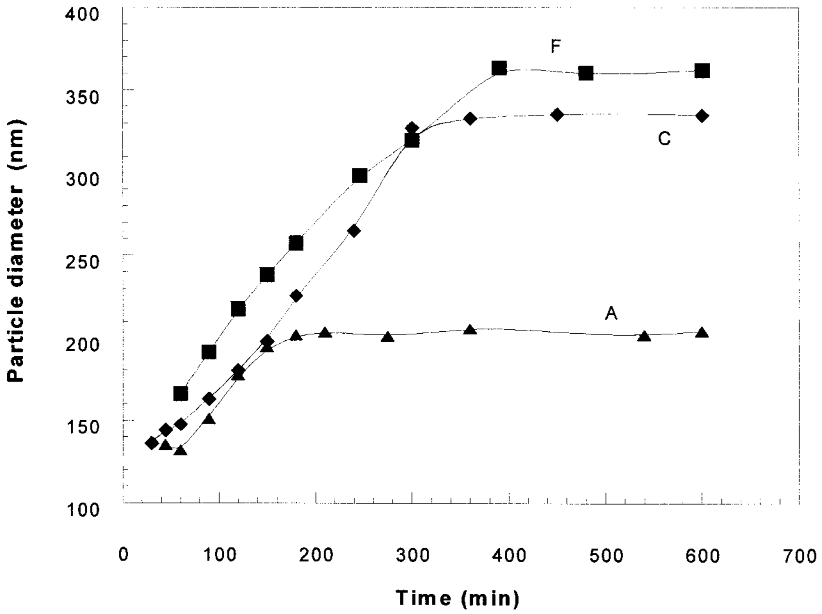

Figure 4. Evolution of the particles diameter during the polymerization of styrene with C (◆), A (▲), and F (■) as surfactants.

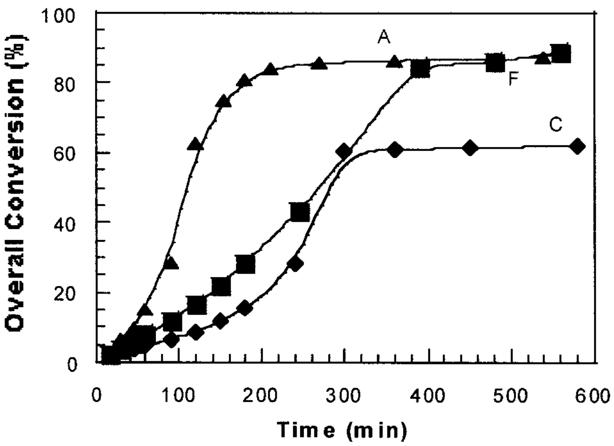

Figure 5. Evolution of the overall conversion during the polymerization of styrene with C (◆), A (▲), and F (■) as surfactants.

but cannot copolymerize with styrene. Under identical experimental conditions ([surfactant], [initiator], solvent, temperature) the kinetics of the polymerization and the characteristics of the obtained particles are totally different for the two kinds of stabilizer. The use of *ω*-styrenyl PS-*b*-PEO macromonomer increases the number of particles (Figure 3) of smaller size (Figure 4). This indicates that A participates in the polymerization and is permanently grafted onto the particle stabilizing the particles from the early stage of the polymerization.

The conversion vs time curves are shown in Figure 5. They are typical of those obtained in dispersion polymerization. After an initial period during which the rate of polymerization is rather slow, it then steeply increased and remained nearly constant until the end. These features indicate that polymerization first occurred in the continuous medium before proceeding within the particle phase. As conversion increased, the viscosity within each particle built up, decreasing the diffusion-controlled rate of termination and in turn accelerating propagation. Similar behavior has been reported for the dispersion polymerization in which maleate[10] and methacryloyl-based poly(ethylene oxide)[16] macromonomers were used as reactive surfactants.

The final conversion reached 85% in polymerizations carried out in the presence of the macromonomer A but only 60% in the presence of the unreactive copolymer C. These differences can be attributed to the number of particles generated in each of the two systems; the fact that A may be irreversibly trapped upon stabilization of a nascent particle tends to promote the production of a larger number of particles, so that the number of radicals penetrating each particle and then the rate of termination are likely smaller in the case of A than in C. Another possible explanation may be related to the difficulty of styrene diffusing through the particle surface; physically adsorbed C copolymers are likely to cause more steric hindrance than covalently attached surfactants A because some of the latter may be buried inside the particle.

Particles resulting from the stabilization by C exhibit an isometric distribution (Figure 6a), whereas those stabilized by A show a broader distribution of size (Figure 6b). The difference between the two systems certainly arises from the possibility for the micelles resulting from the aggregation of A-type surfactants to readily homopolymerize when penetrated by a radical; decreasing the concentration of surfactant A may prevent the formation of micelles and produce mainly monodisperse particles (Figure 6c). Such PS-*b*-PEO-based micelles have been already observed[6,20] in an ethanol–water mixture under similar conditions.

The amount of coagulum at the end of polymerization was always found close to zero whatever the stabilizer (A or C) used. Nevertheless, particles obtained with C as stabilizer seem to exhibit a lower stability toward ultracentrifugation than those stabilized with reactive stabilizers. Indeed, unlike latex stabilized by A, those obtained with C coagulate (% coagulum > 40%) upon centrifugation.

Effect of Chemical Nature of the Polymerizable Group. To investigate the effect of the macromonomer reactivity on the dispersion formed, two different macromonomers functionalized with styrenyl (A) and maleate (F) polymerizable groups were used as stabilizers. The maleic entity cannot homopolymerize and is known

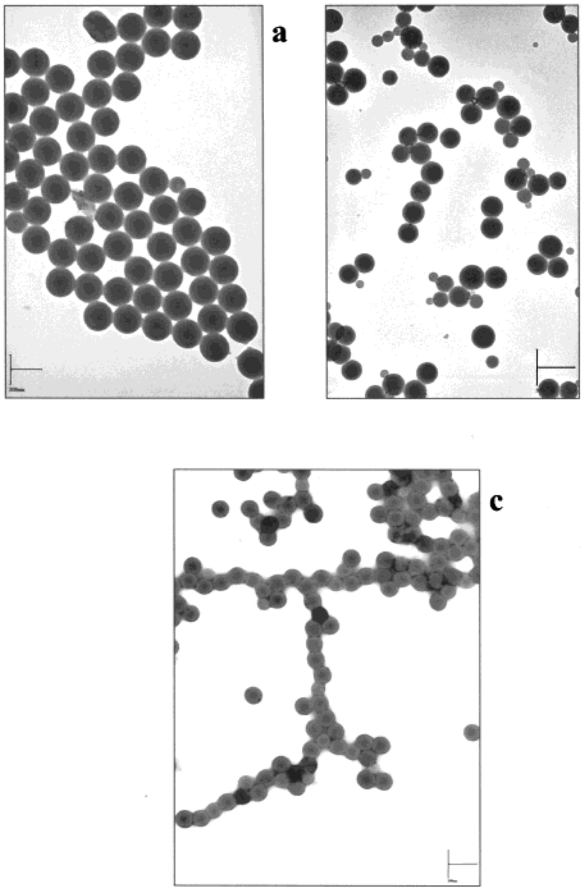

Figure 6. TEM micrographs of polystyrene particles stabilized by (a) C (m_C = 500 mg), (b) A (m_A = 500 mg), and (c) A ($m_{A\cdot}$ = 187 mg).

to exhibit a lower reactivity than styrenyl unsaturation.[21]

Macromonomers functionalized with a maleate group generate larger particles than those produced in the presence of A (Figure 4). This result could be explained by later stabilization due to lower reactivity and better solubility of F in the medium; the critical molar mass, at which the nuclei are formed, increases.

F exhibits a much higher critical micellar concentration[19] than A (25 times higher), and under the conditions used, F-type surfactants cannot produce polymerizable micellar aggregates; therefore, the particles formed are rather monodisperse (Figure 7a).

On the other hand, the reactivity of the maleate group decreased, the rate of polymerization although the overall conversion in monomer (85%) approached that found for the particles synthesized in the presence of A-type surfactants (Figure 5).

Effect of Amphiphilic Feature of the Macromonomer. The role played by the amphiphilic character of the macromonomer on the colloidal stabilization was also examined. A series of dispersion polymerizations were thus carried out in the presence of both non-surface-active macromonomer (PEO >96%) (H) and amphiphilic macromonomer A.

Figure 8 shows that particles of smaller size were obtained using A instead of H as surfactants. This suggests that A is a better stabilizer; because of its amphiphilic character, A adsorbs onto the particles from the onset until the end of nucleation, after which the number of particles remains constant. The particle then grows to a predictable size. In contrast, with H the actual stabilizer is the copolymer formed by reaction with styrene so that adsorption occurs progressively, favoring the formation of particles of larger size.

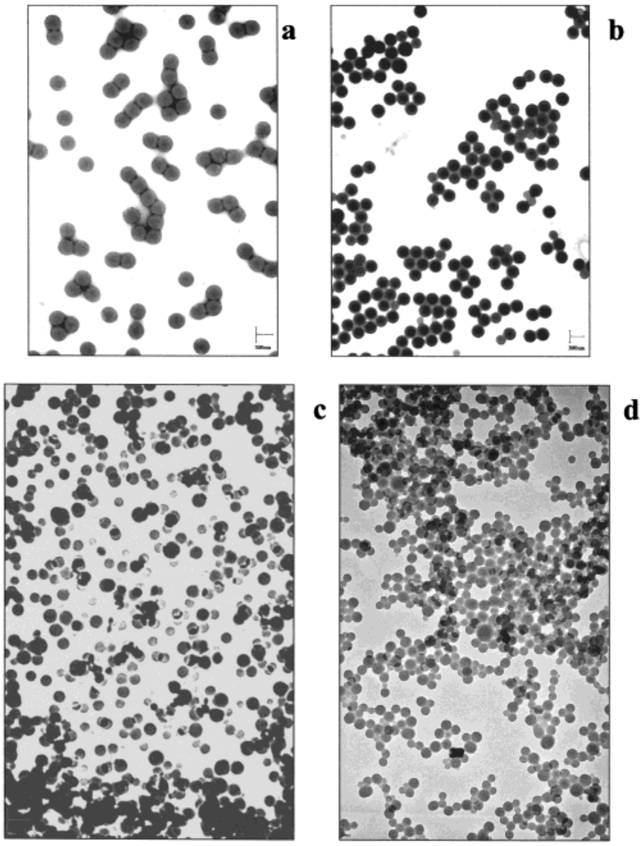

Figure 7. TEM micrographs of polystyrene particles stabilized by (a) F (m_F = 500 mg), (b) H (m_H = 500 mg), (c) B (m_B = 500 mg), and (d) D (m_D = 500 mg).

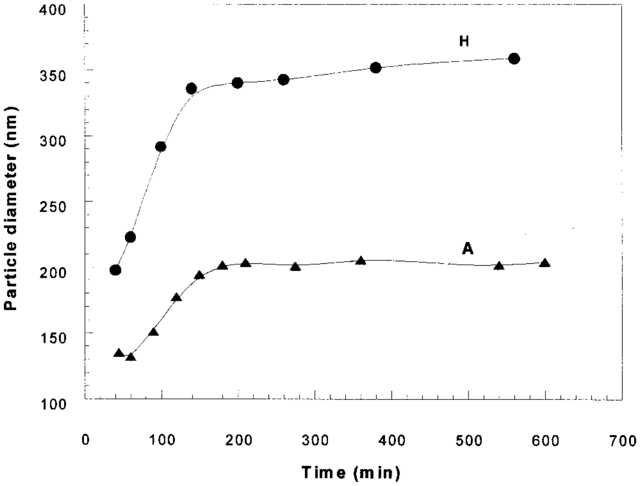

Figure 8. Evolution of the particles diameter during the polymerization of styrene with A (▲) and H (●) as reactive surfactants.

Despite this difference, the kinetics of polymerization in the presence of H and A are very similar as shown in Figure 9. This implies that the size of the hydrophilic block does not affect the rate of polymerization.

Because H cannot self-aggregate into micelles, a separate nucleation process cannot occur, and therefore particles of rather narrow size distribution (Figure 7b) were obtained.

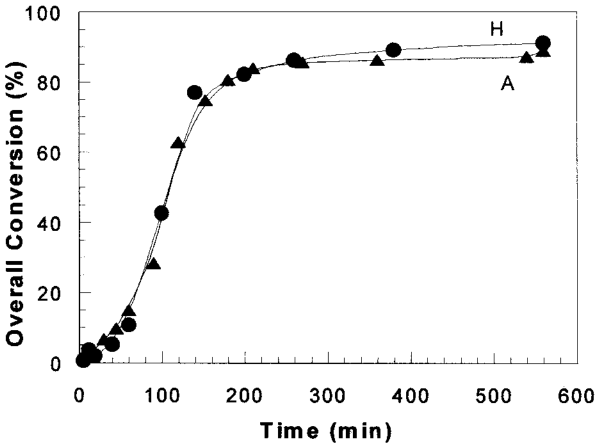

Figure 9. Evolution of the overall conversion during the polymerization of styrene with A (▲) and H (●) as reactive surfactants.

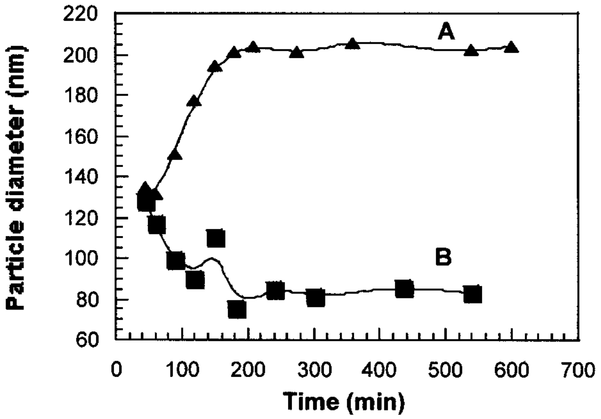

Figure 10. Evolution of the particles diameter during the polymerization of styrene with A (▲) and B (■) as reactive surfactants.

Effect of Molar Mass of the Stabilizer. The molar mass of the stabilizer is another very crucial factor that governs the size of the particles formed. The effect of this parameter was investigated using two PS-*b*-PEO macromonomers of different molar masses, namely 6600 g/mol (A) and 17 800 g/mol (B), but of the same composition (PEO = 75%) and similar polymerizable group.

Figure 10 shows that the particle size tends to decrease as the molar mass of the stabilizer increases. One reason for this tend may be the larger surface area occupied by stabilizers of higher molar mass. An additional reason may be the larger hydrophobic block in B favors the adsorption of the macromonomer onto the latex and enhances the efficiency of the stabilization. In that event, the nucleation steps ends at an early stage of the polymerization and therefore produces smaller particles. Another explanation should be that stabilizer of higher molar mass reaches the critical value at an early stage of polymerization, providing earlier nucleation and smaller particles.

Surprisingly, as polymerization goes on and macromonomers are consumed, the average particle diameter decreases (Figure 10). This result can be accounted for the formation at the beginning of the polymerization of macromonomer-based micelles and their subsequent disappearance from the medium, especially in the case where these amphiphilic stabilizers contain a large hydrophobic block.

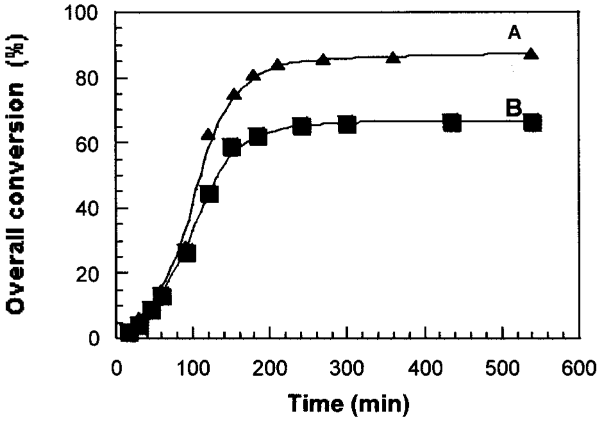

Figure 11. Evolution of the overall conversion during the polymerization of styrene with A (▲) and B (■) as reactive surfactants.

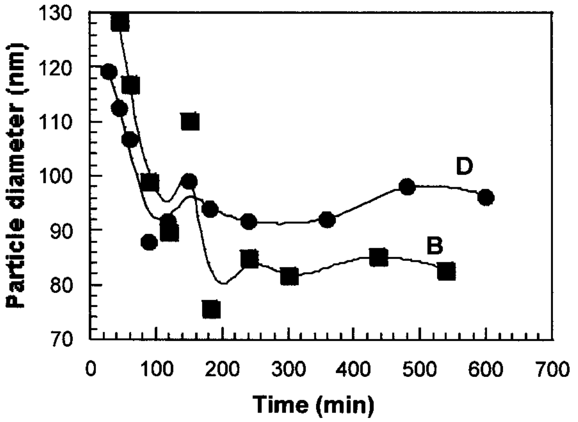

Figure 12. Evolution of the particles diameter during the polymerization of styrene with D (●) and B (■) as reactive surfactants.

As expected, the rate of polymerization was not affected by the size of the stabilizer (Figure 11). The lower final overall conversion with B may be explained by steric hindrance due to a hydrophobic block.

Likewise, the size distribution of particles was not drastically changed upon varying the molar mass of the stabilizer as shown in Figures 6b and 7c.

Effect of the Structure of the Stabilizer. The influence of the molecular architecture of the stabilizer on the outcome of the dispersion polymerization of styrene was also investigated. The fact that gemini-type surfactants exhibit better dispersing performances than conventional surfactants[22] prompted us to examine the potential of gemini-type PS-*b*-PEO_2 macromonomers (D) as surfactant and compare their behavior with that of linear homologues.

As shown in Figures 12 and 13, the gemini-type surfactants affect neither the kinetics nor the particle size. In addition, despite its higher cmc, D seems to self-aggregate into micelles and gives rise to a separate nucleation process (Figure 7d). One way to suppress such side nucleation and improve the size distribution particles would be to decrease the hydrophobic block size or reduce the reactivity of the polymerizable entity. This study is currently in progress in our laboratory.

Conclusion

Five PS-*b*-PEO macromonomers with various molecular features, including different polymerizable groups,

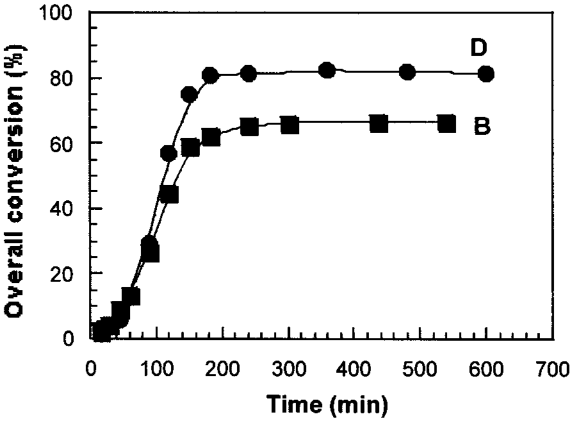

Figure 13. Evolution of the overall conversion during the polymerization using macromonomers D (●) and B (■) as reactive surfactants.

compositions, molar masses, and structures, were used as reactive surfactants in the dispersion polymerization of styrene. Despite the tendency of some of them to self-aggregate into micelles, it is possible to produce relatively monodisperse polystyrene particles using these macromonomers as stabilizers. Low molar mass copolymers exhibiting high critical micellar concentration were best suited to stabilize and generate particles with narrow size distribution. In contrast, PS-*b*-PEO macromonomers of larger size did not qualify from this application because the exchange between micelles and unimers was too slow, which favored a separate nucleation process and resulted in particles with a broad size distribution.

In this study it was found that the use of amphiphilic macromonomers results in an incorporation yield of the stabilizer and produces latexes of better stability than those stabilized by hydrophilic macromonomers. However, the self-association of amphiphilic macromonomers in polar media may bring about a secondary nucleation and afford particles with a broader size distribution.

Experimental Part

Materials. Styrene (Aldrich, 99%) was distilled under reduced pressure to remove all impurity. 2,2′-Azobis(isobutyronitrile) (AIBN) (Janssen Chemica, 98%), hydroquinone (Aldrich, 99%), toluene, and ethanol were used as received.

Synthesis of Stabilizer. The macromonomers were synthesized via anionic polymerization. The PS block was first obtained, and then the PEO block was grown. Depending on the type of unsaturation (styrenyl or maleate), the polymerizable group was introduced upon deactivation of carbanionic or oxanionic species with an appropriate electrophilic unsaturated reactant. In this way, macromonomers with controlled and narrow molar masses distribution and high functionalization could be obtained. The synthesis of these macromonomers was described in previous papers.[7,8,23] Characteristics pertaining to these macromonomers are given in Table 1. This table reports the size of the PS and PEO blocks, the percent of the PEO part, the molar mass of the block macromonomer, and the critical micelle concentration (cmc). On the other hand, Figure 1 shows the molecular structures of the different families of macromonomers.

Dispersion Polymerization. All the experiments were carried out following the recipe below.

The dispersion polymerizations were carried out at 70 °C in a 250 mL glass reactor under a nitrogen atmosphere and stirring. In a typical synthesis, styrene (14 g, 0.135 mol) and the macromonomer (0.5 g) were dissolved in ethanol (100 g) in the presence of water (44 g) at 70 °C. After purging with nitrogen, a solution of AIBN (0.35 g, 2.13 mmol) in styrene (2 g, 0.019 mol) was added to the reactor. After 12 h the polymerization was terminated by additing hydroquinone (0.3 g, 2.7 mmol).

Latex Characterizations. Before characterizing the samples by ^{1}H NMR, the particles resulting from dispersion polymerization were dried and then washed with hot methanol (Soxhlet extraction) for 5 h. In this way unreacted stabilizer and reacted, but soluble species could be removed.

For kinetic studies, aliquots were sampled out from the reactor with a syringe at different polymerization times.

The conversion in styrene was determined by gas chromatography using dodecylundecane (1 mL) as internal standard.

The overall conversions (both styrene and macromonomer) of the polymerization were determined by gravimetry,[7] that is, by determination of the weight of the polymer formed after a given time (on cleaned latex).

The conversion in macromonomer at a given time was determined by ^{1}H NMR on the basis of the amount incorporated into the particle, taking into account the conversion in styrene.

The number of particles (per milliliter of latex) was calculated according to the classical equation $N_p = 6\tau/\Pi D_p{}^3 d_p$, where τ is the polymer content in g/mL, d_p is the polymer density in g/mL, and D_p is the diameter of particles in cm.

The variation of the particle size during polymerization was monitored using photon correlation spectroscopy (Malvern zetasizer 3000). Before measurements, the latexes were diluted about 100 times in an ethanol−water mixture to minimize multiple scattering caused by high concentration.

After completion of polymerization, some selected dried samples were analyzed using transmission electron microscopy (TEM, H7000 FA Hitachi). The D_w/D_n values were determined over 200 particles.

The cmc measurements were carried out using a KSV Sigma 70(KSV Instruments Ltd.) tensiometer.[19] Briefly, weighed amounts of macromonomer were dissolved in a 250 mL volumetric flask containing water at room temperature and equipped with a magnetic stirrer. The cmc was measured following the change in the surface tension of the aqueous solution with the concentration of the added macromonomer. The cmc value was determined from the intersection point of the two lines obtained by linear regression of the experimental data.

^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker AC 200FT apparatus.

SEC analysis was performed at 20 °C in THF (0.7 mL/min) on a Varian apparatus equipped with a refractive index/UV dual detection and fitted with four TSK columns (250, 1500, 10^4, 10^5 Å). Polystyrene molar masses were determined by using linear polystyrene as the calibration standard. A trace of hydroquinone added to the samples was used as the internal flow marker reference.

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