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ORIGINAL CONTRIBUTION

F. Corcos
E. Bourgeat-Lami
C. Novat
J. Lang

Poly(styrene-*b*-ethylene oxide) copolymers as stabilizers for the synthesis of silica–polystyrene core–shell particles

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F. Corcos · E. Bourgeat-Lami (✉)
C. Novat
Laboratoire de Chimie et Procédés de Polymérisation
CNRS-CPE, Bâtiment 308 F, B.P.2077
43 Boulevard du 11 Novembre 1918
F-69616 Villeurbanne Cedex, France

J. Lang
Institut Charles Sadron
CNRS-ULP Strasbourg
6 Rue Boussingault
F-67083 Strasbourg Cedex, France

Abstract Following previous works [1, 2], silica–polystyrene core–shell particles have been synthesized by dispersion polymerization of styrene in an ethanol/water mixture in the presence of a poly(styrene-*b*-ethylene oxide) block copolymer as stabilizer. Besides the formation of composite core–shell particles, a large number of free latex particles that do not contain silica were also formed. This number decreases as the size of the silica beads decreases from 300 to 29 nm in diameter, and becomes very low compared to the number of composite particles for the smallest silica beads used. In every case, the composite particles could be easily separated from the free latex particles by centrifugation, providing a material made of regular core–shell composite particles. On the basis of the mechanisms involved in dispersion polymerization, hypotheses were formulated to account for the formation of the silica–polystyrene composite particles.

Key words Block copolymers stabilizers · Dispersion polymerization · Silica · Polystyrene · Core–shell composite particles

Introduction

It has been shown recently [1, 2] that encapsulation of silica beads by polystyrene (PS) can be achieved by dispersion polymerization in an aqueous ethanol medium, when silica surfaces are grafted with the coupling agent 3-(trimethoxysilyl)propyl methacrylate (MPS). In these previous studies, we were mainly interested in the parameters that influenced the composite particle size and morphology, for instance, the size and concentration of the silica beads. For small silica beads, a large number of silica beads is present in each composite particle, whereas this number decreases as the size of the silica beads increases, and becomes close to 1 for silica beads larger than 450 nm. Simultaneously, the composite particles become more irregular in shape. In order to have real control of the morphology of the composite particles, and in particular to obtain only one silica bead per composite particle, whatever the silica bead size, modifications of the experimental conditions are necessary. In addition to the solvent composition, or to the nature and concentration of monomer and initiator, one of the main parameters that governs the size and stability of the latex particles, during and after polymerization, is the nature and concentration of the stabilizer. In the previous studies, poly(*N*-vinyl pyrrolidone) (PVP) was used as a stabilizer for the composite particles. Here, we investigate block copolymers of PS and polyethylene oxide (PEO). Drastic changes in the morphology of the composite particles are observed compared to the morphology obtained with PVP. In the literature, there have been reports of only a few studies using block copolymer stabilizers for dispersion polymerization in polar media. In addition to the work of Terada et al. [3], who described the dispersion polymerization of styrene in the presence of poly(styrene-*b*-vinyl acetate) copolymers in ethanol, and that of Baines et al. [4], who used poly(2-(dimethylamino)ethyl methacrylate-*b*-alkyl methacrylate) copolymer stabilizers, the only other relevant work in this field is that of Winzor et al.

[5], who investigated a series of poly(styrene-*b*-ethylene oxide) (PS/PEO) copolymers as steric stabilizers for the dispersion polymerization of styrene in methanol. In the present study, we describe the use of similar block copolymers for the synthesis of silica–PS composite latexes. The morphology and composition of the composite particles is followed by transmission electron microscopy (TEM) as a function of the size of the silica beads and the concentration of the stabilizer. In order to explain the observed evolution of the morphology in the presence of the block copolymer and, in particular, to understand the role of stabilization in the formation of the composite particles, a preliminary study was carried out in the absence of silica beads. The results of the polymerization performed in presence of the silica beads, under otherwise identical experimental conditions, are given. The observed evolutions are discussed in the light of the mechanism currently adopted to explain the process of dispersion polymerization.

Experimental

Materials

Absolute ethanol, ammonium hydroxide, tetraethyl orthosilicate for the preparation of the silica beads, the coupling agent, MPS, the monomer, styrene, the initiator, 2,2′-azobis(isobutyronitrile) (AIBN), and the stabilizer, PVP K30 (M_w = 40 000), have the same origin as in the previous work [1].

Copolymer characterization

The (PS/PEO) copolymers were supplied by Goldschmidt. Two copolymers were used, having a PS/PEO molecular weight ratio given by the manufacturer of 1000/3000 and 3000/3000, and named SE 1030 and SE 3030, respectively. In the present work, molecular weights and molecular weight distributions of the copolymers were determined by size-exclusion chromatography (SEC) with a Waters 600 apparatus using tetrahydrofuran as the eluant at a flow rate of 1 ml/min and Shodex columns. A Waters R410 refractive index detector was calibrated with monodisperse PS standards; therefore, the molecular weights corresponded to those of PS equivalents. The molar ratio of the styrene to the ethylene oxide units of the copolymers was determined by ^{1}H NMR spectroscopy using a Bruker AC 250 MHz instrument and $CDCl_3$ solutions. The ratio was calculated by comparing the peak integral between 6.2 and 7.3 ppm corresponding to the styrenic protons with that centered around 3.65 ppm due to the protons of the ethylene oxide units. Molecular weight ratios were deduced from the molecular weights determined by SEC and the molar ratios given by the NMR analysis. The characteristics of the PS/PEO block copolymers are given in Table 1. Micellar solutions of the copolymers were prepared by dissolving the copolymers in an ethanol/water mixture with an ethanol-to-water weight ratio of 94.5/5.5. Gentle warming was required to assist dissolution. Micelle diameters were measured using a Malvern Nanosizer instrument working at a fixed scattering angle of 90°.

Adsorption isotherm of the copolymers on the silica surface

A series of solutions with desired concentrations of the block copolymer SE 3030 in water was prepared and the solutions were added to the silica dispersion in a glass vial with a cap. The mixture was equilibrated by shaking at room temperature for 24 h. After equilibration, the solid was separated by centrifugation and the supernatant was analyzed by UV spectroscopy (UVIKON 922 spectrophotometer) using a calibration curve.

Table 1 Characteristics of the poly(styrene-*b*-ethylene oxide) (*PS/PEO*) block copolymers

PS/PEO	Manufacturer		This work		
	M_n (g/mol)	Composition	M_n (g/mol)^a	M_w/M_n^a	Composition^b
SE 1030	4000	1000/3000	4520	1.15	990/3530
SE 3030	6000	3000/3000	6200	1.24	2600/3600

^{a} Determined by size-exclusion chromatography analysis using PS standards
^{b} Determined by ^{1}H NMR spectroscopy

Dispersion polymerization

The polymerizations were performed in a mixture of ethanol and water with an ethanol/water weight ratio of 94.5/5.5. The silica beads were synthesized according to the method of Stöber et al. [6]. They were grafted with MPS by stirring a mixture of alcosol (silica dispersion in alcohol) and MPS for several days at room temperature. The dispersion was purified by dialysis to eliminate free MPS, as done previously [1]. In all cases the dispersion polymerization was carried out in a batch process, which means that all the compounds were added to the ethanol/water mixture at the beginning of the polymerization. The concentrations (in weight per 100 g solvent, i.e., the mixture of ethanol and water) of the various components used in the synthesis were 10% styrene, 0.1% AIBN, 1.5% silica when polymerization was performed in the presence of silica beads, 2% PVP K30 stabilizer, and variable concentrations, between 0.3 and 2%, of the stabilizer PS/PEO.

Particles size and morphology

Images of the silica beads and of the PS latexes, synthesized in the absence and in the presence of silica beads, were obtained by TEM. A drop of a diluted dispersion (about 0.01 wt%) was put on a carbon film supported by a copper grid and placed, after air drying, in the vacuum chamber of a Philips CM10 electron microscope. All the diameters, i.e., the diameter of the silica beads, $D_p(SiO_2)$, that of the latex particles free of silica beads, D_p(free), and that of composite particles containing silica beads, D_p(composite), were determined from the TEM images. The diameters were averaged in each instance over a great number of particles: between 50 and 100. In the cases where the composite particles exhibited a core–shell morphology, it was possible to determine from the TEM micrographs the thickness of the shell, i.e., which corresponds to half the difference between D_p(composite) and $D_p(SiO_2)$.

Particle number and polymer partition between free latexes and composite particles

The synthesis using the block copolymer stabilizers in the presence of the silica beads described here can result in the simultaneous formation of composite particles, i.e., latex particles containing silica beads and free latex particles that do not contain silica. In addition, most of the composite particles studied here, using PS/PEO as a stabilizer, contain only one silica bead (this is illustrated in Fig. 2b). In this case, the composite particle number, N_p(com-

Table 2 Diameter, $D_p(SiO_2)$, of the silica beads, number, $N_p(SiO_2)$, of silica beads, diameter, D_p(composite), of the composite particle, shell thickness, e, around the composite particle, ratio, e/R_p, of the polymer shell thickness over the radius, R_p, of the composite particle, weight ratio, E, of the polymer forming the shell over the total quantity of polymer synthesized, diameter, D_p(free), and number, N_p(free), of the free latex particles, and mean number, N_a, of silica beads per composite particle. Silica beads: 1.5 wt%; Styrene, 10 wt%; SE 3030, 2 wt%[a]

Silica beads		Composite particles				Free latex particles		N_a^c
$D_p(SiO_2)$ (nm)	$N_p(SiO_2)^b$ (nm)	D_p(composite) (nm)	e (nm)	e/R_p	E (wt%)	D_p(free) (nm)	$N_p(\text{free})^b$	
300	4.7×10^{14}	414	57.0	0.28	15.5	58	5.8×10^{17}	0.0008
247	7.8×10^{14}	368	57.5	0.31	20.8	57	5.4×10^{17}	0.0014
108	1.0×10^{16}	166	29.0	0.35	36.5	54	3.7×10^{17}	0.0260
29	5.2×10^{17}	68	19.5	0.57	92.0	55	6.9×10^{16}	0.9700

[a] Grams per 100 g solvent
[b] Per liter of dispersion
[c] Calculated using Eq. (A3)

posite), is precisely equal to the number, $N_p(SiO_2)$, of silica beads. This last number is directly determined from $D_p(SiO_2)$ and the silica concentration. Knowing this number and the size of the composite particles determined by TEM, one can deduce the amount of polymer which constitutes the shell and compare it to the total amount of polymer synthesized (this comparison is made using the ratio, E, of the amount of shell polymer over the total amount of polymer synthesized, see Tables 2, 3). The total amount of PS is determined by drying a known quantity of dispersion and subtracting the amount of silica and stabilizer contained in the solid. The concentration of polymer forming the free latex particles can be easily obtained from the difference between the amount of polymer synthesized and that of the polymer which constitutes the shell. Then, one can deduce the number of free latex particles, N_p(free), from their size and the concentration of the free polymer. Knowing the number and the diameter of the silica beads, the diameters of the composite particles and of the free latex particles, an average number, N_a, of silica beads per particle, can be calculated. The definition and the mathematical expression of the different N_a values are given in the Appendix.

Composite particle recovery

In order to obtain latexes containing only composite particles with core–shell morphologies, the free latex particles were separated from the composite particles by centrifugation of the original dispersion at 15 000 rpm for 15 min and redispersion into the ethanol/water mixture. The operation was reproduced until the serum was no longer turbid. The absence of residual free latex particles was confirmed by TEM.

Results

Polymerization in the absence of silica beads

Influence of the nature of the stabilizer

In the first series of experiments, we studied the influence of the composition of the block copolymer stabilizers on the size of the particles and on the molecular weight of the polymers formed in the absence of silica beads. The results are compared to those obtained with the PVP K30 homopolymer. Table 4 shows that the size of the latex particles formed in the presence of the SE 3030 copolymer is smaller than the size obtained with the SE 1030 stabilizer. On the other hand, both of the PS/PEO stabilizers give particle sizes lower than that observed with PVP K30. Mean diameters of 62 and 150 nm were obtained with SE 3030 and SE 1030, respectively, while larger particle sizes, of 750 nm, were obtained with PVP K30. These results seem to indicate that the copolymers are better stabilizers for the PS particles than PVP K30, when used at the same weight concentration. However, one must note that the molecular weight of the block copolymers is 7–10 times smaller than that of PVP. Thus, the number of block copolymer molecules in the dispersion is 7 times larger for SE 3030 and 10 times larger for SE 1030 than the number of PVP molecules. Nevertheless, the decrease in the size of the latex particles, when using the block copolymer stabilizers, is not only due to an increase in the number of stabilizing molecules since SE 1030, which corresponds to the larger molar concentration, gives the larger particle size. Indeed, one must also take into consideration the fact that the block copolymers have a PS segment that has a great affinity for the PS latex particles and certainly plays a role in their stabilization. A better coverage of the latex particles by the block copolymer is probably obtained when the length of the PS block is increased which is the case for the stabilizer SE 3030 when compared to SE 1030 (30 styrene monomer units for SE 3030 compared to ten for SE 1030). In addition, the other block of the copolymer is composed of a PEO chain, which is soluble in the aqueous alcoholic medium, and, thus, the copolymer can behave as a classical surfactant. Consequently, the block copolymer SE 1030, which has a shorter PS chain, is more soluble in the polymerization medium than the SE 3030 copolymer, and has, therefore, a lower partition coefficient in favor of the PS latex particles. It is clear that the amphiphilic character of the block copolymer molecules plays an important role in the steric stabilization mechanism of

Table 3 Concentration of the stabilizer SE 3030, diameters, $D_p(SiO_2)$, of the silica beads, number, $N_p(SiO_2)$, of silica beads; diameter, D_p(composite), of the composite particle, polymer shell thickness, e, around the composite particle, ratio, e/R_p, of the polymer shell thickness over the radius, R_p, of the composite particle, weight ratio, E, of the quantity of polymer forming the shell over the total quantity of polymer synthesized, diameter, D_p(free), and number, N_p(free), of the free latex particles, and mean number, N_a, of silica beads per composite particle. Silica beads: 1.5 wt%[a], styrene, 10 wt%[a]

SE 3030[a]	Silica beads		Composite particles				Free latex particles		N_a
	$D_p(SiO_2)$ (nm)	$N_p(SiO_2)$[b]	D_p(composite) (nm)	e (nm)	e/R_p	E (wt%)	D_p(free) (nm)	N_p(free)[b]	
2	300	4.7×10^{14}	414	57.0	0.28	15.5	58	5.8×10^{17}	0.0008[c]
0.3	300	4.7×10^{14}	519	109.5	0.43	36	175	1.75×10^{16}	0.026[c]
2	108	1.0×10^{16}	166	30.5	0.37	36.5	54	3.7×10^{17}	0.026[c]
1	108	1.0×10^{16}	205	48.5	0.47	54	74	1.55×10^{17}	0.061[c]
0.5	108	1.0×10^{16}	240	66.0	0.55	83	125	1.3×10^{16}	0.43[c]
2	29	5.2×10^{17}	68	19.5	0.57	92	55	6.9×10^{16}	0.97[c]
1	29	5.2×10^{17}	124	–	–	–	–	0	6 [d]
0.5	29	5.2×10^{17}	193	–	–	–	–	0	22.7[d]

[a] Grams per 100 g solvent
[b] Per liter of dispersion
[c] Calculated using Eq. (A3)
[d] Calculated using Eq. (A4)

the latex particles. Indeed, in comparison to PVP, which is believed to involve in situ grafting of the growing PS chains to obtain the true stabilizer [7–10], the PS/PEO copolymers can easily offer an effective steric stabilization at a very early stage of polymerization and thus, provide a better control of the particle size. Experimental evidence of such amphiphilic character has been described in the literature for block surfactants very similar to ours, and has been used in the stabilization of oil-in-water emulsion polymerizations [11]. Critical micellar concentrations (cmc) of PS/PEO block copolymers in water as low as 1 mg/l have been obtained by Wilhelm et al. [12], using fluorescent probe techniques, but so far little has been done on the characterization of such block copolymers in alcoholic media. As a matter of fact, the determination of the cmc using conventional techniques, for instance, surface tension measurements or fluorescent probe methods, seems difficult to perform in alcohol. Nevertheless, in the present work, evidence for the presence of micellar aggregates is given by the bluish color of the copolymer solutions and an attempt has been made to determine their size by dynamic light scattering (DLS). DLS measurements indicate micelles with diameters between 60 and 34 nm for the SE 3030 copolymer and between 36 and 19 nm for the SE 1030 copolymer, when the temperature is raised from 19 to 58 °C. We recall that the diameters of PS/PEO block copolymer aggregates in methanol, having a molar ratio of 1840/6800, 5800/13 500 and 10 000/29 400, were found to be 16, 26, and 43 nm by Winzor et al. [5].

Table 4 Diameter, D_p, obtained by transmission electron microscopy (*TEM*) of the PS latex particles synthesized in the absence of silica, number-average, M_n and weight-average, M_w, molecular weights and polydispersity, M_w/M_n, of PS for the latex particles as a function of the nature of the stabilizer

Stabilizer[a]	PVP K30	SE 1030	SE 3030
D_p (nm) (TEM)	750	150	62
M_n (g/mol)	29 000	79 100	98 400
M_w (g/mol)	109 000	220 400	188 200
M_w/M_n	3.8	2.8	1.9

[a] 2 wt % (grams per 100 g solvent)

In addition to changes in particle size, Table 4 indicates that the molecular weights of the synthesized PS molecules are larger when the block copolymers are used as stabilizers instead of PVP. This is probably due to the larger number (smaller size) of particles present in the dispersion at the end, but also during polymerization, in the presence of the block copolymer stabilizers. As a result of this larger number of particles, there are fewer oligoradicals which enter each particle per unit time, and, therefore, there is a larger probability for an individual polymer chain to grow for a longer time before termination occurs when the block copolymers are used as stabilizers [13–15].

Influence of the stabilizer concentration

The SE 3030 stabilizer, which proved to be the best stabilizer of the two copolymers, was chosen in order to study the influence of the copolymer concentration on particle size and PS molecular weights. Three different concentrations of the SE 3030 block copolymer were used, namely, 2, 1 and 0.5 wt% (in grams per 100 g of solvent). Particles with increasing sizes were obtained as reported in Table 5 and as illustrated in Fig. 1. The increase in particle size with decreasing concentration of stabilizer can be regarded as the consequence of the diminution in the number of stabilizing molecules. It is believed that early in the polymerization reaction, primary polymer particles associate with each other until there is sufficient stabilizer on the particles to achieve steric stabilization. Consequently, a lower stabilizer concentration results in a lower number of particles with larger sizes. Similar trends have already been described in the literature [4, 5, 15–22] for other stabilizers including block copolymers [5] and PVP [17, 18]. Nevertheless, remember that in addition to the number of stabilizing molecules, the nature of the stabilizer must also be taken into consideration. Indeed, the extrapolation of the curve of Fig. 1 to 0.38 wt%, which corresponds to a number of SE 3030 molecules equal to the number of PVP molecules at 2 wt%, indicates that it will certainly not be possible to obtain, with this SE 3030 concentration, a diameter as high as 750 nm, which is the diameter of the latex particles found with PVP. As a consequence of the increased particle size when decreasing the concentration of the PS/PEO stabilizers, one observes a decrease in the molecular weight and a broadening of the molecular weight distribution.

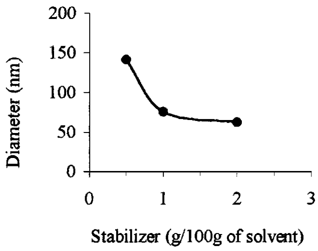

Fig. 1 Variation in the diameter of the latex particles synthesized without silica beads as a function of the concentration of the SE 3030 block copolymer. The concentrations of the other components (in weight per 100 g solvent) are ethanol, 94.5 wt%, water, 5.5 wt%, styrene, 10 wt%, and 2,2′-azobis(isobutyronitrile) (*AIBN*), 0.1 wt%

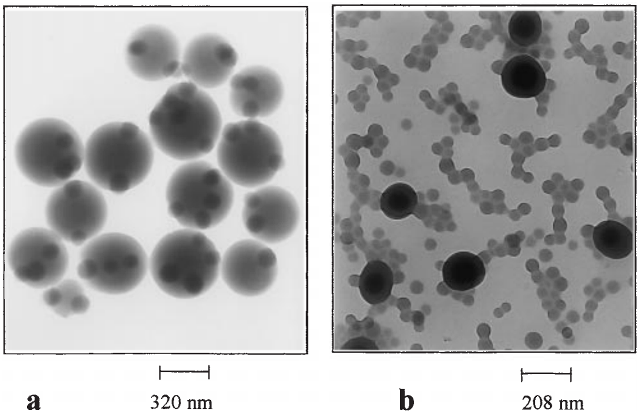

Fig. 2 Transmission electron microscopy (*TEM*) micrographs of latex particles synthesized with **a** poly(*N*-vinyl pyrrolidone) and **b** SE 3030 stabilizers. The diameter of the silica beads is 108 nm. The concentrations (in weight per 100 g solvent) are silica beads, 1.5 wt%, stabilizer, 2 wt%, styrene, 10 wt%, and AIBN, 0.1 wt%

Polymerization in the presence of silica beads

Comparison to PVP

Figure 2 shows TEM micrographs of PS particles synthesized in the presence of 108-nm diameter silica beads grafted with MPS, using either PVP (Fig. 2a) or the SE 3030 block copolymer (Fig. 2b) stabilizers. With both stabilizers, all the silica beads are encapsulated by PS; however, two important differences appear which concern the number of silica beads per latex particle, and the morphology of the composite particles. When PVP is used as the stabilizer, all the particles are composite particles and contain at least one silica bead. In accordance with a previous study [2], an average number, N_a, of silica beads per particle of 4 can be calculated using Eq. (A4) given in the Appendix. In contrast when PS/PEO is used as the stabilizer, there is a great number of latex particles without silica beads (free latex particles) and, concurrently, each composite particle contains only one silica bead. Consequently, the average number of silica beads per particle drastically decreases from 4 to 0.026 (Table 2). In addition, one can also observe in Fig. 2b that the PS forms a regular shell around the composite particles, which has not been observed for the composite particles synthesized so far with PVP as a stabilizer [1, 2]. The only case where a regular shell was obtained around the silica beads with PVP as a stabilizer was for large silica beads of diameters above 300 nm, i.e., much larger than the ones used here, and with a weight ratio (polymer)/(silica bead) also much higher than in the present work [2].

Table 5 Diameter, D_p, of the PS latex particles synthesized in the absence of silica, number-average, M_n, and weight average, M_w, molecular weights, and polydispersity, M_w/M_n, of PS for the latex particles as a function of the concentration of the stabilizer SE 3030

	SE 3030 stabilizer concentration		
	0.5 wt%[a]	1 wt%[a]	2 wt%[a]
D_p (nm) (TEM)	141	75	62
M_n (g/mol)	73 700	81 300	98 500
M_w (g/mol)	313 000	241 800	191 300
M_w/M_n	4.2	3	1.9

[a] grams per 100 g solvent

Effect of the silica bead size

The size of the silica beads used in the polymerization has a drastic effect on the nature of the latex particles

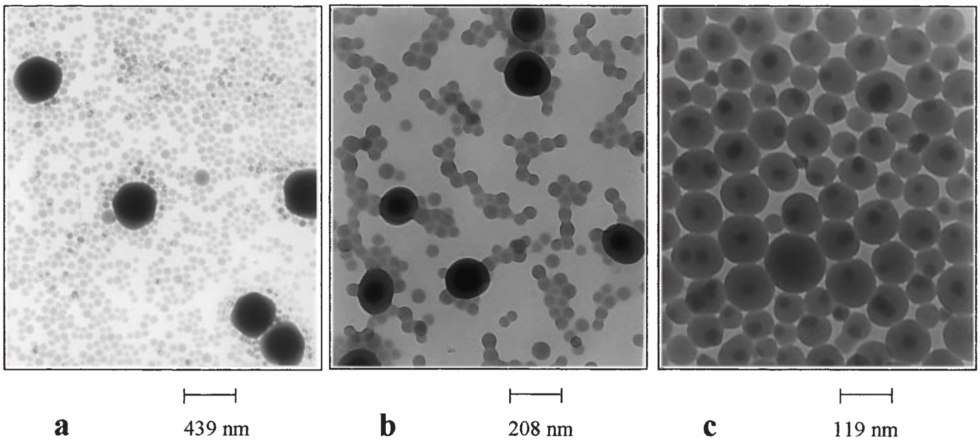

Fig. 3 TEM micrographs of latex particles synthesized in the presence of silica beads with a diameter of **a** 247 nm, **b** 108 nm, and **c** 29 nm and SE 3030 as stabilizer. The concentrations (in weight per 100 g solvent) are silica beads, 1.5 wt%, stabilizer, 2 wt%, styrene, 10 wt%, and AIBN, 0.1 wt%

formed. This is illustrated in Fig. 3 which shows TEM micrographs of the particles obtained using the SE 3030 block copolymer stabilizer, in the presence of silica beads with diameters of 300 nm (Fig. 3a), 108 nm (Fig. 3b), and 29 nm (Fig. 3c), respectively. The scales of these three figures are different in order to present distinctively, in each case, the silica beads and their shell of PS. Although Fig. 3 is a limited view of the outcome of the synthesis, examination of many micrographs allows us to say that the micrographs in Fig. 3 are really representative of the samples. In the three cases, a uniform coating of polymer around the silica beads is observed, the relative thickness of which increases when decreasing the size of the silica beads. For the largest silica beads, a true core–shell morphology is observed while the smallest silica beads of the series are more or less well centered into the composite particles (Fig. 3c). In addition to the silica–PS core–shell particles, one can also see in Fig. 3 small free PS latex particles whose size is smaller than the size of the composite particles. It clearly appears from Fig. 3a and b that the number of free polymer particles is significantly higher than the number of composite particles when large silica beads are involved, and decreases when decreasing the size of the silica beads (Fig. 3c). The diameter of the composite particles, the size and the number of the free latex particles, as well as the absolute (e) and the relative (e/R_p) thickness of the polymer shell around the silica beads, determined as described in the experimental part, are reported in Table 2. The values in Table 2 confirm that the polymer shell becomes progressively larger compared to the radius of the silica beads when decreasing the silica bead size (e/R_p increases), which means that the quantity of polymer which serves to form the shell increases compared to the total quantity of polymer formed (E increases), and becomes close to 100% with the smallest silica beads of diameter 29 nm. At the same time, the number of free latex particles decreases while the total particle number (composite particles and free latex particles) remains almost constant and is independent of the size of the silica beads. As a consequence of the diminution in the number of free latex particles as the size of the silica beads decreases, the average number, N_a, of silica beads per particle (given by Eq. A3 in the Appendix) increases (N_a is nearly equal to 1 for silica beads with a diameter of 29 nm). In contrast very low value of N_a is obtained with the large silica beads because of the large number of free latex particles formed in that case.

Effect of the stabilizer concentration

The effects of the concentration of the stabilizer SE 3030 on the different parameters described above which characterize the composite and the free latex particles are given in Table 3. One of the most interesting results is again obtained by the variation of the ratio, E, of the amount of shell–polymer over the total amount of polymer synthesized, as the stabilizer concentration varies. Table 3 shows that with the largest silica beads used (300 and 108 nm in diameter), E increases when the stabilizer concentration decreases. This indicates that a decrease in the concentration of stabilizer facilitates the growth of the shell–polymer around the silica beads at the expense of the free latex particles. As a consequence, the diameter of the composite particles, D_p(composite), the shell thickness, e, and the ratio, e/R_p, increase, when the stabilizer concentration decreases. At the same time N_a increases, due to the decrease in N_p(free). The decrease in N_p(free) is due to both the decrease in the amount of polymer which constitutes the free latex particles and to the increase in their diameter when decreasing the stabilizer concentration in the reaction medium. For the smallest silica beads of the series (29 nm in diameter), and for concentrations of stabilizer below 2 wt% relative to the solvent, Table 3 shows that the morphology of the latex particles differs completely from the previous one. First, no free latex particles are formed and, second most of the composite particles contain more than one silica bead. The average number of silica beads per composite particles (given in this case by Eq. A4 in the Appendix), increases from 1 to 23 as the stabilizer concentration decreases from 2 to 0.5 wt%. This result is qualitatively comparable to the result found with small silica beads and PVP as stabilizer, but at a higher PVP concentration [2].

Core–shell composite particles

We recall that only spherical core–shell composite particles of equal size, with a silica core at the center of the composite particles, can give films made of a polymer matrix containing a regular, hexagonal, arrangement of silica beads. These films are supposed to give mechanical or optical properties different from those given by films with silica beads distributed randomly. One of the goals in our studies on encapsulation of inorganic particles by polymers is to synthesize perfectly spherical core–shell composite particles of equal size. We have shown previously [1, 2] that regular core–shell particles were rarely obtained with PVP as a stabilizer, even in the best cases. Indeed, encapsulation of only one silica bead by PS was observed only when the diameter of the silica beads was greater than 300 nm and the concentration of styrene in the reaction medium was sufficiently high to completely cover the surface of the silica beads; however, even in that case, the composite particles were neither perfectly spherical nor of equal size. In addition, the silica beads were not perfectly in the center of the composite particles. In the present study we obtained real silica–PS core–shell particles using the block copolymer SE 3030 as a stabilizer. Free latex particles that do not contain silica beads are formed simultaneously, but they can be easily separated from the core–shell particles by centrifugation as shown in Fig. 4. This figure represents TEM micrographs of core–shell composites after elimination of the free latex particles as described in the Experimental part. In Fig. 4a, the diameter of the silica beads is 300 nm, while it is only 108 nm in Fig. 4b–d. Figure 4b and c represents the images of the same sample imaged at different magnifications, while Fig. 4d is obtained by decreasing the amount of stabilizer. In every case, one can observe that a regular shell of polymer surrounds all the silica beads. As expected, and according to what has been described before, it clearly appears from Fig. 4a and b that the thickness of the shell increases when decreasing the diameter of the silica beads. A further increase in the shell thickness is observed for a given silica bead size when decreasing the amount of stabilizer (Fig. 4b, d). In addition, one can see in Fig. 4a that, for the largest silica beads, the composite particles are ordered into a regular hexagonal arrangement, which indicates a low degree of polydispersity in the size of the core–shell composite particles. A poorer organization is observed when lowering the size of the silica beads because, in that case, the silica beads are not perfectly regular in size and/or in shape. It will probably be possible to obtain more-ordered structures starting from silica beads with lower polydispersity. Moreover, modification of the experimental conditions by increasing for instance, the monomer concentration, changing the solvent composition and the number of silica beads or by decreasing the stabilizer concentration even more, will certainly lead to the production of different core–shell particles with different volume ratios of the shell over the core.

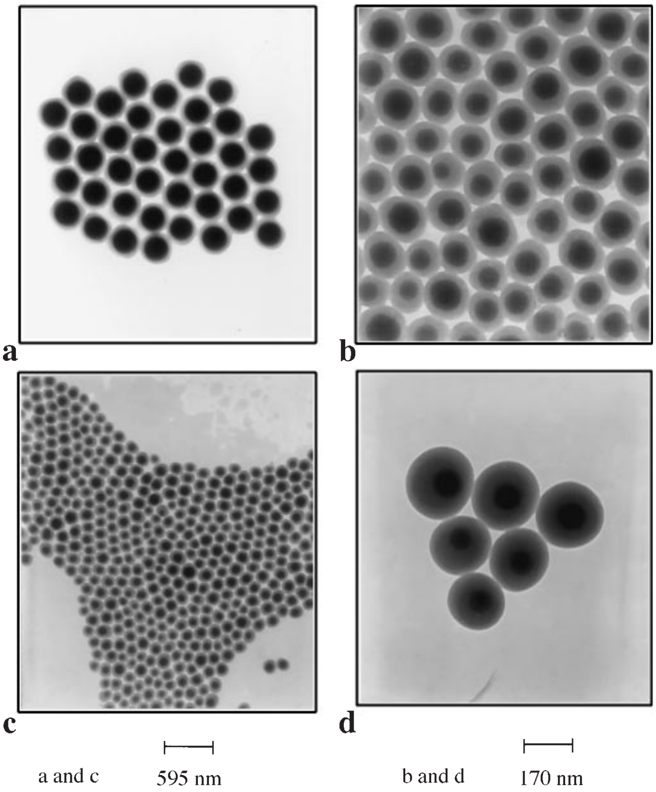

Fig. 4a–d TEM micrographs of composite particles obtained after elimination of the free latex particles by centrifugation/redispersion in the aqueous alcoholic medium. Diameters of the silica beads: **a** 300 nm and **b–d** 108 nm. Stabilizer concentrations: 2 wt% **(a–c)** and 1 wt% **(d)**, relative to the solvent

Discussion

The mechanism of dispersion polymerization has already been extensively studied and discussed by several authors, in particular by Paine [8, 13, 14], Lok and Ober [9], and has been reviewed by Barrett [7]. Several features are characteristic for dispersion polymerization. The polymerization is initiated in the continuous phase, where the monomer and the initiator are soluble. As the polymer chains grow, they reach a molecular weight at which they are no longer soluble. Then, they associate with other growing polymer chains in the continuous phase to form small polymer aggregates. These small aggregates grow, either by addition of other polymer chains or other small polymer aggregates and form small latex particles which become stable when they are prevented from flocculation by the stabilizer present in the continuous phase and adsorbing on their surface. These small, stable, latex particles form the nuclei of the final latex particles. For polymers with low solubility in the solvent used, the stage of particle formation is normally completed very quickly (a few seconds or less) and, if the amount of stabilizer available in the continuous phase is sufficient to cover and stabilize the growing latex particles, their number stays unchanged during the rest of the polymerization. It is known that the solvency of the continuous phase for the polymer or the nature and concentration of the stabilizer strongly influence, for instance, the duration of particle formation or the number and the size of the particles formed. Besides nucleation, other processes can also intervene, such as renucleation, which occurs mainly in feed processes when an excess of stabilizer is added or aggregation of latex particles due to a lake of available stabilizer in a batch reaction.

Only a simplified description of the mechanisms involved in dispersion polymerization is given here. In this limited frame, we present some hypotheses concerning the role played by the silica beads in the mechanism of dispersion polymerization of styrene in the presence of SE 3030 stabilizer. First, it is obvious that the coupling agent MPS renders the silica surface partially hydrophobic. Next, the adsorption isotherm shown in Fig. 5 indicates that the PS/PEO block copolymers partition between the continuous phase and the silica beads. The adsorption of the block copolymer increases the hydrophobic character of the silica surface. Thus, even before the polymerization, due to the grafting of MPS and to the adsorption of SE 3030, the silica surface presents loci for the adsorption of oligoradicals, insoluble polymer chains, and even monomers. Then, copolymerization of the adsorbed species can take place at the silica surface by reaction with the methacrylate group of the coupling agent, giving polymer chemically linked to silica [1]. It is, therefore, clear that there is competition between, on the one hand, formation of small aggregates and stabilized latex particles in the continuous phase and, on the other hand, adsorption of oligoradicals, insoluble polymer chains, monomers, and copolymerization at the silica surface. As a consequence, when the number and, therefore, the surface of the silica beads increase, the probability of polymerizing around the silica beads should increase at the expense of the formation of free latex particles in the continuous phase. This is, indeed, seen in the micrographs shown in Fig. 3, and in the results reported in Table 2, which indicate that the most successful encapsulation is obtained with the smallest silica beads, i.e., those which offer the largest surface area in the dispersion. Moreover, as a part of this work, we have obtained results indicating that this competition arises very early during polymerization. Indeed, such competition is clearly evidenced if one observes, by TEM, samples taken at very low conversion times. This has been done in particular in the case of large silica beads (300 nm in diameter). A schematic representation of the TEM images obtained at 4% conversion with large silica beads is given in Fig. 6. This scheme indicates that, in addition to the presence of a very large number of free latex particles, whose diameter does not exceed 20 nm, very small polymer particles attached to the silica surface have been formed, the size of the particles being comparable to the size of the free latex particles. The fact that the size of the particles synthesized on the surface of the silica beads is very similar to the size of the free latex particles seems to indicate that the growth of both types of particles started at about the same time, i.e., at the beginning of the polymerization; however, at the present time, it is very difficult to say whether, during the very early stage of the polymerization, the polymer particles observed on the silica surface result from the adsorption of oligoradicals and insoluble growing polymer chains or if they result from the capture of nuclei or larger stable latex particles already formed in the continuous phase.

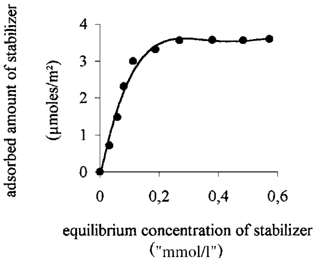

Fig. 5 Adsorption isotherm of the SE 3030 stabilizer on the silica surface grafted with 3-(trimethoxysilyl)propyl methacrylate. Silica concentration 15 g/l, and diameter 300 nm

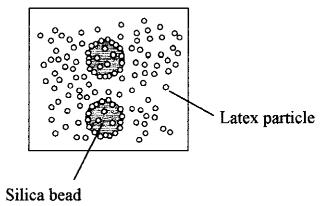

Fig. 6 Schematic representation of the composite particles at very low conversion (4%) using SE 3030 as stabilizer (2 wt% relative to the solvent)

Nevertheless, we have estimated that the total particle number, i.e., the number of free latex particles and of polymer particles attached to the silica surface, is between 4×10^{17} and 8×10^{17} per liter of dispersion. This number corresponds approximately to the number of particles synthesized in the absence of silica, i.e., 6×10^{17} (calculated from the results given in Table 4). Thus, it can be reasonably assumed that the total particle number is independent of the presence of the silica beads and that, as a consequence, it is determined very early during polymerization. However, the partition of the polymer particles between the continuous phase and the silica beads is very dependent on the silica surface, which itself depends on the size and concentration of the silica beads. Fewer free nuclei are formed in the continuous phase when a large silica surface area is involved in the reaction medium. The free nuclei continue to grow normally in the continuous phase as they do in the absence of silica. Consequently, when the silica surface is varied, the number of free latex particles changes considerably while the size of the free latex particles does not change fundamentally as shown in Table 2 and Fig. 3. Notice, however, that a decrease in the diameter of the free latex particles from 62 nm (without silica) to 55 nm (in the presence of the silica beads), corresponds to a decrease of 30% in their volume, which indicates a tendency of the silica surface to capture, during the polymerization process, more insoluble polymer chains and/or monomers than they should do in order to strictly let the free latex particles grow as if there were no silica in the medium. On the silica surface, the attached polymer continues to grow until a regular and continuous shell is obtained from the coalescence of the neighboring growing particles. The formation of a regular shell is indeed possible in this case because, from the beginning of the reaction, there is a large number of growing particles on the surface of the silica beads. Up to now, it has been assumed implicitly that the captures occur in the very early stage of the polymerization. The possibility that stable latex particles aggregate on the silica surface during the later stages of the polymerization cannot be completely discarded at the present time. However, although it is experimentally very difficult to evidence what occurs, especially at the beginning of the polymerization either in the continuous phase or at the silica surface, more systematic TEM investigations on samples taken in the course of the polymerization will be made in order to obtain evidence for a better understanding of the mechanism of dispersion polymerization occurring in the presence of silica beads.

Conclusion

The polymerization of styrene using the block copolymer PS/PEO (3000/3000) as stabilizer in the presence of 29–300-nm diameter MPS-grafted silica beads has the following characteristics:

1. All the silica beads are encapsulated with PS
2. There is only one silica bead per composite particle
3. Free latex particles are formed but their number decreases as the diameter of the silica beads decreases, and becomes very small compared to the number of composite particles when the diameter of the silica beads is 29 nm and then almost all the polymer synthesized constitutes the shell of the composite particles.

An attempt has been made to explain these results which involve the competition between the formation of nuclei in the continuous phase and the adsorption of oligomers or insoluble chains at the silica surface, at the early stage of the polymerization. As the surface of the silica beads increases, an increasing number of oligoradicals and insoluble polymers, which should form nuclei in the continuous phase, are captured by the silica beads. As a consequence of this capture, the number of free nuclei and, therefore, of free latex particles decreases, whereas the quantity of polymer forming the shell of the composite particles increases. Whatever the size of the silica beads, it is easy to separate the free latex particles from the composite particles and to obtain a material made of regular silica–PS core–shell latex particles of equal size. All these results indicate a new route for the synthesis of organic–inorganic core–shell particles.

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Appendix

The average number, N_a, of silica beads per latex particle is defined as the ratio of the number of silica beads over the total number of latex particles (containing silica beads or not). N_a is therefore given by

$$N_a = \frac{N_p(\mathrm{SiO_2})}{N_p(\mathrm{composite}) + N_p(\mathrm{free})} , \tag{A1}$$

where $N_p(\mathrm{SiO_2})$, $N_p(\mathrm{composite})$, and $N_p(\mathrm{free})$ are the number of silica beads, composite latex particles (containing one silica bead or more), and free latex particles (containing no silica beads) in a given volume of dispersion.

1. When each composite particle contains only one silica bead (Fig. 3), then $N_p(\mathrm{composite}) = N_p(\mathrm{SiO_2})$, and Eq. (A1) becomes

$$N_a = \frac{N_p(\mathrm{SiO_2})}{N_p(\mathrm{SiO_2}) + N_p(\mathrm{free})} , \tag{A2}$$

Eq. (A2) indicates that N_a is equal to 1 when there are no free latex particles in the dispersion after polymerization and that N_a decreases when the number of free latex particles increases. Since N_p(free) is given by the ratio of the total amount of polymer in the free particles (determined as described in the Experimental section) over the mass of a free latex particle (determined from its mean diameter measured by TEM), one can easily show that N_a can be calculated from the relation

$$N_a = \frac{D_p(\text{free})^3}{D_p(\text{free})^3 - D_p(\text{composite})^3 + (1 + w \times \rho_{SiO_2}) \times D_p(SiO_2)^3} \tag{A3}$$

where D_p(free), D_p(composite), and $D_p(SiO_2)$ are the diameters, measured by TEM, of the free latex particles, of the composite particles, and of the silica beads, respectively, w is the ratio of the weight of the total polymer synthesized over the weight of the total amount of silica beads present in a given volume of dispersion, ρ_{SiO_2} is the density (1.8 g/cm^3) of the silica beads, and the density of PS is assumed to be 1.

2. When there are no free latex particles in the dispersion after polymerization, and if one assumes that the composite particles (which may then contain more than one silica bead) are spherical, one can then easily show that the average number of silica beads per composite particle can be calculated from the relation

$$N_a = \frac{D_p(\text{composite})^3}{(1 + w \times \rho_{SiO_2}) \times D_p(SiO_2)^3}\ , \tag{A4}$$

where the diameters D_p(composite) and $D_p(SiO_2)$ are determined by TEM. Notice that in this case $N_a \geq 1$. This situation has been met in the present study only with the smallest-sized silica beads used in the polymerization reaction (Table 3).

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