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Reactive Surfactants in Heterophase Polymerization.[†] 2. Maleate Based Poly(ethylene oxide) Macromonomers as Steric Stabilizer Precursors in the Dispersion Polymerization of Styrene in Ethanol−Water Media

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ABSTRACT: The dispersion polymerization of styrene in ethanol−water mixtures has been investigated. The reactions were carried out in the presence of maleate based poly(ethylene oxide) macromonomers as steric stabilizer precursors: R-MA-EO$_n$-R′, with R = H or n-$C_{12}H_{25}$, MA = maleic acid, n = 34, 42, and 49, and R′ = H or CH_3. Nearly monodisperse polystyrene particles from 900 to 2000 nm in diameter were obtained. The structure and the concentration of the macromonomer, and the polarity of the solvent, affect the particle size and the particle size distribution. The location of the macromonomer, its conversion, and its incorporation yield in the particles throughout the entire polymerization are discussed. Maleate macromonomers react quickly to yield very low molecular weight styrene copolymers. Some of the copolymers take part in the stabilization of the particles as weakly adsorbed species. Hydrophilic macromonomers are well suited for dispersion polymerization, but the incorporation of these macromonomers into the polymer particles is not improved if they have an amphiphilic structure.

Introduction

Micron-size polymer particles have found a wide variety of applications in coatings, inks, dry toners, instrument calibration, chromatography, biomedical treatment, biochemical analysis, and microelectronics.[1−3] The preparation of monodisperse particles in the range of 1−20 μm is particularly challenging because it is just between the limits of particle size by conventional emulsion polymerization (0.1−0.7 μm) and suspension polymerization (20−1000 μm).

The two-step "swollen emulsion polymerization" developed by Ugelstad and co-workers, using swelling promoters, was the first successfully applied technique for producing monodisperse polymer particles in the range of 0.2−1.5 μm. Using that kind of technique, highly monodisperse polymer particles up to 50 μm could be prepared by a multistage process.[4,5] The Vanderhoff group also used successive seeding methods in order to obtain monodisperse micron-size particles.[6,7] The above-mentioned procedures, however, are time-consuming and often difficult to carry out. One of the advantages of emulsifier-free emulsion polymerization is that it can be used for the preparation of polymer seeds with rather large particles in order to reduce the ulterior swelling steps.[8]

Precipitation polymerization has also been used for the preparation of monodisperse polymer particles larger than 1 μm, for example, the production of poly(diethylene glycol dimethacrylate) microspheres.[9]

Omi et al. proposed a modification of the suspension process which yielded a broad range of bead sizes. Rather than a conventional stirred-tank reactor, a microporous glass membrane was used to obtain uniform monomer droplets.[10]

Dispersion polymerization in polar media is an alternative route to prepare monodisperse polymer particles in the 1−20 μm size range. This is a simple and efficient one-step method, originally developed in industry for the production of stable polymeric particles in hydrocarbon solvents. During the dispersion polymerization, the polymer precipitates from an initially homogeneous reaction mixture containing monomer, initiator, steric stabilizer, and solvents. Under favorable conditions, monodisperse polymer particles stabilized by a steric barrier of dissolved polymer are formed. The early work, mainly done in nonaqueous media such as aliphatic hydrocarbons, was thoroughly reviewed by Barrett.[11] Most of the studies dealt with polymer particles in the 0.1−2 μm size range.

More recently, several authors have investigated the dispersion polymerization of monomers (especially styrene[12,13] and methyl methacrylate[14,15]) in polar media (mainly alcohol/water mixtures) using polymeric steric stabilizers soluble in such media (e.g., poly(vinylpyrrolidone),[16,17] poly(acrylic acid),[18−20] poly(2-ethyl-2-oxazoline),[21] or (hydroxypropyl)cellulose[22]) in order to examine the influence of several experimental parameters on the particle size and particle size distribution. The aim was to improve and to understand the conditions which yield large, monodisperse polymer particles. When one uses a precursor polymer which contains sites for chain transfer of radicals, such as poly(acrylic acid), (hydroxypropyl)cellulose, or poly(vinylpyrrolidone), a graft copolymer can be produced *in situ* during dispersion polymerization. However, the effect of this grafting mechanism on particle formation is quite complicated and depends largely on the polymerization parameters. Moreover, competition is likely to appear between the adsorption of the graft copolymer and that of the precursor polymer. A few comprehensive studies on the preparation of monodisperse particles up to 12 μm have been reported,[23,24] and a rather simple mechanistic model to predict particle size has been proposed by Paine.[25] However, the mechanisms involved in dispersion polymerization remain poorly understood.

AB or ABA block copolymers are a second type of steric stabilizers which can be used in dispersion

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polymerization.[26,27] Poly(styrene-*b*-ethylene oxide) was recently used by Winnik and co-workers in the dispersion polymerization of styrene in methanol.[28] Provided that a selective solvent for the block copolymer is used as the continuous phase, these copolymers can be adsorbed onto the surface of the particles formed in order to achieve their stabilization. Unfortunately, for such systems, broad or bimodal distributions were often observed.

Another approach to achieve the particle formation and their subsequent stabilization is to use macromonomers. Macromonomers can be prereacted to form graft copolymers, which will be introduced in the reaction medium afterward. ICI used macromonomers to make preformed graft copolymer stabilizers. They synthesized a poly(12-hydrostearic acid) macromonomer with a methacrylate end group. This macromonomer was copolymerized with methyl methacrylate to obtain a preformed comb−graft copolymer, which was successfully used as stabilizer in nonaqueous dispersions of methyl methacrylate.[11] Macromonomers can also be allowed to react *in situ* during the dispersion polymerization to form graft copolymers. This is a simple and flexible method for producing monodisperse micron-sized polymer particles. For instance, PEO macromonomers are commonly used in the ICI aqueous dispersion process, the "Aquersymer" process, in order to produce ion-free acrylic latices with superior stability and film forming properties compared to conventional charge stabilized latices.[29]

Recently, PEO[30−32] and poly(2-oxazoline)[33,34] macromonomers with styrenic or methacryloyl end groups have been used in the dispersion polymerization of styrene or methyl methacrylate in polar media. Homopolymerization of macromonomers is unfavorable because it can lead to a high proportion of soluble polymers in the continuous phase.

In this paper, we present a study of the dispersion polymerization of styrene in ethanol−water mixtures using PEO maleic macromonomers. At variance with the macromonomers quoted above, these maleic compounds cannot homopolymerize and are thus expected to be less prone to the formation of soluble polymers. Actually, recent works by Tauer have concluded that anionic maleic reactive surfactants could be used in emulsion polymerization of styrene with a very high incorporation yield.[35]

Experimental Section

Materials. Styrene (Aldrich, 99%) was purified by distillation at reduced pressure. Poly(vinylpyrrolidone) (PVP-K30) (Aldrich, M_w = 40 000 g/mol), 2,2′-azobis(isobutyronitrile) (AIBN) (Janssen Chimica, 98%), 2,2′-azobis(2,4-dimethylvaleronitrile) (ADVN) (Vazo 52, Du Pont, 98%), potassium persulfate ($K_2S_2O_8$) (Aldrich, 99%), poly(ethylene glycol) monomethyl ether (PEO) (Aldrich, M_w = 2000 g/mol), polyethoxy nonylphenol (NP40) (Sigma), and maleic anhydride (Aldrich, 99%) were used as received. Ethanol/H_2O (95/5 v/v) (EtOH 95°) (Docks des alcools) and absolute ethanol (EtOH) (Prolabo, p.a.) were used without purification. Deionized water was used throughout this work.

Characterizations. Particle size and size distribution were measured with three techniques. Dynamic light scattering (DLS) was performed on a Brookhaven Instruments BI8000, at a fixed angle of 90° at 20 °C. A disk centrifuge photosedimentometer (DCP) (BI-DCP Brookhaven particle sizer) turned out to be more accurate than the former technique in the particle size range studied (600−2500 nm). Furthermore, the polydispersity (D_w/D_n) could be determined by the disk centrifuge system BI-DCP and not by the BI8000.

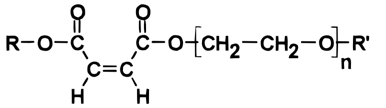


Figure 1. Structure of macromonomer and surfmers. Macromonomer **I**: R = H, R′ = CH_3, n = 49. Surfmer **II**: R = $CH_3(CH_2)_{11}$-, R′ = H, n = 34; Surfmer **III**: R = $CH_3(CH_2)_{11}$-, R′ = H, n = 42.

Transmission electron microscopy (TEM) was carried out on a Hitashi HU12.

Molecular weight distributions were determined by size exclusion chromatography (SEC) on a PSS gel mixed B column (Waters 510 apparatus) using tetrahydrofuran (THF) as eluent (flow rate: 1 mL/min). Detection was performed by using a refractive index detector Waters R410 and an UV spectrometer at 254 nm.

^1H NMR analyses were conducted on a Bruker AC250 sprectrometer at 250 MHz in $CDCl_3$.

Synthesis of Macromonomers. First, 41.03 g (0.0205 mol) of PEO (M_w = 2000 g/mol) freeze-dried from benzene, and 3.353 g (0.0342 mol) of maleic anhydride were introduced in a 250 mL three-neck flask equipped with a gas supply (N_2) and a condenser. The mixture was stirred and kept for 4 h at 80 °C. After addition of 80 g of chloroform, the solution was precipitated in cold diethyl ether (1 L) and the product was recovered by filtration. One more cycle of precipitation from chloroform was applied in order to purify the obtained macromonomer **I** (Figure 1). The product was finally dried at reduced pressure at 40 °C. ^1H NMR, δ (ppm): 3.38 (s, 3H, OCH_3); 3.6 (m, $(4n-2)$H, CH_2 (PEO chain except the first methylene group)); 4.37 (t, 2H, CH_2 (first methylene group)); 6.28 (d, J = 12.3 Hz, 1H, =CH); 6.33 (d, J = 12.3 Hz, 1H, =CH). No isomerization of the double bond into the fumaric derivative was noted. The degree of polymerization of the PEO chain (n) was determined by titration with a NaOH solution (0.02 M): the result was n = 49, which is in good agreement with the ^1H NMR analysis (n = 52).

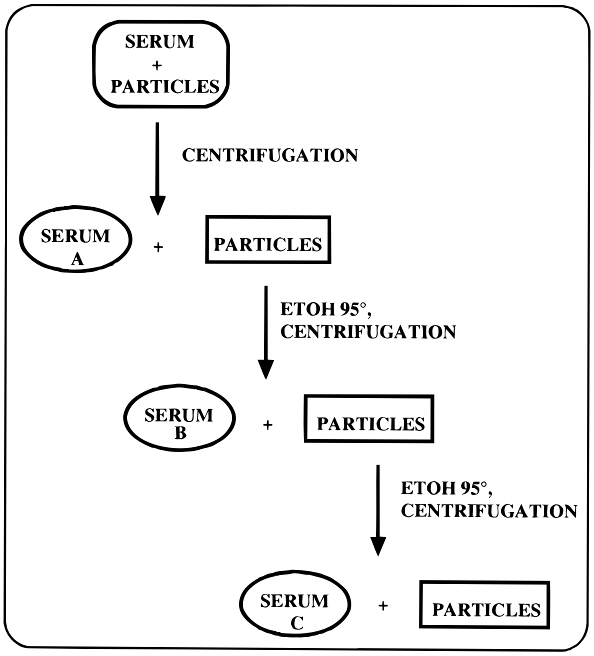
Synthesis of Surfmers. The preparation of the macromonomers with amphiphilic properties, the so-called *surfmers*, is described elsewhere.[36] Commercial fatty alcohols were reacted with maleic anhydride in a melted state to form the hemiester, which was used as a precursor in the polymerization of ethylene oxide, according to a heterogeneous catalytic process.[37] Two products (surfmer **II** and surfmer **III**) (Figure 1), with the same hydrophobic part but with different PEO chain lengths, were synthesized.

Dispersion Polymerization. Dispersion polymerization was carried out in a double walled glass reactor (250 mL) fitted with a gas supply (N_2), a condenser, and a glass stirrer. In a typical batch process, 0.505 g of macromonomer **I** was dissolved in 44.74 g of water and 101.46 g of EtOH 95°. After purging with nitrogen for one night, the mixture was heated at 70 °C, and a solution of 0.337 g of AIBN in 16.34 g of styrene was added to the reactor. The reaction medium was always clear at the beginning of the polymerization. The mixture was stirred at 250 rpm, and polymerization proceeded for 24 h. Conversion of styrene was determined by gravimetry.

In a "seed and feed" process, 14.21 g of water, 61.39 g of EtOH 95°, and 0.0639 g of surfmer **III** were charged in the reactor and purged with nitrogen. The mixture was heated at 56.4 °C, and a solution of 0.194 g of ADVN in 6.40 g of styrene was added to the reactor. After 30 min of reaction, two solutions were simultaneously added over a period of 3 h 30 min: one containing 0.136 g of ADVN in 4.26 g of styrene, the other consisting of 0.2658 g of surfmer **III** in 3.16 g of water and 13.64 g of EtOH 95°. Then, the reaction was allowed to proceed for 24 h.

Cleaning Procedure for the Latices. The washing process is summarized in Scheme 1. After polymerization, the dispersion was centrifuged for 30 min at 15 000 rpm (Beckman, Avanti 30 centrifuge), whereafter the supernatant was carefully removed. The adsorbed species were extracted from the polystyrene particles by redispersing the particles in fresh EtOH 95°. Then, the dispersion was centrifuged again, and a

Scheme 1. Cleaning Procedure for the Latices



new cycle of dispersion/centrifugation was applied. The supernatants and the cleaned particles were finally dried at 40 °C at reduced pressure and analyzed by NMR.

Adsorption of Surfmers onto Polystyrene Particles in Ethanol–Water Media. A seed of polystyrene particles was prepared by emulsion polymerization. NaCl (1.3 g) dissolved in 1800 g of water was charged into a glass reactor (2000 mL), similar to the one described before. After purging with nitrogen for 1 h, the solution was heated at 70 °C and vigorously stirred at 350 rpm. Then, 1.5 g of initiator $K_2S_2O_8$ and 185 g of styrene were added and polymerization proceeded for 24 h.

This seed latex (D_n = 673 nm, D_w/D_n = 1.004 (TEM)) was cleaned by ion exchange with a mixture of anionic and cationic resins, until the conductivity was 3 μS/cm. Then, the seed latex was cleaned by serum replacement in an ultrafiltration system (Millipore Minitan System) equipped with PVDF membranes (pore size: 200 nm) and fed with a mixture of EtOH/H_2O (70/30 v/v), so that the serum was gently exchanged from water to the EtOH/H_2O mixture. The stability of the seed latex after this operation (dry solid content: 5.12%) was checked by a DCP analysis: particle size and size distribution remained unchanged. The adsorption of the surfmers **II** and **III** on the seed particles was conducted as follows: various quantities of surfmer were added to a known quantity of latex in 10 mL glass bottles, and the bottles were gently shaken for 24 h. Afterwards, the latex was centrifuged at 15 000 rpm for 30 min. The precipitate was dried at reduced pressure at 40 °C and analyzed by NMR in order to determine the fraction of surfmer physically adsorbed on the polystyrene particles. The same procedure was applied to study the adsorption of NP40.

Results and Discussion

In this paper, we describe the dispersion polymerization of styrene in ethanol–water mixtures using maleic PEO macromonomers as stabilizer precursors. Moreover, macromonomers with amphiphilic properties, the so-called *surfmers* (a combination of *surf*actant and mono*mer*), will be applied to investigate the effect of the macromonomer structure. Special attention is paid to the location of the macromonomer, its conversion, and its incorporation yield into the particles during the entire polymerization. This will lead to a better understanding of the mechanism of stabilization.

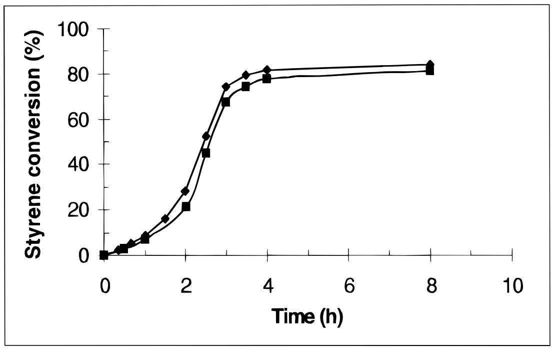


Figure 2. Conversion–time curve for the dispersion polymerization of styrene in EtOH/H_2O (70/30 v/v) using different types of stabilizer: ♦: Macromonomer **I**; ■: PVP-K30 (see Table 1 for the recipes).

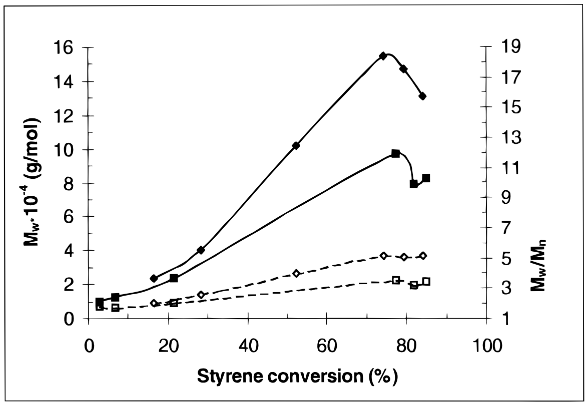


Figure 3. Weight average molecular weight (M_w) (continuous line) and polymolecularity index (M_w/M_n) (dotted line) versus styrene conversion for the dispersion polymerization of styrene in EtOH/H_2O (70/30 v/v) using different types of stabilizer: ♦: macromonomer **I**; ■: PVP-K30 (see Table 1 for the recipes).

Reactivity of PEO Maleic Derivatives in Dispersion Polymerization. Comparison between PVP-K30, PEO Macromonomer, and NP40 as Stabilizers. First, macromonomer **I** was applied in the dispersion polymerization of styrene in an EtOH/H_2O mixture. The kinetics as well as the characteristics of the obtained particles have been compared with a similar experiment where PVP was used as the polymeric stabilizer. The conversion–time curve (Figure 2) shows that, in both cases, a gel effect occurs at about 20% styrene conversion, indicating that the locus of polymerization changes from the continuous phase to the particle phase. This is accompanied with a rise of the molecular weight and a broadening of the molecular weight distribution (Figure 3). After 80% styrene conversion, the monomer concentration in the polymer particles is so low that the system can become glassy, so that the continuous phase is restored as the main locus of polymerization. As a result, the molecular weight of the resulting particles decreases. As shown in Table 1, the system with the macromonomer leads to larger particles than the PVP system, to a narrower size distribution and to the absence of coagulation. These results indicate that large polymer particles with narrow size distribution, can be obtained without any floc by using the macromonomer **I** at lower concentrations (3 wt %) than the more conventional stabilizer PVP-K30, which is usually used at more than 8 wt % for styrene.[16] This illustrates the usefulness of such macromonomers in dispersion polymerization.

In order to investigate the effect of the polymerizable group of macromonomer **I** on the mechanism of stabi-

Table 1. Effect of Different Types of Stabilizers on Particle Size and Size Distribution[a]

	styrene conversion (%)	D_n (nm)[d]	D_w/D_n	coagulum[e]
macromonomer **I**[b]	84.2	1860	1.04	0
PVP-K30[b]	85.2	979	1.13	3.9
NP40[c]	61	1990	1.72	>20

[a] Dispersion polymerization of styrene in EtOH/H_2O (70/30, v/v). Total solid content: 10.8%; AIBN: 2 wt % for the total monomers. $T = 70$ °C. [b] Stabilizer: 3.1 wt % for styrene. [c] Stabilizer: 20 wt % for styrene. [d] DCP analysis. [e] wt % for styrene.

Table 2. The Stabilization Characteristics as a Function of Styrene Conversion[a]

	styrene conversion (%)					
	4.9	16.3	28.1	74.2	79.5	84.2
incorporation yield (%)	0.6	1.2	1.9	2.9	2.8	3.3
adsorbed species (%)						8.6
D_n (nm) of swollen particles	924	1311	1513	1885	1911	1933
surface area/molecule (Å^2/molecule)	1226	1285	1087	1087	1177	1042 (286)[b]

[a] Dispersion polymerization of styrene in EtOH/H_2O (70/30, v/v). Total solid content: 10.8%; macromonomer **I**: 3.1 wt % for styrene; AIBN: 2 wt % for the total monomers. $T = 70$°C. [b] If both incorporation and adsorption are taken into account.

lization, an experiment was carried out with a conventional nonionic surfactant NP40 (Table 1), which is able to adsorb weakly onto the particles (see also Figure 6), but which is unable to copolymerize with styrene. This nonionic surfactant turned out to be a poor stabilizer even in large quantities. Highly polydisperse particles were obtained, and coagulation occurred immediately after stopping the impeller. This leads to the conclusion that the copolymerization of the macromonomer **I** with styrene is essential for the stabilization of the polymer particles. In other words, the true stabilizer is the copolymer formed *in situ*. Styrene offers hydrophobicity to the copolymers, which results in a stronger adsorption of the copolymers onto the particles.

Analysis of the Reaction Medium. In order to clarify the mechanism of stabilization involved in the dispersion polymerization with the macromonomer, the macromonomer conversion and the location of the formed copolymers were also determined at any moment of the polymerization. In fact, the macromonomer may be (1) unreacted, in the continuous phase, (2) reacted but still in the continuous phase as soluble species, (3) reacted and weakly adsorbed (physically adsorbed), (4) reacted and strongly adsorbed (chemically anchored), (5) buried in the particles (this last case is unlikely to happen because the PEO chain can reorient at the surface of the particles when they are swollen with styrene monomer).

For this purpose, a centrifugation technique was used in order to separate the particles from the serum and to clean the particles from the physically adsorbed species (Scheme 1). In step A, only species 1 and 2 (see above) remained in the serum. In the following steps using EtOH 95° as diluent, which is a better solvent than the reaction solvent, species 3 is desorbed. Two cleaning cycles were sufficient: desorption in step C represented less than 3 wt % of the total species found in the serum. The NMR analysis of the serum and of the polymer particles after centrifugation gave us useful information about the chemical composition of each phase and the macromonomer conversion. Combination of the NMR results and the material balance allowed us to calculate both the adsorption yield of the macromonomer as well as its incorporation yield into the particles. Here, the adsorption yield is defined as the amount (%) of macromonomer weakly adsorbed on the particles (species 3), whereas the incorporation yield is defined as the amount (%) of macromonomer chemically anchored to the particles (species 4 and 5).

The results obtained for the macromonomer **I** are shown in Table 2. At the end of the polymerization, the incorporation yield is very low, i.e., 3.3%. At this point, however, the macromonomer conversion is more than 90%. Furthermore, a small fraction of the macromonomer is weakly adsorbed, whereas the major part (88.1%) is lost in the serum. This means that only 11.9% of the macromonomer actually takes part in the stabilization of the polymer particles.

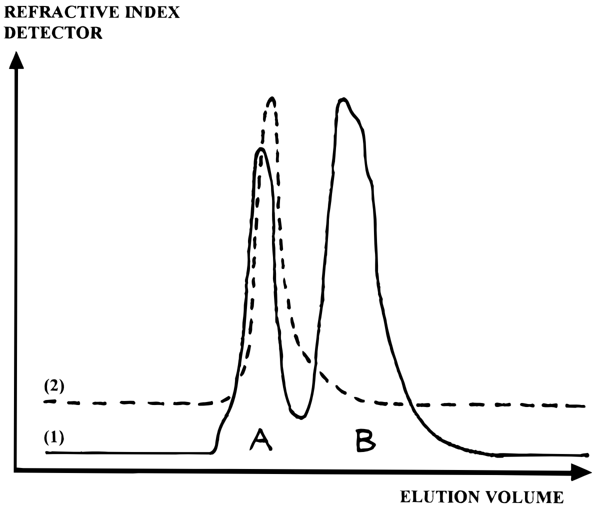


Figure 4. (1) SEC analysis of the soluble species in the serum. **A**: Soluble copolymers; **B**: styrene oligomers. (2) SEC analysis of macromonomer **I**.

Characterization of the Soluble Species and Kinetics of Copolymerization. The soluble species, which remained in the serum at the end of the polymerization, were analyzed by SEC (Figure 4). This was very useful in order to detect styrene oligomers, whose molecular weight varied from about 200 to 1100 g/mol, indicating that the critical degree of polymerization for the precipitation of oligomers in this medium is more than *ca.* 10 styrene units. Moreover, the molecular weight of the copolymers appeared to be very low, less than twice the molecular weight of the macromonomer, indicating that there was only one macromonomer unit per copolymer chain. Several reasons for the low molecular weight of the soluble copolymers can be proposed, such as the thermodynamic repulsion (or incompatibility) between the PEO chain of the macromonomer and the polystyrene macroradical,[38] the occurrence of enhanced termination caused by high radical concentrations (organized aggregates, inefficient capture), and to a lower extent, a transfer reaction to ethanol.[30] Dealing with transfer reaction to PEO chains, Rempp et al.[39] have already checked that, in the polymerization with styrene, transfer reaction onto the PEO chain ($M_w = 1800$ g/mol) could be disregarded if [macromonomer] $\ll$ [styrene], which is the case in our work.

Also, the soluble copolymers were separated from the styrene oligomers by precipitation in diethyl ether. The

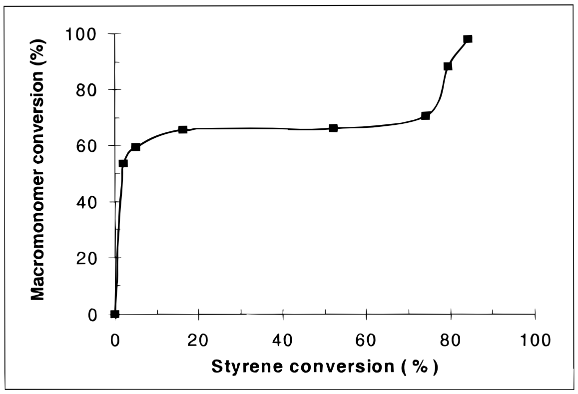


Figure 5. Macromonomer conversion during the dispersion polymerization of styrene in EtOH/H_2O (70/30 v/v). Total solid content: 10.8%; macromonomer **I**: 3.1 wt % for styrene; AIBN: 2 wt % for the total monomers. T = 70 °C.

NMR analysis revealed that the styrene content in the soluble copolymers was extremely low. These results are consistent with the tendency of this system to form alternating copolymers, and which have already been reported for styrene and maleic derivatives.[40,41]

More information could be obtained by studying the macromonomer conversion during the course of the polymerization. First, the curve of the macromonomer conversion versus styrene conversion (Figure 5) suggests that the reaction loci are transferred from the continuous to the particle phase early after the beginning of the polymerization and restored in the continuous phase at high conversion. Similar events were also reported by Capek et al.,[38] who investigated the kinetics of the dispersion polymerization of styrene in EtOH/H_2O mixture (80/20 v/v) using PEO macromonomers with a styrene or a methacrylate end group. In our case, the macromonomer reacts very rapidly at the beginning of the polymerization: about 50% macromonomer conversion is achieved at only 2% styrene conversion. Similar behavior was observed with the maleic surfmer **III**. This very high reactivity is in agreement with the observed tendency to form alternating copolymers.

All these observations lead to the conclusion that the formation of low molecular weight and low styrene contents copolymers is the reason why the incorporation yield is not as high as expected.

These results differ a lot from those of Stähler,[42] who studied the emulsion polymerization of styrene using an anionic maleic surfmer as stabilizer. In their case, the surfmer has been consumed mainly during the third stage of the emulsion polymerization, after the monomer droplets disappear. The difference from our results can be partly ascribed to the applied process. In dispersion polymerization, the mixture is initially homogeneous, so that copolymerization can occur. Later on, partitioning of styrene and AIBN (or oligo-radicals) takes place between the particles and the continuous phase. The partition coefficient for styrene, defined as the ratio $[\text{styrene}]_{(\text{particle})}/[\text{styrene}]_{(\text{continuous medium})}$, was evaluated to be about 5.[43] The partition coefficient for AIBN has not been determined, but other authors,[44,45] have shown that the average number of oligo-radicals per particle might be relatively high due to the large particle size and the high viscosity within the particles. This implies that the polymerization of styrene now proceeds mainly inside the particles. As a result, copolymerization is unfavored during the growth stage of the particles. In contrary, in emulsion polymerization, the reaction medium is heterogeneous at the beginning of the polymerization. Moreover, Stähler used AIBN as initiator, which is scarcely soluble in water. Thus, at the beginning of the emulsion polymerization, the partitioning of the reactants is such that the copolymerization with the surfmer is unfavored. A change in the locus of polymerization from the particle volume to the particle–water interface with increasing conversion is thought to be responsible for the copolymerization during the third stage of the polymerization. In addition, in their case, the surfmer used does not contain PEO chain, and the polymerization is carried out in the absence of ethanol, so that neither PEO/PS incompatibility nor transfer reaction to solvent can influence the copolymerization. All this leads to a high incorporation yield, as shown by the surface tension of the final latex being almost that of pure water.

Surface Coverage of the Particles by PEO chains. The coverage of the particles by chemically bounded PEO chains is an important feature in the understanding of the mechanism of stabilization. The values of the incorporation yield allowed us to determine the surface area per macromonomer molecule at the surface of the particles during the polymerization (Table 2). For the calculation of the particle diameter, polymer particles are supposed to be nearly monodisperse throughout the polymerization, and partitioning of both styrene monomer and ethanol between continuous and polymer phase is taken into account.[43] This approach indicated that the surface area occupied by an anchored PEO chain remained nearly constant (about 1100 Å^2/molecule) during the whole polymerization.

In order to discuss this value, we can treat the PEO chain as a rigid sphere with random coil dimensions, affixed on the surface of the polymer particle. In this case, the surface area covered by a single PEO chain of macromonomer **I** can be estimated as 1065 Å^2 by using the following equation, where n is the mean number of ethylene oxide units in the PEO chain of the macromonomer:[32]

$$S = (5\pi/3)[0.16 \times (44n)^{0.585}]^2 \qquad (1)$$

Although this value of 1065 Å^2 is determined in methanol at 25 °C while we have worked in ethanol–water mixtures at 70 °C, it is interestingly very similar to the value of 1100 Å^2 determined from the incorporation yield of the macromonomer (Table 2). This means that the surface coverage by anchored PEO chains is almost 100% when the coil conformation model is applied. As a result, the particle surface is completely covered by PEO chains, so that the particles are sterically stabilized against coagulation.

According to the de Gennes model,[46] when the surface becomes crowded with PEO chains, the polymer coils can be deformed into brushes. Also, the thickness of the grafted layer is increased, improving the steric stabilization of the particles. Indeed, the study of the adsorption of PEO surfactant molecules (Figure 6) gave values in the range 100–150 Å^2/molecule when the surface of polystyrene particles was saturated by the surfactant. Considering the value of 150 Å^2/molecule as a reference (i.e., surface coverage = 100%) for the brush conformation of PEO chains containing around 45 ethylene oxide units, the value of 1100 Å^2/molecule then corresponds to a surface coverage of about 9% related to the brush conformation. It suggests that the stability of the particles is far from the optimum. Nevertheless, the surface area per molecule is 286 Å^2/molecule (Table 2) when both the anchored species

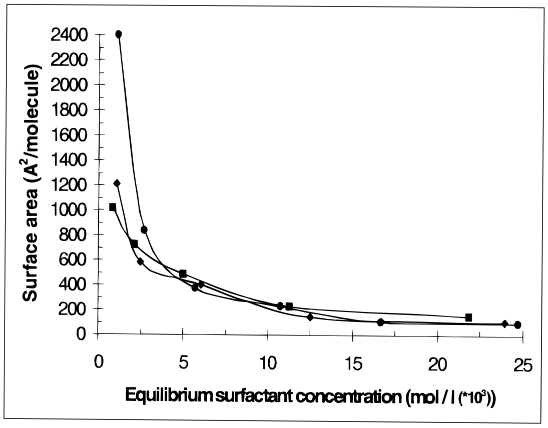


Figure 6. Adsorption of the surfmers and a conventional nonionic surfactant onto polystyrene particles, in EtOH/H_2O (70/30 v/v). ♦: surfmer **II** ; ■: surfmer **III**; ●: NP40.

(incorporation yield) as well as the weakly adsorbed species (adsorption yield) are taken into account. This means that the physically adsorbed species are in large part responsible for the stability of the particles: the surface coverage related to the brush conformation becomes significant (about 53%) if these species are considered. It results that the flocculation of the latex is effectively prevented. It is important to note that if the surface of the particles were to become saturated with stabilizer, secondary particle formation would be likely to occur, and monodisperse particles would no longer be obtained.[25]

Effect of Various Parameters on the Dispersion Polymerization Using PEO Macromonomers as Stabilizers. Macromonomer Structure. The surfmer **III** was used in order to determine the effect of its amphiphilic properties on dispersion polymerization. As shown in Table 3, smaller particles were obtained when using this surfmer instead of the macromonomer **I**. It suggests that the surfmer acts as a better stabilizer. Indeed, due to its amphiphilic properties, it is able to adsorb very early onto the particles, i.e., during the nucleation step which determines the particle number and hence the final particle size. Moreover, it needs to copolymerize with less styrene units, compared to the hydrophilic macromonomer **I**, before being captured by the particles. However, the incorporation yield was not improved by using the surfmer **III**. Also, the surface coverage by incorporated PEO chains is worse than with the macromonomer **I**. These results are quite unexpected. Nevertheless, other studies[34,47] also suggest that hydrophilic reactive stabilizer precursors, i.e., without amphiphilic properties, are very effective in dispersion polymerization, but the comparison with similar amphiphilic products was not carried out.

In the "seed and feed" experiment, although the final surfmer conversion is again more than 90%, the slow addition of the surfmer **III** does not significantly improve the incorporation yield. This indicates that the presence of seed particles does not favor the formation of enriched styrene copolymers. Indeed, despite the amphiphilic properties of the surfmer, its ability to adsorb onto seed particles in the alcoholic medium is very low, so that copolymerization at the particle–serum interface is limited.

Some work is now in progress in our laboratory in order to study the use of macromonomers and surfmers with a styrene or a methacryloyl end group. Indeed, the change in the reactivity of the macromonomer with styrene is thought to be a key factor to improve the incorporation yield.

Macromonomer Concentration. The surfmer **II** was used at different concentrations, and the results are summarized in Table 4. As expected, the higher the concentration of surfmer, the smaller the particle size is. This is caused by an increase in the amount of available stabilizer. Otherwise, although the incorporation yields do not vary significantly, the surface coverage of the particles by the PEO chains of the surfmer is increased. This means that the increase in the amount of stabilizer is more pronounced than the rise of the total surface area of the produced particles. Also, both the decrease as well as the rather high value of the size distribution index indicate a lack of stabilization that can be attributed to the relatively short PEO chain length of the surfmer **II** ($n = 34$). Narrower size distribution was obtained with the surfmer **III** ($n = 42$) (Table 3).

The surface area covered by a single PEO chain of surfmer **II** can be estimated as 695 Å² (coil conformation) by using eq 1. Moreover, the study of the adsorption of the surfmer **II** onto polystyrene particles gave a value of approximately 107 Å²/molecule when the surface was saturated by the surfactant (Figure 6). We will choose this value as a reference (i.e., surface coverage = 100%) for the brush conformation. Consequently, at a surfmer concentration of 6% by weight based on styrene, the surface coverage by anchored PEO chains is about 98% related to the coil conformation and only 15% related to the brush conformation. Considering both the anchored and the adsorbed species, the surface coverage related to the brush conformation increases to about 68%, showing that the physically adsorbed species are again responsible for a large part in the stability of the particles.

Moreover, higher molecular weight and higher polymerization rate were obtained with the smaller particles. This is explained by an increase in the capture efficiency for the small particles, so that the polymerization inside the particles becomes dominant and the gel effect becomes more significant.

Solvent Composition. The surfmer **III** ($n = 42$) was applied with different water content in the diluent. As shown in Table 5, the particle size decreases with increasing amounts of water. This is commonly explained as follows: the critical degree of polymerization, at which the nuclei are formed, decreases while increas-

Table 3. Effect of the Structure of the Macromonomers on Particle Size and Incorporation Yield[a]

	styrene conversion (%)	D_n (nm)[b]	D_w/D_n	incorporation yield (%)	surface area (Å²/molecule)
surfmer **III**	75.4	1170	1.04	3.0	1312
seed and feed[c]	*74.6*	*1590*	*1.13*	*3.3*	*904*
macromonomer **I**	98	2040	1.04	3.3	1008

[a] Dispersion polymerization of styrene in EtOH/H_2O (70/30 v/v), using surfmer **III** or Macromonomer **I** as stabilizer. Total solid content: 10.8%; stabilizer: 3.1 wt % for styrene; AIBN: 2 wt % for the total monomers; $T = 70$ °C. [b] DCP analysis. [c] Seed and feed dispersion polymerization of styrene in EtOH/H_2O (80/20 v/v).

Table 4. Effect of the Concentration of the Macromonomers on Particle Size, Incorporation Yield, and Molecular Weight[a]

concentration of surfmer **II**, wt % for styrene	styrene conversion (%)	D_n (nm)[b]	D_w/D_n	incorporation yield (%)	surface area (Å^2/molecule)	$M_w \times 10^{-4}$ (g/mol) (M_w/M_n)
6	76.6	1240	1.19	2.5 8.6[c]	705 157[d]	10.9 (4.62)
14	89.3	910	1.12	2.7	436	16.6 (6.36)

[a] Dispersion polymerization of styrene in EtOH/H$_2$O (70/30 v/v), using different concentrations of surfmer **II** as stabilizer. Total solid content: 10.8%; AIBN: 2 wt % for the total monomers; $T = 70$ °C. [b] DCP analysis. [c] Adsorption yield (%). [d] If both incorporation and adsorption are taken into account.

Table 5. Effect of the Composition of the Solvent on Particle Size and Incorporation Yield[a]

solvent composition: EtOH/H$_2$O v/v	styrene conversion (%)	D_n (nm)[b]	D_w/D_n	incorporation yield (%)	surface area (Å^2/molecule)
80/20	58.6	1540	1.03	2.3	1218
70/30[c]	75.3	1150	1.04	3.1	1312
60/40[c]	80	949	1.34	4.6	1156

[a] Dispersion polymerization of styrene for different compositions of the solvent. Total solid content: 10.8%; surfmer **III**: 3.1 wt % for styrene; AIBN: 2 wt% for the total monomers; $T = 70$ °C. [b] DCP analysis. [c] TEM photographs of the particles are shown in Figure 7.

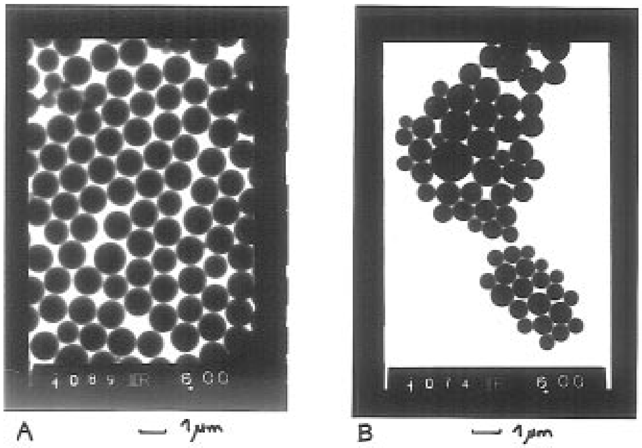


Figure 7. TEM photographs of polymer particles prepared by dispersion polymerization of styrene using surfmer **III** in EtOH/H$_2$O: 70/30 v/v (A); 60/40 v/v (B).

ing the polarity of the solvent; hence more nuclei are produced and the particle size decreases.[34] However, the reverse was observed for the dispersion polymerization of *n*-butyl methacrylate in methanol–water media.[32] Such discrepancies mean that much remains to be done in order to understand the mechanism of particle formation in dispersion polymerization. In a 60/40 v/v ethanol–water medium, the initial mixture is initially heterogeneous at 70 °C (droplets of styrene are present), so that a competition between dispersion and suspension polymerization occurs, leading to a very wide size distribution as seen on Figure 7. Moreover, the incorporation yield gently rises with the water content, but it is counterbalanced by the decrease in the particle size, so that the surface coverage is almost constant.

Conclusions

Polymer particles with narrow size distributions have been obtained by dispersion polymerization of styrene in ethanol–water media, using PEO maleic macromonomers as steric stabilizer precursors. The particle size ranged from 900 to 2000 nm in diameter, and even larger particles could be obtained by this method. Various parameters, such as the structure and the concentration of the macromonomer, and the polarity of the solvent, affect the particle size and the particle size distribution. Although the macromonomer conversion is almost complete at the end of the polymerization, the fraction of macromonomer really incorporated into the particles turned out to be very low. Some of the copolymers formed *in situ* also take part in the stabilization of the particles as weakly adsorbed species, but a large fraction of the copolymers remains in the continuous phase as soluble species. This is explained by the unusual reactivity of the maleic macromonomer, which yields very low styrene contents copolymers. Also, the incompatibility between PEO and polystyrene supresses the propagation of the copolymer macroradical. Surprisingly, the amphiphilic properties of the surfmers do not improve the incorporation yield, indicating that the hydrophilic reactive stabilizer precursors, i.e., without amphiphilic properties, are better suited for dispersion polymerization.

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