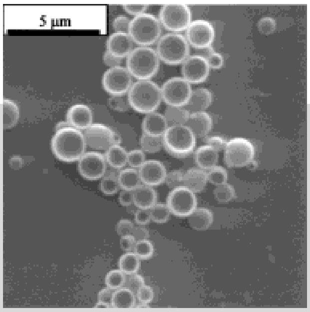
The Generation of Nanoparticles in Miniemulsions

By *Katharina Landfester**



A versatile method for the generation of nanoparticulate metals, ceramics, and polymers based on synthesis in miniemulsions—highly stable small droplets in a continuous phase—is presented here. It is revealed that in addition to nanoparticles, encapsulated materials, polymer capsules (see Figure), and hollow particles can also be obtained by careful selection of the starting materials.

1. Introduction

The formation and application of nanoparticles composed of polymeric or inorganic material enjoys great popularity in academia and industry. Many different approaches are used for the generation of nanoparticles in order to obtain the required properties. Practically all processes used, i.e., the sol–gel process[1,2] or the microemulsion technique[3] for the preparation of inorganic particles and emulsion polymerization[4] for the preparation of polymer particles, are based on kinetic control during preparation; the particles are built from the center to the surface, and the particle structure is governed by kinetic factors. Because of the dictate of kinetics, serious disadvantages such as lack of homogeneity and restrictions as to the compositions accessible have to be accepted. Therefore, it has been a dream for a long time to take advantage of potential thermodynamic control for the design of nanoparticles, as well as the concept of "nanoreactors" where the essential ingredients for the formation of the nanoparticles are present in the initial reaction mixture.[3,5] It is stressed that particle formation in nanoreactors takes place in a highly parallel fashion, i.e., the synthesis is performed in 10^{18}–10^{20} nanocompartments, which are separated from each other by a continuous phase. However, previous systems investigated show serious restrictions and failure mechanisms, as recently discussed.[6]

The idea of polymerization in a nanoreactor is technically realized in high perfection for suspension polymerization, where droplets in the micrometer range are created that can be polymerized without change of particle identity.[7] The suspension principle was adapted by Ugelstad et al.[8] to obtain smaller droplet sizes; they scaled down the droplet size to several hundred nanometers by shearing the system.

In this research news article a recent development is described in which the availability of high shear devices such as ultrasonicators and high-pressure homogenizers in combination with applied physical chemistry has allowed the droplet or nanoreactor diameter to be decreased to 30–100 nm, while still preserving the integrity of each single nanodroplet. Importantly, the developed concept is not restricted to a single procedure (such as radical polymerization in water), but is widely applicable to the generation of nanoparticulate metals, ceramics, or new polymers via a liquid/liquid technology both in direct (aqueous solvent) and inverse (organic or hydrocarbon solvent) situations.

2. Miniemulsions

A system where small droplets with high stability in a continuous phase are created by using high shear[9–11] is classically called a "miniemulsion". One of the tricks to obtaining stability of the droplets is the addition of an agent that dissolves in the dispersed phase, but is insoluble in the continuous phase. The small droplets can be hardened either by subsequent polymerization or by decreasing the temperature (if the dispersed phase is a low-temperature melting material). For a typical oil-in-water miniemulsion, an oil, a hydrophobic agent (or several), an emulsifier, and water are homogenized by high shear (see Fig. 1) to obtain homogeneous and monodisperse droplets in the size range of 30 to 500 nm. Based on the miniemulsion principle, the preparation of new nanoparticles that could not be prepared in heterophase processes to date will be delineated in this paper. The potential and the high impact of using miniemulsions for new technological developments will be presented.

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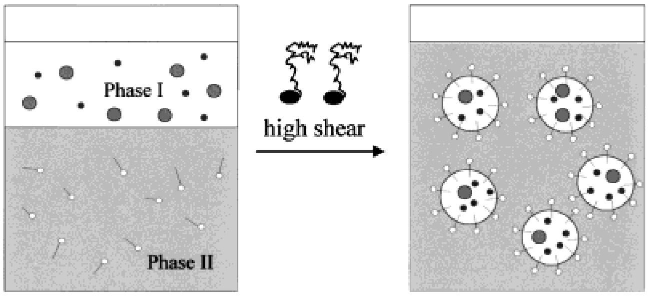

Fig. 1. The miniemulsion principle.

2.1. Creation of Stable Miniemulsions

When creating a miniemulsion, the homogenization step is of high importance since fairly monodisperse small droplets need to be obtained. Homogenization can be achieved using an ultrasonicator (for the miniemulsification of small quantities in a lab-scale batch process) or a high-pressure homogenizer (for larger scales). At the beginning of homogenization, the polydispersity of the droplets is still quite high, but through constant fusion and fission processes induced by the high shear, the size, and polydispersity decrease until the miniemulsion reaches a steady state.[12] The process of homogenization can be followed by different methods, e.g., by turbidity or surface tension measurements. In the given example in Figure 2, a constant value indicates when the steady state is reached in the two experiments. The surface tension reaches high values, indicating that the coverage of the droplets by surfactant molecules is very low. Indeed, incomplete coverage of droplets by surfactant molecules is an important characteristic of miniemulsions and shows that the surfactant is very efficiently used. It has been observed that the coverage of surfactant depends on the droplet size: The smaller the droplets, the higher the coverage in order to obtain stable droplets. The exact size of the droplet can be selectively adjusted by the type and amount of surfactant used for stabilization. Anionic and cationic surfactants allow the formation of monodisperse droplets between about 30 and 200 nm; non-ionic oligomeric or polymeric surfactants are suitable for the formation of droplets between about 100 and 800 nm.

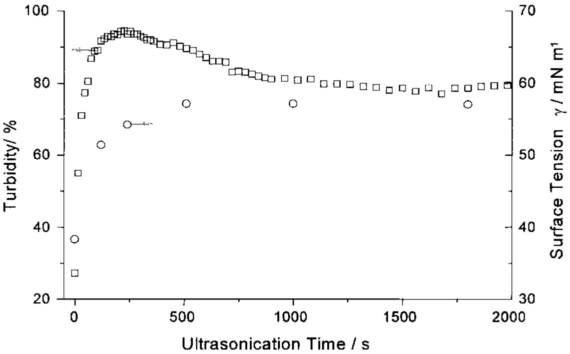

Fig. 2. Homogenization process followed by surface tension and turbidity measurements.

Such minidroplets were previously regarded as a rather unstable dispersion state of matter for two droplet growth mechanisms:

- Ostwald ripening (τ_1 mechanism),
- collisions (coalescence) (τ_2 mechanism).

Suppression of these two processes is required for the formation of a stable miniemulsion. Coalescence can be controlled by the effective use of a surfactant. Ostwald ripening can be efficiently suppressed by addition of a hydrophobic agent to the dispersed phase. This agent cannot diffuse from one droplet to the other and some agent is trapped in each droplet; this provides an osmotic pressure inside the droplets, which counteracts the Laplace pressure. The effectiveness of the hydrophobe increases with decreasing water solubility in the continuous phase.

This mechanism has already been used for the stabilization of fluoroalkane droplets by addition of perfluorodimorphineopropane, which results in an effective and stable blood substitute.[13]

A variety of molecules can be used as hydrophobes and can be chosen so that they also add a useful property to the final product, i.e., they could be dyes, plasticizers, or cross-linkers.

The addition of an ultrahydrophobe does not completely block droplet growth (because of a still finite solubility, the existence of droplet collisions, and surfactant-assisted transport), but slows it down remarkably. The final state to be expected is given by the balance of osmotic pressure and Laplace pressure. Since the Laplace pressure directly after miniemulsification is usually larger than the osmotic pressure, the miniemulsion tends to grow on the timescale of days to weeks. Due to the timescale involved, this growth is usually not of relevance for synthetic applications, but it is also possible to handle it in a thermodynamic fashion. This can be done either by increasing the amount of osmotic agent, by increasing the particle size, or by adding a second dose of surfactant after dispersion (to lower the surface tension and the related Laplace pressure).[12]

The extremely high stability of those nanodroplets as well as the absence of exchange of material between the droplets (in the case of low solubility in the continuous phase) can be illustrated graphically by classical color reactions such as the formation of Prussian Blue or nickel murexid in inverse miniemulsion systems. One miniemulsion with droplets containing a murexid solution, and another miniemulsion containing a Ni^{2+} solution are mixed and, as can be seen from Figure 3, the mixed miniemulsion (represented at 0 s) remains red: no nickel murexid complex is formed. This indicates that droplets with murexid and droplets with Ni^{2+} coexist and no fusion/fission process takes place. If, as a comparison, one performs the same experiment with two microemulsions, immediate reaction takes place because the low interfacial tension of close to zero leads to high dynamic processes in the system. The droplets in microemulsions do not retain their identity, in miniemulsions they do. This is because in miniemulsions higher

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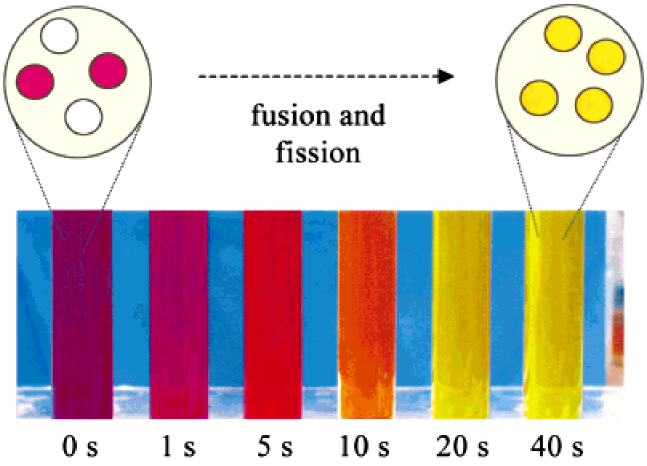

Fig. 3. Mixing and subsequent sonication of two miniemulsions, one containing murexid solution, the other one Ni^{2+}.

energy is required for this process, e.g., ultrasonication. In this case, fusion and fission processes are induced and it can be seen that with increasing ultrasonication time the miniemulsion turns yellow. The overall droplet size does not change.

Because of this, each miniemulsion droplet can indeed be treated as a small nanoreactor. This enables a whole set of new reactions leading to nanoparticles as well as the synthesis of nanoparticles hybrids that were previously not accessible. Some examples will be given in the following to show the wide applicability.

3. Nanoparticle Generation

3.1. Synthesis of Inorganic Nanoparticles from Miniemulsified Molten Salts

There are many salts or metals with low melting point. These systems can be heated above their melting points and can be miniemulsified in organic solvents. Cooling below the melting temperature then results in recrystallization of the particles. The formation of high-melting materials can be achieved by further reaction in which the low-melting material is used as a precursor. One example is shown in Figure 4 where Fe_2O_3 particles are obtained from molten $FeCl_3$ droplets by adding a base. Using a mixture of Fe^{2+}/Fe^{3+} allows the preparation of magnetic particles. Well-defined zirconia particles in an organic phase can also be obtained by miniemulsifying the low-melting precursor $ZrOCl_2$.[14]

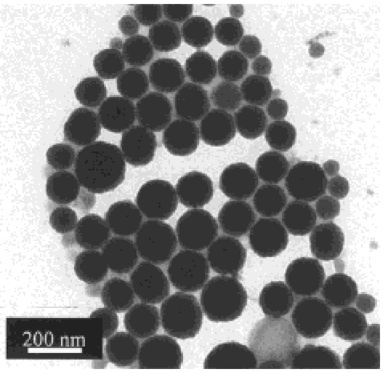

Fig. 4. Fe_2O_3 obtained from molten $FeCl_3$ droplets by addition of a base.

3.2. Latexes from Non-radical Polymerization Processes

The same procedure of miniemulsification can be performed to obtain polymer particles. Hydrophilic monomers are miniemulsified in an organic phase and hydrophobic monomers in water. Hardening of the droplets can then be achieved by subsequent polymerization in each droplet. The type of polymerization is not just limited to radical reactions: polyaddition or polycondensation reactions can also be carried out in such miniemulsion droplets. As one example, polymeric particles formed via polyaddition of a diepoxide and a diamine are shown in Figure 5.[15] Particles such as these may be well suited to dentures.

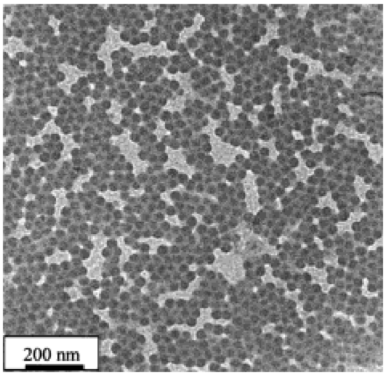

Fig. 5. Particles obtained by polyaddition in miniemulsion.

3.3. Generation of Encapsulated Inorganics

The first two examples showed the fabrication of either pure inorganic or pure polymeric particles. It is of course of high interest to combine the inorganic and the polymeric part in order to obtain hybrid particles. If the inorganic particles shown in the first example are dispersed in a monomer and if this dispersion is subjected to miniemulsification, polymeric particles that fully encapsulate inorganic material are obtained. The polymeric shell effectively protects the inorganic particle. It is possible to incorporate just one (large) inorganic particle per polymer particle as was shown in the case $CaCO_3$;[16] one can also cover a larger carbon black aggregate by a thin polymeric layer (see Fig. 6a),[17] or one can incorporate many small particles, e.g., magnetite particles, in each polymer particle (see Fig. 6b).[18] Successful incorporation has been proven by many techniques. The dispersion with encapsulated carbon black may, for example, be used for ink jet printing, and the magnetic particles may be used for medical applications, e.g., for the destruction of cells via magnetic fields.

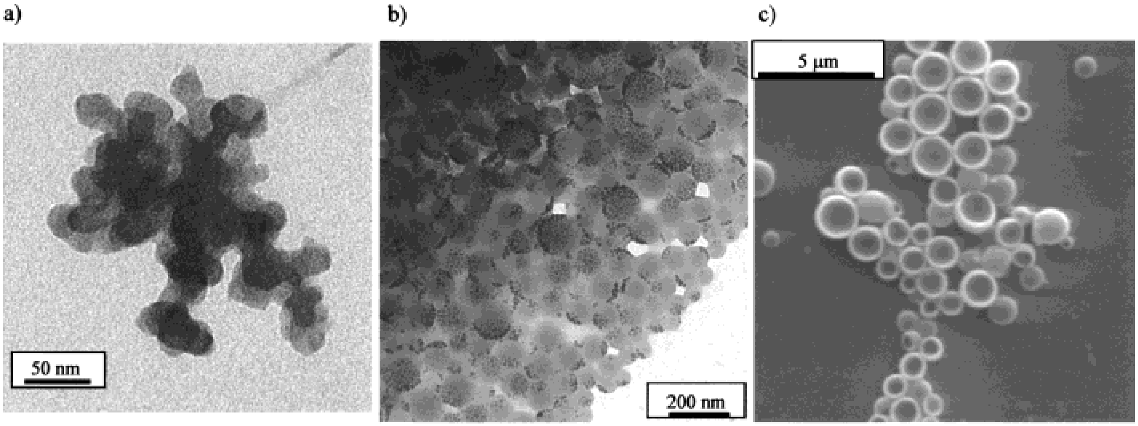

Fig. 6. Encapsulation of materials by the miniemulsion process: a) carbon black aggregates, b) magnetite, c) a liquid to form nanocapsules.

3.4. Direct Generation of Polymer Capsules and Hollow Particles

It has been shown that the encapsulation process is not limited to solid materials, but also liquids that are insoluble in the polymeric shell material can be encapsulated in order to obtain nanocapsules. For the synthesis, a monomer and an oil are chosen in such a way that the two components are miscible in the monomeric state. But as soon as polymerization takes place, phase separation occurs. The differences in the hydrophilicities of the oil/polymer and polymer/water interfaces have to be designed so that the formation of nanocapsules is favored (Fig. 6c).[19] The wall can either be formed so that no leakage occurs, or it can be formed as a permeable shell that allows controlled release, e.g., of a perfume or a medicine.

4. Conclusion

Dispersion of liquid matter in stable nanodroplets into a miniemulsion opens new vistas for the synthesis of homogeneous inorganic particles using fluid precursor systems. Not only inorganic particles but also liquids can be encapsulated in a subsequent second miniemulsion step in a polymer shell in order to avoid leakage. This protects the interior against external influences, but may also protect the environment, e.g., the human body, against toxic materials. A permeable shell allows the controlled slow release of substances into the environment. The miniemulsion principle can also be exploited to obtain polymer particles. The strength of miniemulsions is that polymeric nanoparticles consisting of polymers or polymer structures that are not accessible using other types of heterophase polymerization can be produced.

The use of miniemulsions in materials science is rapidly increasing—there are many possibilities for the design of new particles covering many applications in different fields. One may envisage single molecules trapped and crystallized in each droplet, thus enabling new types of physico-chemical experiments and handling of complex matter.[6]

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