Emulsion Polymerization of Styrene Using Conventional, Polymerizable, and Polymeric Surfactants. A Comparative Study

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ABSTRACT: The emulsion polymerization of styrene is investigated, employing analogous conventional, polymerizable, and polymeric cationic surfactants ("polysoaps"). The polymerization and the properties of the latexes depend sensitively on the emulsifier and on the charge of the initiator. There is no visible correlation between the properties of the final latexes and the properties of the emulsifiers such as surface activity, solubilization capacity, or the ability to stabilize the initial monomer emulsion. When a cationic initiator is employed, all emulsifiers lead to stable monodisperse latexes, except for polysoaps with low hydrophobe content. The polymerizable, as well as the polymeric emulsifiers, yield latex solutions with very high surface tensions, different from the use of the standard surfactant. In contrast, the use of an anionic initiator can pose difficulties. The polymerizable emulsifier is efficiently fixed to the latex by copolymerization, being mostly consumed in the early stage of the reaction. Also, small amounts of the polysoaps are grafted onto the latexes during the reaction.

Introduction

The typical reaction mixture in emulsion polymerization consists of water, of the monomer, and of a water-soluble initiator which are completed by an emulsifier. The role of the emulsifier is crucial and multifold, intervening in the stabilization of the starting emulsion, as well as in particle nucleation and growth, and also in the stabilization of the final latex.[1]

In consequence, much work has been devoted to the variation of the nature of the emulsifier, which is normally a low molar mass surfactant. Variations include, for example, "emulsifier-free" recipies, in which the surfactants are created in situ. This is realized either by copolymerization of a hydrophilic comonomer or by oligomerization of the hydrophobic monomer by a hydrophilic, generally an ionic initiator fragment. Also, the use of (co)polymerizable surfactants has been studied,[2,3] representing a compromise between a classical and an emulsifier-free emulsion polymerization.

The particular interest in such systems derives, in addition to other reasons, from the intrinsic immobilization of the emulsifier on the latex particles.[3] Hindered desorption of the emulsifier from the latex should improve the latexes' stability and facilitate "core-shell" procedures. Also, it should prevent the migration and accumulation of the emulsifier (e.g., near the surface) after the filming of the latex, which deteriorates the performance of the final polymer products.

As an alternative to a covalent binding of the emulsifier onto the latex particles by copolymerization, strong adsorption of polymeric surfactants may be considered. Different molecular architectures of such polymeric surfactants can be envisaged (Figure 1), which should give rise to different behavior.[4] Amphiphilic block copolymers can be viewed as oversized surfactants ("macrosurfactants") as they preserve the bipolar architecture of low molar mass surfactants. Hydrophobic aggregation typically occurs intermolecularly, and the large blocks allow for steric stabilization, beside electrostatic stabilization if the hydrophilic block is charged. In contrast, amphiphilic graft copolymers tend to aggregate intramolecularly, due to the possibilities to minimize hydrophobic contacts within the macromolecule. Therefore, the emulsifier is rather thought to produce a thin protective coating on the latex surfaces. Very long grafts are required for steric stabilization. The so-called "polysoaps" consist of individual surfactant fragments tied together, as obtained, for example, by polymerization of reactive surfactants. Similar to graft copolymers, aggregation takes place intramolecularly. Due to their molecular structure, an even thinner protective coating on the latex surface can be assumed intuitively. This renders the possibility for steric stabilization less clear. Actually, the picture has much similarity to "crew-cut" micelles.[5]

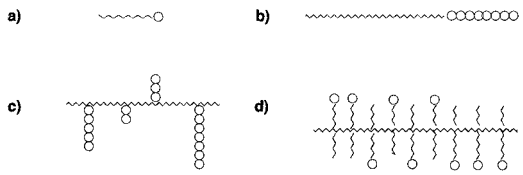

Figure 1. Schematic structure of low molar mass surfactants, macrosurfactants, amphiphilic graft copolymers, and polysoaps.

Whereas the use of amphiphilic block copolymers[6,7] and of amphiphilic graft copolymers[8−10] in emulsion polymerization has been studied occasionally, the use of polysoaps has been hardly explored so far.[11,12] Beside the possible improvement of the emulsifier's adsorption strength, the particular architecture of polysoaps might also give rise to modified nucleation and particle growth mechanisms.[1,13] Assuming, for example, nucleation in the homogeneous phase, the adsorption of surfactant fragments may become a cooperative process. Or, in the later stages of polymerization when the latex particles are growing, the dense covalent linkage of the surfactant

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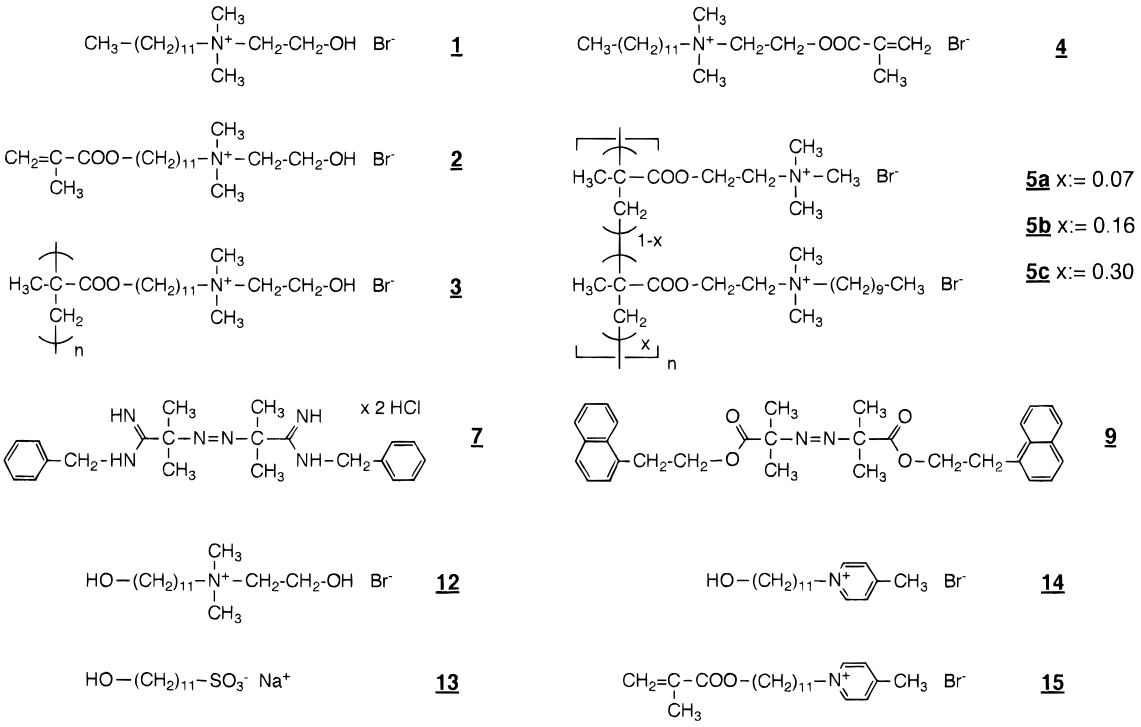
Table 1. List of Emulsifiers and Initiators Used



fragments to a polymer chain may prevent their uniform distribution at the surface of the latex particles or, instead this may cause patching of the surfactants, thus modifying, for example, the "limited coagulation process".[1]

Therefore, we were interested to learn about the ability of polysoaps to function as emulsifier in emulsion polymerization. As such systems depend on numerous parameters which render an absolute evaluation difficult, the polymerization of a model styrene emulsion was studied for a series of analogous polymerizable surfactants and polysoaps (Table 1). *N*,*N*-Dimethyl-*N*-(2-hydroxyethyl)-*N*-dodecylammonium bromide (**1**) was chosen as reference low molar mass surfactant. Similar cationic surfactants have been frequently used in model studies of emulsion polymerization of styrene, as well as of its microemulsion polymerization.[14−16]

In the polymerizable surfactant **2**, the terminal methyl group of the reference surfactant **1** is replaced by a methacryloyl moiety. The corresponding homopolymer is polysoap **3**, which belongs to the so-called "tail end-type" geometry, because the polymer backbone is attached to the end of the hydrophobic chain.[17] Because of the importance of polymer geometry for the property of polysoaps,[4] analogous polysoaps **5a**−**c** of "head-type" geometry were studied, too. In these copolymers, the backbone is attached to the hydrophilic head group.[18] The copolymer series is made from polymerizable surfactant **4** and from ((methacryloyloxy)ethyl)trimethylammonium bromide (**6**). The series is characterized by an increasing content of hydrophobic chains. The cationic comonomer **6** is needed to act as "main chain spacer," assuring the water solubility of copolymer series **5**, as found in other polysoaps of head-type geometry.[4,19−21] The hydrophobe content of copolymer **5c** is very close to the maximum which still allows solubility of such head-type polysoaps in water.[18]

Experimental Section

Materials. All solvents used were analytical grade. Water was deionized and subsequently purified by a Milli-Q water purification system. Styrene was destabilized and purified by distillation prior to use. Initiator (2,2′-dimethyl-2,2′-azo-*N*-benzylpropionamidine) hydrochloride (VA-552) (**7**) was a gift from Wako Chemicals and was recrystallized from acetone. Potassium persulfate **8** was recrystallized from water. (2-(Methacryloyloxy)ethyl)trimethylammonium bromide (**6**) was a gift from B. Schlarb. The synthesis of monomers **2** and **4** is described elsewhere.[17]

For the preparation of the polysoaps, the initiator 2,2′-dimethyl-2,2′-azo-2-(1-naphthyl)ethyl propionate) (**9**) was used. Molar masses could thus be estimated by end-group analysis of the naphthyl fragment via UV spectroscopy ($\lambda = 284$ nm, $\epsilon = 9100$ L mol^{-1} cm^{-1} in ethanol), assuming 1.2 naphthyl end groups/macromolecule as determined for poly(methyl methacrylate) prepared under identical conditions.[22] The polymerization of **2** in ethanol at 60 °C yields polysoap **3** of M_n = 115 000 (DP_n = 280) and polysoap **3*** with the lower molar mass of M_n = 24 000 (DP_n = 59).

Prepared analogously from methacrylates **4** and **6**, copolymers **5a**−**c** were purified as described.[17,18] The compositions of the copolymers given in Table 1 are average values according to elemental analysis, ^{1}H-NMR spectroscopy in CD_3OD and FT-IR spectroscopy (using the bands at 2925 and 1730 cm^{-1}). The compositions determined by the different methods are in good agreement. They correspond well to the compositions of the monomer feed. End-group analysis of the naphthyl fragments of initiator **9**[22] gives average molar masses of M_n = 85 000 for **5a**, M_n = 110 000 for **5b**, and M_n = 60 000 for **5c** i.e., the copolymers contain approximatively 330, 400, and 210 cationic groups/chain.

N,*N*-Dimethyl-*N*-dodecyl-*N*-(2-hydroxyethyl)ammonium bromide (**1**) is synthesized by reacting 150.9 g (0.59 mol) of 1-bromodecane with 276 g (3.10 mol) of *N*,*N*-dimethylethanolamine 4 days at 80 °C under argon. Repeated crystallization from ethyl acetate yields 115 g (56%) of colorless, hygroscopic powder. ^{1}H-NMR (200 MHz, $CDCl_3$, δ in ppm): 0.85 t (3H, $-CH_3$), 1.23 m (18H, $-(CH_2)_9-$), 1.73 m (2H, $-CH_2-C-N^+$), 3.35 s (6H, N^+-CH_3), 3.4−3.6 m (2H, $-CH_2-N^+$), 3.7 m (2H, N^+-CH_2-C-O-), 4.1 m (2H, $-CH_2-O-$).

N,*N*-Dimethyl-*N*-(11-hydroxyundecyl)-*N*-(2-hydroxyethyl)-ammonium bromide (**12**) is made by reacting 2.15 g (0.024 mol) of dimethylaminoethanol with 5.5 g (0.0219 mol) of 11-bromoundecanol in 50 mL of acetone for 48 h. Precipitation by cooling and recrystallization from acetone/methanol (9/1, v/v) gives 5.31 g (71%) of colorless powder, mp = 163 °C. ^{1}H-

NMR (200 MHz, $CDCl_3$, δ in ppm): 1.2−1.35 m (14H, $-(CH_2)_7-$), 1.45 m (2H, $-C-CH_2-C-N^+$), 1.66 m (2H, $-O-C-CH_2-C-$), 3.17 s (6H, $-CH_3$), 3.37 m (2H, $-(C)_7-C-CH_2-N^+-$), 3.53 m (4H, $-O-CH_2-C-C-$, $-N^+-CH_2-C-O-$), 3.95 m (2H, $-N^+-C-CH_2-O-$).

Sodium 11-hydroxyundecylsulfonate (**13**) is obtained by reacting a suspension of 15g (0.12 mol) of Na_2SO_3, 0.1 g of $Na_3PO_4 \cdot 12H_2O$, 0.05 g of aniline, and 4.82 g (0.019 mol) of 11-bromoundecanol in 100 mL of water for 22 h at 140 °C in an autoclave. Extraction of the evaporated mixture by hot $CHCl_3$ and recrystallization gives 1.8 g (37%) of colorless powder. ^{1}H-NMR (200 MHz, D_2O, δ in ppm): 1.2−1.45 m (14H, $-(CH_2)_7-$), 1.52 m (2H, $-CH_2-C-SO_3$), 1.71 m (2H, $-O-C-CH_2-$), 2.88 t (2H, $-CH_2-SO_3$), 3.58 t (2H, $-O-CH_2-$).

N-(11-Hydroxyundecyl)-4-methylpyridinium bromide (**14**) is prepared by refluxing 1.86 g (0.020 mol) of 4-methylpyridine with 5.03 g (0.020 mol) of 11-bromoundecanol in 50 mL of ethanol for 48 h. Repeated recrystallization from acetone gives 4.64 g (67%) of colorless, hygroscopic powder. ^{1}H-NMR (200 MHz, $CDCl_3$, δ in ppm): 1.2−1.45 m (14H, $-(CH_2)_7-$), 1.6−1.8 m (4H, $-CH_2-C-N^+$, $-O-C-CH_2-$), 2.75 s (3H, aryl$-CH_3$), 3.50 t (2H, $-O-CH_2-$), 4.97 t (2H, $-CH_2-N^+-$), 7.95 d, 9.33 d (2H + 2H, $-CH=$, aromatic).

N-((11-methacryloyloxy)undecyl)-4-methylpyridinium bromide (**15**) is made by refluxing 2.44 g (0.026 mol) of 4-methylpyridine and 8.40 g (0.026 mol) of 11-bromoundecyl methacrylate[17] in 40 mL of acetonitrile for 48 h. Flash chromatography of the reaction mixture on silicagel (eluent: $CHCl_3$/CH_3OH 7/1 v/v) yields 6.1 g (57%) of viscous, hygroscopic oil. ^{1}H-NMR (200 MHz, $CDCl_3$, δ in ppm): 1.2−1.45 m (14H, $-(CH_2)_7-$), 1.5−1.7 m (2H, $-O-C-CH_2-$), 1.7−2.2 m (5H, $-CH_2-C-N^+$, $=C-CH_3$), 2.6 s (3H, aryl$-CH_3$), 4.05 t (2H, $-O-CH_2-$), 4.85 t (2H, $-CH_2-N^+-$), 5.50 s (1H, CH=C−COO, trans), 6.05 s (1H, CH=C−COO, cis), 7.85 d, 9.25 d (2H + 2H, $-CH=$, aromatic).

Emulsion Polymerization Procedures. Emulsion polymerizations were carried out in a 200 mL three-neck glass reactor equiped with magnetic stirrer (cylindrical bar 3 cm and stirring speed 500 rpm), dropping funnel and reflux condenser in an argon atmosphere. The reactor was charged with 3.24 mmol of emulsifier (based on the amount of ionic groups) and 150 mL of water. It was thermostated at 46 °C in the case of cationic initiator **7** and at 56 °C in the case of anionic initiator **8**. Styrene (16.5 g, 158 mmol) was added dropwise within 20 min under stirring, and the emulsion was deoxygenated by bubbling argon for 30 min. Finally, a solution of 0.79 mmol of initiator (=0.5 mol % relative to the monomer) in 12 mL of deoxygenated water was added rapidly via a dropping funnel. The start of the initiator addition is taken as $t = 0$ min. Samples of known volume are taken at given times of the polymerization by a hypodermic syringe. The samples were discharged in a flask containing a small amount of hydroquinone and chilled in an ice bath to inhibit further polymerization.

Analytical Methods. Monomer conversions were determined by converting the unreacted styrene with excess bromine into 1,2-dibromoethylbenzene. The residual bromine was reduced with excess KI ($Br_2 + 2KI \rightarrow 2KBr + I_2$). The iodine thus formed is titrated by aqueous sodium thiosulfate ($I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$) using starch as indicator:[23] to a suspension of 0.2 g of NaBr and 2 mL of saturated aqueous NaBr were added 0.5 mL of the styrene emulsion (taken after vigorous shaking) and 30 mL of methanol, followed by 10 mL of 0.1 M bromine−bromide reagent (made of 5.5 mL of bromine and 100 g of NaBr in 1 L of methanol; the exact Br_2 concentration is determined by titration with 0.05 M aqueous $Na_2S_2O_3$). The mixture is reacted for 45 min at ambient temperature. Then, 5 mL of a 10 wt % aqueous solution of KI was added and the mixture was immediately titrated with 0.05 M aqueous $Na_2S_2O_3$.

Polymer yields were determined gravimetrically. Generally, the polymers were isolated by lyophilizing the reaction mixture, solubilizing the residue in 10 mL of $CHCl_3$, and precipitating into methanol. The recovered polymer was dried for 48 h at 60 °C in vacuo.

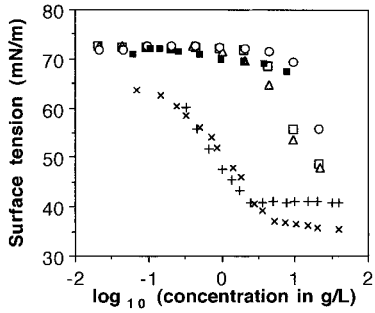


Figure 2. Surface activity of the low molar mass emulsifiers and of the polysoaps: (×) **1**, (+) **2**, (■) **3**, (○) **5a**, (□) **5b**, (△) **5c**.

FT-IR spectra of KBr pellets were recorded with a Nicolet Model 205 spectrometer. NMR spectra were recorded by a Varian Gemini (300 MHz) spectrometer. Microanalysis were performed by the University College of London. Differential scanning calorimetry (DSC) (DSC7, Perkin-Elmer) applied heating and cooling rates of 10 °C/min.

Molar masses of the polystyrenes were measured by GPC (Waters, UltraStyragel, eluent THF). The column combination (2 × linear, 2 × 1000 Å) was calibrated with polystyrene standards of narrow molar mass distribution (TSK standards, Tosoh Corp.).

Surface tensions γ were determined at 20 ± 1 °C with a manual tensiometer Krüss 8501 (De Noüy method). If a styrene phase separated in the early stage of the polymerizations, as occasionally seen, measurements were done on the aqueous phase of these samples.

The stability of the latexes against electrolytes were studied by pouring 30 μL of latex into 1.5 mL of $Ca(ClO_4)_2$ solutions of varying concentration ranging from 10^{-1} to 10^{-4} mol/L. The turbidity of these solutions was compared visually to samples diluted by pure water.

Particles sizes of polystyrene latexes were determined by photon correlation spectroscopy using a light-scattering spectrometer equipped with an ionized krypton laser (λ = 647.1 nm). Samples were diluted by pure water to make sure that multiple scattering does not contribute significantly to the signal and to reach the "ideal gas" limit where the interactions between particles are negligible. For the latex volume fractions below 0.2% that were measured, no concentration effects were observed. Samples are conditioned in cylindrical glass cells of 6 mm diameter which are placed in a larger cell containing Decalin and are thermostated at 25 °C. Detection is performed using a photomultiplier moving from an angle of 20°−160°. The photocurrents are analyzed using a correlator with 72 channels. The sample time could be varied from 100 ns to 0.9 s. Correlation functions of the scattered intensity are analysed by a computer using a second-order cumulant expansion. From the variation of the characteristic relaxation time with the scattering angle, the diffusion coefficient is deduced and then the Stokes−Einstein relation is applied to calculate the average hydrodynamic diameter of the latex particles.

Scanning electron microscopy used a Hitachi S-570 electron microscope (10 kV acceleration). Latexes were diluted two−seven times by water and then spread on a glass slide. After drying, the samples are sputtered with Au/Pd (15 nm thickness). Particle diameters were estimated by measuring the outer diameter and substracting 30 nm for the metal coating.

Results and Discussion

Surface Activity and Solubilization Capacity of the Emulsifiers. The surface activity of the various emulsifiers is illustrated in Figure 2. The break point of the curve of **1** at the concentration of 4.9 g/L (0.015 mol/L) indicates the critical micelle concentration (CMC). This value is slightly higher than the CMC of monomer **2** of 2.4 g/L (0.0059 mol/L).[17] The CMC value of **1** fits smoothly into the series of *N*,*N*-dimethyl-*N*-dodecyl-*N*-(2-hydroxyalkyl)ammonium bromides reported recently[24]

and compares well with the CMCs of 0.015 mol/L of dodecyltrimethylammonium bromide[24] and those of 0.017 mol/L of emulsifier **4**.[17] The surface tension γ of 38 mN/m at the CMC is comparable to the one of **2** of 40 mN/m; however, γ decreases slowly but continously above CMC.

The polysoaps **3** and **5a**−**c** behave differently compared to their low molar mass analogs (Figure 2). Up to 1 wt %, tail-end polysoap **3** is hardly surface active at the air−water interface. In contrast, head-type copolymers **5a**−**c** increasingly reduce the surface tension at high concentrations with increasing hydrophobe content. These findings agree well with the previously reported behaviors of homopolymers of **2** and those of copolymers of structure **5** which are prepared with 2,2′-dimethyl-2,2′-azopropionitrile (AIBN).[18] The role of the hydrophobic fragments from initiator **9** is therefore negligible for the surface activity of the polysoaps.

The solubilization capacities of polymers such as **3** and **5a**−**c** for various hydrophobic dyes were studied previously, demonstrating the absence of a CMC.[18,25,26] The tail-end polysoap **3** exhibited always substantially higher capacities than did the head-type analogs **5**. Within the latter, solubilization capacity increases with the hydrophobe content (i.e., from **5a** to **5c**). From these studies it can be deduced that the solubilization capacities of the conventional surfactant **1** and those of the polymerizable surfactant **2** are comparable to or even higher than those of polysoap **3**. Accordingly, solubilization capacities should increase in the series **5a** < **5b** < **5c** < **3** ≤ **2**, **1**.

Stabilization of Styrene-in-Water Emulsions. The model system investigated contains 10 wt % of styrene, 2 mol % of emulsifier (relative to styrene), and 0.5 mol % of initiator. The emulsifier concentrations are therefore always higher than the CMCs (cf. Figure 2). In order to compare the stabilities of the starting emulsions, the mixtures were vigorously stirred for 1 h at room temperature and then quickly poured into a test tube where the demixing of the upper styrene phase was followed. If no emulsifier is employed, the emulsions demix almost instantaneously, and the phase separation is complete within a few seconds.

The presence of classical, low molar mass surfactants improves the stability of the emulsion considerably. When employing the cationic surfactant **1**, the complete demixing of the styrene emulsion requires 20 min. For comparison, emulsions made with the anionic surfactant sodium dodecyl sulfate **10** demix within 7−8 min, and emulsions made with the zwitterionic surfactant 3-(*N*-dodecyl-*N*,*N*-dimethyl)ammoniopropanesulfonate (**11**) demix even more rapidly.

In comparison, emulsions prepared with the polysoaps **3** and **5a**−**c** are less stable. Demixing is complete after about 2 min for all polysoaps, independent of their individual structure. Recalling the marked differences in surface activity at the air−water interface and in solubilization capacity, none of these parameters can therefore be determinant for the stabilization of the emulsions. The results also imply that efficient stirring is crucial for performing emulsion polymerizations employing polysoap emulsifiers.

Surfactant monomer **2** proved to be an extremely efficient emulsifier, outweighing the other surfactants by far. Several days were required until complete demixing of the emulsions was reached. Comparably good performance is observed for the related surfactant monomer **15** of tail-end type geometry and for the analog **4** of head-type geometry. In contrast, the analogous surfactants **12**−**14**, which bear a terminal hydroxyl group instead of the methacrylate residue, are very poor emulsifiers, leading to demixing within 30 s. Therefore, the exceptional stabilizing effect of **2** cannot be due to the general presence of a second terminal polar group. It must be linked to the presence of the methacrylate moiety.

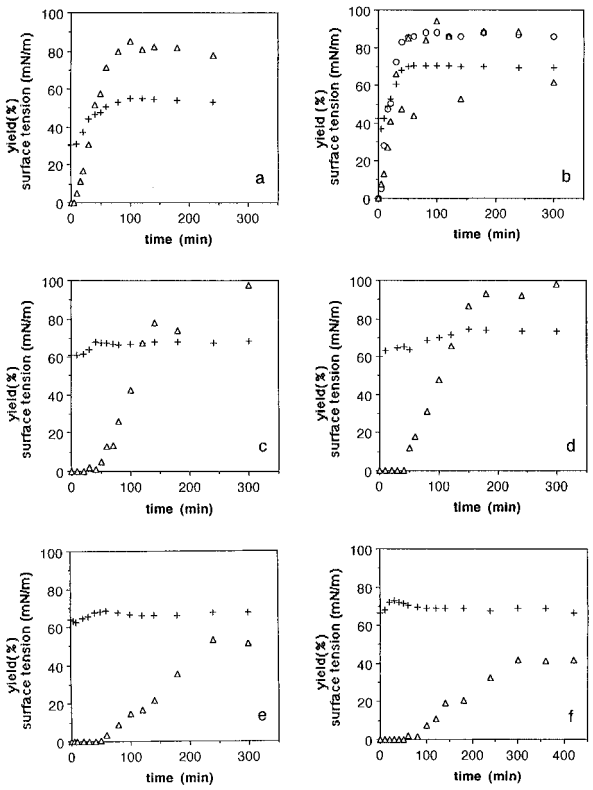


Figure 3. Time-yield curves (△) (isolation by precipitation) and time−surface tension curves (+) for the emulsion polymerization of styrene at 46 °C, using cationic initiator **7** and emulsifier (a) standard surfactant **1**; (b) polymerizable surfactant **2**, (○) time conversion curve; (c) polysoap **3** (homopolymer); (d) polysoap **5c** (hydrophobe content 30 mol %); (e) polysoap **5b** (hydrophobe content 16 mol %); and (f) polysoap **5a** (hydrophobe content 7 mol %).

Although the clarification of the effect will require a more profound study, it may be speculated that a "loop conformation" at the styrene−water interface is reponsible for the exceptional stabilization of the emulsions. Such a conformation has been postulated before,[27,28] taking into account the well-known interaction of carbonyl moieties with ammonium groups (cf. also ref 17). The back-bended methacryloyl group could then act as "covalently bound cosurfactant".

Emulsion Polymerization. *Emulsion Polymerization Using a Cationic Initiator.* In the first series of investigations, cationic initiator **7** was used to start emulsion polymerization of styrene at 46 °C. In these studies, the charge of the initiator is the same as the charge of the emulsifiers employed. The polymerizations were followed by monitoring monomer conversion, polymer yield and surface tension of the reaction mixture. Except for using polymerizable surfactant **2** (see below), the agreement between monomer conversion and polymer yield was excellent. Time-conversion and time-yield curves are shown in Figure 3, and the characteristics of the final latexes are listed in Table 2.

Employing the reference surfactant **1**, monomer conversion is complete after about 100 min (Figure 3a). The

Table 2. Characteristics of the Final Latexes Obtained with Different Emulsifiers, Using Cationic Initiator 7 at 46 °C

emulsifier	$R_p(\times 10^2)$ (mol/L s)	γ final (mN/m)	M_w	d_H (nm)	d_n (nm)	PDI
1	1.11	54	254 000	69	68	1.09
2	2.64	70		53	43	1.12
3	0.65	69	90 000	76	86	1.05
3*	0.53		94 000	79		
5a	0.16	69	33 000	188	158	1.02
5b	0.24	68	46 000	199	133	1.12
5c	0.69	72	71 000	97	90	1.10

R_p = rate of polymerization at 20% conversion of styrene. d_H = hydrodynamic diameter (by dynamic light scattering). d_n = number average diameter (by SEM). PDI = polydispersity index.

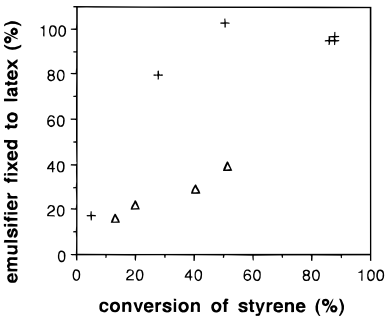


Figure 4. Percentage of the initial amount of polymerizable emulsifier **2** fixed to the latex with increasing conversion of styrene (from IR spectra and elemental analysis data of latexes, using the time-conversion data of Figure 3b). Key: + = cationic initiator **7**; △ = initiator $K_2S_2O_8$.

initially low surface tension of the starting emulsion increases in the course of the reaction. This is attributed to the progressive adsorption of the emulsifier on the latex particles, as generally observed in classical systems.

The use of the polymerizable surfactant **2** gives comparable results (Figure 3b) (i.e., high polymerization rates and yields). The surface tension increases in the course of the reaction even up to 70 mN/m (i.e., close to that of pure water). Noteworthy, the polymerization of styrene is not hindered by the use of the polymerizable surfactant, as reported in some cases.[29−33] Also, initial homopolymerization of **2** prior to the emulsion polymerization of styrene can be excluded because the reactions performed in the presence of **2** and of its homopolymer **3** differ strongly (Figures 3b,c).

To verify copolymerization of styrene with **2**, the isolated polymers were analyzed by IR spectroscopy. The intensity of the C=O stretching band at 1725 cm^{-1}, indicative of **2**, was compared to the intensity of the aromatic C−H deformation band at 756 cm^{-1}. The decreasing intensity of the C=O band with increasing conversion of styrene demonstrates the preferential incorporation of **2** into the latex particles during the early stage of the polymerization. The amounts of emulsifier fixed to the latex could be calculated by calibrating the IR data by elemental analysis of samples isolated at low conversions, in which the high emulsifier content enables acceptable precision (Figure 4). Accordingly, the reactive emulsifier **2** is consumed more rapidly than styrene, but consumption is only complete at about 50% overall conversion.

The preferential consumption of **2** in the early stage of the emulsion polymerization is easily rationalized if we assume reactivity ratios of styrene and methacrylate **2** which are similar to the ones of styrene with methyl methacrylate ($r_1 = 0.52$ and $r_2 = 0.47$)[34] and initiation in the homogeneous phase. The solubility of styrene in water at 46 °C is in the order of 0.004 mol/L%[16] compared to a concentration of **2** of 0.022 mol/L. In any case, the results imply efficient and rather complete fixation of the polymerizable emulsifier on the latex by preferential, but gradual incorporation. The formation of water-soluble homopolymers is avoided. The methacrylate **2** seems therefore better suited for emulsion polymerization of styrene than the frequently studied reactive olefin surfactants[29−32,40,41] or acrylamides.[42] Obviously, there is neither a need for strictly alternating copolymerization of the monomer and the emulsifier as suggested recently[2,43−45] nor for ideal azeotropic copolymerization.[40,46−49]

Copolymers of styrene with surfactant **2**, which are soluble in methanol, are presumably the origin of some analytical problems encountered. Monomer conversion and polymer yield correspond only when lyophilizing the reaction mixture, weighing the residue, and then subtracting the weights of emulsifier, inhibitor, and initiator (Figure 3b). When monitoring the polymer yield, however, by the standard procedure, that is, by final precipitation into methanol, the apparent yields were much lower than monomer conversions.

Emulsions prepared with polysoaps **3** and **5a**−**c** consisted of large droplets of styrene, which demix very rapidly when stopping the stirring. In addition, an upper styrene phase which was progressively consumed was often observed during the polymerization. Nevertheless, high polymerization rates and high yields were obtained using homopolymer **3** or copolymer **5a** (Table 2 and Figures 3c−d), though the rate is somewhat slower than that when using emulsifiers **1** and **2**. However, within the copolymer series **5** (Figures 3d−f), polymer yields and polymerization rates decrease strongly with decreasing hydrophobe content (i.e., **5c** > **5b** > **5a**). Typically, for all polysoaps employed, the reaction mixtures exhibit high surface tensions from a very early stage of the polymerization on. This is in agreement with the low surface activity of the polymeric emulsifiers at the concentration used (cf. Figure 2). The final surface tensions of latexes are very close to the surface tension of pure water (72 mN/m).

The effect of the molar mass of the polysoaps seems to be small. The use of polysoap sample **3*** of substantially lower molar mass ($M_n = 24 \times 10^3$) gives virtually the same results as the use of sample **3** ($M_n = 115 \times 10^3$). This finding corresponds to the negligible effect of molar mass of amphiphilic graft copolymers in emulsion polymerization.[8]

Remarkably, the use of all polysoaps leads to induction periods that were not observed when employing low molar mass emulsifiers **1** and **2**. The length of the induction period varied somewhat from experiment to experiment. No obvious explanation can be given for this phenomenon. There is no indication for impurities in the analytical data (NMR, IR, TLC, and microanalysis). Also, different charges of polysoaps, as well as samples submitted to repeated purification procedures, behave the same. Furthermore, the use of a different initiator, $K_2S_2O_8$, reduces the induction period although its decomposition rate is slower (cf. Figure 5, and discussion below). Therefore, an accidental inhibition by impurities is most improbable. Rather, the induction periods point to a modified, considerably slowed down nucleation mechanism.

Emulsion Polymerization Using an Anionic Initiator. In a second series of experiments, the anionic initiator

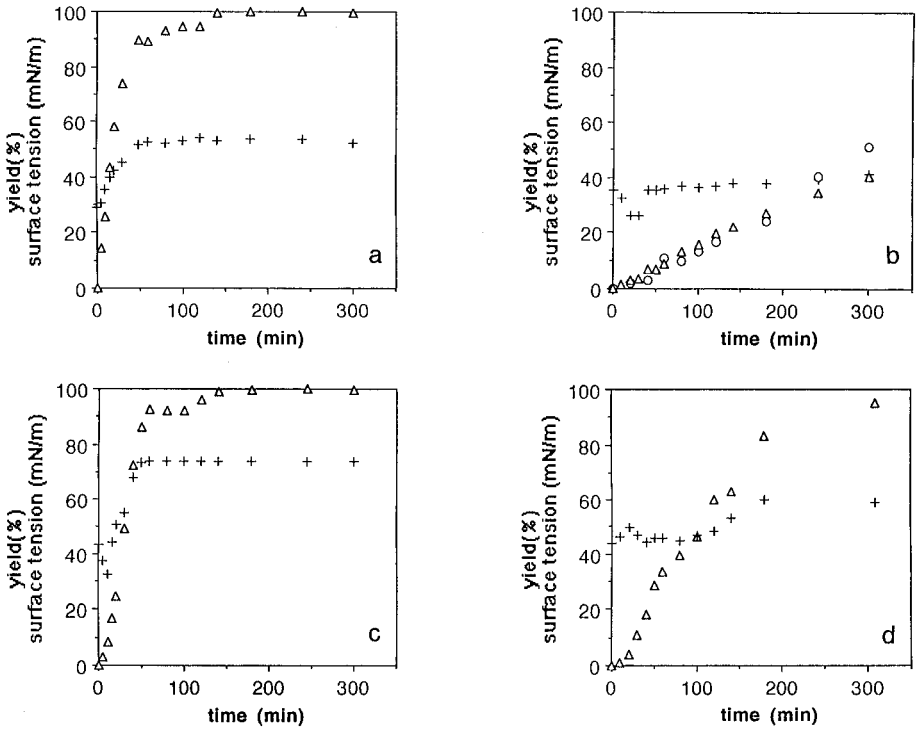


Figure 5. Time-yield curves (△) (isolation by precipitation) and time−surface tension curves (+) for the emulsion polymerization of styrene at 56 °C, using anionic initiator $K_2S_2O_8$ (**8**) and emulsifier (a) standard surfactant **1**; (b) polymerizable surfactant **2**, (○) time conversion curve; (c) polysoap **3** (homopolymer); and (d) polysoap **5c** (hydrophobe content 30 mol %).

Table 3. Characteristics of the Final Latexes Obtained with Different Emulsifiers, Using Anionic Initiator $K_2S_2O_8$ at 56 °C

emulsifier	$R_p(\times 10^2)$ (mol/L s)	γ final (mN/m)	M_w	d_H (nm)	d_n (nm)	PDI
1	2.54	53	1,240,000	73	74	1.02
2	0.13	44		268	779	
3	1.94	72	1,420,000	108	58	1.09
5c	0.69	59	1,780,000	988	617	

R_p = rate of polymerization at 20% conversion of styrene. d_H = hydrodynamic diameter (by dynamic light scattering). d_n = number average diameter (by SEM). PDI = polydispersity index.

$K_2S_2O_8$ (**8**) was used to start emulsion polymerization (Figure 5 and Table 3). Here, the charge of the initiator is opposite to the that of the cationic emulsifier employed. As initial experiments conducted at 46 °C showed only low reaction rates due to the slow initiator decomposition, the studies with **8** were performed at 56 °C.

With the reference emulsifier **1**, emulsion polymerization proceeded very similar when initiating by $K_2S_2O_8$ instead of by cationic **7** (cf. Figures 3a and 5a). This is also true for the tail end-type polysoap **3**, except for the shorter induction period observed (cf. Figures 3c and 5c). The induction period is shortened for the use of the head-type polysoap **5c**, too, but here the polymerization rate is considerably slowed down (Figure 5d). Also, the comparably low surface tension of the starting emulsion increases only up to 60 mN/m in the course of the reaction.

Most important differences are found in the case of polymerizable surfactant **2** when using $K_2S_2O_8$ instead of the cationic initiator **7** (cf. Figures 3b and 5a,b). Polymerization rate and yield are very low, and aggregated polymer separates from the latex at longer reaction times (>80 min). The low polymer yields are real and not due to problematic polymer recovery as discussed above: titration of residual styrene confirmed low monomer conversion, identical to the polymer yield. Following the copolymerization of styrene and **2** by IR analysis of the polymers, the data demonstrate again the preferential incorporation of **2** during the early stage of the polymerization (Figure 4). However the overall amount of **2**, which is incorporated, is markedly reduced when initiating by $K_2S_2O_8$. Also, the surface tension of the reaction mixture remains almost constant throughout the entire polymerization. Thus, the value for the final latex is particularly low (cf. Tables 2 and 3).

The difficulties in preparing latexes with the polymerizable emulsifier and, to a lesser degree, with the head-type polysoap when initiated by K_2SO_8 are striking. Considering possible reasons, we may imagine an efficient scavenging of the anionic initator radicals by the cationic monomer **2**, thus interfering with the polymerization of styrene. The resulting ampholytic/zwitterionic oligomers should be poorly soluble only, thus accumulating at the interface. This could explain the low surface tensions found. The zwitterionic character should also reduce electrostatic repulsion between polymer particles, which would explain the low stabilities of such latexes. In fact, the use of the polymerizable zwitterionic surfactant *N*-((11-methacryloyloxy)undecyl)-*N*,*N*-dimethylammoniopropanesulfonate, which is the zwitterionic analog to **2**, does not yield stable polystyrene latexes.[35] However, these putative explanations are speculative: no particular difficulties were reported in a study concerning polymerizable zwitterionic emulsifiers.[36] The same is true for a study of the copolymerization of cationic polymerizable emulsifiers with methylmethacrylate in water.[20]

Somewhat similarly to the problems when using the polymerizable emulsifier, one could also imagine a strong electrostatic attraction of the anionic initiator to the polysoaps being polycations. But surprisingly, only polysoap **5c** of the head type behaves poorly under these conditions, whereas polysoap **3** of the tail end type still provides good results. This geometry effect is difficult

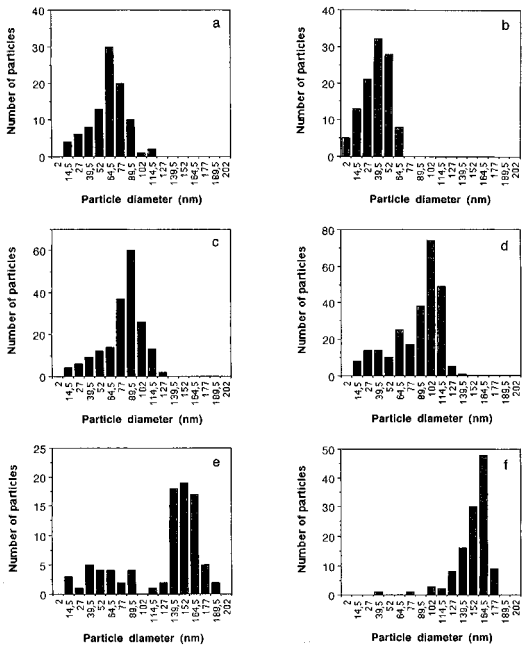


Figure 6. Particle size distribution (from electron microscopy) of polystyrene latexes obtained with cationic initiator **7**, using as emulsifier (a) standard surfactant **1**, (b) polymerizable surfactant **2**, (c) polysoap **3** (homopolymer), (d) polysoap **5c** (hydrophobe content 30 mol %), (e) polysoap **5b** (hydrophobe content 16 mol %), and (f) polysoap **5a** (hydrophobe content 7 mol %).

to explain. Like the induction periods observed, this difference may point to a modified nucleation mechanism when using polysoaps, but at present this is speculative.

In a recent study on the use of cationic head-type polysoaps based on poly(*N*-alkyl-*N*-methyl-*N*,*N*-diallylammonium chloride) copolymers for microemulsion polymerization of styrene,[11] a similar retardation effect was seen when using $K_2S_2O_8$. Comparisons are limited as the styrene content was much lower, and considerable amounts of low molar mass cosurfactants were used. But still, the similarity is remarkable. An analogous retardation of the emulsion polymerization of methylmethacrylate was observed, too, when using charged amphiphilic block copolymers and initiators of opposite charge (e.g., cationic block copolymers and $K_2S_2O_8$ or anionic block copolymers and a cationic initiator[37]). No satisfactory explanation could be given for these systems either.

Characterization of the Latexes. *Sizes and Size Distribution.* The size of the latex particles and their size distributions were studied by SEM and dynamic light scattering (Tables 2 and 3, Figures 6−8). Within the limits of precision, the results from the different methods well agree.

When using the cationic initiator **7**, all emulsifiers gave latexes with narrow particle size distributions (Table 2 and Figure 6). Considering the problems related to the sputtering of the SEM samples with a thin metal layer, the real size distributions may be even narrower. Relatively large particles are formed when using polysoaps **5a** and **5b**. Both have low hydrophobe contents and perform rather poorly, as judged from the low polymerization rates and overall conversions (Figures 3e−f). For the other emulsifiers, small particles of below 100 nm diameter are obtained. Comparing in detail, particle sizes decrease with the use of polysoaps **3**−**5c** > reference **1** > polymerizable emulsifiers **2**. For

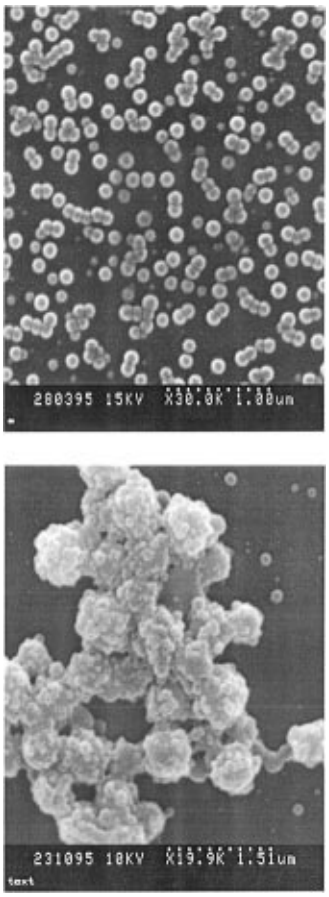


Figure 7. SEM micrographs of polystyrene latexes obtained with polysoap **5c**: (a) using cationic initiator **7**, (b) using anionic initiator $K_2S_2O_8$ (**8**).

the latter, however, the size distribution is slightly broadened.

When exchanging the cationic initiator **7** with anionic $K_2S_2O_8$ (**8**), the situation differs dramatically (cf. Tables 2 and 3). Only latexes prepared with reference **1** appear virtually unchanged. The use of tail end-type polysoap **3** still produces latex particles of narrow size distribution (Figure 8 and Table 3). But the particles are much smaller according to SEM (see below for the apparent differences between diameters determined by SEM and by dynamic light scattering). In contrast, very broad size distributions containing very large particles were obtained with emulsifiers **2** and **5c** (Table 3 and Figures 8b,d), as indicated visually by the strong whiteness of the latexes. The SEM micrographs suggest that the large particles obtained with **5c** result from the aggregation of smaller primary ones (Figure 7), differing from the use of cationic initiator **7**.

Recently, oligo(acrylic acid-*co*-dodecylacrylate) with ca. 30 mol % of hydrophobic chains was employed for the emulsion polymerization of styrene using $K_2S_2O_8$, which is an initiator of identical charge.[12] Formally, the oligomer corresponds to a head−type polysoap, with a hydrophobe content comparable to that of polysoap **5c**. But the molar mass of the "polymeric" emulsifiers was very low with $M_n = 1300$ (i.e., there were in average only 3 hydrophobic chains per emulsifier). Although a much higher amount of emulsifier was used than in our work, the latexes showed bimodal size distributions. This was putatively attributed to the simultaneous polymerization of styrene within the "polymeric micelles" and within the shrinking monomer droplets. After seeing our results with polysoaps **5a**−**c** using

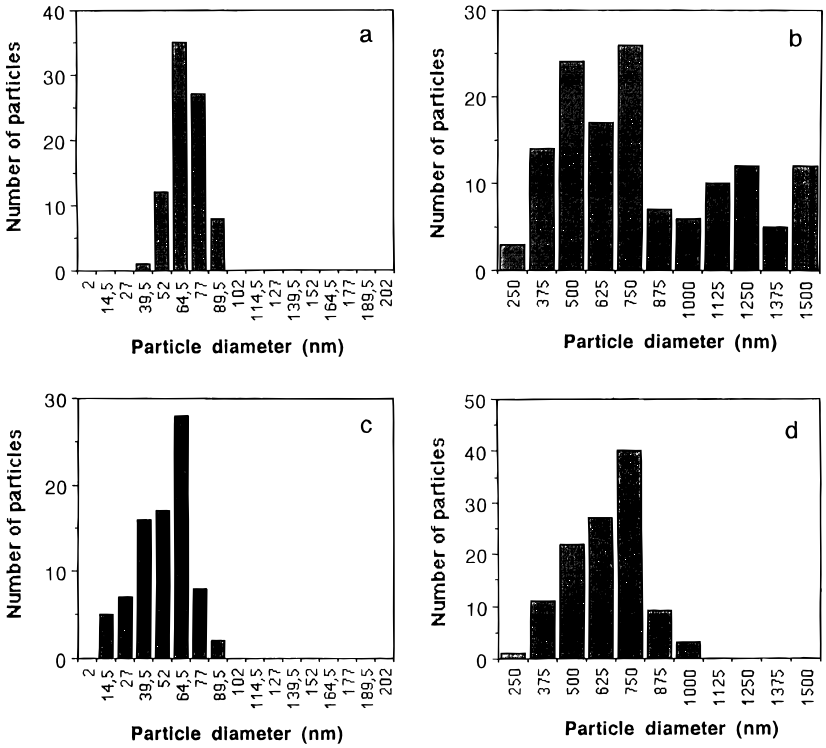


Figure 8. Particle size distribution (from electron microscopy) of polystyrene latexes, obtained with anionic initiator $K_2S_2O_8$ (**8**), using as emulsifier (a) standard surfactant **1**, (b) polymerizable surfactant **2**, (c) polysoap **3** (homopolymer), and (d) polysoap **5c** (hydrophobe content 30 mol %).

initiator **7**, we decided that there must be a different explanation. Perhaps, the bimodal distributions derive from the high polydispersity of the emulsifier. In any case, true polysoaps give obviously monomodal, narrow size distributions.

Stability. Using the cationic initiator **7**, stable latexes were obtained for all emulsifiers, irrespective of the relative stability or instability of the starting styrene emulsions. Under ambient conditions, the latexes are stable for at least 2 years. Exposure to stress by freezing and thawing results in complete precipitation of the latexes prepared with the nonpolymerizable surfactant **1**. In contrast, latexes made with the polymerizable surfactant **2**, as well as with the polysoaps **3** and **5a**−**c**, could be partially redispersed after thawing, thus demonstrating improved stability.

Stability against electrolyte was probed by adding increasing amounts of $Ca(ClO_4)_2$: Ca^{2+} ions bind strongly to anionic surfaces, whereas ClO_4^- ions bind strongly to cationic surfaces. For all emulsifiers used, the latexes start to flocculate at concentrations of about 10^{-2} mol/L of $Ca(ClO_4)_2$. This is also true for latexes made using polysoaps **5a** and **5b** with low hydrophobe content, although increased turbidity points to aggregation starting at salt concentrations as low as 10^{-4} mol/L. Best stabilities are obtained with reference **1** and polymerizable **2** which can tolerate up to 2×10^{-2} mol/L of salt, but the advantage compared to polysoaps **3** and **5c** is small. Therefore, in contrast to the poor stabilization of the starting monomer emulsions, the use of polysoaps does not cause inherent problems for the stability of the final latexes, at least if an initiator of identical charge is used. This is in contradiction to some elder assumptions.[42] Clearly, the polysoaps studied of both geometries (i.e., tail end- and head-type) are useful emulsifiers.

The use of the anionic initiator $K_2S_2O_8$, however, may cause problems, although the oppositely charged emulsifier is employed in large excess (3.24 mmol vs 0.79 mmol). In particular the use of polymerizable emulsifier **2** resulted in unstable latexes. Some aggregated polymer separates from the latex already during the reaction, and a large fraction of the latex flocculates after a few days. This explains the discrepancy between the diameters of the latex particles as determined by SEM and dynamic light scattering in Table 3, as the latter experiments were performed on the supernatant latex after 2 months of storage. Latexes made with the head-type polysoap **5c** are somewhat more stable than the ones made with polymerizable **2**, but partial flocculation occurs within a few months, too.

Latexes with a good long−term stability were only obtained with the reference **1** and polysoap **3**. Stored under ambient conditions, the latexes were stable for at least for 2 years. Still, a closer look to the macroscopically stable latexes revealed that only the ones made with **1** are fully stable and that particle sizes stay constant. Though latexes made with polysoap **3** do not precipitate within 2 years, an initial particle growth upon storage is observed which approaches a final value (Figure 9). Again, this growth may explain the apparent discrepancy between the diameters measured by SEM and dynamic light scattering (Table 3).

The stability against electrolytes of these latexes was probed by added $Ca(ClO_4)_2$, too. The latexes made using reference emulsifier **1** and polysoap **3** exhibit comparable stabilities tolerating $(1-2) \times 10^{-2}$ mol/L of salt. This compares well to the latexes made with the cationic initiator. However, latexes made with emulsifier **2** and **5c** are extremely sensitive to the addition of salt. Even the remaining supernatant latex solutions, after about 2 weeks of storage, flocculate at salt concentrations of 10^{-4} mol/L.

Characterization of the Polystyrenes. The molar masses of the polystyrenes obtained were studied by GPC (Tables 2 and 3). Prior to analysis, all samples were

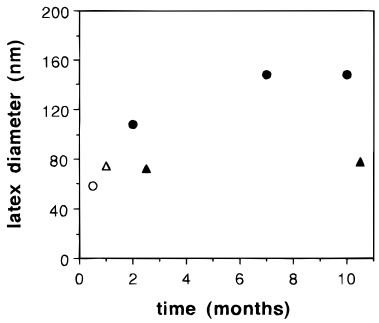


Figure 9. Evolution of particle size of polystyrene latexes with storage time, when prepared with anionic initiator $K_2S_2O_8$ (**8**), using as emulsifier standard surfactant **1** (△ and ▲) and polysoap **3** (○ and ●). Open symbols, number average from SEM data; full symbols, hydrodynamic diameter calculated from dynamic light-scattering data.

purified by precipitation into methanol. This may imply some fractionation, but without the purification step the emulsifiers interfere with the analysis. No meaningful values can be given for the use of the polymerizable surfactant **2**, because the copolymerization with styrene leads to copolymers of unknown retention behavior.

Using cationic initiator **7**, polystyrenes made with reference **1** gave values of M_w of 150 000 at low conversions which increase to 250 000 for the final latex. A comparable analysis for the use of polymerizable emulsifier **2** and polysoaps **3** and **5a**−**c** was not possible because, even if purified, the polystyrenes obtained were partially insoluble in the eluent THF. This effect is particularly pronounced at low conversions. In the case of **2**, this observation can be easily explained by the incorporation of the ionic monomer **2** by copolymerization into the polymers (cf. Figure 4). In the case of the polysoaps, we have to assume partial grafting on polystyrene. In fact, FT-IR spectra of the precipitated polymers exhibit a small signal at about 1730 cm^{-1}, indicative for the ester carbonyl group of the polysoaps, which could not be removed by repeated precipitation. Analysis of the THF soluble fractions exhibited complex polymodal distributions at low conversions, which render a meaningful interpretation of the evolution of the data with increasing styrene conversion difficult. This may be due to small amounts of grafted polysoaps, promoting effects like aggregation in solution, or adsorption to the column material. Therefore, even the figures for the final latexes should be taken with some care. Nevertheless, comparing the data for the different emulsifiers in Table 2, the molar masses of the polystyrenes increase with decreasing size of the latex particles (i.e., with increasing particle number). This is expected from theory.

Generally, the emulsion polymerizations using the anionic initiator $K_2S_2O_8$ at 56 °C gave considerably higher molar masses than those given when using the cationic initiator **7** at 46 °C (cf. Tables 2 and 3). The differences in molar masses obtained when employing reference emulsifier **1** appear reasonable if we assume for a given latex diameter inverse proportionality between the degree of polymerization and the rate of generation of the initiating radicals, because the decomposition rates of the two initiators differ sufficiently[38,39] (**7** at 46 °C in water, $k_d = 7.3 \times 10^{-6}$ s^{-1}; $K_2S_2O_8$ at 56 °C in water, $k_d = 1.8 \times 10^{-6}$ s^{-1}).

As seen when using the cationic initiator, and as postulated by theory, the molar mass of the polystyrenes increases with decreasing particle diameter when $K_2S_2O_8$ is used with emulsifiers **1** and **3** (Table 3). However, the molar mass of polystyrenes obtained with emulsifier **5c** are the highest within the series, though the particle sizes measured are the largest. This inconsistency may be explained by the aggregation of this latex (cf. Figure 7). Possibly, the primary latex particles formed with emulsifier **5c** are very small, thus leading to high molar mass polystyrene.

Analysis of the polystyrenes by DSC showed for all samples glass transition temperatures T_g of 104 °C, independently of using conventional surfactant or polysoaps as emulsifiers. Only polystyrenes made employing polymerizable emulsifier **2** exhibited slightly lower glass transition temperatures T_g of 102−103 °C, T_g increasing with overall conversion. In parallel, the height of the glass transition increases. This last observation fits into the copolymerization behavior of styrene and **2** (cf. Figure 4). However, it should have been expected that T_g increases with incorporation of the ionic comonomer, which is not observed: homopolymer **3** does not show a T_g below its decomposition temperature of about 210 °C.[17] Possibly, the copolymers are phase separated from the pure polystyrene but do not show a separate detectable transition. This may be due to the small percentage of copolymer present or to a large width of the glass transition.

Conclusions

All three types of emulsifiers studied, "classical" surfactants and polymerizable surfactants, as well as polysoaps, are useful in emulsion polymerization. Notably, the hitherto virtually not studied polysoaps compare well with their analogous conventional emulsifiers. Polymerization rates and yields are high, and stable latexes with small, monodisperse particles can be prepared. Whether the nucleation mechanism when using polysoaps is or is not similar to conventional emulsion polymerizations remains an open question. This point may be worthwhile investigating, given the importance for copolymerization or core-shell procedures.

The various emulsifier types show individual features, and their relative performances change with the reaction conditions. This implies that a judicious choice of the emulsifier type will be advantageous for a given problem. For example, the use of initiators of opposite charge causes problems when employing polymerizable emulsifiers and, to a lesser extent, when using polysoaps but does not affect conventional surfactants. On the other hand, polymerizable emulsifiers or polysoap emulsifiers improve the stability of the latexes. Also, the final latex suspensions exhibit very high surface tensions of about 70 mN/m. This is attributed to the efficient fixation of the emulsifier on the latexes, by copolymerization, in the case of the polymerizable emulsifier, or primarily, by adsorption and, to a small extent, by grafting in the case of the polysoaps.

Note Added in Proof: Microemulsion polymerization of styrene with a similar reactive surfactant was reported most recently.[50]

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