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Characterization of aqueous micellar solutions of amphiphilic block copolymers of poly(acrylic acid) and polystyrene prepared via ATRP. Toward the control of the number of particles in emulsion polymerization

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Abstract

A series of diblock, triblock and star-block copolymers composed of polystyrene and poly(acrylic acid) were synthesized by ATRP. The structure of the copolymers, the size of the blocks and the composition were varied, keeping however a short polystyrene block and a poly(acrylic acid) content larger than 60 mol% to allow solubility in alkaline water. Their micellization was studied by static and dynamic light scattering and the influence of their structural characteristics on the aggregation number, N_{agg}, was examined at low salt concentration and alkaline pH. It was shown that micelles were in thermodynamic equilibrium and that N_{agg} followed the power law $N_{agg} \sim N_A^{-0.9} N_S^2$ (with N_A, the total number of acrylic acid units in the copolymer and N_S, the total number of styrene units), that is characteristic of amphiphile micelles formed from strongly segregated block copolymers. Moreover, N_{agg} was independent of salt concentration in the investigated range. The same copolymers were previously used as stabilizers in emulsion polymerization [Macromolecules 34 (2001) 4439]. The final latex particle concentration, N_p, was compared with N_m, the initial micelle concentration. This enabled us to conclude that among the block copolymers studied, those with high acid content behaved like low molar mass surfactants. In contrast, those with low acid content formed stable micelles that could be directly nucleated to create latex particles, allowing a good control over N_p.

Keywords: Amphiphilic block copolymers; Atom transfer radical polymerization; Emulsion polymerization

1. Introduction

Aqueous emulsion polymerization [1,2] is a widely applied process for free-radical polymerization because it is environmentally safe, it offers many technical advantages and it produces polymer latexes that can be used directly for a variety of applications. Surfactants are needed to stabilize the suspension of submicron particles. They are usually low molar mass surface active molecules, that have actually some drawbacks. For instance, because of their high mobility, they can migrate at the polymer/substrate interface during film formation, leading to a poor adhesion of the water-borne coating. When used in large concentration during the emulsion polymerization reaction, they can cause continuous or secondary nucleation, resulting in broad particle size distribution. To overcome these drawbacks, reactive surfactants were proposed in the past [3,4]. These molecules bear a reactive group able to react during one of the elementary steps of a radical polymerization (initiation, propagation, chain transfer), hence leading to a covalent incorporation of the surface active molecules into the polymer chains. Another possibility is to use amphiphilic copolymers [5,6]. In this case, there is no covalent bonding, but a strong anchoring of the hydrophobic segment(s) at the particle surface. The non-ionic copolymers based on poly(ethylene oxide) and either polystyrene or poly(methyl methacrylate) have been the most studied [5]. A new trend is now to use amphiphilic polyelectrolytes that provide electrosteric stabilization [7]. Among them, amphiphilic polyelectrolyte block copolymers are particularly interesting. Even though they have not yet been very extensively studied for the purpose of latex stabilization, the few examples reported in literature demonstrate that they are

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very powerful stabilizers in emulsion polymerization [7]. They can be considered as the macromolecular counterparts of small-molecule surfactants and form micellar aggregates in selected solvents. In aqueous emulsion polymerization, the hydrophobic blocks can anchor onto the particle surface while the hydrophilic blocks extend into the water-phase and create a well-defined hydrophilic shell. Besides the advantages of reduced mobility and high efficiency, another goal has been quite recently considered. It is the possibility to use the block copolymer micellar solution as a seed for an emulsion polymerization. The purpose is to directly control the final number of particles, that generally depends on many parameters in the presence of traditional surfactants and cannot be easily predicted [8,9].

In recent work, we have used diblock, triblock and star-block copolymers of polystyrene and poly(acrylate salt) as stabilizers in emulsion polymerization. We have selected copolymer compositions with low polystyrene content that allowed an easy solubilization in water, without the need of an organic cosolvent. The purpose was to correlate the final number of latex particles (N_p) obtained in various experimental conditions with the structural parameters of the block copolymers. N_p was shown to be proportional to $[\text{copolymer}]^\alpha$ over a wide concentration range. The value of the exponent 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 approximately 75 mol% and decreased to 0.3 when the hydrophilic content was increased. A low value of α means that several copolymer micelles are needed to stabilize a given latex particle; in other words, non-nucleated micelles play the role of stabilizer reservoir, which is usually the case with low molar mass surfactants. In contrast when $\alpha = 1$, every latex particle might originate from a single micelle. This trend can be correlated with the exchange dynamics of the stabilizer. The results obtained with various initiator concentrations, temperatures and ionic strengths corroborated this observation and let us conclude that the important point to explain the evolution of α with the copolymer composition was the competition between direct nucleation of the micelles and exchange of the block copolymers between the micelles and the polymer/water interface that continuously expands in the system upon particle growth. The time scale of this exchange (which is very fast for small-molecule surfactants) was on the same order of magnitude as the initiation step for emulsion polymerizations carried out in the presence of block copolymers. The most hydrophilic block copolymers behaved quite similarly to low molar mass classical surfactants, with a fast exchange. In contrast the most hydrophobic ones led to micelles that were sufficiently stable to be directly nucleated. In the latter case, the final number of particles was supposed to match the initial number of micelles. Thus, a good prediction of N_p can be anticipated and this possibility was successfully applied for emulsion copolymerizations of methyl methacrylate and *n*-butyl acrylate at 45 wt% solid [10].

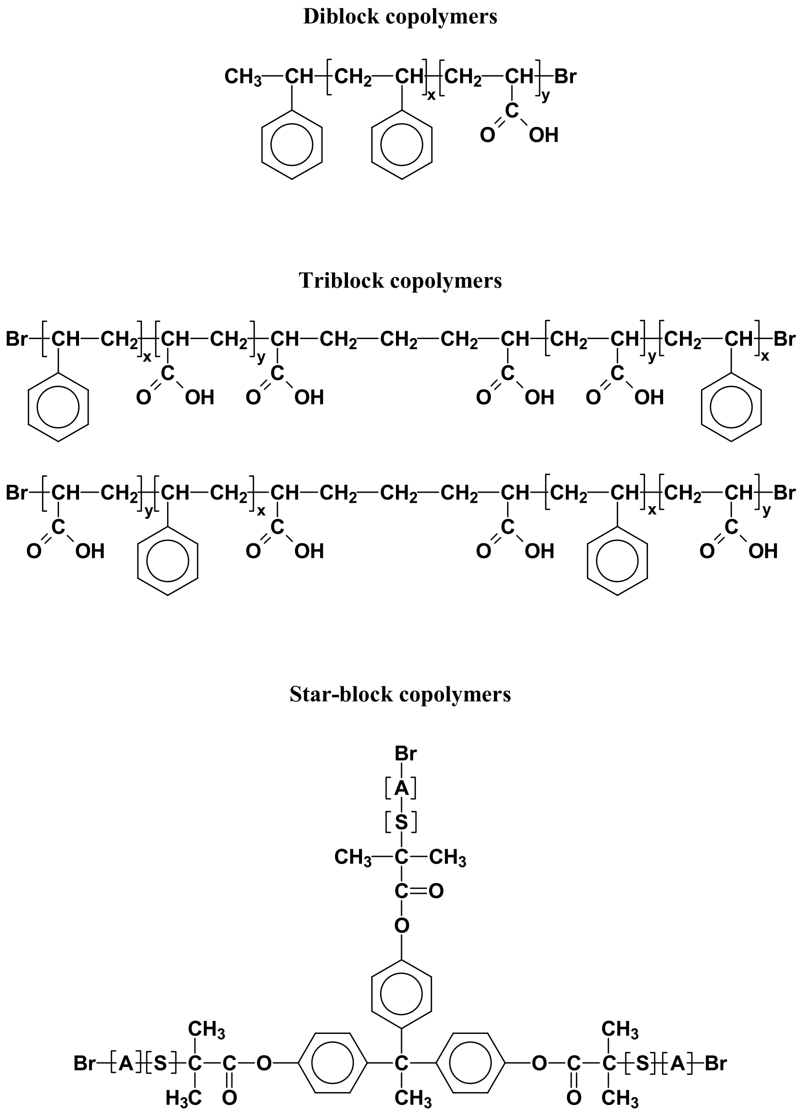
The purpose of the present work was to study, by static and dynamic light scattering, the structure of the micellar solutions of the amphiphilic copolymers previously employed as stabilizers in emulsion polymerization and to establish a correlation with the number of particles in the latexes [9]. These techniques were used under similar experimental conditions as those selected for the emulsion polymerization process, except the temperature.

Similar diblock copolymers with a short polystyrene segment have already been studied in the past by Eisenberg et al. [11–14] and more recently by Van der Maarel et al. [15,16]. The former study gave us information about the critical micelle concentration (cmc) that was found below 10^{-5} mol l^{-1} for all diblock copolymers with polystyrene block having more than 11 units [11,13]. In addition, the effect of the structural parameters on the aggregation number N_{agg} was also studied by static light scattering (SLS). The dependence of the aggregation numbers on the poly(acrylic acid) block length was studied [14]. In 2.5 mol l^{-1} NaCl solution, it was observed that for very short polystyrene block (6 units), the aggregation numbers were strongly affected by the poly(acrylic acid) block length: it decreased with increasing poly(acrylic acid) block length. However, as the polystyrene block length was increased (up to 11–23 units), the effect of the poly(acrylic acid) block length on the aggregation numbers was the reverse, but remained quite low: the aggregation numbers slightly increased as the poly(acrylic acid) block length increased. The effect of the insoluble block length on the aggregation numbers was shown to be much larger than that of the poly(acrylic acid) block. Indeed, for different poly(acrylic acid) block lengths (85–170–350 units), the aggregation numbers increased strongly with the polystyrene block length in a linear way.

2. Experimental section

2.1. Synthesis of the amphiphilic block copolymers

All of the block copolymers studied in this work have been prepared via atom transfer radical polymerization (ATRP) [17] of styrene and *tert*-butyl acrylate. Short polystyrene block and molar fraction of *tert*-butyl acrylate above 60 mol% were purposely targeted to get water soluble amphiphilic block copolymers after hydrolysis (no need of a cosolvent). Description of the synthesis has already been published [18]. Subsequent hydrolysis of the ester groups was performed as follows. The block copolymers were dissolved in dichloromethane and a five-fold molar excess (with respect to the ester groups) of trifluoroacetic acid (Aldrich, 99%) was added. The mixture was stirred at room temperature for 24 h. When hydrolyzed, the copolymers precipitated in dichloromethane. They were separated by



Scheme 1. Structure of the amphiphilic copolymers of polystyrene and poly(acrylic acid) presented in Table 1.

filtration, washed with dichloromethane, thoroughly dried at 50 °C, and characterized using proton NMR in d6-DMSO solution. Complete hydrolysis was always observed. Structure of the amphiphilic copolymers of polystyrene and poly(acrylic acid) is shown in Scheme 1 and in Table 1.

2.2. Preparation of the micellar solutions

The copolymers in the acidic form did not dissolve directly in water. They had to be ionized and heated to obtain clear solutions. The block copolymers were introduced into an aqueous solution of K_2CO_3. The pH of all solutions was above 7 (complete neutralization of acrylic acid units) and in most of the cases except $C_s = 0.005\ \mathrm{mol}^{-1}$, the concentration of acrylic acid units was below the salt concentration. The samples were heated during 45 min at 70 °C for complete solubilization. At that stage, the acrylic acid units were in the potassium salt form. Thus, in the following, the block copolymers will be named $PS_x–PAK_y$ (with x and y the number of styrene and acrylate units, respectively). It should be emphasized that further heating of the solutions was not necessary since SLS analysis showed that longer preparation time did not affect the micelle structure by contrast to what was previously measured by Khougaz et al. [14] for equivalent copolymers.

2.3. Refractive index increment measurement (dn/dC_p)

Refractive index increment values, dn/dC_p, have been measured with a Waters R403 differential refractometer operating at 20 °C with white light. Solutions of NaCl have been used to calibrate the refractometer. Prior to measurements, the salted solutions of the copolymers have been dialyzed for 5 days on a Pectra/Por membrane with a cut-off of 1000 Da according to the protocol proposed by Khougaz et al. [14]. The dialysate has then been used for diluting the solutions whose concentrations have been determined by

Table 1
Structural characteristics of the diblock (PS_x–PAK_y), triblock (PAK_y–PS_x–PAK_y and PS_x–PAK_y–PS_x) and three arm star-block ((PS_x–PAK_y)$_3$) copolymers with the acrylic acid units in the potassium salt form

Copolymer	N_S	N_A	Molar fraction of AK units	M_w (g mol^{-1})[a]	M_w/M_n[b]
PS_{10}–PAK_{21}	10	21	0.68	4000	1.20
PS_{10}–PAK_{56}	10	56	0.85	8200	1.14
PS_{10}–PAK_{100}	10	100	0.91	17,300	1.44
PS_{16}–PAK_{55}	16	55	0.77	9900	1.29
PS_4–PAK_{50}–PS_4	8	50	0.86	7900	1.24
PAK_{52}–PS_9–PAK_{52}	9	104	0.92	14,200	1.14
PAK_{76}–PS_9–PAK_{76}	9	152	0.94	23,700	1.34
PAK_{50}–PS_{16}–PAK_{50}	16	100	0.86	18,300	1.44
(PS_5–PAK_9)$_3$	15	27	0.64	5500	1.19

N_A is the total number of acid units in the copolymers and N_S is the total number of styrene units.

[a] Weight average molar mass of the block copolymers (from size exclusion chromatography) [8,17].

[b] Polydispersity index of the block copolymers [8,17].

UV spectroscopy. We estimate the relative error on the values of dn/dC_p to be equal to 12%. The experimental data are reported in Table 2; because of the 12% error, the same $dn/dC_p = 0.14$ ml g^{-1} was used for all of the micellar solutions at 20 °C. At 70 °C, dn/dC_p was 0.16 ml g^{-1}.

2.4. Static light scattering

Light scattering measurements were done by using an ALV-5000 multibit, multitau full digital correlator in combination with a Malvern goniometer and an ALV-800 photomultiplier. The vertically polarized incident light is emitted by an Ar-ion laser and has a wavelength (λ) of 514.5 nm. All of the measurements have been performed at 20 °C unless otherwise specified. Prior to measurements, solutions were filtered through 0.45 μm Millipore filters. SLS measurements allow the determination of structural parameters such as the weight average molar mass (M_w) and the radius of gyration (R_g) of the particles investigated. Moreover, thermodynamical parameters such as the second virial coefficient (A_2) are also accessible. For diluted solutions of weakly interacting systems, the excess scattering intensity ($I - I_{sol}$) for a given polymer concentration (C_p), at given scattering angle (θ) is indeed related to M_w, R_g and A_2 according to Eq. (1).

Table 2
Refractive index increment (dn/dC_p) of the various block copolymers presented in Table 1

Copolymer	C_s (mol l^{-1})	dn/dC_p (ml g^{-1})
Diblocks		
PS_{10}–PAK_{21}	0.020	0.152
PS_{10}–PAK_{56}	0.020	0.144
PS_{10}–PAK_{100}	0.020	0.131
PS_{10}–PAK_{100} (70 °C)	0.020	0.160
PS_{10}–PAK_{100}	0.036	0.138
PS_{16}–PAK_{55}	0.005	0.161
PS_{16}–PAK_{55}	0.020	0.133
PS_{16}–PAK_{55}	0.036	0.156
Triblocks		
PS_4–PAK_{50}–PS_4	0.020	0.154
PAK_{52}–PS_9–PAK_{52}	0.020	0.144
PAK_{76}–PS_9–PAK_{76}	0.020	0.135
PAK_{50}–PS_{16}–PAK_{50}	0.020	0.157
Star block		
(PS_5–PAK_9)$_3$	0.020	0.132

$C_s = [K_2CO_3]$; when non-specified, $T = 20$ °C. Estimated error = 12%.

$$\frac{KC_p}{R_\theta} = \left(\frac{1}{M_w} + 2A_2C_p\right)\left(1 + \frac{q^2R_g^2}{3}\right) \tag{1}$$

$R_\theta = R_{tol}[(I - I_{sol})/I_{tol}]$ is the Rayleigh ratio determined using toluene as a reference ($R_{tol} = 0.33 \times 10^{-4}$ cm^{-1}) [19]. K is an optical constant defined as

$$K = \frac{4\pi^2 n_{tol}^2 \left(dn/dC_p\right)^2}{\lambda^4 N}$$

where n_{tol} is the refractive index of toluene and N is the Avogadro's number. q is the wave vector $q = (4\pi n/\lambda)\sin(\theta/2)$ with n being the refractive index of the solvent. The concentrations investigated ranged from $C_p = 0.2$ to 6.5 g l^{-1} which corresponds to values far above the cmc expected for these systems [11]. θ values ranged from 30 to 140°. Finally, the Zimm procedure has been used to determine M_w and R_g [20].

2.5. Dynamic light scattering (DLS)

The intensity autocorrelation functions $g_2(t)$ obtained from DLS were analyzed in terms of a continuous distribution of relaxation times:

$$g_1(t) = \int_0^\infty A(\tau)\exp(-t/\tau)d\tau \tag{2}$$

Here $g_1(t)$ is the normalized electric field autocorrelation function related to $g_2(t)$ via the so-called Siegert relationship [21]. The REPES routine was used to obtain $A(\tau)$ without assuming a specific shape [22]. Correlation functions are characterized by a single peaked relaxation time distribution. The average relaxation time are q^2-dependent and can be used to calculate an apparent diffusion coefficient $D = (q^2\tau)^{-1}$. In the diluted range, the concentration dependence of D is given by

$$D = D_0(1 + k_D C_p) \tag{3}$$

where D_0 is the translation diffusion coefficient extrapolated to zero concentration and k_D is the dynamic second virial coefficient. The hydrodynamic radius R_H can be calculated using the Stokes–Einstein relation

$$R_H = \frac{kT}{6\pi\eta D_0} \tag{4}$$

where η is the viscosity of the solvent, k, the Boltzmann's constant and T is the absolute temperature.

3. Results and discussion

3.1. Characterization by static light scattering

3.1.1. The polyelectrolyte effect

In the systems investigated, the presence of electrostatic interactions which are promoted at low salt concentration can lead to the so-called 'polyelectrolyte effect'. Its consequence on light scattering data can be important like strong upturns in the scattering curves at low q values or like the presence of slow modes in the distribution of relaxation times. Förster et al. [23] have shown that a key parameter to consider was the ratio of polyelectrolyte monomer units concentration to salt concentration. The polyelectrolyte effect appears for flexible systems when this ratio is larger than 1, whereas for dense polyelectrolytes such as stars or brushes, charge renormalization shifts the critical ratio to values much larger than 1 [24]. In our experiments, the highest value encountered is roughly 9 (polymer PS_{16}–PAK_{55} at $C_p = 6.5$ g l^{-1} in 0.005 M K_2CO_3). For this system and for all of the other investigated ones, we have detected neither upturns in the scattering intensity at low q, nor slow modes. In these conditions, the addition of salt has been estimated to be sufficient to screen intermicellar electrostatic interactions.

3.1.2. Determination of the aggregation number (N_{agg})

As already said, SLS technique gives some characteristics of the amphiphilic block copolymers in aqueous solution, namely M_w, the weight average molar mass of the scattering entities in solution. Results are reported in Table 3 for the various block copolymers studied at 20 °C and for one of them at 70 °C, with various K_2CO_3 concentrations. As expected, M_w of the scattering entities in solution were much larger that M_w of the individual block copolymers, indicating aggregation. We can determine a weight average aggregation number (N_{agg}) according to Eq. (5).

$$N_{agg} = \frac{M_{w,aggregates}}{M_{w,copolymer}} \tag{5}$$

The structure of these aggregates is discussed below.

3.1.3. Influence of C_s, the K_2CO_3 concentration

The effect of C_s on the aggregation behavior and aggregate structure was studied for two diblock copolymers, PS_{10}–PAK_{100} and PS_{16}–PAK_{55}. As seen in Table 3, C_s in the range 0.005–0.072 mol l^{-1} did not have any significant effect neither on R_g nor on N_{agg}. This trend is rather different

Table 3
Characterization by SLS of the micellar solutions of the various amphiphilic block copolymers presented in Table 1

Copolymer	C_s (mol l^{-1})	R_g (nm)	M_w (g mol^{-1})	N_{agg}[a]	R_c (nm)	b (nm)	b' (nm)
Diblocks							
PS_{10}–PAK_{21}	0.020	26	8.3×10^5	209	4.3	1.07	1.07
PS_{10}–PAK_{56}	0.020	26	1.2×10^6	143	3.8	1.14	1.14
PS_{10}–PAK_{100}	0.020	25	1.0×10^6	59	2.9	1.32	1.32
PS_{10}–PAK_{100} at 70 °C	0.020	25	1.4×10^6	79	3.1	1.25	1.25
PS_{10}–PAK_{100}	0.036	27	1.2×10^6	69	3.0	1.28	1.28
PS_{16}–PAK_{55}	0.005	27	3.2×10^6	327	5.9	1.16	1.16
PS_{16}–PAK_{55}	0.020	33	3.2×10^6	333	5.9	1.15	1.15
PS_{16}–PAK_{55}	0.036	28	3.5×10^6	348	6.0	1.14	1.14
PS_{16}–PAK_{55}	0.072	35	3.3×10^6	336	6.0	1.15	1.15
Triblocks							
PS_4–PAK_{50}–PS_4	0.020	26	1.8×10^5	22	1.9	1.44	1.02
PAK_{52}–PS_9–PAK_{52}	0.020	25	2.5×10^5	18	1.9	1.55	1.09
PAK_{76}–PS_9–PAK_{76}	0.020	24	2.1×10^5	9	1.5	1.74	1.23
PAK_{50}–PS_{16}–PAK_{50}	0.020	23	1.2×10^6	63	3.4	1.52	1.08
Star block							
$(PS_5$–$PAK_9)_3$	0.020	67	3.5×10^5	63	3.3	1.49	0.86

$C_s = [K_2CO_3]$; when non-specified, $T = 20$ °C.

[a] Calculated according to Eq. (5).

from earlier results obtained by Eisenberg et al. [14] for similar diblock copolymers with longer polyelectrolyte segment. For instance, N_{agg} increased from 12 to 26 for a diblock copolymer PS_6–$PANa_{180}$, when NaCl concentration was increased from 0.025 to 2.5 mol l^{-1}. For the copolymer PS_{23}–$PANa_{300}$, N_{agg} increased from 87 (for [NaCl] = 0.05 mol l^{-1}) to 150 (for [NaCl] = 0.25 mol l^{-1}) and then leveled off for larger concentrations. The range of salt concentration was however above that used in this work. At low salt concentration (below [NaCl] = 0.010 mol l^{-1}) the aggregation number of poly(*t*-butylstyrene)$_{26}$-*b*-poly(sodium styrene sulfonate)$_{413}$ was independent of the salt concentration and decreased at high salt (>0.1 mol l^{-1}) [25]. Similarly, in a more recent study, Förster et al. [24] have shown that N_{agg} of poly(ethylethylene)$_{144}$-*b*-poly(styrene sulfonic acid)$_{136}$ was also independent of salt concentration for [NaCl] below 0.1 mol l^{-1}, but, in contrast to the latter work, it significantly increased above. In conclusion, in the range of salt concentration used in this study, the absence of effect of C_s on the aggregation behavior of the selected diblock copolymers is not unexpected; they remained in the osmotic brush regime, with probably a strong stretching of the polyelectrolyte chains [26] as it will be discussed later from DLS data.

3.1.4. *Influence of the copolymer structure at a given* $C_s = 0.020$ mol l^{-1}.

At a given salt concentration and a given temperature (20 °C), the effect of structure (diblock, triblock, star-block) and composition of the block copolymers can be studied from data reported in Table 3. For the series of diblock copolymers, R_g did not vary significantly, in contrast to N_{agg}, which was strongly dependent upon the block lengths. Indeed, for diblocks with the same polystyrene segment (10 units, PS_{10}–PAK_{21}, PS_{10}–PAK_{56} and PS_{10}–PAK_{100}), N_{agg} decreased from 209 to 59 when the number of acid units in the polyelectrolyte block increased from 21 to 100. For the diblocks PS_{10}–PAK_{56} and PS_{16}–PAK_{55} with the same polyelectrolyte block, N_{agg} increased from 143 to 333 with the increase in polystyrene length from 10 to 16 units. A very similar trend was found for the triblock copolymers: N_{agg} increased when the size of the hydrophobic block(s) was increased, and decreased when the size of the polyelectrolyte block(s) was increased. At higher salt concentration however, the effect of the hydrophilic block of diblock copolymers with similar polystyrene length was found by Eisenberg et al. [14] to be less pronounced. This systematic dependence of N_{agg} with the length of both blocks is characteristic of amphiphile micelles, as shown before by Förster et al. [27] and indicates that the aggregates are in thermodynamic equilibrium. The quantitative dependence of N_{agg} upon N_A (total number of acid units in the copolymer) and N_S (total number of styrene units) is illustrated in Fig. 1. The scaling relationship $N_{agg} \sim N_A^{-\alpha} N_S^{\beta}$ was used with $\beta = 2$, as predicted by the theory for amphiphile micelles [27]. To obtain data points collapsing onto the same straight line, the triblock and star-block copolymers were mentally cut into, respectively, two and three similar diblocks. For this purpose, N_{agg}, N_A and N_S were modified according to the following procedure. For the triblocks, N_A and N_S were divided by 2 and N_{agg} multiplied by 2; for the star $(PS_5 - PAK_9)_3$, N_A and N_S were divided by 3 and N_{agg} was multiplied by 3. As seen in Fig. 1, all of the data points follow the same straight line with the slope = −0.9. The exponent $\alpha = 0.9$ is very close to the 0.8 value previously obtained for strongly segregated diblock and triblock copolymers as well as for low molar mass surfactants [27]. These results show that the triblock and star-block copolymers form micelles in a similar way as diblock copolymers, their aggregation behavior being determined by the same parameter.

In these systems of amphiphile micelles, the parameter that controls the aggregation is the interchain distance b between corona copolymers. The distance b can be calculated assuming b^2 is the surface area of one copolymer at the core/corona interface. For amphiphile micelles, b depends only on the length of the hydrophilic chains and increases as N_A increases. The values of b can be calculated as follows (Eq. (6)).

$$b^2 = \frac{4\pi R_c^2}{N_{agg}} \tag{6}$$

R_c is the micellar core radius which can be calculated assuming a spherical geometry and the space filling condition (Eq. (7)).

$$\frac{4}{3}\pi R_c^3 = N_{agg} N_S v_0 \tag{7}$$

v_0 is the molar volume of a styrene monomer unit. The values of b are reported in Table 3. If one considers only the

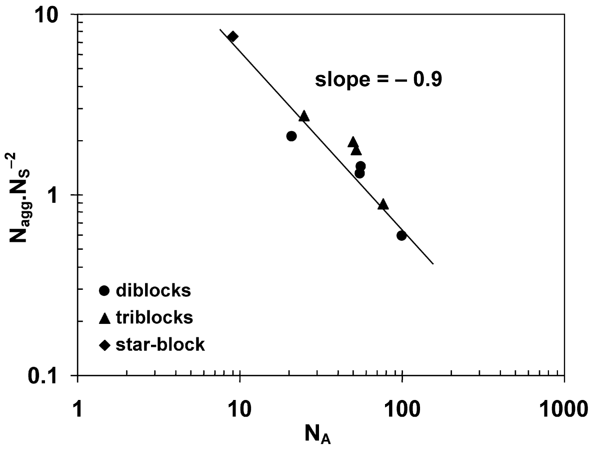


Fig. 1. $N_{agg}N_B^{-2}$ vs N_A for all of the diblock, triblock and star-block copolymers ($T = 20$ °C; $C_s = [K_2CO_3] = 0.020$ mol l^{-1}). The triblock and star-block copolymers data have been recalculated for equivalent diblock copolymer (see text).

diblock copolymers, b was independent of N_S (comparison of $PS_{10}-PAK_{56}$ and $PS_{16}-PAK_{55}$) and increased as N_A increased for a given N_S ($PS_{10}-PAK_{21}$; $PS_{10}-PAK_{56}$; $PS_{10}-PAK_{100}$). At this stage, comparison with the other structures cannot be done directly. The parameter b can then be recalculated to b', the interchain distance between individual hydrophilic segments. In the case of triblock copolymers that are equivalent to two diblocks one has $b'^2 = b^2/2$ and for three-arm stars that are equivalent to three diblocks, $b'^2 = b^2/3$. The values of b' are also reported in Table 3. For all structures, if the parameter b' governs the aggregation behavior, then it should follow the simple relationship $b' = b'_0 N_A^{\varepsilon}$ [27]. The good agreement with this power law is illustrated in Fig. 2, which allows to calculate $b'_0 = 0.62$ nm ($b_0'^2 = 0.38$ nm^2) and $\varepsilon = 0.15$. The exponent ε corresponds to $\alpha/6$, which comes from purely geometric considerations (indeed, from Eqs. (6) and (7), one calculates $N_{agg} = 36\pi v_0^2 N_S^2 b^{-6}$; with $N_{agg} \sim N_A^{-\alpha} N_S^{\beta}$ and $\beta = 2$, one gets $b \sim N_A^{\alpha/6}$; $\alpha/6 = 0.9/6 = 0.15$). The value found for b'_0 is quite small with respect to those reported for other systems. For instance diblocks of polystyrene and poly(methacrylic acid) in water–dioxane solution [28] exhibited $b'_0 = 1.52$ nm. The small values found for b' and b'_0 indicate a very high polyelectrolyte brush density on the hydrophobic core of the micelles. Again, this can be related to the stretched structure of the polyacrylate segments at low salt concentration, and will be confirmed below by DLS.

3.2. Characterization by dynamic light scattering: conformation of the polyelectrolyte chains inside the corona

DLS enabled us to determine R_H, the hydrodynamic radius of the micelles (see Table 4). By subtracting the contribution of the micellar core to R_H, the thickness of the hydrophilic corona (δ_c) can be estimated. With fully stretched polyelectrolyte chains, an upper limit of this thickness (δ_c^*) can be determined knowing the degree of polymerization of the polyelectrolyte chains and assuming the length of a monomer to be equal to 0.25 nm [29]. These results are given in Table 4. Since δ_c is very close to δ_c^*, one can conclude to a rather stretched conformation for the charged segments inside the corona. As seen previously, this last result is a direct consequence of the high surface density.

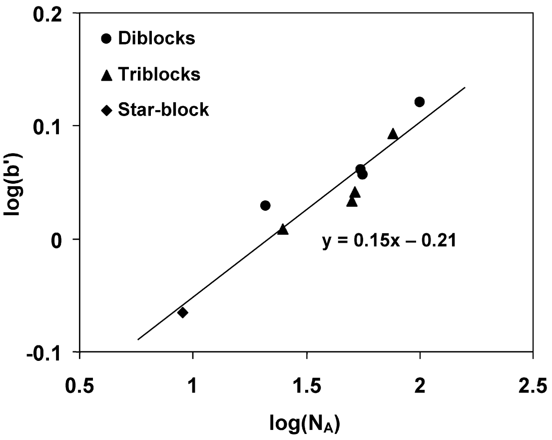


Fig. 2. Logarithmic plot of b' vs N_A for all of the diblock, triblock and star block copolymers ($T = 20$ °C; $C_s = [K_2CO_3] = 0.020$ mol l^{-1}). The triblock and star-block copolymers data have been recalculated for equivalent diblock copolymer (see text).

3.3. Correlation with emulsion polymerization and number of latex particles

In Table 5 are reported our previous results concerning styrene emulsion polymerizations performed in the presence of the amphiphilic block copolymers studied here [9,10]. To discuss the efficiency of the micellar solutions to act as a seed, it is interesting to compare N_c, the average number of copolymer molecules per latex particle, with N_{agg}, the micelle aggregation number. The N_c/N_{agg} ratio gives also the indication about the final particle concentration with respect to the initial micelle concentration (N_m, l^{-1}) since $N_c/N_{agg} = N_m/N_p$. It is obvious that the N_c/N_{agg} ratio is an approximative value, since N_{agg} was not determined under exactly the same experimental conditions as those of the emulsion polymerizations. In particular, elevated temperature and presence of styrene are the two main parameters that might affect structure of the micelles in the initial step of the polymerization. Effect of temperature has been studied for copolymer $PS_{10}-PAK_{100}$ (Table 3): N_{agg} increased from 59 to 79 when temperature was raised from 20 to 70 °C. Concerning the presence of styrene, no experimental data could be collected by SLS. However, it is anticipated that swelling of the micelle hydrophobic core with styrene might lead to a rearrangement resulting in an increase of N_{agg}, in the same way as N_{agg}

Table 4
Characterization by DLS of the micellar solutions of the various amphiphilic block copolymers presented in Table 1

Copolymer	C_s (mol l^{-1})	R_H (nm)	$\delta_c = R_H - R_c$ (nm)	δ_c^{*a} (nm)
Diblocks				
$PS_{10}-PAK_{21}$	0.020	10	5	5
$PS_{10}-PAK_{56}$	0.020	15	11	14
$PS_{10}-PAK_{100}$	0.020	23	20	25
$PS_{10}-PAK_{100}$	0.036	24	21	25
$PS_{16}-PAK_{55}$	0.005	21	15	14
$PS_{16}-PAK_{55}$	0.020	21	15	14
$PS_{16}-PAK_{55}$	0.036	22	16	14
$PS_{16}-PAK_{55}$	0.072	22	16	14
Triblocks				
$PS_4-PAK_{50}-PS_4$	0.020	11	9	6
$PAK_{52}-PS_9-PAK_{52}$	0.020	11	9	13
$PAK_{76}-PS_9-PAK_{76}$	0.020	13	11	19
$PAK_{50}-PS_{16}-PAK_{50}$	0.020	21	17	13

$C_s = [K_2CO_3]$; $T = 20$ °C.

[a] Upper limit of δ_c, calculated by $0.25N_A$ for the diblock copolymers and $0.25N_A/2$ for the triblocks.

Table 5
Emulsion polymerizations of styrene at 70 °C using the amphiphilic block copolymers as stabilizers: final characteristics of the latexes Refs. [9,10]

Copolymer	Concentration		C_s = [K_2CO_3] (mol l^{-1})	R_H (DLS) (nm)	α[a]	N_c[b]	N_{agg}[c] (20 °C)	N_c/N_{agg}
	wt% vs styrene	10^{-4} (mol l^{-1})						
PS_{10}–PAK_{21}	0.78	3.11	0.020	35	0.98	394	209	1.9
	1.12	4.04		31		408		2.0
	1.63	6.53		27		396		1.9
	2.23	8.97		26		448		2.1
	2.45	8.82		23		395		1.9
PS_{10}–PAK_{56}	0.25	0.50	0.020	51	0.77	177	143	1.2
	0.56	1.11		38		183		1.3
	1.01	2.01		35		239		1.7
	1.96	3.94		31		313		2.2
	2.41	4.87		28		300		2.1
	3.80	7.80		24		288		2.0
PS_{10}–PAK_{100}	0.50	0.61	0.020	47	0.64	214	59	3.6
	0.82	1.00		46		280		4.8
	1.06	1.30		39		362		6.1
	1.62	2.00		42		432		7.3
	2.38	2.96		30		379		6.4
	2.41	3.00		32		400		6.8
	2.43	3.03		30		402		6.8
	3.00	3.76		31		492		8.3
	3.86	4.88		31		495		8.4
PS_{16}–PAK_{55}	0.49	0.88	0.005	48	0.86	314	327	1.0
	1.06	1.92		40		348		1.1
	1.12	2.03		36		290		0.9
	2.04	3.72		33		388		1.2
	2.65	4.86		29		383		1.2
PS_{16}–PAK_{55}	0.25	0.46	0.020	59	1.0	351	333	1.1
	0.52	0.93		50		312		1.0
	0.71	1.28		42		310		0.9
	1.13	2.03		40		348		1.1
	1.39	2.50		33		295		0.9
	1.98	3.57		31		295		0.9
	2.41	4.38		28		320		1.0
PS_{16}–PAK_{55}	0.51	0.91	0.036	60	1.0	583	348	1.7
	1.48	2.66		42		576		1.7
	2.04	3.69		36		559		1.6
PAK_{52}–PS_9–PAK_{52}	0.24	0.28		55	0.37	126	18	7.0
	0.84	0.99		47		276		15
	1.71	2.04		43		434		24
PAK_{76}–PS_9–PAK_{76}	0.68	0.58		60	0.27	384	9	43
	0.95	0.80		58		498		55
	1.54	1.31		55		677		75
	2.47	2.13		51		974		108
	2.90	2.52		51		1172		130
	3.38	2.94		49		1244		138
(PS_5–PAK_9)$_3$	0.56	1.57		52	0.98	747	63	12
	0.86	2.40		40		557		9
	1.18	3.32		43		845		13
	1.48	4.17		38		757		12
	1.98	5.60		33		653		10
	2.44	6.96		32		762		12

Initiator: [$K_2S_2O_8$] = 0.005 mol l^{-1}; solid content = 10 wt%; the micellar solutions were prepared according to the procedure described in Section 2.

[a] In $N_p \sim [\text{copolymer}]^{\alpha}$.

[b] N_c is the average number of block copolymer molecules per particle. It was calculated by $N_c = [\text{copolymer}]/N_p$ with N_p the particle concentration in the latex, calculated according to $N_P = (6\tau)/[\pi d_p(2R_H)^3]$ (τ is the polymer content in the latex, obtained by gravimetry and d_p = 1.05 g cm^{-3} is the polystyrene density).

[c] From data in Table 3.

increases with N_S^2. As a consequence, before polymerization starts, the micellar solutions might reach a new thermodynamic equilibrium state with N_{agg} being slightly larger than determined at low temperature and in the absence of styrene.

In our previous study of emulsion polymerization [9,10], we showed that N_p was proportional to $[\text{copolymer}]^\alpha$, with α depending upon the copolymer composition (see Section 1). Since $[\text{copolymer}] \times N = N_m \times N_{agg}$, one has $N_p \sim (N_m \times N_{agg})^\alpha$ that can also be written as Eq. (8).

$$\frac{N_m}{N_p} \sim N_{agg}^{-\alpha} N_m^{1-\alpha} \tag{8}$$

Eq. (8) means that, for a given copolymer with $\alpha = 1$, $N_m/N_p = N_c/N_{agg}$ is independent of N_m, while for smaller values of α, N_m/N_p should increase when N_m (and hence copolymer concentration) is increased.

When data presented in Table 5 are examined, it appears that for copolymers with α close to 1 (typically above 0.7), N_c/N_{agg} was also close to 1 (generally comprised between 1 and 2) and remained constant over the whole copolymer concentration range. This is true for copolymers PS_{10}–PAK_{21}, PS_{10}–PAK_{56}, and PS_{16}–PAK_{55} at all salt concentrations. This trend means that every single copolymer micelle existing in the initial stage of the emulsion polymerization is nucleated into a latex particle. The fact that N_c/N_{agg} remained slightly above 1 is most probably related to the change in micelle structure as discussed above. When the concentration of copolymer was increased, the number of micelles increased also in the same proportion, as well as the final number of particles. Exchange dynamics of the PS_{10}–PAK_{21}, PS_{10}–PAK_{56}, and PS_{16}–PAK_{55} stabilizers were sufficiently slow with respect to the nucleation step so that the copolymers did not contribute to stabilization of the newly created interfaces. Star-block copolymer $(PS_5$–$PAK_9)_3$ gave somehow contradictory results: although $\alpha = 0.98$ and N_c/N_{agg} did not vary with copolymer concentration, the latter value was unexpectedly large. This would mean that micellar solutions of $(PS_5$–$PAK_9)_3$ were strongly affected by the emulsion polymerization medium. The polyelectrolyte blocks are probably too short in this case for good stabilization and swollen micelles would exhibit exceptionally large aggregation numbers (approximately 700). For the other block copolymers with α lower than 1, N_c/N_{agg} increased with copolymer concentration as the consequence of the fast exchange dynamics, resulting in a continuous redistribution of the copolymer molecules during the nucleation step between the newly created interfaces and the still existing micelles. It should however be noted that N_c/N_{agg} remained usually quite low (ranging from 3 to 9 for copolymer PS_{10}–PAK_{100} with $\alpha = 0.64$, from 7 to 24 for PAK_{52}–PS_9–PAK_{52} with $\alpha = 0.37$, and from 43 to 138 for PAK_{76}–PS_9–PAK_{76} with $\alpha = 0.27$, under usually a similar concentration range). This explains the high efficiency of amphiphilic copolymers as latex particle stabilizers.

4. Conclusion

Static and dynamic light scattering were used to examine the structure of micellar aqueous solutions of a series of diblock, triblock and star-block copolymers synthesized via ATRP and composed of polystyrene and poly(acrylic acid). All of the copolymers had short polystyrene block and exhibited a polyacrylic acid content larger than 60 mol% to allow solubility in alkaline water. The influence of the structural characteristics of the copolymers on the aggregation number, N_{agg}, was examined at low salt concentration and alkaline pH. The value N_{agg} followed the power law $N_{agg} \sim N_A^{-0.9} N_S^2$ (with N_A, the total number of acrylic acid units in the copolymer and N_S, the total number of styrene units), that is characteristic of amphiphile micelles, formed from strongly segregated block copolymers. Moreover, N_{agg} was independent of salt concentration in the investigated range. It was concluded that micelles were in a thermodynamic equilibrium state, which is a key condition to ensure reproducibility of the latex characteristics when these copolymers are used as stabilizers in emulsion polymerization. The final latex particle concentration, N_p, obtained via styrene emulsion polymerization and determined in a previous study was compared with N_m, the initial micelle concentration. The results enabled us to conclude that among the block copolymers studied, those with high acid content behaved like low molar mass surfactants, precluding a direct prediction of N_p. In contrast, those with low acid content formed micelles that could be directly nucleated to create latex particles, allowing thus a good control over N_p. Among the studied structures, the diblock copolymers combine easy synthesis along with high stabilizing efficiency. The PS_{16}–PAK_{55} diblock copolymer is probably the best choice.

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