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Adsorption of block copolymers at latex surface and their utilization in emulsion polymerization

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Abstract

Amphiphilic block copolymers have been investigated for their utilization in emulsion polymerization of butyl methacrylate. Special attention has been paid to the adsorption mechanism of the block copolymers from systematic measurements of equilibrium adsorption isotherms. A series of well-defined water-soluble amphiphilic block copolymers, composed of poly(butyl methacrylate) and poly(sodium methacrylate) blocks, were synthesized by anionic polymerization of butyl methacrylate and *tert*-butyl methacrylate followed by the thermal deprotection of the *tert*-butyl ester groups and final hydrolysis. The number density of emulsion polymer particles N_P varied as [copolymer]$^{\alpha}$, α lying between 0.44 and 0.73 according to the hydrophilic content of the copolymers. In contrast with SDS taken as a reference emulsifier, the adsorption of the copolymers was very strong and this provided quite an efficient stabilization of the polymer particles during emulsion polymerization, even at low concentrations ($<10^{-4}$ mol L^{-1}) and low coverages ($<10\%$ of the interfacial area).

Keywords: Amphiphilic block copolymers; Emulsion polymerization; Adsorption isotherm

1. Introduction

Colloidal dispersions [1] have to be stabilized against coagulation by means of a suitable surface chemistry which often involves adsorption of surface active materials, surfactants or polymers. A repulsive potential energy barrier is required in order to counterbalance the Van der Waals attractions between colloidal particles. Electrostatic repulsion by chemically attached or adsorbed charged materials is one way that has been formally described in the classical DLVO theory [2]. The second classical mean is the steric stabilization by polymeric surfactants. Both mechanisms can be combined using polyelectrolytes as electrosteric stabilizers.

Conventional surfactants are often required in emulsion polymerization recipes, especially when small particle sizes are aimed at. The very classical system which has received much attention is the emulsion polymerization of styrene with sodium dodecylsulfate (SDS) as emulsifier. There are several major drawbacks with the use of classical surfactants such as foaming of the formulations, slow migration of emulsifier to the surfaces of water-borne organic coatings (paints). Most emulsifiers are also more or less irritant or hazardous. These troubles arise from the availability of emulsifier molecules that are partly dissolved in the aqueous phase and not tightly adsorbed to the latex particles. The emulsifier concentration in the aqueous phase lies between one-tenth of the *cmc* and the *cmc* itself and these molecules are in fast equilibrium with the adsorbed ones, meaning that they should not been eliminated from the formulation. The replacement of conventional emulsifiers by block copolymers may appear beneficial because the *cmc* of such polymeric surfactant are very low and their adsorption is strong to irreversible. Many block copolymers have been studied as stabilizers in the emulsion polymerization [1,3–8]. For example, polystyrene-*graft*-polyoxyethylene and polystyrene-*block*-polyoxyethylene were used in emulsion polymerization of styrene, poly(methyl methacrylate)-*block*-polyoxyethylene triblock copolymers were used as

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stabilizers in emulsion polymerization of different monomers (styrene, methyl methacrylate…). The effect of varying blocks lengths and monomer types was investigated through latex characteristics such as particles diameter, number of particles, amount of coagulum, average molar mass and its distribution.

The main differences in the surface-active properties of block copolymers with respect to conventional surfactants are the low *cmc* and the slow adsorption kinetics [8]. These characteristics involve large modifications in the mechanisms of emulsion polymerization with respect to the classical styrene—SDS system used as a reference case. Thus, SDS molecules are able to adsorb very rapidly onto the growing polymer particles; the characteristic time for adsorption is much shorter than the polymerization time scale, so that it is considered that the adsorption equilibrium is satisfied every time during polymerization. The consequence is a high coverage of the growing particles and a progressive transfer of micellized surfactant to the particles surface. The number of polymer particles is therefore less than the initial number of micelles, even if the nucleation mechanism is micellar. Smith and Ewart [9] have established a theoretical relationship between the final number density of particles in the emulsion N_P, and the concentration of surfactant as $N_P \propto [\text{surfactant}]^{\alpha}$. This power law with $\alpha=0.6$ agrees quite well with experimental data for the polymerization of styrene with the SDS surfactant at concentrations above the *cmc* [10]. Values of α below 0.6 are found for more polar monomers; a power law is still most often observed and remains the scheme used for comparing different surfactants. Actually, the Smith and Ewart's power law is based on several assumptions. One of them states that the nucleation of new particles stops when the total area of the latex particles has increased enough so as to adsorb all the micellar surfactant. This hypothesis implies that the surfactant molecules organized in micelles are instantaneously available to stabilize the newly created interfaces. In respect with their macromolecular structure, amphiphilic block copolymers should not behave similarly to small molecule surfactants. For the emulsion polymerization of styrene in presence of triblock copolymers, Ni et al. [11], observed the linear relationship described above with $\alpha=0.4$. As the surfactant concentration decreased below the *cmc*, the high stabilizing efficiency was lost and particle diameter increased significantly. Burguière et al. [12], showed that in the case of very slow dynamics of exchange of block copolymers with hydrophilic content less than 85 mol%, α was larger than 0.6. In the extreme case of frozen micelles (no exchange), the number of final particles should be the same as the initial number of micelles, so that $\alpha=1$ [13]. Burguière et al. [12], also observed α as low as 0.3 for triblock copolymers. The low values of α were correlated to simultaneous homogeneous and micellar nucleation mechanisms.

When block copolymers are used as emulsifiers in the emulsion polymerization recipes, they contribute both to the polymer particles size and to the colloidal stabilization itself. The delayed adsorption of block copolymers may lead to poor stability during the first stage of the polymerization and subsequent coagulation. But coagulation reduces the total interfacial area and causes an increased adsorption compared to a hypothetical well-stabilized system. The different parameters (adsorbed amount per unit area, total interfacial area) which vary during the polymerization time are strongly interrelated. As a consequence, it is difficult to investigate the influence of the molecular parameters of the block copolymers. The investigation of the equilibrium adsorption of block copolymers of different chemical structure on the same polymer particles allows a more direct investigation into structure—activity relationships.

The present work aims at studying the effect of adsorption of block copolymers in the emulsion polymerization of a moderately non-polar monomer. This investigation was made with a series of model poly(butyl methacrylate)-*block*-poly(methacrylic acid) block copolymers (PBMA-*b*-MAA) of varying molecular composition. They were used as emulsifiers for the emulsion polymerization of butyl methacrylate. The investigated polymers are ionized in basic aqueous medium and provide electrosteric stabilization. The investigation was restricted to water-soluble copolymers that spontaneously aggregate as micelles. The starting formulation of the emulsion polymerization was therefore at equilibrium with respect to the state of the polymeric surfactant; this choice eliminated the micelle formation process as a parameter of relevance. The equilibrium adsorption of the copolymers on poly(butyl methacrylate) latex particles (prepared by means of emulsifier-free polymerization) was investigated independently so as to help in a discussion on the mechanisms of emulsion polymerization and structure–activity relationships.

2. Experimental section

2.1. Materials

Butyl methacrylate (BMA, Aldrich) and tert-butyl methacrylate (tBMA, Aldrich) were vacuum-distilled over CaH_2 and stored under a nitrogen atmosphere at −20 °C. The crown ether 11,12-dibenzo-1,4,7,10,13,16-hexacyclooctodeca-2,11-diene (DB18C6 from Acros), 4,4′-azobis-(4-cyanopentanoic acid) (from Acros) were used as received. THF was distilled over sodium metal. The diphenylmethylsodium Ph_2CHNa initiator was prepared at room temperature by reacting diphenylmethane with a solution of sodium naphthalene in THF prepared from sodium and naphthalene at room temperature. Dialysis tubing (Sigma) was washed (water, Na_2S solution, acidified water, hot water) according to the manufacturer recommendations.

2.2. Analytical techniques

Molar masses and molar mass distributions were measured by size exclusion chromatography (SEC) in THF eluent with a Waters apparatus equipped with a Plgel 5 μm mixed-D column and a refractometric detector using polystyrene standards for the calibration. ^{1}H NMR analyses of the copolymers were performed using a 250 MHz AC200 Bruker spectrometer. The PBMA-*b*-tBMA precursor block copolymers were analysed in $CDCl_3$ (or in CD_3OD solution at 330 K). The amphiphilic PBMA-*b*-MAA block copolymers were analysed in DMSO-d6 (or in CD_3OD at 330 K). The PBMA block length was calculated from the area of the peaks of the αCH_2 protons of the ester group ($\delta = 4.05$ ppm) and aromatic protons of initiator residue. The PtBMA block length was determined by subtracting the calculated area pertaining aliphatic protons of PBMA-block from the area of all aliphatic protons ($\delta = 0.8$–2.2 ppm). Thermogravimetric analyser TGA 2950 from DuPont Instruments and IR spectrometer Nexus from Nicolet were used to monitor the thermal modification of copolymers.

For emulsion polymerization, the particles average diameter was measured by dynamic light scattering (DLS) at a 90° angle using a Brookhaven device equipped with a Spectra Physics Argon laser. Each reported diameter value was an average over 20 measurements.

The titration method used for the determination of adsorption isotherms was the following: samples containing the latex and the block copolymer were equilibrated for 24 h, centrifuged in a Beckman J2-21 ultracentrifuge, and the supernatant was titrated with a HCl solution with a Radiometer Analytical TIM880 titration manager equipped with a ABU52 Biburette.

Dynamic surface tension of block copolymer solutions was measured with a Krüss DSA10 tensiometer. An air bubble was formed at the tip of an inverted stainless steel needle immersed in the copolymer solution; the digital picture of the bubble was taken with the video camera and analyzed for its shape, giving the surface tension as a function of time.

2.3. Synthesis and characterization of the block copolymers

PBMA-*b*-MAA block copolymers were prepared in three steps shown in Scheme 1: PBMA-*b*-tBMA synthesis by anionic polymerization, thermal cleavage of the *tert*-butyl ester, and hydrolysis of the anhydride formed in the second step. The PBMA-*b*-tBMA block copolymers were prepared by anionic polymerization of BMA and tBMA in THF initiated by Ph_2CHNa in the presence of DB18C6 at -20 °C [14]. A 1 L four-neck jacketed reactor, equipped with an internal coil condenser, a stopcock septum inlet, a graduated funnel and a thermometer, was cooled by circulating ethanol, through the condenser and the jacket, so as to ensure homogeneous cooling inside the solution. A typical polymerization was performed as follows: 4×10^{-3} mol of DB18C6 was introduced into the reactor, the equipment was dried by argon/vacuum cycles, 500 mL of THF was transferred into the reactor by capillary technique and 8.8 mL of the initiator solution (4.4×10^{-3} mol of Ph_2CHNa) was poured with the graduated funnel. After cooling at desired temperature (-20 °C), 0.035 mol of BMA was slowly added with a syringe in a first step, after a delay of two minutes for polymerization at full conversion, 0.21 mol of t-BMA was subsequently added. The anionic chain ends were deactivated after 2 min by adding acidified methanol. The polymer was recovered by precipitation into a methanol/water (4/1 v/v) mixture and analysed by SEC and ^{1}H NMR. Residual traces of crown ether were eliminated by flash chromatography in ethyl acetate, affording polymer with more than 95% yield. The analytical data, namely molecular weight, polydispersity and block lengths are reported in Table 1.

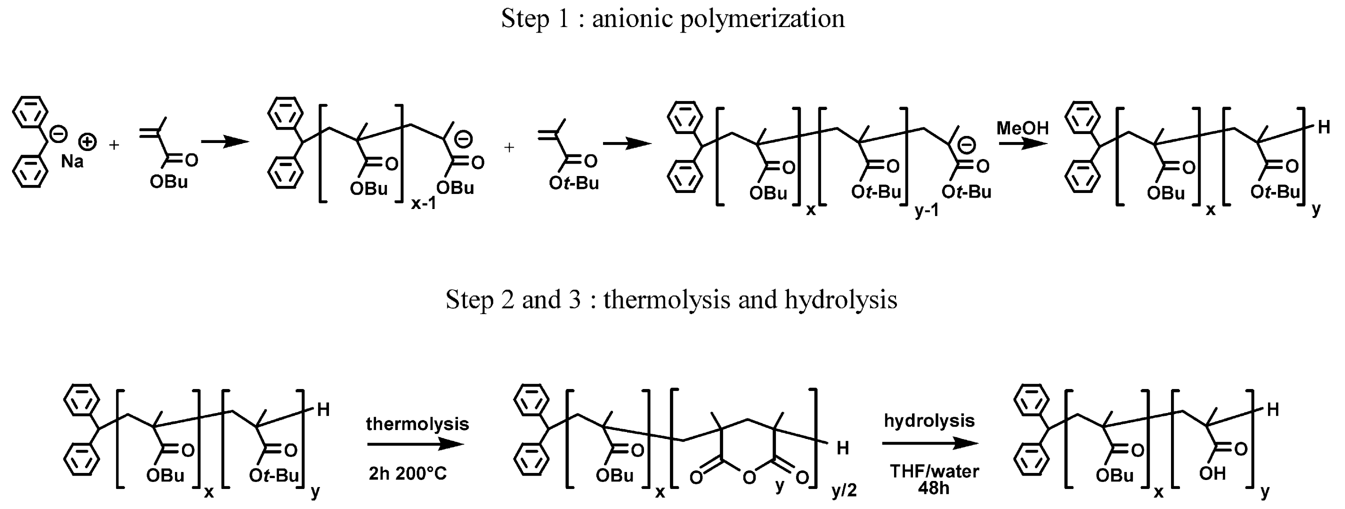
The dry PBMA-*b*-tBMA block copolymers were heated at 200 °C during 2 h under nitrogen atmosphere for thermal cleavage of the *tert*-butyl ester, giving both acid and anhydride formation [15], as observed by IR spectroscopy (Fig. 1). For a test run with PtBMA homopolymer, the C=O band of the ester group at 1724 cm^{-1}, was replaced by the anhydride bands at 1759 and 1803 cm^{-1} and the acid band at 1701 cm^{-1}; the band at 1701 cm^{-1} was the only remaining band after hydrolysis. Thereafter, the copolymers were dissolved in THF with a 10-fold molar excess of water with respect to *tert*-butyl ester groups, and the mixture was heated at reflux for 24 h. The solvents were eliminated in a rotating evaporator and the copolymers were thoroughly dried at 80 °C. Analyses by means of ^{1}H NMR and IR spectroscopy (Table 2) indicated full conversion into the acid.

2.4. Preparation of the micellar solutions of the copolymers

The copolymers in the acidic form could be dissolved directly in water within a period of one day to one week, depending on the concentration and the composition. Total elimination of water was impossible: the copolymers contain between 2 and 10 wt% of water. So the concentration of the solution was determined by NaOH 0.1 N titration.

2.5. Emulsion polymerization procedure

Batch emulsion polymerizations in presence of block copolymers were performed in a 250 mL three-neck round-bottom reactor immersed in a thermostated oil bath and equipped with a reflux condenser, a nitrogen inlet and a thermometer. A typical procedure was as follows. The micellar solution ($V_{tot} = 130$ mL) de-oxygenated by bubbling nitrogen for 1 h. Then, 15 mL of BMA and an aqueous solution of initiator (0.3 g dissolved in 10 mL) were introduced successively. The pH of polymerization medium was set always between 8 and 9 by adding 0.6 mL of



Scheme 1. Synthesis and structure of PBMA-*b*-PMAA

ammonium hydroxide 5.0 N for full ionization of the carboxylic acid units. The polymerizations were stopped after 3 h.

Batch emulsion polymerization without emulsifier was performed following the same general procedure. The PBMA latex of 380 nm average diameter had 8.5 wt% solid content. Latex cleaning was carried out by dialysis: dialysis tubing was filled with 100 mL of polymer suspension and immersed in 3 L of deionized water. Water was renewed five times over a period of 4 days. Latex was concentrated to 12 wt% by rotating evaporator since dilution occurred during dialysis. The residual concentration of carboxylic acid from initiator in the supernatant was reduced from 1.6×10^{-2} mol L^{-1} to 7×10^{-3} mol L^{-1} after dialysis of concentrated latex.

2.6. Characterization of the latexes

The solid content τ of the final latexes were determined by weighting the dry latex. The particles diameter D was measured by DLS. The final number density of particles N_P (L^{-1}) was calculated according to ($\rho = 1.02\times10^6$ g m^{-3} being the PBMA density):

$$N_P = \frac{6\tau}{\pi\rho D^3} \tag{1}$$

2.7. Adsorption isotherms

Adsorption isotherms were determined by the solution depletion method. The adsorbed amount was determined by titration of the supernatant after sedimentation of the particles by ultracentrifugation. The titration of the supernatant containing the free block copolymers and other water-soluble species was carried out by pH-metry. Typically, 1–6 mL of copolymer solution was added to 10 mL of latex; final volume was completed to 16 mL by adding distilled water. After a 3 days delay of equilibration, the samples were centrifuged at 20,000 rpm during 1 h. 10 mL of supernatant were titrated by HCl 0.1 N. The adsorbed amount Γ (mol m^{-2}) was calculated from the concentrations of copolymer before [COPO]$_i$ and after adsorption [COPO]$_f$, the particles area A and the sample volume V according to:

$$\Gamma = \frac{([\mathrm{COPO}]_i - [\mathrm{COPO}]_f)V}{A}, \quad A = \frac{6\tau'}{\rho D} \tag{2}$$

The particles area was calculated from their diameter D and the solid content of diluted latex τ'. The final concentration of copolymer was calculated from the titration data for the latex with adsorbed copolymer (sample) and latex alone (Fig. 2) according to:

Table 1
Composition of PBMA$_x$-*b*-tBMA$_y$ precursor block copolymers as analyzed by ^{1}H NMR and SEC

PBMA$_x$-*b*-tBMA$_y$	NMR			SEC	
	x	*y*	*x*+*y*	*x*+*y*	M_w/M_n
8/16	8.1	12.5	20.6	31.1	1.08
8/32	7.8	32.4	40.2	47	1.04
8/64	7.2	58.2	65.4	84.2	1.03
16/64	16.6	60	76.6	97.2	1.04
32/64	33.1	60.4	93.5	110	1.04

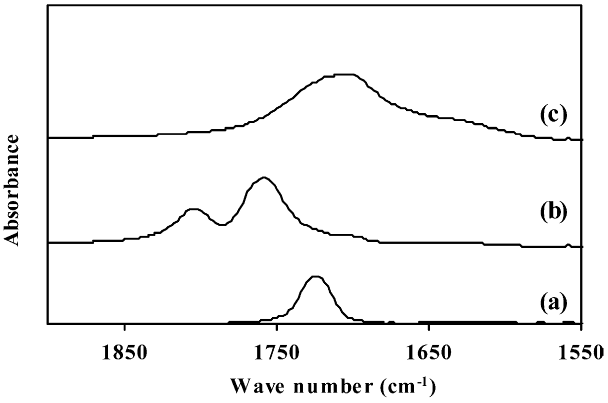


Fig. 1. IR spectra of PtBMA homopolymer (a) precursor, (b) thermolysis at 200 °C and (c) hydrolyzed.

$$[\mathrm{COPO}]_\mathrm{f} = \left(\frac{(V_{2,\mathrm{S}} - V_{1,\mathrm{S}})}{V_{\mathrm{total,S}}} \times [\mathrm{HCl}] - \frac{(V_{2,\mathrm{L}} - V_{1,\mathrm{L}})}{V_{\mathrm{total,L}}} \times [\mathrm{HCl}] \times k\right) / PD_{\mathrm{MAA}} \quad (3)$$

where V_{total} was the volume of titrated sample, V_1 and V_2 were the equivalent volumes of acid corresponding to the titrations of excess strong basic species (OH^-) and carboxylates respectively; subscripts S and L referred to the sample and bare latex. k was the dilution factor of the latex and PD_{MAA} was the polymerization degree of the PMAA block.

3. Results and discussion

3.1. The slow adsorption kinetics measurements at the air/water interface

The kinetics of adsorption from aqueous copolymers solutions to the air-water interface have been assessed from dynamic surface tension measurements. The example of a PBMA_{16}-*b*-MANa_{32} solution at a concentration of 200 μmol L^{-1} is given in Fig. 3. Starting from the fresh surface of a newly created bubble of air in the copolymer solution, the surface tension continuously decreased from the surface tension of pure water (72.0 mN m^{-1}) to a nearly constant value taken as the equilibrium surface tension. The kinetics were so slow that equilibrium was hardly reached even after several days equilibration. The slow adsorption equilibration of copolymer solution is indeed well known but it is poorly documented because measurements are so difficult and tedious. This phenomenon has somehow discouraged *cmc* measurements by means of surface tension measurements [8]. On the same grounds, the dynamics of exchange between unimers and micelles are very slow even for water-soluble copolymers. The adsorption is slow as compared to conventional surfactants because of the macromolecular nature of the copolymers that involves a low diffusion coefficient of the copolymers in solution and the low *cmc* of such polymeric surfactant. The slow exchange between micelles of polystyrene-*block*-poly(sodium methacrylate) copolymers similar to the present ones has already been studied by fluorescence measurements [16]. At room temperature, similar results were obtained as the exchange rate constants could not be estimated. The surface tension measurements have also shown that the *cmc* of the present copolymers were in the μmol L^{-1} range, in agreement with the values reported in the literature for similar copolymers [17–19]. The concentrations of copolymer used in the emulsion polymerization recipes were every time much larger that the *cmc*. Lastly, the equilibrium

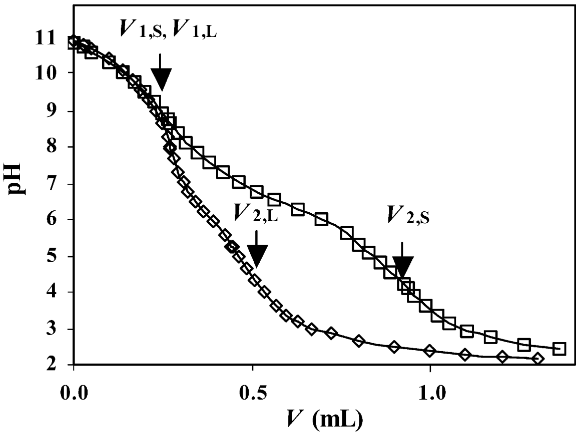


Fig. 2. Example of titration curves: (◇) bare latex and (□) sample.

Table 2
Composition of PBMA_x-*b*-MAA_y as analyzed by ^{1}H NMR

PBMA_x-*b*-MAA_y	*x*	*y*	Composition (mol% MAA)
8/16	8.9	16	64.5
8/32	9.2	33.8	78.6
8/64	8.3	62.2	88.2
16/64	20	70.7	77.9
32/64	33.3	60.5	64.5

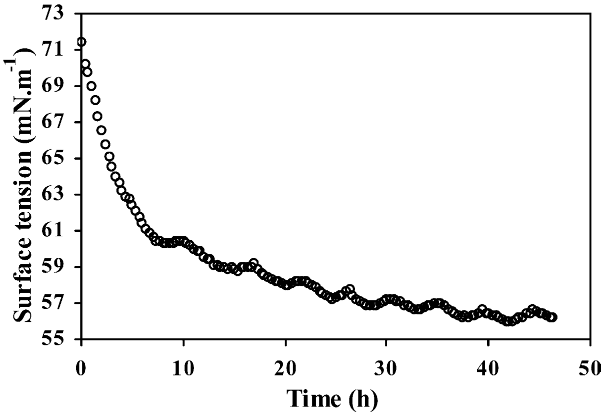


Fig. 3. Surface tension measurement of a 200 μmol L^{-1} PBMA_{16}-*b*-MANa_{32} solution.

surface tensions above the *cmc* were quite high, in the 50–60 mN m^{-1} range, suggesting a poor coverage of the surface by the hydrophobic block. For comparison, the equilibrium surface tension of a sodium dodecyl sulfate (SDS) solution in pure water above the *cmc* is 32.5 mN m^{-1} [20] and the time scale for adsorption leading to the surface tension lowering is in the 10 ms range [21]. Thus, block copolymers differ from conventional surfactants such as SDS in many instances. This is reflected in their behavior as emulsifiers in emulsion polymerization of moderately non-polar monomers such as styrene or *n*-butyl methacrylate. However, the adsorption kinetics onto the surface of polymer particles is not as slow as at the air-water interface because of the different geometry: a dispersion of droplets against a planar macroscopic surface.

3.2. Adsorption isotherms on latex surface

The adsorption of the series of amphiphilic copolymers at the interface between PBMA latex particle and water was investigated by the depletion method using the titration of the supernatant after sedimentation of the particles by ultracentrifugation. The adsorption isotherms, that is, the adsorbed amount (mol m^{-2}) as a function of the residual concentration (mol L^{-1}) have been built for each copolymer at concentrations above the *cmc* (Fig. 4). The adsorption isotherms were similar in shape: a very strong adsorption took place at low concentrations of copolymer, which was followed by a plateau at higher concentrations. Because of the very low residual concentrations after adsorption from dilute solutions, it was not possible to measure with accuracy the steep rise of the adsorption at low concentrations. The residual concentration was zero within experimental accuracy, which means irreversible adsorption for this part of the adsorption isotherm. The plateau which was observed at higher concentrations was not perfectly flat as it could be expected for a surface where surface sites were fully occupied by adsorbed molecules. This behavior was characteristic of a hindered adsorption phenomenon where the macromolecules already adsorbed hinder further adsorption. Such a behavior is quite frequent for the adsorption of polymers. The present data were strongly reminiscent of the two regimes described by Alexander and de Gennes for the adsorption of end functional polymers and block copolymers [22,23]. The "mushroom" (dilute) regime with a strong affinity for the surface was observed at low concentrations, where the surface was either bare or not too much crowded, leading to a steep increase of the adsorption. The "brush" (semi-dilute) regime at higher concentrations was characterized by a low affinity for the surface because lateral interactions between adsorbed macromolecules hindered the adsorption of additional macromolecules. The macromolecules got stretched in a direction perpendicular to the surface. The low affinity manifested by a low slope of the adsorption isotherm which characterized the balance of the free energy of adsorption of the PBMA blocks on the PBMA latex and the entropic term of the conformational free energy of the PMANa blocks that stretched radially. Such a behavior has already been observed with block copolymers for various surfaces and solvents [24–27]. Depending on the copolymer structure, the adsorption strength and adsorbed amount at the plateau were quite different. For PBMA$_8$-*b*-MANa$_{16}$ and PBMA$_8$-*b*-MANa$_{32}$, the strength of the adsorption was very strong as indicated by high value of the adsorbed amount at vanishing residual concentrations. A slight but significant positive slope was observed at higher concentrations. Nevertheless, for PBMA$_{32}$-*b*-MANa$_{64}$ which showed a lower adsorption, the accuracy of measurements was poorer, so that the slope in the brush regime was difficult to assess. The present results were at variance with adsorption isotherms described as Langmuir-type by some authors [28,29] where the adsorbed amount rapidly increased with polymer concentration up to a plateau region. The slopes were 3–7×10^{-8} m for PBMA$_8$-*b*-MANa$_{64}$, PBMA$_{16}$-*b*-MANa$_{64}$ and PBMA$_{32}$-*b*-MANa$_{64}$, 0.8–1×10^{-7} m for PBMA$_8$-*b*-MANa$_{32}$ and 0.8–1.7×10^{-7} m for PBMA$_8$-*b*-MANa$_{16}$. These phenomena has already been described and explained by the stretching of macromolecules [30]. As the PMANa block length increased, the adsorbed amount on the 'plateau' decreased. When the PBMA block length was increased, the adsorbed amount on the plateau remained constant. When the results were expressed in weight concentration, adsorb amount did not significantly vary and were close to 0.1–0.3 mg m^{-2}. This meant that adsorption was controlled by steric effect at the level of the hydrophilic blocks: on the plateau region, the coverage by copolymers was limited by the PMANa chain radius. Layer thickness of copolymers are currently under investigation by static and dynamic light scattering.

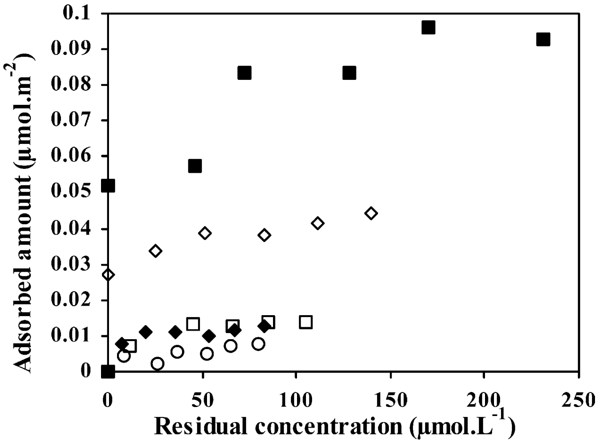


Fig. 4. Adsorption isotherms, adsorbed amount versus residual concentration: (■) PBMA$_8$MANa$_{16}$, (◇) PBMA$_8$-*b*-MANa$_{32}$, (○) PBMA$_8$-*b*-MANa$_{64}$, (◆) PBMA$_{16}$-*b*-MANa$_{64}$, (□) PBMA$_{32}$-*b*-MANa$_{64}$.

The surface area per macromolecule at the latex surface was:

$$a = \frac{10^{18}}{\Gamma_{\max} N_{\mathrm{Av}}} \quad (4)$$

where $\Gamma_{\max}$ was the maximum adsorbed amount (μmol m^{-2}) taken as the extrapolation of the adsorption isotherm to $C_{\mathrm{res}}=0$. It was expected that the surface be completely covered with non-perturbed PMANa blocks at this point of the adsorption isotherm. The surface area a plotted against the weight average molar mass M_w in a double logarithmic plot was linear (Fig. 5). Half of the slope was 0.58, slightly higher than the exponent 0.5 of the law $R_G \,\alpha\, M_w^{1/2}$ corresponding to Θ-solvent conditions in bulk solution. The section of a free poly(sodium methacrylate) homopolymer coil in aqueous solution can be calculated from its radius of gyration ($\alpha = \pi R_G^2$). The areas calculated from radii of gyration of PMANa in dilute aqueous solutions taken from the literature were close to the linear behavior (Fig. 5) although the molar masses were much higher and the ionic strengths were also variable (PMANa $M_w=$ 13,000 g mol^{-1}, NaCl 10^{-1} M [31]; PMANa $M_w=$ 130,000 g mol^{-1}, NaCl 10^{-1} M [32]; PMANa$_{0.8}$H$_{0.2}$ $M_w=440{,}000$ g mol^{-1}, NaCl $10^{-2}/10^{-3}$ M and $M_w=$ 202,000 g mol^{-1}, NaCl 10^{-2} M [33]). Additional data coming from viscosity measurements in 2 M $NaNO_3$ solutions [34] were also reported in Fig. 5; the gyration radius $\langle r^2\rangle^{1/2}$ was calculated from these data with the help of its relationship with the intrinsic viscosity [35] and the Mark–Houwink relationship (Eq. (5)), giving Eq. (6):

$$[\eta] = \frac{\phi \langle r^2\rangle^{3/2}}{M_w}, \quad [\eta] = K M_w^{\alpha} \quad (5)$$

$$\langle r^2\rangle^{1/2} = \left(\frac{K}{\phi}\right)^{1/3} M_w \quad (6)$$

The reported values of the Mark–Houwink coefficients were $K=4.49\times10^{-4}$, $\alpha=0.65$ and $\phi=2.1\times10^{21}$ (according to the units used in [34]) is a universal constant [35]. Let us notice that $\alpha=0.65$ in the Mark–Houwink equation gives an exponent $(\alpha+1)/3=0.55$, close to the exponent 0.58 found in the present adsorption data.

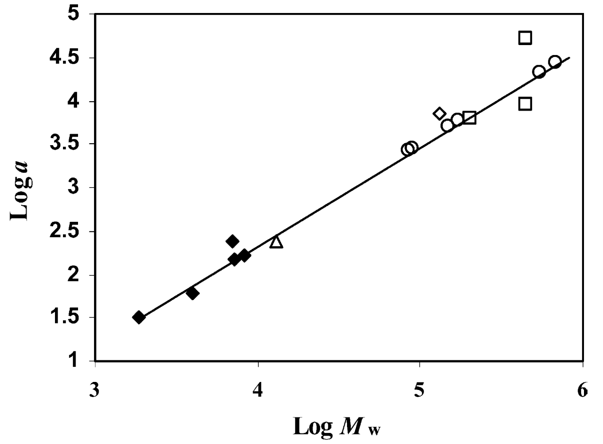


Fig. 5. Logarithmic plot of surface area (nm^2) versus weight average molar mass of poly(sodium methacrylate): (◆) experimental, (◇) [32], (■) [33], (△) [31] and (□) [34]. The line is the linear regression to the present adsorption data only.

This good agreement between molecular area in the adsorbed layer and in dilute bulk aqueous solutions showed that the conformation of the adsorbed PMANa block was the same as in 3-dimensional solution, that is, non-perturbed by the presence of the surface and the neighboring adsorbed molecules.

3.3. *Efficiency of the block copolymers as stabilisers in emulsion polymerization*

The amphiphilic block copolymers were tested as stabilizers in the free-radical emulsion polymerization of butyl methacrylate. They proved to be powerful electrosteric stabilizers, resulting in stable latexes and small particles. The smallest particle diameters that could be reached were 60 nm against 380 nm for the emulsifier-free polymerization carried out according to the same recipe and temperature. Very small amount of flocculated latex (coagulum) were found at the end of the polymerization. The stabilizing efficiency can be evaluated from either the final number density of stabilized particles N_P or the stabilized surface area per macromolecular chain a. Both these later parameters are related; N_P was calculated from the diameter and solid content but the evaluation of a required information from the adsorption isotherm that have been reported in the previous section. Table 3 reports characteristic data as the molar concentration, the weight fraction with respect to the monomer, the solid content, the particle average diameter and the number density of particles as calculated from Eq. (1). All block copolymers contained more than 60 mol% of methacrylic acid units so as to ensure water solubility. These amphiphilic block copolymers have structures that enable them to adsorb or anchor onto the particle surface, while the charged hydrophilic segments are well extended in the water phase and ensure electrosteric stabilization. As evidence, even very small weight fractions of stabilizer with respect to the monomer (less than 1 wt%) lead to relatively small diameters and a large number of particles. The number density of particles N_P was examined first as a function of the molar concentration for the different copolymers in the usual way since the theoretical work of Smith and Ewart. Figs. 6 and 7 show respectively the influence of the hydrophilic block length for a constant number of butyl methacrylate units and the influence of the hydrophobic block length for a constant number of methacrylic acid units. In the range of studied concentrations, the highest number of particles was obtained for PBMA$_{16}$-*b*-MANa$_{64}$ but the copolymer PBMA$_8$-*b*-MANa$_{64}$ with the shortest hydrophobic block exhibited better efficiency at low concentration ($<10^{-4}$ mol L^{-1}). Smith and Ewart [9]

Table 3
Emulsion polymerizations of butyl methacrylate in presence of amphiphilic block copolymers: final characteristics of the latexes

PBMA$_x$-*b*-MAA$_y$	Concentration		D (nm)	τ (g L^{-1})	N_P (10^{17} L^{-1})	Γ (µmol m^{-2})	C_{res} (µmol L^{-1})
	wt % vs. BMA	10^{-4} mol L^{-1}					
8/16	0.08	0.28	143	87.1	0.56	0.006	0
	0.1	1.4	96	101.2	2.14	0.019	0
	1	3.36	77	90.1	3.70	0.036	0
	2	8.34	67	91.6	5.70	0.072	60
8/32	0.2	0.38	120	88.7	0.96	0.006	0
	0.45	0.96	95	88.6	1.93	0.013	0
	1	2.12	83	75.9	2.49	0.024	0
	3	6.36	71	92.2	4.82	0.048	150
8/64	0.06	0.073	145	86.6	0.53	0.001	0
	0.13	0.18	124	87.8	0.86	0.003	0
	0.4	0.55	115	87.1	1.07	0.007	0
	1	1.36	92	89.6	2.15	0.013	40
16/64	0.005	0.054	149	85.6	0.48	0.0005	0
	0.02	0.22	115	90.4	1.11	0.003	0
	0.4	0.43	92	91.3	2.20	0.0049	0
	1	1	77	89.0	3.65	0.0095	10
	3	3	67	91.4	5.69	0.015	130
32/64	0.3	0.18	127	89.5	0.82	–	–
	1	0.90	80	91.4	3.34	–	–
	2	1.80	74	89.0	4.11	–	–
	3	2.70	65	91.3	6.22	–	–

have first established the proportionality between N_P and [surfactant]$^{\alpha}$ (with $\alpha=0.6$) for small surfactant molecule (SDS) and over a wide range of concentrations above the critical micellar concentration (*cmc*). In this study, the *cmc* values have not been still experimentally determined with accuracy, but the *cmc* of similar copolymers reported in several studies were generally below 10^{-5}–10^{-6} mol L^{-1} [16–19]. For all copolymers, linear relationships of log(N_P) versus log[surfactant] were observed, indicating that the data followed the same power law as described above. The α exponent depended upon the copolymer composition. The exponent ranged from 0.44 to 0.73 as the hydrophilic content was increased (Fig. 8) and did not significantly depend on the length of the hydrophobic block. The theoretical value $\alpha=0.6$ was observed for the styrene monomer, but departures from this exponent have been observed for more polar monomers and were not considered as failure of the theory. $\alpha=0.44$ obtained for the most hydrophilic copolymers was close to the value $\alpha=0.5$ considered as following the theory of Smith and Ewart for the butyl methacrylate monomer in presence of SDS [36]. But this apparent agreement with the theory looked fortuitous; this did not mean that the present system fulfilled the hypotheses of the Smith and Ewart theory. In particular, the hypothesis of fast equilibration of the surfactant does not

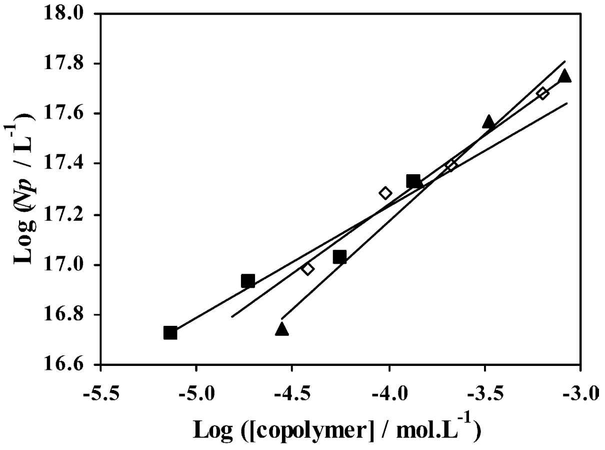


Fig. 6. Logarithmic plot of N_P, number density of particles versus the concentration of block copolymer: (▲) PBMA$_8$-*b*-MANa$_{16}$, (◇) PBMA$_8$-*b*-MANa$_{32}$, (■) PBMA$_8$-*b*-MANa$_{64}$.

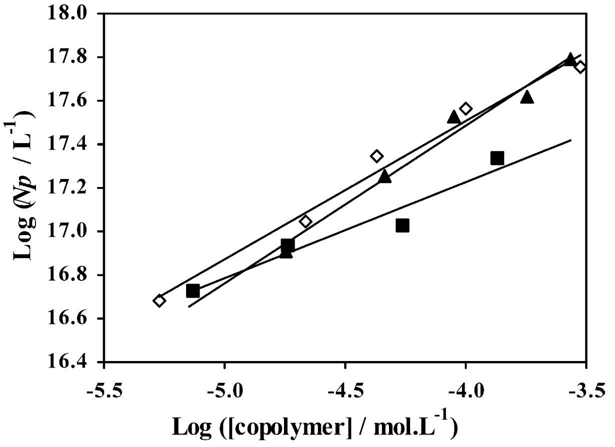


Fig. 7. Logarithmic plot of N_p, number density of particles versus the concentration of block copolymer: (■) PBMA$_8$-*b*-MANa$_{64}$, (◇) PBMA$_{16}$-*b*-MANa$_{64}$, (▲) PBMA$_{32}$-*b*-MANa$_{64}$.

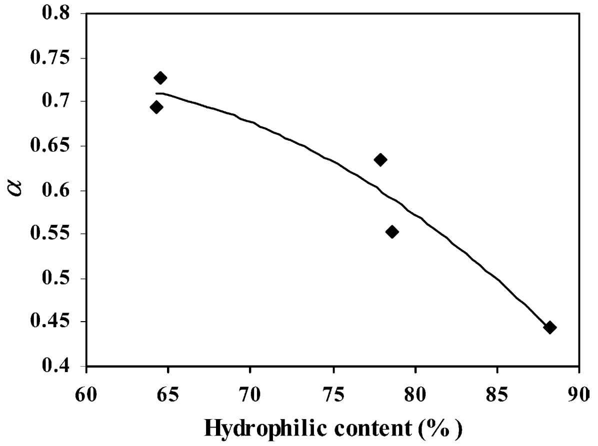


Fig. 8. Evolution of α exponent versus the hydrophilic content of block copolymers. The line is a guide for the eyes only.

hold for copolymers. Burguière et al. have ruled out the mechanism of Smith and Ewart in the case of block copolymers by showing experimentally that the order with respect to the initiator was 0 [12]. The mechanism by which the number of polymer particles is lower than the initial number of micelles is necessarily different of the fast surfactant adsorption of the classical theory of Smith and Ewart. The exponents laid between that of frozen micelles where all the micelles acted as nucleation sites for particles ($\alpha = 1$) and $\alpha \approx 0.5$. The Smith and Ewart value was not a lower limit however since α exponents as low as 0.3 had already been measured for the polymerization of styrene [12].

3.4. The particle formation mechanism and relationship between adsorbed amount and particle diameter

The adsorption level at the end of emulsion polymerization was inferred from the adsorption data which were collected with the surfactant-free latex made of the same PBMA polymer. Thus, the following system of two equations (adsorption isotherm and balance of copolymer amounts before and after adsorption) was solved for the adsorbed amount Γ and the residual concentration of copolymer C_{res}:

$$\Gamma = f(C_{\mathrm{res}}) \tag{7}$$

$$[\mathrm{COPO}]V = C_{\mathrm{res}}V + \Gamma A \tag{8}$$

where [COPO] was the introduced concentration of copolymer, V the volume of water and A the total area of the latex particles. The adsorbed amount determined in that way corresponded to the equilibrium state reached after the polymerization has been completed; this was the upper bound since the adsorbed amount on the growing particles during the polymerization was lower than the equilibrium value in case of slow adsorption.

The adsorption isotherm of SDS has already been determined on polystyrene (PS) latex particles [37] and values of PS particle diameters versus SDS concentration were also reported in the literature [38]. The adsorbed amounts of SDS on PS particles at the end of emulsion polymerization were calculated using the same method as described above. The results are reported in Tables 3 and 4 and the diameters of the latex particles are plotted as a function of relative coverage in Fig. 9. Relative coverage was the ratio of the adsorbed amount to the adsorbed amount at full coverage taken at the plateau of the adsorption isotherm; it represented the fraction of latex surface area that was covered by the copolymer. As the relative coverage increased, particles average diameter first decreased very fast and thereafter hardly reached 60 nm at the about 40% relative coverage. It might be possible to synthesize smaller particles by increasing the copolymer concentration of the polymerization recipe but only a small decrease of diameter could be expected according to the observed trends. Moreover, there was a significant residual concentration of copolymer in the aqueous phase at the end of the polymerization, which meant that copolymer was still available for reducing the particle size. Obviously, the particle size was no longer controlled by the copolymer concentration but by another concentration-independent parameter in this concentration domain. Even when the surface was covered to completion, the most hydrophilic copolymer PBMA_8-*b*-MANa_{64} seemed to be a poor stabilizing surfactant, as the lowest diameter was significantly higher. Interestingly, the copolymers were able to stabilize particles at very low relative coverage (<10%), whereas coverages larger than about 20–25% were required to obtain low diameter particles (~100 nm) by emulsion polymerization in the presence of SDS. For most lower copolymer concentrations, the residual concentration of copolymer was vanishingly small (below the detection limit of the titration method) and the final coverage was not complete. Under such stabilizer-starved conditions, the copolymers were quite efficient in allowing the creation of new area that they did not cover. Coagulation of particles might have occurred during the nucleation period; but it has been limited by the few copolymer molecules that were present on the particle surface.

An α exponent lower than 1 indicated that the number of final particles is lower than the number of initial micelles. Since there was no residual copolymer inside the aqueous

Table 4
Diameter and adsorption data for emulsion polymerization of styrene with SDS emulsifier as calculated from literature data

[SDS] (mol L^{-1})	D (nm)	Γ (µmol m^{-2})	C_{res} (10^{-3} mol L^{-1})
0.004	130	0.75	0.84
0.008	85	0.95	1.25
0.024	57	1.95	3.6
0.048	49	3	10
0.072	44	3	30

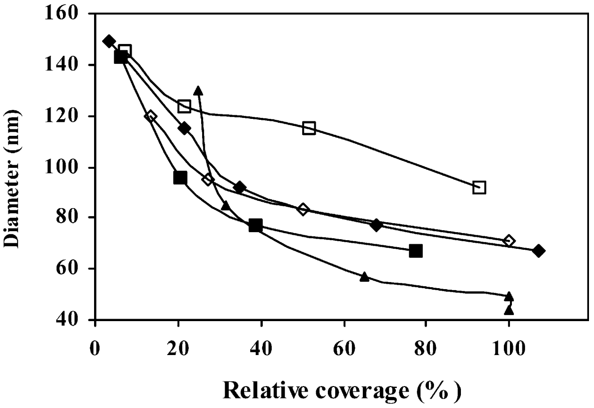


Fig. 9. Evolution of PBMA particle diameter determined by light scattering as a function of relative coverage for different surfactants: (■) $PBMA_8$-*b*-$MANa_{16}$, (◇) $PBMA_8$-*b*-$MANa_{32}$, (□) $PBMA_8$-*b*-$MANa_{64}$, (♦) $PBMA_{16}$-*b*-$MANa_{64}$ and (▲) SDS. The lines are guides for the eyes only.

phase, micelles have been lost. This did not result from copolymer diffusion from micelles to growing particles because the kinetics of adsorption were too slow. Since adsorption of copolymer was very low, micellar nucleation was a likely mechanism by which stabilized particles could be formed. Particles formed by homogeneous nucleation mechanism coagulated with copolymer-covered particles and this contributed to the particle growth. Lastly, a possible event of coagulation of poorly covered particles lead to a larger particle with a better coverage, the final state being the same as if copolymer molecules have migrated from one particle to another. One tentative mechanism of copolymer migration was therefore associated with limited coagulation.

Quite an efficient materials exchange mechanism is the migration of the monomer because of its significant solubility in water. Thus, particles growth requires that the monomer molecules leave the monomer-swollen non-nucleated micelles in order to enter the nucleated particles. The surfactant diffusion to the particles surface destroys the non-nucleated micelles in the case of small surfactant molecules like SDS but this mechanism is not operative with copolymer micelles. A likely mechanism by which the monomer content of micelles leaves them and fills the growing particles is Ostwald ripening. According to this phenomenon well known in the field of emulsion and miniemulsion polymerization, the organic molecules (oil, monomer) leave the smaller droplets and enter the larger ones, so that the large particles grow at the expense of the small ones that finally disappear. The driving force of this mechanism is the difference of monomer concentration in equilibrium with a small droplet of pure monomer and a larger one, which is described by the Kelvin law:

$$\ln\left(\frac{C(r)}{C(\propto)}\right) = \frac{2\gamma V_{\mathrm{mol}}}{rRT} \tag{9}$$

where $C(r)$ and $C(\propto)$ are the equilibrium concentrations near a particle of radius r and near a flat surface, respectively (V_{mol} = molar volume, γ = interfacial tension). As observed previously, the surface tension of the copolymer solutions were not very low ($\gamma = 56\ \mathrm{mN\ m^{-1}}$) and this suggested that the copolymers were also not powerful in decreasing the interfacial tension between the monomer droplets and water. This enhances the sensitivity of the equilibrium concentration $C(r)$ to the droplet size, and therefore accelerates Ostwald ripening. The copolymer content of empty micelles that might be still present at the end of polymerization slowly adsorb to the bare part of the particles surface, ensuring the long term stability of the suspension. That way, the emulsion polymerization with block copolymer stabilizers has strong resemblances with a miniemulsion polymerization process where the hydrophobe that limits Ostwald ripening has not been added.

4. Conclusion

Amphiphilic block copolymers composed of a poly(butyl methacrylate) hydrophobic block and a poly(sodium methacrylate) hydrophilic block have been investigated for their utilization in emulsion polymerization of butyl methacrylate. The block copolymers were obtained by thermal modification of block copolymer precursors of PBMA-*b*-tBMA synthesized by anionic polymerization. Only water-soluble copolymers were investigated as the chemical composition was varied from 64 to 88 mol% of methacrylic acid units. The measurements of the number density of emulsion polymer particles for various copolymer contents of the polymerization recipe and the determination of the equilibrium adsorption isotherms gave insight on the mechanisms of nucleation and growth of the polymer particles. The comparison of the behavior of such block copolymers of different block lengths with respect to the well-known SDS allowed to point out the main differences coming from the slow adsorption rate of copolymers.

A Smith–Ewart type power law $N_P\ \alpha\ [\mathrm{COPO}]^{\alpha}$ was followed in every case with α exponent varying from 0.44 to 0.73 as the hydrophilic content of the copolymers was decreased. The α values can be correlated by a competition between homogeneous and micellar nucleation but the mechanism proposed by Smith and Ewart did not hold because the copolymer exchange between micelles and growing particles was very slow. It was proposed that the final number of particles lower than the number of starting micelles was caused by limited coagulation during the nucleation period and/or easy monomer transfer from non-nucleated micelles to the growing particles by means of an Ostwald ripening effect.

The equilibrium adsorption on PBMA latex surface was very strong to irreversible at low coverages and hardly increased at higher coverages because of lateral interactions between adsorbed macromolecules in the so-called brush regime of adsorption. The interfacial area per copolymer at the beginning of the brush regime was the same as the circular section of a non-perturbed coil a poly(sodium methacrylate) in aqueous solution.

The adsorbed amounts at the end of the emulsion polymerization were evaluated from adsorption isotherms determined on PBMA latex synthesized by surfactant-free polymerization, showing that the block copolymers appeared quite efficient in stabilizing the emulsion of polymer particles. The copolymers were able to provide efficient stabilization down to a relative coverage of the particles surface of the order 5–10%. This is much lower than for a classical surfactant like SDS requiring at least 25% relative coverage for ensuring the colloidal stability of the particles during the polymerization course. The efficient electrosteric stabilization mechanism of block copolymers compensates the low adsorbed amount and slow adsorption rate, allowing the stabilization at such low coverages.

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