Formulation and Stability Mechanisms of Polymerizable Miniemulsions

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ABSTRACT: Polystyrene latexes in a size range of 30−180 nm can be synthesized by polymerization in miniemulsions where the particle size responds to the amount of the surfactant sodium dodecyl sulfate (SDS) which was varied between 0.5 and 50 wt % with respect to monomer. Turbidity and surface tension measurements were used to characterize the miniemulsification by ultrasonication and the approach to a steady state of droplet size. Since size equilibrium seems to be established by a rate equation of collision-induced droplet fusion and ultrasound fission, miniemulsions realize the minimal droplet size for the distinct amount of surfactant; i.e., they are "critically stabilized" with respect to collisions (τ_2 process). Complete stability against Ostwald ripening (τ_1 process) is obtained by the addition of a hydrophobe, which was varied over a broad structural range. The efficiency of this hydrophobic agent is given mainly by a very low water solubility. The growth of the critically stabilized miniemulsion droplets is usually slower than the polymerization time; therefore in ideal cases, a 1:1 copy of droplets to particles is obtained, and the critically stabilized state is frozen. The critical surface coverage of these particles with SDS molecules was determined and depends strongly on the particle size: the smaller the particle size, the higher the required surface coverage with surfactant. The good accessibility of these systems allows to establish a general relation between the macroscopic surface tension of the latex and the microscopic coverage of the particles which is expected to hold true for all latexes. Finally, the characteristics of polymerization in miniemulsions were compared with those of the corresponding processes in macro- and microemulsions.

Introduction

Miniemulsions are classically defined as aqueous dispersions of relatively stable oil droplets within a size range of 50−500 nm prepared by shearing a system containing oil, water, a surfactant, and a so-called "cosurfactant".[1] Polymerization in carefully prepared miniemulsions results in latex particles which have about the same size as the initial droplets,[2] as recently shown by a combination of SANS, surface tension measurements, and conductometry.[3] This means that the appropriate formulation of a miniemulsion suppresses coalescence of droplets and Ostwald ripening, and a virtually 1:1 copying process of the droplets to the particles concerning their sizes can be obtained. In the case of low water solubility of the monomer, monomer molecules in the water phase and in the droplets can exchange to a low extent, but a pseudo-equilibrium is established.[4]

In most cases, miniemulsion recipes are based upon the anionic sodium dodecyl sulfate (SDS) in combination with selectively oil-soluble "cosurfactants". Recently, it was also possible to examine systematically the influence of cationic and nonionic surfactants.[5] It was shown that such miniemulsion formulations use surfactants in a by far more efficient way than microemulsion polymerizations and that they are as efficient as the best emulsion polymerization recipes.

A very important factor for the formulation of stable miniemulsions is the choice of the appropriate "cosurfactant": the substances described in the literature are usually cetyl alcohol, hexadecane,[6−8] dodecyl mercaptan,[9] or reactive alkyl methacrylates.[10] It was also shown[11] that the presence of minor amounts of high molecular weight polystyrene positively influences the polymerization behavior of styrene miniemulsions, i.e., faster polymerization and smaller particle sizes are obtained, and it was speculated about the reasons of this effect.[12] The term "cosurfactant" is rather misleading because in most cases the agent is not a "cosurfactant" in the traditional sense. A cosurfactant by definition[13,14] is a surface-active agent that acts in addition to the surfactant by further lowering the interfacial energy but that cannot form micellar aggregates by itself. Sometimes for the formulation of miniemulsions it is not an amphiphile at all, and barely water-soluble hydrophobes are even much more effective. Hexadecane is not placed on the interface and does not change the interfacial energy.[3] Up to now, there is much speculation about the role of the hydrophobic agent. It is obvious that the Ostwald ripening process is hindered. Long-term stabilities of the miniemulsions are described in the literature,[15] but the reason is not elaborated on. The discussion includes explanations such as the hydrophobes (as hexadecane) acting as "superswelling" agents, whereas the fatty alcohols are assumed to influence the rigidity of the oil/water interfaces or lower the interfacial energy.

In this paper, we will give a more general description of the working principle of miniemulsions and the occurring stability limits by detailed examination of the following points:

1. We will characterize the efficiency of the dispersion process by measuring the turbidity and the interfacial tension in dependence of ultrasonication time. In addition, it is tested whether the particle size depends on the amount of dispersed phase. The dispersion state is related to the droplet stability or coalescence as detected by the final latex size after different equilibration times. This is used to establish a kinetic model of miniemulsion formulation and to introduce the principle of "critical stability".

2. Both the chemical nature and character of the hydrophobic additive in the miniemulsification process are varied over a broad range, and the influence on the final latex size is examined. The chemical variation

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allows exclusion of the importance of a special interaction of the hydrophobe with the interface, whereas variation of the amount enables the evaluation of the influence of the hydrophobe on the osmotic pressure. Variation of the hydrophobe includes substances that are interesting from the application side since it can remain in the final polymer, e.g., oligomeric plasticizers.

3. The amount of surfactant per monomer (the surfactant-to-monomer ratio *S*) will be systematically varied in order to establish a typical relation of the minimum latex size on the surfactant ratio for the anionic model surfactant sodium dodecyl sulfate (SDS).

4. The amount of surface coverage of the final miniemulsion latexes with surfactant molecules is determined by surfactant titration. The resulting interfacial tension of the particle allows the estimation of a Laplace pressure as the relevant driving force for Ostwald ripening.

5. It will be checked whether Laplace pressure and osmotic pressure created by the hydrophobe counterbalance each other in the droplets. A qualitative scenario for the formation and stability of miniemulsions based on both osmotic and colloidal collision stability will be given.

Experimental Section

Synthesis of the Latexes. A 6 g sample of styrene and the respective amount of hydrophobe were mixed and added to a solution of sodium dodecyl sulfate (SDS) in 24 g of water. After stirring for 1 h, the miniemulsion was prepared by ultrasonicating the emulsion for a distinct time, e.g. 120 s, at level 5 with a ultrasonic disintegrator type UD-20 by Techpan. For polymerization, the temperature was increased to 72 °C, and 120 mg of potassium persulfate (KPS) was added. In the case of AIBN as an initiator, 150 mg of AIBN was added to the oil phase prior to ultrasonication, and the reaction temperature was kept at 65 °C. The reaction is usually completed after 2 h, as determined by calorimetry.[5]

Analytical Methods. All measurements regarding the surface tension and the interfacial tension were performed with the K12 processor–tensiometer from Krüss employing the DuNöuy-Ring method. The radius of the Pt–Ir ring RI12 was 9.545 mm, and the wire had a radius of 0.185 mm. Each measurement was repeated 10 times, and the obtained values were corrected with the Zuidema and Waters correction.[16]

The surfactant titration of the latex to determine surface coverage was carried out by successively adding 0.2 mL of a 12 g L^{-1} surfactant solution to 40 mL of the latex. Following each addition the latex was stirred for 60 s, and the surface tension was measured.

The particle sizes were measured using a Nicomp particle sizer (model 370, PSS Santa Barbara, CA) at a fixed scattering angle of 90°. The turbidity measurements were carried out by a process turbiditymeter (FSC 402, Mettler Toledo, Switzerland) with a sensor for high turbidity values which is sensitive to the backscattered light. This sensor was placed directly into 300 mL of a miniemulsion in a 500 mL beaker in order to avoid backscattering from the glass walls. The wavelength of the light was 880 nm.

Results

Miniemulsification Process. To establish a reproducible dispersion procedure, the time of ultrasonication under otherwise unchanged experimental parameters was varied to determine the dependence of the droplet size versus time. The ultrasonication time was chosen to be in the range of 15 s up to 30 min, and the approach to steady state was monitored by both turbidity and surface tension measurements. As shown in Figure 1, the turbidity increased within the first 180 s, decreased afterward, and is constant after about 1000 s of ultrasonication. The surface tension increases from 38 mN m^{-1} before ultrasonication up to 57 mN m^{-1} after 450 s. This high surface tension shows that in the miniemulsion no free micelles are present, and the coverage of the droplets is incomplete. For the polymerization process, we can assume that micellar nucleation is very unlikely. The point that the surface tension levels off earlier is presumably related to the fact that the surface tension is sensitive to the overall surface area of the droplets, whereas the turbidity is also sensitive to the droplet size distribution. Note that in this experiment a 5-fold load compared to the usual recipes was used to slow down the dispersion process.

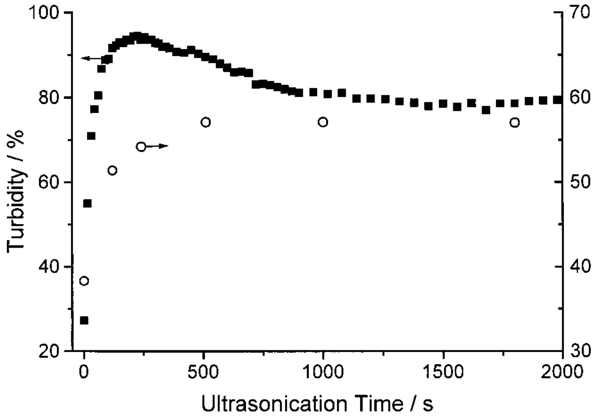

Figure 1. Turbidity and surface tension as a function of the ultrasonication time.

Table 1. Dependence of the Ultrasonication Time on the Particle Diameter[a]

latex	ultrasonication time [min]	diam [nm]	std dev σ	γ [mN m^{-1}]
TIME-1	0.5	135	0.089	63.2
TIME-2	1	112	0.163	66.3
TIME-3	2	96	0.038	67.8
TIME-4	5	87	0.116	68.5
TIME-5	10	84	0.138	68.6
TIME-6	20	83	0.098	68.7

[a] Miniemulsions were formulated by 6 g of styrene, 250 mg of hexadecane, 72 mg of SDS, and 24 g of water.

Afterward, these miniemulsions were rapidly polymerized within 10 min and the most 2 h, and the resulting polymer particles were characterized by dynamic light scattering after dilution. These data are summarized in Table 1.

The temperature during miniemulsification was varied from 0 to 60 °C and does not have a systematic effect on the particle size. It is worth mentioning that the stability of the resulting miniemulsion depends on the degree of dispersion: a system in the steady state with the related smaller particles shows a stronger tendency to aggregation as compared to a less well-dispersed system. This is due to a lower surface coverage with surfactant as well as a higher collision rate of the smaller droplets.

The reaching of the steady state depends on the total shear applied to the systems; the duration and the degree of ultrasonication are connected to each other.

This process was characterized by polymerizing the miniemulsions after different delay times, resulting in the latex diameters shown in Figure 2. A stable situation is reached after some hundred hours where particle size apparently stops to change, and it is assumed that

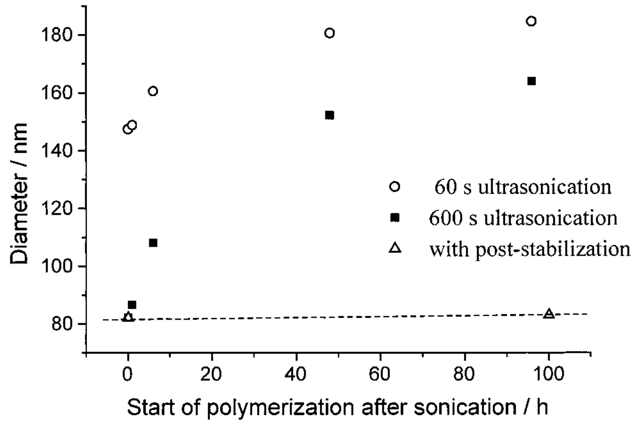

Figure 2. Influence of a delay time between the ultrasonication and the polymerization on particle size.

a colloidally stable situation is reached. The polydispersity of these matured miniemulsions is very low and can reach values as small as 5% Gaussian width. A less well sonicated system obviously reaches the same limiting value, but the change in size is smaller. This maturing process ought to be compared with the overall polymerization time which is for miniemulsions usually between 10 min and 2 h; therefore, the change in particle size remains unobserved in rapid procedures.

A very important deduction of this scenario is that miniemulsions can be stabilized by adding a second aliquot of surfactant after the miniemulsification. This second load, if small enough, is not used to increase the droplet number but to complete the surface coverage of each minidroplet. It has to be noted that the surface should not be fully covered in order to avoid the formation of new (and therefore smaller) droplets by the existence of micelles. Indeed, a miniemulsion which was brought by secondary surfactant addition to 45 mN m^{-1} surface tension did not undergo maturation, as also shown in Figure 2. This step to bypass the per se "critical stabilization" of a miniemulsion might become very important for the transfer of such processes in production and technology.

As a matter of principle, there are two different processes that can provide an instability of emulsions: by diffusion from smaller to larger droplets (Ostwald ripening) or by collisions of droplets. An easy way to distinguish between an osmotically controlled steady state dominated by Ostwald ripening (τ_1 mechanism) or a state controlled by collision rates and colloidal stability (τ_2 mechanism) is a variation of the amount of the dispersed phase.

Miniemulsions with different solids contents of 5, 10, 15, 20, and 25% were prepared (20 min of ultrasonication) by varying only the water content and by keeping the monomer-to-surfactant-to-hydrophobe ratio constant, and the particle sizes of the polymerized particles were measured to be 67, 70, 78, 83, and 88 nm, respectively (Figure 3). We expect the particle size to increase with decreasing volume fraction for a τ_1 process, whereas particles become smaller with decreasing amount of dispersed phase for a τ_2 process. Therefore, we can deduce that the steady-state droplet size in miniemulsification is established by a rate equilibrium of the fission of droplets by ultrasound and droplet fusion due to insufficient colloidal stability. Exchange of monomers via the continuous phase after droplet formation is of secondary importance.

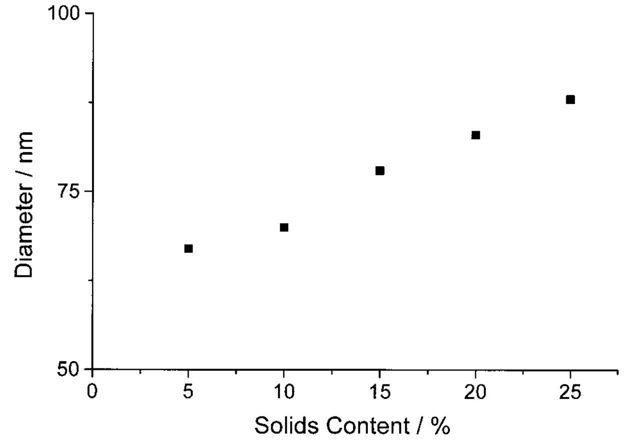

Figure 3. Dependence of the diameter with increasing solids content.

This kinetic mechanism also explains the comparably fast approach to the steady state of dispersions as well as the observed maturing, which presumably is due to collision processes. Since a steady state is the product of a rate equilibrium at a distinct concentration and temperature, the system is per definition "critically stabilized": smaller droplets with a lower surfactant coverage already have fused whereas all larger droplets were split. This underlines that miniemulsions make use of the surfactant in the most efficient way possible.

The Role of the Hydrophobe and Its Efficiency. Since previous work has excluded the possibility of the "cosurfactant" hexadecane to act as a surface-active agent,[2] it is assumed that the use of a small percentage of a hydrophobe allows to build up an osmotic pressure in the droplets which provides stability against Ostwald ripening, i.e., suppresses the dominance of a τ_1 mechanism. In other words, if the hydrophobic molecules are confined in each miniemulsion droplet, a change in droplet size by evaporation (or diffusion) of monomer causes the osmotic pressure to increase with decreasing radius R as $\Pi \sim R^{-3}$ (whereas the Laplace pressure just goes with R^{-1}), which effectively stops the shrinkage or growth, respectively. It is evident that the less water-soluble the hydrophobe is, the more effective it is as an osmotic pressure agent.

On that basis, a wide variety of hydrophobes were selected, and a number of miniemulsion latexes were prepared leaving all experimental parameters constant except for the nature of the hydrophobe. In most cases the molar ratio of hydrophobe to monomer was chosen to be 1:52. In the case of hexadecane, different concentrations of the hydrophobe were investigated. All formulations were compared on the basis of the size and polydispersity of the freshly polymerized latexes. These data are summarized in Table 2.

It is found that all "ultrahydrophobes" (water solubility less than 10^{-7} mL mL^{-1}) can be employed as very effective osmotic agents, and miniemulsions are obtained. In addition, the particle size after polymerizing the minidroplets does not or does just weakly depend on the amount of the hydrophobe. This was already shown by other groups.[8,10,17] It was found that a minimum molar ratio of the hydrophobe to the monomer of about 1:250 is required in order to be able to build up an osmotic pressure in the droplets. This also explains the fact that a small amount of a high molecular weight polymer, e.g. styrene, can barely act as an osmotically stabilizing agent.[18] In the case that the

Table 2. Variation of the Hydrophobe and Its Influence on Latex Characteristics[a]

latex	hydrophobe	surfactant	diam [nm]	std dev σ	γ [mN m^{-1}]	A_{surf} [nm^2]
ISMEHD1	hexadecane (20 mg)	SDS	108.5	0.132	67.5	2.63
ISMEHD3	hexadecane (100 mg)	SDS	108.2	0.077	67.4	2.64
ISMEHD4	hexadecane (250 mg)	SDS	101.5	0.115	67.2	2.81
ISMEHD6	hexadecane (400 mg)	SDS	100.6	0.096	67.4	2.84
NBME8	decahydronaphthaline (166 mg)	SDS	78.3	0.245	68.4	3.63
NBME9	octamethylcyclotetrasiloxane (338 mg)	SDS	108.7	0.210	58.9	2.64
NBME10	tetraethylsilane (160 mg)	SDS	99.0	0.099	68.2	2.79
NBME11	perfluoromethyldecalin (573 mg)	SDS	88.3	0.173	67.8	3.23
NBME12	hexafluorobenzene (212 mg)	SDS	86.2	0.262	69.2	3.30
NBME13	olive oil (526 mg)	SDS	79.6	0.317	52.8	3.56
FTME98	polyester[b] (100 mg)	SDS	82.0	0.238	50.1	3.43

[a] Amounts of 6 g of styrene, 72 mg of SDS, and 24 g of water were kept constant. The polymerization was started with 120 mg of KPS. [b] $M_w = 1.33 \times 10^4$ g mol^{-1} synthesized from adipinic acid and 1,6-hexanediol.

absolute value of the osmotic pressure would control the droplet size, by doubling the amount of the hydrophobe, the diameter would decrease by a factor of 2. Therefore, it is not the absolute osmotic pressure which influences the particle size, but the bare presence of a hydrophobe. The typical diameter of those droplets and the corresponding latexes is about 80 nm, with a rather narrow particle size distribution. The siloxanes produce slightly larger particles of about 110 nm in diameter, but these molecules are also known to be attracted by the latex surface which modifies the hydrophobe distribution in some unknown way. We have also determined the surface tension of the final latexes (against air), and indeed for all hydrophobes that are also surface-active a lowered surface tension was found.

Table 2 also includes the data of the particle surface area per SDS molecule A_{surf}, which was calculated according to the procedure described earlier[5] assuming that the equilibrium concentration of surfactant is molecularly dissolved.

Variation of the Amount of Surfactant and Particle Size Control. Steady-state miniemulsification leads to critically stabilized minidroplets, and the size depends directly on the surfactant concentration. Due to the fact that the surface tensions of the miniemulsion and the resulting latex are very similar to each other and that the particle sizes are equivalent as measured earlier by SANS,[3] we will extrapolate the latex surface properties to those of the droplets. For verification, latexes using miniemulsion polymerization were synthesized in a very broad range of surfactant-to-monomer ratios S (weight ratio of SDS to monomer) in the range of $0.015 < S < 0.5$, keeping the latex concentration at 20 wt % and ultrasonicating up to the steady-state limit. The employed surfactant-to-monomer ratios connect the previous limits of emulsion polymerization and microemulsion polymerization.

By changing the surfactant concentration, one can reproducibly obtain latexes with diameters between 30 and 180 nm (Table 3). A latex with 32 nm is already translucent and very close in size to what was obtained in a microemulsion polymerization, using no hydrophobe but a 4-fold amount of a SDS/alcohol mixture (compare to El-Aasser's microemulsion:[19] $S = 1.87$, $d = 30$ nm).

Plotting the particle diameter versus the inverse weight fraction of the surfactant $(W_M + W_{surf})/W_{surf}$ (with W_M and W_{surf} the weight of monomer and surfactant, respectively) gives a line where the slope is directly related to the surface area per surfactant molecule.[20] The SDS miniemulsion data are shown in Figure 4.

Table 3. Characteristics of the Latexes Synthesized with Different Amounts of SDS[a]

latex	SDS	S	diam [nm]	std dev σ	A_{surf} [nm^2]	γ [mN m^{-1}]
DOME26	3.000	0.500	32.4	0.285	0.20	32.0
KLME69	1.512	0.252	42.2	0.211	0.32	34.9
KLME68	1.019	0.170	46.0	0.203	0.44	43.5
KLME67	0.619	0.103	55.2	0.220	0.60	47.4
KLME66	0.407	0.068	64.5	0.156	0.79	51.6
KLME64	0.296	0.049	81.7	0.181	0.97	59.0
KLME82	0.208	0.035	81.5	0.319	1.21	60.4
KLME65	0.148	0.025	67.1	0.201	1.62	62.4
KLME83	0.126	0.021	88.9	0.279	1.84	63.5
KLME84	0.088	0.015	94.4	0.105	2.47	67.1
KLME85	0.060	0.010	107.7	0.100	3.18	69.0
KLME86	0.032	0.005	133.8	0.251	4.80	70.3
KLME87	0.016	0.003	180.3	0.177	7.12	70.1

[a] The amounts of styrene, hexadecane, and water were kept constant.

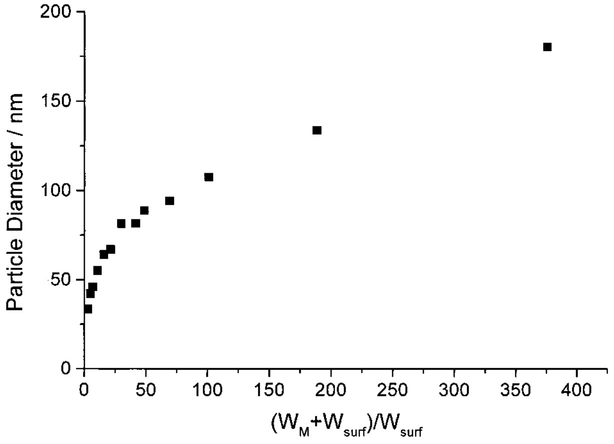

Figure 4. Particle size versus surfactant concentration for the SDS latexes with KPS as initiator.

Contrary to microemulsions, the slope changes continuously, indicating a decreasing surface coverage with increasing particle size. The A_{surf} data as calculated from particle size and the stoichiometry are depicted in Figure 5.

It is seen that the whole range from a dense surfactant monolayer ($A_{surf} \approx 0.4$ nm^2) down to very incompletely covered latex particles ($A_{surf} \approx 7$ nm^2) is observed. Below $S = 0.01$ or 1% surfactant, the dispersions start to become unstable, indicated by an increasing amount of coagulum, which is presumably related to the very low surface coverage with surfactant. On the other hand, A_{surf} values of 0.2 nm^2 indicate the presence of free surfactant micelles or multilayer adsorption, which are not considered in these simplified area calculations. It is also derived that A_{surf} depends in a very systematic fashion on the particle size which is described by two straight lines; the intercept at about $d = 80$ nm

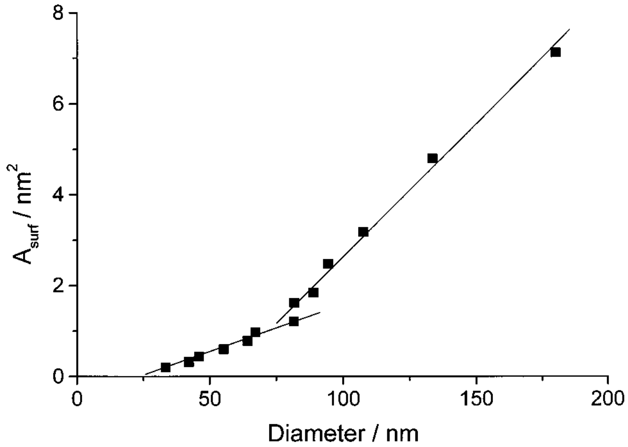

Figure 5. A_{surf} versus the diameter of the particles.

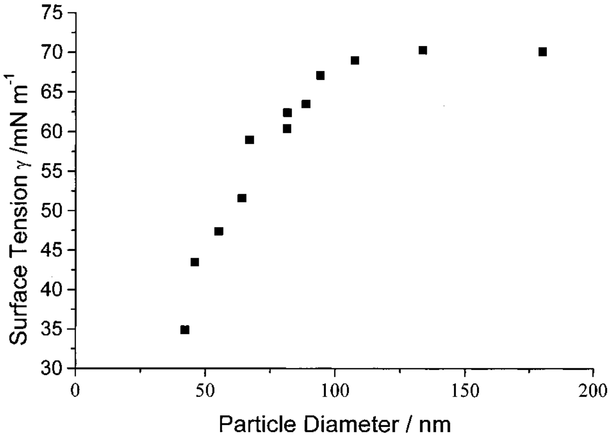

Figure 6. Surface tension versus particle diameter. SDS as surfactant and KPS as initiator were used.

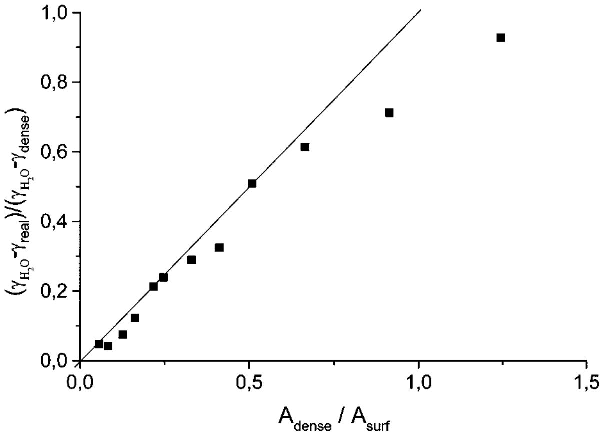

Figure 7. Correlation between the surface tension γ_{real} and the surface coverage A_{surf}.

indicates a change in the surfactant distribution or the stabilizing potentials which cannot be further specified now.

Since the surface tensions of the each initial miniemulsion and the corresponding final latex are very similar to each other, we deduce that the surfactant distribution of surfactant molecules on the droplets or particles, on the water/air interface, and in the solution is alike. Therefore, we base the following discussion on the correspondence principle of miniemulsions and their latexes. The different surface coverages are again explained by the "principle of critical stabilization": small droplets with their high number densities and lower absolute droplet-to-droplet distance rely on a dense surfactant layer to stay stable whereas big droplets tolerate to be less well protected. This point again underlines that collision stability as compared to osmotic stability is the limiting factor governing the formation of miniemulsions.

Surface Tension and Latex Coverage. It is a matter of course that the different surface coverages of the latex particles with surfactant (a molecular property) are also reflected in the corresponding surface tensions of the latexes against air γ (a macroscopic property), which are also given in Table 3. The relation of γ and the latex diameter is plotted in Figure 6.

An increase of the surface tension with increasing diameter is observed. Particles with diameters exceeding 100 nm have a surface tension close to pure water; i.e., there is practically no free surfactant left in the solution. This is due to the fact that the bare particle surface is so large that adsorption equilibrium ensures a very low surfactant solution concentration, and the surface tension also being controlled by the equilibrium concentration of free surfactant is close to the one of pure water.

Smaller droplets, on the other hand, need a higher surface coverage in order to reach stability. The resulting polymer particles also show the same high surface coverage. Thus, the corresponding equilibrium concentration of surfactant is rather high, but the concentration usually stays well below the cmc value; i.e., in most miniemulsions, there are no free micelles. Just as in the case of the highest surfactant loads, $S = 0.5$, a dense surface layer and a γ typical for a micellar phase are observed. We take this value as a definition that we leave the composition region of the miniemulsification process.

The good accessibility of latex particles with different surfactant densities opens the possibility to correlate the macroscopic surface tension with the microscopic latex coverage. The easiest way to do so is to compare the relative effects: if we assume that a completely covered particle/water interface ($A_{surf} = A_{dense}$) is in equilibrium via solution with a completely covered latex/air surface (the saturation value γ_{dense} for SDS is known to be 35 mN m^{-1}), and if we also assume that a naked latex surface corresponds to a bare water surface γ_{water} (72 mN m^{-1}), then we can plot all experimental value pairs γ_{real} and A_{surf} as

$$\frac{\gamma_{H_2O}-\gamma_{real}}{\gamma_{H_2O}-\gamma_{dense}}=\frac{A_{dense}}{A_{surf}} \qquad (1)$$

In this curve, the origin (0,0) represents a bare particle surface whereas the point (1,1) stands for the completely covered latex. The experimental values are shown in Figure 7, where a $A_{dense} = 0.4$ nm^2 was assumed.

It is seen that all data follow a straight line interpolating between the two limits, and it can be derived that the interfacial energy of an incompletely covered latex is simply given by a sum law. No excess contributions become visible. Only at very low surface coverage of the particles is a deviation from the straight line observed. This simple law should be valid for all latex dispersions and establishes the basis to recalculate the surfactant surface coverage from the macroscopic surface tension by eq 1.

The recalculation of latex interface energies also allows one to calculate an accurate Laplace pressure p_{Laplace} inside the original miniemulsion droplet by

$$\frac{3\gamma_{\mathrm{LL}}}{R} = p_{\mathrm{Laplace}} \tag{2a}$$

with

$$\gamma_{\mathrm{LL}} = \frac{A_{\mathrm{dense}}}{A_{\mathrm{surf}}}\gamma_{\mathrm{LL,dense}} + \left(1 - \frac{A_{\mathrm{dense}}}{A_{\mathrm{surf}}}\right)\gamma_{\mathrm{LL,naked}} \tag{2b}$$

with the droplet radius R and γ_{LL} being the interface energy of oil droplet and water phase. $\gamma_{\mathrm{LL,naked}}$ and $\gamma_{\mathrm{LL,dense}}$ are the interfacial tensions at the water/styrene interface without and with SDS coverage and are determined to be 35 mN m^{-1} and 2 mN m^{-1}, respectively. For a typical recipe, e.g., $S = 0.012$ ($R = 50$ nm and therefore $\gamma_{\mathrm{LL}} = 30$ mN m^{-1}), this results in a Laplace pressure of 18 bar as a maximum driving force for Ostwald ripening.

This Laplace pressure is counterbalanced by an osmotic pressure which is given by

$$\Pi_{\mathrm{osm}} = \frac{RTc}{M} \tag{3}$$

For $S = 0.012$, this results in 4.5 bar or an osmotic pressure well below the Laplace pressure. Therefore, it is important to note that the droplet size is not given by an effective zero droplet pressure, i.e., $p_{\mathrm{Laplace}} - \Pi_{\mathrm{osm}} = 0$, which would represent a “real” thermodynamic equilibrium state. A state of equal effective pressure in each droplet, however, also stabilizes the miniemulsions effectively against Ostwald ripening; this corresponds to finding the minimum of free energy under the constraint of constant droplet number. The reason for that is that the osmotic pressure increases with decreasing droplet size with R^{-3} (for immobile ultrahydrophobes), whereas the balancing Laplace pressure just goes with R^{-1}. The creation of smaller and bigger droplets from a homogeneous population therefore is connected with a loss in free energy and does not occur. This again underlines the earlier statement that miniemulsions are thermodynamically stable against Ostwald ripening (although the effective pressure is not zero), whereas colloidal or collision stability is the factor which primarily governs the droplet number and the related latex size for each surfactant and monomer concentration.

Comparison of Polymerization in Miniemulsions with Emulsion Polymerization and Microemulsion Polymerization. Because miniemulsions are formally very similar to emulsions and microemulsions, a discussion on the basis of the above given findings is meaningful to differentiate between the different kinds of heterophase polymerization.

The differences between emulsion polymerization and miniemulsion polymerizations are obvious: in emulsion polymerization, the latex particle does not correspond to the primary emulsion droplet, and the size is established by kinetic processes where kinetic parameters such as the temperature or the amount of initiator play a predominant role. These factors remain unseen in miniemulsion polymerization where the latexes are essentially a polymerized copy of the original droplets, the size of which is essentially given by the dispersion process and droplet stability, but not by polymerization parameters.

Both polymerization in microemulsions and in miniemulsions start from a highly dispersed state, and in critical situations a differentiation can be a little bit more delicate. However, a list of points for checking can be given:

1. Steady-state dispersed miniemulsions are osmotically stable but critically stabilized with respect to colloidal stability. Microemulsions are, on the other hand, in an equilibrium with respect to both τ_1 and τ_2 processes.
2. The interfacial energy between the oil and water phase in a microemulsion is close to zero, which is not the case for a miniemulsion. The surface coverage of the microemulsion phases by surfactant molecules is complete, whereas it is not for a miniemulsion.
3. The formation of a miniemulsion requires high mechanical agitation to reach a steady state given by a rate equilibrium of droplet fission and fusion, whereas formation of microemulsions is usually spontaneous.
4. The osmotic stability of miniemulsion droplets results from an osmotic pressure in the droplets which controls the solvent or monomer evaporation. The osmotic pressure results by the addition of a hydrophobe which has an extremely low water solubility. This crucial prerequisite is usually not present in microemulsions but can be added to increase the stability. It is also expected that such microemulsions undergo structural changes to establish a situation of zero effective pressure instead of zero Laplace pressure. Such “osmotically stabilized microemulsions” are, however, out of the scope of the present contribution.
5. During the polymerization, the original droplets of microemulsions usually grow, whereas in miniemulsions this growth can be suppressed. This is due to the fact that a growing polymer chain, formed at the beginning in just some of the droplets, modifies the thermodynamics, for instance by its osmotic pressure and its conformational entropy. The rapid monomer and surfactant exchange results in a growth of the initially formed droplets. In miniemulsions the monomer diffusion is balanced by a high osmotic background of the hydrophobe which makes the influence of the polymer less serious.
6. The amount of surfactant required to form a polymerizable miniemulsion with SDS was between $0.005 < S < 0.25$, which is well below the surfactant amounts required for microemulsions. For high S values, there might occur some overlap, but also in these regions, the miniemulsions represent the state with higher dispersity, as indicated by their surface tensions or characteristic sizes.

Conclusion

We have shown that polymerization of styrene in miniemulsions stabilized with 0.5–50 wt % SDS relative to the monomer resulted in stable polymer dispersions with particle diameters between 30 and 180 nm and narrow particle size distribution. By on-line turbidity measurements and off-line determination of surface tension in the unpolymerized miniemulsion with monomer droplets, it was found that miniemulsions reach a steady state after a certain sonication time.

Steady-state miniemulsification results in a system “with critical stability”; i.e., the droplet size is the product of a rate equation of fission by ultrasound and fusion by collisions, and the minidroplets are as small as possible for the time scales involved. It turned out that the droplet growth by monomer exchange or τ_1 mechanism is effectively suppressed by addition of a very hydrophobic material, whereas droplet growth by collisions or the τ_2 mechanism is subject to the critical conditions mentioned above. It is however possible to obtain long-term colloidal stability of miniemulsions by addition of an appropriate second dose of surfactant after the dispersion step.

The hydrophobe turns out to be the key component for miniemulsification, and the predominant requirement for this agent is an extremely low water solubility (less than 10^{-7} mL mL^{-1}), independent of its chemical nature. Both the amount and the type of hydrophobe were varied over a broad range, and essentially all systems turned out to produce stable miniemulsions with similar structural characteristics. The fact that the amount of the hydrophobe does not have any impact on the particle size led us to the conclusion that not the absolute value of the osmotic pressure but the bare presence of this agent is decisive. Variation of the hydrophobe included oligomeric esters, which are valuable additives for film formation (plasticizers) and which—opposite to hexadecane—are allowed to remain in the final product.

Usually the growth of minidroplets is slower than the polymerization time, and a situation very close to a 1:1 copying of the droplets to particles is obtained, freezing the critically stabilized state. The surface coverage with SDS molecules of this state depends strongly on the particle size and can be determined by surfactant titrations and surface tension measurements. The smaller the droplets are and the more collisions they undergo, the more dense the coverage of the particles with surfactant needs to be to keep the miniemulsion stable. That way it was possible to determine the maximum surface area per SDS molecule in dependence of the particle size and latex concentration. We also established a relation between macroscopic latex surface tension and microscopic surface coverage, which is expected to hold true for all polystyrene/SDS/water dispersions.

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