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Recent Developments in Miniemulsions –

Formation and Stability Mechanisms

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SUMMARY: Polystyrene latexes in a size range of 30 nm to 180 nm can be synthesized by polymerization in miniemulsions. Since size equilibrium seems to be established by a rate equation of collision induced droplet fusion and ultrasound fission, miniemulsions realize the minimal particle 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 hydrophobe agent is mainly given by its very low water solubility. The growth of the critically stabilized miniemulsion droplets is usually slower than the polymerization time, and a 1:1 copy of the particles is obtained, 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 surface coverage with surfactant is required in order to realize the critically-stable state.

Introduction

Nowadays, we know at least three different groups of emulsion polymerization techniques, namely the macro-, mini- and microemulsion polymerization. In the *macroemulsion* (or conventional emulsion) polymerization one starts from large monomer droplets and surfactant micelles in the water phase. During the polymerization, the monomer diffuses through the water phase, and particles with a diameter of usually larger than 100 nm are formed. Due to the increase of the interfacial area, the surface tension of a latex increases with polymerization. In *miniemulsion* polymerization1), relatively stable oil droplets with interfacial tensions larger than zero and droplet sizes within a size range of 50 to 500 nm are prepared by shearing a system containing oil, water, surfactant, and a water insoluble hydrophobe. These minidroplets can be polymerized to polymer latex particles, ideally in a 1:1 copying process. The identity of the monomer droplets before and the particles after the polymerization was recently shown by a combination of SANS, surface tension measurements and conductometry2). The diffusion of monomer through the water phase is suppressed by the

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addition of a hydrophobe to the monomer phase. Due to a constant low coverage of the droplets and particles with surfactant, the surface tension remains constantly high. Depending on the choice of the surfactant, particles with an anionic, cationic or nonionic surface can be polymerized$^{3)}$.

The third type of emulsions are the *microemulsions*. They are thermodynamically stable with an interfacial tension at the oil/water interface close to zero. The high amount of surfactant which is required for the preparation leads to complete coverage of the particles, and therefore the surface tension of the microemulsion reaches the minimum value. During the polymerization, the particle size increases and results in latexes of 5 to 50 nm$^{4)}$, in coexistence with empty micelles.

In this paper, we will focus on the stability mechanisms for the formation of miniemulsions. A main interest is set on the role of the hydrophobe. It has been reported recently that the hydrophobe acts as an osmotic agent and therefore suppresses Ostwald ripening$^{5)}$. The growth of the droplets by collision is still possible until the osmotic pressure and the Laplace pressure is equilibrated.

Results

In the miniemulsification process, the oil phase consisting of monomer and a hydrophobe is dispersed in the water phase by means of an adequate amount of surfactant by fast stirring and the efficient use of ultrasonication: small droplets in the size range of 30 –500 nm with sufficient stability are created. The size of the droplets directly after the miniemulsification mainly depends on the amount and type of the surfactant and the ultrasonication time. The efficiency of the miniemulsification process was characterized by measuring the turbidity and the interfacial tension in dependence of ultrasonication time$^{5)}$. It was figured out that an ultrasonication time of 10 min is required for a system containing 18 g of styrene, 750 mg of hexadecane, 226 mg of SDS and 72 g of water in order to obtain a steady state with a constant droplet size. A further reduction of particle size is not obtained.

In principle, for dispersed droplets after this miniemulsification, there are two mechanisms which can lead to changes in the particle number and particle size: the growth by Ostwald ripening (τ_1 process) and the growth by collisions between the droplets (τ_2 process).

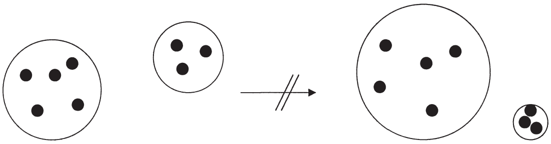
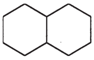
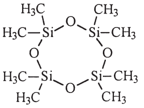
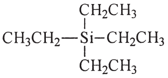
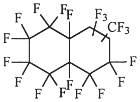
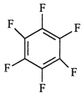


Figure 1: *The hydrophobe suppresses Ostwald ripening. The driving force is to avoid an off-balance of the osmotic pressure.*

Table 1: *Characteristic of latexes synthesized with varying hydrophobes.*

hydrophobe	diameter [nm]	γ [mN m^{-1}]	A_{surf} [nm^2]
$CH_3-(CH_2)_{14}-CH_3$	102	67.2	2.81
	78	68.4	3.63
	109	58.9	2.64
 $Si(CH_2CH_3)_4$	99	68.2	2.79
	88	67.8	3.23
	86	69.2	3.30
olive oil	79.6	52.8	3.56
polyester	82	50.1	3.43

Growth by Ostwald ripening

By using hydrophobes for the preparation of miniemulsions, the stability of the emulsions is significantly enhanced. As standard hydrophobes hexadecane and cetylalcohol were used[6-8]. The use of agents such as alkyl mercaptanes[9] and blue dye[10] also has been reported. To our knowledge, the hydrophobe suppresses Ostwald ripening efficiently by creating an osmotic pressure in each droplet. The most important requirement of the hydrophobe is its low water solubility. In Fig. 1 the effect of the osmotic pressure is shown schematically. In the case of monomer diffusion from the smaller droplet into the larger droplet (the usual Ostwald ripening) the pressure in the smaller droplet would increase more than the Laplace pressure driven by the droplet interfacial tension, and the process is therefore inhibited. The chemical nature of the hydrophobic additive in the miniemulsification process was varied over a broad range, and the influence on the final latex size was examined (Tab. 1). The chemical variation allows exclusion of the importance of a special interaction of the hydrophobe with the interface. Variation of the hydrophobe includes substances which are interesting from the application side since they can remain in the final polymer, e.g. oligomeric plastizisers.

Growth by collision

The growth of the droplets by collisions (τ_2 process) was monitored at different times after the miniemulsification5). This way, the droplet stability or coalescence of the minidroplets was characterized by the size of the polymerized latexes after different equilibration times. Being in the steady state of miniemulsification, a system with 6 g of styrene, 250 mg of hexadecane, 24 g of water and 72 mg of SDS results in a particle size of 82 nm if the polymerization is carried out with 120 mg of KPS directly after 5 min of sonication. Depending on the delay time between the miniemulsification and start of the polymerization reaction, the particles grow up to a maximum size of 180 nm.

It was also proven that the droplet size depends on the amount of dispersed phase. With decreasing dispersed phase, the particle size also decreases. Miniemulsions with different solid contents of 5, 10, 15, 20, and 25 % were prepared (20 min of ultrasonication), and the particle sizes of the polymerized particles were measured to be 67, 70, 78, 83 and 88 nm, respectively. This can be explained by the decreased number of collisions induced by fusion processes during the ultrasonication, the fission of droplets is more effective.

Coverage of the particles

The amount of surfactant per monomer, S, is systematically varied in order to establish for the anionic model surfactant sodium dodecyl sulfate (SDS) the relation between the minimum latex size and the surfactant ratio. The surface coverage of the final miniemulsion latexes with surfactant molecules is determined by surfactant titration. It was found that the surface area per molecule SDS increases with increasing particle size (Fig. 2). This means that the smaller the particles are, the more surfactant per interfacial area is required to obtain a steady state after miniemulsification. For particles with a size of about 180 nm, one SDS molecule per 5.5 nm^2 interfacial area is necessary, whereas for particles with an diameter of less than 50 nm the value is less than 0.4 nm^2, indicating that a close to

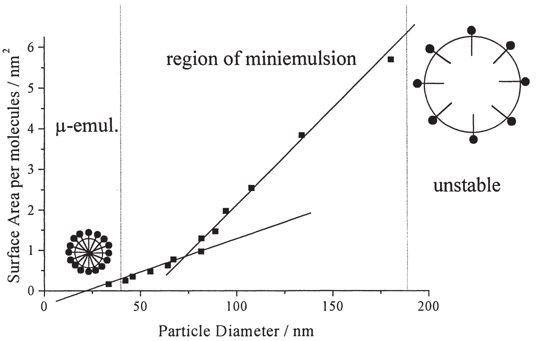


Figure 2: Dependence of the surface area per SDS molecule on the particle size. The smaller the particles are, the more surfactant is required to obtain stable systems.

complete coverage of the particles is achieved. By definition, we are leaving the region of miniemulsion at full coverage of the particles, the emulsion with smaller droplets stabilized by SDS has to be understood as an osmotically stabilized microemulsion. On the other side, particles larger than 180 nm cannot be obtained by steady state miniemulsification (rate equilibrium) since the systems become unstable and we are leaving the region of miniemulsions.

Pressure balance

It was checked whether Laplace pressure produced by the interfacial energy and osmotic pressure created by the hydrophobe counterbalance each other in the droplets. The variation of the amount of the hydrophobe enables the evaluation of the influence of the hydrophobe on the osmotic pressure. In the case of pressure balance, the particle size should decrease by a factor of 2 if the amount of the hydrophobe is doubled (see equation 1)

$$\Pi_{osm} V = \gamma_{LL} A$$
$$\Pi_{osm} \frac{4}{3}\pi R^3 = \gamma_{LL} 4\pi R^2 \qquad \text{(eq 1)}$$
$$\frac{\Pi_{osm} R}{3} = \gamma_{LL}$$

Contrary to this, it was found that the amount of hydrophobe does not significantly influence the particle size. This means that directly after the miniemulsification, the pressure balance is not obtained. The Laplace pressure can be larger than the osmotic pressure as shown in Fig. 3 by plotting the radius versus γ_{LL} for the theoretical and real case.

With increasing the ultrasonication time, the difference increases indicating larger differences between the Laplace pressure and the osmotic pressure. The system starts to equilibrate the pressure during the waiting time between ultrasonication and polymerization. This principle can be used to establish a kinetic model of miniemulsion formulation and to support the principle of "critical stability" presented above. After the miniemulsification, the system usually is

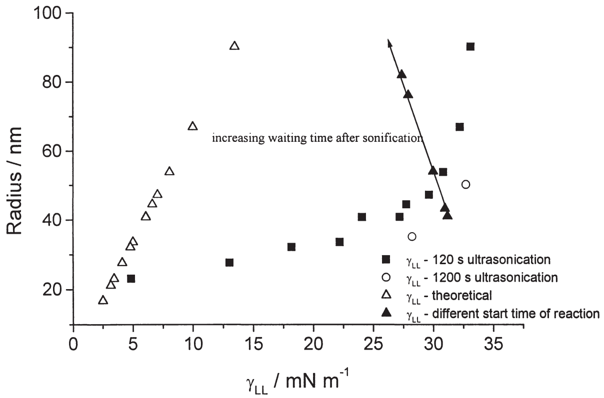


Figure 3: γ_{LL} is plotted versus the radius indicating that the Laplace pressure is larger than the osmotic pressure.

osmotically stable, but critically stabilized against particle collisions. To reach a stable state, the system cannot grow by monomer transport, but only by collisions until the osmotic pressure and the Laplace pressure counterbalance. At each point, the critically stabilized miniemulsion can be polymerized in a approximately 1:1 copying process under retention of its actual state since the polymerization time is usually faster than the growth by collisions: The critically stabilized state is frozen. A stable state with a pressure balance can also be obtained by adding a second charge of surfactant after the sonication to poststabilize the system effectively. Here, even after waiting times of some days before starting the polymerization, the size of the particles does not change any more.

Comparison Microemulsion - Miniemulsion

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 check points 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 particles results from an osmotic pressure in the particles which controls the solvent or monomer evaporation. The osmotic pressure results from 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.
5. During the polymerization, the 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

particles. 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 $0.005 < S < 0.25$ (S is the surfactant to monomer ratio), 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

It is shown that 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 timescales involved. It turned out that the droplet growth by monomer exchange or τ_1 mechanism is effectively suppressed by the addition of a very hydrophobic material, whereas droplet growth by collisions or the τ_2 mechanism is subject to the critical conditions. It is however possible to obtain long-term colloidal stability of miniemulsions by addition of an appropriate amount of surfactant for poststabilization. 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 (plastisizers) 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. The smaller the particles 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.

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