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ORIGINAL CONTRIBUTION

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Synthesis of polymer particles and nanocapsules stabilized with PEO/PPO containing polymerizable surfactants in miniemulsion

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Abstract We describe the miniemulsion polymerization of vinyl monomers stabilized in the presence of the polymerizable anionic surfactant Tego XP-1008 and the polymerizable nonionic surfactant Tego XP-1007. Different amounts of polymerizable surfactants and various types of initiators were used to investigate the size and the stability of the final latex particles by transmission electron microscopy and dynamic light-scattering measurements. The grafting of the polymerizable surfactants onto the surface of the latex particles was checked by NMR and XPS measurements and was found to be efficient. Finally, polymerizations of appropriate formulations containing divinylbenzene with the polymerizable surfactant Tego XP-1008 in the presence of a larger amount of hydrophobic agent produced nanocapsules.

Keywords Miniemulsion · Polymerizable surfactant · Surfmer · Polymer nanoparticles · Nanocapsules

Introduction

Surfactants play a very important role in stabilization of colloids during polymerization processes and later in storage. In the last decades, polymerizable surfactants have attracted much attention. Efficient polymerizable surfactants, so-called surfmers, are covalently bonded onto the latex particle they stabilize [1–3]. The properties of the resulting latexes such as resistance to freeze-thaw cycles or electrolyte addition [4, 5] are significantly improved. When the latex is used for film formation, the surfmer does not migrate to the interfaces. Thus, the adhesion properties of the film are not lowered as it happens if using a conventional surfactant, which is physically adsorbed onto the surface of the particle.

In emulsion polymerization, some amount of the surfmer may be buried inside the final latex due to the mechanism of the polymerization [6]. According to Schoonbrood and Asua [7], a surfmer behaves in emulsion polymerization in an optimum way if it is not reactive at the beginning and more reactive toward the end of the reaction. It involves that the copolymerization parameter of the surfmer and the monomer is a key factor in the control of the latex stability. This can be avoided by performing a miniemulsion polymerization where the surfmer molecules are situated on the surface of the droplets already at the beginning of polymerization. The size of the droplets do not change during the polymerization and therefore, the surfactant can be built in the polymer chain any time. Boisson et al. [8] studied the miniemulsion polymerization of styrene and methyl methacrylate with the polymerizable surfactant vinylbenzylsulfosuccinic acid sodium salt. Stable latexes were obtained with either 2,2′-azoisobutyronitrile (AIBN) or potassium persulfate (KPS) as initiator. It was estimated by surface tension measurements that 50 to 75% of the surfactants remained fixed onto the surface of the particles. Latexes polymerized with KPS were found to be more stable toward electrolytes and freeze-thaw tests. The authors explained the increase in stability by a gain of steric stabilization when KPS was the initiator, completing the electrostatic stabilization given by the sulfonate group of the surfactant.

Guyot et al. [9] carried out miniemulsion polymerization of methyl methacrylate (MMA) and styrene with the polymerizable surfactants produced from the reaction between succinic anhydride and either hydroxypropylmethacrylate

or hydroxyethylmethacrylate. The pure surfmers showed a poor surface activity according to surface tension measurements. Thus, a mixture of the surfmer with sodium dodecyl sulfate (SDS) was used to stabilize the miniemulsion droplets. The surfmers employed are highly soluble in water; therefore some surfmers remained in the water phase and were not polymerized. The grafting efficiency of the surfmer increases when the amount of SDS in the mixture of surfactants was higher. The prepared latexes exhibited good resistance to freeze-thaw tests.

Another group [10] successfully used a monofluoroalkyl maleate as a surfmer to stabilize miniemulsion copolymerization of styrene and *n*-butyl methacrylate. The size of the particles could be controlled by the concentration of the surfmer. The authors blended the synthesized particles with styrene–butadiene copolymer latex to produce the composite films. These films show more hydrophobic properties compared to the films made of pure styrene–butadiene latexes.

In this contribution, we will show that poly(ethylene oxide)-poly(propylene oxide) (PEO-PPO)-based polymerizable surfactants can also be used successfully in miniemulsion polymerization. On the one hand, an anionic surfactant with a phosphate group will be used; on the other hand, a nonionic surfactant. It will be shown that the anionic surfactant can also be used for the production of nanocapsules.

Experimental part

Materials

The monomers styrene, butyl acrylate (BA) (both form Merck), and divinylbenzene (Sigma-Aldrich) were distilled under reduced pressure prior to use. SDS (Alfa Aesar), *n*-hexadecane (HD) (Merck), 2,2′-azobis(4-methoxy-2, 4-dimethyl valeronitrile) (V70, Wako), AIBN, and KPS (both purchased from Fluka) were used. The anionic surfactant Tego XP-1008 (M_n~1150 g·mol^{-1}), a phosphate-terminated polyethylene oxide-co-polypropylene oxide with vinyl groups and nonionic Tego XP-1007 (M_n~1100 g·mol^{-1}), a polyethylene oxide-co-polypropylene oxide with vinyl groups were kindly provided by Degussa Goldschmidt GmbH. The structures are given in Fig. 1. Demineralized water was used throughout the work.

Preparation of the miniemulsions

The total amount of 6 g of the monomer(s), 250 mg of *n*-HD for the synthesis of particles or 3 g of monomer, and 3 g of HD for the synthesis of nanocapsules were mixed with 200 mg of AIBN (Tego XP-1008) or 100 mg of V70 (Tego XP-1007) and added to a solution of known amounts of the polymerizable surfactant in 24 g of water. The mixture was preemulsified by magnetic stirring for 1 h and then miniemulsified by ultrasonication for 120 s with a Branson sonifier W450 Digital at 90% amplitude (1/2-in. tip). To avoid the polymerization and, especially in the case of V70, decomposition of the initiator due to heating, the mixture was cooled with an ice-bath during sonication. The miniemulsion was subsequently transferred to an oil-bath at 75°C (Tego XP-1008) or 45°C (Tego XP-1007). If the water-soluble initiator KPS was used for the synthesis, the initiator was added after miniemulsification. The polymerization was performed for 20 h at a stirring rate of 500 rpm. For comparison between X-ray photoelectron spectroscopy (XPS) measurements, a reference latex was synthesized with SDS instead of the surfmer using the same experimental conditions as described above.

Analytical methods

The particle size was measured by photon correlation spectroscopy using a Nicomp particle sizer (model 370, PSS, Santa Barbara, CA, USA) at a fixed scattering angle of 90°. The data were processed using the cumulants method. Transmission electron microscopy (TEM) was performed with a Phillips 400T TEM spectrophotometer operating at 80 kV. One droplet of a diluted latex sample was placed onto a 400-mesh carbon-coated copper grid and left to dry

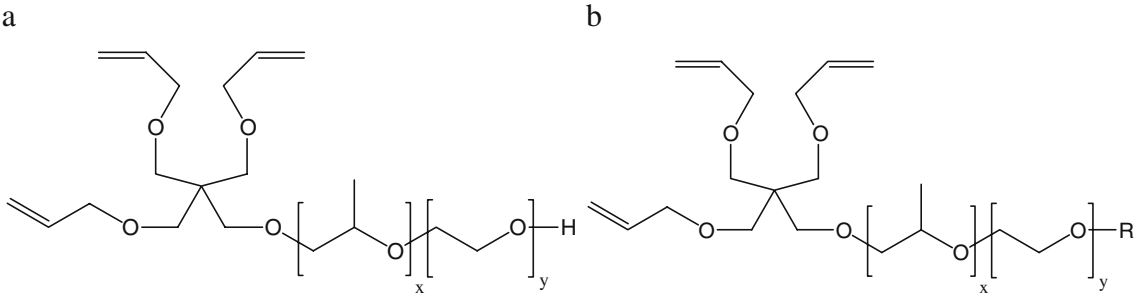

Fig. 1 Chemical structures of **a** the nonionic polymerizable surfactant Tego XP-1007 and **b** the ionic polymerizable surfactant Tego XP-1008 with *R* = phosphate

Table 1 Characteristics of the miniemulsion latexes in the presence of Tego XP-1008

Sample	Surfactant [wt%][a]	Initiator	Monomer(s) [g]	Diameter [nm][b]	Surface tension [mN·m^{-1}]	Solid content [%]	M_w [kg mol^{-1}]
1	0.6	AIBN	Styrene: 6	200	68	17	45
2	1.1	AIBN	Styrene: 6	166	67	19	48
3	1.2	AIBN	Styrene: 6	150	68	20	59
4	2.25	AIBN	Styrene: 6	126	65	20	94
5	2.8	AIBN	Styrene: 6	112	67	20	85
6	3.9	AIBN	Styrene: 6	109	66	20	92
7	5.3	AIBN	Styrene: 6	98	66	19	86
8	7.8	AIBN	Styrene: 6	86	65	19	86
9	10.4	AIBN	Styrene: 6	88	62	18	104
10	2.9	AIBN	Styrene: 3 BA: 3	129	67	15	70
11	4.5	AIBN	Styrene: 3 BA: 3	112	65	20	73
12	2.9 (SDS)	AIBN	Styrene: 3 BA: 3	76	69	20	96
13	4.5 (SDS)	AIBN	Styrene: 3 BA:3	66	68	19	95
14	1.1	KPS	Styrene: 6	151	68	20	52

[a]Amount related to the dispersed phase
[b]Diameter determined by DLS measurements

under air. No further contrasting was applied. Scanning electron microscopy (SEM) micrographs were obtained with a DSM 962 SEM (Zeiss, Germany). A thin layer of Au/Pd alloy (about 5 nm) was sputtered onto the dry samples prior to imaging. Gravimetric measurements were performed with a Kern RH 120-3 gravimeter to measure the solid content of the latexes. Surface tension measurements of the latexes were carried out at 25°C using a DCAT11 tensiometer from Dataphysics, employing the Du Noüy ring method. The radius of the Pt-Ir ring is 9.4425 mm and the wire radius is 0.185 mm. Each measurement was repeated ten times and the average value was taken as a result. Latexes were dialyzed against demineralized water several times using Millipore membranes (Amicon Ultra-4 exclusion M_w of 30,000) in a Sigma centrifuge at 3,900 rpm for 25 min until the conductivity of water remains constant at a value below 3 μS/cm. Four dialyze cycles were found to be enough to fulfill the previous requirement. XPS analysis was performed using an X-Probe 206 spectrometer (Surface Science Instruments, USA). The binding energies were referenced to hydrocarbon at 285.0 eV. The emission angle of electrons was set at 55° with respect to the sample, which results in an information depth of about 10 nm. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded on a Bruker Avance 400 spectrometer at 400 MHz in deuterated chloroform solvent using trimethylsilyl as internal standard. Gel permeation chromatography (GPC) experiments were performed with chloroform on Waters–Styragel columns (pores sizes 105, 104, 103, and 106 A) using a Waters 410 differential refractometer and a Viscotek H502B detector. The molecular weights were calculated on the basis of narrow molecular weight distribution polystyrene standards using PSS (Mainz) software.

Results and discussion

In the present work, we studied the behavior of two kinds of polymerizable polyethylene–polyproylene based surfactants (anionic and nonionic) in miniemulsion polymerization. First, we examined the influence of the amount of polymerizable surfactant on the polymerization yield, average particle size, and molecular weight of the resulting latexes. In addition, the effect of monomer composition was studied with the anionic surfactant Tego XP-1008.

Both surfactants, the anionic Tego XP-1008 and the nonanionic Tego XP-1007, could be used to obtain stable miniemulsions. The polymerization was initiated inside the droplets by using the oil-soluble initiator AIBN or V70 [2,2′-azobis(4-methoxy-2,4-dimethyl valeronitrile)]. The

Table 2 Characteristics of the miniemulsion latexes for the particles synthesis in the presence of nonionic surfactant Tego XP-1007

Six grams of styrene was used in all the syntheses; the initiator was V70
[a]Amount related to the dispersed phase
[b]Diameter determined by DLS measurements

Sample	Surfactant [wt%][a]	Diameter [nm][b]	Surface tension [mN·m^{-1}]	Solid content [%]	M_w [kg mol^{-1}]
A1	0.6	217	46	2	616
A2	1.2	159	45	3	627
A3	2.0	135	41	5	571
A4	2.4	132	41	8	520
A5	3.0	129	40	13	320
A6	3.6	125	40	16	314
A7	5.3	122	39	16	372

characteristic data of the latexes stabilized by Tego XP-1008 and Tego XP-1007 are summarized in Tables 1 and 2, respectively.

According to the solid content measurements, high conversions were obtained after the polymerizations, indicating that the polymerizable surfactants do not interfere negatively with the radical polymerization reaction.

In the case of using the anionic surfactant Tego XP-1008, stable particles with a diameter of 200 nm could be obtained by using only 0.6wt% of surfactant. This diameter is almost twice as large than the diameter obtained with SDS, which can be explained by the lower hydrophobicity of the PPO chain compared to the $C_{12}H_{25}$-chain. With increasing surfactant amount, the particle size decreases as expected.

The log–log plot of the hydrodynamic diameter vs the concentration of surfactant (Fig. 2) indicates that the size of the particles decreases quasilinearly with the amount of surfactant employed in the miniemulsion polymerization. This behavior is similar to the one observed with conventional surfactants [11]; however the particles are larger than in the case of other ionic surfactants like SDS or CTMA-Cl. This can be attributed to the nature of the surfactant where on the PEO-PPO chain one phosphate group is located. GPC measurements listed in the Table 1 show that the molecular weight is quite low but slightly increasing with increasing surfactant concentration from M_w=50,000 to 100,000 g·mol^{-1}. The quite high surface tension of the latexes obtained with Tego XP-1008 (see Table 1) is independent on the amount of surfactant. This indicates a low concentration of molecular surfactant dissolved in the continuous phase, which is due to the grafting of the surfactant onto the polymer particles.

Also copolymer particles consisting of styrene and BA can successfully be stabilized (sample 10 and 11). Here, the particle size is slightly larger compared to the pure styrene stabilized with the same surfactant (Tego XP-1008), and much smaller than the comparable SDS stabilized samples (sample 12 and 13).

The use of hydrophilic KPS as initiator does not influence the particle size, which clearly speaks for a true miniemulsion process where the particle size should be independent of the locus of initiation (sample 14).

The synthesis of polystyrene particles in the presence of nonionic polymerizable surfactant Tego XP-1007 was performed at 45°C with the oil-soluble initiator V70. This initiator was chosen because of its low decomposition temperature ($T_{1/2}$=30°C) to prevent a latex coagulation caused by the presence of a cloud point at 53°C. In all runs, more than 95% of the monomer was converted to polymer. However, the latexes obtained with low amounts of nonionic polymerizable surfactant (less than 3wt%) con-

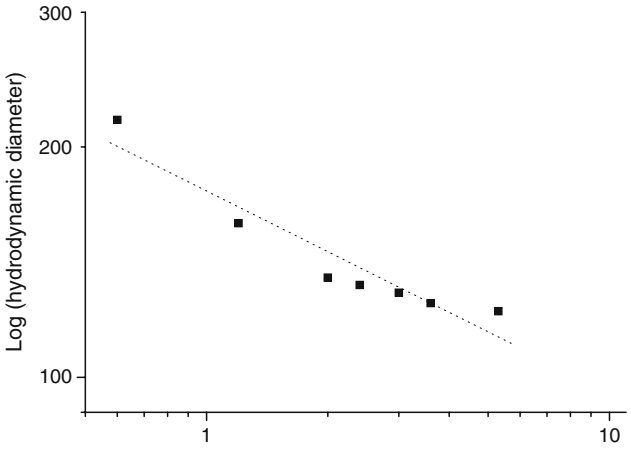

Fig. 3 Evolution of the hydrodynamic diameter in a function of the amount of Tego XP-1007

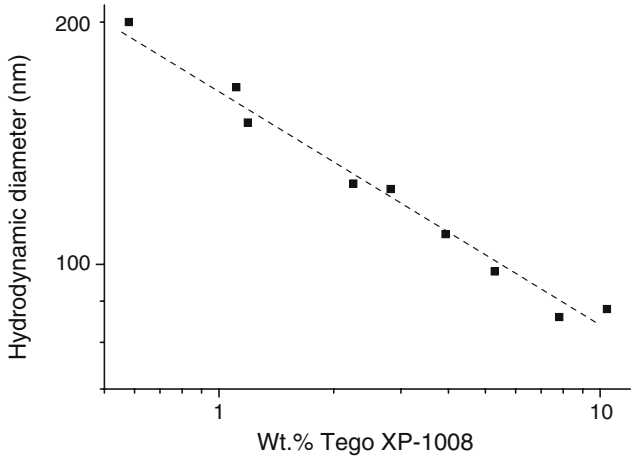

Fig. 2 Evolution of the hydrodynamic diameter in a function of the amount of Tego XP-1008

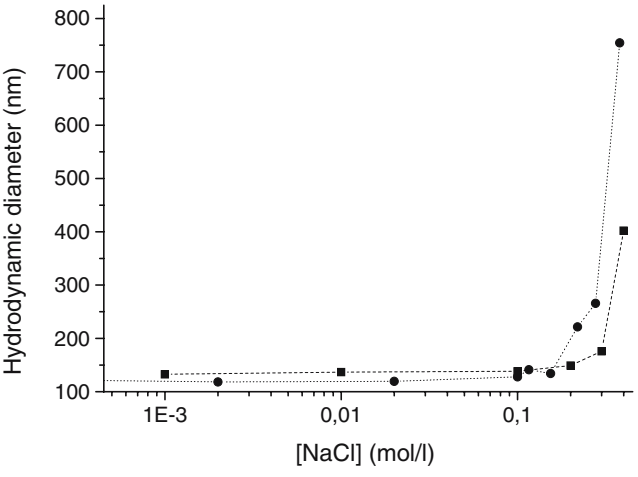

Fig. 4 Evolution of the hydrodynamic diameter of latex 4 (*squares*) and 5 (*spheres*) upon addition of electrolyte (Tego XP-1008 used as surfactant)

tained a lot of coagulum at the end of polymerization (up to 80% as it can be seen from the solid content). The average size of the particles decreases significantly with an increase of the surfactant concentration as shown in Fig. 3. The same trend was found for the GPC results (see Table 2) where the average molecular weight of the polymer particles increases with a decrease of the Tego XP-1007 amount in the reaction mixture, which indicates an influence of the surfactant with the polymerization process.

In contrast to the values of the anionic latex, the surface tension values of polystyrene latexes prepared with nonionic Tego XP-1007 are relatively low, corresponding almost to the critical micelle concentration value (42 mN m^{-1}). As shown by NMR experiments, this is not due to unreacted surfactant but can be probably attributed to surfactant molecules which do not carry double bonds.

Stability of the miniemulsions

In the case of using Tego XP-1008, the use of either AIBN or KPS as initiator leads to the stable particles with no significant change in the particle size. Also, the particles

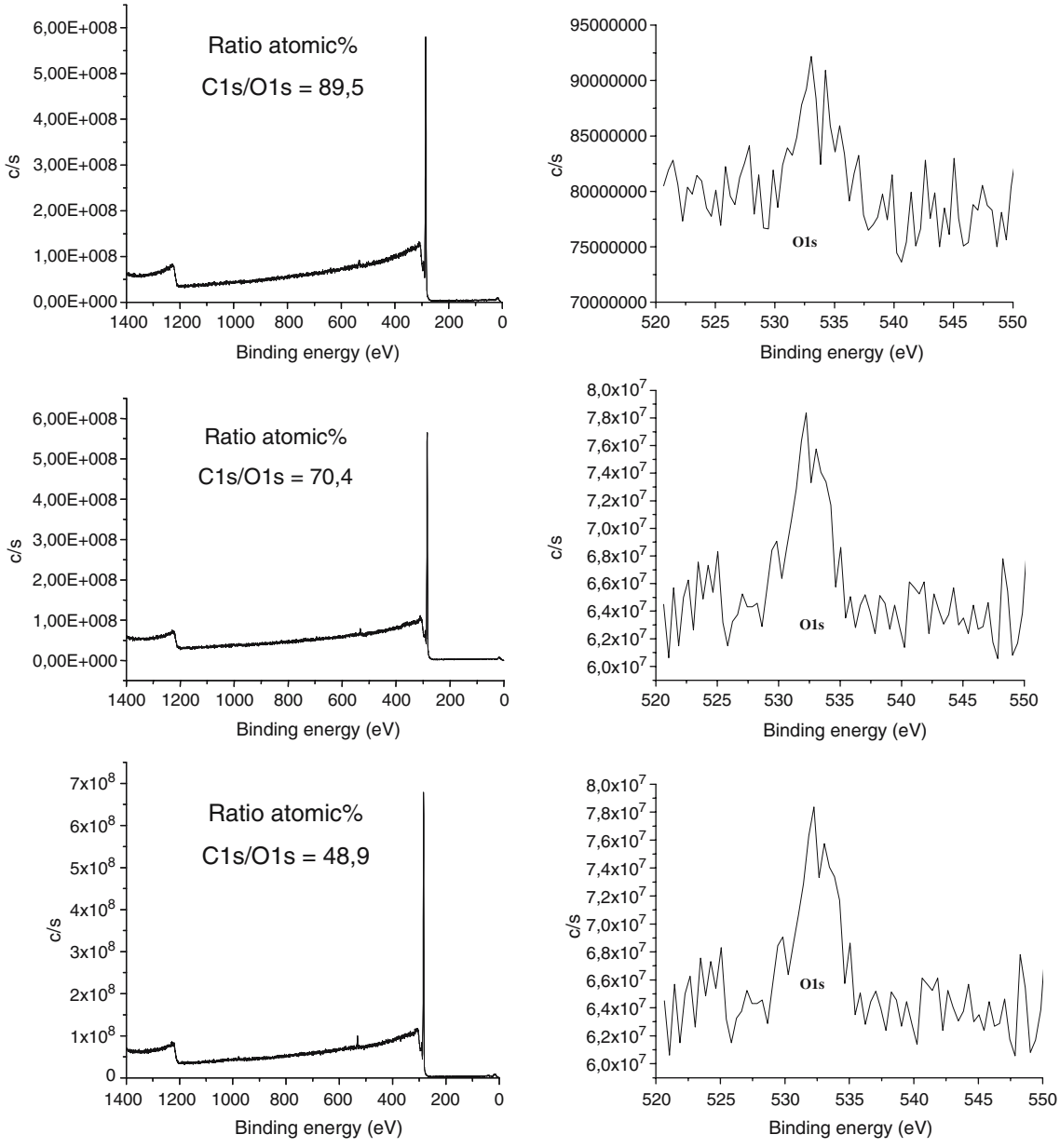

Fig. 5 XPS spectra of the polymers, ratio atomic percent and focus on the O1s signal. **a**–**b** Sample with SDS, **c**–**d** sample 2, **e**–**f** sample 5

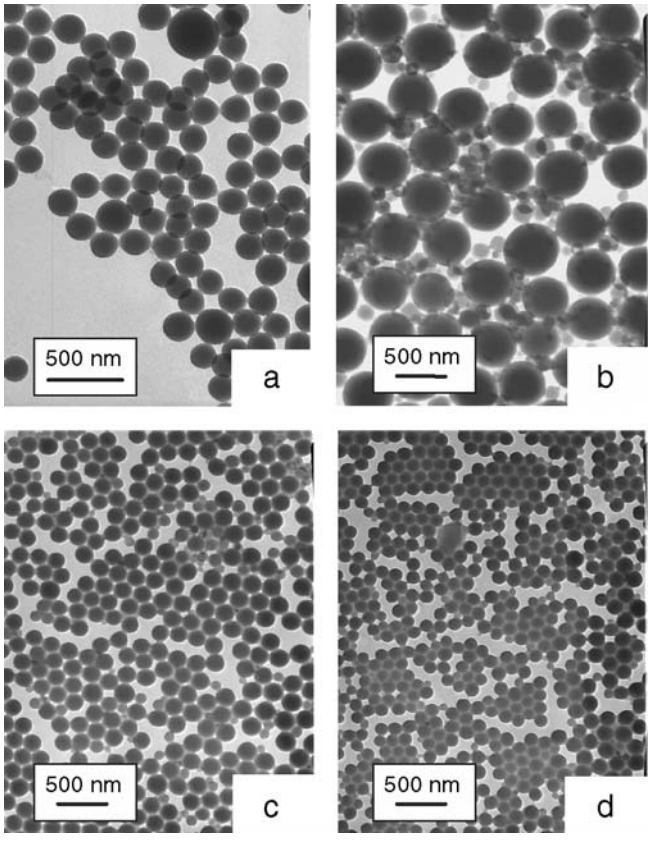

Fig. 6 TEM micrographs of the polymer particles: **a** sample 5 (Tego XP-1008), **b** sample A1, **c** sample A4, **d** sample A7 (Tego XP-1007)

synthesized with more than 3wt% of Tego XP-1007 resulted in stable particles. Photon correlation spectroscopy was also applied to study the behavior of the latexes synthesized with either Tego XP-1008 or Tego XP-1007 toward the addition of NaCl solutions (Fig. 4). The measurements were performed at several concentrations of the salt solutions allowing us to find the critical coagulation concentration (CCC) of the latex by dichotomy. Polystyrene latexes obtained with nonionic surfactant Tego XP-1007 were stable even in 1 mol l^{-1} NaCl solution. For latexes stabilized with Tego XP-1008, the CCC values were found by extrapolation of the curves presented in Fig. 4: CCC=0.25 and 0.28 mol l^{-1} for samples 4 and 5, respectively.

In addition, all latexes show high stability during dialysis experiments, which is expected from the surfactant covalently bonded to the particles.

Grafting of the polymerizable surfactant onto the particles

^{1}H-NMR spectroscopy was carried out on the latexes to check the reactivity of the double bonds of the surfmer toward the polymerization. It could be shown that the double bonds of the surfactant are completely converted in all the samples.

Furthermore, XPS measurements were conducted on the latex particles obtained with Tego XP-1008 to investigate the grafting efficiency of the surfmer onto the particle surfaces. We performed XPS on three different samples: (1) not dialyzed reference sample prepared with SDS as a surfactant and (2) dialyzed latex samples, i.e., sample 2 (low concentration of surfmer) and sample 5 (high concentration of surfmer). Unfortunately, the phosphor atom of the surfmer could not be seen with accuracy for the sample 2. Nevertheless, results shown in Fig. 5 provide information on the oxygen atom content, which is more present in the surfmer. In fact, oxygen is contained in the oligo(ethylene oxide) and oligo(propylene oxide) parts. As expected for a successful grafting of the surfmer onto the particles, sample 5 has higher oxygen content than sample 2. Both samples contain more oxygen than the nondialyzed sample prepared with SDS, which contains four atoms of oxygen in its molecule. This means that a high amount of surfmer is still on the particles despite the repeated dialysis.

Morphology of the particles

The morphology of the nanoparticles was analyzed by using TEM. In the case of Tego XP-1008, the particles are

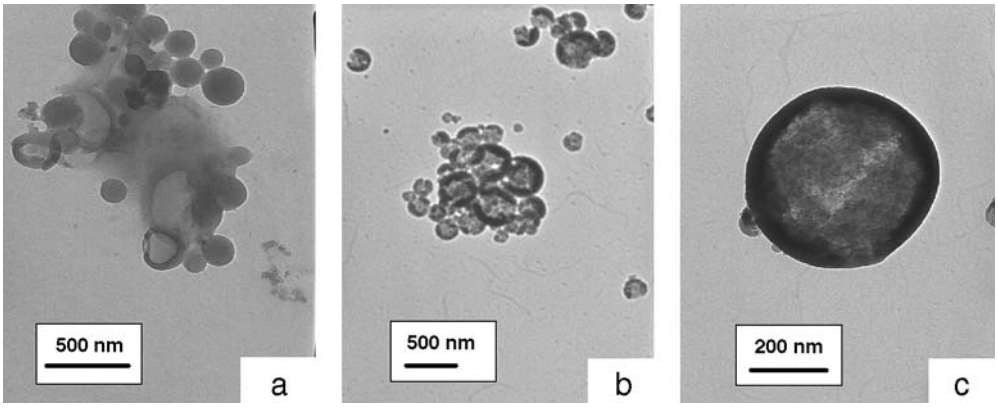

Fig. 7 TEM micrographs of samples prepared with Tego XP-1008: **a** sample 15, **b**–**c** sample 18

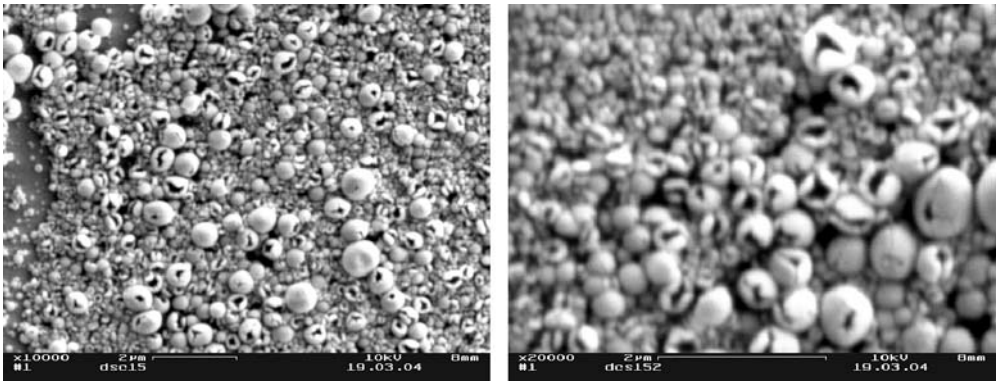

Fig. 8 SEM micrographs of the poly(divinylbenzene) capsules from sample 18

relatively monodisperse as seen in the TEM of sample 5 in Fig. 6a. Also, in the case of using higher amounts of Tego XP-1007, monodisperse particles of spherical morphology are detected (Fig. 6c and d). In the case of low surfactant concentration, a clearly bimodal distribution with particles of about 400 nm and particles of about 100 nm is seen (Fig. 6b) indicating that the amount of surfactant is not enough to stabilize small particle sizes.

Synthesis of nanocapsules

In a next step, the anionic polymerizable surfactant Tego XP-1008 was used for the preparation of hollow nanocapsules by the miniemulsion technique. As reported earlier, nanodroplets consisting of the hydrophobic oil and the monomer were created, then during the polymerization phase, separation occurs because the polymer is immiscible with the hydrophobe, thus allowing the formation of the polymeric shell [12].

In the case of Tego XP-1008, HD was used as hydrophobic oil. The polystyrene latex stabilized by 2.2wt% (sample 15) of the surfmer results in a mixture of capsules and polymer particles (approximately 50/50% in number as detected by TEM, see Fig. 7a). With increasing amount of surfactant, the average particle size and also the average molecular weight decrease, but there was still a mixture of nanocapsules and particles (not shown). The reference cited above [12] indicates clearly that the encapsulation is facilitated by the use of either a more hydrophilic monomer than styrene (e.g., MMA) or the addition of a hydrophilic comonomer. In [13], capsules of polystyrene are produced also with the help of an additional hydrophilic monomer. Thus, we used divinylbenzene as the monomer, which is more hydrophilic than styrene. TEM micrographs in Fig. 7 and the SEM micrographs in Fig. 8 clearly show a hollow capsule structure. With increasing amount of surfactant to 5.2wt%, the nanocapsule size can be decreased from 240 to 190 nm. The relatively high values of surface tension reported in Table 3 indicate that the HD is not present on the air surface and thus did not demix with the water phase. To our knowledge, it is the first time that a synthesis of hollow capsules in the presence of a polymerizable surfactant is reported. The TEM and SEM micrographs shown in Figs. 7 and 8 confirm the success of the synthesis.

Conclusion

We synthesized latexes by miniemulsion in the presence of polymerizable surfactants. Polystyrene and poly(styrene-co-butyl acrylate) particles stabilized by these surfactants were found to be stable. The plot of the particle size of the latexes vs the concentration of surfactant had the same appearance than with the normal nonpolymerizable surfactants. XPS measurements performed on dialyzed samples show that the polymerizable surfactant was grafted onto the surface of the latexes during the polymerization. These

Table 3 Characteristics of the miniemulsion latexes for the capsules synthesis; an initiator AIBN was used

Sample	Surfactant [wt%][a]	Monomer/ hexadecane [g/g]	Diameter [nm][a]	Surface tension [mN·m^{-1}]	Solid content [%]	M_w [kg·mol^{-1}]
15	2.2	Styrene: 3 HD: 3	174	60	10	70
16	3.9	Styrene: 3 HD: 3	150	58	10	31
17	5.2	Styrene: 3 HD: 3	146	57	9	30
18	2.3	DVB: 3 HD: 3	241	60	10	–
19	4.0	DVB: 3 HD: 3	195	60	10	–
20	5.2	DVB: 3 HD: 3	187	58	10	–

[a]Amount related to the dispersed phase
[b]Diameter determined by DLS measurement

results demonstrate well the efficiency of the polymerizable surfactants investigated. It is remarkable that the stable nanocapsules could be synthesized with the anionic surfactant Tego XP-1008 when using divinylbenzene as a comonomer.

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