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Miniemulsions for Nanoparticle Synthesis

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Miniemulsions are specially formulated heterophase systems consisting of stable nanodroplets in a continuous phase. The narrowly size distributed nanodroplets of 50 to 500 nm can be prepared by shearing a system containing oil, water, a surfactant, and an osmotic pressure agent which is insoluble in the continuous phase. Since each of the nanodroplets can be regarded as a batch reactor, a whole variety of reactions can be carried out starting from miniemulsions clearly extending the profile of classical emulsion polymerization. This articles gives an overview about the mechanism of formation of and polymerizations in miniemulsions and reviews the current standing of the field for both the synthesis of new polymers and of dispersed hybrid systems.

Keywords. Polymer latex, Miniemulsion, Heterophase polymerization, Polymer nanoparticles, Composite particles

1
Introduction

The synthesis and application of polymeric nanoparticles dispersed in a continuous media enjoy great popularity in academy and industry. This is due to a number of reasons. On the one hand the formulation of polymers without the use of organic solvents is of high importance because of security, health, and environmental reasons. Consequently, the formulation in an environmentally friendly solvent, in general water, is highly desired. This is why polymer science is confronted with the problems of dispersing or synthesizing more and more polymers in water, although dispersion in water might interfere with the polymerization process.

On the other hand, there is a technological trend towards a high solid content of polymer formulations, e.g., to minimize shrinkage effects or to shorten processing times. A high polymer content at reasonable processing viscosities can only be obtained by polymer dispersions, either in water or hydrocarbon solvents.

As a third advantage, polymer particles in dispersions allow one to control or imprint an additional length scale into a polymer bulk material, given by the diameter of the particle, which is offered by the process of film formation. That way, polymer materials can be generated employing rational structure design not only on the molecular scale, but also on the mesoscale.

Usually or most widely applied, polymer latexes are made by emulsion polymerization [1]. Without any doubt, emulsion polymerization has created a wide field of applications, but in the present context one has to be aware that an inconceivable restricted set of polymer reactions can be performed in this way. Emulsion polymerization is good for the radical homopolymerization of a set of barely water-soluble monomers. Already heavily restricted in radical copolymerization, other polymer reactions cannot be performed. The reason for this is the polymerization mechanism where the polymer particles are the product of kinetically controlled growth and are built from the center to the surface, where all the monomer has to be transported by diffusion through the water phase. Because of the dictates of kinetics, even for radical copolymerization, serious disadvantages such as lack of homogeneity and restrictions in the accessible composition range have to be accepted.

There are a variety of other techniques to generate polymer dispersions, such as polymerization of microemulsions, suspension polymerization, or the generation of secondary dispersions by precipitation, which will be discussed in more detail below. All of them found their applications which, however, cannot really be extended to more general procedures in polymer science since they are handicapped by serious disadvantages such as excessive use of surfactant, insufficient colloidal stability, or costly procedures. It is therefore an idealized concept in heterophase polymerization to generate small, homogeneous, and stable droplets of monomer or polymer precursors, which are then transferred by (as many as possible) polymer reactions to the final polymer latexes, keeping their particular identity without serious exchange kinetics being involved. This means that the droplets have to become the primary locus of the initiation of the polymer reaction. Then, polymerization or polyaddition should proceed as in a hypothetical bulk state, where the continuous phase is still good to transport initiators, side products, and heat. This is a state we call 'nanoreactors', since every droplet behaves as an independent reaction vessel without being seriously disturbed by all the other events.

With the concept of 'nanoreactors' one can take advantage of an additional mode control for the design of nanoparticles where both thermodynamic aspects as well as shear history enter the particle size and the inner structure of the latexes or hybrid particles. The polymerization in such nanoreactors takes place in a highly parallel fashion, i.e., the synthesis is performed in 10^{18}–10^{20} nanocompartments per liter that are separated from each other by a continuous phase. In miniemulsion polymerization, the principle of small nanoreactors is realized as demonstrated in Fig. 1.

In a first step of the miniemulsion process, small stable droplets in a size range between 30 and 500 nm are formed by shearing a system containing the dispersed phase, the continuous phase, a surfactant, and an osmotic pressure agent. In a second step, these droplets are polymerized without changing their identity.

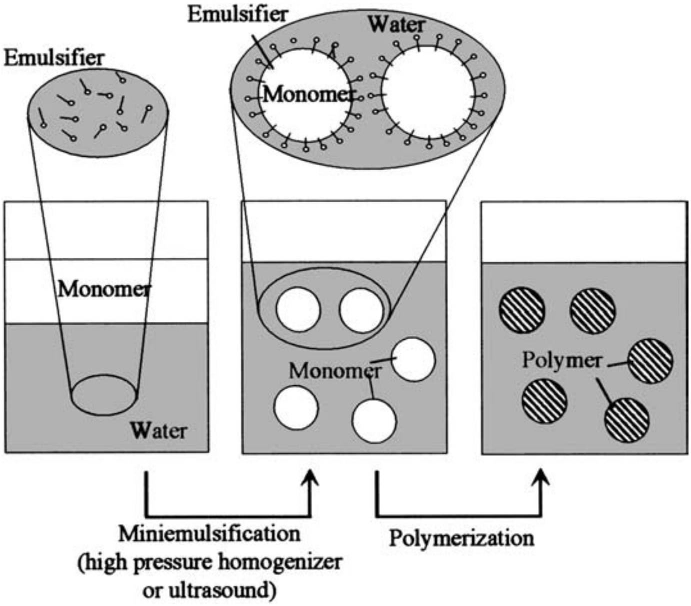

Fig. 1. The principle of miniemulsion polymerization

The main focus of this article is a detailed description of the working principles of miniemulsions, the examination of kinetics during the polymerization process, and the generation of different particle structures by appropriate handling of interface effects. It will be shown that miniemulsions are indeed not restricted to radical polymerization in water, but open the way to new polymers via a liquid/liquid technology both in direct (aqueous solvent) and inverse (organic or hydrocarbon solvent) situations. It will be shown that this principle is also highly favorable for the generation of nanoparticulate metals and ceramics, and for the encapsulation of nanoparticles into polymer shells to generate nanocomposites with high stability and processibility.

2
Miniemulsions and Miniemulsion Polymerization

2.1
Emulsion Stability Against Ostwald Ripening, Collisions, and Coalescence

Emulsions are understood as dispersed systems with liquid droplets (dispersed phase) in another, non-miscible liquid (continuous phase). Either molecular diffusion degradation (Ostwald ripening) or coalescence may lead to destabilization and breaking of emulsions. In order to create a stable emulsion of very small droplets, which is, for historical reasons, called a miniemulsion (as proposed by Chou et al. [2]), the droplets must be stabilized against molecular diffusion degradation (Ostwald ripening, a unimolecular process or τ_1 mechanism) *and* against coalescence by collisions (a bimolecular process or τ_2 mechanism). Stabilization of emulsions against coalescence can be obtained by the addition of appropriate surfactants, which provide either electrostatic or steric stabilization to the droplets.

Mechanical agitation of a heterogeneous fluid containing surfactants always leads to a distribution of droplet sizes results. Even when the surfactant provides sufficient colloidal stability of droplets, the fate of this size distribution is determined by their different droplet or Laplace pressures, which increase with decreasing droplet sizes resulting in a net mass flux by diffusion between the droplets. If the droplets are not stabilized against diffusional degradation, Ostwald ripening occurs which is a process where small droplet will disappear leading to an increase of the average droplet size [3].

In 1962, Higuchi and Misra examined the quantitative aspects of the rate of growth of the large droplets and the rate of dissolution of the small droplets in emulsion for the case in which the process is diffusion controlled in the continuous phase [4]. It was proposed that unstable emulsions may be stabilized with respect to the Ostwald ripening process by the addition of small amounts of a third component, which must distribute preferentially in the dispersed phase [4]. The obtained stability in miniemulsions is said in the literature to be *metastable* or *fully stable*. The stabilization effect by adding a third component was recently theoretically described by Webster and Cates [5]. The authors considered an emulsion whose droplets contain a trapped species, which is insoluble in the continuous phase, and studied the emulsion's stability via the Lifshitz-Slyozov dynamics (Ostwald ripening).

The rate of Ostwald ripening depends on the size, the polydispersity, and the solubility of the dispersed phase in the continuous phase. This means that a hydrophobic oil dispersed as small droplets with a low polydispersity already shows slow net mass exchange, but by adding an 'ultrahydrophobe', the stability can still be increased by additionally building up a counteracting osmotic pressure. This was shown for fluorocarbon emulsions, which were based on perfluorodecaline droplets stabilized by lecithin. By adding a still less soluble species, e.g., perfluorodimorphinopropane, the droplets' stability was increased and could be introduced as stable blood substitutes [6, 7].

2.2
Techniques of Miniemulsion Preparation and Homogenization

In order to obtain emulsification, a premix of the fluid phases containing surface-active agents and further additives is subjected to high energy for homogenization. Independent of the technique used, the emulsification includes first deformation and disruption of droplets, which increase the specific surface area of the emulsion, and second, the stabilization of this newly formed interface by surfactants.

In early papers, miniemulsions were prepared by using mechanical homogenization, e.g., by simple stirring or by the use of an omni-mixer and an ultra-turrax. However, the energy transferred by these techniques is not sufficient to obtain small and homogeneously distributed droplets [8]. A much higher energy for the comminuting of large droplets into smaller ones is required, significantly higher than the difference in surface energy $\gamma\Delta A$ (with γ the surface/interfacial tension and ΔA the difference between former and the newly formed interface), since the viscous resistance during agitation absorbs most of the energy.

In high force dispersion devices, ultrasonication is used today especially for the homogenization of small quantities, whereas rotor-stator dispersers with special rotor geometries, microfluidizers, or high-pressure homogenizers are best for the emulsification of larger quantities.

Power ultrasound emulsification was first reported in 1927 [9]. There are several possible mechanisms of droplet formation and disruption under the influence of longitudinal density waves [10–12]. Cavitation is the mechanism generally regarded as crucial under practical conditions [13, 14]. Parameters positively influencing cavitation in liquids improve emulsification in terms of smaller droplet size of the dispersed phase right after disruption. Imploding cavitation bubbles cause intensive shock waves in the surrounding liquid and the formation of liquid jets of high velocity with enormous elongational fields [15]. This may cause droplet disruption in the vicinity of the collapsing bubble. However, the exact process of droplet disruption, due to ultrasound as a result of cavitation, is not yet fully understood.

Using a high-pressure homogenizer with an orifice valve [16], it was shown that the time droplets spend in the laminar flow is long enough for a large number of disruption steps to take place subsequently, because the deformation time is much lower than the mean residence time in the elongation flow. During the deformation and break-up of a single droplet, almost no surfactant molecule adsorbs at the newly forming interface because the adsorption time is longer than one disruption step. This is why a special mechanical design to ensure either highly turbulent flow after disruption or sufficient residual times in the elongational flow is necessary to enable surfactant adsorption at the newly formed droplets. Then the disruption process can be facilitated by the presence of surfactants.

In direct miniemulsions, the droplet size is in turn determined by the amount of oil and water, the oil density, the oil solubility, and the amount of surfactant. It is found for direct miniemulsions that the droplet size is initially a function of the amount of mechanical agitation [17, 18]. The droplets also change rapidly in size throughout sonication in order to approach a pseudo-steady state, assuming a required minimum amount of energy for reaching this state is used. Once this state is reached, it was found that the size of the droplet does not change any more. At the beginning of homogenization, the polydispersity of the droplets is still quite high, but by constant fusion and fission processes the polydispersity decreases, and the miniemulsion then reaches a steady state (see Fig. 2) [19].

The process of homogenization can be followed by different methods, e.g., by turbidity, by conductivity, and by surface tension measurements. With increasing time of ultrasound, the droplet size decreases and therefore the entire oil/water interface increases. Since a constant amount of surfactant has now to be distributed onto a larger interface, the interfacial tension as well as the surface tension at the air/emulsion interface increases since the droplets are not fully covered by surfactant molecules. The surface tension can reach a value

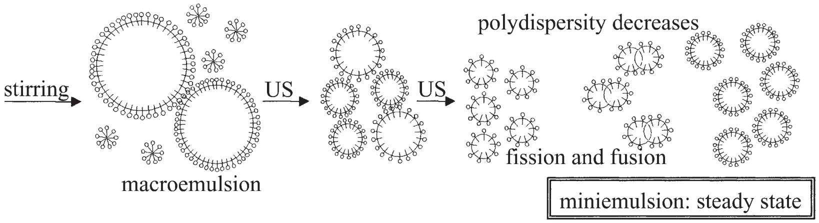

Fig. 2. Scheme for the formation of a miniemulsion by ultrasound (US)

close to 60 mN m^{-1}, indicating that the coverage of the droplets is indeed very low (calculated as 10% of a dense layer). The conductivity of the system is characterized by the surfactant and its distribution between the different bound states only. The conductivity due to free surfactant molecules, to surfactant micelles as well as the conductivity of charged dispersion droplets will also differ significantly. Increasing the droplet number during ultrasonication will decrease the free surfactant molecules and micelles; this is always accompanied with a strong decrease of the conductivity till an equilibrium is reached as seen in Fig. 3. The surface tension and the conductivity measurements are sensitive to the total oil/water interface, but both techniques can hardly distinguished between polydisperse and monodisperse systems as long as the overall interfacial area in the system is the same. Supplementing turbidity measurements (included in Fig. 3), which are sensitive to the size and size distribution of the droplets, equilibrate later than the surface tension or conductivity measurements, indicating the complexity of the underlying equilibration process.

The droplet size and size distribution seems to be controlled by a Fokker-Planck type dynamic rate equilibrium of droplet fusion and fission processes, i.e., the primary droplets are much smaller directly after sonication, but colloidally unstable, whereas larger droplets are broken up with higher probability. This also means that miniemulsions reach the minimal droplet sizes under the applied conditions (surfactant load, volume fraction, temperature, salinity, etc.), and therefore the resulting nanodroplets are at the critical borderline between stability and instability. This is why miniemulsions directly after homogenization are called 'critically stabilized' [19, 20]. Practically speaking, miniemulsions potentially make use of the surfactant in the most efficient way possible.

2.3
Influence of the Surfactant

Colloidal stability is usually controlled by the type and amount of the employed surfactant. In miniemulsions, the fusion-fission rate equilibrium during sonication and therefore the size of the droplets directly after primary equilibration depends on the amount of surfactant. For sodium dodecylsulfate (SDS) and styrene at 20% dispersed phase, it spans a range from 180 nm (0.3% SDS relative to styrene) down to 32 nm (50 rel.% SDS) (Fig. 4a). Again, it is anticipated that rapidly polymerized latexes also characterize the parental miniemulsion. As

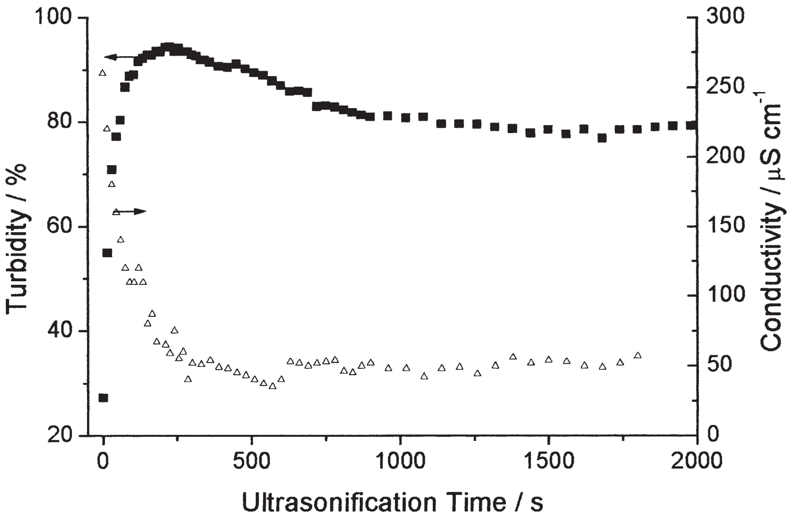

Fig. 3. Homogenization process followed by surface tension and conductivity measurements until a steady state is reached

compared to emulsion- and microemulsion polymerization, those particles are – with respect to the amount of used surfactant – very small, comparable to the best emulsion polymerization recipes. A latex with a particle size of 32 nm is already translucent and very close to the size, which was obtained in a microemulsion polymerization process with no hydrophobe, but the fourfold amount of a SDS/alcohol mixture [21].

The area per surfactant molecule on the particle surface, A_{surf}, also show a strong dependence on the particle size. It is seen that the entire range from a dense surfactant monolayer (A_{surf} about 0.4 nm^2) for small particles to very incompletely covered latex particles (A_{surf} about 7 nm^2) is obtained (see Fig. 4b). This reflects the fact that smaller particles have at comparable volume fractions a higher particle number density, a shorter averaged surface-to-surface distance, a higher relative mobility, and lower potential barriers, and therefore rely on denser surfactant layers to become colloidally stable. Since surfactant layer densities also influence the chemistry of such objects, e.g., permeation rates through the interface or enrichment of polar components within the droplet, this effect is important to remember: certain effects and reactivities might depend on the droplet size and work better for larger particles, which is somewhat counterintuitive.

It is a matter of course that the different surfactant coverages are also reflected in the corresponding surface tensions γ of the latexes (see Fig. 4b). An increase of the surface tension with increasing diameter is observed. The miniemulsions based on polystyrene particles exceeding 100 nm have a surface tension of close to the one of pure water (72 mN m^{-1}). This is due to the fact that the bare particle surface is so large that adsorption equilibrium ensures a very low surfactant solution concentration. Smaller particles with their higher sur-

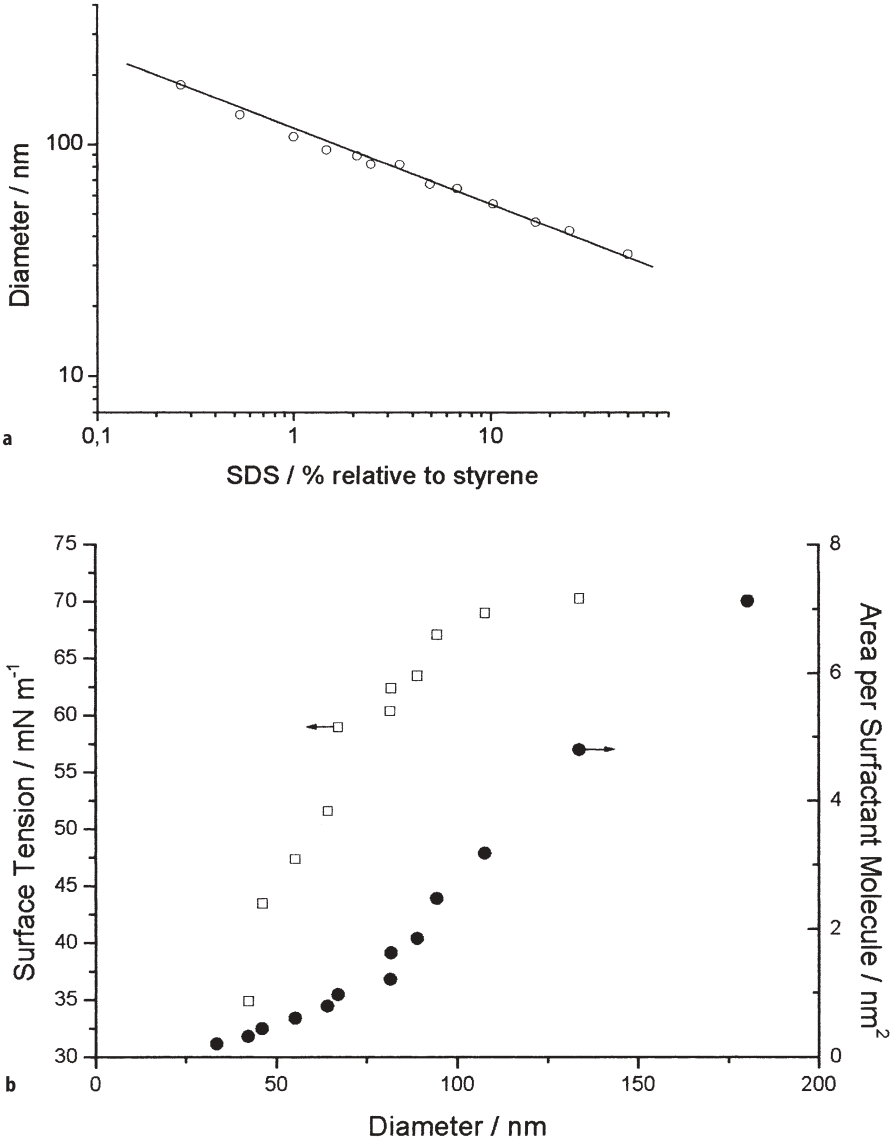

Fig. 4. **a** Polystyrene particle size vs amount of SDS (KPS as initiator); **b** Surface tension of the latexes and coverage of the particles in dependence of particle size

face coverage also have a higher equilibrium concentration of free surfactant, but the concentration usually still stays well below the critical micelle concentration value (cmc). This means that in miniemulsions there are no free micelles present. This is very important for the chemical reactivity and the polymerization kinetics in such systems. Just in the case of the highest surfactant load (50% SDS), a dense surface layer and a γ value typical for a micellar phase are observed. Here we leave the composition region for well-defined miniemulsions.

2.4
Influence of the (Ultra)hydrophobe

As stated above, the destabilization of nanodroplets by Ostwald ripening after the homogenization process can be efficiently slowed down by an addition of a hydrophobic agent to the dispersed phase, which now counteracts the droplet or Laplace pressure of the droplet. The agent has to be chosen so that it is trapped in each droplet and cannot diffuse from one droplet to the other. The effectiveness of the hydrophobe increases with decreasing water solubility in the continuous phase and there is a low but finite hydrophobe content in order to become operative to efficiently suppress Ostwald ripening. Many ultrahydrophobes can be used for the formulation of miniemulsions: beside hexadecane as a model [22, 23], other alkanes with different chain lengths [24], hydrophobic dyes [25], hydrophobic comonomers [26, 27], chain transfer agents [28, 29], hydrophobic initiators [30, 31], plasticizers, silanes, siloxanes, isocyanates, polyester, fluorinated alkanes [20], or other additives are effective agents to prevent Ostwald ripening. Long chain alcohols which acts as a hydrophobe and a cosurfactant at the same time [32, 33] are less effective.

A steady-state of miniemulsification is reached if an efficient homogenization process is performed and an adequate amount of hydrophobe is used. After stopping sonication, a rather rapid and minor equilibration process has to occur where the effective chemical potential in each droplet (which can be expressed as an effective net pressure) is equilibrating. Since the droplet number after sonication is fixed, the averaged size is also not influenced by this process, but the droplet size distribution usually undergoes very fast change. It can be calculated that the Laplace pressure within the resulting nanodroplets and the osmotic pressure created by the hydrophobe are still far away from being equal: the Laplace pressure is still larger than the osmotic pressure. It was found 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 time scales involved [19].

The Laplace pressure p_{Laplace} and the osmotic pressure can be calculated as shown in [20]. For a typical hexadecane concentration of 2 mol% relative to styrene, this results in an osmotic pressure of 4.5 bar, which is usually well below the Laplace pressure of 12 bar in a typical miniemulsion system (1.7% SDS relative to styrene, ca. 100 nm diameter). This means that right after steady-state miniemulsification 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, but it is rather characterized by a state of equal pressure in all droplets. Minor statistical differences of the pressure directly after sonication are presumably rapidly equilibrated, since changing the particle size leads to an adaptation of the Laplace pressure with R^{-1}, whereas the osmotic pressure goes with R^{-3}. This means that minor changes in size change the pressure balance significantly.

The equality of droplet pressures makes such systems insensitive against net mass exchange by diffusion processes (after the very fast equilibrium process at the beginning), but the net positive character of the pressure makes them sensitive to all changes of the droplet size. Experimental observations were made [19] that steady-state homogenized miniemulsions, which are critically stabilized, undergo droplet growth on the timescale of hundreds of hours, presumably by collisions or by hydrophobe exchange. The droplets seem to grow until a zero effective pressure is reached. Accordingly to Webster and Cates these miniemulsions are then fully stable [5]. It is, however, possible to obtain immediate long-term colloidal stability of miniemulsions by addition of an appropriate second dose of surfactant after the dispersion step. This dose is not used to increase the particle number, but goes to the bare interface of the preformed miniemulsion droplets in order to decrease the interfacial tension between the oil and the water phase and to decrease the coupled Laplace pressure. Such post-stabilized miniemulsions do not change their droplet size on the timescale of days and even several months. This leads to the conclusion that most miniemulsions described in the literature are indeed thermodynamically only metastable, i.e., with respect to conservation of particle number they are in a local minimum of the chemical potential, which, however, is deep enough to allow chemical reactions without significant change of the particle size and structure.

The particle size of rapidly polymerized minidroplets does not or does just weakly depend on the amount of the hydrophobe [34–36]. It was found that doubling the amount of hydrophobe does not decrease the radius by a factor of 2 (as expected from a zero effective pressure), it is just that the effective pressure (pressure difference) has to be the same in every droplet, a mechanism which in principle does not depend on the amount of hydrophobe [19]. However, a minimum molar ratio of the hydrophobe to the monomer of about 1:250 is required in order to build up a sufficient osmotic pressure in the droplets exceeding the influence of the first formed polymer chains. This also explains the fact that a small amount of high molecular weight polymer, e.g., polystyrene, can barely act as an osmotic stabilizing agent; here stabilization can only be achieved for the time of polymerization [37, 38].

The investigation of the droplet size is also an important issue in the literature. The size of the *polymer particles* is easily determined by light scattering or microscopic methods since the dispersions can be diluted without changing the particles. Few attempts have been made at measuring *droplet sizes* in emulsions directly. Ugelstad et al. [24] and Azad et al. [39] stained miniemulsions with OsO_4 and used transmission electron microscopy. However, the treatment can alter the sizes. Goetz and El-Aasser [40] made some attempts to determine droplet sizes using light scattering and transmission electron microscopy. Miller et al. [41] used capillary hydrodynamic fractionation (CHDF). Nevertheless, for those measurements the emulsions had to be diluted, which seriously changes the system. Even if the emulsion is diluted with monomer-saturated water [42], the size of the droplets will change slightly due to different solubility effects.

Measurement of characteristics of the emulsion droplets in concentrated media is indeed a difficult task. Some indirect methods have been used. The interfacial area and therefore the droplet size were determined by measuring the critical micelle concentration of miniemulsions [43]. Erdem et al. determined droplet sizes of concentrated miniemulsions via soap titration, which could be confirmed by CHDF measurements [44]. Droplet sizes without diluting the system can much better be estimated by small angle neutron scattering (SANS) measurements [23].

2.5
Inverse Miniemulsions

The concept of emulsion stabilization is not restricted to direct miniemulsions, but it could also be extended to inverse miniemulsions where the osmotic pressure is built up by an agent insoluble in the continuous oily phase, a so-called 'lipophobe'. Ionic compounds, simple salts or sugars, show a low solubility in organic solvents and can be used as lipophobes in water-in-oil miniemulsions [45]. Another adaptation of the process is that for the dispersion of polar monomers in non-polar dispersion media; surfactants with low HLB (hydrophilic-lipophilic balance) values are required. A number of surfactants were screened, including standard systems such as $C_{18}EO_{10}$, sodium bis(2-ethylhexyl)-sulfosuccinate (AOT), sorbitan monooleate (Span80), and the nonionic block copolymer stabilizer poly(ethylene-*co*-butylene)-*b*-poly(ethylene oxide) (PE/B-EO) consisting of hydrophilic and hydrophobic block lengths of about 3700 g mol^{-1}, respectively. PE/B-EO turned out to be most efficient due to its polymeric and steric demanding nature, providing maximal steric stabilization which is the predominant mechanism in inverse emulsions. A comparison of the direct and inverse miniemulsion is given in Fig. 5.

The extraordinarily high droplet stability against exchange processes can be demonstrated in a very illustrative way by the formation of a nickel murexid complex inside the droplets: One miniemulsion with droplets containing a Murexid solution, and one miniemulsion containing a $Ni(NO_3)_2$ solution are mixed. As seen in Fig. 6a, the mixed miniemulsion stays orange-red for weeks, which indicates that the droplets with the different species stay separated as colloidal entities on the time scale of most chemical reactions. Repetition of the same experiment with two microemulsion or micellar solutions would lead to an immediate reaction because of unblocked droplet exchange. In miniemulsions, the exchange can be stimulated by mechanical energy, such as ultrasonication used to prepare the original miniemulsions. In this case, fusion and fission processes are induced, and with increasing ultrasonication the miniemulsion indeed turns yellow (see Fig. 6b).

Also in the inverse case, the droplet size throughout the miniemulsification process runs into an equilibrium state (steady-state miniemulsion) which is characterized by a dynamic rate equilibrium between fusion and fission of the

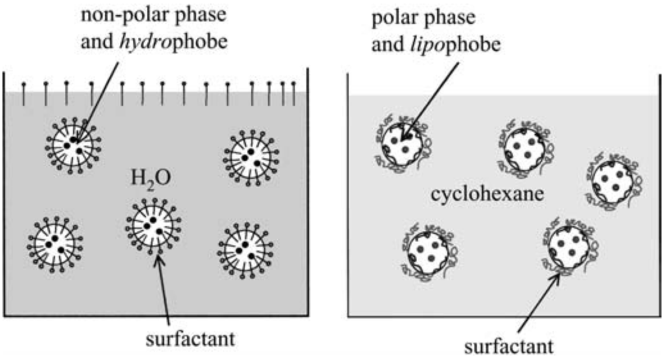

Fig. 5. Comparison between direct and inverse miniemulsion

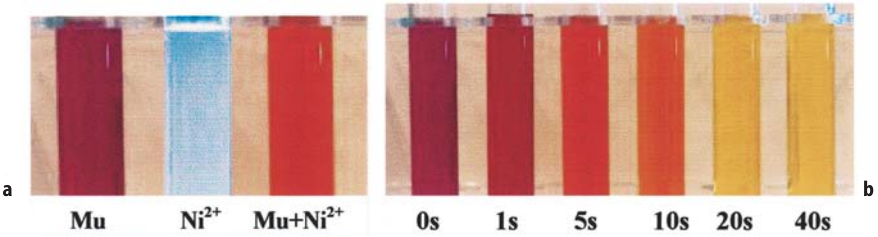

Fig. 6. **a** Mixing of two inverse miniemulsions, one containing Murexid solution, the other one Ni(NO$_3$)$_2$; **b** Mixed miniemulsion of b during the process of ultrasonication

droplets, as it can be determined by turbidity measurements. High stability of the droplets *after* the high shear treatment, however, is obtained with the osmotic agent. The type of lipophobe has no influence on the stability of the inverse miniemulsion. The droplet size depends, unlike in regular miniemulsions, on the amount of osmotic agent [46]. It seems that in inverse miniemulsions the droplets experience shortly after miniemulsification a real zero-effective pressure situation (the osmotic pressure counterbalances the Laplace pressure) which makes them very stable. This is speculatively attributed to the different stabilization mechanism and mutual particle potentials, which make a pressure equilibration near the ultrasonication process possible. This is why it is believed that inverse miniemulsions are not critically stabilized, but are fully stable systems.

Nevertheless, for inverse miniemulsions the surfactant is used in a very efficient way, at least as compared to inverse microemulsions [47,48] or inverse suspensions [49] which are used for subsequent polymerization processes. Again, the surface coverage of the inverse miniemulsion droplets with surfactant is incomplete and empty inverse micelles are absent. Again this is important for the interpretation of the reaction mechanism.

The fusion/fission mechanism of minidroplet formation also results in the typical triangular relation between the amount of surfactant, the resulting particle size, and the surface coverage. With increasing amount of the surfactant, the particle size decreases. The smaller the particles, the higher the coverage of the particles by surfactant. For inverse miniemulsions these relations also depend on the amount of hydrophobe.

2.6
Preservation of Particle Identity Throughout Miniemulsion Polymerization

The idea of miniemulsion polymerization is to initiate the polymerization in each of the small stabilized droplets, without major secondary nucleation or mass transport processes involved. Preservation of particle number and particle identity is therefore a key issue. Therefore, the growth of minidroplets is ideally slower than the polymerization time, and a situation very close to a 1:1 copying of the monomer droplets to polymer particles is obtained. From today's point of view, it is either possible to polymerize a freshly prepared, steady-state miniemulsion with minimal particle size, freezing the critically-stabilized state by rapid polymerization, or by adding an adequate second dose of surfactant (controlled by surface tension measurements to saturate the particle surface avoiding the presence of free micelles). The growth of the minidroplets is then effectively suppressed, and polymerization avoids any 'racing' situation.

The preservation of particle character and size throughout polymerization itself is very hard to determine. The size of the final polymer particles is easily determined by light scattering or microscopic methods since the dispersions can be diluted without changing the particle size. Measurements of the emulsion droplets in concentrated media on the other hand are a very difficult task and have already been discussed above.

Indirect techniques, such as conductivity measurements and the determination of the surface tension were carried out to get more information about the surfactant distribution during the polymerization and were applied to characterize the droplet or particle sizes before and after the polymerization without diluting the system [23]. As a powerful method small angle neutron scattering experiments were applied to characterize the droplet or particle sizes before and after the polymerization without diluting the system [23].

2.7
Surfactant Variation

The majority of the recipes described in the literature are based on the anionic sodium dodecylsulfate (SDS) as a model system. The possibility of using cationic surfactants such as octadecyl pyridinium bromide for the preparation of miniemulsions was first exploited in 1976. However, the emulsions were prepared by stirring and the resulting emulsions showed broadly distributed droplet sizes [2, 39, 50]. Recent work on steady-state miniemulsions showed that cationic and nonionic surfactants form well-defined miniemulsions for further miniemulsion polymerization processes, resulting in narrow size distributed stable cationic and nonionic latex particles [51]. Similar molecular amounts of the simple cationic surfactant, cetyltrimethylammonium bromide or chloride

(CTAM-Br or -Cl), compared to the anionic surfactant, SDS, result in similar particle sizes showing that the particle size is essentially controlled by a limit of the surfactant coverage of the latex particles. From surface tension measurement results, this surface coverage was determined to be of the order of 30%, which proves the very efficient use of surfactants in the miniemulsification process. A new class of cationic surfactants with sulfonium headgroups was also effectively employed for the synthesis of miniemulsions. The ring-opening reaction of epoxides with thioethers, followed by addition of organic acids, is a versatile approach towards a broad variety of different sulfonium surfactant structures. By use of a wide variety of accessible reactants, the sulfonium surfactant architecture was varied in terms of (a) the hydrophobic chain length, (b) the counterion of the sulfonium headgroup, (c) the structure of the sulfonium headgroup, and (d) the surfactant architecture, i.e., single-chain or bola- or star-shaped surfactants [52].

Nonionic miniemulsions can be made by using 3–5% of a poly(ethylene oxide) derivative as surfactant, resulting in larger, but also very well defined latexes [51]. Chern and Liou used a nonionic surfactant nonylphenol polyethoxylate with an average of 40 ethylene oxide units per molecule [53]. Particle sizes between 135 and 280 nm were realized. The particle size mainly depends on the type and amount of the hydrophobe and therefore on the degree of the suppression of Ostwald ripening [53].

Capek described the use of a macromonomer in miniemulsion polymerization [54]. Lim and Chen used poly(methyl methacrylate-*b*-(diethylamino)ethyl methacrylate) diblock copolymer as surfactant and hexadecane as hydrophobe for the stabilization of miniemulsions [55]. Particles with sizes between about 150 and 400 nm were produced. It is possible to create stable vinyl acetate miniemulsions employing nonionic polyvinyl alcohol (PVA) as surfactant and hexadecane as hydrophobe [56].

The favorable use of an amphiphilic graft copolymer comprised of octadecyl acrylate and acrylic or methacrylic acid groups for the formation of polystyrene miniemulsion latexes has been demonstrated in our laboratory by Baskar et al. [57] The comb-like polymers had molecular weights of about 4×10^4 g mol^{-1}. In this case, the polymer acts as a surfactant and a hydrophobe at the same time which is of large industrial significance. Since those polymers neither dissolve homogeneously in monomer or water, the polymers are anticipated to be located only at the oil-water interface [57]. Compared to the surface-active cetyl alcohol, the water solubility is shown to be very low, which ensures the stability of the miniemulsion droplets.

By variation of the relative amount of the surfactant, it was possible to vary the particle size over a wide range [58]. Figure 7 shows that, depending on the type of the surfactant, different size ranges can be achieved. Latexes synthesized with ionic surfactants, e.g., sodium dodecyl sulfate (SDS), CTAB, or the C_{12} sulfonium surfactant show about the same size-concentration curve, i.e., the efficiency of the surfactants and the size dependent surface coverage is very similar, independent of the sign of charge. The efficiency of the nonionic surfactants is lower in contrast to the ionic ones and the whole size-concentration curve is shifted to larger sizes. This is attributed to the lower efficiency of the steric sta-

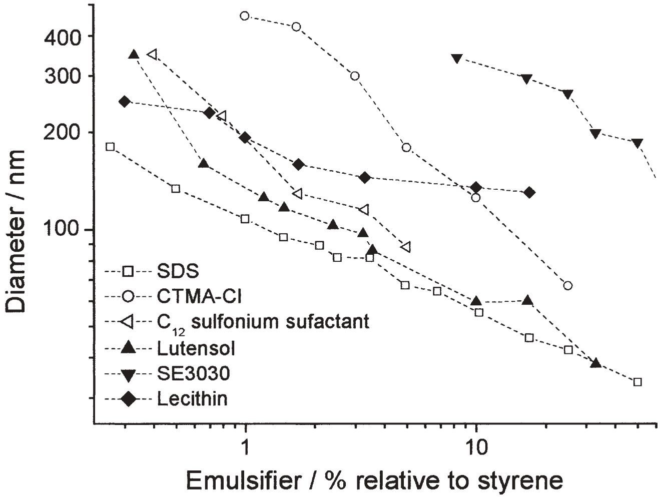

Fig. 7. Variation of the particle size by changing the amount and type of surfactant in a styrene miniemulsion

bilization as compared to electrostatic stabilization and the fact that steric stabilization relies on a more dense surfactant packing to become efficient. As can be derived from the surface tension of the latexes and surfactant titrations, the nonionic particle surfaces are, nevertheless, incompletely covered by surfactant molecules and the latexes show surface tensions well above the values of the saturated surfactant solution where saturated surfactant layers occur. Also, the biosurfactant lecithin can be used for the preparation of stable miniemulsions.

2.8
Checklist for the Presence of a Miniemulsion

In some crucial cases it might be not obvious whether the system represents a miniemulsion or not. Therefore a short checklist summarizing the characteristics of miniemulsions is provided:

1. Steady-state dispersed miniemulsions are stable against diffusional degradation, but critically stabilized with respect to colloidal stability.
2. The interfacial energy between the oil and water phase in a miniemulsion is significantly larger than zero. The surface coverage of the miniemulsion droplets by surfactant molecules is incomplete.
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.
4. The stability of miniemulsion droplets against diffusional degradation results from an osmotic pressure in the droplets, which controls the solvent or monomer evaporation. The osmotic pressure is created by the addition of a substance, which has extremely low water solubility, the so-called hydrophobe. This crucial prerequisite is usually not present in microemulsions, but

can be added to increase the stability. Such miniemulsions can still undergo structural changes by changing their average droplet number to end up in a situation of zero effective pressure, however, on very long time scales. This secondary growth can be suppressed by an appropriate second dose of surfactant added after homogenization.

5. Polymerization of miniemulsions occurs by droplet nucleation only.
6. During the polymerization, the growth of droplets in miniemulsions can be suppressed. In miniemulsions the monomer diffusion is balanced by a high osmotic background of the hydrophobe, which makes the influence of the firstly formed polymer chains less important.
7. The amount of surfactant or inherent surface stabilizing groups required to form a polymerizable miniemulsion is comparably small, e.g., with SDS between 0.25 and 25% relative to the monomer phase, which is well below the surfactant amounts required for microemulsions.

3
Radical Polymerizations of Miniemulsions

3.1
Mechanisms and Kinetics in Miniemulsion Polymerization

In miniemulsion polymerization the nucleation of the particles mainly starts in the monomer droplets themselves. Therefore, the stability of droplets is a crucial factor in order to obtain droplet nucleation. The better the droplets are stabilized against Ostwald ripening, the higher is the droplet nucleation.

In Fig. 8 the calorimetric curve of a typical miniemulsion polymerization for 100-nm droplets consisting of styrene as monomer and hexadecane as hydrophobe with initiation from the water phase is shown. Three distinguished intervals can be identified throughout the course of miniemulsion polymerization. According to Harkins' definition for emulsion polymerization [59–61], only intervals I and III are found in the miniemulsion process. Additionally, interval IV describes a pronounced gel effect, the occurrence of which depends on the particle size. Similarly to microemulsions and some emulsion polymerization recipes [62], there is no interval II of constant reaction rate. This points to the fact that diffusion of monomer is in no phase of the reaction the rate-determining step.

The first interval is the interval of particle nucleation (interval I) and describes the process to reach an equilibrium radical concentration within every droplet formed during emulsification. The initiation process becomes more transparent when the rate of polymerization is transferred into the number of active radicals per particle $\bar{n}$, which slowly increases to $\bar{n}\approx 0.5$. Therefore the start of the polymerization in each miniemulsion droplet is not simultaneous, so that the evolution of conversion in each droplet is different. Every miniemulsion droplet can be perceived as a separate nanoreactor, which does not interact with others. After having reached this averaged radical number, the polymerization kinetics is slowing down again and follows nicely an exponential kinetics as known for interval III in emulsion polymerization or for suspension polymer-

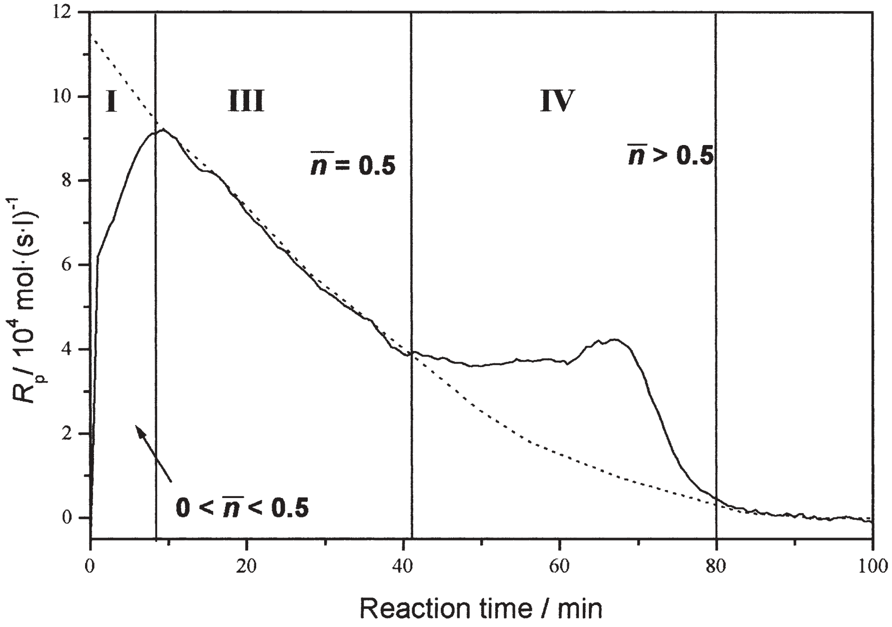

Fig. 8. Calorimetric curve of a typical miniemulsion polymerization consisting of 20% styrene in water, 1.2% SDS (relative to styrene), and KPS as initiator

ization. As reasoned by the droplet nucleation mechanism, only the monomer in the droplet is available for polymerization, which is exponentially depleted from the reaction site. The average number of radicals per particle, $\bar{n}$ during interval III is quite accurately kept at 0.5, implying that the on/off mechanism known from emulsion polymerization [63] upon entry of additional radicals into such small latex particles is strictly valid.

The boost found in interval IV is the typical gel-peak well known also from suspension polymerization, which is due to the viscosity increase inside the particles and the coupled kinetic hindrance of the radical recombination. This is also reflected in a steep rise of $\bar{n}$.

3.2
Droplet Size

The polymerization kinetics is governed by the droplet size. Tang et al. found that the polymerization of styrene miniemulsions created by the microfluidizer was faster than that of miniemulsions created by the omnimixer [64]. This behavior can mainly be attributed to the different droplet size prior to polymerization. In the first case, the droplets are smaller than in the second case [65]. Fontenot and Schork observed similar behavior for MMA miniemulsions. With increasing shear and increasing concentration of surfactant, the polymerization rate increases [22]. This again can be explained by different sizes of the initial droplets.

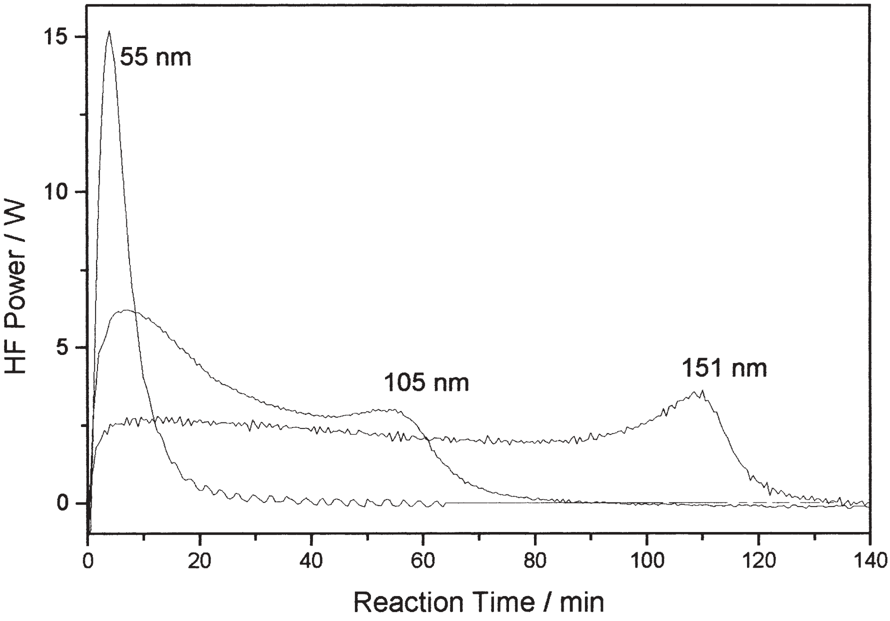

Fig. 9. Calorimetric curves for styrene miniemulsion polymerizations with different SDS contents, e.g., different particle sizes (0.3 rel.% SDS leads to 151-nm, 1.0 rel.% SDS to 105-nm, and 10 rel.% SDS to 55-nm particles)

In steady-state or mechanically equilibrated miniemulsions, the droplet size can be easily varied by variation of the amount of surfactant. Depending on the droplet size of the miniemulsions, we obtained calorimetric curves with various kinetic features which are shown in Fig. 9 [66]. Disregarding the complexity of the kinetics and the existence of the three intervals, the reaction time to reach 95% conversion depends as a rule of thumb about linearly on the particle size and thus varies between 20 and 120 min.

Independent of the size of the droplets, interval I (see also Fig. 8) has a similar duration and takes about 5 min, which again supports the concept that this interval is only influenced by processes in the continuous aqueous phase which do not depend on the droplet size. The maximum reaction speed, however, shows a strong particle size dependence and is proportional to the particle number, i.e., the smaller the particles are, the faster is the reaction.

3.3
Initiators

For miniemulsion polymerization, the initiator can be either oil- or water-soluble. In the case of an oil-soluble initiator, the initiator is dissolved in the monomeric phase prior to miniemulsification. Then the reaction starts within the droplets. This is comparable to suspension polymerization where the initiation is carried out in the large droplets. Because of the finite size of the miniemulsions droplets, radical recombination is here the problem to face. Also a water-soluble initiator can be used to start the polymerization from the water phase. The start from the continuous phase is similar to the conventional emulsion polymerization where usually water-soluble initiators are used.

It was found that the chain length of the resulting polymer is inversely proportional to the square root of the initiator concentration [66], underlining that the reaction in miniemulsion is rather direct and close to an ideal radical polymerization. It could be shown that the amount of initiator used for polymerizing the latex does not have an effect on the number of nucleated droplets which shows that droplet nucleation is by far the dominant mechanism over the whole range of initiator concentrations.

For the styrene/hexadecane system, the amount of initiator does not have an effect on the particle number, but in the case of more water-soluble monomers, for example MMA and vinyl chloride [67], secondary particle formation was observed. Here, the amount of new particles increases with the concentration of the water-soluble initiator. Homogeneous nucleation in the water phase can be restrained by using a water-soluble redox initiator, e.g., $(NH_4)S_2O_8/NaHSO_3$ at lower temperature (45°C) [68] or even more efficiently by using an interfacial acting redox initiator (cumene hydroperoxide/Fe^{2+}/ethylenediamine tetraacetate (EDTA)/sodium formaldehyde sulfoxylate (SFS)) [69, 70] to initiate the miniemulsion polymerization. The hydrophobic radicals decrease the homogeneous nucleation in the aqueous phase.

The miniemulsion polymerization also allows the use of oil-soluble initiators which is the preferential choice for monomers with either high water solubility (e.g., MMA in order to prevent secondary nucleation in the water phase) or for monomers with an extremely low water solubility (e.g., LMA) where the monomer concentration in the water phase is not high enough to create oligoradicals which can enter the droplets.

The ability of initiators with different water solubilities, namely lauroyl peroxide (LPO), benzoyl peroxide (BPO) and 2,2′-azoisobutyronitrile (AIBN) in stabilizing monomer droplets against degradation by molecular diffusion and their efficiency for polymerization was investigated [30]. Upon heating, the initiator decomposes, and a sufficiently long polymer chain will be formed only when a single radical appears. 'Single radicals' refer to radicals that appear in the monomer droplets one at a time as opposed to pair generation in which, due to initiator decomposition, two radicals appear in the monomer droplet at the same time. Single radicals can be formed by desorption of one of the radicals formed by initiator decomposition and by entry of a radical from the aqueous phase. This makes oil-soluble initiators effective only when one or both of the formed radicals are sufficiently hydrophilic to undergo desorption. Comparing different oil-soluble initiators, the probability of nucleation is much larger for AIBN than in the cases of LPO and BPO.

4

Different Polymerization Reactions in Miniemulsions

The process of miniemulsion allows in principle the use of all kinds of monomers for the formation of particles, which are not miscible with the continuous phase. In case of prevailing droplet nucleation or start of the polymer reaction in the droplet phase, each miniemulsion droplet can indeed be treated as a small nanoreactor. This enables a whole variety of polymerization reactions that lead to nanoparticles (much broader than in emulsion polymerization) as well as to the synthesis of nanoparticle hybrids, which were not accessible before.

4.1

Radical Homopolymerization in Regular Miniemulsions

As a model monomer for radical homopolymerization of hydrophobic monomers, styrene is described in many papers. The polymerization of acrylates and methacrylates is also well known. It could also be shown that the miniemulsion process also easily allows the polymerization of the ultrahydrophobic monomer lauryl methacrylate without any carrier materials as necessary in emulsion polymerization [71].

Not only hydrophobic but also fluorinated monomers were applied for the synthesis of latexes in the size range of 100–250 nm by employing rather low doses of protonated surfactants [72]. As a model system, the fluorine-containing monomer tridecafluorooctyl methacrylate ($CH_2{=}C(CH_3)CO_2(CH_2)_2(CF_2)_6F$) was used for the miniemulsion procedure. Indeed, this monomer could be miniemulsified using perfluoromethyldecaline or the polymerizable heptadecafluorodecyl methacrylate ($CH_2{=}C(CH_3)CO_2(CH_2)_2(CF_2)_8F$) as hydrophobes and the standard hydrocarbon surfactant sodium dodecyl sulfate (SDS). The use of this simple standard surfactant is worth mentioning, since most other recipes relied on fluorinated surfactants or long chain alkyl surfactants (dense packing). Already at surfactant loads as low as 0.66 rel.% (weight percent SDS relative to the dispersed phase), a stable miniemulsion could be obtained. Due to the low water solubility of the monomer, it was not possible to perform initiation from the water phase, and the polymerization was started inside the droplets by using AMBN (2,2′-azobis(2,4-dimethylbutyronitrile)) as a hydrophobic initiator. With 0.66 rel.% SDS, coagulate-free latexes with particle diameters of about 200 nm were obtained. The size of the final particles could be easily decreased by increasing the amount of surfactant from about 200 nm (0.66% SDS) to 100 nm (5.33% SDS). As compared to polystyrene latexes made under similar conditions, all fluoromethacrylate latexes are slightly larger, thus expressing the more hydrophobic surface and the connected higher packing density of surfactant required for stabilization. On the other hand, the latexes are smaller than those made from lauryl methacrylate (see Fig. 10a), which we interpret with a higher average surface energy for the fluoromethacrylate due to the fact that methacryloyl units are also pointing to the water phase.

The hydrophobic monomer vinylnaphthalene also forms at temperatures above its melting temperature miniemulsions and the miniemulsion droplets can be polymerized, resulting in polymer particles with a refractive index of the polymer particles of 1.6818 which is one of the highest known for polymers (see Fig. 10b). Since the scattering intensity for particles with the same diameter is proportional to $\Delta(n_1-n_2)^2$ (where n_1 and n_2 are the refractive indexes of the particles and the continuous medium respectively), the scattering intensity of polynaphthalene latex particles is twice as high ($\Delta(n_1-n_2)^2=0.1213$) as for styrene latex particles with the same size ($\Delta(n_1-n_2)^2=0.0660$).

The polymerization of more hydrophilic monomers is also possible, as shown for MMA and vinyl acetate [36, 56, 73]. In the case of monomers with a pronounced water solubility, the nucleation in water should be efficiently suppressed in order to avoid secondary nucleation in the water phase. This can be achieved, e.g., by using an oil-soluble initiator and the polymerization of acrylonitrile or by adding a termination agent to the continuous phase. A typical calorimetric curve of MMA polymerization using a hydrophobic initiator shows a fast conversion.

PVC latex particles consisting of two size populations can be generated in a miniemulsion polymerization. The mechanism for the formation of two discrete particle families relies upon polymerization of two distinct kinds of droplets [74].

4.2
Formation of Particles in Non-Aqueous Solvents

It was shown that the principle of aqueous miniemulsions could be transferred to non-aqueous media [45]. Here, polar solvents, such as formamide or glycol, replace water as the continuous phase, and hydrophobic monomers are miniemulsified with a hydrophobic agent, which stabilizes the droplets against molecular diffusion processes. It turned out that steric nonionic surfactants based on poly(ethylene oxide) tails are far more efficient than ionic stabilizers,

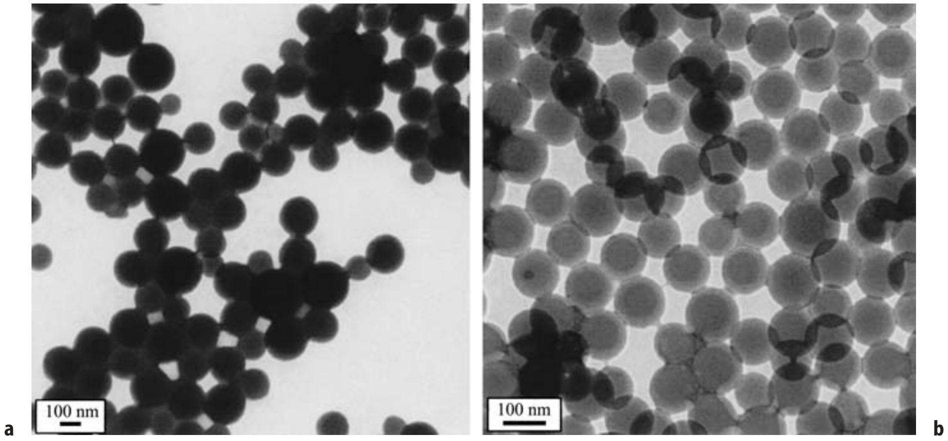

Fig. 10a,b. TEM photographs: **a** polylaurylmethyacrylate latex particles; **b** polynaphthalene latex particles which is speculatively attributed to a low degree of ion solvation and degree of dissociation in formamide. It is possible to make particles as small as 70 nm, which is unusually small for non-aqueous heterophase polymerization techniques. An increase of the particle size with decreasing amounts of surfactant is detected. For the polymerization of the monomer droplets, both AIBN and KPS were employed as initiators. AIBN dissolves in both organic phases leading to an aggregation of the particles since the polymerization can be started simultaneously and uncontrolled in the droplets and in the continuous phase. The hydrophilic initiator KPS, however, turned out to be suitable, since it starts the polymerization controlled from the continuous phase.

4.3
Formation of Particles in Inverse Miniemulsion

In the case of inverse systems, hydrophilic monomers such as hydroxyethyl acrylate, acrylamide, and acrylic acid were miniemulsified in non-polar media, e.g., cyclohexane or hexadecane [45, 46]. Rather small and narrow distributed latexes in a size range between 50 nm<d<200 nm were synthesized with nonionic amphiphilic block copolymers. Depending on the system, the surfactant loads can be as low as 1.5 wt% per monomer, which is very low for an inverse heterophase polymerization reaction and clearly underlines the advantages of the miniemulsion technique.

For the moderately hydrophilic hydroxyethyl methacrylate, cyclohexane and hexadecane were chosen as the continuous phase. As initiators, PEGA200 which is soluble in the monomer phase, but not in cyclohexane, turned out to be applicable. AIBN which is mainly soluble in the cyclohexane phase could also be successfully used. KPS cannot be employed as initiator due to solubility problems. Small amounts of water act as lipophobe, and it could be shown by turbidity measurements that the addition of water increases the emulsion stability.

Rather small latex particles in the size range between 80 nm and 160 nm and narrow size distributions are obtained. The systems are stable down to 1.6 wt% surfactant relative to the monomer; at lower amounts the systems tend to coagulate. With increasing amount of surfactant, the particle size decreases as expected. The area per surfactant molecule, A_{surf}, decreases with decreasing particle size and follows the same trend as in the case of direct miniemulsions shown earlier. This means that again the surface coverage is a function of the particle size: for smaller particles more surfactant is required in order to obtain stable latexes. It is remarkable that the final dispersions are stable for longer time even at low surface coverage.

For the synthesis of acrylamide in a miniemulsion polymerization process, the solid crystalline monomer has to be dissolved in water, and therefore a higher amount of water was applied for the synthesis. As the continuous phase, cyclohexane or IsoparM were chosen. The miniemulsions after sonication show only a low stability (less than 1 h) without the addition of a strong lipophobe (1 mol/l NaCl); its presence increases the stability of the miniemulsions to the timescale of several days. A polymerization started with AIBN from the continuous phase resulted in stable polymer dispersions, as shown in Fig. 11.

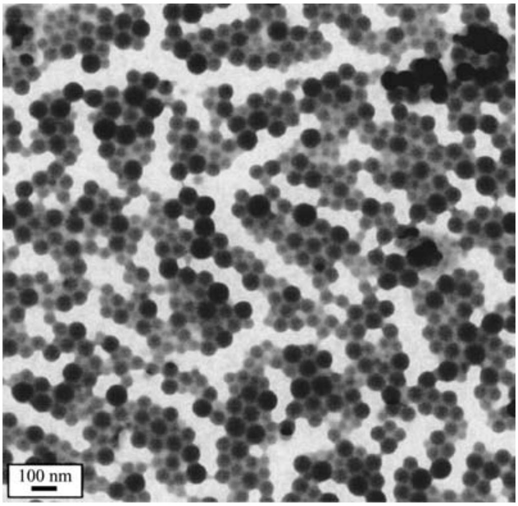

Fig. 11. Hydrophilic polyacrylamide particles obtained in inverse miniemulsion polymerization in IsoparM

The high homogeneity and rather well-defined character of those latexes is clearly observed. Again, already surfactant loads as low as 1.8% relative to the dispersed phase result in stable latexes. The particle size is getting smaller with increasing amounts of the surfactant, and the surface area per surfactant molecule A_{surf} is between 18 nm^2 at low surfactant amounts (1.8 rel.%) and 7 nm^2 for higher surfactant amounts (7.1 rel.%), depending on the particle size.

Acrylic acid was polymerized in inverse miniemulsions together with 4 wt% of the crosslinking agent diethylene glycol diacrylate in order to obtain homogeneous polyelectrolyte microgels, which can be redispersed and characterized in water. However, the solubility of acrylic acid in cyclohexane is not negligible. The addition of water to acrylic acid already decreases the solubility of acrylic acid in cyclohexane significantly. Therefore, a 5 mol/l NaOH solution at a 1:1 ratio NaOH solution/acrylic acid was used in order to shift the partitioning of acrylic acid more into the water phase. NaOH not only acts as a lipophobe, but also neutralizes the acid, which leads to a higher hydrophilicity of the component. Starting from a critical surfactant amount of 2.5 rel.% to prevent the formed polymer particles from aggregation, stable latex particles of about 100 nm diameter were produced. Increasing the surfactant amount leads to smaller particles. The surfactant efficiency or the stabilized area per surfactant molecule, A_{surf}, is very high. In the case of low surfactant concentration, A_{surf} is as big as 25 nm^2 per stabilizing molecule and decreases to 13.2 nm^2 in the case of higher amounts of surfactant.

As compared to classical inverse heterophase polymerization techniques such as polymerization in inverse microemulsions [47] or dispersion polymerization [75, 76], polymerization of inverse miniemulsions is favored by the very efficient use of surfactant and the copying process from the droplets to the particles. This leads to a homogeneous structure and composition of the resulting particles (no kinetic effects are involved). The latter feature is especially important for homogeneous crosslinking or copolymerization in inverse heterophase polymerization.

4.4
Nanocrystalline Polymers

Polyacrylonitrile, which is a semicrystalline polymer, can be used for many engineering applications, such as fiber spinning or for housing and package applications. A peculiarity of polyacrylonitrile is that it is insoluble in its monomer. This makes it very difficult to homopolymerize acrylonitrile in an emulsion polymerization process since nucleated polymer particles cannot grow by monomer swelling.

Polymerization in miniemulsion is a very suitable technique to avoid this problem since each droplet acts as a nanoreactor. As a result, pure polyacrylonitrile (PAN) nanoparticles were obtained in the size range 100 nm<d<180 nm depending on the amount of surfactant as usually observed in miniemulsion systems (2.0 rel.% SDS leads to 180-nm particles, 6 rel.% to 98-nm particles) [77]. As compared to a standard styrene miniemulsion system, it has to be considered that the solubility of acrylonitrile in water is rather high (7.35%). For a miniemulsion with 20 wt% acrylonitrile, just about 70% of the monomer is located inside the droplets, whereas 30% is dissolved in the water phase. This is no restriction for a miniemulsion polymerization process, and the use of a hydrophobic initiator 2,2′azobis(2-methylbutyronitrile) allows the preservation of the droplets as the reaction sites by droplet nucleation (see Fig. 12). Initiation of the

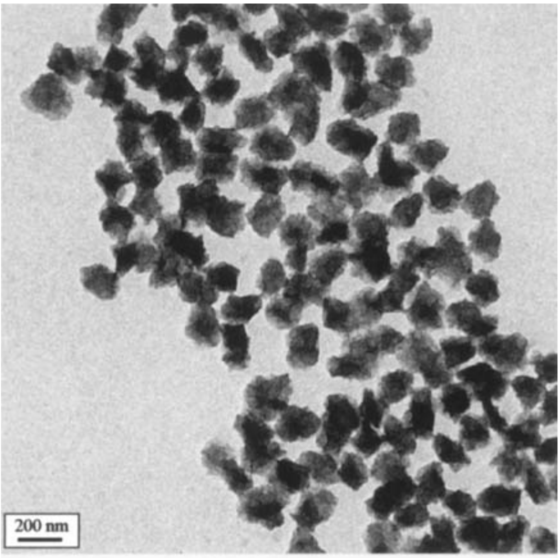

Fig. 12. Transmission electron micrograph of PAN latex particles

miniemulsion in the water phase would lead to polymerization in the water phase and secondary nucleation of new polymer particles. However, it has to be noted that the more SDS is used and therefore the smaller the droplets are, the more difficult it is to control the fast polymerization within the droplets.

Due to the insolubility of the polymer in the monomer, the formed polymer precipitates and crystallizes during the polymerization within the droplets; ca. 10-nm large polymer nanocrystals are formed. Pure PAN latexes have a crumpled appearance where the single polymer nanocrystals remain in the final structure and are easily identified by their sharp edges and flat surfaces.

4.5
Radical Copolymerization

4.5.1
Hydrophobic/Hydrophobic Copolymers

Miniemulsion copolymerization of a 50:50 styrene/methyl methacrylate monomer mixture, using hexadecane as hydrophobe, was carried out by Rodriguez et al. [78]. The mechanism of mass transfer between miniemulsion droplets and polymer particles in the miniemulsion copolymerization of styrene-methyl methacrylate (AIBN as initiator, hexadecane as hydrophobe) was studied, analyzing the mass transfer of highly water-insoluble compounds from miniemulsion droplets to polymer particles by both molecular diffusion and collisions between droplets and particles [79, 80].

Copolymerization of styrene and butyl acrylate was successfully carried out by Huang et al. using the redox initiator system $(NH_4)_2S_2O_8/NaHSO_3$ at lower temperature [68]. The rate of the miniemulsion polymerization increases with increasing butyl acrylate concentration and decreases with increasing styrene concentration. This was attributed to differences in the water solubility. The lower water solubility of styrene either increases the desorption rate of the radicals or reduces the radical absorption of the monomer droplet [81].

Inaba et al. prepared a series of model styrene/butyl acrylate copolymer latexes with glass transition temperatures at room temperature. The functional monomer 2-(3-isopropenylphenyl)-2-methylethylisocyanate (TMI) was used as monomer/crosslinking agent for further film formation. A small amount of methacrylic acid was introduced in some formulations in order to enhance the crosslinking reaction. A redox initiation system was used to reduce premature crosslinking during the polymerization [82].

The copolymerization of monomers where one of the monomers acts as the hydrophobe was reported by Reimers and Schork [26]. MMA was copolymerized with *p*-methylstyrene, vinyl hexanoate, or vinyl 2-ethylhexanoate. The resulting copolymer composition tended to follow the predictions of the reactivity ratios, i.e., the reaction progresses as a bulk reaction. In contrast, copolymer compositions obtained from the (macro)emulsion copolymerizations tended to be more influenced by the relative water solubility of the comonomer and mass transfer. Wu and Schork used monomer combinations with large differences in reactivity ratios and water solubility: vinyl acetate/butyl acrylate, vinyl acetate/dioctyl maleate, and vinyl acetate/*N*-methylol acrylamide. The miniemulsion system follows more closely the integrated Mayo-Lewis equations than the comparable emulsion system [73].

The copolymer composition in miniemulsion copolymerization of vinyl acetate and butyl acrylate during the initial 70% conversion was found to be less rich in vinyl acetate monomer units [34]. Miniemulsion polymerization also allowed the synthesis of particles in which butyl acrylate and a PMMA macromonomer [83, 84] or styrene and a PMMA macromonomer [85] were copolymerized. The macromonomer acts as compatibilizing agent for the preparation of core/shell PBA/PMMA particles. The degree of phase separation between the two polymers in the composite particles is affected by the amount of macromonomer used in the seed latex preparation.

In a previous chapter the polymerization of fluorinated monomers in miniemulsion polymerization was shown. The fluorinated monomers can also be copolymerized with protonated monomers. It was shown in our laboratory that miniemulsification of such mixed monomer species allows one to perform efficient copolymerization reactions with standard hydrophobic and hydrophilic monomers in a common heterophase situation, resulting either in core-shell latexes or in statistical copolymers. In contrast to the pure fluorinated polymers, these copolymers dissolve in organic solvents but still show the profitable interface properties of the fluorinated species. In order to obtain a negatively charged surface, the surfactant SDS and small amounts of acrylic acid were used, whereas positively charged particles are expected to be obtained by cetyl trimethylammonium chloride as surfactant and MADQUAT as polymerizable comonomer. In all cases, coagulum-free and stable polymer latexes were obtained. It could be shown that the use of AA or MADQUAT did not significantly affect the particle size. However, the size distribution is broader than for the pure fluorinated polymer particles. An increase in the surfactant amount leads often to bimodal distributions; 1.3% surfactant seems to be well suited.

4.5.2
Amphiphilic Copolymers

Small amounts of carboxylic monomers (acrylic acid (AA) or methacrylic acid (MAA)) [86] or 2-hydroxyalkyl methacrylates [87] could be easily used in a styrene miniemulsion polymerization, using DMA or SMA as hydrophobe and SDS as emulsifier.

The polymerization process of two monomers with different polarities in similar ratios is a difficult task due to the solubility problems. Using the miniemulsion process, it was possible to start from very different spatial monomer distributions, resulting in very different amphiphilic copolymers in dispersion [88]. The monomer, which is insoluble in the continuous phase, is miniemulsified in order to form stable and small droplets with a low amount of surfactant. The monomer with the opposite hydrophilicity dissolves in the continuous phase (and not in the droplets). As examples, the formation of acrylamide/methyl methacrylate (AAm/MMA) and acrylamide/styrene (AAm/Sty) copolymers was chosen using the miniemulsion process. In all cases the syntheses were performed in water as well as in cyclohexane as the continuous phase. If performing the synthesis in water, the hydrophobic monomer with a low water solubility (styrene or methyl methacrylate) mainly forms monomer droplets, whereas the hydrophilic monomer acrylamide with a high water solubility will be mainly dissolved in the water phase. In the case of inverse miniemulsion, the hydrophilic monomer is expected to form the droplets, whereas the hydrophobic monomer is dissolved in the continuous phase.

Starting from those two dispersion situations, the locus of initiation is expected to have a great influence on the reaction products and the quality of the obtained copolymers. Therefore three different initiators were used, an oil-soluble initiator (e.g., 2,2′azobis(2,4-dimethylvaleronitrile (ADVN)), an interfacial active initiator (e.g., PEGA200), and a water-soluble initiator (e.g., potassium peroxodisulfate (KPS)) in order to initiate the polymerization selectively in one of the phases or at the interface.

In the system AAm/MMA, the best copolymer with respect to low content of homopolymers, low blockiness, and good redispersibility in polar and non-polar solvents was obtained in inverse miniemulsion with initiation in the continuous phase cyclohexane. In this case, the MMA chains grow in the continuous phase till they become insoluble and precipitate onto the AAm-droplets which enables the radicals to cross the interface; then AAm units can be added to the polymer chain. In the system AAm/Sty, the best copolymer was also obtained in the inverse miniemulsion process, but using interfacial initiation. This leads to almost homopolymer free copolymer samples with low blockiness indicating a fast change of the growing radical between the phases in order to add Sty and AAm units. A copolymerization in the direct miniemulsion with water as continuous phase using the interfacial initiator PEGA200 (see Fig. 13) results in a higher homo-AAm content. This can be attributed to the fact that the initiator

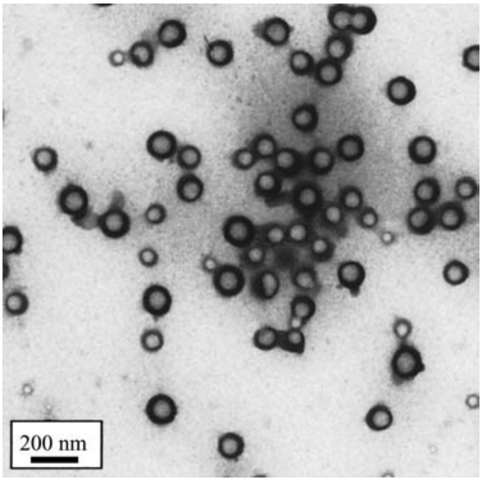

Fig. 13. TEM micrograph of the PMMA/AAm copolymer obtained in a direct miniemulsion polymerization with interfacial initiation stained with RuO_4

due to its hydrophilicity has a slightly higher tendency to be in the water phase where AAm units can be captured. In order to obtain also in this direct case a statistical copolymer, the hydrophilicity of the interfacial initiator will be changed by in further experiments.

4.6
Catalytic Chain Transfer in Miniemulsion

The employment of a cobalt catalytic chain transfer agent in miniemulsion polymerization allows the direct control of the molecular weight [89]. The solubility of the cobalt catalyst was found to have a large influence on the mechanism of the reaction. Cobaltoxime boron fluoride partitions approximately equally between the water and oil phases. In this case, the reaction was found to be extremely sensitive to the selection of the initiator, displaying poor catalytic activity in the presence of oxygen-centered radicals (derived from potassium sulfate), which can be explained by a poisoning and/or deactivation of the catalyst. By contrast, tetraphenylcobaltoxime boron fluoride resides exclusively in the oil phase. The catalytic activity proved to be independent of the initiator type, as the catalyst does not come in direct contact with the initiator-derived radicals. Therefore, miniemulsions allow effective isolation from the initiator radicals, thereby allowing a batch reaction to proceed without significant loss of catalytic activity.

4.7
Controlled Free-Radical Miniemulsion Polymerization

Living free-radical polymerization represents a promising technique to produce polymers with highly controlled structures. Different possible systems known from bulk polymerizations have been used in miniemulsions. The living free radical polymerization of, e.g., styrene via the miniemulsion approach allows one to eliminate the drawback of the bulk system where an increase in polydispersity was found at high conversions due to the very high viscosity of the reaction medium [90].

Four different approaches for controlled radical polymerization have been adapted to the miniemulsion polymerization process:

1. The controlled free-radical miniemulsion polymerization of styrene was performed by Lansalot et al. and Butte et al. in aqueous dispersions using a *degenerative transfer process* with iodine exchange [91, 92]. An efficiency of 100% was reached. It has also been demonstrated that the synthesis of block copolymers consisting of polystyrene and poly(butyl acrylate) can be easily performed [93]. This allows the synthesis of well-defined polymers with predictable molar mass, narrow molar mass distribution, and complex architecture.
2. In a *stable free-radical polymerization* (SFRP), the initiated polymer chains are reversibly capped by a stable radical, for example, the 2,2,6,6-tetramethylpyridin-1-oxyl radical (TEMPO). Stable PS dispersions via miniemulsion polymerization were prepared by MacLeod et al. with an optimized ratio

and amount of surfactant, hydrophobe, nitroxide and KPS as initiator at 135°C [94]. TEMPO in combination with BPO was used by Prodpran et al. [95]. Utilizing TEMPO-terminated oligomers of polystyrene also results in stable latexes, but the particle size distribution is unexpectedly broad [96]. In order to decrease the reaction temperature below 100°C, an acrylic β-phosphonylated nitroxide in combination with the KPS/$Na_2S_2O_5$ redox initiator system was used [97].

3. *Living radical polymerizations* in miniemulsions have also been conducted by de Brouwer et al. using reversible addition-fragmentation chain transfer (RAFT) and nonionic surfactants [98]. The polydispersity index was usually below 1.2. The living character is further exemplified by its transformation into block copolymers.
4. *Reverse atom transfer radical polymerization* (ATRP) of butyl methacrylate was successfully conducted in miniemulsions by Matyaszewski et al. using the water-soluble initiator V50 and the hydrophobic ligand 4,4′-di(5-nonyl)-4,4′-bipyridine (dNbpy) to complex the copper ions. Although the forming radical mediator Cu(II) complex had a large water-partitioning coefficient, the rapid transfer of Cu(II) between the organic and aqueous phases assured an adequate concentration of the deactivator in the organic phase. As a result, controlled polymerization was achieved [99, 100].

5
Hybrid Nanoparticles by Miniemulsion Technologies

5.1
Polymer-Polymer Hybrids

Water-insoluble materials such as resins by dissolution or dispersion can be incorporated easily in the organic phase by using the miniemulsion process. Miniemulsion copolymerizations were carried out with acrylic monomers (methyl methacrylate, butyl acrylate, and acrylic acid) in the presence of alkyd resin in order to produce stable polymer-polymer hybrid latex particles incorporating an alkyd resin into acrylic coating polymers [42]. Throughout the reaction, the resin simultaneously acts as a hydrophobe and allows the stabilization of the miniemulsion. The double bonds served as grafting sites of the alkyd onto the polyacrylate and predominantly poly(acrylate-*g*-alkyd) was formed [101]. Despite a high degree of crosslinking (>70%), residual double bonds were still present in the polymer-polymer hybrid latex for curing reactions during film formation [102].

Polymerizing acrylic monomers in the presence of oil-modified polyurethane leads also to a grafting onto the polyacrylics, resulting in dispersions suitable for stable water-borne latexes with good adhesion properties and fair hardness properties [103].

Oil-acrylate hybrid-emulsions were formed using the fatty-acid hydroperoxides as initiator system for the miniemulsion polymerization of acrylate. The initiation took place at the droplet interface and resulted in the formation of triglycide modified polyacrylate molecules which act as compatibilizers between the oil and the PMMA phase, resulting in more homogeneous particles [104].

5.2
Encapsulation of Pigments by Direct Miniemulsification

For the encapsulation of pigments by miniemulsification, two different approaches can be used. In both cases, the pigment/polymer interface as well as the polymer/water interface have to be carefully chemically adjusted in order to obtain encapsulation as a thermodynamically favored system. The design of the interfaces is mainly dictated by the use of two surfactant systems, which govern the interfacial tensions, as well as by employment of appropriate functional comonomers, initiators, or termination agents. The sum of all the interface energies has to be minimized.

For a successful incorporation of a pigment into the latex particles, both type and amount of surfactant systems have to be adjusted to yield monomer particles, which have the appropriate size and chemistry to incorporate the pigment by its lateral dimension and surface chemistry. For the preparation of the miniemulsions, two steps have to be controlled (see Fig. 14). First, the already hydrophobic or hydrophobized particulate pigment with a size up to 100 nm has to be dispersed in the monomer phase. Hydrophilic pigments require a hydrophobic surface to be dispersed into the hydrophobic monomer phase, which is usually promoted by a surfactant system 1 with low HLB value. Then, this common mixture is miniemulsified in the water phase employing a surfactant system 2 with high HLB, which has a higher tendency to stabilize the monomer (polymer)/water interface.

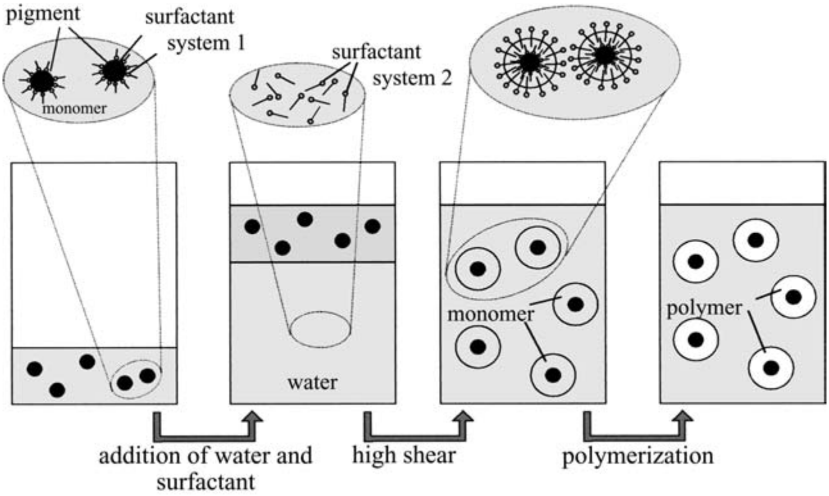

Fig. 14. Principle of encapsulation by miniemulsion polymerization

Erdem et al. described the encapsulation of TiO_2 particles via miniemulsion in the two steps. First, TiO_2 was dispersed in the monomer using the OLOA 370 (polybutene-succinimide) as stabilizer [105]. Then this phase was dispersed in an aqueous solution to form stable submicron droplets [106]. The presence of TiO_2 particles within the droplets limited the droplet size. Complete encapsulation of all of the TiO_2 in the colloidal particles was not achieved; the encapsulation of 83% of the TiO_2 in 73% of the polymer was reported. Also the amount of encapsulated material was very low: a TiO_2 to styrene weight ratio of 3:97 could not be exceeded [107, 108].

Nanoparticulate hydrophilic $CaCO_3$ was effectively coated with a layer of stearic acid as surfactant system 1 prior to dispersing the pigments into the oil phase [58]. The -COOH groups act as good linker groups to the $CaCO_3$, and the tendency of the stearic acid to go to the second polymer/water interface was found to be low. Then 5 wt% of $CaCO_3$ based on monomer could be completely encapsulated into polystyrene particles [58]. It was shown that the weight limit was given by the fact that, at this concentration, each polymer particle already contained one $CaCO_3$ colloid, which was encapsulated in the middle of the latex particle (Fig. 15a).

The encapsulation of magnetite particles into polystyrene particles was efficiently achieved by a miniemulsion process using oleoyl sarcosine acid [109] or the more efficient oleic acid as first surfactant system to handle the interface magnetite/styrene, and SDS to stabilize the interface styrene/water, thus creating a polymer-coated ferrofluid (Fig. 15b). Since the magnetite particles were very small (ca. 10 nm), each polymer particle was able to incorporate many inorganic nanoparticles. A content of 20 wt% could be incorporated in this way.

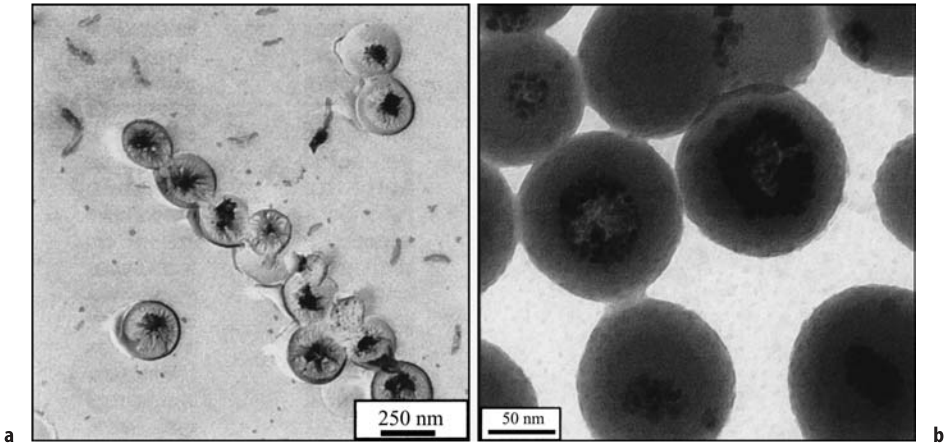

Fig. 15. **a** Encapsulation of one colloid per polymer particle: $CaCO_3$ nanoparticles in PS latex particles; **b** Encapsulation of many colloids per polymer particle: Fe_3O_4 in PS particles

5.3
Encapsulation of Carbon Black by Co-Miniemulsion

Since carbon black is a rather hydrophobic pigment (depending on the preparation conditions), the encapsulation of carbon black in the latexes by direct dispersion of the pigment powder in the monomer phase prior to emulsification is again a suitable way [58]. Here, full encapsulation of non-agglomerated carbon particles can be provided by the appropriate choice of the hydrophobe. In this case the hydrophobe not only acts as the stabilizing agent against Ostwald ripening for the miniemulsion process, but also mediates to the monomer phase by partial adsorption. However, this direct dispersion just allows the incorporation of 8 wt% carbon black since the carbon is still highly agglomerated in the monomer. At higher amounts, the carbon cluster broke the miniemulsion, and less defined systems with encapsulation rates lower than 100%, which also contained pure polymer latexes, were obtained.

To increase the amount of encapsulated carbon to up to 80 wt%, another approach was developed [110] where both monomer and carbon black were independently dispersed in water using SDS as a surfactant and mixed afterwards in any ratio between the monomer and carbon. Then this mixture was cosonicated, and the controlled fission/fusion process characteristic for miniemulsification destroyed all aggregates and liquid droplets, and only hybrid particles being composed of carbon black and monomer remain due to their higher stability [110]. This controlled droplet fission and heteroaggregation process can be realized by high energy ultrasound or high pressure homogenization as was shown earlier.

TEM and ultracentrifuge results showed (see Fig. 16) that this process results in effective encapsulation of the carbon with practically complete yield: only rather small hybrid particles, but no free carbon or empty polymer particles, were found. It has to be stated that the hybrid particles with high carbon contents do not possess spherical shape, but adopt the typical fractal structure of carbon clusters, coated with a thin but homogeneous polymer film. The thickness of the monomer film depends on the amount of monomer, and the exchange of monomer between different surface layers is – as in miniemulsion polymerization – suppressed by the presence of an ultrahydrophobe.

Therefore the process is best described as a polymerization in an adsorbed monomer layer created and stabilized as a miniemulsion (‘ad-miniemulsion polymerization’). The process is schematically shown in Fig. 16.

5.4
Encapsulation of a Liquid – Formation of Nanocapsules

The polymerization in miniemulsion can also be performed in the presence of an oil, which is inert to the polymerization process. During polymerization, oil and polymer can demix, and many different structures such as an oil droplet encapsulated by a polymer shell, sponge like architectures, or dotted oil droplets can be formed. The formation of such structures is known from classical emul-

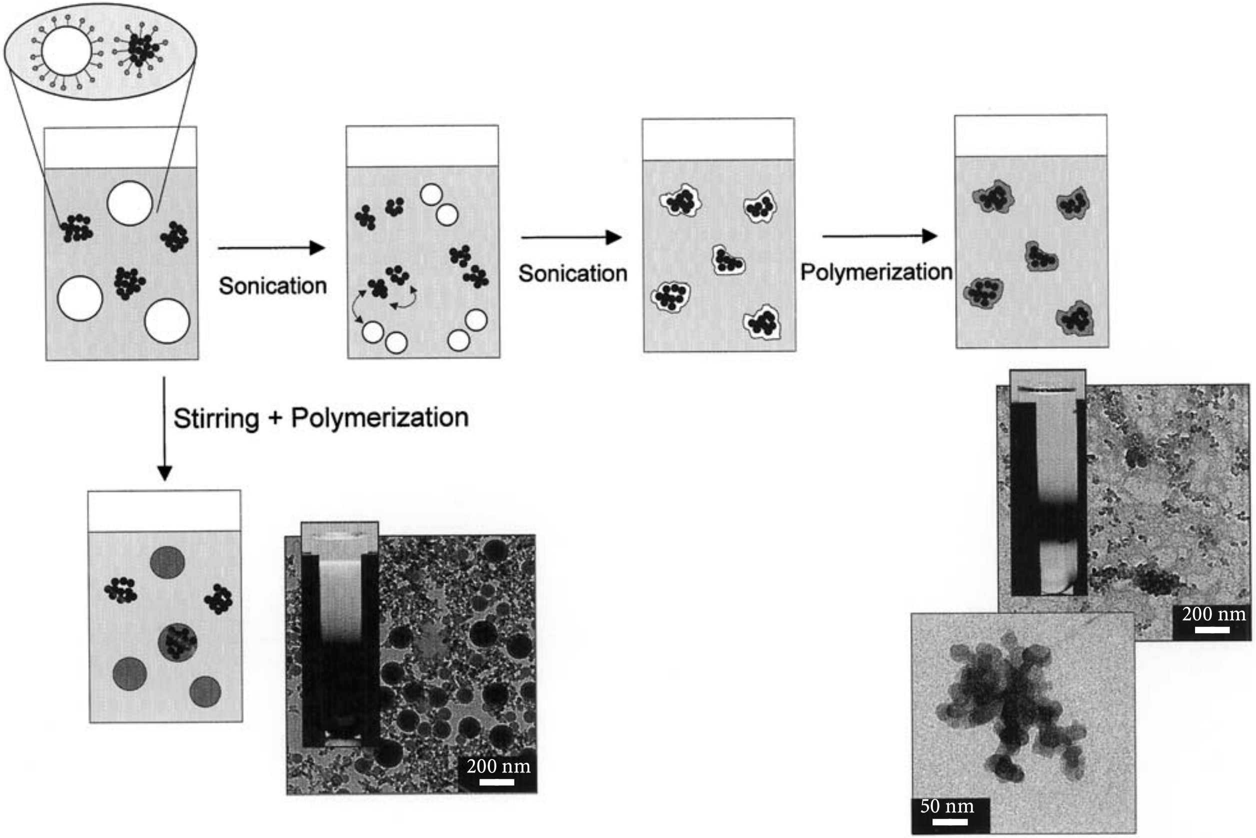

Fig. 16. Principle of co-miniemulsion where both components have to be independently dispersed in water and mixed afterwards. The controlled fission/fusion process in the miniemulsification realized by high energy ultrasound or high pressure homogenization destroys all aggregates and liquid droplets, and only hybrid particles being composed of carbon black and monomer remain due to their higher stability

sion polymerization, but is usually kinetically controlled [111–113]. The synthesis of hollow polymer nanocapsules as a convenient one-step process using the miniemulsion polymerization, however, has the advantage of being thermodynamically controlled [114].

The chemical control of the expected particle morphology for an encapsulation process is a system with a complex parameter field. The particle morphology reacts sensitively on the chemical nature of the emulsifier, the polymer, and the oil, as well as on additives such as an employed additional hydrophobe, the initiator, or possible functional comonomers. It is obvious that the development of the final morphology in polymer microparticles also involves the mobility or diffusion of at least two molecular species influenced by some driving force to attain the phase-separated structure. The ease of movement may be related to the phase viscosity, but in this approach the main emphasis is laid on the driving force, which is the Gibbs free energy change of the process.

It was found that the nanocapsules are formed in a miniemulsion process by a variety of monomers in the presence of larger amounts of a hydrophobic oil. Hydrophobic oil and monomer form a common miniemulsion before polymerization, whereas the polymer is immiscible with the oil and phase-separates throughout polymerization to form particles with a morphology consisting of a hollow polymer structure surrounding the oil. The differences in the hydrophilicity of the oil and the polymer turned out to be the driving force for the formation of nanocapsules.

In the case of poly(methyl methacrylate) (PMMA) and hexadecane as a model oil to be encapsulated, the pronounced differences in hydrophilicity are suitable for direct nanocapsule formation. PMMA is regarded as rather polar (but is not water soluble), whereas hexadecane is very hydrophobic so that the spreading coefficients are of the right order to stabilize a structure in which a hexadecane droplet core is encapsulated in a PMMA shell surrounded by water [114]. In the state of miniemulsion, the monomer and the hexadecane are miscible, but phase separation occurs during the polymerization process due to the immiscibility of hexadecane and PMMA. Miniemulsions were obtained by mixing the monomer MMA and hexadecane at varying ratios together with the hydrophobic, oil-soluble initiator AIBN and miniemulsifying the mixture in an aqueous solution of SDS. After polymerization polymer capsules were obtained as shown in Fig. 17a. Nanocapsules with an increased shell stability can be obtained by using up to 10 wt% of EGDMA as crosslinking agent. It is a fortunate experimental situation that the particle size in this reaction does not change with the amount of the anionic surfactant SDS or the nonionic surfactant Lutensol AT50 (a hexadecyl modified poly(ethylene glycol)). This means that with increasing surfactant load the surface coverage also increases, and the interfacial tension at the droplet/water interface decreases. That way, the influence of the systematic variation of one of the interface tensions on the particle morphology was examined, and a continuous morphological change towards engulfed structures was found (Fig. 17b) [114].

In the case of styrene as monomer and hexadecane as model oil, the cohesion energy density of the polymer phase is closer to that of the oil and therefore the structure of the final particles depends much more on the parameters, which

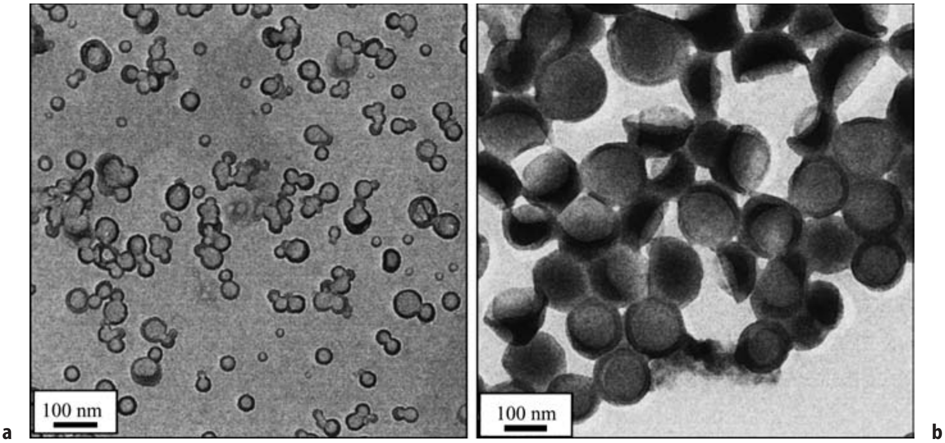

Fig. 17. **a** TEM micrographs of nanocapsules with an MMA to HD ratio of 1:1 using SDS as surfactant; **b** Coexistence of nanocapsules and capped particles in the case of using the surfactant Lutensol AT50

critically influence the interfacial tensions. A variety of different morphologies in the styrene/hexadecane system can be obtained by changing the spreading parameter. This was done by changing the monomer concentration, the type and amount of surfactant, as well as the initiator and the functional comonomer.

The best results were obtained by using the block copolymer surfactant SE3030 together with the nonionic initiator PEGA200 which supports interface stabilization and improves the structural perfection (Fig. 18a) of the polystyrene capsule morphology.

Another very powerful approach to improve the perfection of the capsules is the addition of a comonomer to the oil phase. Depending on the polarity of the monomer, it will enter one of the two interfaces (polymer/water or polymer/oil) and reduce the corresponding interfacial tensions and spreading coefficients. It was shown that the very hydrophobic comonomer lauryl methacrylate, which is expected to minimize the interfacial tension between styrene and the hexadecane phase, has no significant effect on the resulting morphology of the particles, meaning that this interfacial energy is of minor importance since it is already quite low. On the other hand, the slightly more hydrophilic MMA and the very hydrophilic AA affect the interfacial tension of styrene to water, and here a pronounced influence on the morphology was found. The influence depends on the partitioning coefficient: for MMA about 50 wt% of monomer was needed to create only close-to-perfect capsules, whereas 1 wt% of AA was sufficient in order to saturate the capsule surface with carboxylic groups, and hollow shell structures with constant capsule thickness were found (Fig. 18b). There is, however, a minor fraction of small homogeneous polymer latexes which we attribute to secondary nucleation due to the high content of water-soluble acrylic acid.

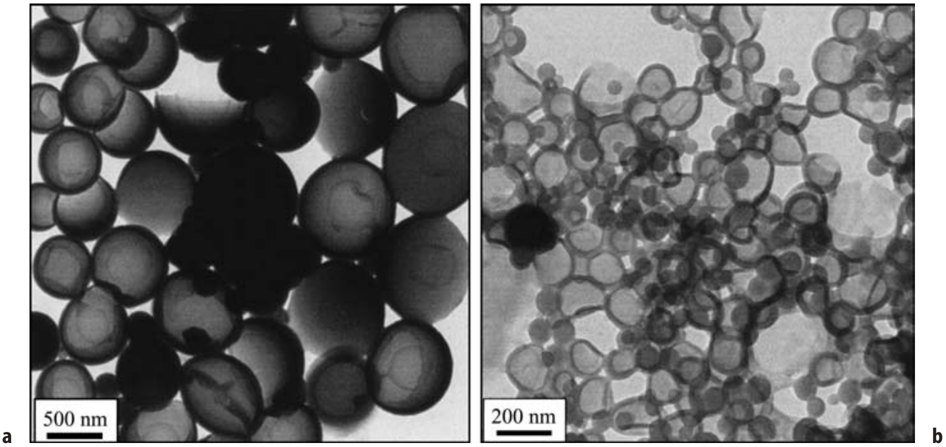

Fig. 18a,b. TEM micrographs of PS/hexadecane: **a** with SE3030 as surfactant and PEGA200 as initiator; **b** with AA as comonomer

5.5
Surface Coating of Miniemulsions with Inorganic Nanoparticles and Crystalline Building Blocks

In many cases gas permeation or chemical sensitivity of polymer capsules is still too high to be efficient for encapsulation. Here the employment of crystalline inorganic materials, such as clay sheets of 1.5 nm thickness, can be recommended. Since those clay sheets are fixed like scales onto the soft, liquid miniemulsion droplet, the resulting objects are called 'armored latexes' [115]. Since clays carry a negative surface charge, miniemulsions stabilized with cationic sulfonium-surfactants represented a convenient way to generate those armored latexes or crystalline nanocapsules. Due to their high stability against changes in the chemical environment, it is possible to use miniemulsion droplets themselves, but also polymerized latex particles as templates for such a complexation process. As a result, the liquid droplets or the polymer particles are then completely covered with clay plates and therefore film formation or coalescence is prevented. A synthetic monodisperse model clay with small lateral extensions was employed. As a result, the liquid droplets or the polymer particles are then completely covered with clay plates, which is also macroscopically visible by the absence of film formation or coalescence. However, complexation with the clay plates alone was not always sufficient to prohibit the release of low T_g polymer (e.g., PBA) or liquid material. In order to glue further together the single clay sheets, silicic acid was used as a 'mortar'. Therefore the stability of the shells can be increased by a condensation reaction with silicic acid, which reacts with itself, but also with residual surface OH-groups of the clay. In this case, film formation is indeed completely suppressed as shown by TEM for dried sample with PBA as template (Fig. 19a). The figure shows intact nanocapsules still filled with PBA with about the same size as found previously in solution. To receive an emptied, purely in-

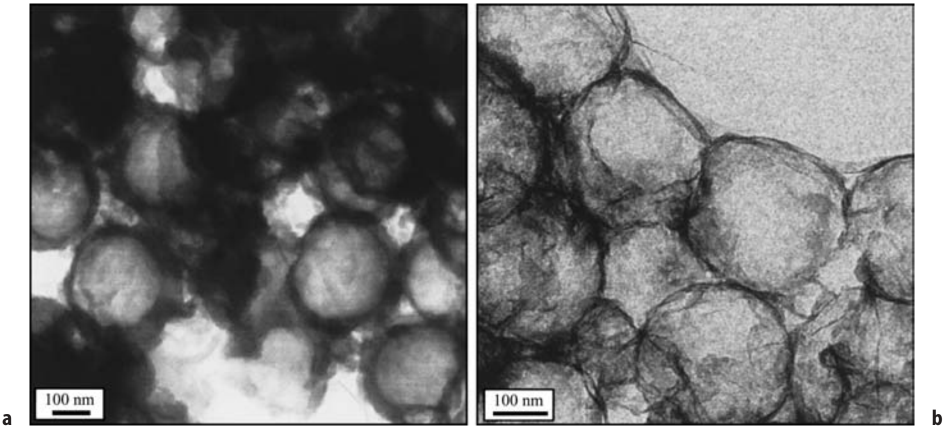

Fig. 19a,b. TEM of armored latexes: **a** sealed clay on PBA template particles; **b** sealed clay on PMMA template particles after removal of the PMMA in the core

organic shell, PMMA latex particles were used as templates. By intense illumination with the electron beam, PMMA depolymerizes to MMA, which uses or creates little pores in the shell to evaporate under the TEM high vacuum conditions. Figure 19b shows such emptied capsules as obtained by electron degradation. In any case the inorganic structure has not disintegrated; this means that the colloidal 'laying of bricks' was successful. These 'armored' droplets and latexes particles could be of high interest for pressure sensitive adhesives or as a new type of filler with unconventional chemical and mechanical performance.

5.5.1
Miniemulsions with Silica Nanoparticles

Switching from the very hydrophilic clays towards other inorganic nanoparticles, e.g., colloidal silica, leads, in the interplay with polymerization in miniemulsions, into a potential structural complexity, which covers the whole range from embedded particles (such as in the case of the calcium carbonate and carbon blacks) to surface bound inorganic layers (such as in the case of the clays). For basic research they are ideal systems to analyze complex structure formation processes in emulsions, since the original droplet shows a structure which is essentially established by molecular forces and local energy considerations, and which is ideally just solidified into a polymer structure.

It was discussed that the structure created by the ternary system oil/water/nanoparticle follows the laws of spreading thermodynamics, as they hold for ternary immiscible emulsions (oil 1/oil 2/water) [114, 116, 117]. The only difference is that the interfacial area and the curvature of the solid nanoparticle has to stay constant, i.e., an additional boundary condition is added. When the inorganic nanoparticles possess, beside charges, also a certain hydrophobic character, they become enriched at the oil-water interface, which is the physical base of the stabilizing power of special inorganic nanostructures, the so-called Picker-

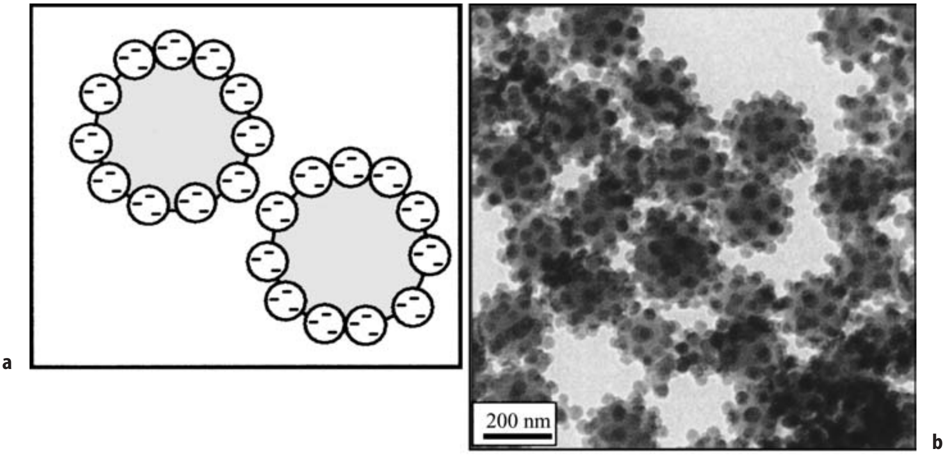

Fig. 20. **a** Scheme for using silica particles as stabilizer for monomer droplets of miniemulsions(Pickering stabilization); **b** Represents a latex with a monomer to silica ratio of 1:0.32

ing-stabilizers [118–120]. This means that the surface energy of the system oil/nanoparticle/water has to be lower than the sum of the binary combinations oil/water and water/nanoparticle to enable superstructure formation to occur. Since all three terms can be adjusted by the choice of the monomer and the potential addition of surfactants, this spans a composition diagram with a variety of morphologies to occur. Silica nanoparticles are quite ideal as model nanoparticles for the systematic examination of compositional phase behavior since they are easy to obtain and to control with respect to their surface structure and interacting forces. The latter is done either by variation of pH, which changes the surface charge density, or by adsorption of cationic organic components, changing the polarity of the objects.

It was shown that silica nanoparticles in the absence of any surfactant could act as a Pickering stabilizer for a miniemulsion process [121]. The high quality and small overall particle size obtained only under alkaline conditions (pH=10) and in presence of the basic comonomer 4-vinylpyridine which acts as an aminic coupler [122, 123] is shown in Fig. 20. The particle size depends on the amount of silica in the expected way: the higher the silica content, the smaller the resulting stable hybrid structures. Comparably small compound particles in the size range between 120 nm and 220 nm in diameter with rather narrow size distribution were obtained [121], speaking for the high stabilization power of the silica particles as Pickering stabilizers. This underlines the surface activity of the silica nanoparticles under the applied conditions and the kinetic-free, equilibrium type structure of a miniemulsion latex particle. Since these systems are free of low molecular weight surfactants and all chemical side products which might act as a surfactant, the measured surface tension was as high as 71.4 mN m^{-1}, which is practically the value of pure water.

The addition of a surfactant (nonionic, anionic, or cationic) to the same system resulted in a more complex zoo of structures [121]. Nonionic surfactants are preferentially bound to the silica nanoparticles due to a preferential interaction between the silica and the ethylene oxide chains [124], which screens any interaction with the monomer mixture. Also the addition of the anionic sodium dodecyl sulfate (SDS) leads to electrostatic repulsion and a competition between surfactant and silica nanoparticles. The most pronounced morphology changes are observed with the cationic surfactant cetyltrimethylammonium chloride (CTMA-Cl). Due to charge coupling as well as induced dipole interaction, this surfactant strongly binds to silica over the whole pH-range. The surfactant is mainly adsorbed by the silica, but under standard conditions there is not enough CTMA in the recipe to counterbalance the negative charges of the system at pH=10. In the presence of 4-vinylpyridine, the strong acid-base interaction gives an additional stability. Therefore, at pH=10 a hedgehog morphology is found with a small overall diameter of 90 nm.

At higher CTMA concentrations exceeding the amount adsorbed onto the silica, a different morphology was found. Starting from a calculated surface coverage of 75%, the silica particles become incorporated into the droplets, and stable hybrid structures are obtained. The hybrids now have a raspberry morphology; however, they are rather heterogeneous with respect to loading with silica [121].

6
Non-Radical Polymerizations in Miniemulsion

6.1
Polyaddition

As already indicated in the introduction, the existence of stable, isolated nanodroplets, in which chemical reactions may, but do not have to, depend on droplet exchange (the so-called 'nanoreactors'), enables the application of the miniemulsion process in a much broader range.

In contrast to the process of creating a secondary dispersion as was used for the preparation of, e.g., polyurethanes and epoxide resins, it was shown that the miniemulsion polymerization process allows one to mix monomeric components together, and polyaddition and polycondensation reactions can be performed *after* miniemulsification in the miniemulsified state [125].

The principle of miniemulsion polymerization to polyadditions of epoxy-resins was successfully transferred to mixtures of different epoxides with varying diamines, dithiols, or diols which were heated to 60°C to form the respective polymers [125]. The requirement for the formulation of miniemulsions is that both components of the polyaddition reaction show a relatively low water solubility, at least one of them even below 10^{-5} g l^{-1}. The diepoxide bisphenol-A-diglycidylether was successfully used as epoxy component. In order to vary the obtained polymeric structure, tri- and tetra-functionalized epoxides were also used. As amino components a NH_2 terminated poly(propylene oxide) with M_w=2032 g mol^{-1}, 4,4′-diaminobibenzyl, 1,12-diaminododecane, and 4,4′-diaminodicyclohexylmethane were applied. As other addition components beside amine, 1,6-hexanedithiol and Bisphenol A were used. The hydrophobic component, which is required for the formulation of stable miniemulsions, is usually the applied epoxide itself, which has a very poor water solubility and provides sufficient retardation of the Ostwald ripening. The addition of a typical hydrophobe like hexadecane does not improve the miniemulsion stability indicating that monomer exchange is not the rate-determining step. The final polymers reveal molecular weights of about 20,000 g mol^{-1} with a dispersity of close to 2. This means that unexpectedly ideal reaction conditions are preserved during the reaction in miniemulsion, and that the proximity of the interface to water does not really disturb the reaction. Crosslinked epoxy network could be obtained by the reaction of both amine hydrogens, e.g., the molar ratio of diepoxide to diamine was chosen to be 2:1. SDS and the block copolymer SE3030 turned out to be very efficient surfactants for the polyaddition systems. With increasing amount of surfactant, the particle size decreases as expected. Using SDS as surfactant for the stabilization of the Epikote E828/Jeffamin D2000 system, the particle size ranges from 245 nm (1.7 wt% SDS relative to the monomer mixture) down to 83 nm (42 rel.% SDS). For the latexes of Epikote E828 and 1,12-diaminododecane synthesized with SDS, the particle size also shows the expected trend: with increasing amount of surfactant the particle size decreases from 816 nm (0.85 rel.% SDS) to 36 nm (25 rel.% SDS).

In general, it turned out that with increasing hydrophobicity of the reaction partner, the particle sizes also decrease, and small particles with a diameter down to 30 nm can be synthesized from a number of most hydrophobic combinations. This is about the minimal size which can be made by radical processes, i.e., we reach a limit given by the fundamental laws of colloidal stability. Figure 21a shows as a typical example the reaction product of Epikote E828 and 4,4′-diaminobibenzyl: small particles with a relatively narrow size distribution are obtained.

It was also shown that polyurethane latexes can be made by direct miniemulsification of a monomer mixture of diisocyanate and diol in an aqueous surfactant solution followed by heating (see Fig. 21b) [126]. This is somewhat special since one might expect a suppression of polymerization by side reactions between the very reactive diisocyanates and the continuous phase water. Therefore, it is important that the reaction between diisocyanate and diol has to be slower than the time needed for the miniemulsification step and the side reaction of the diisocyanate with water in the dispersed state has to be slower than the reaction with the diol. The functional groups (isocyanate to alcohol groups) were employed in a 1:1 molar ratio. IR spectra of the reactants and the resulting product show the disappearance of the isocyanate group after reaction (peak at 2300 cm^{-1}). The amide vibration at 3300 cm^{-1}, the carbonyl vibration at 1695 cm^{-1}, and the vibration at 1552 cm^{-1} are strong evidence for the formation of a polyurethane. The side reaction with water, leading to urea groups within the polyurethane, was also identified by the characteristic vibration at 1643 cm^{-1}, but turned out to be of secondary importance.

Polyaddition was also performed using chitosan stabilizer with two biocompatible costabilizers, Jeffamine D2000 and Gluadin, and a linking diepoxide in presence of an inert oil and it results, via an interface reaction, in thin but rather stable nanocapsules. Since both water and oil soluble aminic costabilizers can be

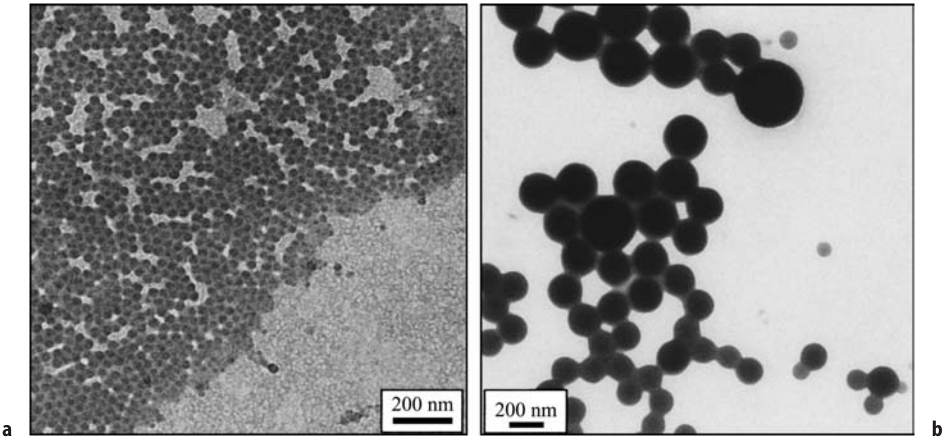

Fig. 21. a Typical latex obtained in a polyaddition process in miniemulsion (Epikote E828 (bisphenol-A-diglycidylether) and 4,4′-diaminobibenzyl); **b** TEM micrograph of a polyurethane latex obtained by isophorone diisocyanate and 1,12 dodecanediol

used, these experiments show the way to a great variety of capsules with different chemical structure. These capsules are expected to be biocompatible and biodegradable and might find applications in drug delivery [127].

6.2
Anionic Polymerization

For the anionic polymerization of phenyl glycidyl ether (PGE) in miniemulsion, Maitre et al. used didodecyldimethylammonium hydroxide as an 'inisurf', which acts as a surfactant and an anionic initiator by means of its hydroxy counterion at the same time [128]. As revealed by ^{1}H NMR and FTIR, genuine α,ω-dihydroxylated polyether chains were produced. The average molecular weight could be increased by varying the initiator concentration, type and concentration of surfactants, or by adding an alcohol as costabilizer. With increasing conversion, the polymer chain length increased but remained small, with a critical polymerization degree of $DP_{max}=8$.

6.3
Metal Catalyzed Polymerization Reactions

Ethylene can be polymerized using an aqueous miniemulsion consisting of an organo-transition metal catalyst at ethylene pressures of 10–30 bar and temperatures of 45–80°C resulting in large particles of about 600 nm [129]. A maximal productivity of 2520 kg PE per g atom active metal was achieved, which represents about 60% of the productivity of the same catalyst when used in ethylene suspension polymerization in organic phase.

7
Inorganic Miniemulsions

Miniemulsification is not restricted to organic monomers. It was shown that it can also be applied for low melting salts and metals to obtain salt or metal colloids of high homogeneity with diameters between 150 nm and 400 nm [130]. This is regarded as a very important development, since it allows the synthesis and handling of inorganic or metallic powders and their incorporation into coatings, inks, or nanocomposites by simple polymer technologies.

The extension of miniemulsions from water or polar monomers as a dispersed phase in oils or hydrocarbons as a continuous phase to salt melts or concentrated salt solutions is nevertheless demanding, since those liquids show higher cohesion energies, surface tensions, and mutual attractions than the corresponding organic matter. For that, a well-chosen steric stabilizer has to be employed, the polar part of which has to be miscible with salt melts, whereas the hydrophobic part has to be sufficiently long and tightly packed to provide sufficient steric stabilization. Again, it turned out that amphiphilic block copolymers [131] with poly(ethylene oxide) block are best suited. For the salt, one can choose from a wide variety of salts or metals, which melt below boiling or chemical decomposition of the continuous phase (which can easily be as high as 250–300°C). It is also possible to use highly concentrated salt solutions in water or to decrease the melting point by adding ternary components to the salts.

As an example, iron(III) chloride hexahydrate was melted by heating above 37°C and miniemulsified in the continuous phase (IsoparM, cyclohexane, etc.) to a stable miniemulsion using at least 5 wt% (with respect to salt) of the block copolymer stabilizer. Decreasing the temperature leads to nanoscopic salt crystals dispersed in a continuous oil phase. The average size of these particles is about 350 nm, a typical number for inverse dispersions.

Pure zirconyl chloride octahydrate melts and degrades at 150°C, but the melting temperature of the salt can easily be reduced by adding water to the salt. A 3:1 $ZrOCl_2$/water mixture melts at about 70°C. The molten salt was added to IsoparM at 75°C. A stable miniemulsion was obtained using 10 wt% of the block copolymer poly(ethylene-*co*-butylene-*b*-ethylene oxide) (PE/B-EO), which transforms throughout cooling in a dispersion of separate $ZrOCl_2$ nanocrystals. TEM pictures show (see Fig. 22a) that the particles are of uniform polyhedral crystalline shape.

For the preparation of nanosized metal dispersions the same procedure of high shear forces was used to prepare miniemulsions. Molten metals have very strong cohesion forces, which make them very difficult to disperse in an organic phase by conventional techniques. Gallium (mp=30°C) was melted at 45°C and emulsified in IsoparM by using 10 rel.% P(E/B-*bock*-EO). The miniemulsion was cooled to room temperature, and solid gallium particles with a size of 150 nm were obtained. Miniemulsification was also applied to disperse low melting alloys, like Wood's metal (mp=70°C) or Rose's metal (mp=110°C). Because of the very high density difference of the metal (ϱ (Wood's metal)=9.67 g cm^{-3}) and the continuous phase (ϱ (IsoparM)=0.87 g cm^{-3}), the weight-content of the metal was increased to 50 wt% (with respect to the overall dispersion) to obtain relevant volume fractions (for TEM see Fig. 22b).

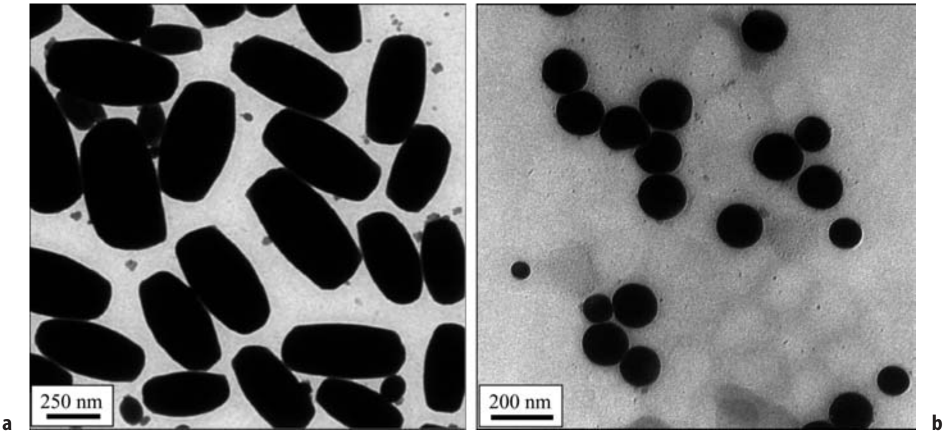

Fig. 22a,b. Particles obtained in an inverse miniemulsion process consisting of: **a** $ZrOCl_2.8H_2O$; **b** Wood's metal

The formation of high-melting materials can be achieved by a further reaction where the low-melting material is used as a precursor. These are subsequently transferred in a particle-by-particle fashion to the final product by reaction or precipitation, very similar to polymerization reactions of organic monomers. In the dispersed state heterophase reactions such as precipitations or oxidations can be performed, which essentially occur under preservation of the colloidal entities as single nanoreactors.

Addition of a base (pyridine or methoxyethylamine), which can mix with the continuous phase to the cyclohexane-salt miniemulsion under stirring, provides reaction to oxides and hydroxides, e.g., from iron(III) chloride hexahydrate to iron(III) oxide. Here the crystal water steps into the reaction, while pyridine from the continuous phase neutralizes the eliminated HCl. Obviously, the interface area of the miniemulsion is high enough in order to allow this reaction.

Formation of Fe_2O_3 is accompanied with an increase of the particle density ($\varrho(Fe_2O_3)=5.24\ \mathrm{g\,cm^{-3}}$). However, light scattering values and TEM pictures show that the droplets do not shrink as a whole, but show a hollow aggregate structure with interstitial cavities between primary particles (Fig. 23a). The particle size in cyclohexane could be varied by changing the amount of surfactant between 240 nm (20 rel.% TEGO EBE45 surfactant) to 370 nm (5 rel.%) and in IsoparM between 150 nm (42.5 rel.%) and 390 nm (5 rel.%).

The confinement of two species in stoichiometric amounts within the nanodroplets also allows the synthesis of mixed species. A mixture of Fe^{2+} and Fe^{3+} salts leads to the formation of magnetite, Fe_3O_4. The final dispersion with a particle size of 200 nm is black and shows magnetic properties. As is seen in the TEM pictures (Fig. 23b), the superstructure composed of 10-nm nanoparticles as determined by WAXS is anisotropic (lemon shaped), and constituting needle shaped nanocrystals, can be identified inside the particles, arranged as bundles along the main axis of the 'lemons'.

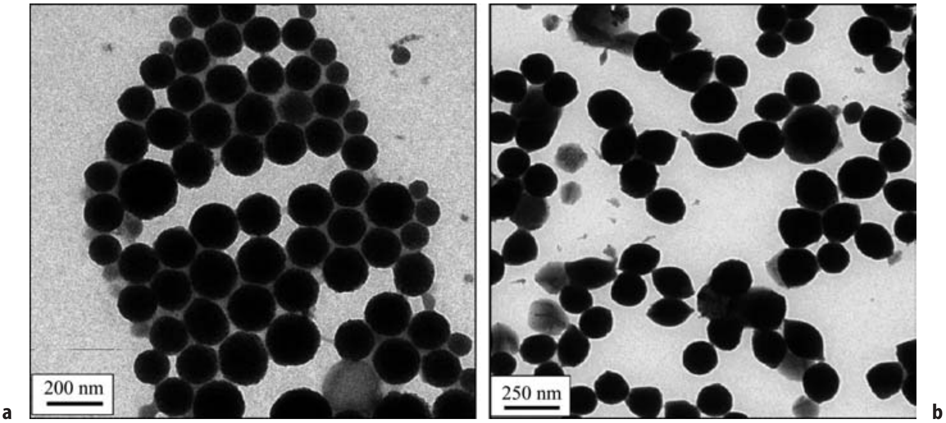

Fig. 23a,b. Reaction products of molten iron salt miniemulsions ('inorganic polymerizations'): **a** Fe_2O_3 particles obtained from $FeCl_3$ droplets; **b** Fe_3O_4 particles obtained from $FeCl_2/FeCl_3$ droplets

8
Conclusion

The main aim of this work was to summarize and combine recent progress in the field of miniemulsion. It was shown that the use of high shear, appropriate surfactants, and the addition of a hydrophobe in order to suppress the influence of Ostwald ripening are key factors for the formation of the small and stable droplets in miniemulsion. The kinetics of the reaction in the small separated nanodroplets was discussed in detail. It was shown that the strength of miniemulsion is the formation of polymeric nanoparticles consisting of polymers or polymer structures, which are hardly accessible by other types of heterophase polymerization. Non-radical polymerizations and the formation of hybrid materials by the encapsulation of inorganic materials or liquids are some examples which show the wide applicability of miniemulsions for technologically relevant problems. With the miniemulsification of molten inorganic materials in a subsequent reaction, the miniemulsions cross the border of polymers and open new possibilities in fabrication of solid particles for material science.

In my opinion, the field of miniemulsion is still on its rise in polymer and material science since there are numerous additional possibilities both for fundamental research and application. As a vision one may think of single molecules trapped and crystallized in each small droplet, which enables new types of physico-chemical experiments and handling of complex matter [132]. Since miniemulsions allow a very convenient and effective separation of objects in compartments of the size of 30–300 nm in diameter, some general new perspectives for polymer chemistry are opened. In miniemulsion droplets, it is in principle possible to isolate complex polymers or colloids strictly from each other and to react each single molecule for itself with other components, still working with significant amounts of matter and technically relevant mass fluxes. This was called ‘single (polymer) molecule chemistry’ [133]. In this mode of operation, single molecule chemistry usually takes place in a highly parallel fashion, where the 3D-space is compartmentalized to small, nanometer-sized subunits or ‘nanoreactors’ in each of which the same reaction takes place, each on a single molecule. Although this is hardly used in classical chemistry, it is the regular case in biochemical reactions since practically all reactions take place in different compartmentalized areas of the cell [134]. The approach is not restricted to organic synthesis, but includes more complex physicochemical processes such as protein folding, which mainly takes place as a single molecular event in the nanocompartments [135]. Mimicking these processes in polymer chemistry would open a door to gain a better control of the outcome of a demanding complex process or chemical reaction.

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