# Polyreactions in miniemulsions

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## Abstract

Miniemulsions are specially formulated heterophase systems where stable nanodroplets of one phase are dispersed in a second, continuous phase. It is delineated that miniemulsions rely on the appropriate combination of saturated high shear treatment, surfactants, and the presence of an osmotic pressure agent insoluble in the continuous phase. The droplet diameter is adjusted by the type and amount of surfactant, the volume fraction of disperse phase, and the general dispersion problem and lies between 30 and 500 nm. Since each of those droplets can be regarded as an individual batch reactor, a whole variety of polymerization reactions can be performed starting from miniemulsions, clearly extending the profile of classical emulsion polymerization. This article gives an overview about the mechanisms of formation of and polymerization in miniemulsions and reviews the current standing of the field for both the synthesis of new polymers and disperses hybrid systems from heterophase situations. © 2002 Elsevier Science Ltd. All rights reserved.

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# 1. Introduction

The synthesis and application of polymer nanoparticles dispersed in a non-solvent, so-called polymer latexes, experiences a scientific 'renaissance' in polymer science. This is due to a number of reasons. On the one hand, a general trend in society towards 'no organic volatiles' because of security, health, and

environmental reasons makes formulations of polymers in 'healthy' solvents, in general water, necessary. This is why polymer science is confronted with the problems to disperse or to synthesize more and more polymers in water, although a dispersion in water might interfere with the polymerization process. A second driver for this development is the 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 in hydrocarbon solvents. Thirdly, scientists have learned that polymer dispersions are a possibility 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 'for free'. That way, polymer materials can be generated employing rational structure design not only on the molecular scale, but also on the mesoscale, and superior rubbers or shock resistant thermoplastics are obtained.

Usually or most widely applied, polymer latexes are made by emulsion polymerization [1]. It is not the point to dismiss emulsion polymerization, since it has created an incredible wealth and 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. Strictly spoken, emulsion polymerization is good for the radical homopolymerization of a set of barely water-soluble monomers, but already heavily restricted in radical copolymerization, let alone all other polymer reactions. The reason for this is the polymerization mechanism where the polymer particles are the product of a 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 dictate 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 is a variety of other techniques to generate polymer dispersions, such as polymerization of microemulsions, suspension polymerization, or the generation of secondary dispersions by precipitation or solvent assisted emulsification, which will be discussed in more detail later. All of them are however seized by serious disadvantages such as excessive use of surfactant, insufficient colloidal stability, or costly procedures so that they found their applications, which however cannot really be extended to be used as a more general procedure in polymer science.

It is therefore a long-standing 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 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 droplets 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 size and 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 which are separated from each other by the continuous phase.

It will turn out that this situation is realized to a wide extend for miniemulsion polymerization, as schematically illustrated in Fig. 1.

Although there are already a few overviews of the field of miniemulsion [2–4], it is the attempt of the
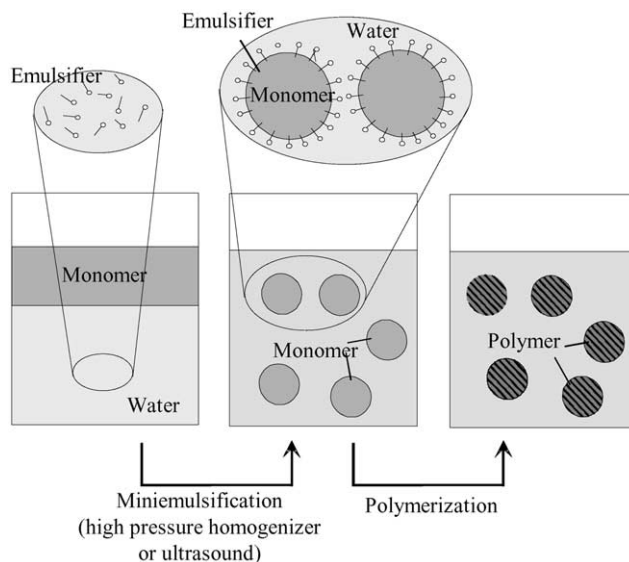
Fig. 1. The principle of miniemulsion polymerization.

present review to grab the exploding understanding and experimental developments which occurred especially in the last years to allow an actual assessment of the status and the possibilities of the field. The main focus is laid on a detailed description of the working principles of miniemulsions, the examination of the kinetics during the polymerization process, and the generation of different particle structures by appropriate handling of interface effects. It will be shown that miniemulsions indeed are not restricted to radical polymerization in water, but opens the way to new polymers via a liquid/liquid technology both in direct (aqueous solvent) and inverse (organic or hydrocarbon solvent) situations. We also will show that the principle is highly favorable for the simple generation of metal and ceramic nanoparticles, and for the encapsulation of nanoparticles into polymer shells to generate nanocomposites with high stability and processability.

## 2. Miniemulsions

### 2.1. Emulsion stability against Ostwald ripening, collisions, and coalescence

A stable emulsion of very small droplets is for historical reasons called a miniemulsion (as proposed by Chou et al. [5]). To create such a state, the droplets must be stabilized both against molecular diffusion degradation (Ostwald ripening, a monomolecular process or $\tau_1$ mechanism) and against coalescence by collisions (a bimolecular process or $\tau_2$ mechanism).

When an oil-in-water emulsion is created by mechanical agitation of a heterogeneous fluid containing surfactants, a distribution of droplet sizes results. Even when the surfactant provides sufficient colloidal stability of droplets, the fate of the droplet distribution is determined by their different droplet or Laplace pressure, which increases with decreasing droplet size, resulting in a net mass flux by diffusion. If the droplets are not stabilized against diffusional degradation, small ones will disappear,

increasing the average droplet size. It was shown that this disappearance can be very fast for small droplets [6].

The quantitative aspects of the rate of growth of the large particles and the rate of dissolution of the small particles in emulsion were theoretically examined by Higuchi and Misra [7]. It was shown that the emulsion stability was proportional to the particle volume. Kabalnov et al. [8] demonstrated by statistical analysis of experimental data that the changes of the particle size distribution function is in accordance with the predictions of the Lifshitz–Slezov theory. Extension for fluorocarbon emulsions were made later [9]. Due to the low water solubility, the fluorocarbon emulsions exhibit a higher stability.

The idea or concept that unstable droplets of aerosols or fog can be stabilized by the presence of a non-volatile third component was first formulated by Köhler [10]. A thermodynamic description of this phenomenon was later given by LaMer and Gruen [11], still for the aerosol case. These old treatises are usually not considered, and it is the merit of Reiss and Koper to review also this original literature in a recommendable article describing different thermodynamic scenarii of nanodroplet evolution in equilibrium with a gas phase [12].

In 1962, it was proposed that unstable emulsions (a transfer of knowledge to the liquid/liquid situation) may be stabilized with respect to the Ostwald ripening process by the addition of small amounts of a third component which must be preferentially located in the dispersed phase [7]. This stabilization effect was recently theoretically described by Webster and Cates [13]. They considered an emulsion whose droplets contained a trapped species (insoluble in the continuous phase) and studied the emulsion's stability via the Lifshitz–Slezov dynamics (Ostwald ripening). They extended the treatment of Kabalnov et al. [8] and derived a general condition on the mean initial droplet volume which ensures stability, even when arbitrary polydispersity is present in both size and composition of the initial droplets. They distinguished 'nucleated' coarsening, which requires either fluctuations about the mean field equations or a tail in the initial droplet size distribution, from 'spinodal' coarsening in which a typical droplet is locally unstable. A weaker condition for stability, previously suggested by Kabalnov et al., is sufficient only to prevent spinodal coarsening and is best viewed as a condition for metastability. The emulsion evolution is driven by the competition between the osmotic pressure of the trapped species and the Laplace pressure of droplets.

This is of high importance for the production of stable emulsions and miniemulsions. The increased stability is technologically used in other fields such as anesthetic/analgesic emulsions, the stability of which is provided by a white mineral or other ripening inhibitors [14].

The rate of Ostwald ripening depends on the size, the polydispersity and the solubility of the dispersed phase in the continuous phase. This means 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 building up additionally 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 [15,16].

Davis et al. [17] described that the added material reduces the total vapor pressure as defined by Raoult's law. As in the case of the pure oil system, smaller droplets will have a slightly higher vapor pressure (or solubility) than the larger ones. In order for the system to reach equilibrium, the constituting oil will leave the small droplets and pass to larger droplets. This loss will cause an increase in the mole fraction of the ultrahydrophobe in the small droplets and a decrease in the large droplets. Thus, the small droplets will have an osmotically reduced vapor pressure with respect to the larger droplets, which

will continue until pressure equilibrium is obtained. In no case, particles can disappear by this mechanism.

Besides the molecular diffusion of the dispersed phase, destabilization of emulsions can also occur by collision and coalescence processes. The handling of this problem is the standard question in colloid science and as usually solved by addition of appropriate surfactants which provide either electrostatic or steric stabilization to the droplets.

## 2.2. Techniques of miniemulsion preparation and homogenization

Mechanical emulsification starts with a premix of the fluid phases containing surface-active agents and further additives. The emulsification includes two mechanistic steps: first, deformation and disruption of droplets, which increase the specific surface area of the emulsion, and secondly, the stabilization of this newly formed interfaces by surfactants.

Mechanical homogenization of the emulsions to miniemulsions can be obtained by different methods. In the first miniemulsion articles, simple stirring was used. The use of an omni-mixer and ultraturrax is also described in earlier articles. However, the energy transferred by these techniques is not sufficient in order to obtain small and homogeneously distributed droplets [18]. 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 $\gamma$-surface/interfacial tension and $\Delta A$—the newly formed interface, since the viscous resistance during agitation absorbs most of the energy and creates heat [19,20]. As high force dispersion devices, today ultrasonication is used especially for the homogenization of small quantities, whereas a rotor–stator disperser with special rotor geometries, a microfluidizer or high-pressure homogenizers is favorable for the emulsification of higher quantities. Different machines are commercially available for emulsification.

Using a high-pressure homogenizer with an orifice valve [21], 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 nearly no surfactant molecule adsorbs at the newly forming interface, because adsorption time is longer than one disruption step. This is why a special mechanical design to ensure either high turbulent flow after disrupture or sufficient residual times in the elongational flow are necessary to enable surfactant adsorption at the newly formed droplets. Then, the total disruption process can be facilitated by surfactant.

Power ultrasound emulsification was first reported in 1927 [22]. There are several possible mechanisms of droplet formation and disruption under the influence of longitudinal density waves [23–25]. One is the formation of droplets as a consequence of unstable oscillations of the liquid–liquid interface. These capillary waves may occur only if the diameter of droplets to be disrupted is sufficiently larger than the wavelength of the capillary waves. For common systems of oil and water, this wavelength is in the range 10 μm [26], which is the typical size of droplets in a premix for continuous emulsification, and is therefore unlikely to occur. This has also been concluded by Neduzhii [27] who studied the influence of sound frequencies on emulsification. A mechanism related to that of capillary waves is the oscillation and subsequent disruption of whole droplets due to the action of sound. The corresponding resonance size is again in the region of some 10 μm. This process has to be taken into account only for the small fraction of droplets with diameters exactly matching the resonance frequencies. With respect to a usually
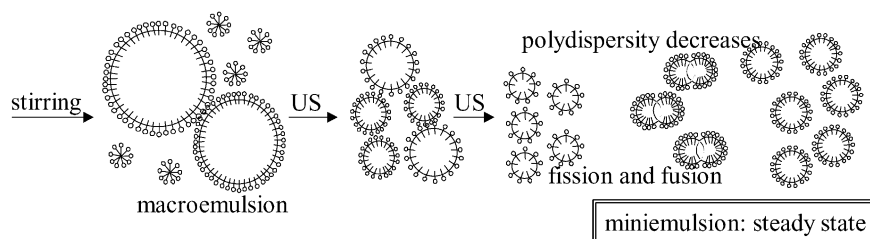
Fig. 2. Scheme for the formation of miniemulsion by ultrasound.

broad droplet size distribution in an emulsion premix, a broad range of sound frequencies would be a precondition for this mechanism to become effective.

Cavitation is the mechanism generally regarded as crucial under practical conditions [28,29]. 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 intense shock waves in the surrounding liquid and the formation of liquid jets of high velocity with enormous elongational fields [30]. However, the exact process of droplet disruption due to ultrasound as a result of cavitation is not yet fully understood. At constant energy density, the droplet size decreases when adding stabilizers, whereas the viscosity of the oil in w/o emulsions has no effect [31]. This clearly speaks for strong elongational flow components. For industrial purposes, it is possible to scale-up the sonifier by using a large-scale equipment [29].

In miniemulsions of monomers relevant for the polymerization purposes described here, the droplet size is in turn determined by the amount of monomer and water, the monomer solubility, and the amount of surfactant. It was found that the initial droplet size is a function of the mechanical agitation [32,33]. The monomer droplets change quite rapidly in size also throughout sonication in order to reach a pseudo-steady state. Once this state is reached, the size of the monomer droplet is no longer a function of the amount of applied mechanical energy, assuming a required minimum is used. In the beginning of homogenization, the polydispersity of the droplets is still quite high, but by constant fusion and fission processes, the polydispersity decreases, the miniemulsion reaches then a steady state (Fig. 2) [34].

The process of homogenization can be followed by different methods, e.g. by turbidity and by surface tension measurements. With increasing time of ultrasound, the droplet size decreases, and therefore the entire interface oil/water increases. Since a constant amount of surfactant has to be distributed now at a larger interface, the interface tension as well as the surface tension at the air/dispersion interface increases. In the example given in Fig. 3, the surface tension reaches a value close to $60\,\mathrm{mN\,m^{-1}}$ indicating that the coverage of the droplets is indeed very low (calculated as 10% of a dense surfactant layer). This limiting value however depends on the size of the droplets [34]. The surface tension measurement is sensitive to the total interface oil/water, but it can hardly be distinguished between polydisperse and monodisperse systems as long as the interfacial area 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 measurements indicating the complexity of the underlying equilibration process.

All experimental details really speak for a picture where the droplet size and size distribution are controlled by a Fokker–Planck type dynamic rate equilibrium of droplet fusion and fission processes, i.e. the primary droplets directly after sonication are much smaller, but colloidally unstable, whereas larger
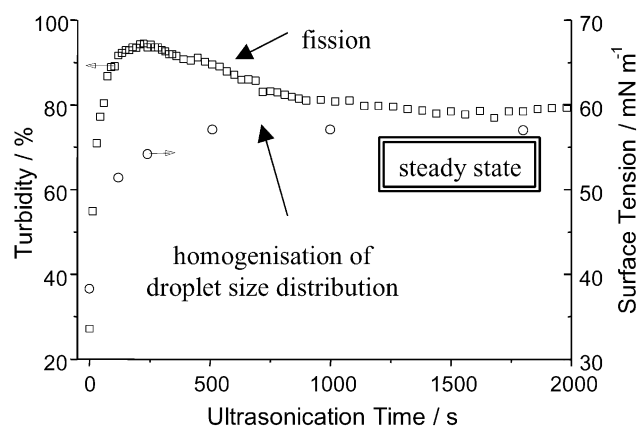
Fig. 3. Homogenization process followed by surface tension and turbidity measurements. Reaching of the steady state.

droplets are broken up with higher probability. This also means that miniemulsions come to the minimal particle sizes under the applied conditions (surfactant load, volume fraction, temperature, salinity, etc.), that is, that the resulting nanodroplets are at the critical borderline between stability and instability. This is why miniemulsions were already called 'critically stabilized' [34,35]. Practically speaking, it is that miniemulsions potentially make use of the surfactant in the most efficient way possible.

Another experiment underlining this dynamic rate equilibrium is a variation of the amount of the dispersed phase. Typically, the particle size increases with decreasing volume fraction when a $\tau_1$ process or osmotic stability is the limit, whereas the particles become smaller with decreasing amount of the dispersed phase for a $\tau_2$ process where collision rates are rate determining.

Miniemulsions with different solid contents between 5 and 25% were prepared by varying only the water content and by keeping the monomer/surfactant ratio constant (1.7 rel% sodium dodecyl sulfate, SDS). The ultrasonication time was chosen deeply in the saturation limit in order to ensure the reaching of the steady state, and the droplets were rapidly polymerized to reflect the original dispersion state as
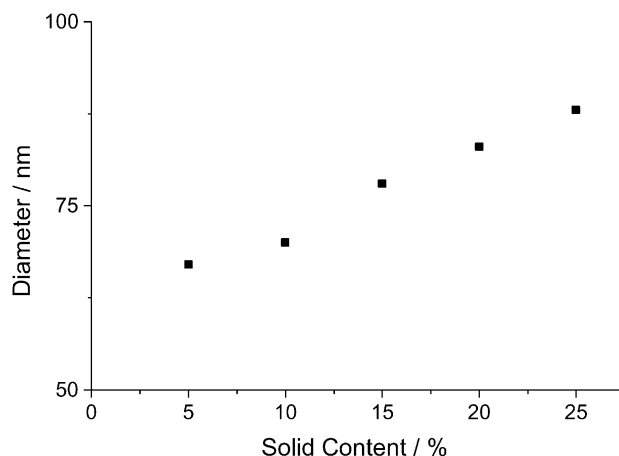


Fig. 4. Dependence of the particle diameter with increasing solids content (SDS: 1.7% relative to monomer styrene).

a)



b)
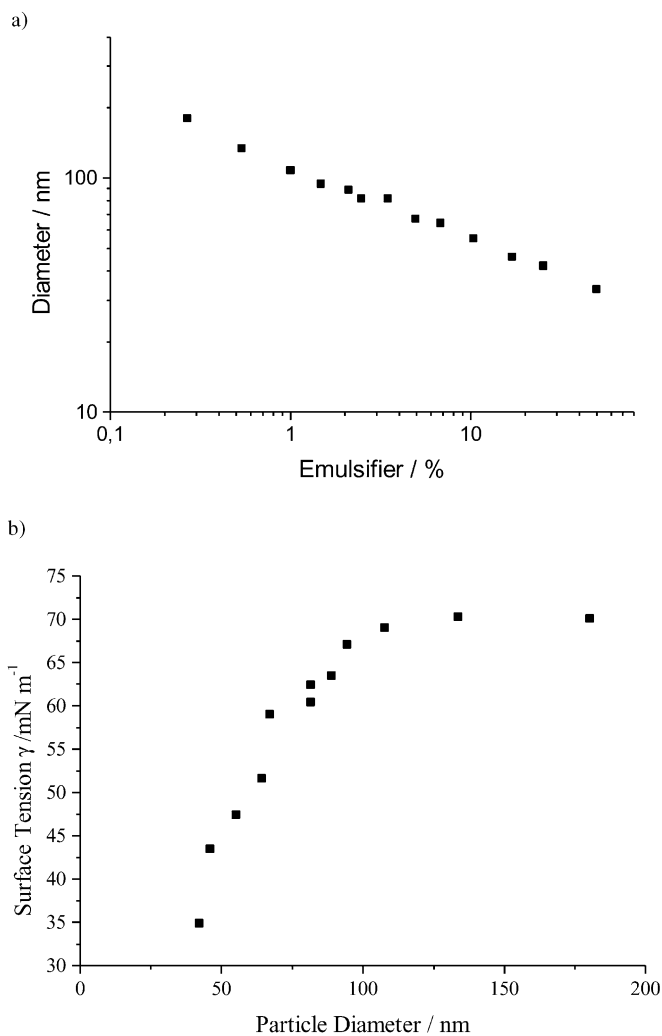


Fig. 5. (a) Polystyrene particle size versus amount of SDS (KPS as initiator) and (b) surface tension of the latexes in dependence of size.

close as possible. With increasing solid content, the particle size increases from 67 nm (5% solid content) to 88 nm (25% solid content) (Fig. 4). Therefore, it can be deduced that in appropriately formulated miniemulsions, it is indeed the colloidal stability which sets the limits, and that neither Ostwald ripening nor insufficient mechanical dispersion are problems, anymore.

## 2.3. Influence of the surfactant

Colloidal stability is usually controlled by the type and amount of employed surfactant. In this section, we will only discuss the typical relations using SDS as a model surfactant. A comparison of different surfactants is described in detail in Section 2.7.
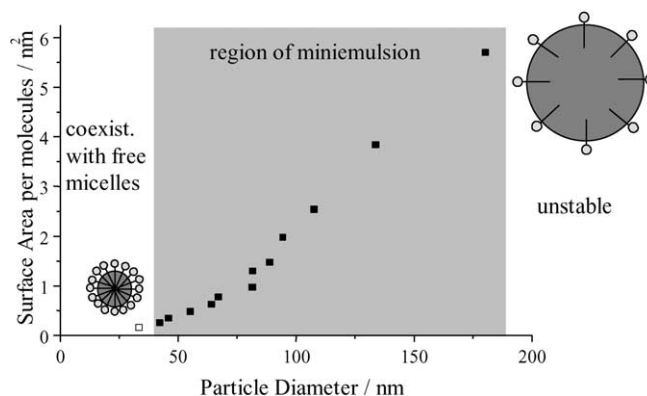
Fig. 6. $A_{surf}$ and surface tension versus the diameter of the particles.

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 SDS and styrene at 20 wt% disperse phase, it spans a range from 180 nm (0.3 rel% SDS relative to styrene) down to 32 nm (50 rel% SDS) (Fig. 5). Again, it is anticipated that rapidly polymerized latexes also characterize the parental miniemulsion. As compared to emulsion- and microemulsion polymerizations, 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 [36].

From the stoichiometry of the reaction and the particle size, one can calculate the averaged stabilized oil–water surface area per surfactant molecule, $A_{surf}$, which is a good measure for the efficiency of the surfactant.

The $A_{surf}$ values show also a strong dependence on the particle size. It is seen that the entire range from a dense surfactant monolayer (about 0.4 nm$^2$) for small particles to very incompletely covered latex particles (Fig. 6) is obtained. 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 remind: certain effects and reactivities might depend on droplet size and work better for larger particles, which is somewhat counterintuitive.

$A_{surf}$ values of 0.2 nm$^2$ calculated at very high surfactant loads indicate the presence of free micelles or multilayer adsorption which is not considered in these simplified area calculations. Here, we certainly leave the region of clean miniemulsions. On the other hand, surfactant ratios below 0.3 rel% create colloidally unstable systems, and again, the region of an operative 'miniemulsion mode' is left.

It is a matter of course that the different surfactant coverages are also reflected in the corresponding surface tensions $\gamma$ of the latexes (Fig. 5(b)). An increase of the surface tension with increasing diameter is observed. The miniemulsion-based polystyrene latexes exceeding 100 nm size have a surface tension close to the one of pure water. This is due to the fact that the bare particle surface is so large that

adsorption equilibrium ensures a very low concentration of free surfactants. Smaller droplets with their higher surface coverage have also a higher equilibrium concentration of free surfactant, but the concentration usually stays well below the cmc value. To repeat this in other words: in miniemulsions, there are no free micelles present. This is very important for the chemical reactivity and the polymerization kinetic in such systems.

Just in the case of the highest surfactant load of this series (50 rel% SDS), a dense surface layer and a $\gamma$ value typical for a micellar phase are observed. However, here we already left the composition range of well-defined miniemulsions.

## 2.4. Influence of the (ultra)hydrophobe

It was already stated earlier that the destabilization of the nanodroplets by Ostwald ripening can efficiently be slowed down by an addition of a hydrophobic agent to the dispersed phase which counteracts the droplet or Laplace pressure of the droplet. It is important to choose an agent, which can hardly diffuse from one droplet to the other and therefore is trapped in each droplet. The effectiveness of the hydrophobe increases with decreasing water solubility in the continuous phase, and there is a low but final hydrophobe content in order to become operative. For the hydrophobic agent, the term 'costabilizer' might also be used, but the notation 'cosurfactant' which is also used in the literature is rather misleading and should be avoided because in most cases, the agent is not surface active. A cosurfactant by definition [37,38] is a surface-active agent which acts in addition to the surfactant by further lowering the interfacial energy, but which cannot form micellar aggregates by itself.

Using an adequate amount of hydrophobe and undergoing an efficient homogenization process, a steady-state miniemulsification is reached. 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 particle number is fixed, also the averaged size is not influenced by this process, but the particle size distribution. It is assumed that this process is very fast and is usually not accessed by the experiment. It can be calculated that the Laplace pressure within the resulting nanodroplets and the osmotic pressure created by the hydrophobe are still far from being equal: the Laplace pressure is still larger than the osmotic pressure.

If we calculate the Laplace pressure by $2\gamma_{LL}/R = p_{Laplace}$ with the surface tension $\gamma_{LL}$ calculated from the surface coverage (as done in Ref. [34]), we obtain a value of about 12 bar as a maximum driving force for Ostwald ripening [35]. The osmotic pressure counteracting the Laplace pressure is given by $\Pi_{osm} = RTc/M$, which results in 4.5 bar, as calculated from typical literature recipes. Therefore, the droplet size after steady-state miniemulsification is not given by an effective zero droplet pressure, i.e. $p_{Laplace} - \Pi_{osm} = 0$ (which indeed would represent a real thermodynamic equilibrium), but 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 adaptation of the Laplace pressure with $R^{-1}$, whereas the osmotic pressure goes with $R^{-3}$, that means the minor changes in size already significantly change the pressure balance.

The equality of droplet pressures makes such systems insensitive against net mass exchange by diffusion processes (after the very fast equilibration process at the beginning), but the net positive character of the pressure makes them sensitive to all other changes of droplet size. It is an experimental observation [34] that steady-state homogenized miniemulsions which are critically stabilized undergo
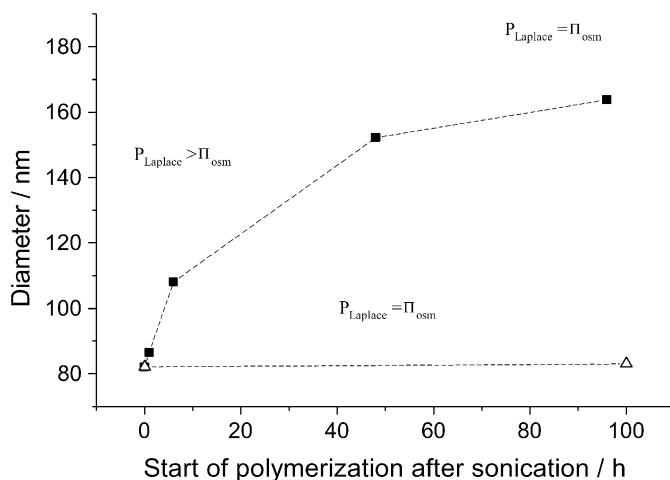
Fig. 7. Growth of miniemulsion droplets after steady-state ultrasonication (■). Post-stabilization (△) allows to keep the droplet size.

very slow droplet growth on the time scale of hundreds of hours, presumably by collisions or hydrophobe exchange. The droplets seem to grow until a zero effective pressure is reached (Fig. 7). 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 interface tension between the oil and the water phase and the coupled Laplace pressure. Such post-stabilized miniemulsions do not change their droplet size on the time scale of hours and even months (Fig. 7). This leads to the conclusion that most miniemulsions described in the literature are only thermodynamically 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 in 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. It is not that doubling the amount of hydrophobe 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.

The insensitivity of the amount of the hydrophobe on the particle size is well documented in the literature [39–41]. It was found that the 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 firstly 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 a stabilization can only be achieved for the time of polymerization [42,43].

Another good test for the hypothesis of 'equal effective pressure' is given by the following experiment: two miniemulsion with a different amount of hydrophobe, but otherwise unaltered physico-chemical characteristics are mixed together. In this case, the droplets with the lower hydrophobe content shrink, whereas the size of the droplets with the higher hydrophobe content increase till the chemical

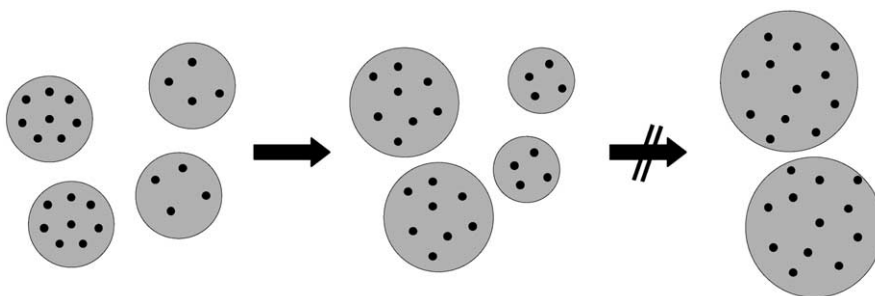Fig. 8. Different hydrophobe loads allow the generation of bimodal particle size distribution, the number of droplets does not change.

potential in all droplets is equilibrated. Ideally, a bimodal dispersion is created (Fig. 8), but the number of droplets does not change.

The choice of potential ultrahydrophobes is widespread: beside hexadecane as a model, hydrophobic dyes, comonomers, plastisizers or other additives can be used. Silanes, siloxanes, isocyanates, polyester, fluorinated alkanes and many others turned out to be very efficient in suppressing Ostwald ripening (see Table 1; for an overview of literature cases, see also Table 2). It is evident that the less water-soluble the hydrophobe is, the more effective it is as an osmotic pressure agent.

In the following, we also want to point to the primary literature where specific questions of miniemulsification or specific choices of hydrophobic materials are discussed.

Ugelstad et al. [44] were able to show that as the chain length of the hydrophobe increased, the stability of the miniemulsion increased. Delgado reported a plateau of stability of hexadecane (HD)/SDS miniemulsions at a molar ratio of 4:1. However, Fontenot and Schork could not confirm this ideal ratio between hexadecane and SDS [45]. Indeed, since the hexadecane does not interact with the SDS at the interface, but is homogeneously distributed in the droplets [46], the existence of an optimal ratio between hexadecane and SDS is not likely.
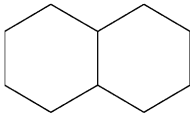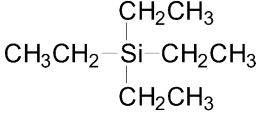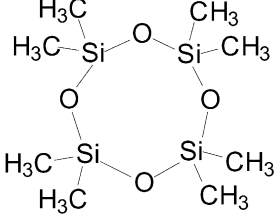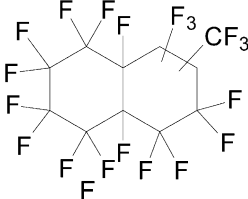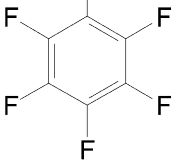
Fontenot [32] reported in detail the use of polymer as hydrophobe. Polymers would make an ideal hydrophobe for numerous reasons, e.g. high water insolubility and monomer compatibility. It was shown that the use of polymer as hydrophobe allows to stabilize the droplets sufficiently for the course of polymerization [42].

Reimers et al. [47] showed by a model that polymerizable miniemulsions with an added polymer and swollen polymer particles can be seen in a similar way. Interdroplet (or interparticle) mass transfer is governed by the thermodynamic driving force for this process, which, in turn, is related to the interfacial energy and the energies of mixing and elastic deformation when the droplets contain a polymer or other swelling agents or a hydrophobe. Such emulsions are not thermodynamically stable, but they can be thought to be kinetically stable in the sense that Ostwald ripening of the small droplets is sufficiently retarded so as to allow nucleation and polymerization of the droplets before significant diffusional degradation of the droplet population has taken place.

Another standard choice of a stabilizing additive which acts as a hydrophobe and a cosurfactant at the same time are long-chain alcohols. The addition of cetyl alcohol to a oil/water/SDS system was found to lead to emulsions which are more stable than emulsion only with SDS [48]. The interfacial tension at the styrene/water interface in the presence of mixed surfactants (SDS/cetyl alcohol or CTMA/cetyl alcohol)

Table 1
The use of different hydrophobes in styrene miniemulsion with 1.2% SDS relative to styrene

| Hydrophobes | Diameter (nm) | Surface tension of the final latexes (mN m$^{-1}$) |
|---|---|---|
| $CH_3-(CH_2)_{14}-CH_3$ | 92 | 68.7 |
| Oligostyrene $M_w = 1000$ g mol$^{-1}$ | 93 | 68.2 |
| decalin (bicyclic structure) | 78 | 68.4 |
| triethylsilane: $CH_3CH_2-Si(CH_2CH_3)_2-CH_2CH_3$ | 99 | 68.2 |
| octamethylcyclotetrasiloxane (cyclic Si–O ring with CH$_3$ groups) | 109 | 58.9 |
| perfluorodecalin (fluorinated bicyclic structure, CF$_3$) | 88 | 67.8 |
| hexafluorobenzene (F-substituted benzene) | 86 | 69.2 |
| Olive oil | 80 | 52.8 |
| Polyester | 82 | 50.1 |

has been determined to be between 5 and 13 mN m$^{-1}$, while the apparent interfacial tensions between the aqueous phase and the resulting interfacial layer were less than 1 mN m$^{-1}$ [49]. It could be shown that with increasing chain length of the alcohol, the interfacial tension also increased. Lack et al. [50] examined the interfacial aspects of miniemulsion stability for cetyl or lauryl alcohol and concluded the overall droplet stability using cetyl alcohol is not comprised solely of diffusional stability. Since cetyl alcohol shows an amphiphilicity and influences the interfacial tension, it seems to act as a co*surfactant* (as known in microemulsions) more than a hydrophobe.

Table 2
Some selected examples of miniemulsion polymerization reported in the literature (A103, polyoxyethylenated nonylphenol half ester of sulphosuccinic acid; AA, acrylic acid; Alipal CO-436, ammonium salt of sulfated nonylphenoxy poly(ethylenoxy) ethanol; AMBN, 2,2′-azobis(2-methylbutyronitrile); APS, ammonium persulfate; BuA, butyl acrylate; BPO, benzoyl peroxide; CA, cetyl alcohol; COD-Ni(0), bis(cis,cis, 1,5 cyclooctadiene) nickel(0); DDM, dodecyl mercaptane; DMA, dodecyl methacrylate; DOM, dioctyl maleate; Dowfax 8390, disulfonated alkyl diphenyl oxid sodium salt; EHA, ethylhexyl acrylate; EHMA, ethylhexyl methacylate; HD, hexadecane; KPS, potassium persulfate; MAA, methacrylic acid; miniEP, miniemulsion polymerization; MMA, methyl methacrylate; NMA, n-methylol acrylamide; NP-40, nonyl polyethoxylate with 40 EOs per molecule; NE-40, polymerizable nonyl polyethoxylate with 40 EOs per molecule; OPB, octadecyl pyridinium bromide; PB/Et-co-PEO, poly(butylene/ethylene-co-ethyleneoxide); PS, polystyrene; SDS, sodium dodecyl sulfate; SG1, N-tert-butyl-N-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide; SMA, stearyl methacrylate; V50, 2,2′-azobis(2-amidino propane) dihydrochloride; V59, 2,2′-azobis(2-methyl-butyronitril); VAc, vinyl acetate)

| Monomer | Hydrophobe | Surfactant | Homogenization | Initiator | Comments | References |
|---|---|---|---|---|---|---|
| Styrene | CA | SDS | Stirring | KPS | First article about droplet nucleation | [51] |
| Styrene, EHMA | $C_{10-18}OH$ | SDS, CTMA-Br | | | Interfacial characteristics by spin drop | [230] |
| St/MMA | HD | SDS | Ultrasonication | | Interparticle monomer diffusion transport in miniemulsions | [74] |
| Toluene chlorobenzene alkanes | CA | SDS | Sonication | | Role of water solubility of the oil phase | [52] |
| *Different hydrophobe* | | | | | | |
| Styrene | HD, LPO | SDS | Sonication | AIBN, BPO, LPO | LPO as hydrophobe, single radical formation, probability of nucleation, molecular weight distribution | [61,145] |
| Styrene | Blue dye (Blue 70) | SDS | Microfluidizer | NaPS | Stabilization by dye, 60% of the droplet are nucleated | [57] |
| Styrene | DMA | NP-40 | Microfluidizer | NaPS, AIBN | Use of non-ionic surfactant, DMA as hydrophobe | [86] |
| Styrene | SMA | NP-40/SDS | Microfluidizer | NaPS | Suppression of Ostwald ripening using DMA or SMA | [60] |
| MMA | DDM | SDS | Ultrasonication | KPS | DDM retards Ostwald ripening | [55] |
| MMA | PMMA | SDS | Sonication | KPS | Predominant droplet nucleation in polymer is used as hydrophobe | [42] |
| MMA | LPO | SDS | Sonic dismembrator | LPO | Initiator as hydrophobe | [62] |
| MMA | PMMA | SDS | Sonication | KPS | Robust droplet nucleation, initiator concentration, retarder in water phase, agitation | [43] |

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Table 2 (*continued*)

| Monomer | Hydrophobe | Surfactant | Homogenization | Initiator | Comments | References |
|---|---|---|---|---|---|---|
| Styrene | DMA, SMA | SDS, NP-40, NE-40 | Microfluidizer | | Ostwald ripening for different hydrophobes | [59] |
| *Artificial latexes* | | | | | | |
| Epoxy resin | | | | | Artificial latex | [106] |
| Rubber latexes (core) | CA | | Homogenizer | – | Artificial core latexes by miniemulsification, semicontinuous polymerization for shell | [105] |
| *Swelling method* | | | | | | |
| Styrene | Alkanes, chlorobenzene | OPB | | | Swelling method, large (up to 50 μm) monodisperse PS particles | [44,96] |
| *Polymerization during sonication* | | | | | | |
| Styrene | | SDS | | Ultrasonic irradiation | Continuous ultrasonication | [98] |
| *Different monomer* | | | | | | |
| VAc | HD, PVAc, PMMA | PVOH Vinol 205 (polyvinyl alcohol) | Sonic dismembrator | NaPS | Non-ionic surfactant, kinetics by conductance | [88] |
| Vinyl chloride | $C_{16}/C_{18}$ alcohol | SDS | 700 piig | AIVN, KPS | Bimodal PVC particles | [150] |
| Ethylene | | SDS | Stirring + pressurized | COD-Ni(0) | | [210] |
| Acrylonitrile | HD | SDS | Sonication | V59 | Nanocrystalline polymers | [158] |
| Vac, MMA | HD | SHDS | Sonication | NaPS | Copolymer | [39] |
| VAc/BA, DOM or NMA | HD | SDS | Sonication | KPS | Copolymer consisting of monomers with different reactivity ratios | [147] |
| Styrene, AA, MAA | DMA, SMA | SDS | Microfluidizer | NaPS | Copolymer hydrophobic–hydrophilic | [165] |
| AA, MAA, HEMA, acrylamide | NaCl | PB/Et-*co*-PEO | Ultrasonication | KPS, V59 | Inverse miniemulsions | [75] |
| *Kinetics* | | | | | | |
| Styrene | CA | SDS | Microfluidizer | AMBN | 2,5-Dihydroxy-1,4-benzene disulfonic acid as inhibitor | [144] |
| Styrene/MMA | HD | SDS | | KPS, AIBN | Water-insoluble DTBHQ | [159] |

Table 2 (*continued*)

| Monomer | Hydrophobe | Surfactant | Homogenization | Initiator | Comments | References |
|---------|-----------|-----------|----------------|-----------|----------|-----------|
| Styrene | CA/PS | SDS | Ultrasonication/microfluidizer | KPS | Effects of polymer type | [134] |
| Styrene | CA/PS | SDS | Ultrasonication/microfluidizer | KPS | Kinetics | [135] |
| Styrene | CA/PS | SDS | Omni-mixer, ultrasonication, microfluidizer | KPS | Effects of shear on homogenization on kinetics | [136] |
| Styrene | CA/PS | SDS | Ultrasonication | KPS | Kinetics, effect of polymer in minidroplets, calorimetry, TEM | [131] |
| Styrene | CA/PS | SDS | Ultrasonication | KPS | Evolution of particle size distribution, calorimetry, TEM | [128,130, 132,133] |
| Styrene | CA/AMBN | SDS | Ultrasonication + microfluidizer | AMBN | Single radical generation, enhanced stabilization by AMBN, calorimetry | [143] |
| *Living free radical polymerization* | | | | | | |
| Styrene | PS, $C_6F_{13}I$ | SDS | Ultrasonication | ACPA, AIBN | Degenerative transfer process | [169] |
| Styrene | PS, $C_6F_{13}I$ | SDS | Ultrasonication | ACPA/$C_6F_{13}I$ | Degenerative transfer process: block copolymers | [171] |
| Styrene | HD | SDBS | | KPS/TEMPO | SFRP with TEMPO, $T = 135\,°C$ | [172] |
| Styrene | HD | Dowfax 8390 | Ultrasonication | TEMPO/BPO | SFRP with TEMPO, $T = 125\,°C$, with TTTOPS, TEMPO terminated oligomeric styrene | [173,174] |
| Styrene | HD, CA | SDS | Ultrasonication | KPS/$Na_2S_2O_5$, SG1 | SFRP, $T = 90\,°C$ | [175] |
| Styrene, MMA | HD, CA | SDS | Ultrasonication | AIBN or V-40/dithiobenzoates | RAFT | [177] |
| BMA | HD | Brij 98 | Ultrasonication | V50/dNbpy/CuBr | ATRP | [178] |
| MMA | HD | SDS | Ultrasonication bath (180 W) | AIBN/KPS | Chain transfer agent | [167] |
| *Hybrid latexes* | | | | | | |
| Alkyd resin, MMA, BuA, AA | HD | SDS | Sonication | KPS | Hybrid particles, resin coated by polymer | [70] |

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Table 2 (*continued*)

| Monomer | Hydrophobe | Surfactant | Homogenization | Initiator | Comments | References |
|---|---|---|---|---|---|---|
| Sunflower oil, MMA | HD | SDS | Sonication + high-pressure homogenizer | Fatty-acid hydroperoxide/ $Fe^{2+}$/SFS/SDTA | Triglyceride modified polyacrylate | [182] |
| Styrene, MMA or BuA/ hexadecane | HD | SDS, Lutensol AT50 | Sonication | PEGA, KPS, AIBN | Formation of nanocapsules | [191] |
| Styrene/$TiO_2$ | HD/PS | SDS | Sonication + microfluidizer | KPS | Encapsulation, 3% $TiO_2$ | [184,231] |
| Sytrene/$CaCO_3$ | HD | SDS | Sonication | KPS | Encapsulation of $CaCO_3$ | [90] |
| Styrene/carbon | Polyester | SDS | Sonication | KPS, AIBN | Encapsulation of carbon black by cosonication | [187] |
| *Other types of polymerization* | | | | | | |
| Diamine/ diepoxide | HD | SDS, Lutensol AT50 | Sonication | – | Polyaddition reactions in miniemulsion | [209] |
| Disocyanates/ diols | HD | SDS | Sonication | – | Polyurethane in miniemulsions | [232] |
| *Processing* | | | | | | |
| Styrene/2-EHA/MAA | HD | SDS, A103 | Ultrasonication | KPS | High solids content batch miniEP | [214] |
| MMA | HD | SDS | Ultrasonication | APS | Continuous miniEP | [222] |
| MMA | HD | SDS | | APS | Continuous miniEP | [221] |
| BuA | HD | SDS | Ultrasonication and microfluidizer | APS, KPS | High solids (60–70%) by two step polymerization (semicontinuous miniEP); 1. seeded miniEP; 2. semicontinuous miniEP | [216] |
| Styrene/ EHMA/MAA | HD | SDS/Alipal CO-436 | Ultrasonication | KPS | High solids content, comparison mini- and conventional semicontinuous miniEP | [215] |

Ugelstad et al. [48,51] and Chou et al. [5] obtained the best stability for styrene and benzene mini-emulsion at a molar ratio of ionic surfactant to cetyl alcohol between 1:1 and 1:3. Brouwer et al. [52] studied the effect of the water solubility of the dispersed phase on the stability of miniemulsions prepared by dispersing oil in a gel-phase using simple mixing. They concluded that the ease of formation of miniemulsions (with cetyl alcohol, CA) increases with increasing water solubility, but the overall stability of miniemulsions decreases with increasing water solubility.

Ugelstad et al. [51] were able to show that as the chain length of the costabilizer or hydrophobe increased, the stability of the miniemulsion also increased. Choi et al. [53,54] determined the effect of alcohol chain length and the ratio of long-chain alcohol (CA) to SDS on the stability by observing the amount of oil separated after centrifugation and after aging. The best result was obtained for a ratio CA/SDS of 3:1, and the miniemulsion stability increases with increasing fatty alcohol chain length. In the case of cetyl alcohol, a better stability can be provided by using a small amount of additionally added polymer in order to build-up an osmotic pressure in the particles.

Hexadecane or cetyl alcohol is undesirable for a commercial applications. Therefore, a variety of other substances acting as a hydrophobe have been employed. For example, also dodecyl mercaptane (DDM) can be included in the recipe, which acts as a hydrophobe and chain transfer agent. Miniemulsions with dodecyl mercaptane [55,56] as hydrophobe showed a high stability. Results indicate that DDM retards Ostwald ripening and allows the production of stable miniemulsions.

Relatively stable styrene miniemulsions were prepared by using a water-insoluble, low molecular weight blue dye (Blue 70) as the hydrophobe [57].

Water-insoluble comonomers can also be used to impart diffusional stability to the miniemulsion droplets [58]. Styrene miniemulsions could be stabilized by using reactive hydrophobes, such as dodecyl methacrylate (DMA) or stearyl methacrylate (SMA) [59]. The effectiveness of these hydrophobes strongly depends on their solubility in water. The higher the water solubility of the hydrophobe is, the greater is the extent of Ostwald ripening occurring in the miniemulsion. The solubilities can be estimated and lead to the following ranking: CA > DMA > SMA > HD. In the case of DMA, both Ostwald ripening and creaming could not be neglected for miniemulsions upon aging at 35 °C, whereas no appreciable Ostwald ripening and creaming was detected for SMA containing miniemulsions [60].

The ability of initiators with very low water solubility, namely lauroyl peroxide (LPO), in stabilizing monomer droplets against degradation by molecular diffusion was investigated and compared to the behavior of benzoyl peroxide (BPO) and azobis(isobutyronitrile) (AIBN) [61]. Only LPO was water-insoluble enough to stabilize the droplets efficiently against degradation by molecular diffusion.

Miniemulsion polymerizations using LPO as the stabilizing hydrophobe have also been carried out by Reimers and Schork [62]. Diffusional instability was reduced to the point where nucleation in the monomer droplets and polymerization could be carried out before significant diffusional degradation took place.

The stability of miniemulsion systems has been studied the using shelf-life stability [56,63–65] and ultracentrifugation stability studies [66] and by measuring levels of free surfactant.

Measuring the droplet size is an important issue also 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. [44] and Azad et al. [67] stained miniemulsions with $OsO_4$ and used transmission electron microscopy. However, the treatment can alter the sizes. Goetz and El-Aasser [68] made some attempts to determine droplet sizes using light scattering and transmission electron microscopy. Miller

et al. [69] observed by CHDF that for cetyl alcohol systems there is a period of rapid average droplet size increase followed by a region in which the droplet size increases slowly. This behavior was not found in the case of hexadecane. 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 [70], the size of the droplets will change slightly due to different solubility effects. The high shear during CHDF measurements can also lead to coalescence of the droplets.

Measurements of characteristics of the emulsion droplets in a 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 (styrene/DMA/SDS/water) and it was compared to emulsions (styrene/SDS/water) [71], Erdem et al. determined droplet sizes on concentrated miniemulsions via soap titration which could be confirmed by CHDF measurements [72]. Droplet sizes without diluting the system can be estimated by SANS measurements [46]. In this case, the system consists of deuterated oil droplets in protonated water in order to have a large scattering contrast.

The characterization of the occurring transport processes between the droplets through the water phase is also a subject of literature. An exchange of oil without any effect on the final sizes of the droplets is called compensated transfer [73]. Non-compensated transfers are the classical mechanisms of Ostwald ripening and coalescence. Whereas the non-compensated transfer is suppressed in mini-emulsions by the addition of a hydrophobe, the compensated transfer can still be observed. It was shown for a mixture of two emulsions, one with tetradecane droplets and the other one with 1-bromo tetradecane droplets, that this process is faster by at least an order of magnitude than the corresponding non-compensation process, e.g. Ostwald ripening.

Two miniemulsions, one consisting of MMA and another consisting of styrene, were used to show that monomer transport between miniemulsion droplets takes place [74]. However, it has to be noted that droplets consisting of different monomers are used. Therefore, the exchange is also driven by a chemical potential.

## 2.5. Inverse miniemulsions

The concept of emulsion stabilization is not restricted to direct miniemulsions, but can 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 [75]. Another adaptation of the process is that for the dispersion of polar monomers in non-polar dispersion media, surfactants with low HLB values are required. A number of surfactants was screened, including standard systems such as $C_{18}E_{10}$, sodium-bis(2-ethylhexyl)-sulfosuccinate (AOT), sorbitan monooleate (Span 80), and the non-ionic block copolymer stabilizer poly(ethylene-*co*-butylene)-*b*-poly(ethylene oxide) (TEGO EBE45, see Fig. 9). TEGO EBE45 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.

Here, the extraordinarily high droplet stability against exchange can be demonstrated in a very illustrative way by the formation of Prussian Blue: one miniemulsion with droplets containing a $FeCl_3$ solution, and one miniemulsion containing a $[Fe(CN)_6]^{4-}$ solution are mixed. As it is seen in Fig. 10(a), the mixed miniemulsion stays colorless for weeks, which indicates that the droplets with $FeCl_3$ and the droplets with $[Fe(CN)_6]^{4-}$ stay separated as colloidal entities on the time scale of most

Poly[(ethylene-co-butylene)-b-(ethylene oxide)]



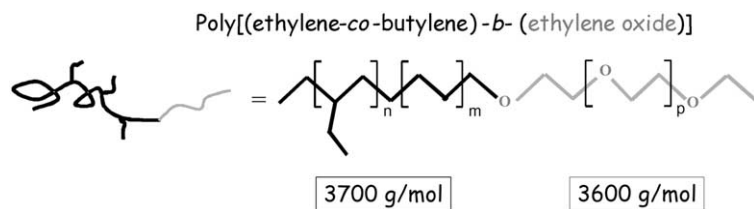3700 g/mol          3600 g/mol

Fig. 9. Schematic presentation of an amphiphilic block copolymer employed in inverse miniemulsions.

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 blue (Fig. 10(b)).

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 droplets. It can be determined by turbidity measurements. As expected and in accordance with a droplet fission/droplet fusion picture, the approach to the steady state of turbidity is very similar for the systems with salt or without salt as an osmotic agent.

A high stability of the droplets after the high shear treatment however is just obtained with the osmotic agent. The type of lipophobe has no influence on the stability of the inverse miniemulsion. The droplet size depends, contrary to regular miniemulsions, on the amount of osmotic agent [76]. It seems that in inverse miniemulsions, the droplets experience 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 makes a
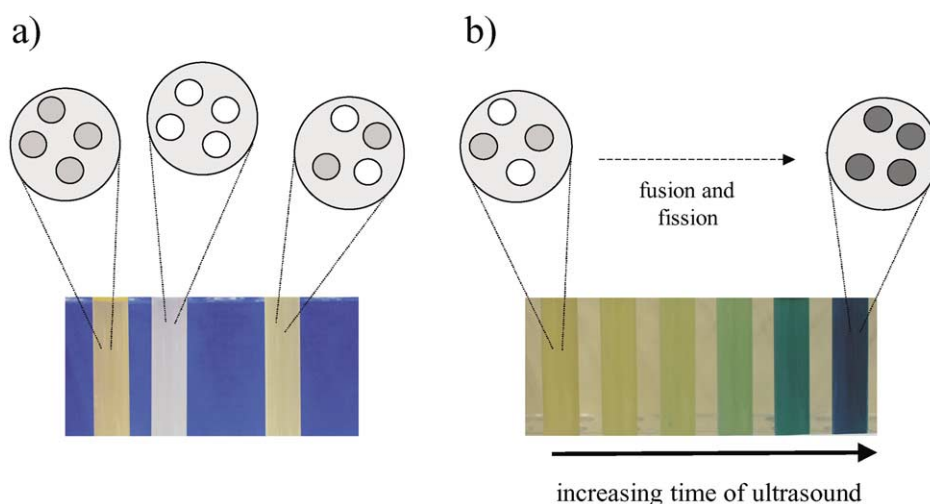


Fig. 10. (a) Mixing of two inverse miniemulsions, one containing FeCl$_3$ solution, the other on [Fe(CN)$_6$]$^{4-}$. (b) Controlled fusion and fission of the droplets during ultrasonication.

pressure equilibration near the ultrasonication process possible. This is why we believe that inverse miniemulsions are not critically stabilized, but are stable systems.

Nevertheless, also for inverse miniemulsions the surfactant is used in a very efficient way, at least as compared to inverse microemulsion [77,78] or inverse suspension polymerization [79]. Again, the surface coverage of the inverse minidroplets with surfactant is incomplete. Values of about 40 mN m$^{-1}$ are found for the interface tension of an inverse latex in cyclohexane to water [76], while the interfacial tension of pure cyclohexane/water was determined to be ca. 50 mN m$^{-1}$ (see also Ref. [76]), and a concentrated TEGO EBE45/cyclohexane solution shows 20 mN m$^{-1}$, being taken as the saturation value for the point of inverse micelle formation. This translates into a surface coverage of the inverse droplets of only 30%, and that 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 are, the higher is the coverage of the particles by surfactant. For inverse miniemulsions, these relations depend in addition 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. Ugelstad et al. [51] first published results where droplets with sizes of less than 0.7 μm were nucleated leading to polystyrene latexes. The homogenization was obtained by stirring, SDS was used as surfactant, CA was used as cosurfactant/hydrophobe, and a broad distribution of particles. A continuation of this early work showed that the addition of cetyl alcohol increases the stability of the droplets [48]. It was stated that this type of polymerization leads to a broad size distribution, which however with a current view is due to the imperfection of the homogenization at that time. The preparation of still broad distributed droplets using hexadecyltrimethylammonium bromide/cetyl alcohol mixtures was published by El-Aasser et al. [80]. The use of sonication for the homogenization process in miniemulsions was introduced in 1979 [81]. The term miniemulsion was created later by Chou et al. [5].

Also for the rather imperfect recipes of the early days, the growth of minidroplets is 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 the present 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. Measurement of the emulsion droplets in a concentrated media on the other hand is a very difficult task and was already discussed earlier.

Indirect techniques, such as conductance measurements and the determination of the surface tension

are regularly applied to get more information about the surfactant distribution during the polymerization. Small angle neutron scattering experiments [46] were applied to characterize the droplet or particle sizes before and after the polymerization without diluting the system [46]. It was found that the part of the scattering function describing the particle form does not change, whereas inner droplet structure and interparticle potentials do change. With SANS, it was also checked that a small amount of added polystyrene does not have an effect on the droplet size and the droplet size distribution. The neutron scattering experiment were also used to determine that the hexadecane is located homogeneously within each droplet and has no cosurfactant character.

## 2.7. Surfactant variation

The majority of the recipes described in the literature is based on the anionic SDS as a model system.

The possibility of using cationic surfactants, such as octadecyl pyridinium bromide for the preparation of miniemulsions was firstly exploited in 1976. However, the emulsions were prepared by stirring, and the resulting emulsions showed broadly distributed droplet sizes [67]. El-Aasser reported also on the use of cationic surfactant to create miniemulsions [5,82]. Recent work on steady-state miniemulsions showed that cationic surfactants form well-defined miniemulsions latexes with narrow size distribution and high stability [83]. From surface tension measurement results, the surface coverage was determined to be of the order of 30%, which proved the high efficiency of surfactants also in cationic miniemulsions. Two cationic counterion-coupled gemini surfactants, so-called cocogems, which were shown to be extremely efficient in the formation of microemulsions [84], resulted in only a moderate activity in miniemulsification: rather large latex particles with a close-to-complete surfactant layer were obtained. This shows that the underlying energetical rules of micro- and miniemulsions are different and that efficiency relies on different surfactant properties. It is speculated that for miniemulsions the ability to form dilute surfactant layers is advantageous, whereas low absolute interface energies and a high area requirement per surfactant is favorable for microemulsions. A new class of cationic surfactants with sulfonium headgroups was also effectively employed for the synthesis of miniemulsion polymers [85].

Non-ionic miniemulsions can be made by using 3–5% of a poly(ethylene oxide) derivate as surfactant, resulting in larger, but also very well-defined latexes [83]. Chern and Liou used a non-ionic nonylphenol polyethoxylate [86]. Particle sizes between 135 and 280 nm were realized. The particle size was reported to depend mainly on the type and amount of the hydrophobe, and therefore on the degree of the suppression of Ostwald ripening [86].

Capek described the use of macromonomer in miniemulsion polymerization [87]. Lim and Chen used poly(methyl methacrylate-*b*-(diethylamino)ethyl methacrylate) diblock copolymer as surfactant and hexadecane as hydrophobe for the stabilization of miniemulsions [65]. Particles with sizes between about 150 and 400 were produced. It is possible to create stable vinyl acetate miniemulsions employing non-ionic polyvinyl alcohol (PVOH) as surfactant and hexadecane as hydrophobe [88].

The favorable use of an amphiphilic statistical copolymer comprised of octadecyl acrylate and acrylic or methacrylic acid groups for the formation of polystyrene miniemulsion latexes has been demonstrated by Baskar et al. [89]. In this case, the polymer acts as a surfactant and a hydrophobe at the same time, which is industrially important. Since those polymers dissolve homogeneously neither in monomer nor in water, the polymers are anticipated to be located only at the oil–water interface.

By variation of the relative amount of surfactant to monomer, the particle size can be varied over a wide range [90]. Fig. 11 shows that depending on the type of the surfactant different size ranges are
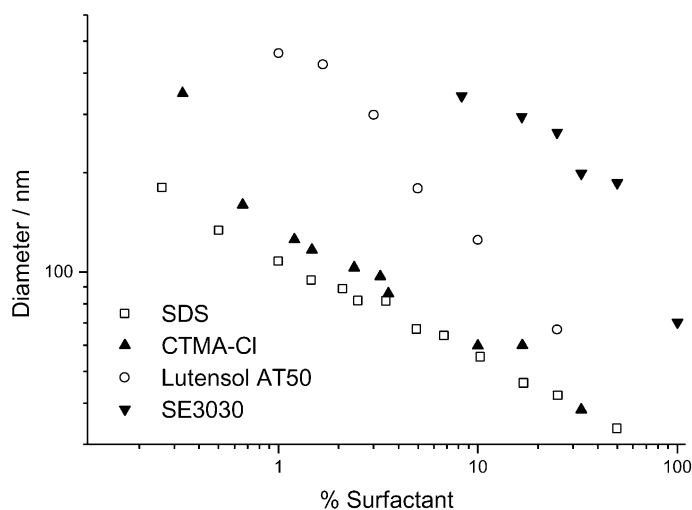
Fig. 11. Variation of the particle size by changing the relative amount and type of surfactant in a styrene miniemulsion at a volume fraction of the dispersed phase of 0.2.

accessible. Latexes synthesized with SDS and cetyltrimethylammonium bromide show about the same size–concentration curve, i.e. the efficiency of the surfactant and the size dependent surface coverage are very similar, independent of the sign of charge.

The efficiency of the two non-ionic surfactants is lower, and the whole size–concentration curve is shifted to larger sizes. The polydispersity of the latexes is also generally broader for the non-ionic systems. This is attributed to the lower efficiency of the steric stabilization 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 surface tension measurements of the latexes and surfactant titrations, the non-ionic particles are nevertheless incompletely covered by surfactant molecules and show surface tensions well above the values of saturated surfactant layers. Also for the non-ionic systems, the surface coverage depends on size: the coverage of the particles with surfactant increases with decreasing particle size (Fig. 6).

To check the assumption that the curves depicted in Fig. 11 represent borderlines of maximal efficiency, we tried to decrease the electrostatic stability by addition of various amounts of salt to the aqueous phase. By adding NaCl to an otherwise standardized styrene/HD miniemulsion, the particle size increases from 80 to almost 200 nm due to electrostatic screening and the coupled reduced stability (Fig. 12).

## 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, we want to provide a short checklist summarizing the characteristics of miniemulsions:

1. Steady-state dispersed miniemulsions are stable against diffusional degradation, but critically stabilized with respect to colloidal stability.
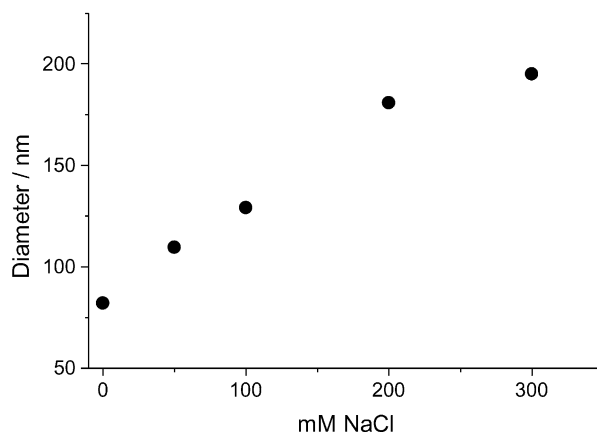
Fig. 12. Influence of the addition of NaCl on the particle size (6 g styrene, 250 mg hexadecane, 72 mg SDS, 100 mg KPS).

2. The interface 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 an extremely low solubility in the continuous phase. This crucial prerequisite is usually not present in microemulsions, but can be added also there 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.

## 2.9. Differences between macro-, mini-, microemulsion and suspension polymerization

Miniemulsions are not defined by a size range, but by a mode of operation. Therefore (see Section 2.8), miniemulsion polymerization can be in most cases easily differentiated from other techniques of heterophase polymerization types, namely the microemulsion-, emulsion-, and suspension polymerization. For illustration, a scheme of the different processes is shown in Fig. 13.

The polymerization in microemulsions starts from a thermodynamic stable, spontaneously formed state which relies on high amounts of special surfactant systems or mixtures which possess an interfacial
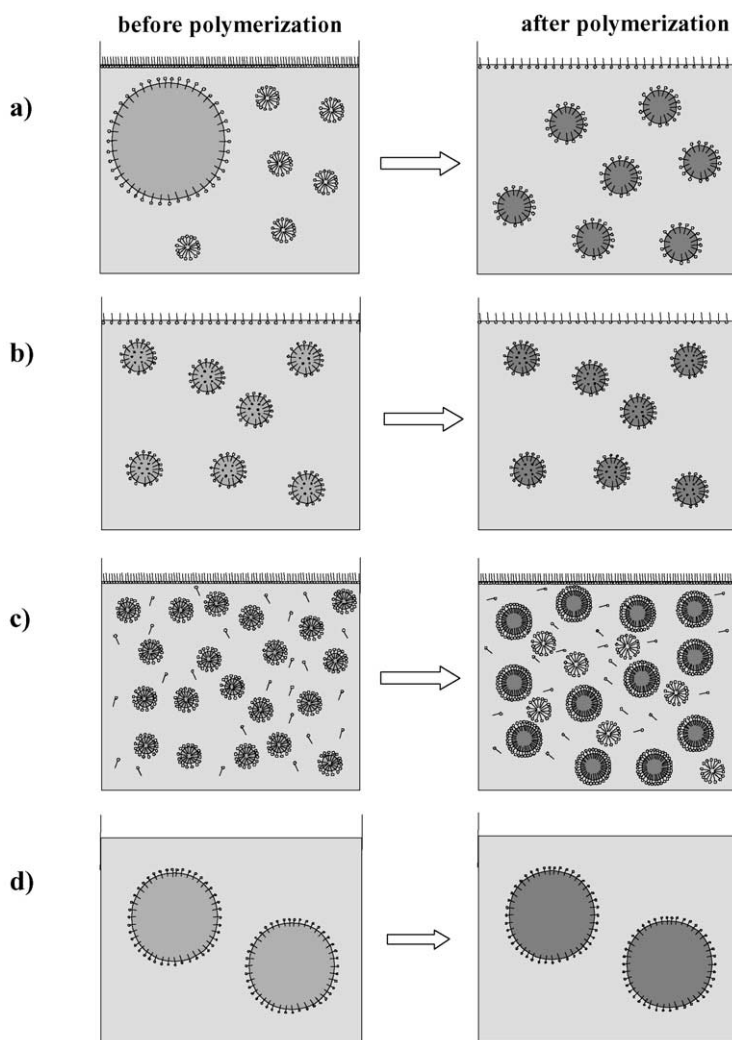
Fig. 13. Comparison of different heterophase polymerization processes: (a) emulsion polymerization; (b) miniemulsion polymerization; (c) microemulsion polymerization; (d) suspension polymerization.

tension at the oil/water interface close to zero. Contrary to that, miniemulsions are critically stabilized, require high shear to reach a steady state, and the interfacial tension is much larger than zero. The high amount of surfactant which is required for the microemulsion preparation also leads to a complete surfactant coverage of the particles. Since the initiation cannot be obtained in all microdroplets simultaneously, the first polymer chains are formed only in some droplets. The osmotic and elastic influence of these chains destabilize the fragile microemulsions and usually lead to an increase of the particle size, the formation of empty micelles, and secondary nucleation. The final product are very small latexes 5–50 nm in size, in coexistence with a majority of empty micelles. For more details about microemulsions, the reader is referred to the review literature [77,91,92].

In emulsion polymerization, the polymerization starts from a situation where large monomer droplets

stabilized by surfactant and empty or monomer-swollen surfactant micelles coexist. The water-soluble initiator forms oligoradicals with the slightly water-soluble monomer units, until the oligoradicals are hydrophobic enough either to enter the micelles or to nucleate particles from the continuous phase. During polymerization, the monomer diffuses from the larger monomer droplets through the water phase to the micelles in order to sustain polymer particle growth until the monomer droplets have vanished. Particles with a diameter of usually larger than 100 nm are formed. Due to the increase of the interfacial area, the surface tension of a latex increases with polymerization.

The differences between emulsion polymerization and miniemulsion polymerization are also obvious. In emulsion polymerization, the latex particle does not correspond to the primary emulsion droplet, and the size is established by kinetic processes where kinetic parameters such as the temperature, the amount of initiator, the nucleation rate as well as nanoparticles stability play a predominant role. These factors remain unseen in miniemulsion polymerization where the latexes can essentially be understood as polymerized copies of the original droplets, the size of which is given by the dispersion process and droplet stability, but not by any polymerization parameter.

Suspension polymerization involves much larger monomer droplets (1 $\mu$m–1 mm) dispersed in the continuous phase. Nucleation occurs predominantly in the droplets, and each polymerizing droplet behaves as an isolated batch polymerization reactor. This principle of microreactors is very similar to the idea of miniemulsions. Indeed, the main difference is the size and stability of the formed particles. The notation 'suspension polymerization' is reserved for systems where nucleation occurs in the monomer droplets, and the average number of radicals per particle $\bar{n}$ throughout polymerization is very high ($10^{2-6}$). Due to the very large particle sizes involved, the coupled droplet pressures are rather low, and Ostwald ripening occurs at a much lower rate. This is also why addition of hydrophobes is not common in suspension polymerization.

## 2.10. Miniemulsion related processes

Beside the clearly identified cases of microemulsion-, miniemulsion-, emulsion-, and suspension polymerization, literature describes a variety of mixed cases which are somewhat related to miniemulsion and are therefore listed later.

### 2.10.1. Swelling method

Ugelstad et al. [44,93] described a technique where stable monomer emulsions are obtained by homogenizing a highly water-insoluble compound (a hydrophobe) with water and emulsifier followed by swelling the dispersed phase with more than 200 times its own volume of monomer. Polymer particles consisting of pure polymer are usually only capable of absorbing 0.5–5 times their own volume of low molecular weight compounds. Calculations based on an extended Flory–Huggins equation predict that if the particles contain a substantial amount of an oligomer which is water-insoluble, one may expect an enormous increase in the swelling capability. A swelling with monomer up to a v/v ratio of >1000 is reported leading to monodisperse, porous particles. It was shown that the entry rate coefficient for small ratios of polymer to monomer is about one to two orders of magnitude smaller than the value expected in an equivalent 'normal' emulsion polymerization latex [94]. A two-step procedure [95,96] is described: in a first step, relatively small monodisperse polymer particles are swollen with a low molecular weight, highly water-insoluble compound and then with monomer mixtures, followed by polymerization. This method allows preparation of highly monodisperse particles

of more than 50 μm diameter with a standard deviation of less than 2%. The particles have found application as standards in immunoassays and in liquid chromatography.

Monomer emulsions with excellent long-time stability were obtained by diffusional swelling of vinyl chloride monomer into performed, stable polydisperse preemulsions of water-insoluble oils or monodisperse, oligomer styrene seed particles [97].

### 2.10.2. Polymerization during sonication

Briggs and Grieser described the preparation of polystyrene latexes with ultrasonic initiation [98]. For the polymerization, no further initiator is added, the radicals formed as a consequence of the cavitation process were sufficient as initiating species. The process can be understood as the in situ polymerization of small droplets created by ultrasonication, i.e. in a state at the fusion–fission equilibrium and near the pressure balanced miniemulsion. The droplets are relatively unstable, since no hydrophobe is present, but they are continuously regenerated due to the permanent application of ultrasound. Very small latexes with a sizes of about 50 nm were obtained.

### 2.10.3. Bibette process

Monodisperse emulsions of intermediate sized droplets with a high stability can be obtained by shearing a crude, polydisperse emulsion at high concentrations with a well-defined low shear rate, as it is available in a Couette apparatus. Sufficient viscosity of the premixed emulsion and the related dissipation of mechanical energy are absolutely necessary to end-up with a monodisperse emulsion. It was found that the thinner the gap in the Couette apparatus ix, the more monodisperse is the final emulsion. The final drop size depends on the applied shear rate, the viscoelasticity of the premixed emulsion, and the interfacial tension between the dispersed and the dispersing phase [99,100]. In principle, this process allows us to establish monodisperse emulsions with larger droplet sizes up to the micron range, and polymerization of the Bibette emulsions can be performed according to the general principles predominantly leading to droplet nucleation. The use of mixing tools, such as the ultraturrax or just stirring does not result in a narrow distribution since the homogeneity of shear is not sufficient.

### 2.10.4. Polymerization of emulsions made by membrane emulsification

The formation of emulsions with droplets having a narrow droplet size distribution is also obtained by membrane emulsification. The droplets can possess a high stability when the droplets are uniform and a hydrophobe is added; and again, hexadecane has been employed for this purpose [101]. The droplet size can be varied by pressing the crude preemulsions through membranes with different pore sizes, but also the membrane material and process parameters such as the membrane pressure and the viscosity of the continuous phase influence the droplet sizes. The polymerization of such emulsion can lead to monodisperse polymer particles.

Omi et al. reported the synthesis of fairly monodisperse polystyrene microspheres using a particular microporous glass membrane [102,103]. Several pore sizes from 0.5 to 18 μm were employed for the preparation of stable emulsions. The reaction mechanism is similar to that of an ordinary suspension polymerization with the advantage that an initial narrow size distribution of the droplets is retained throughout the polymerization. The addition of sodium nitrite prevented secondary nucleation in the water phase, so that each droplet indeed behaved as an isolated locus of polymerization.

Relatively uniform biodegradable polylactide microspheres were prepared by employing the same

membrane emulsification technique [104]. In this case, polylactide was dissolved in dichloromethane, and a hydrophobe was also added. This mixture was dispersed in aqueous phase by SDS and poly(vinyl alcohol), and the solvent was evaporated. This process is similar to the following procedure of producing secondary dispersions via miniemulsion.

### 2.10.5. Secondary polymer dispersions

Latexes can also be prepared as secondary dispersions. Here, build-up of the polymer is performed in an organic solvent, followed by emulsification of the low viscosity polymer solution. In a last step, the organic solvent is removed from the emulsion resulting in polymer dispersion. For the generation of very small particles, it is possible to use emulsification procedures which indeed are similar to the above-described miniemulsification.

Rubber latexes can be prepared by direct emulsification of the corresponding polymers [105]. The preformed polymers were dissolved in toluene, and added as a solution to the aqueous mixed emulsifier solution under stirring and subsequent homogenizing. The solvent was subsequently removed by distillation. The preparation of a secondary dispersion of epoxy resin/curing agent is also described in order to obtain positively charged latex particles for coating purposes [106].

## 3. Radical polymerizations of miniemulsions

### 3.1. Mechanistics and kinetics in miniemulsion polymerization

#### 3.1.1. Nucleation

In principle, three particle nucleation mechanisms are currently discussed in the literature for heterophase polymerizations: micellar nucleation, homogeneous nucleation and droplet nucleation.

In the micellar nucleation mechanism, the radical enters a micelle, which is swollen with monomer, and reacts with the monomer to form a polymer chain. Further monomer diffuses from other monomer-swollen micelles, which serve as monomer reservoirs. This mechanism seems to be typical for microemulsion polymerizations started from the continuous phase. Because of its nature, it can only occur at concentrations of free surfactant above the critical micelle concentration of the applied surfactant. For miniemulsion polymerization, the micellar nucleation mechanism is therefore very unlikely.

The homogeneous nucleation is of importance for the so-called surfactant-free emulsion polymerization, but could also be a possible mechanism in miniemulsion polymerization. In this case, the latex seeds are formed from aggregating oligomers in the water phase [107], and the monomer is transported to the nucleation site by diffusion. Usually, this mechanism is sensitive to the overall initiator concentration and depends on the solubility of the employed monomer. It is discussed to be of minor significance in styrene miniemulsions, too [108].

The droplet nucleation mechanism suggests that the droplets formed during the emulsification step are polymerized via radicals which enter the monomer droplets. Monomer diffusion to the reaction sites is of no kinetic importance in the case of batch miniemulsion polymerizations since there is already the maximal concentration of monomer at all reaction sites. For an ideal miniemulsion system, droplet nucleation is expected to be the dominant mechanism. Due to the statistics of radical entry and overall size, every single droplet is nucleated; the particle number does not change
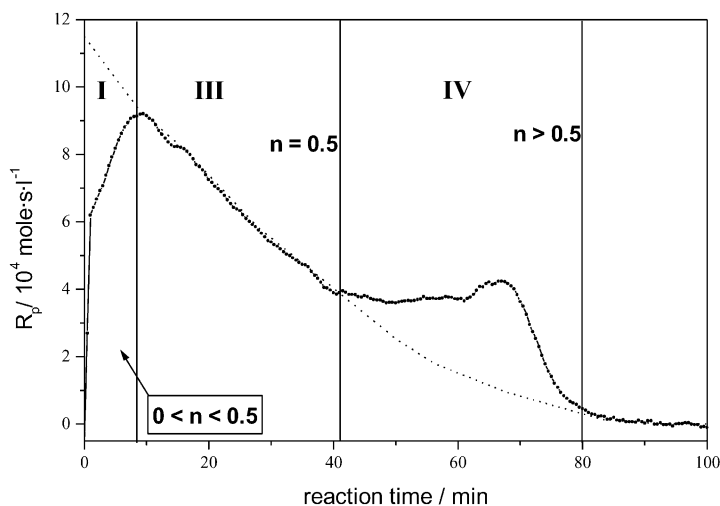
Fig. 14. Calorimetric curve of a typical miniemulsion (styrene, SDS, KPS as initiator) taken from Ref. [108].

during the polymerization. This mechanism also explains the successful usage of oil-soluble initiators in miniemulsion polymerization.

It is an agreed upon fact that in miniemulsions the nucleation of the particles mainly starts in the monomer droplets themselves but the relative importance of homogeneous nucleation is less clear. Choi et al. [109] described that only 20% of the droplets are nucleated (CA as cosurfactant/hydrophobe). Chern et al. determined that 55% (DMA as hydrophobe [110]) to 60% (blue dye as hydrophobe [57]) are nucleated, whereas Reimers and Schork reported a droplet nucleation of 95% (HD as hydrophobe). The seemingly marginal difference towards complete droplet nucleation disturbs the special advantages of miniemulsion latexes (polymer compositions, dissolved molecules) due to the different sizes and compositions of the secondary nucleated particles. Mixed modes of particle nucleation depend on the miniemulsion system. In the case of styrene miniemulsion stabilized with NP-40 and DMA as hydrophobe, it was found that with increasing DMA- or decreasing NP-40-concentration and initiator content, monomer droplet nucleation becomes more important [86].

### 3.1.2. Kinetics of droplet nucleation and polymer growth

To get an insight into the polymerization mechanism of miniemulsion polymerization, several studies have focused on the particle size development during the polymerization and its dependence on the initiator amount [108]. Generally, it can be stated that droplet nucleation is the predominant nucleation mechanism when the particle size is independent of the initiator concentration. In this case, also the overall reaction rate should not depend on the amount of initiator and only be influenced by the number of droplets, e.g. their size.

Conductance data during the polymerization were also used to support the droplet nucleation as the primary mechanism of particle formation [45].

In Fig. 14, the calorimetric curve of a typical miniemulsion polymerization with styrene and hexadecane as hydrophobe is shown. Three distinguished intervals can be identified throughout the course of miniemulsion polymerization. According to Harkin' definition for emulsion polymerization
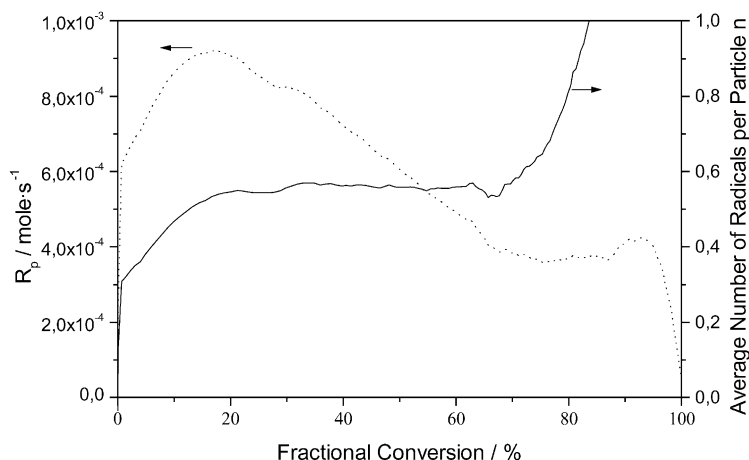
Fig. 15. The evolution of the average number of radicals per particles during a typical miniemulsion using styrene (KPS as initiator).

[111–113], only intervals I and III are found in the miniemulsion process. Additionally, an interval IV describes a pronounced gel-effect, the occurrence of which depends on particle size. Similarly to microemulsions and some emulsion polymerization recipes [114], there is no interval II of constant reaction rate. This points again 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. As seen from the integration of the heat curve, this interval ends at rather low conversions (max 10%) so that indeed every droplet can nucleate before unbalanced mass transfer can play a crucial role. The length of this interval of about 8 min in the case of KPS is by far too long to be caused by the direct entry of persulfate radicals, as it can be calculated from simple kinetic considerations. Experiments with cationic and non-ionic initiators hint to the fact that such highly hydrophilic radicals with their hydration water shell cannot penetrate the hydrophobic droplets [108]. Instead of that, the sulfate radical reacts first with a few monomer units which are molecularly dissolved in the water phase, until a sufficient hydrophobicity for phase transfer is reached. This is very similar to the initiation step in emulsion or dispersion polymerization, as discussed by Tauer and Kühn [107,115] and Barrett [116]. Because of the low styrene concentration in water, this process inevitably takes some minutes.

The initiation process becomes more transparent when the rate of polymerization is transferred (by the known particle number and the known absolute rate constants) into the number of active radicals per particle, $\bar{n}$, which slowly increases to $\bar{n} \approx 0.5$ (Fig. 15). This slow increase of $\bar{n}$ is due to a slow radical flux through the droplet interface.

After having reached this averaged radical number, the polymerization kinetics is slowing down again and follows nicely an exponential kinetics (dotted line in Fig. 14), as known for interval III in emulsion polymerization or for suspension polymerization. As reasoned by the droplet nucleation mechanism, only the monomer in the droplet is available for polymerization, and this 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 [117] upon entry of additional radicals into such small latex particles is 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 radical recombination. This also reflects in a steep rise of $\bar{n}$ during this interval.

The differences between miniemulsion and emulsion were also examined for the polymerization of methyl methacrylate using hexadecane as hydrophobe and KPS as initiator by conductance measurements [45]. In the case of miniemulsions, the conductance did not change significantly; in the case of emulsion, it increases throughout the reaction. This difference leads to a different importance of initiator and surfactants for the formation of new particles. Droplet nucleation in the case of miniemulsions was shown to induce a limit on the number of particles in the reactor.

The amount of hexadecane was reported to have an influence on the kinetics. With increasing amount of hexadecane, the polymerization rate decreases [118]. This is discussed to be due to a decrease in the concentration of monomer in the polymer particles as hexadecane promotes swelling in the miniemulsion droplets, and therefore changes particle size [119]. On the other hand, Delgado et al. have reported that even though the hexadecane plays an important role in the distribution of the monomer between the different phases during the copolymerization process, it does not greatly influence the kinetics in the bulk [120,121].

The predominance of droplet nucleation was also shown for the miniemulsion system using DDM. When stable miniemulsions with DDM as hydrophobe were initiated, particle formation occurred predominately by monomer droplet nucleation [55]. It was found by light scattering measurements that the number of droplets is close to the number of particles implying they are the droplets that are being nucleated. The number of particles in a predominately droplet nucleated polymerization only weakly depends on variation of the amount of initiator. A small increase of the number of particles with increasing DDM is due to some surfactant characteristics of the mercaptane.

Chern and Liou believed that the oil-soluble initiator AIBN in a miniemulsion using SMA or DMA as hydrophobes promotes nucleation in the monomer droplets [122]. Increasing the level of AIBN or SDS enhances formation of particle nucleation via homogeneous nucleation.

The first mathematical model for miniemulsions composed of styrene was developed by Chamberlain et al. [123]. This model was based on the mathematical treatment by Hawkett et al. [124]. It was assumed that polymer particles were formed only upon the entry of free radicals into the monomer droplets, and each entry event resulted in a polymer particle. Chamberlain's et al. work showed that the rate coefficient for radical entry ($\rho$) to the monomer droplets has an order of magnitude lower than the value determined for the seeded emulsion polymerization in order to fit the experimental data obtained for miniemulsion polymerizations using dodecanol as costabilizer.

A computer simulation which can be applied to many monomers in mini- and emulsion polymerization processes was given by Fontenot and Schork [125] taking into consideration many parameters and effects, such as radical absorption, desorption and number balance.

### 3.1.3. Kinetics with cetyl alcohol as a costabilizer

Due to the multiple role of cetyl alcohol in such reaction recipes, the reported observations are less cohesive and sometimes contradictory. A common feature of miniemulsion polymerizations with cetyl alcohol as costabilizer is the relatively long nucleation interval of the reaction as indicated by the long rise to a rate maximum [109,123,126]. This phenomenon has been attributed to a reduced radical

absorption rate possibly caused by the interfacial layer formed by the mixed emulsifier at the droplet–water interface. It has been postulated that a reduced radical absorption rate into monomer droplets is due to the fact that the entering oligomer must first displace a surfactant molecule from the surface of the particle. Since surfactant/cosurfactant-rich surfaces have a lower free energy than surfactant/polymer-rich ones, this should be thermodynamically hindered [94]. Another possible cause for a reduced radical absorption rate is the lowering of the monomer concentration in the aqueous phase due to the presence of cetyl alcohol thus slowing the polymer radical growth in the aqueous phase. Thus, the effect of cetyl alcohol on the entry and exit of radicals in emulsion polymerization was studied, but no conclusive picture was obtained [127].

Miller et al. [128] studied the mechanism of the miniemulsion polymerization of styrene through a combination of calorimetry and transmission electron microscopy using cetyl alcohol as the costabilizer. It was shown by CHDF [129] that the standard deviation increases with increasing conversion. The results suggest that the miniemulsion polymerization using cetyl alcohol as the costabilizer features a long, slow nucleation period. The length of this nucleation time is a function of the initiator concentration, while the conversion at which nucleation ceases was determined to be between 40 and 60%. It has also been noted that in the case of CA only 20% of the droplets capture radicals [109], and that therefore these droplets grow throughout polymerization.

This shows the imperfection of miniemulsion systems stabilized by CA. It is our opinion that although CA simplifies the formation of a miniemulsion (by lowering the interface tension and with it the ease of mechanical dispersion), but exhibits a heavy compensation by influencing chemistry and kinetics in a very negative way.

### 3.1.4. Influence of added polymer on kinetics

Predissolving polystyrene into styrene monomer prior to miniemulsification using cetyl alcohol as costabilizer has been shown to result in a large reduction in the particle size and the coupled increase in the polymerization rate, as compared to similar systems with no predissolved polymer [130]. In the case of hexadecane, the enhancement was much less pronounced. This phenomenon for cetyl alcohol mini-emulsions has been termed 'enhanced droplet nucleation'. It was considered that the system consists of small, stable preformed monomer-swollen particles which are able to efficiently capture aqueous phase radicals [131]. It was shown that the addition of polystyrene to the miniemulsions increases the number of polymer particles produced. Compared to a miniemulsion only with CA as costabilizer, more droplets become particles. Considering the very low nucleation efficiency of about 0.2 for the bare CA system, it has to be stated that the added polymer obviously removes for an unknown reason one of the typical deficiencies of CA.

The number of polymer particles was independent of the concentration of initiator if polymer was added to the miniemulsion, whereas the final number of particles varied with the 0.31 power of the initiator concentration in the absence of polymer [132]. Particles prepared in the presence of polymer also showed a rather narrow particle size distribution, whereas a very broad particle size distribution was found for the pure CA system. The miniemulsion with polymer followed the kinetics of the Smith–Ewart case 1 and/or 2.

Some early experiments first suggested that the disrupture of the SDS/CA interfacial barrier by the polymer to promote radical entry might be the responsible effect [133]. Later, it was shown that varying the molecular weight and the end group of the polymer had no influence on the kinetics, contracting the simple picture [134]. Since measurements of the droplet size with CA as costabilizer, but without added

polymer, indicate droplet degradation and unstable droplet size distribution [135,136] independent of the type of mechanical preparation, it was suggested that the predominant cause of enhanced droplet nucleation by the polymer is that the polymer adds extra stability to the miniemulsion droplets and ensures the preservation of droplet number prior to polymerization [137,138].

It was shown that the use of polymer (without CA) as hydrophobe on the other hand provides sufficient stabilization throughout the course of polymerization [42]. During polymerization, predominantly droplet nucleation was found. The polymerizations of these polymer-stabilized miniemulsions were also found to be less sensitive to variations in the recipe. This was evident in the rate of polymerization and in the particle number [43].

### 3.1.5. Influence of droplet size on the kinetics

The effect of homogenization on the kinetics was studied by Tang et al. [139]. The polymerization of miniemulsions created by the microfluidizer is faster than of miniemulsions created by the omni-mixer. This is mainly attributed to the different droplet sizes prior to polymerization. In the first case, the droplets are much smaller than in the second case. It has to be mentioned that these experiments were done with CA as costabilizer.

Tang et al. also carried out a comparative study to evaluate other parameters of styrene miniemulsions on the polymerization kinetics [126], such as the type of hydrophobe, the means and temperature of homogenization, but they all can be related to differences in the particle size. The results also showed that when the SDS concentration is above its cmc, the overall rate of conventional polymerization is faster than that of the miniemulsion system. However, it is the opposite when the SDS concentration is below the cmc [126]. Fontenot and Schork observed similar behavior for MMA miniemulsions. With increasing shear and concentration of surfactant, the polymerization rate increases [45]. This again can be explained by different sizes of the initial droplets.

In steady state or mechanically equilibrated miniemulsions, the droplet size is easily varied by variation of the amount of surfactant. Depending on the droplet size of the miniemulsions, calorimetric curves with various kinetic features were obtained, which are shown in Fig. 16(a) [108]. Disregarding the complexity of the kinetics and the existence of the three intervals, the reaction time to reach 90% conversion depends as a rule of thumb about linearly on the particle size and thus varies between 20 and 120 min (Fig. 16(b)).

Independent of the size of the droplets, interval I 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, the faster is the reaction. It is underlined that polystyrene latexes can be completely polymerized within 20 min, as long as the particle size is small enough.

The gel-peak is not observed for the smallest particles ($d = 50$ nm) and is getting more and more pronounced for the larger particles. In addition, its onset also depends on particle size (at 45% conversion for a 150 nm latex and at 60% for a 100 nm latex). Both intensity and onset show that the gel-effect is a bulk effect and not found close to the particle surface where the radical flux is still in equilibrium.

Even though the particle number of the latexes increases drastically, the number of radicals per particle in interval III is about constant at 0.5, which underlines the on/off-mechanism due to radical flow is valid. It is worth underlining that within the 20 min of overall reaction time (50 nm latexes), one can calculate (from the molecular weight of the formed polymer chains) that just about 60 radicals have
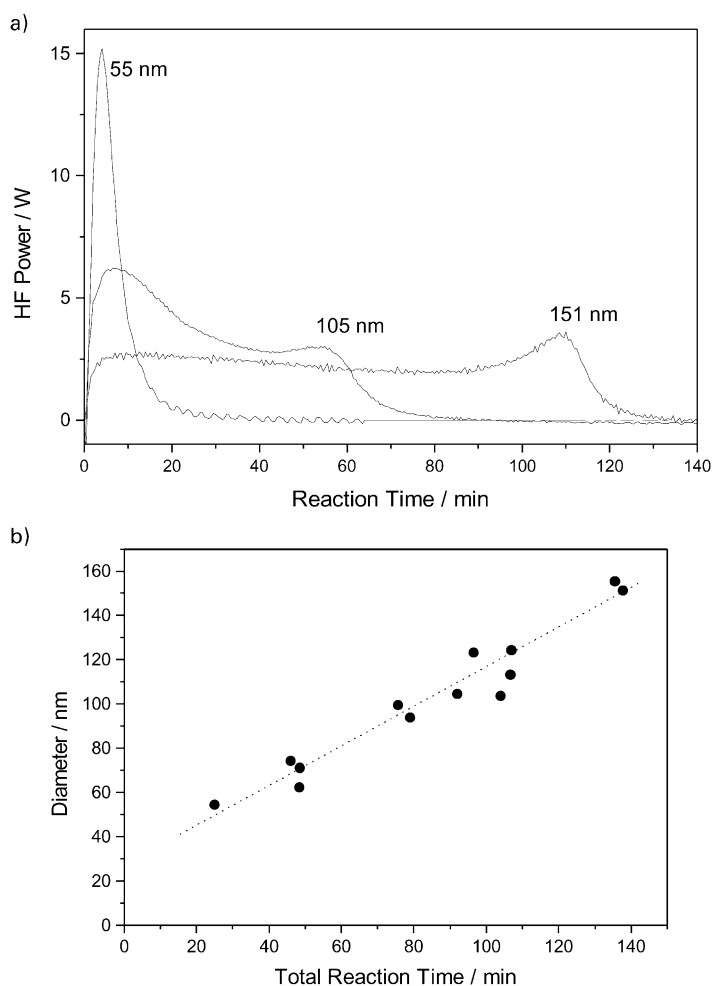
Fig. 16. (a) Calorimetric curves for styrene miniemulsions with different SDS contents in order to obtain different particle sizes. (b) Dependence of the time to reach 95% conversion on the diameter of the resulting polystyrene latex (KPS as initiator).

crossed the particle interface. One can also calculate that this found effective radical flow is comparably low; just a fraction of the radicals created by initiator decomposition in the continuous phase end-up in the hydrophobic particles.

## 3.2. 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. Because of the finite size of the 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 mainly water-soluble initiators are used.
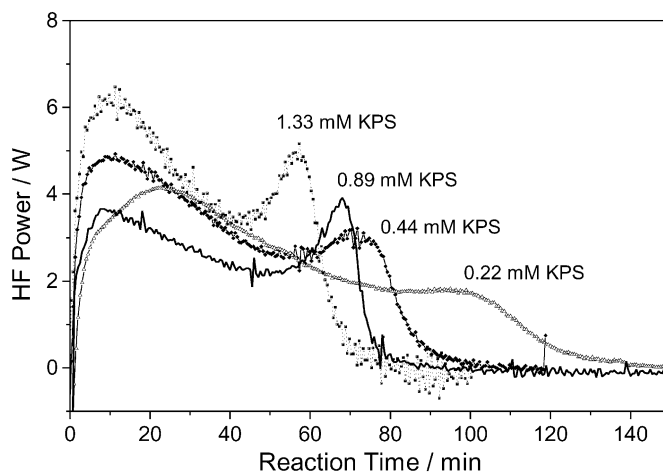
Fig. 17. Calorimetric curves for styrene miniemulsions with different amounts of initiator.

### 3.2.1. Water-soluble initiators

The formation of free primary radicals takes place in the water phase. Varying the initiator concentration leads to surprisingly similar reaction profiles, as revealed by calorimetry (see Fig. 17, taken from Ref. [108]). The particle nucleation interval, interval I, is longer when less initiator is present. In the case of the lowest concentration of this series, it takes about 20 min to reach the radical equilibrium, whereas for all other reactions, there seems to be a threshold below which interval I cannot be further shortened. Once all the droplets are nucleated, the monomer is steadily consumed (interval III). The average radical number per particle $\bar{n} = 0.5$ during interval III is independent of the amount of initiator, and an increase of the initiator concentration cannot result in an acceleration of the polymerization process in this interval. Only the frequency of the on/off-process is changed. It was also found that the chain length of the resulting polymer is inversely proportional to the square root of the initiator concentration [108] underlining that the reaction in miniemulsion is rather direct and close to an ideal radical polymerization.

The onset of the gel-effect (interval IV) however depends on the amount of initiator: the higher the initiator concentration, the earlier and the more pronounced the gel-peak. This observation is in accordance with a higher radical stream through the interface, which should also go with the square root of concentration.

For the styrene/hexadecane system, the amount of initiator does not have an effect on the particle number, i.e. droplet nucleation is by far the dominant mechanism over the whole range of initiator concentrations. This is not necessarily the case, since an increased initiator concentration also results in an increased probability for homogeneous nucleation. In the case of more water-soluble monomers, for example, MMA and vinyl chloride [97], secondary particle formation was observed. Here, the amount of new particles increases with the concentration of the 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) [140] or even more efficiently by using an interface active redox initiator (cumene hydroperoxide/$Fe^{2+}$/EDTA/formaldehyde sulfoxide) to initiate the miniemulsion polymerization [141,142].

### 3.2.2. Oil-soluble initiators

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 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 LPO, BPO and AIBN in stabilizing monomer droplets against degradation by molecular diffusion and their efficiency for polymerization was investigated in Ref. [61]. 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 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.

Miniemulsions can also be initiated and stabilized by the more hydrophobic 2,2′-azobis(2-methyl-butyronitrile), AMBN, which simultaneously acts as an initiator and a hydrophobe. It was noted that the rate of polymerization significantly increases as the surface area of the monomer droplet increases [143]. A radical flux out of the particle is expected. In the case of KPS, the polymerization rate decreased compared to conventional emulsion polymerization, whereas it increased in the case of AMBN. Using the hydrophobic initiator AMBN and the water-soluble 2,5-dihydroxy-1,4-benzene disulfonic acid in styrene miniemulsions (prepared with CA/SDS) resulted in enhanced polymerization rates and increased the droplet nucleation [144]. The evolution of the molecular weight distribution in the batch mini-emulsion polymerization of styrene initiated by different oil-soluble initiators reveals the molecular weight remains roughly constant at the beginning of the polymerization and increased significantly at the end due to the gel-effect. A fairly good agreement between experimental results and model predictions was found [145].

Some monomers, such as the ultrahydrophobic lauryl methacrylate, require for homopolymerization the use of hydrophobic initiators.

## 4. Different polymerization reactions in miniemulsions

The process of miniemulsion allows that in principle all kind of monomers can be used 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 which lead to nanoparticles (much broader than in emulsion polymerization) as well as the synthesis of nanoparticle hybrids which were not accessible before. Table 2 summarizes a number of examples.

### 4.1. Radical homopolymerization in regular miniemulsions

As a model monomer for the radical homopolymerization of oily monomers, styrene is described in many papers. The polymerization of acrylates and methacrylates are also well known. The miniemulsion
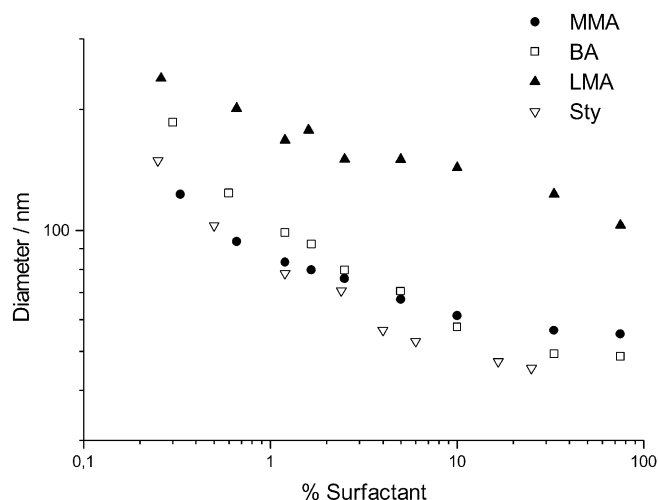
Fig. 18. The use of different monomers in miniemulsion: the dependence of the surfactant concentration on the particle size.

also allows easily the polymerization of the ultrahydrophobic monomer lauryl methacrylate without any carrier materials as necessary in emulsion polymerization [146].

The polymerization of more hydrophilic monomers is also possible, as shown for MMA and vinyl acetate [41,88,147]. In the case of monomers with the 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 by using a oil-soluble initiator see also 3.2.2. (oil-soluble initiators) and 4.4. (polyacrylonitrile) or the addition of a termination agent to the continuous phase.

In Fig. 18, the ability to control particle size by the surfactant concentration (here SDS is employed) for different monomers is shown. For MMA, BA and styrene, similar size-relative surfactant concentration curves are detected, whereas the hydrophobic monomer LMA leads to larger particles. This is due to the larger interfacial tension between the monomer and the water phase which has to be compensated by a higher coverage by surfactant molecules.

Elbing et al. described the polymerization of vinyl stearate in small droplets. Since the emulsions were optically clear or opalescent, they called them in their first paper microemulsions [148]. In their second paper, they switched to the term miniemulsion because the droplets were much larger than micelles [149]. However, the term microemulsion is more appropriate, because the droplets are thermodynamically stable, and they are not osmotically stabilized. As usually observed in microemulsion, the droplets show an increase of size during polymerization.

PVC latex particles consisting of two size populations are generated in a miniemulsion polymerization. The mechanism for the formation of two discrete particle families relies upon polymerization of two distinct kinds of droplets [150]. Large particles are formed by homogenization of a mixture of monomer and a water-insoluble initiator. Smaller droplets are formed by swelling of soap/alcohol (SLS–alcohol and cetyltrimethylammonium bromide–alcohol) miniemulsion droplets. Polymerizable miniemulsion droplets arise when alcohol in excess of 2:1 soap/alcohol stoichiometry is utilized in its preparation. This difference appears to be due to a liquid-to-solid phase change in the forming particles during the course of polymerization [151].

## 4.2. Formation of particles in non-aqueous polar solvents

It was shown that the principle of aqueous miniemulsions can be transferred to non-aqueous media [75]. Here, polar solvents, such as formamide or glycol replace the water as the continuous phase, and hydrophobic monomers are miniemulsified with an ultrahydrophobic agent which stabilizes the droplets. It turned out that steric non-ionic surfactants based on poly(ethylene oxide) tails are by far more efficient than ionic stabilizers, which is speculatively attributed to a low degree of ion solvation and degree of dissociation in formamide. It was possible to make particles as small as 70 nm, which is unexpectedly small for non-aqueous heterophase polymerization techniques. An increase of particle size with decreasing amounts of surfactant is detected. For the polymerization of the monomer droplets, both AIBN or KPS as initiators were employed. AIBN which dissolves in both organic phases leads to an aggregation of particles. The hydrophilic initiator KPS however turned out to be suitable, since it only starts the polymerization controlled from the homogeneous phase.

It is noted that the surface tension measurements of both the initial miniemulsion and the final latex indicate incomplete surface coverage of the latexes and clean droplet nucleation as the dominant initiation mechanism.

The high boiling solvent glycol represents an alternative continuous phase for some other synthetic concepts, such as the controlled radical polymerization thus allowing polymerization temperatures well above 100 °C without pressurizing the reaction. Miniemulsions made in glycol allowed production of latexes with a diameter as small as 193 nm [75]. Again, an initiator had to be selected which just dissolves in one of the phases. The solubility of KPS in both the monomer and the glycol is too low to be efficient, whereas AIBN dissolves in both phases and leads to coagulation. For glycol, the non-ionic polyethylene oxide-based azo-initiator PEGA200 [152] turned out to be the appropriate choice.

For further application, it has to be noted that formamide and glycol latexes can easily be diluted with water, preserving the stability of the systems. This can also be used to characterize the latexes in water, avoiding the problems of dynamic light scattering with the high viscosity solvent glycol.

## 4.3. Formation of particles in inverse miniemulsion

In the case of inverse systems, hydrophilic monomers, such as hydroxyethyl methacrylate, acrylamide, and acrylic acid were miniemulsified in a non-polar media, e.g. cyclohexane or hexadecane [75,76]. Rather small and narrow distributed latexes in a size range $50 < d < 200$ nm were made with the non-ionic amphiphilic block copolymers described in Fig. 9. 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 initiator, 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 due to solubility problems. The use of AIBN as initiator results in a smaller particle size than the use of PEGA200. 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 inverse latex particles in the size range between 80 and 160 nm and narrow size distributions are obtained. The systems are stable down to 1.6 wt% surfactant with respect to monomer,
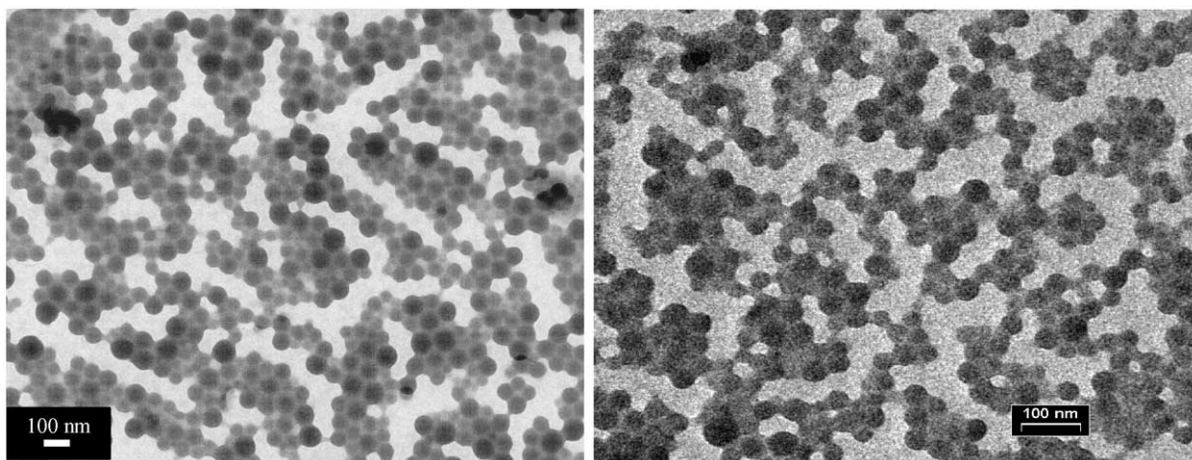
Fig. 19. Hydrophilic polymer particles obtained in inverse miniemulsion polymerization in Isopar: (a) polyacrylamide; (b) poly(acrylic acid).

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. It is remarkable that the final dispersions are stable for longer time even at low surface coverages.

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 was chosen. The miniemulsions after sonication show only a low stability (less than 1 h) without the addition of a strong lipophobe (1 M NaCl), which increases the stability of the miniemulsions to the time scale of several days to months. Polymerization with AIBN from the continuous phase resulted in stable polymer dispersions, as shown in Fig. 19.

The high homogeneity and rather well-defined character of those latexes are clearly observed. Again, already surfactant loads as low as 1.8 rel% with respect 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%) and 7 nm$^2$ for higher surfactant amounts (7.1%), depending on particle size.

Acrylic acid was polymerized in the inverse miniemulsions together with 4 wt% of the crosslinking agent diethylene glycol diacrylate in order to obtain homogeneous polyelectrolyte microgels which can be also redispersed and characterized in water. In this case, the solubility of acrylic acid in cyclohexane is not negligible. For a formulation of a stable inverse acrylic acid containing miniemulsion, both a 1 M NaCl solution and a 5 M NaOH solution (charging up the monomer) were employed as ultralipophobes. Using the 5 M NaOH solution, the partitioning of acrylic acid was shifted to the water phase, and only 7% of the acrylic acid was found in the cyclohexane phase.

Starting from a critical surfactant amount of 2.5 rel% to prevent the formed polymer particles from aggregation, stable latexes of about 100 nm diameter were produced. Increasing the surfactant amount leads to smaller particles. The surfactant efficiency or stabilized area per surfactant molecule, $A_{surf}$, is very high. In the case of low surfactant concentration, $A_{surf}$ is as high as 25 nm$^2$/stabilizer.

The quality and the low polydispersity of the particles are illustrated by the picture shown in Fig. 19(b). Those particles have an averaged size of 50 nm and a polydispersity of less than 10%.

This example proves that a high monomer solubility in the continuous phase is not a serious hindrance for the miniemulsion polymerization. Since the interfacial tension of the miniemulsion and of the final latex to water are very similar, it is expected that droplet nucleation is still the main initiation mechanism for AIBN and KPS as the initiators.

Due to the crosslinking, the particles could be dried and redispersed in water under retention of their particular identity. Here, rather monodisperse particles with a diameter of 218 nm are found, i.e. a swelling of the microgels by a volume factor of 80 occurs. This is rather typical for polyelectrolyte microgels in salt free solutions [153,154].

As compared to classical inverse heterophase polymerization techniques such as polymerization in inverse microemulsions [77] or dispersion polymerization [155,156], 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 is a very interesting polymer for many engineering applications, such as fiber spinning or for housing and package application. Even though it is produced in a radical polymerization process as a mainly atactic polymer, it has the tendency to form crystallites, the crystallinity degree is reported to be between 28 and 34% [157]. 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 further 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 results, it is possible to obtain pure polyacrylonitrile (PAN) nanoparticles in the size range $100 < d < 180$ nm depending on the amount of surfactant (2.0 wt-rel% SDS compared to monomer leads to 180 nm particles, 6 rel% to 98 nm particles) [158]. As compared to a standard styrene miniemulsion, 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. As already shown for acrylic acid in cyclohexane, this is no restriction for a miniemulsion polymerization process, as the use of a hydrophobic initiator (V59) allows preservation of the droplets as the reaction sides (droplet nucleation). During the reaction the entire monomer of the water phase is consumed, as shown by NMR measurements, and the droplets are expected to grow by the amount of monomer consumed from the water phase.

Due to the insolubility of the polymer in the monomer, the formed polymer precipitates and crystallizes during the polymerization within the droplets. 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 (Fig. 20).

The crystallinity of the particles was determined by wide-angle X-ray scattering to be 26%. A continuous transition between the crumpled and a smooth spherical morphology can be obtained by copolymerizing acrylonitrile with increasing amounts of styrene.
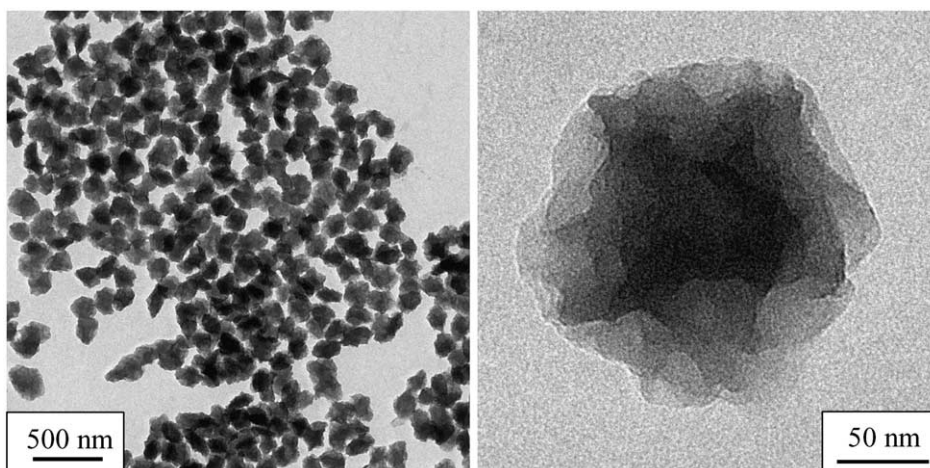
Fig. 20. Transmission electron micrograph of PAN latex particles.

## 4.5. Radical copolymerization

Miniemulsion copolymerization of 50:50 styrene/methyl methacrylate monomer mixture, using hexa-decane as hydrophobe, was carried out. An increase in the hexadecane concentration or an increase in the sonication time led to smaller particle sizes, and therefore a faster polymerization was obtained [159]. The mechanism of mass transfer between miniemulsion droplets and polymer particles in the miniemul-sion copolymerization of styrene–methyl methacrylate (AIBN as initiator, hexadecane as hydrophobe) was studied, and a mathematical model was developed. The model includes the mass transfer of highly water-insoluble compounds from miniemulsion droplets to polymer particles by both molecular diffu-sion and collisions between droplets and particles [74,160].

Copolymerization of styrene and butyl acrylate were successfully carried out using the redox initiator system $(NH_4)_2S_2O_8$/NaHSO_3 at lower temperature [140]. The rate of the miniemulsion polymerization increases with increasing butyl acrylate concentration and decreases with increasing styrene concentra-tion. 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 [161].

Inaba et al. prepared a series of model styrene/*n*-butyl acrylate copolymer latexes with glass transition temperatures at room temperature. The functional monomer dimethyl *m*-isopropenyl benzyl isocyanate (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 [162].

The copolymerization of monomers where one monomer acts as the hydrophobe was reported [58]. MMA was copolymerized with *p*-methyl styrene, vinyl hexanoate, or vinyl 2-ethylhexanoate. The resulting copolymer composition tended to follow the predictions of the reactivity ratios, i.e. the reaction progresses such as a bulk reaction. In contrast copolymer compositions obtained from the 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: vinylacetate/butyl acrylate, vinylacetate/dioctyl maleate, and vinyl acetate/*n*-methylol acrylamide. The miniemulsion system follows more closely the integrated Mayo–Lewis equations than the comparable emulsion system [147].

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 [39]. The dynamic mechanical properties of the copolymer films showed less mixing between the butyl acrylate-rich core and the vinyl acetate-rich shell in the miniemulsion latexes compared to the conventional latex films.

The miniemulsion polymerization allowed the synthesis of particles in which PBuA and PMMA macromonomer were copolymerized [163,164]. The macromonomer acts as compatibilizing agent for the preparation of core/shell PBuA/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. Interfacial tension is considered one of the main parameters controlling the particle morphology in composite particle.

In the case of small amounts carboxylic monomers (AA or MAA) [165] or 2-hydroxyalkyl methacrylates [166] in a styrene miniemulsion polymerization, using DMA or SMA as hydrophobe and SDS as emulsifier, a mixed mode of particle nucleation, namely droplet nucleation and homogeneous nucleation, was observed. In the case of DMA, the homogeneous nucleation plays a crucial role since the osmotic stability of the droplets is not fully ensured, whereas in the case of the more hydrophobic SMA, the droplets show a higher stability, and therefore droplet nucleation was favored. It has to be noted that the authors used the water-soluble initiator sodium persulfate which can easily capture the acrylic acid in the water phase. From our point of view, it is advised in the case of monomers with a high water solubility to use hydrophobic initiators in order to prevent secondary nucleation in the water phase (see also: oil-soluble initiators).

## 4.6. Catalytic chain transfer in miniemulsion

The employment of a cobalt catalytic chain transfer agent in miniemulsion polymerization allows directly to control the molecular weight [167]. The solubility of the cobalt catalyst was found to have a large influence on the mechanism of the reaction. Cobaltoxime boron fluoride (COBF) partitions approximately equally between the water and oil phase. 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), explained by a poisoning and/or deactivation of the catalyst. Contrary to this, tetraphenylcobaltoxime boron fluoride (COPhBF) stays exclusively in the oil phase. The COPhBF 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 of the catalyst 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 styrene via the miniemulsion approach allows

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 [168].

Four different approaches for controlled radical polymerization have been adapted to the mini-emulsion polymerization process:

(a) The controlled free radical miniemulsion polymerization of styrene was performed in aqueous dispersions using a *degenerative transfer process* with iodine exchange [169,170]. 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 [171]. This allows the synthesis of well-defined polymers with predicable molar mass, narrow molar mass distribution, and complex architecture.

(b) In a *stable free radical polymerization* (SFRP) the initiated polymer chains are reversible capped by a stable radical, for example, the 2,2,6,6-tetramethyl pyridin-1-oyxl radical (TEMPO). Stable PS dispersions by miniemulsion polymerization are prepared with an optimized ratio and amount of surfactant, hydrophobe, nitroxide and KPS as initiator at 135 °C [172]. TEMPO in combination with BPO was used by Prodpran et al. [173]. They carried out the polymerization at 125 °C in pressure bottles. The kinetics were followed as a function of the [TEMPO]/[BPO] ratio. At a TEMPO to BPO 3:1 molar ratio, polymers with the lowest polydispersity (1.3) were achieved. Utilizing TEMPO-terminated oligomers of polystyrene results also in stable latexes, but the particle size distribution is unexpectedly broad [174]. 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. It was demonstrated that water-soluble alkoxyamines were initially formed during the induction period and were progressively transferred into the organic phase. In unbuffered systems, a decrease of the pH during the reaction leads to an increased rate of polymerization together with a low initiator efficiency which is due to side reactions of the nitroxide and the initiator system. At neutral pH the side reactions can be suppressed [175]. Theoretical aspects of controlled radical polymerization in miniemulsion were examined by Charleux [176]. An analytical expression of the rate of irreversible termination is proposed as a function of particle size and is compared with the rate of termination in bulk. For large particles, the polymerization kinetics was found to be similar in bulk and in miniemulsions. In contrast for small particles, owing to slower terminations, the concentration of released nitroxide was shown to be smaller in miniemulsion than in bulk, leading thus to a lower proportion of dead chains, a faster polymerization, and a broader molar mass distribution.

(c) *Living radical polymerizations* in miniemulsions have also been conducted using reversible addition-fragmentation chain transfer (RAFT) [177]. The miniemulsion stability was found to be a key issue, and the authors' system was only stable with non-ionic surfactants. The polydispersity was usually below 1.2. The living character is further exemplified by the formation of block copolymers. The increased polymerization rate of the compartimentalized miniemulsion system leads to an improved block copolymer purity compared to that of homogeneous systems. It was shown that living radical polymerization could be conducted simultaneously with conventional radical polymerization in a single reactor leading to a blend of latex particles with completely different characteristics. This again underlines the strict separation of the single droplets (nanoreactors) throughout the reaction cascade.

(d) *Reverse atom transfer radical polymerization* (ATRP) of butyl methacrylate was successfully conducted in miniemulsions 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 [178,179].

## 5. Hybrid nanoparticles by miniemulsion technologies

### 5.1. Polymer–polymer hybrids

Miniemulsification enables the incorporation of major amounts of water-insoluble materials, such as resins by dissolution or dispersion in the organic phase. 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 [70]. Throughout the reaction, the resin simultaneously acts as a hydrophobe and allows the stabilization of the miniemulsion. It was found that the double bonds that served as grafting sites of the alkyd onto the polyacrylate were mostly those near acid groups. The predominant form was poly(acrylate-*g*-alkyd resin) which also confirms the monomer droplet nucleation mechanism [180]. Kinetics studies showed that as the relative resin content increased, the polymerization rate decreased. In a purely acrylic system, complete conversion was found.

Tsavalas et al. [181] showed in a similar system that despite of a high degree of crosslinking ($>70\%$), residual double bonds were present in the polymer–polymer hybrid latex for curing reactions during film formation. The presence of unsaturated resin was found to favor chain-transfer reactions at higher conversions leading to both, inhibition of the reaction and grafting [181]. The in situ grafting between a polyester resin and an acrylic polymer in a nearly zero-VOC environment offers a novel, water-based, crosslinkable latex coating incorporating properties from both water- and solvent-based systems.

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 [64].

Oil-acrylate hybrid-emulsions were formed using the fatty-acid hydroperoxides as initiator system for the miniemulsion polymerization of acrylate. During polymerization, nucleation takes place in the monomer-oil droplet. The use of fatty-acid hydroperoxides as oil-soluble initiators in combination with the redox system ROOH/SFS/EDTA–$Fe^{2+}$ leads to an initiation at the droplet interface and results in the formation of triglycides modified polyacrylate molecules. These molecules act as compatibilizers between oil and the PMMA phase resulting in more homogeneous particles. The diffusion of the fatty-hydroperoxide molecules from the oil phase to the oil–water interface probably determines the rate of polymerization. Only a small number of the available sites for crosslinking of the oils are used for initiation of the miniemulsion polymerization, and therefore the autooxidative crosslinking properties of the oils remain unchanged [182].

### 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 state. The design of the interfaces is mainly dictated by the use of two surfactant systems which govern the interfacial
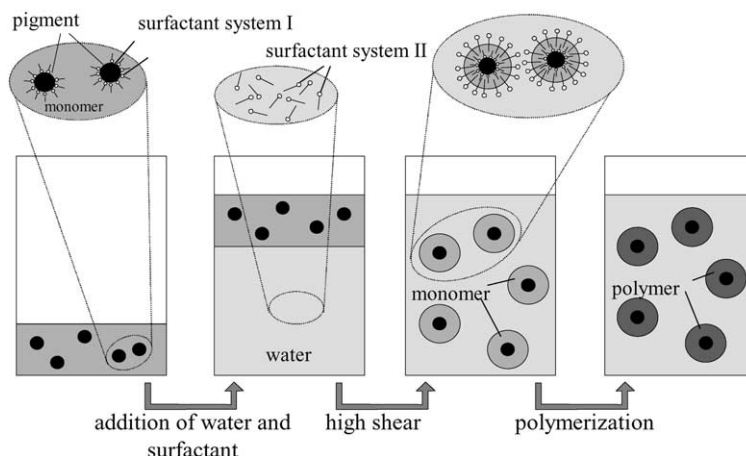
Fig. 21. Principle of encapsulation by miniemulsion polymerization.

tensions, as well as by employment of appropriate functional comonomers, initiators, or termination agents. The sum of all interface energies has to be minimized.

In order to achieve the incorporation of a pigment into the latex, both type and amount of surfactant have to be adjusted to yield monomer droplets 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 (Fig. 21). First, the already hydrophobic or hydrophobized particulate pigment with a size of up to 100 nm has to be dispersed in the monomer phase. Hydrophilic pigments require a hydrophobic surface to be dispersed in 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.

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 [183,184]. The presence of $TiO_2$ particles within the droplets limited the droplet size, and complete encapsulation was not achieved (encapsulation taxes were reported to be between 73 and 83%). Also the amount of encapsulated material was very low: a $TiO_2$ to styrene weight ratio of 3:97 could not be exceeded [185].

Nanoparticulate hydrophilic $CaCO_3$ was coated with a layer of stearic acid prior to dispersing the pigments into the oil phase [90]. 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. Five weight percentage of $CaCO_3$ could be completely encapsulated into polystyrene particles. 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 (Fig. 22(a)).

The encapsulation of the magnetite particles into polystyrene particles was efficiently achieved by a miniemulsion process using oleoyl sarcosine acid [186] 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. 22(b)). Since the magnetite particles were very small (ca. 10 nm), each polymer particle was able to incorporate many inorganic nanoparticles.
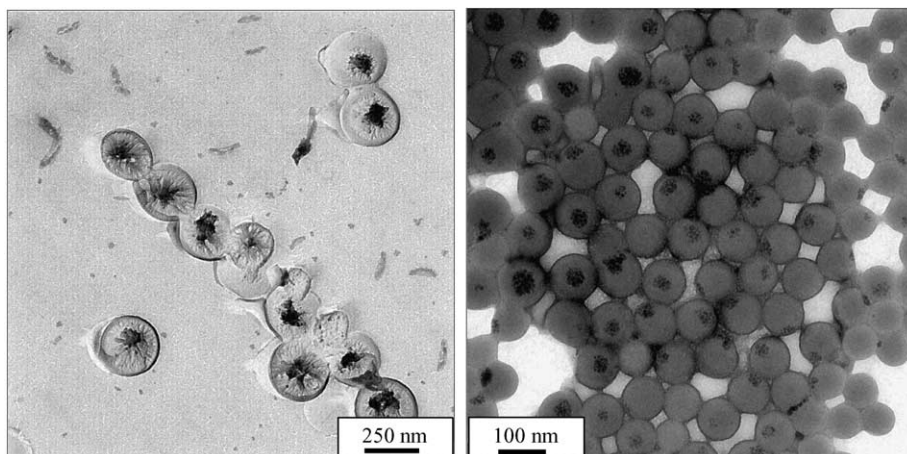
Fig. 22. (a) Encapsulation of one colloid per polymer particle: CaCO$_3$ nanoparticles in PS latexes. (b) Encapsulation of one colloid per polymer particle: Fe$_3$O$_4$ in PS latexes.

## 5.3. Encapsulation of carbon black by 'ad-miniemulsion polymerization'

Since carbon black is a rather hydrophobic pigment (depending on preparation conditions), 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 [90]. Here, full encapsulation of non-agglomerated carbon particles can be provided by appropriate choice of the hydrophobe. In this case, the hydrophobe not only acts as the stabilizing agent for the miniemulsion process, but also mediates to the monomer phase by partial adsorption. As a side product, this also prevents the formation of solid carbon–carbon aggregates. The main drawback of the direct dispersion of carbon black in the monomer is that the carbon is still highly agglomerated in the monomer, and a maximum of 8 wt% carbon black was incorporated. 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 [187]. Here, 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 remained due to their higher stability. This controlled droplet fission and heteroaggregation process can be realized by high-energy ultrasound or high-pressure homogenization as it was discussed earlier in this review.

TEM and ultracentrifuge results showed 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.
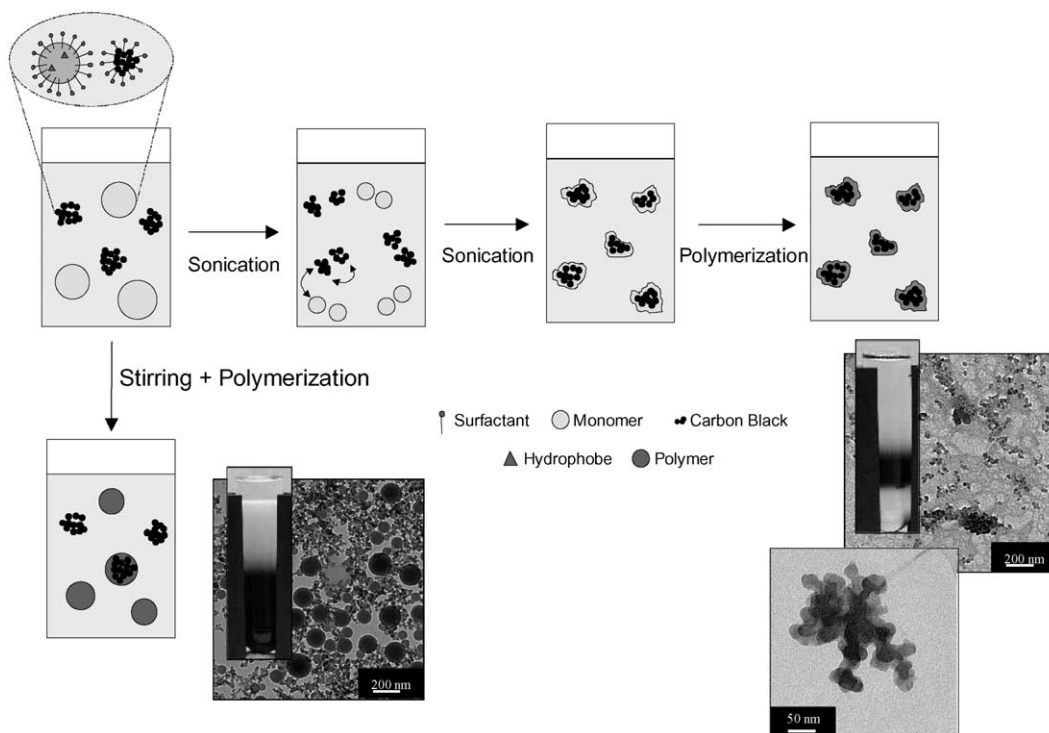
Fig. 23. Principle of co-miniemulsion where both components have to be independently dispersed in water and mixed afterwards. The controlled fission/fusion process in the miniemulsification realized by high energy ultrasound or high-pressure homogenization destroys all aggregates and liquid droplets, and only hybrid particles being composed of carbon black and monomer remain due to their higher stability.

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. 23.

The structural homogeneity of the encapsulation process is characterized by sedimentation experiments in a preparative ultracentrifuge. In a density gradient, it is simple to differentiate between the low-density polymer phase, the high-density pure carbon phase and all intermediates which are the encapsulated species with different layer thickness and layer perfection. For the experiment, sucrose solutions of different densities were layered, building up a density gradient from 1.0 to 1.3 $g\,cm^{-3}$. As shown in Fig. 23, the sample without sonication treatment (comparable to a potential product made by emulsion polymerization) consist of different species, at least a white band being composed of carbon-free polymer particles and a black fraction with densities larger than 1.13 $g\,l^{-1}$. The density distribution of this mixed fraction is obviously very large and covers species from bare, not encapsulated carbon (at the bottom, density larger than 1.3 $g\,cm^{-3}$) to well-encapsulated species. In the case of cosonication, only one particle fraction with a narrow density distribution (1.2 $g\,l^{-1}$) is detected, indicating that all formed particles do show a very similar carbon/polymer composition or degree of encapsulation. At the same time, the absence of pure polystyrene particles or pure pigment aggregates is clearly illustrated.

The completeness of the surface coverage of the encapsulated products can be analyzed by BET

measurements on the dialyzed and dried products. For the pure carbon black used in the experiment, the BET surface area was determined to be $250 \, \mathrm{m^2 \, g^{-1}}$. A pure PS latex with a diameter of 100 nm shows a BET surface area of about $50 \, \mathrm{m^2 \, g^1}$. For the dialyzed and dried carbon/styrene hybrid made by the ad-miniemulsion polymerization process, a BET surface area of $58 \, \mathrm{m^2 \, g^{-1}}$ was determined, which speaks for the close-to complete encapsulation of the carbon, blocking the inner micropores for adsorption [187].

As the ultrahydrophobe for this process which provided both osmotic stability of the monomer ad-layer and an efficient binding to the monomer, a hydrophobic polyurethane turned out to be a favorable choice. The optimum amount was found to be 3 wt% of polyurethane. For comparison, also hexadecane was employed (4 wt%), but the particles turned out to be larger and bimodal. For further application of those systems as water-based inks or colorants, the presence of hexadecane is disadvantageous.

For the instantaneous formation of a cohesive, carbon containing film, encapsulation with polymers with a low glass transition temperature are preferred. In case of butyl methacrylate (BMA) as the encapsulating monomer (contains both a pendant hydrophobe and a carbonyl-group known to interact with carbon surfaces), different carbon black pigments with different surface polarity could be efficiently encapsulated, and the resulting hybrid particle sized were as low as 60 nm [187]. Obviously, BMA with its hydrophobe/carbonyl character is better suited for carbon surface stabilization and encapsulation than the aromatic styrene. Those systems are extremely interesting for high resolution electronic printing applications.

## 5.4. Encapsulation of a liquid—formation of polymer nanocapsules

Polymerization in miniemulsion can also be performed in the presence of an oil which has to be inert to the polymerization process. After polymerization, oil and polymer can demix, and a variety of 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 emulsion polymerization, but is usually kinetically controlled [188–190]. The synthesis of hollow polymer nanocapsules as a convenient one-step process using the miniemulsion polymerization however has the advantage to be thermodynamically controlled [191].

First work describing the behavior of two immiscible oils in water on the base of thermodynamic considerations was published by Torza and Mason [192]. They showed that the resulting equilibrium configuration of two immiscible liquid droplets, designed as phase 1 and 3, suspended in a third immiscible liquid phase 2, is readily predicted from the interfacial tensions $\sigma_{ij}$ and spreading coefficients $S_i = \sigma_{jk} - (\sigma_{ij} + \sigma_{ik})$. In terms of the convention $\sigma_{12} > \sigma_{23}$ ($S_1 < 0$) phase 1 is completely engulfed by phase 3 when $S_2 < 0$ and $S_3 > 0$, no engulfing occurs when $S_2 > 0$ and $S_3 < 0$; and $S_1, S_2, S_3 < 0$ leads to partial engulfing and formation of two-phase droplets with three interfaces the shapes of which can be calculated. The three different equilibrium configurations are illustrated in Fig. 24.

The chemical control of the expected particle morphology for an encapsulation process is a system with a complex parameter field. Recognizing the dramatic effect that common emulsifiers have on the interfacial tension between water and organic liquids or solids, it is not surprising to find that the preferred particle morphology reacts sensitively on the chemical natures 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.
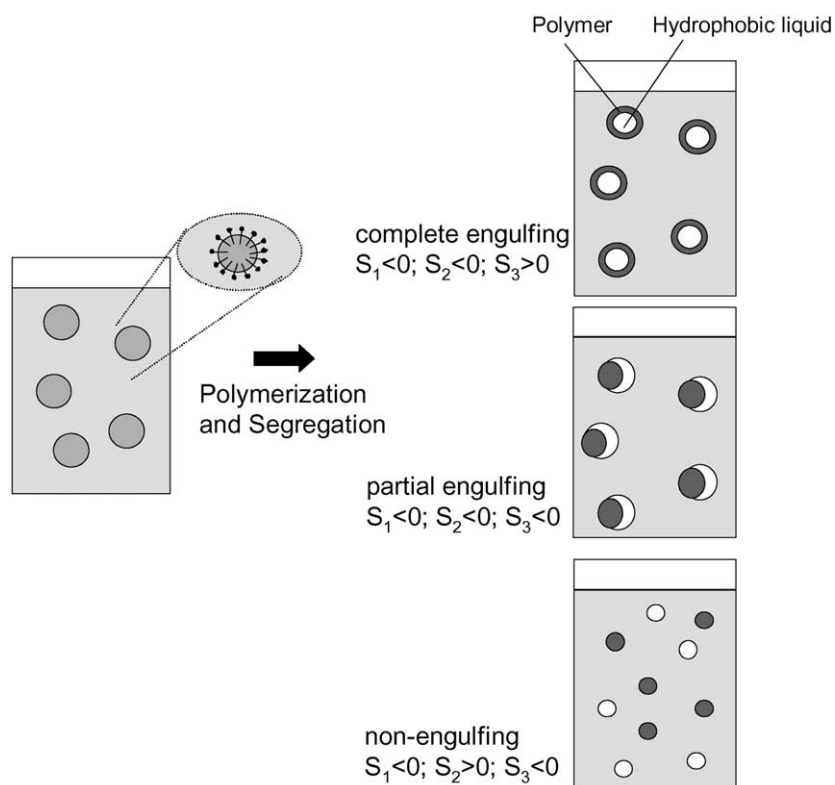
Fig. 24. Possible equilibrium configurations corresponding to the three sets of $S_i$. The continuous medium is phase 2.

An analysis of the thermodynamics of this situation has also been developed by Sundberg and co-workers [193]. Sundberg also discussed [194] that the influence of the surfactant and the nature of the incompatible polymers on polymer particle morphology is seen through their individual and collective effects upon the interfacial tensions. Several apparently different morphologies (hemispherical, sandwich, multiple lobes) have been found to coexist at the same time within a single emulsion, suggesting that they may be simply different states of phase separation and not thermodynamically stable, unique morphologies. Chen and co-workers developed a thermodynamically based model to describe the free energy differences between different possible particle structures [195].

Experimentally, it turned out that for the preparation of polymer particles in aqueous media consisting of two phases, the following parameters can be employed:

- the differences in the hydrophilicity of the monomers and polymers and the solubility of the monomers and polymers in the aqueous phase [196,197];
- the compatibility of the formed polymers [198];
- type and amount of initiator [199];
- temperature [200].

In the case of PMMA and hexadecane as a model oil to be encapsulated, the pronounced
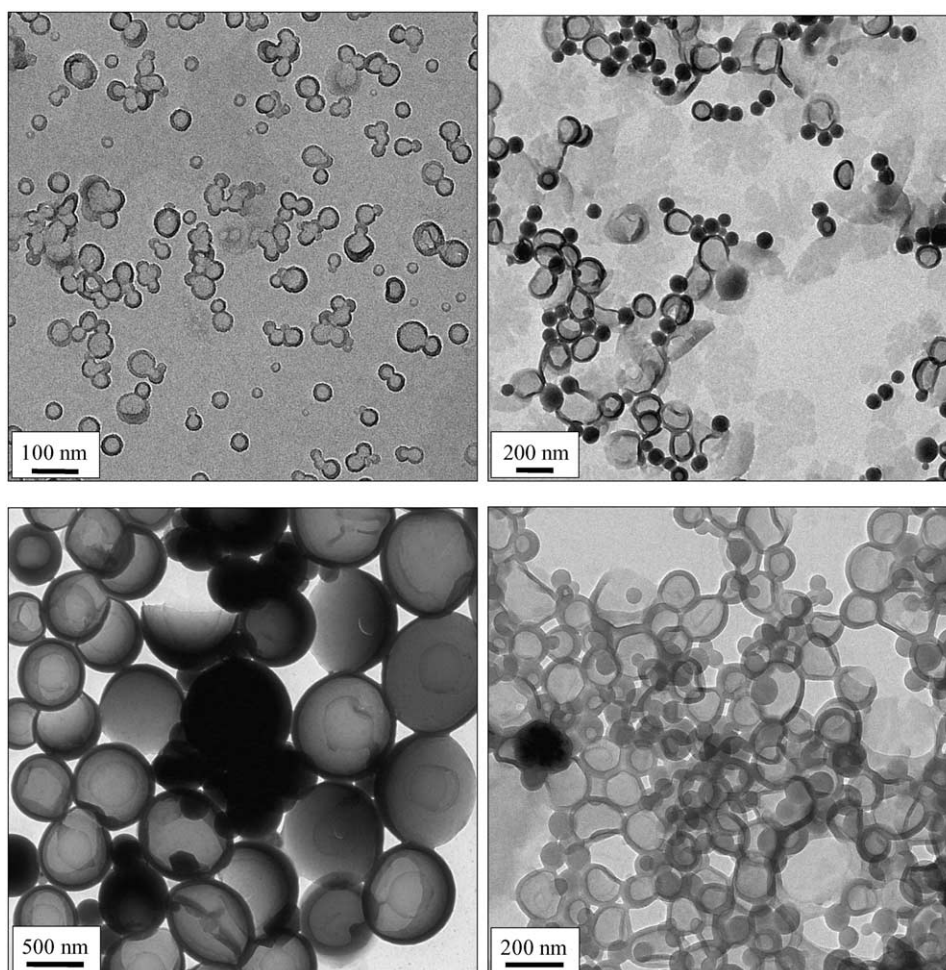
Fig. 25. TEM micrographs of nanocapsules. (a) PMMA/hexadecane/SDS; (b). PS/hexadecane/SE3030/KPS; (c) same as (b), but with PEGA 200; (d) acrylic acid as a comonomer.

differences in hydrophilicity are suitable for direct nanocapsule formation. PMMA is regarded as rather polar (but is not water-soluble), whereas hexadecane is very unpolar so that the spreading coefficients are of the right order to stabilize a structure in which a hexadecane droplet core is encapsulated by a PMMA shell surrounded by water [191]. The miniemulsions were obtained by mixing the monomer MMA and hexadecane together with the hydrophobic, oil-soluble initiator AIBN and miniemulsifying the mixture in an aqueous solution of SDS. The polymerization leads to polymer capsules with 160 nm diameter and a narrow particle size distribution (less than 15% gaussian width), as shown in Fig. 25(a). 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. Since MMA is rather water-soluble ($150 \, \text{mM} \, l^{-1}$) the use of the hydrophobic initiator AIBN is advised, otherwise secondary nucleation of pure PMMA particles from the water phase may occur. Nanocapsules with a higher shell stability can be obtained by using up

to 10 wt% of EGDMA as crosslinking agent. The particle size of the hollow latexes is not affected by the crosslinker.

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 non-ionic surfactant Lutensol AT50 (a hexadecyl modified poly(ethylene glycol)). This means that with increasing surfactant load also the surface coverage 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 particle morphology was examined, and a continuous morphological change towards engulfed structures was found [191].

In the case of styrene as a 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 more sensitive on the parameters which influences the interfacial tensions critically. A variety of different morphologies in the styrene/hexadecane system can be obtained by changing the spreading parameter. This was done by changing monomer concentration, type and amount of surfactant, as well as initiator and functional comonomer.

The employment of a block copolymer made of polystyrene and poly(ethylene oxide) (SE 3030) to stabilize the styrene/water interface lead in a certain composition range to the formation of capsules however sometimes with imperfect or broken up shape (Fig. 25(b)).

Employment of a non-ionic initiator PEGA200 which supports interface stabilization improves the structural perfection (Fig. 25(c)) of the polystyrene capsule morphology. In the SEM, one can see that most of the nanocapsules are collapsed and regular bowls with a continuous uniform shell are obtained. This leads to the deduction that the hexadecane was incorporated in the center of the particle. Some of the hollow spheres are still intact. In the AFM, some collapsed nanocapsules are detected as bowls, some as pancakes. There are also some particles with 'explosion holes' as a consequence of the release of the hexadecane under the high vacuum conditions of TEM.

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 affected the interfacial tension of styrene to water, and here, a pronounced influence on the capsule morphology was found. The influence depends on the partitioning coefficient: for MMA, about 25 wt% of monomer were needed to create close-to perfect capsules, whereas already 1 wt% of AA was sufficient to saturate the capsule surface with carboxylic groups, and hollow shell structure with constant capsule thickness were found (Fig. 25(d)). There is however a minor fraction of small homogeneous polymer latexes, which we attribute to secondary nucleation due to the very high content of water-soluble acrylic acid.

## 5.5. Surface coating of miniemulsion 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, employment of crystalline inorganic materials, such as clay sheets with 1.5 nm thickness can be recommended. Since those clay sheets are fixed like scales onto the soft, liquid
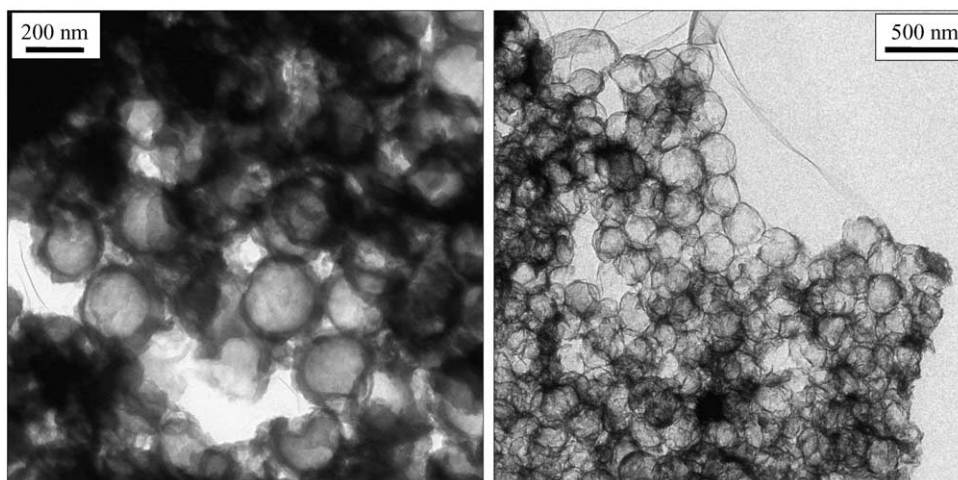
Fig. 26. TEM of armored latexes: (a) sealed clay on PBA and (b) sealed clay on PMMA, after removal of PMMA.

miniemulsion droplet, the resulting objects were called 'armored latexes' [201]. 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 also against changes in the chemical environment, it was possible to use miniemulsion droplets themselves (but also already polymerized latex particles) as templates for the plating procedure. Fig. 26(a) shows the outcome of such a plating process.

Here, 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.

In some cases, it is necessary to connect the tiles and seal the inorganic nanocapsule by a subsequent condensation reaction with silicic acid which reacts with itself, but also with residual surface OH-groups of the clay plates. To prove the successful construction of the hollow shell structure, the polymer template was removed and the freestanding capsule analyzed. This was done by using a PMMA mini-emulsion latex as a template, which depolymerizes by increased illumination with the electron beam in TEM.

Fig. 26(b) shows the emptied crystalline hulls as obtained by electron degradation. The structural preservation of the hollow shells is clearly visible, the inorganic structure has not disintegrated, that is the colloidal 'brick laying' 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.

## 5.6. 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 case of the calcium carbonate and carbon blacks) to surface-bound inorganic layers (such as in case of the clays). For basic research, they are ideal
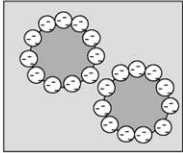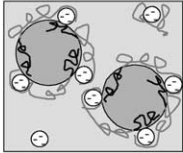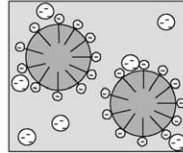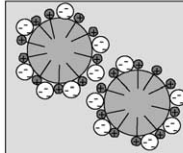
Fig. 27. Different morphologies in a oil/nanoparticle/water system as influenced by different surfactants.

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) [191–193]. The only difference is the interfacial area and the curvature of the solid nanoparticles 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 as so-called Pickering stabilizers [202–204]. In other words, 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 the composition diagram with a variety of morphologies to occur. The most simple possibilities are illustrated in Fig. 27.

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 the silica nanoparticles in the absence of any surfactant could act as a Pickering stabilizer for a miniemulsion process [205]. The high quality and small overall particle size obtained only under alkaline conditions (pH 10) and in presence of the basic comonomer 4-vinylpyridine is shown in Fig. 28.

The compulsory use of an aminic coupler was introduced by Armes [206,207], who made similar looking particles in precipitation polymerization and backed by the fact that 4-vinylpyridine provides at that pH a strong acid–base interaction with the silica. Purely hydrophobic droplets cannot be stabilized using colloidal silicas. Using the miniemulsion polymerization as an easy-to-analyze model, it could be shown that starting from 6 wt% of a basic monomer, the interfacial energy between monomer phase and silica particles becomes favorable, and only a few free silica particles are observed [205].

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 and 220 nm diameter with rather narrow size distribution were obtained, speaking for the
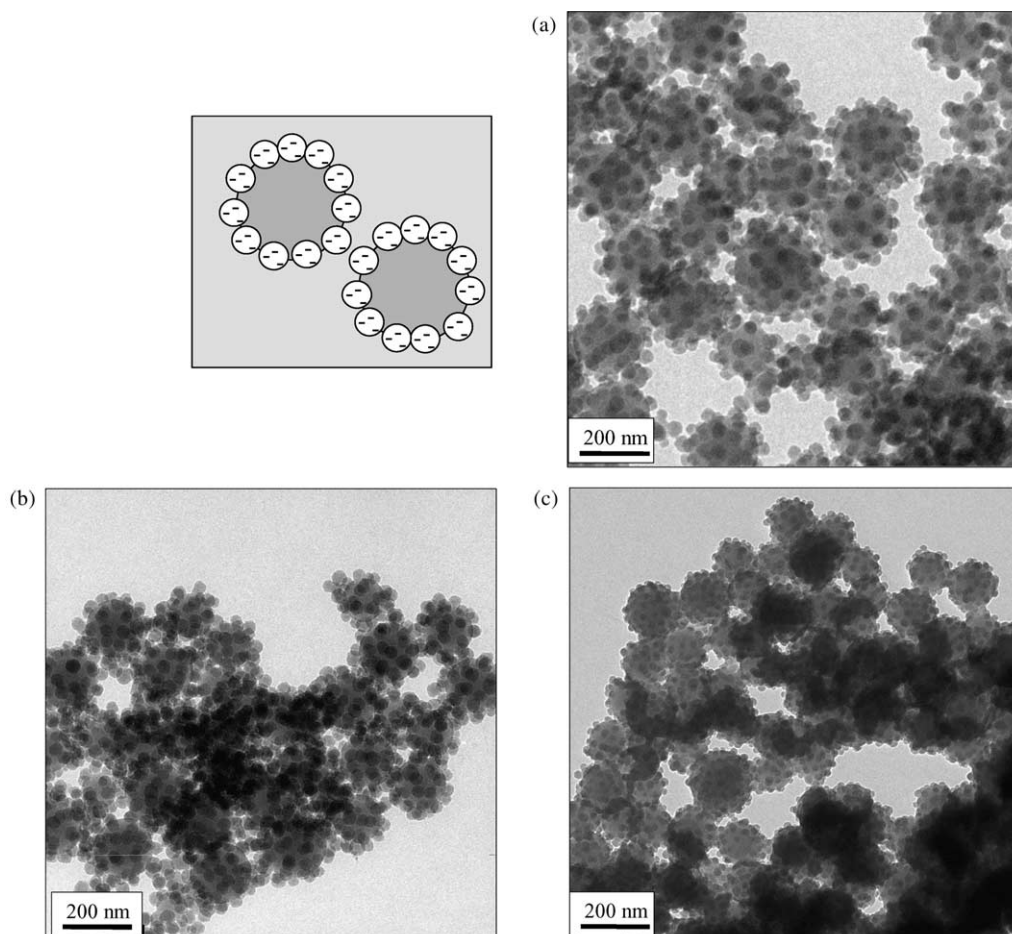
Fig. 28. TEM pictures for latexes using silica particles as stabilizer for monomer droplets (Pickering stabilization): (a) represents a latex with a monomer to silica ratio of 1:0.32; (b) represents a latex with a monomer to silica ratio of 1:0.64; (c) represents a latex with a monomer to silica ratio of 1:1.09. As monomers, a mixture of styrene and 4-vinylpyridin is used.

high stabilization power of the silica particles as Pickering stabilizers. Since these systems are free from 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 $\zeta$-potential of the nanocomposite dispersion versus pH corresponded to the potential of the pure silica-sol.

The addition of a surfactant to the same system resulted in a more complex zoo of structures [205]. Non-ionic surfactants are preferentially bound to the silica nanoparticles due to a preferential interaction between the silica and the ethylene oxide chains [208] which screens any interaction with the monomer mixture. Also addition of anionic SDS leads to electrostatic repulsion and a competition between surfactant and silica nanoparticles. Only at pH 3 (where the silica particles are practically uncharged), coupling between the nanoparticles and the polymer occur, and very small hybrid particles with a diameter of 68 nm are obtained, significantly smaller than those made with a similar recipe without

silica [34]. It is repeated that silica particles alone at pH 3 do not stabilize the emulsion. This means that in this case SDS and the weakly charged silica act in a synergistic fashion, i.e. as surfactant and cosurfactant.

The most pronounced structure changes however were observed with the cationic surfactant cetyl-trimethylammonium chloride (CTMA-Cl). Due to charge coupling as well as induced dipole interaction, this surfactant binds strongly to silica over the whole pH-range. For standard amounts of cationic surfactant in the percent region, there is not enough CTMA in the recipe to counterbalance the negative charges of the system at pH 10, and a hedgehog morphology is found with small overall diameters of 90 nm is found (Fig. 29(a)). $\zeta$-Potential measurements reveal that those compound particles are still negatively charged. The CTMA molecules are presumably arranged in patches between the polymer spheres and the silica particles (Fig. 29(b)). A dense binding of CTMA to the silica results in a hydrophobization of this spot and provides binding to the monomer droplet.

At higher CTMA concentrations exceeding the amount adsorbed onto the silica, a different morphology was found (Fig. 29(c)). Starting from a calculated surface coverage of 75%, the silica particles become incorporated into the droplet. Increasing the amount of surfactant to an apparent complete coverage, the latex particles including the silica become relatively small, but are still well above the corresponding sizes of bare latex particles made under similar conditions or the one of the hedgehogs. The hybrids now have a raspberry morphology however rather heterogeneous with respect to loading with silica. Using ultracentrifugation experiments in a density gradient, a homogeneous distribution of particles within a density range from 1.05 g cm$^{-3}$ (bare polymer) to 1.20 g cm$^{-3}$ (stable hybrids) are found, whereas particles with higher densities (pure silica) are not detected. The occurrence of bare polymer latexes speaks for some imperfections within the sample preparation, and further optimization work is certainly needed prior to application of such hybrid systems, e.g. as a precursor for scratch resistant hybrid coatings.

## 6. Non-radical polymerizations in miniemulsion

### 6.1. Polyaddition reactions in miniemulsions

As already indicated in Section 1, the existence of stable, isolated nanodroplets the chemistry in which may, but does not have to depend on droplet exchange (the so-called nanoreactors) enables the application of the miniemulsion process in a much broader range, For instance, monomeric components are mixed together, and polyaddition and polycondensation reactions can be performed *after* miniemulsification in the miniemulsificated state.

The successful transfer of the principle of miniemulsion polymerization to polyadditions of epoxy-resins was shown in Ref. [209] where mixtures of different epoxides with varying diamines, dithiols or diols were heated to 60 °C to form the respective polymers. The requirement for the formulation of stable miniemulsions is that both components of the polyaddition reaction show relatively low water solubility. The diepoxide Epikote E828, the triepoxide Decanol Ex-314 and the tetraepoxide Ex-411 were successfully used as epoxy components. As amino components Jeffamin D2000 (a NH$_2$ terminated poly(propylene oxide with $M_w = 2032$ g mol$^{-1}$)), 4,4'-diaminobibenzyl, 1,12-diaminododecane, and 4,4'-diaminodicyclohexylmethane. Jeffamine D400 with its lower molecular weight was too water-soluble and could not been used. As other addition components, besides amine, 1,6-hexanedithiol and
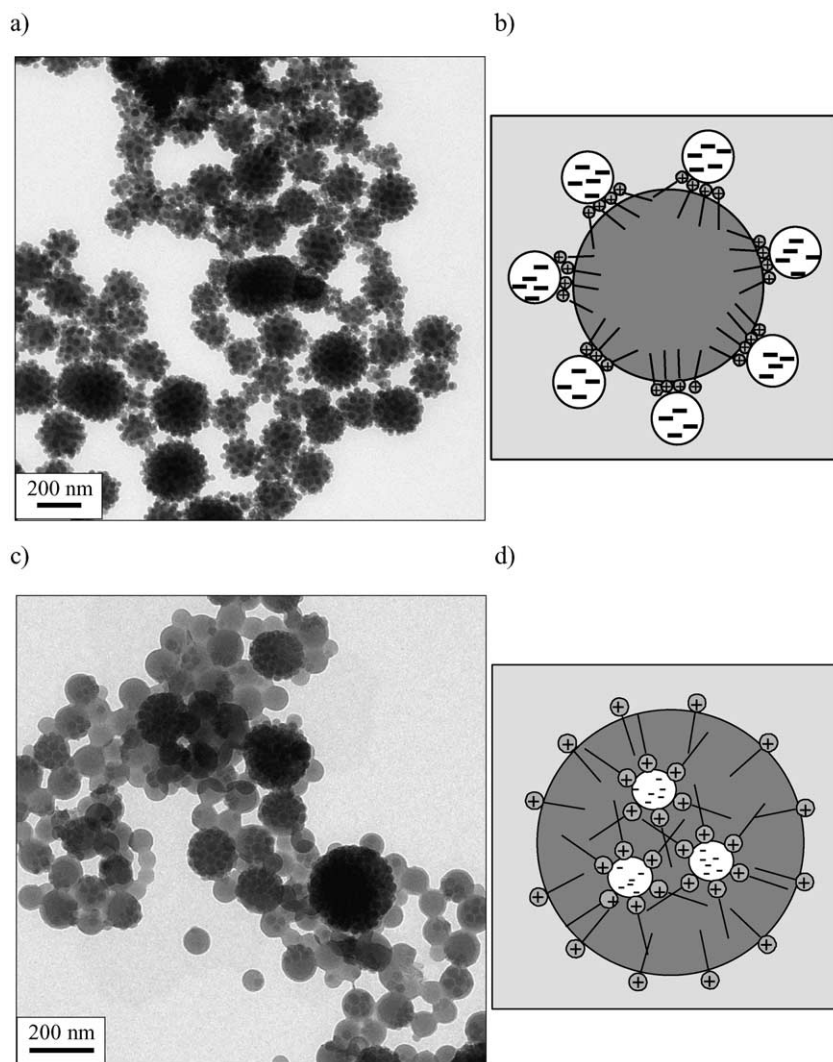
Fig. 29. The use of the cationic CTMA-Cl as surfactant. (a) Hedgehogs found at low amounts of surfactant. (b) Patches of CTMA presumably act as a coupler. (c) Encapsulated silica particles found at higher CTMA concentration. (d) This is due to a complete hydrophobization of the silica surface by surfactant adsorption.

Bisphenol A were used. The hydrophobic components, which are required for the formulation of stable miniemulsions, are usually the applied epoxides themselves which have a very poor water solubility and provide a sufficient droplet stabilization. The addition of a typical hydrophobe as hexadecane did not improve the miniemulsion stability. GPC measurements were used to judge the quality of the polyaddition reaction. In case of the dithiol and the bisphenol products, GPC-elution was possible, and 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.
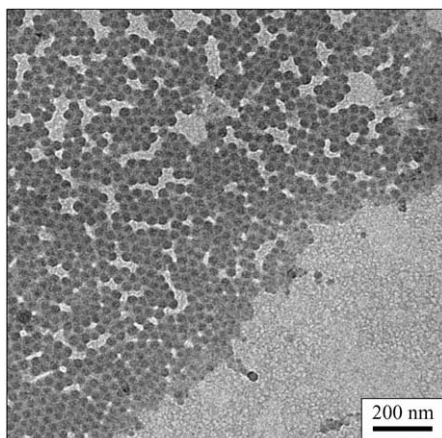
Fig. 30. Typical latex obtained in a polyaddition process in miniemulsion (Epikote E828 (bisphenol-A-diglycidylether) and 4,4′-diaminobibenzyl).

In order to obtain a tightly crosslinked epoxy network by the reaction of both amine hydrogens, the mole ratio of diepoxide to diamine was chosen to be 2:1. For the latexes of Epikote E828 and 1,12-diaminododecane synthesized in a SDS miniemulsion, the particle size show the expected dependence of size on composition: with increasing amount of surfactant the particle size decreases from 816 nm (0.85% SDS) to 36 nm (25%). At low surfactant concentration, the coverage of the particles with surfactant is incomplete, as shown by surface tension measurements.

In general, it turned out that the more hydrophobic the reaction partners the smaller the latexes. Small latex particles with a diameter down to 30 nm can be synthesized from a number of the most hydrophobic combinations. This is also about the minimal size limit, which can be made by radical processes, i.e. we reach a limit given by the fundamental laws of colloidal stability. Fig. 30 shows as a typical example the reaction product of Epikote E828 (bisphenol-A-diglycidyl-ether) and 4,4′-diaminobibenzyl: small particles with a relatively narrow size distribution are obtained.

Using off-stoichiometric ratios of the diepoxide and diamine components (e.g. Epikote E828/Jeffamin D2000 1:1.22) allows to obtain highly functionalized particles with residual primary and secondary amine groups. Such particles with very small dimensions are interesting from a technical point of view, since they can act as a polyfunctional network component (highly precondensated, amine rich coupling component) for a number of applications, e.g. in glues or dental fillings.

Also polyurethanes latexes can be made by direct miniemulsification of a monomer mixture of diisocyanate and diol in an aqueous surfactant solution followed by heating [209]. 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. However, polymer dispersions are obtained when some requirements are fulfilled:

– the reactants have to have a low water solubility;
– the reaction between diisocyanate and diol has to be slower than the time needed for the mini-emulsification step;

– the side reaction of the diisocyanate with water in the dispersed state has to be slower than the reaction with the diol.

For the third requirement, one has to consider that the ratio of diisocyanate molecules located at the droplet/water interface to the molecules inside the droplets is comparably small. It was speculated that after a potential reaction of the interfacial isocyanate molecules with water, the resulting more hydrophilic molecule can form a passivating layer, which slows down further reactions of the isocyanate molecules inside the droplet with the water.

The functional groups (isocyanate to alcohol groups) were employed in a 1:1 molar ratio. IR spectra of the reactants and the resulting product shows 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 evidences 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.

## 6.2. Anionic polymerization

For the anionic polymerization of phenyl glycidyl ether in miniemulsion, didodecyldimethyl-ammonium hydroxide was used as an 'inisurf' which acts as a surfactant and an anionic initiator by means of its hydroxy counterion at the same time. As revealed by $^{1}$H and FTIR, genuine $\alpha, \omega$ 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 a costabilizer. With increasing conversion, the polymer chains increased but remained small, with a critical polymerization degree of $DP_{max} = 8$.

## 6.3. Metal catalyzed polymerization reactions

Ethylene can be polymerized in an aqueous miniemulsion with the aid 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 [210]. A maximal productivity of 2520 kg PE per gram 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, but can also be applied to low melting salts and metals to obtain salt or metal colloids of high homogeneity with diameters between 150 and 400 nm [211]. 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 disperse 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
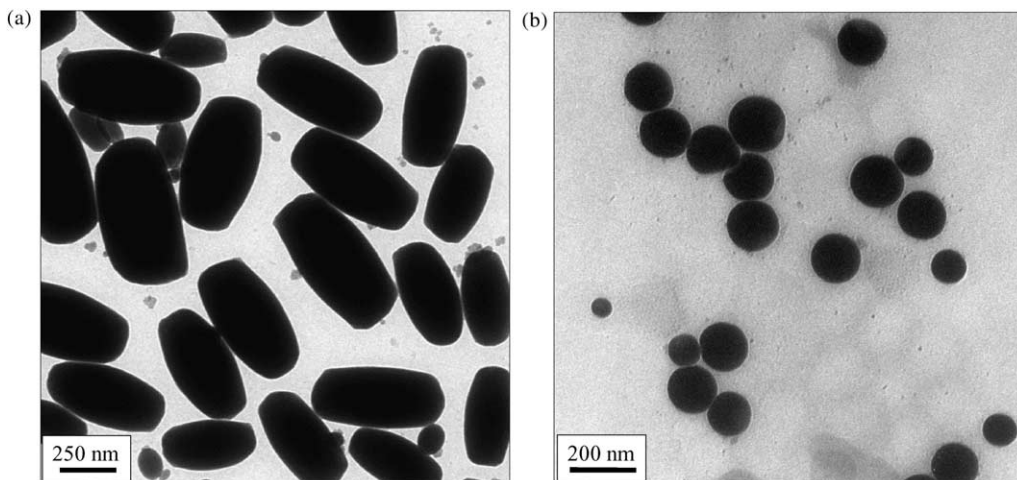
Fig. 31. Particles obtained in an inverse miniemulsion process consisting of (a) $ZrOCl_2 \cdot 8H_2O$ and (b) Woods metal.

of which has to be miscible with salt melts, whereas the unpolar part has to be sufficiently long and tightly packed to provide sufficient steric stabilization. Again, it turned out that amphiphilic block copolymers [212] with a 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 be easily 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.

Examples from Ref. [211] include $Fe(III)Cl_3 \cdot H_2O$ (37 °C), $ZrOCl_2 \cdot 8H_2O$ (−$6H_2O$ 150 °C), gallium (39 °C), and Wood's metal (70 °C). All these systems can be heated above their melting points and can be miniemulsified in organic solvents. Cooling below the melting temperature resulted in recrystallization of the particles however keeping the particulate character or the integrity of the inorganic miniemulsion droplets.

Some examples for such inorganic miniemulsions are shown in Fig. 31.

As an example, iron(III)-chloride hexahydrate was molten by heating above 37 °C and miniemulsified in the continuous phase (Isopar, cyclohexane, etc.) to a stable miniemulsion using at least 5 wt% (with respect to salt) of the block copolymer stabilizer. The process of miniemulsification was followed by turbidity measurements, and steady state was reached after about 200 s for as larger scale experiment. 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. Due to the high density of the particles ($\rho(FeCl_3) = 1.82$ g cm$^{-3}$), sedimentation occurs throughout days, but can be reversed to the single entities by stirring.

A 3:1 $ZrOCl_2$/water mixture melts at about 70 °C. The molten salt was added to Isopar M at 75 °C. A stable miniemulsion was obtained using 10 wt% of the amphiphilic block copolymer TEGO EBE45, which transforms throughout cooling in a dispersion of single $ZrOCl_2$ nanocrystals. TEM pictures show (Fig. 31(a)) that the particles are of uniform polyhedral crystalline shape.

For the preparation of nanosized metal dispersions, the same procedure of high shear forces were 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. Miniemulsification however was
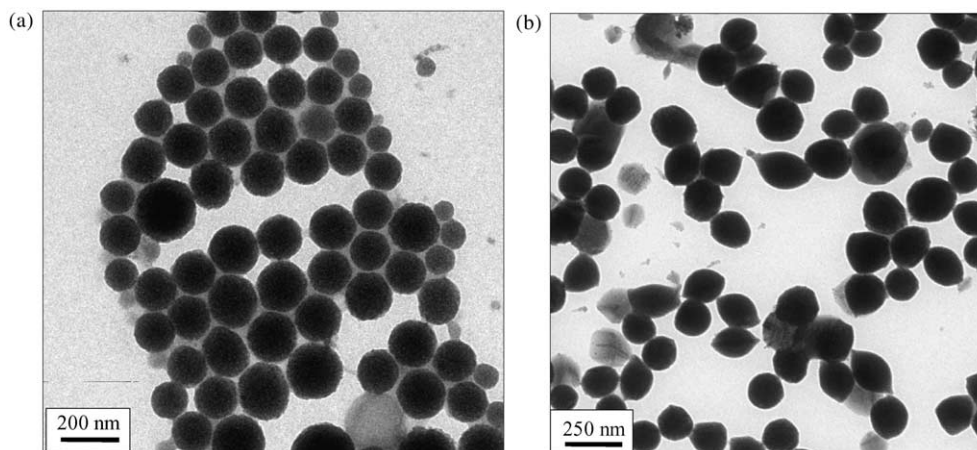
Fig. 32. Reaction products of molten iron salt miniemulsions ('inorganic polymerizations'). (a) $Fe_2O_3$ particles obtained from $FeCl_3$ droplets and (b) $Fe_3O_4$ particles obtained from $FeCl_2/FeCl_3$ droplets.

applied to disperse low melting alloys, like Wood's metal (composition: Bi50, Pb25, Cd12.5, Sn12.5) (mp = 70 °C) or Rose's metal (composition: Bi50, Pb28, Sn22) (mp = 110 °C). Because of the very high density difference of the metal ($\rho$(Wood's metal) = 9.67 g cm$^{-3}$) and the continuous phase ($\rho$(Isopar M) = 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. 31(b)). The resulting dispersions are still stable, and their averaged overall density was determined to be 1.325 g cm$^{-3}$, which goes well with the number calculated from the stoichiometry. The application of these metal dispersions onto paper as a conducting ink results in homogeneous films with metallic gloss and rather high conductivities. For such experiments, the lowest surfactant concentration of 10 wt% with respect to metal seems to be the best suited, since the lower layer thickness of the potentially insulating polymer surfactant leads to better particle contacts and higher conductivities.

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 preservations 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 high 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 particle density ($\rho$($Fe_2O_3$) = 5.24 g cm$^{-3}$). However, light scattering values and TEM pictures show that the droplets do not shrink as a whole, but shows a hollow aggregate structure with interstitial cavities between primary particles (Fig. 32(a)). The particle size in cyclohexane could be varied by changing the amount of surfactant between 240 nm (20 rel% TEGO EBE45 surfactant) and 370 nm (5 rel%) and in Isopar 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 syntheses 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 it is seen in the TEM pictures (Fig. 32(b)), the superstructure 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'.

## 8. Processing aspects of polymeric miniemulsions

### 8.1. High solids content

It was discussed earlier that the stability of miniemulsion latexes depends on the volume fraction of the dispersed phase (Fig. 4). Academic systems are usually made at 10–20 wt% monomer, which however is technologically not interesting. Up to now, pure polystyrene miniemulsion latexes only with solid contents smaller than 45 wt% were reported. The success implementation of miniemulsions with a higher solid content obviously depends on the presence of a hydrophilic component in the monomer phase. Vinyl acetate is hydrophilic enough in order to obtain a high solid content (60%) in a continuous stirred tank reactor (CSTR) [213]. High solids content up to 60% and coagulum-free latexes could also be obtained in a miniemulsion process for the batch and semicontinuous terpolymerization of styrene, 2-ethylhexylacrylate and the hydrophilic methacrylic acid [214]. The stabilization was achieved by an emulsifier mixture of Alipal CO-436 and SDS. The kinetics of the high solids content miniemulsion terpolymerization was found to be slower in the miniemulsion than in the conventional emulsion polymerization which was analogous to the corresponding miniemulsion processes with a lower solid content. The authors also found that the viscosity of the latexes produced by the miniemulsion process was lower and that the maximum solid contents achievable by the miniemulsion process was higher than with conventional emulsion polymerization [215]. Unzue and Asua [119] studied the effect of the operation variables on the feasibility of producing latexes of 65 wt% solids contents by semicontinuous miniemulsion terpolymerization of *n*-butyl acrylate, methyl methacrylate, and the more hydrophilic vinyl acetate. In addition, they studied the effect of the solids content, initiator concentration, feed flow rate, and the amount of the hydrophobe hexadecane on the kinetics of that high solids content polymerization. In a similar approach, but with less emulsifier and only SDS as emulsifier, high solids content latexes were prepared based on the two-stage polymerization [216]. In the first stage, low to medium solids contents seed latexes with a broad particle size distribution were obtained by miniemulsion polymerization, in the second stage, the solids content was increased up to 60–70 wt% using relatively low emulsifier contents. The wide particle size distribution of the first step was crucial to obtain coagulum-free latexes in the second step [217]. Ruckenstein and Kim [218] followed a method developed by Lissant [219,220] to prepare highly concentrated emulsions (higher than 74 wt%) by carrying out gel-like emulsion polymerization of styrene and styrene/methacrylic acid in small centrifuge tubes using an oil-soluble initiator (AIBN) with SDS as an emulsifier.

### 8.2. Continuous miniemulsion polymerization

The continuous miniemulsion polymerization was already described in 1987 by Barnette [221], but

large particles up to 4 μm were obtained. Therefore, this is more a suspension-like polymerization with the use of hexadecane. Two years later, the same group published experimental data on the dynamic behavior of the miniemulsion polymerization of methyl methacrylate in a CSTR [222]. The miniemulsification was prepared continuously and pumped into a batch reactor. The resulting particle sizes were in the range of 100 nm. The dominance of nucleation in monomer droplets in miniemulsion systems was shown to be responsible for the absence of the decaying oscillation transients observed in continuous emulsion polymerization.

Samer and Schork developed a simplified dynamic model which uses a particle number approach to simulate miniemulsion polymerizations for CSTRs in series [223]. The model suggests that particle generation is only a function of the initial droplet concentration, and is independent of the initiator and surfactant concentration. In addition, the number of particles generated in a CSTR is nearly identical to the number of particles obtained in a similar batch miniemulsion. It also turned out that conversion for miniemulsions in a CSTR is much greater than for emulsions. It could be shown for the polymerization of vinyl acetate in a CSTR that the preparation of a miniemulsion is a good strategy to eliminate the oscillatory behavior of CSTR reactors, even in very unfavorable conditions while in conventional emulsion polymerization the opposite was found [224].

### 8.3. Shear stability

Under controlled shear conditions, miniemulsion latexes have been shown to be more stable than similar latexes obtained in conventional emulsion polymerization [225]. The effect has been quantified through the use of a very simplistic kinetic model. A hypothesis has been presented that the shear instability of emulsions results from the presence of a small number of large particles which act as seeds for aggregation. Intentional seeding of mini- and emulsion latexes with larger particles has induced increased shear instability, supporting the hypothesis. Differences in surface characteristics are also possible explanations.

## 9. On the horizon: the concept of 'chemistry on a single polymer' in miniemulsion droplets

The obvious fact that miniemulsions allow a very convenient and effective separation of objects in compartments of the size of 30–300 nm diameter also opens some general new perspectives for polymer chemistry. In miniemulsion droplets, it is in principle possible to isolate complex polymers or colloids strictly from each other and to react each single molecules for itself with other components, still working with significant amounts of matter and technically relevant mass fluxes. This was called 'single (polymer) molecule chemistry' [226].

In this mode of operation, single molecule chemistry usually takes place in a highly parallel fashion, since 3D-space is compartimentalized in small 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 compartimentalized areas of the cell [227]. The approach is not restricted to organic synthesis, but includes more complex physico-chemical processes as protein folding which mainly takes place as a single molecular event in the nanocompartments [228]. Mimicking those processes in polymer chemistry would open a door to gain a better control of the outcome of a demanding complex process or chemical reaction.

The potential advantage of nanoreactors is that a chemical reaction, confined to a nanosized environment, can have a different outcome as compared to the same reaction or process in free 3D-space:

- The size of the structure to be made is limited by the size of the confinement and the number of precursor molecules in each nanoreactor. This is important for polymerizations, precipitations, cross-linking and cyclization reactions.
- The relation between inter- and intramolecular reactions can be shifted. Intramolecular reaction is exclusively obtained as long as there is a single polymer in each nanoreactor. For small confinements, this is guaranteed even at rather high concentrations. In a droplet of 30 nm, a 10 wt% solution of a polymer or protein with $M_w = 850\,000\ \text{g mol}^{-1}$ is essentially single molecular. The principle of compartmentalization, therefore, makes high dilutions for single molecular reactions unnecessary.
- Protein folding, polymer crystallization or more complex processes like DNA hybridization or polymer–polymer complexation and templation occurs under the restriction of having a single polymer chain. This simplifies the topology of the resulting structure.

A conceptual comparison of the miniemulsion system to classical nanoreactors, such as reverse micelles, microemulsions, block copolymer micelles and microgels is given in the literature [226]. It is just summarized that miniemulsions are suitable to design 'real' single molecule experiments, since the lifetime of a single droplet can be on the scale of days to months, whereas efficient reactor filling factors are still of the order of 20–40%, and isolation is as convenient as breaking the miniemulsion.

## 10. Conclusion

The main aim of this review was to provide a critical review of the literature in the fascinating field of miniemulsions. Since this field currently experiences an exponential growth, such a trial is restricted to the knowledge of the authors, and there are certainly some promising activities in miniemulsions, which have to be included in a forthcoming version of such an article.

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 polymer reactions 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 resins, inorganic materials, or liquids are some examples which shows the wide applicability of miniemulsions also for technologically relevant questions. With the miniemulsification of molten inorganic materials with a subsequent reaction, the miniemulsions cross the border of polymers and opens new possibilities in fabrication of solid particles for material science.

To our 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 polymer molecules trapped, handled and folded in each small droplet which enables new types of physico-chemical experiments and handling of complex matter [229].

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