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Amphiphilic gradient poly(styrene-*co*-acrylic acid) copolymer prepared via nitroxide-mediated solution polymerization. Synthesis, characterization in aqueous solution and evaluation as emulsion polymerization stabilizer

Catherine Lefay [a], Bernadette Charleux [a,*], Maud Save [a], Christophe Chassenieux [b], Olivier Guerret [c], Stéphanie Magnet [c]

[a] *Laboratoire de Chimie des Polymères, Université Pierre et Marie Curie—Paris 6, UMR 7610 Associée au CNRS, Tour 44, 1er étage4, Place Jussieu, 75252 Paris Cedex 05, France*
[b] *Physicochimie des Polymères et des Milieux Dispersés (UMR 7615), UPMC-CNRS-ESPCI, 10 rue Vauquelin, 75231 Paris Cedex 05, France*
[c] *ARKEMA, Groupement de Recherches de Lacq, B.P. no 34, 64170 Lacq, France*

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Abstract

A well-defined, amphiphilic poly(styrene-*co*-acrylic acid) copolymer was synthesized in a single step by nitroxide-mediated controlled free-radical copolymerization of styrene and acrylic acid, without protection of the acid groups: $M_n=6500$ g mol^{-1}, $M_w/M_n=1.5$ and a composition of $F_{AA}=0.70\pm0.03$ in acrylic acid. In addition to the good control over molar mass and molar mass distribution, the copolymer exhibited a narrow composition distribution with a slight gradient. Such copolymer was an efficient stabilizer for the emulsion polymerizations of styrene and of mixtures of methyl methacrylate and *n*-butyl acrylate, until 45 wt% solids. A low amount (typically 3–4 wt% based on the monomer(s)) was needed for a good stabilization. This is approximately a decade lower than the required amount of random, amphiphilic copolymers prepared via conventional free-radical polymerization. The performances were, however, below those of analogous diblock copolymers, but the great advantage is the very easy synthetic procedure.

Keywords: Styrene; Acrylic acid; Amphiphilic copolymer

1. Introduction

Amphiphilic, random copolymers are widely industrially produced and used in different applications such as coatings, adhesives, inks etc. Those copolymers are composed of hydrophobic and hydrophilic monomer subunits, randomly distributed along the chains. They are generally synthesized by classical free radical copolymerization in different media and are usually called ASR for alkali-soluble resins when the hydrophilic comonomer possess a carboxylic acid, ionizable at alkaline pH. In particular, the free radical copolymerization of styrene (St) and acrylic acid (AA) is well described in the literature. It was, for instance, performed either in bulk [1,2], in solution in benzene [3] or in emulsion [3–6]. Moreover, some of the ASR containing St and AA are industrially well-known like for instance the Joncryl™ from Johnson Polymer, the Neocryl™ from Neoresins or the Morez™ 101 from Rohm and Haas. Different patents [7–9] describe in more details the synthesis and use of such copolymers as stabilizers for emulsion polymerizations. They were sometimes used in combination with surfactants of low molar mass [10–12]. One of the major drawbacks of the ASR in emulsion polymerization is the requirement of rather high quantity to stabilize the latexes [13–18]. Indeed, and specially when used as the sole surfactant, their concentration ranged from 25 to 45 wt% on the monomer basis, for a latex solids content up to ca. 50% [13–17]. Such low efficiency might be assigned to the poor structural quality of the amphiphilic copolymers, owing to the use of classical free-radical copolymerization for the synthesis. This method, indeed, produces chains with both a broad molar mass distribution and a broad composition distribution. Consequently, even when the average

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* Corresponding author. Tel.: +33 1 44275502; fax: +33 1 44277089.
E-mail address: charleux@ccr.jussieu.fr (B. Charleux).

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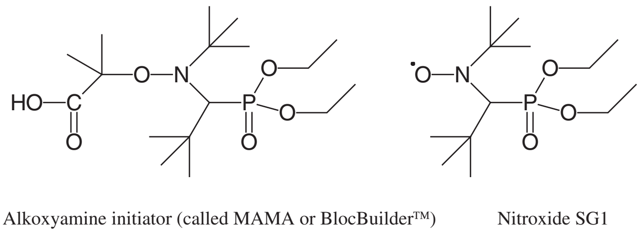
composition and molar mass are appropriate for latex stabilization, a large part of the macromolecules does not efficiently stabilize the emulsion polymerization because of an improper molar mass or an improper hydrophilic/lipophilic balance.

In contrast to the conventional method, controlled free-radical copolymerization is able to yield copolymers that are homogeneous in both molar mass and composition [19–21]. Moreover, as the chains are created simultaneously in the early polymerization stage, they reveal a composition gradient (continuous variation of the comonomer composition along the chain) when the comonomers exhibit a noticeable difference in reactivity [22–26]. Such feature might endow the chains with specific properties, between those of a statistical copolymer and those of a diblock copolymer.

The purpose of this work was thus to improve the structural quality and hence the stabilization properties of amphiphilic random copolymers by using controlled free-radical copolymerization as a synthetic tool. The selected hydrophobic and hydrophilic comonomers were styrene and acrylic acid, respectively. Nitroxide-mediated controlled free-radical polymerization (NMP) was chosen to perform the synthesis, with SG1 as a mediator (Scheme 1), since we recently demonstrated that this nitroxide is well suited to control the copolymerization of styrene and acrylic acid, over a wide composition range, without protection of the acidic groups [27].

The target characteristics of the selected copolymer were a moderate number average molar mass (M_n ranging between 5000 and 10,000 g mol^{-1}) and quite a high hydrophilicity (above 50 mol% of AA) to allow its solubilization in alkaline aqueous solutions. After the full characterization of the copolymer structure and the study by light scattering of its organization in aqueous solution, its efficiency in stabilizing latex particles was tested in emulsion polymerizations. It should be emphasized that the copolymer chain length and composition range were selected in order to closely match the structure of analogous polystyrene-*b*-poly(acrylic acid) diblock copolymers, which exhibited excellent stabilization properties in the emulsion polymerization of styrene [28,29], but which were comparatively more difficult to produce. Indeed, they were prepared in two polymerization steps followed by acidolysis of the ester group of the *tert*-butyl acrylate, used as a hydrophobic precursor of acrylic acid.



Scheme 1. Chemical structure of the alkoxyamine initiator MAMA and of the nitroxide mediator SG1.

2. Experimental part

2.1. Materials

The monomers, styrene (St, Aldrich, 99%), methyl methacrylate (MMA, Acros, 99%) and *n*-butyl acrylate (BA, Aldrich, 99%) were distilled under vacuum before use. Acrylic acid (AA, purest grade, Arkema, stabilized with 200 ppm of hydroquinone) was stored at room temperature and used without further purification. The alkoxyamine initiator (Scheme 1), called MAMA in the following (commercial name is BlocBuilder™, 99% purity) and the nitroxide SG1 (*N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl)-*N*-oxyl, 85% purity) were kindly provided by Arkema. The solvents, 1,4-dioxane (synthesis grade) and dichloromethane (Normapur) were, respectively, supplied by SDS and by Prolabo. Trimethylsilyldiazomethane (2 M solution in hexane) and sodium hydrogen carbonate ($NaHCO_3$, 99.7%) were purchased from Aldrich and potassium persulfate (purity > 99%) from Acros.

2.2. Nitroxide-mediated copolymerization of styrene and acrylic acid

The copolymerization reactions were carried out in 1,4-dioxane solution at 120 °C, according to an already published protocol [27]. The only major difference was the type of alkoxyamine used as an initiator, since here the MAMA (Scheme 1) was chosen instead of the MONAMS [27]. The reactions were performed in a Parr reactor of 300 mL at a stirring rate of 300 rpm. In a typical synthesis, the alkoxyamine initiator MAMA (1.637 g, 4.3×10^{-3} mol) was dissolved in a mixture of styrene (11.50 g, 0.111 mol) and acrylic acid (32.00 g, 0.444 mol, initial molar composition of AA in the comonomer mixture: $f_{AA0}=0.80$). Then, a volume of 145 mL of 1,4-dioxane and 0.0638 g of free SG1 (2.2×10^{-4} mol, 5 mol% based on the initiator) were added. The polymerization solution was transferred into the reactor and deoxygenation was performed at room temperature by nitrogen bubbling for 5 min. Afterward, the reactor was heated at 120 °C and a 2 bar pressure of nitrogen was applied. Time zero for the reaction was arbitrarily taken when the mixture reached 90 °C.

Aliquots were periodically withdrawn during the reaction and cooled in an iced water bath to quench the polymerization. For all of them, the overall monomer conversion was determined by ^{1}H NMR analysis of the raw polymerization medium in acetone d_6 solution. The overall molar conversions (x_{mol}) and the individual conversions of each monomer (x_{AA} and x_{St}) were determined by integrating the peaks corresponding to the vinylic protons, using the broad peak between 6.5 and 7.5 ppm as an internal reference (five aromatic H for styrene and polystyrene, and one vinylic H for the styrene monomer that was subtracted before calculation). The overall weight conversion was calculated from those experimental data [27]. The molar mass of the dried copolymers was determined by size exclusion chromatography after methylation of the AA subunits. The overall molar conversion was used for kinetic analysis (conversion versus time plots), whereas molar masses and polydispersity indexes were plotted as a function of the overall weight conversion.

After 8 h, the reaction yielded a molar conversion of 80% and the final polymerization batch was precipitated in dichloromethane and filtered. The polymer was first dried for 2 days at 60 °C in an oven, and then under vacuum at room temperature. For the purpose of emulsion polymerization, the nitroxide end-group was not removed from the chain-end; actually, the reactions were performed at 70 °C, a temperature that is far too low for the alkoxyamine dissociation (typically above 100 °C).

2.3. Titration of the carboxylic acid groups

The copolymer composition was determined by direct titration of the carboxylic groups with a 0.1 M sodium hydroxide aqueous solution. A precise amount of copolymer (0.115 g) was dissolved in 30 mL of THF and 2 mL of deionized water. Then, the NaOH solution was added dropwise and the pH was followed by a combined pH electrode (XC 100 from Radiometer Analytical). From the mole number of acidic functions in the solution, determined at the equivalent point, the average molar composition of the copolymer in acrylic acid (F_{AA}) was calculated.

2.4. Batch emulsion polymerization of styrene at 10 wt% solids

The free-radical polymerizations of styrene in aqueous emulsion were carried out at 70 °C in a double jacket 250 mL glass reactor, stirred at 300 rpm. The poly(styrene-*co*-acrylic acid) amphiphilic copolymer (weight ranging from 0.10 to 0.80 g; 1–8 wt% based on the styrene content), was added to a 1 M NaOH solution (from 0.81 to 6.48 g, i.e. from 8.1×10^{-4} to 6.5×10^{-3} mol; 1 equiv. NaOH based on the acrylic acid groups) in order to fully neutralize the acidic functions. The solution was then diluted with, respectively, 88–82 mL of deionized water, which already contained $NaHCO_3$ in such an amount that the overall concentration was 0.012 mol L^{-1}. The so-formed alkaline aqueous copolymer solution was then heated at 70 °C in a water bath for 20 min under magnetic stirring to ensure complete copolymer solubilization. After cooling the solution, the pH (which was around 8.5) was adjusted to 10 by the addition of a very small volume of NaOH 1 M. Afterward, the solution was poured into a 250 mL glass reactor thermostated at 70 °C. The stirring rate was 300 rpm. After a 45 mm deoxygenation time by nitrogen bubbling, styrene (10 g, 10 wt% target solids content, previously deoxygenated for 20 min) was added in one shot to the aqueous solution and the mixture was stirred for an additional period of 15 min. The initiator, $K_2S_2O_8$, dissolved in a small quantity of deionized water (0.15 g, 0.006 mol L^{-1} based on the total aqueous volume) was finally poured into the reactor, which triggered the beginning of the reaction. Samples were periodically withdrawn for the 3 h of reaction time, cooled in an iced water bath to stop the polymerization and then analyzed by dynamic light scattering. The conversion was determined by gravimetry after addition of a small amount of hydroquinone to prevent further polymerization upon heating.

2.5. Semi-continuous emulsion polymerizations at 45 wt% solids

The emulsion polymerizations of styrene (45.5 g, 45 wt% target solids content) and of a mixture of methyl methacrylate and *n*-butyl acrylate (35/65 (wt/wt), 45 wt% target solids content) were performed following a semi-continuous addition of the monomers in the reactor already containing the aqueous phase. The latter was composed of 44 g of deionized water, 1.37 g of the poly(styrene-*co*-acrylic acid) stabilizer (3 wt% based on the monomers), 0.012 mol L^{-1} of $NaHCO_3$ and 11.5 g of a 1 M NaOH solution (1.15×10^{-2} mol, 1 equiv. NaOH based on the acrylic acid groups of the stabilizer). The preparation of the amphiphilic copolymer solution was the same as before. The monomers (previously deoxygenated for 45 min) were continuously fed during 4 h into the double jacket 250 mL glass reactor heated at 70 °C and stirred at 300 rpm. The introduction in one shot of the $K_2S_2O_8$ solution (0.09 g dissolved in a small quantity of deionized water, 0.006 mol L^{-1} based on the total aqueous volume) was synchronized with the beginning of the monomer addition and triggered the start of the reaction. At the end of the monomer introduction, a new portion of $K_2S_2O_8$ (0.045 g; 1.66×10^{-4} mol; 0.003 mol L^{-1}) was added and the polymerization was performed for an additional hour. The final latexes were cooled in an iced bath and then analyzed by dynamic light scattering and by gravimetry.

2.6. Analytical techniques

2.6.1. Size exclusion chromatography (SEC)

The average molar mass and molar mass distribution were obtained by SEC in THF with 1 mL min^{-1} flow rate and a polymer concentration of 5 g L^{-1}, after full methylation of the acrylic acid subunits of the copolymers. The experimental procedure used for methylation has already been published [27]. The SEC apparatus is composed of two columns thermostated at 40 °C (PSS SDV, linear M, 8 mm×300 mm; bead diameter: 5 μm; separation limits: 400–2×10^6 g mol^{-1}) and of two detectors: RI (LDC Analytical, refractorMonitor IV) and UV operating at 254 nm (Waters 484). The molar mass characteristics of the poly(styrene-*co*-methyl acrylate) copolymers (M_n, the number average molar mass; M_w, the weight average molar mass; and $PDI = M_w/M_n$, the polydispersity index) were calculated from the differential RI trace, using a calibration curve based on polystyrene standards [30]. The molar masses of the original poly(styrene-*co*-acrylic acid) copolymers were systematically derived and are the ones given in the article.

2.6.2. NMR (250 MHz)

Analyses were performed in 5 mm tubes at room temperature using an AC250 Brucker spectrometer. The chemical shift scale was calibrated on the basis of the solvent signal, i.e. deuterated acetone, at 2.05 ppm.

2.6.3. Liquid adsorption chromatography (LAC)

The methylated copolymers (5 g L^{-1}) were analyzed by LAC in order to investigate the composition distribution since the technique allows the chains to be separated according to their composition, regardless of the molar mass [31]. Separation was carried out at 30 °C on a grafted silica column with a gradient hexane/THF as an eluent at a flow rate of 3 mL min^{-1}. The detection was performed using a UV detector (Waters 481) and an evaporative light scattering detector (DEDL 21, Eurosep).

2.6.4. Light scattering

Alkaline aqueous solutions of the poly(styrene-*co*-acrylic acid) amphiphilic copolymer at different concentrations were analyzed by light scattering. The master solution at a concentration of 25 g L^{-1} (3.8×10^{-3} mol L^{-1}) was prepared with the following components: deionized water (44 g), copolymer (1.376 g, 2.12×10^{-4} mol, $M_n=6500$ g mol^{-1}, $F_{AA}=0.70$), 1 M NaOH solution (11.2 g) and $NaHCO_3$ (0.055 g, 0.012 mol L^{-1}). The solution was prepared as described before in the emulsion polymerization part except that after adjustment of the pH to 10, the solution was heated again in a water bath at 70 °C for 45 min (same duration as the deoxygenation period in the emulsion polymerization). The cooled solution was next analyzed either directly, or after filtration, or after dilution by a solution composed of 250 mL of deionized water, $NaHCO_3$ (0.252 g, 0.012 mol L^{-1}) and a small quantity of 1 M NaOH solution to adjust the pH to 10.

Static (SLS) and dynamic (DLS) 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. The intensity autocorrelation function, $g_2(t)$, and the mean scattered intensity, I, were measured at several wave vector values $q=(4\pi n/\lambda)\sin(\theta/2)$, with n being the refractive index of the solvent and θ being the observation angle ranging from 30 to 140°. The measurements were done at 25 °C if not otherwise specified. The electric field autocorrelation functions $g_1(t)$, related to $g_2(t)$ via the Siegert relation [32], were analyzed using a REPES routine, assuming a continuous distribution of the relaxation times (Eq. (1))

$$g_1(t) = \int_{-\infty}^{+\infty} A(\tau)\exp(-t/\tau)\mathrm{d}\tau \tag{1}$$

In the whole concentration range investigated, the calculated distributions of relaxation times were bimodal. The relaxation times that can be derived for the fast (τ_{fast}) and the slow (τ_{slow}) relaxation processes were q^2-dependent, which allowed the respective translational diffusion coefficient to be calculated, according to: $D_i=(\tau_i q^2)^{-1}$, where i denotes fast or slow. The concentration dependence of D_i is given by: $D_i=D_{0i}(1+k_{Di}C)$ where k_{Di} is the dynamic virial coefficient and D_{0i} is the mutual diffusion coefficient useful to derive the value of the hydrodynamic radius according to $R_{Hi}=kT/(6\pi\eta D_{0i})$, in which k is the Boltzman constant and η the viscosity of the solvent.

2.6.5. Surface tension measurements

The surface tension of alkaline aqueous copolymer solutions was measured with a drop tensiometer (ITC Concept) using the pendant drop method at 25 °C. Solutions with varying copolymer concentrations (from 1.56 to 25 g L^{-1}) were prepared as described in the previous section. The time dependence of the interfacial tension between solution and air was determined by the digital processing of the shape of a drop of the first fluid formed within a quartz cell containing the second fluid (i.e. air). The drop was illuminated by a CCD camera driven by a microcomputer using the Windrop 1.1 software from ITC Concept. After one day of measurement, the surface tension had decreased but never leveled off to a plateau value. For a longer measurement time, the drop fell down and the analysis was stopped.

2.6.6. Analytical techniques to measure the average latex particle size and the particle size distribution

The *z*-average diameter (D_z) of the polystyrene latex particles was measured with a Zetasizer 4 from Malvern, using a 5 mW He–Ne laser at 633 nm.

The polystyrene latex particles were visualized by transmission electron microscopy (TEM, JEOL JEM 100 cx II CHR). The count of 500 particles allowed the number — (D_n), and weight — (D_w) average diameters to be calculated. The number concentration of latex particles per liter of latex was calculated according to Eq. (2), where D_n is the number average particle diameter expressed in centimeter, d_p is the polystyrene density ($d_p=1.05$ g cm^{-3}) [33] and τ_p is the polymer content (g L_{latex}^{-1})

$$N_p(L_{\text{latex}}^{-1}) = \frac{6\tau_p}{d_p\pi D_n^3} \tag{2}$$

3. Results and discussion

3.1. Synthesis and characteristics of the poly(styrene-co-acrylic acid) amphiphilic copolymer

As previously mentioned, the aim of this work was to obtain, in a single polymerization step, a well-defined, amphiphilic poly(styrene-*co*-acrylic acid) copolymer with a moderate number-average molar mass, a narrow molar mass distribution, and a selected hydrophilic/lipophilic balance in order to get easy solubilization in alkaline water. In addition, the copolymer had to exhibit a narrow composition distribution. The model structure was selected on the basis of polystyrene-*b*-poly(acrylic acid) (PSt-*b*-PAA) diblock copolymers, which proved in the past to be excellent stabilizers in emulsion polymerization [28,29]. Actually, one of the best ones had 16 styrene units and 55 acrylic acid units (molar fraction of AA in the copolymer, $F_{AA}=0.77$). For the copolymerization reaction, we started from an initial molar fraction of AA in the comonomer feed of $f_{AA0}=0.80$. Knowing from the previously determined reactivity ratios ($r_{St}=0.72\pm 0.04$ and $r_{AA}=0.27\pm 0.07$) [27] that, at such initial composition, styrene would be consumed faster than acrylic acid, we expected to have an average copolymer composition, F_{AA}, below 0.80 at incomplete conversion.

To control the chain length and chain length distribution, we used SG1-mediated copolymerization of styrene and acrylic acid, with experimental conditions already established in a previous work [27]. The initiator concentration was selected so as to reach a final M_n of 10,100 g mol^{-1} at full monomer conversion. Fig. 1 displays the dependence with the overall weight conversion of the number average molar mass (M_n) and of the polydispersity index (PDI $=M_w/M_n$). It appears that all the criteria of a controlled polymerization were fulfilled: (i) M_n increased linearly with the overall weight conversion until 75% and (ii) the polydispersity indexes remained simultaneously lower than 1.4. Moreover, the SEC chromatograms depicted in Fig. 2 exhibited the expected shift toward higher M_n with the conversion progress. Nevertheless, when the experimental M_n's are compared with the theoretical values, a clear deviation from linearity is observed at high conversion, along with an increase in the polydispersity indexes. Such tendency was assigned to chain transfer to the solvent, 1,4-dioxane. Taking this transfer reaction into account and using an average value of $C_{tr}=4\times 10^{-4}$ for the chain transfer constant in the copolymerization reaction allows the experimental data to be nicely adjusted (see all calculation details in Ref. [34]). This value does not differ so much from that already determined for the homopolymerization of acrylic acid where C_{tr} was 6×10^{-4} [34]. To limit the impact of this side reaction, while recovering a sufficient amount of product, the copolymerization was stopped at 80% conversion. Before purification, the recovered copolymer had $M_n=6300$ g mol^{-1} and $M_w/M_n=1.53$. After purification by precipitation, the final copolymer exhibited the following characteristics: $M_n=6500$ g mol^{-1} and M_w/M_n was approximately the same as before purification, that means close to 1.5. Some small copolymer chains might have thus been eliminated by precipitation.

The average molar fraction of AA in the purified final copolymer was $F_{AA}=0.70\pm 0.03$, as determined by carboxylic group titration (in the following, the copolymer will be referred to as poly($St_{30\%}$-*co*-$AA_{70\%}$)). As expected, the composition drift with respect to the initial comonomer feed composition can be explained by the difference in reactivity of the comonomers, i.e. by the reactivity ratio values ($r_{St}=0.72$ and $r_{AA}=0.27$). On the basis of these reactivity ratios, we simulated the change in copolymer and remaining comonomer compositions with the conversion progress [35] (see Fig. 3). A good agreement of the calculated values of the remaining comonomer composition with the experimental ones obtained

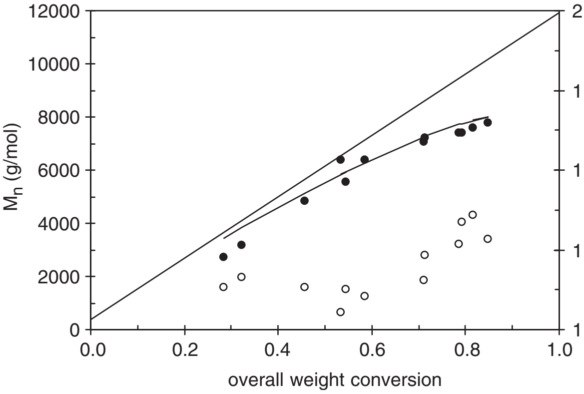


Fig. 1. Number average molar mass, M_n (full symbols), and polydispersity index, M_w/M_n (empty symbols), of the methylated copolymer versus the overall weight conversion, as measured by SEC. The straight line corresponds to the theoretical M_n in the absence of transfer reaction, whereas the curved line corresponds to M_n calculated assuming chain transfer reaction to the solvent 1,4-dioxane, with the average chain transfer constant, $C_{tr}=4\times 10^{-4}$.

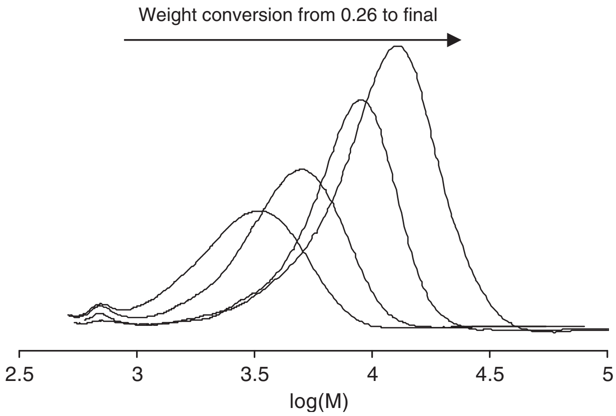


Fig. 2. SEC chromatogram (RI traces) of the methylated copolymer at various overall weight conversions.

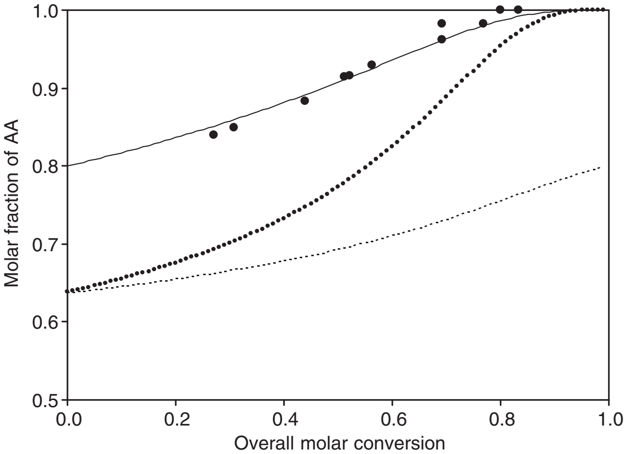


Fig. 3. Theoretical proportion of acrylic acid in the comonomer mixture (—) and in the copolymer (•••: instantaneous composition calculated from the composition equation assuming a terminal copolymerization model; - - -: average composition from conversion 0) as a function of the overall molar conversion (from ^{1}H NMR), on the basis of the reactivity ratios, $r_{St}=0.72$ and $r_{AA}=0.27$, for an initial comonomer composition of $f_{AA0}=0.80$. •: Experimental proportion of acrylic acid in the comonomer mixture (from ^{1}H NMR).

from ^{1}H NMR was observed. This result confirms that the previously determined reactivity ratios are applicable to this system, although a different initiator was used in both studies. This is actually a normal trend since the influence of the initiator might be lost above a given conversion. Consequently, the simulation correctly describes the copolymer composition too. As shown in Fig. 3, the calculated copolymer average composition in acrylic acid starts at $F_{AA}=0.64$ and continuously increases. The instantaneous composition, also displayed in Fig. 3, shows the enrichment in AA units in the copolymer with the conversion increase. Since, in controlled polymerization, conversion is proportional to chain length, the consequence of this is a gradient composition, i.e. a continuous change in local composition along the chain. This was confirmed experimentally by the LAC analyses, performed at different conversions, as reported in Fig. 4 and showing: (i) the net composition drift of the copolymer chains toward higher F_{AA} values with the increase in comonomer conversion, and (ii) the narrow composition distribution.

At the final conversion of 80%, the theoretical average composition is 0.75, which is different from the value $F_{AA}=0.70\pm0.03$ determined experimentally for the purified copolymer by carboxylic acid titration. The purification by precipitation contributed thus to eliminate poly(acrylic acid)-rich chains, most probably formed in the later stage of the polymerization by chain transfer to the solvent.

To summarize, in one polymerization step we achieved the synthesis of a copolymer with the following characteristics, corresponding well to the target: $M_n=6500$ g mol^{-1}, M_w/M_n close to 1.5 and $F_{AA}=0.70\pm0.03$. Due to the difference in reactivity of the comonomers, the copolymer exhibited a gradient composition, with an enrichment in AA from the initiator fragment to the alkoxyamine chain-end. Moreover, the copolymer could be easily dissolved in alkaline aqueous solution, which allowed the properties in the solution state to be examined.

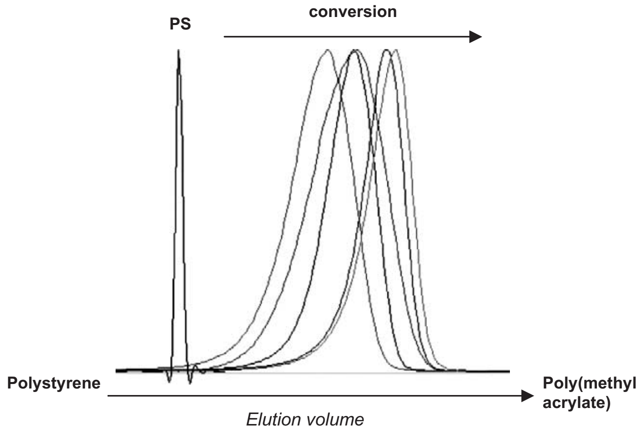


Fig. 4. Liquid adsorption chromatography (LAC) traces of the methylated poly(styrene-*co*-acrylic acid) amphiphilic copolymer obtained at different conversions; the results are compared with a polystyrene standard.

3.2. Study of the poly($St_{30\%}$-*co*-$AA_{70\%}$) gradient copolymer in aqueous solution

As already pointed out in Section 2, the autocorrelation functions measured by dynamic light scattering displayed two diffusive relaxation processes within the whole concentration range investigated (see insert of Fig. 5). Fig. 5 shows the concentration dependence for both diffusion coefficients; the values for the hydrodynamic radii that can be derived for the fast mode and the slow mode of relaxation at infinite dilution are, respectively, $R_H^{fast}=1.2\pm0.2$ nm and $R_H^{slow}=30.6\pm0.6$ nm. It is likely that the fast mode of relaxation corresponds to free polymer chains (the so-called unimers), whereas the slow mode of relaxation corresponds to large size aggregates. The unimers might be deeply compacted by intramolecular association of the styrene subunits, which would explain their very small size. This structuration for the amphiphilic copolymer chains in solution is very different from that generally observed in the case of analogous block copolymers. The particular case of polystyrene-*b*-poly(acrylic acid) diblock copolymers has been previously studied in our group [29]. The system composed of diblock copolymers is often strongly cooperative and the unimers, if they exist, are not easy to observe in solution because of the large proportion of micelles. The majority of the chains of diblock copolymers is thus associated into micelles (for instance, the neutralized PSt_{16}-*b*-PAA_{55} diblock copolymer micelles exhibited an aggregation number of 330–350 at a salt concentration similar to that used here) [29], which is not the case with our gradient copolymers. The chemical structure of the latter could account for this lower cooperativity in terms of aggregation.

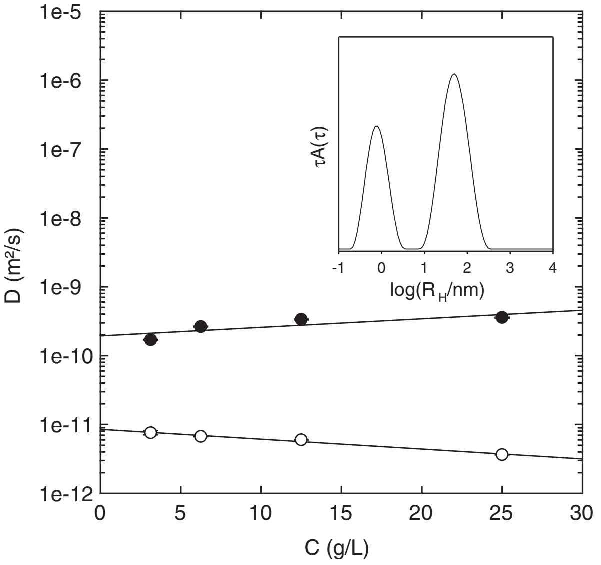


Fig. 5. Concentration dependence of the apparent diffusion coefficient for the slow (open circles) and the fast (closed circles) mode of relaxation. The straightlines correspond to least-squares fits of the data and allow the determination of the hydrodynamic radius for each mode of relaxation (see text). The insert plot displays a typical bimodal distribution of relaxation times obtained from DLS, measured here for $C=25$ g L^{-1} at $\theta=90°$.

It appeared that the aggregates (slow relaxation mode) were not sensitive (in terms of size and contribution to the scattered intensity) to neither heating time during the preparation of the solutions (from 20 min to 61 h at 90 °C; from 3 h to 24 h at 70 °C), nor salt addition (0.5 or 1 M NaCl; 0.5 or 1 M $NaHCO_3$). It should be emphasized that the salt content added to the solution during its preparation was high enough to screen electrostatic interactions. Nevertheless, a puzzling result is that the size of those aggregates was deeply affected by the porosity of the membrane used for filtration (from 0.45 to 0.02 μm). They could thus be disrupted into smaller species by filtration, leading to a sharp decrease of the scattered intensity but keeping the concentration of the solution constant (as measured by UV spectrometry and differential refractometry). As a consequence, it is very likely that the aggregates were not a major component of the system and they implied only a small fraction of the overall concentration. It is very difficult for us to firmly conclude about the exact nature of these aggregates but we could invoke the explanation raised by Sedlak [36] who has attributed the slow mode detected for polyelectrolyte solutions (in pure water and/or in brine) to the existence of metastable multi-chain domains. Our major conclusion is that these aggregates implied only a small fraction of polymer chains (as detailed below from a quantitative analysis of light scattering data). Again, the behavior in solution of our gradient copolymer clearly differed from that of its diblock homologues since varying the heating time during the preparation of the solutions had no influence on their characteristics, which is not the case when frozen structures based on amphiphilic diblocks are considered [37].

A more quantitative picture of this latter fact may result from SLS measurements. The Rayleigh ratio for the solution is given by Eq. (3), where I_{solution}, I_{solvent} and $I_{\text{reference}}$ are the intensity scattered, respectively, by the solution, the solvent (water) and the reference (toluene) with, for the latter, the Rayleigh ratio $= R_{\text{reference}}$

$$R_\theta = \frac{I_{\text{solution}}(\theta) - I_{\text{solvent}}(\theta)}{I_{\text{reference}}(\theta)} R_{\text{reference}} = R_\theta^{\text{fast}} + R_\theta^{\text{slow}} \tag{3}$$

The Rayleigh ratio for the fast and the slow modes of relaxation is given by $R_\theta^i = A^i(\theta) R_\theta$, where $A^i(\theta)$ is the contribution to the scattered intensity of each relaxation process obtained from analysis of the DLS data (see Eq. (1)). The Rayleigh ratio may be related to the weight average molar mass of the scattering entities ($M_{\text{w},i}$) according to:

$$\frac{KC_i}{R_\theta^i} = \left(\frac{1}{M_{\text{w},i}} + 2A_{2,i}C_i\right) P_i(q) \tag{4}$$

K is an optical constant, which depends on the refractive index of the reference (n_{ref}) and on the specific refractive index of the polymer ($\mathrm{d}n/\mathrm{d}C = 0.14$ mL/g) [29] according to Eq. (5), in which $\mathcal{N}_\text{a}$ is the Avogadro's number and $P_i(q)$ is the particles form factor

$$K = \frac{4\pi^2 n_{\text{ref}}^2 (\mathrm{d}n/\mathrm{d}C)^2}{\lambda^4 \mathcal{N}_\text{a}} \tag{5}$$

When considering the fast mode of relaxation, the Eq. (4) may be simplified. Firstly, $P_{\text{fast}}(q) = 1$ since the particles displayed a very small size in solution (this was actually proven by the non angular dependence of R_θ^{fast}). Secondly, since the aggregates poorly contributed to the concentration, one can assume that $C_{\text{fast}} = C$, the overall copolymer concentration. The plot of $KC/R_\theta^{\text{fast}}$ versus C should thus lead to the estimate of the weight average molar mass of the unimers (see Fig. 6). The value was indeed $M_\text{w} = 12{,}700 \pm 2300\ \text{g mol}^{-1}$ in fairly good agreement with the weight average molar mass of the amphiphilic copolymer chains ($M_\text{w} = 10{,}000\ \text{g mol}^{-1}$).

It can thus be concluded that the gradient copolymer with average composition $F_{\text{AA}} = 0.70 \pm 0.03$ did not cooperatively micellize in solution at concentrations below 25 g L ($3.8 \times 10^{-3}\ \text{mol L}^{-1}$) like its block copolymer analogues do, but remained under the form of free unimers compacted by intramolecular association of styrene subunits. A very low amount was actually involved in the formation of loose aggregates, easily broken by filtration, which deeply affected light scattering data despite their small contribution to the concentration. Such conclusions are in agreement with recently reported results on the aqueous solution behavior of poly(styrene-*co*-acrylic acid)-*b*-poly(acrylic acid) copolymers [38].

Even though the studied copolymer had a poor tendency to form aggregates, it exhibited a surface activity as shown by the surface tension measurement displayed in Fig. 7. Whatever the initial copolymer concentration (from 1.56 to 25 g L^{-1}; from 2.4×10^{-4} to $3.8 \times 10^{-3}\ \text{mol L}^{-1}$), the surface tension of the water solution continuously decreased with the analysis time, and no equilibrium plateau was reached even after more than 1 day (Fig. 7A). The surface tension was systematically lower when the copolymer concentration was larger (Fig. 7B) and no transition could be observed. In other words, no apparent

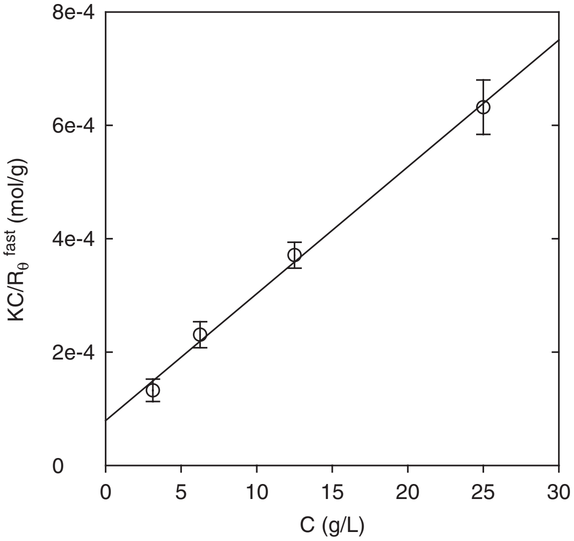


Fig. 6. Concentration dependence of the ratio KC/R_θ for the fast mode of relaxation (see text), the straightline corresponds to a least-square fit of the data.

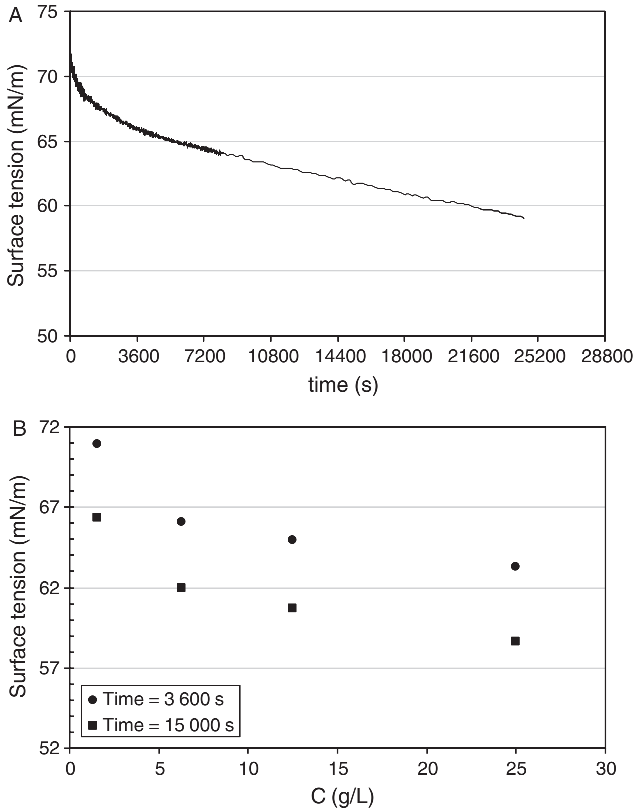


Fig. 7. (A) Surface tension versus time for an aqueous solution of the poly($St_{30\%}$-*co*-$AA_{70\%}$) amphiphilic copolymer (pH 10, [$NaHCO_3$] = 12 mM) at a concentration of 6.25 g L^{-1} (9.6×10^{-4} mol L^{-1}). (B) Surface tension versus copolymer concentration after 3600 and 15,000 s measurement time.

critical micelle concentration could be detected in the studied concentration range, which is fully compatible with the light scattering study. Those results, however, point out the amphiphilic character of the copolymer, which is a good preliminary indication of its stabilization property.

3.3. Use of the poly($St_{30\%}$-co-$AA_{70\%}$) gradient copolymer as a stabilizer in the batch emulsion polymerization of styrene

The gradient copolymer was used as the sole stabilizer in model emulsion polymerizations of styrene. The target solids content of the latexes was 10 wt% and all the polymerizations were performed ab initio, in a batch process. The conditions were selected to allow an easy comparison with our previous work using polystyrene-*b*-poly(acrylic acid) diblock copolymers [28,29]. A first criterion of efficiency was the amount of amphiphilic copolymer necessary to stabilize the latex particles during the polymerization process. A second criterion was the final number of latex particles (N_p) for a given copolymer concentration, i.e. the total surface area stabilized by the copolymer. All results are summarized in Table 1.

From 1 to 8 wt% of copolymer based on styrene, all the final latexes were stable. Such low amount of stabilizer as compared to the usually used ASR, or other amphiphilic random copolymers [13–17], is the good indication of an efficient adsorption at the particle surface of a large majority of the chains in the copolymer sample. This result fully confirms the strong, favorable impact of the narrow composition distribution of the amphiphilic copolymer.

As shown in Table 1, the *z*-average diameter (from DLS) actually decreased when the amount of stabilizer was increased from 1 to 3 wt%, but then reached a plateau. When the particle size distribution is rather broad as it is the case here (see the TEM particle size distributions in Fig. 8; D_w/D_n taken from the TEM analyses ranged from 1.17 to 1.46, see Table 1), DLS cannot be considered as an appropriate method to measure the average diameter as it leads to size discrimination (the smallest particles are not fully taken into account). Consequently, we decided to rely on the TEM analyses and to consider the *n*-average diameter, D_n, derived from this technique. D_n actually continuously decreased when the copolymer concentration was increased. Therefore, increasing the amount of poly($St_{30\%}$-*co*-$AA_{70\%}$) had a strong impact on N_p, which increased proportionally to $[\text{copolymer}]^{0.9}$. Such trend was also corroborated by the polymerization kinetics, as it appeared that the increase in the stabilizer content led to an increase in the conversion rate (Fig. 9), which is the expected behavior as the polymerization rate is proportional to N_p in emulsion polymerization (for all experiments the average number of radicals per particle was the same and close to 0.5) [39].

In conclusion, considering both the particle size and particle size distribution, 3–4 wt% of macromolecular stabilizer seems

Table 1
Model emulsion polymerizations of styrene in the presence of various amounts of the amphiphilic poly($St_{30\%}$-*co*-$AA_{70\%}$) copolymer

wt% copo versus St	[copo]$\times10^4$ (mol L_{latex}^{-1})	D_z (nm) (DLS)	D_n (nm)[a] (TEM)	D_w/D_n[a] (TEM)	N_p (L_{latex}^{-1})$\times10^{-16}$	N_c	A_c (nm^2)
1	1.5	193	130	1.35	7	1400	41
2	3.1	170	123	1.18	10	1900	25
3	4.6	130	92	1.17	23	1200	23
4	6.2	134	94	1.18	22	1700	16
8	12.3	145	75	1.46	43	1700	10

Styrene/water = 10 wt%; [$NaHCO_3$] = 12 mM; [NaOH] = 9–73 mM depending on the amount of copolymer; T = 70 °C; time = 3 h; conversion: 100%. N_p: number of particles per liter of latex, N_c: number of copolymer chains per particle, A_c: surface area occupied by a single copolymer chain at the particle surface (all three values were derived using D_n, TEM).

[a] $D_n = \frac{\sum_i n_i D_i}{\sum_i n_i}$ and $D_w = \frac{\sum_i n_i D_i^4}{\sum_i n_i D_i^3}$.

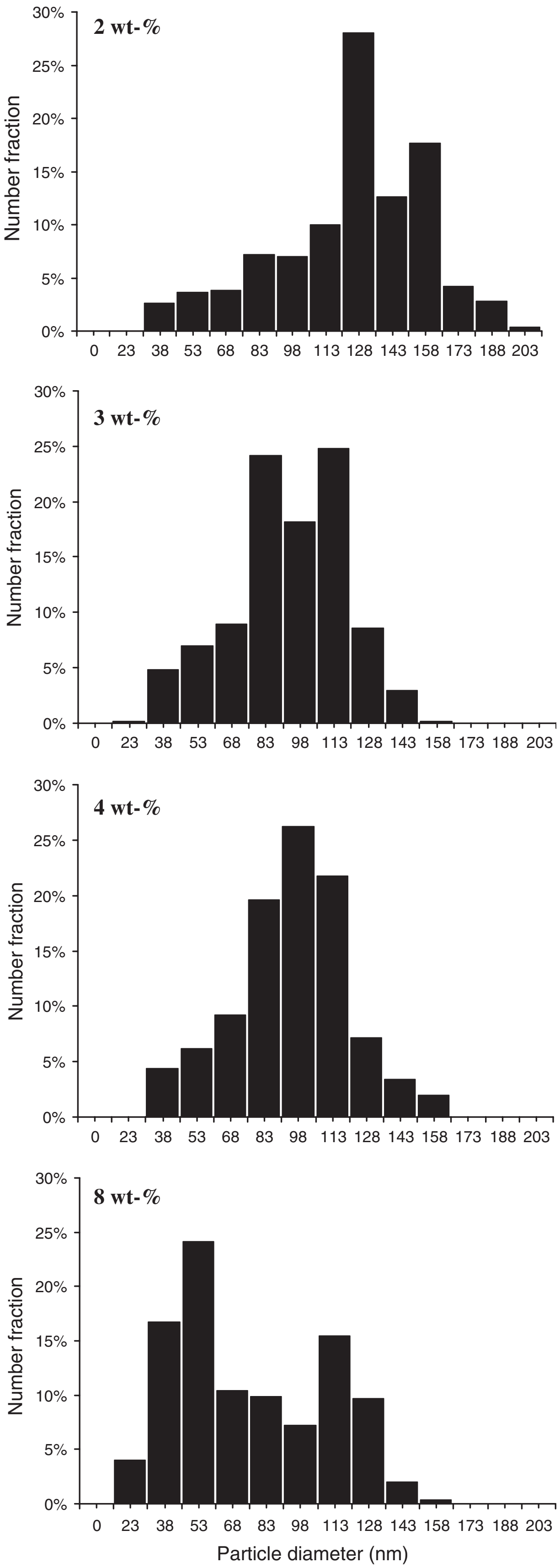


Fig. 8. Particle size number distributions (from TEM) for the polystyrene latexes at 10 wt% solids, containing various amounts (wt% based on styrene) of the poly($\mathrm{St}_{30\%}$-*co*-$\mathrm{AA}_{70\%}$) amphiphilic copolymer as the sole stabilizer.

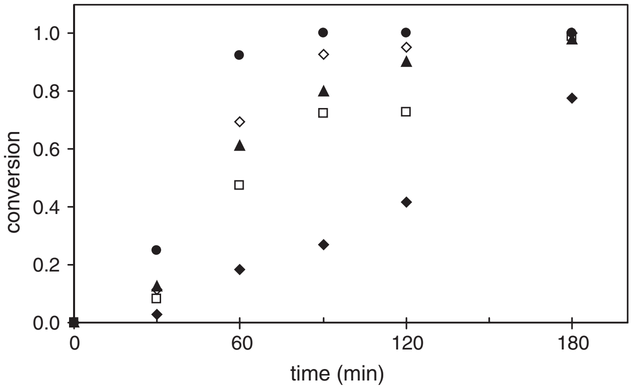


Fig. 9. Conversion versus time for the emulsion polymerizations of styrene with different amounts of the poly($\mathrm{St}_{30\%}$-*co*-$\mathrm{AA}_{70\%}$) amphiphilic copolymer as the sole stabilizer. $T=70$ °C; styrene/water = 10 wt%; $[\mathrm{NaHCO_3}]=12$ mM; $[\mathrm{NaOH}]=9$–73 mM depending on the amount of copolymer. ◆: 1 wt%, □: 2 wt%, ▲: 3 wt%, ◇: 4 wt% and ●: 8 wt%.

to be an optimal amount to obtain stable, 10 wt% solids, polystyrene latexes, in quite a fast polymerization reaction.

The final number of particles in a latex is the direct consequence of the nucleation step. With diblock copolymers, it was concluded that the micelles were playing a direct role in the nucleation mechanism. In some cases, the micelles had a sufficiently long lifetime with respect to the nucleation step, so that they were all turned into a latex particle. In such systems the final number of particles matched the initial number of block copolymer micelles [29]. This was for instance the case for the PSt_{16}-*b*-PAA_{55} diblock copolymer studied before [29]. In contrast, the poly($\mathrm{St}_{30\%}$-*co*-$\mathrm{AA}_{70\%}$) gradient copolymer, which exhibits an overall composition quite similar to that of the aforementioned diblock, mainly dissolves as unimers in alkaline aqueous solution; from light scattering results, the fraction of aggregates was actually very small. A consequence is that the number of particles nucleated and stabilized by the poly($\mathrm{St}_{30\%}$-*co*-$\mathrm{AA}_{70\%}$) gradient copolymer was not as high as that with the PSt_{16}-*b*-PAA_{55} diblock copolymer, as illustrated in Fig. 10. The relationship between

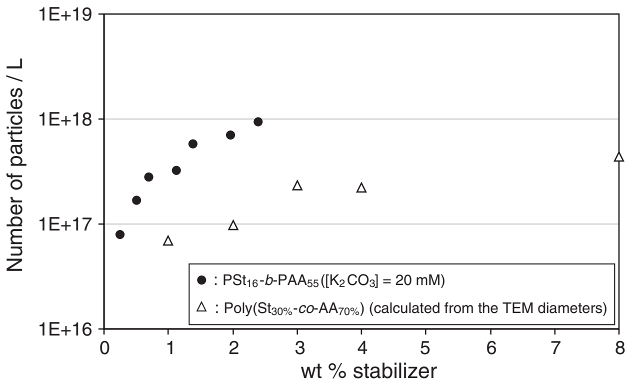


Fig. 10. Number of particles per liter of latex (N_p) as a function of the weight percent of copolymer stabilizer, based on the monomer, for the emulsion polymerization of styrene at 10 wt% solids content (see Table 1 for the experimental conditions and results concerning the gradient copolymer poly($\mathrm{St}_{30\%}$-*co*-$\mathrm{AA}_{70\%}$) and Refs. [28] and [29] for the diblock copolymer PSt_{16}-*b*-PAA_{55}).

the number of particles and the copolymer concentration was, however, very similar for both species (for the gradient copolymer, N_p was proportional to [copolymer]$^{0.9}$, while the exponent ranged from 0.86 to 1.0 for the PSt$_{16}$-*b*-PAA$_{55}$ diblock copolymer, depending on the salt concentration). In the latter case, the number of copolymer chains per particle matched the aggregation number of the micelles (300–350 with 0.020 mol L^{-1} of K_2CO_3) [29], which was a good indication of a direct micellar nucleation mechanism. Differently, one can estimate a number of 1200–1900 chains per particle (Table 1) for the gradient copolymer, assuming that all chains reside at the particle surface (neither burial in the particle core, nor equilibrium solubilization in the aqueous solution). In other words, the average surface area, A_c, occupied by one stabilizer molecule at the particle surface was always smaller for the gradient copolymer than for the diblock (for instance, $A_c = 25$ nm^2 for the former, whereas it was 39 nm^2 for the latter, when an amount of 2 wt% of copolymer was used, based on the monomer; see Table 1). From the differences and similarities of both systems, one might propose two possible nucleation mechanisms for the emulsion polymerizations conducted in the presence of the gradient copolymer. (i) The nucleation exclusively takes place in the aggregates, although in small concentration, and the free unimers adsorb onto the continuously growing particle surface to improve the coverage. This might explain the large number of copolymer chains per particle (even though the number of chains per aggregate might be much smaller) as well as the significantly lower number of particles than in the case of the diblock copolymer stabilizers (Fig. 10). (ii) A homogeneous nucleation mechanism prevails, in which the role of the amphiphilic copolymer would be to adsorb onto the polystyrene surface of the nuclei formed in the aqueous phase, to stabilize them during their growth. Such an assumption is logical in the presence of a large concentration of unimers, but does not clearly support the dependence of the particle number on the copolymer initial concentration. It is nevertheless very likely that both mechanisms coexist in the system.

Table 2
Semi-continuous emulsion polymerizations of styrene and MMA/BA (35/65 wt/wt) in the presence of the amphiphilic poly(St$_{30\%}$-*co*-AA$_{70\%}$) copolymer used as the sole stabilizer

Monomer(s)	Amount of stabilizer (wt% based on the monomers)	Latex description	D_z (nm) (DLS)	Poly[a] (DLS)
St	3	Stable no coagulum	155	0.07
MIMA/BA	3	Stable no coagulum	197	0.06

Solids content = 45 wt%; [$NaHCO_3$] = 12 mM; 1 equiv. NaOH based on the AA groups; $T = 70$ °C; conversion = 100%.

[a] The lower value, the narrower the particle size distribution.

3.4. Use of the poly(St$_{30\%}$-co-AA$_{70\%}$) gradient copolymer as a stabilizer in the semi-continuous emulsion polymerization of St and MMA/BA (35/65 wt/wt) at 45 wt% solids

The semi-continuous emulsion polymerizations performed here were very close to industrial systems. The poly(St$_{30\%}$-*co*-AA$_{70\%}$) gradient copolymer was used in quite a low amount, as it was 3 wt% based on the monomers. At the end of the polymerization, stable latexes were recovered with the diameter given by DLS: $D_z = 155$ and 197 nm for the polystyrene latex and the poly(methyl methacrylate-*co*-*n*-butyl acrylate) latex, respectively (Table 2). In both cases, the particle size distribution was narrow: the polydispersity given by the DLS apparatus was 0.06–0.07.

4. Conclusion

A well-defined, amphiphilic poly(St$_{30\%}$-*co*-AA$_{70\%}$) copolymer was synthesized in a single step by nitroxide-mediated controlled free-radical copolymerization of styrene and acrylic acid, without protection of the acid groups: $M_n = 6500$ g mol^{-1}, $M_w/M_n = 1.5$ and $F_{AA} = 0.70 \pm 0.03$. In addition to the good control over molar mass and molar mass distribution, we showed that the copolymer exhibited a narrow composition distribution with a slight gradient. Such copolymer was an efficient stabilizer for the emulsion polymerizations of styrene and of mixtures of MMA and BA, till 45 wt% solids. Low amounts (typically 3–4 wt% based on the monomer(s)) were needed. This is approximately a decade lower than the required amount of classical random copolymers. The performances were, however, below those of analogous diblock copolymers, but the great advantage is the very easy synthesis. Owing to the broad range of functional monomers able to be polymerized via controlled free-radical polymerization, a great variety of amphiphilic copolymers with high stabilization efficiency is thus achievable.

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