

the sulfonic groups at the polymer backbone with AuCl_4^- anions must be of considerable importance. Despite the considerable research in this field, the reduction mechanism is still a less understood phenomenon.

3.2 Nanoparticle Formation in Template Phases

As already outlined in the chapter above, monodisperse nanoparticles can be obtained by using nucleation processes. However, nucleation processes are strongly limited with regard to the solubility of the nuclei. This means monodisperse nanoparticles can be obtained only in very diluted systems, when in a very short time period many critical nuclei are formed, which grow up and remain on the colloidal level. On the one hand this method is restricted to a limited number of supersaturated systems, and for each of these systems the experimental conditions have to be optimized. On the other hand it becomes very complicated to transfer the process to technical dimensions.

Taken this knowledge into account and the inspiration of nature, the idea was born to use template phases for the formation of well-defined nanoparticles with a narrow size distribution. From biomineralization processes [173], it is well known that proteins and polysaccharides can act as templates for structuring inorganic materials on the nanometer scale. Sikes et al. [174] have shown that proteins, which are essentially polyelectrolytes, extracted from marine shells (in particular the American oyster) can act as inhibitors of all the common scale minerals. Synthetic polyaspartic acid, i.e., an anionic PEL, has a similar effect on the control/inhibition of calcite formation [175]. Collins proposed a tentative model of barium sulfate inhibition in presence of polyaspartic acid and Ca^{++} ions [176].

Generally, the resulting composites offer special optical and mechanical properties. For example, the blaze of colors of pearls can be related to scattering effects on 300 to 500-nm-thin aragonite sheets embedded into a microlaminat consisting of carbohydrates and proteins, and the degree of hardness of teeth and bone to the self-assembly of hydroxyapatite nanoparticles in a microlaminat consisting of proteins and collagen-fibrils. Another example for a self-assembled natural system is Diatomeen, offering a broad spectrum of well-ordered silica structures. An example for the diversity is given in Fig. 3.4.

What we can learn first of all from nature is that we need a self-assembled template phase for producing nanoparticles of defined size and shape. In general, polyelectrolytes can have both a controlling and inhibition function in precipitation processes. Water-soluble polymers, including polyelectrolytes are usually used as a stabilizing or chelating agent in the preparation of metal ultrafine particles. For example, barium ferrite nanoparticles are synthesized by coprecipitation with polyacrylic acid as a protective agent [177]. Hierarchical superstructures by oriented attachment and self-assembly of BaSO_4 nanoparticles triggered by polyacrylates are demonstrated by Antonietti and Cölfen [178]. By using block copolymers with a PEL-block (e.g., poly(ethylene oxide)-block-poly(methacrylic acid)) the polymer controlled crystallization of CaCO_3 leads to highly ordered

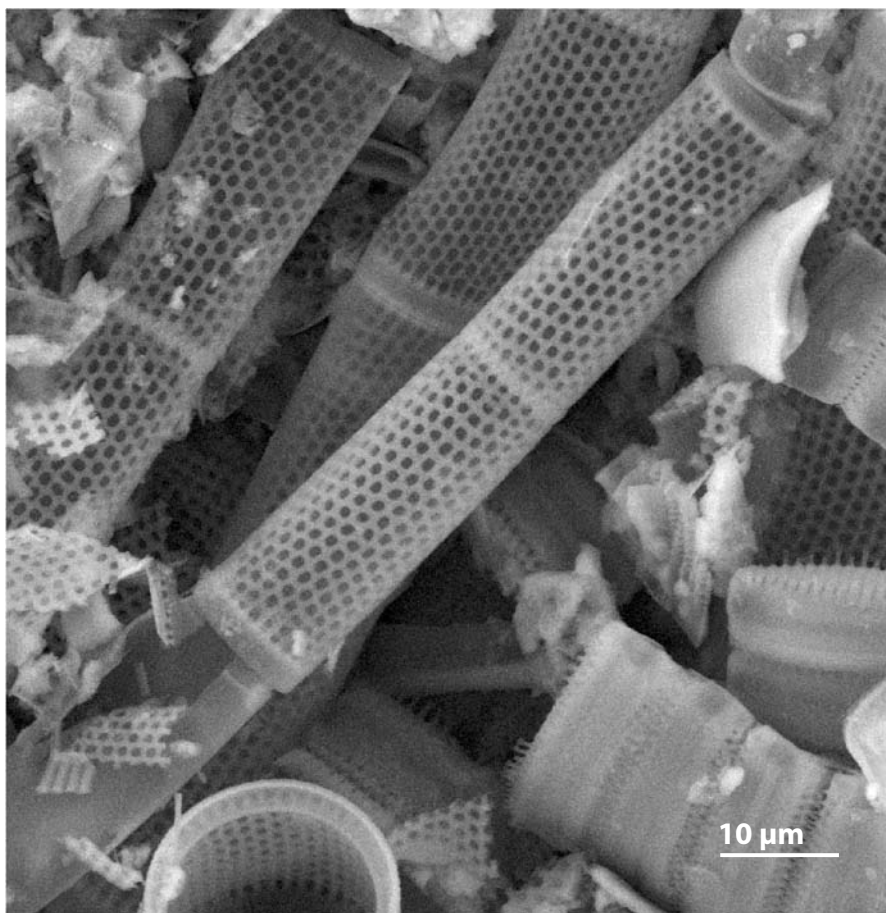


Fig. 3.4. SEM micrograph of Diatomen

supramolecular structures [179]. Furthermore, the PEL can fulfill multiple functions in controlled crystallization processes [180], e.g., block copolymers can yield smaller primary particles, which are initially amorphous [179].

Moreover, there are two strategies to use templates. With the first approach, the template is surrounded by a network-precursor. After network formation, followed by the decomposition of the template a nanoporous material is formed, as a 1:1 replica of the template (Fig. 3.5). This process is called “nanocasting”. As templates, one can use large molecules, i.e., dendrimers or macromolecules, colloidal particles, and amphiphilic systems (e.g., micelles or lyotropic phases). Often supramolecular aggregates of amphiphiles, i.e., surfactants and block copolymers, were used. For example, Göltner et al. developed a method to synthesize mesoporous silica by using a highly concentrated surfactant phase as template [181, 182]. Lyotropic phases of amphiphilic block copoly-

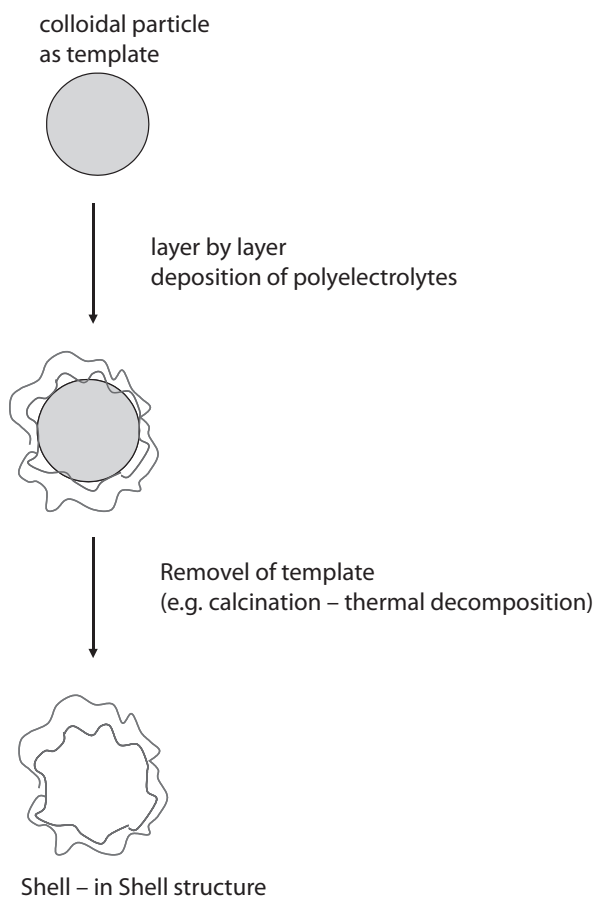


Fig. 3.5. “Nanocasting” by using a spherical template phase

mers were used because of the fact that the pore structures correlate to the block length [183, 184].

The second approach is to use a restricted reaction room as a template phase. Therefore, nanoscale emulsions (i.e., mini- and microemulsions) are of special interest. Furthermore, amphiphilic block copolymers provide a large number of microstructures that can be used to prepare inorganic nanoparticles. Considering the nanoparticle formation in combination to polyelectrolytes, PEL-modified microemulsions and block copolymers with a PEL-block are of special interest.

3.2.1 Miniemulsions as Templates

Emulsions, which refers to droplets of one liquid in another, immiscible one, separated by a surfactant film, can be classified according to the size of the droplets into macroemulsions (with a droplet size $> 1 \mu\text{m}$), and miniemulsions (also called

fine-emulsions and nowadays nanoemulsions) having a significant smaller droplet size between 100 and 1000 nm. However, in all of these different types of emulsions the droplets are stabilized against a coalescence due to a steric, electrostatic or electrosteric stabilization effect (cf. Chap. 4.1), achieved by the addition of surface active materials as emulsifiers. The basic functions of the emulsifier can be described as:

- to help make droplets small, and
- to keep them small by retarding coalescence.

This means the liquids inside the droplets are separated from each other by means of the repulsive forces between the surfactant films and consequently exchange processes are suppressed. Keeping in mind this special behavior, the individual emulsion droplets can be used as templates for particle formation. When the particle formation process is realized inside the droplets and is not directly influenced by droplet–droplet interactions, the primary droplet size is of high relevance.

Therefore, the main problem is to produce monodisperse nanoscale emulsion droplets. Nowadays, this problem is solved by a high energy input, e.g., by means of an ultrasonic treatment, in combination with the addition of hydrophobes to overcome the “Ostwald ripening” [185]. In this way it becomes possible to produce oil-in-water or water-in-oil miniemulsions up to a droplet size of 100 nm. Especially polymer lattices can be successfully produced in such nanoscale droplets. For example, polyurethane latexes can be made by direct miniemulsification of a monomer mixture of diisocyanate and diol in an aqueous surfactant solution followed by heating [185], and polyester/polystyrene hybrid particles can be synthesized in a simple one-pot procedure [186]. By using a three-step preparation route including two miniemulsion processes for example, magnetite can be encapsulated into polystyrene particles [187]. Other examples show that the crystallization process in miniemulsions is quite different from the bulk phase.

3.2.2 Microemulsions as Templates

Microemulsions are thermodynamically stable, isotropic, optically clear solutions of two immiscible fluids, commonly oil and water, containing one or more surface active species. One has to distinguish between normal micellar, i.e., oil-in-water (o/w, L1 phase), reverse micellar (w/o, L2 phase), and bicontinuous microemulsions. The transparent nature of a microemulsion in comparison to a macroemulsion can be related to the very small dimensions of the droplets in the order of 10 to 100 nm. The main difference to all other types of emulsions, including miniemulsions, is the spontaneous, thermodynamically controlled formation of the small droplets induced by the ultra-low interfacial tension. The most essential parameter of a microemulsion is the spontaneous curvature H_0 of the surfactant film.

An unconstrained film of surfactant molecules will adopt a curvature H_0 in its lowest free energy state. Thus, at a constant number of molecules and surface area, a spontaneous formation of microemulsions can be observed at:

$$\left(\frac{\partial G}{\partial H_0}\right) = 0 \quad \text{for } H = H_0 \quad (3.9)$$

where H is defined as the mean curvature at a point of a surface, which can be influenced by the mass ratio of oil-water-surfactant.

For a sphere, H is given by the reciprocal value of the radius R :

$$H = \frac{1}{R} \quad (3.10)$$

The spontaneous curvature H_0 mainly depends on the type of surfactant. However, when the polar head group, and/or the length and number of the hydrophobic tail, or the external conditions are changed, or cosurfactants are added, the spontaneous curvature can be influenced in a characteristic way. For nonionic surfactants, a change of the temperature and for ionic surfactants a change of the ionic strength has profound effects. Taking this knowledge into account, the incorporation of polyelectrolytes in a microemulsion can lead to quite different effects.

Chan and Rosano [188] developed a mathematical model for the formation of oil-in-water microemulsions, based on the total free energy G_T to form a droplet:

$$G_T = G_{SH} + G_A + G_B + G_I \quad (3.11)$$

where G_{SH} is the free energy of the interfacial sheath structure; G_A is the work to expand the interface; G_B the interfacial bending energy; and G_I is the free energy of interaction between the droplets. Thus for a particular set of parameters the system will have two possibly stable states, one at about 15 and another one at about 25 nm. Recently, we were able to show the individual microemulsion droplets by means of ultrahigh-resolution cryo scanning electron microscopy (Fig. 3.6).

One very interesting feature of microemulsions is their use as templates for the production of nanoparticles. Figure 3.7 schematically illustrates the formation of nanoparticles by mixing two adequate w/o microemulsions, containing the water-soluble reactants A and B, respectively. By a simple mixing of the two almost identical microemulsions, the water droplets collide and coalesce, allowing the mixing of the two water-soluble reactants A and B, and the formation of the product AB. Thus, a precipitation reaction can be carried out in the aqueous core of the inverse microemulsion droplets, using the water droplets as nanoreactors. However, the mixing process is very fast, the particle aggregation is realized immediately, and the particles formed are mechanically limited by the size of the water droplets. Since microemulsions are thermodynamically stable, the droplet size is determined by thermodynamic conditions, and consequently the size of the nanoparticles formed, too. When the water-surfactant ratio in the microemulsion is varied, the droplet size can be tuned. In this way, nanoparticles of defined size can be produced, and the method is an improvement over the previously discussed processes. Generally, it becomes possible to produce particles in the 2 to 10-nm diameter range by this procedure. For example, Shah et al. synthesized silver halids (i.e., AgCl, AgBr), superconductors (i.e., YBCO), magnetic materials (i.e., Fe₂O₃, BaFe₁₂O₁₉, and CoFe₂O₄), varistors (ZnO, and ZnO + Bi₂O₃), titanium dioxide and polystyrene nanolatexes [189–194]. Superconductors prepared by the

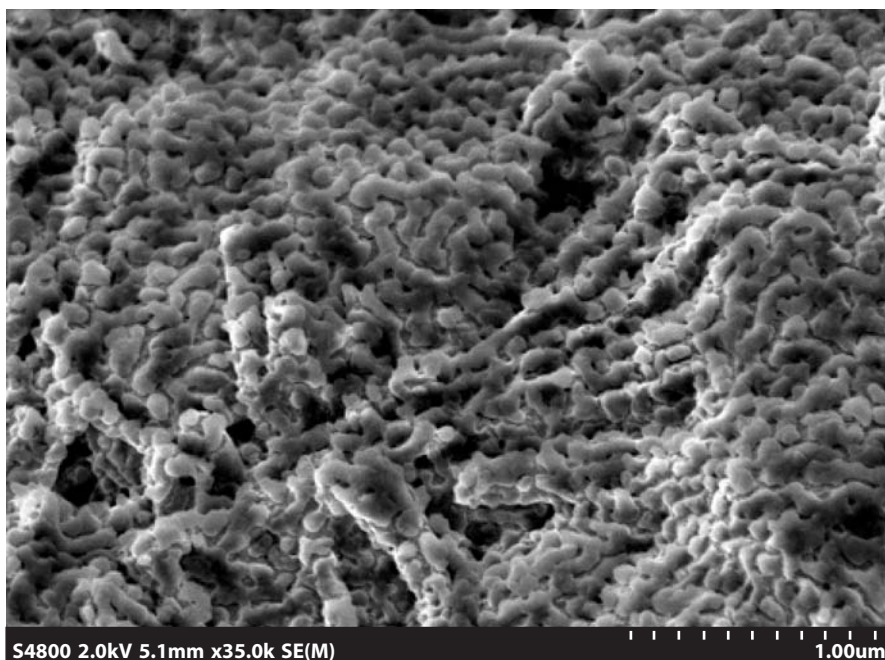


Fig. 3.6. Cryo-SEM micrograph of a water-in-oil microemulsion

microemulsion method show significant changed physical properties, e.g., in the magnetic susceptibility, density of sintered pellets, and the fraction of ideal Meissner signal [195]. A review of the preparation of metal nanoparticles in water-in-oil microemulsions was recently published by Capek [196].

Reverse microemulsions formulated with the anionic surfactant sodium bis(2-ethylhexyl)sulfosuccinate (Aerosol OT, AOT) have been extensively used for the synthesis of inorganic nanoparticles of barium chromate [197], barium sulfate [198], calcium sulfate [199], silica [200], silver [201] and copper [202]. For example, Pileni et al. obtained silver nanoparticles with the application of functionalized surfactant silver bis(2-ethylhexyl)sulfosuccinate (Ag(AOT)) [201], which are organized in nanocrystal self-assemblies in 2D and 3D superlattices [203]. Furthermore, organic nanoparticles of cholesterol, Rhovanil, and Rhodiarome have been synthesized in AOT/heptane/water microemulsions [204]. However, these studies suggest that complex fluids can be used not only to control the size and shape of inorganic nanoparticles but as dynamical systems for the spontaneous organization beyond the mesoscopic length scale. The morphological complexity of BaSO_4 synthesized in AOT microemulsions was demonstrated by Mann et al. [198, 205]. Depending on the reaction condition, crystalline micrometer-long BaSO_4 fibers, filament bundles, highly curved and cone-shaped structures and spindle-shaped aggregates can be observed [205]. These examples show that a direct templating is often difficult to achieve, since the surfactant films, stabilized by weak van der Waals

forces, are often not strong enough to stop the particle-growing process. To overcome this problem, Eastoe et al. [206] incorporated polymerizable surfactants into the system and this approach makes it possible to enclose the nanometer-sized aqueous reaction domains by covalent bonding. The results demonstrate clear advantages of partially polymerized surfactant shells for templating anisotropic inorganic particles from w/o microemulsions.

3.2.2.1 Recovery of Nanoparticles

Another problem that is still open is to recover the nanoparticles from the template without changing the particle dimensions. Due to the high surface energy of nanoparticles, the particles coagulate irreversible when one destroys the reverse micelles without any other protection treatment. Therefore, Kortan et al. reported the preparation of ZnS ultrafine particles modified with thiophenol or phenyltrimethylsilyl selenide [207]. A quantitative study on thiophenol modification and redispersion of CdS nanoparticles was given by Shiojiri et al. [208]. In the redispersion process of CdS nanoparticles, the added thiophenol molecules are considered to have two functions:

- destabilizing the inverse microemulsions and
- binding to the surface of the particles and ejection from the micelles.

Finally, the nanoparticles can be redispersed in non-micellar solvents, e.g., in pyridine, THF, DMF, DMSO, or acetone. The redispersion ratio varied in dependence on the type of non-polar solvent between 10 and 100% [209].

Chemisorptive surfactants such as alkanethiols are known to also enhance gold-particle dispersions and provide opportunities for further chemical modifi-

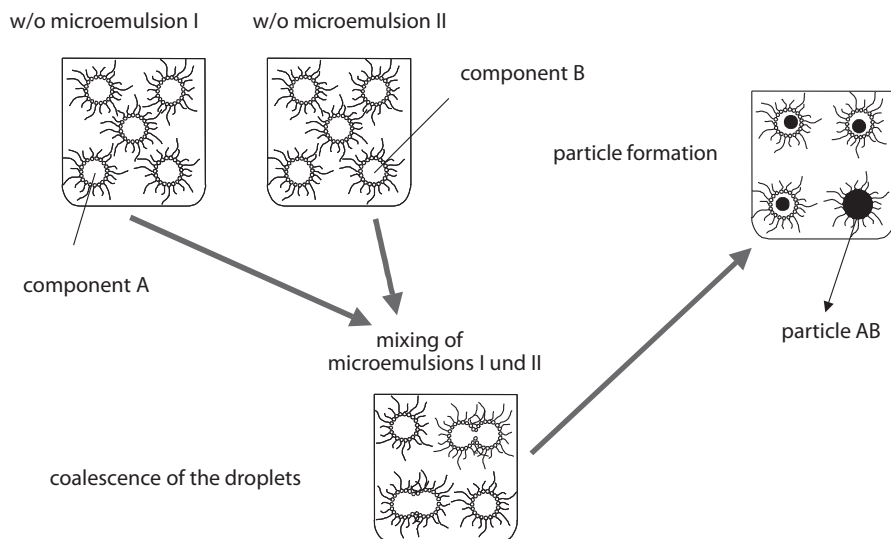


Fig. 3.7. Nanoparticle formation in a microemulsion template phase

cation [210,211]. For example, alkenyl-thiol-stabilized gold nanoparticles can be immobilized covalently onto silicon surfaces [212], and gold nanoparticles stabilized with tetrathiolated resorcinarenes can be extracted from aqueous solutions into nonpolar organic solvents [213].

3.2.2.2 Polyelectrolyte-Modified Microemulsions as Templates

Another approach to produce nanoparticles of defined particle size and particle shape starts from the idea to use polymer-modified microemulsions as templates for the nanoparticle formation process. In this case, the polymer has several functions, which include:

- stabilizing the surfactant film
- controlling the particle growing process
- stabilizing the nanoparticles
- preventing the irreversible coagulation during the process of redispersion

Polyelectrolytes can especially fulfill all of these requirements. However, first of all, polyelectrolytes have to be incorporated into the self-assembled system. Our own investigations have shown that polymers as well as polyelectrolytes can be added to the L2 phases without a macroscopic phase separation up to a polymer concentration in the aqueous phase of 20 or 30% by weight [214,215]. Surprisingly, it is possible to use ionic surfactant-based inverse microemulsions in combination

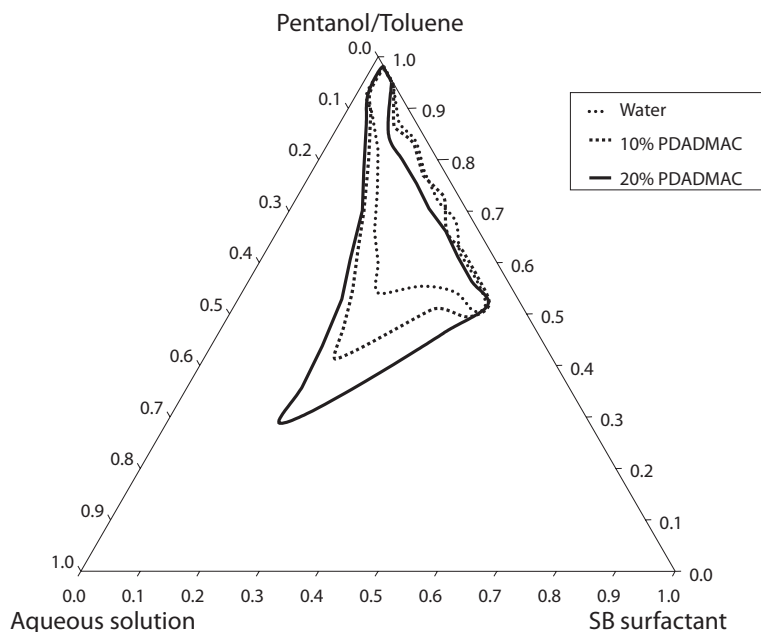


Fig. 3.8. “Boostering” effect of a cationic polyelectrolyte (PDADMAC) on the increase of the area of the inverse microemulsion phase (SB – surfactant having a sulfobetaine head group)

with oppositely charged polyelectrolytes. For example, the cationic polyelectrolyte poly(diallyldimethylammonium chloride) (PDADMAC) can be incorporated into the water droplets of the SDS-based (anionic) microemulsions [214], and the anionic polyelectrolytes Na-polyacrylate (Na-PAA) or Na-carboxymethylcellulose (Na-CMC) into CTAB-based (cationic) reverse microemulsion droplets [216]. Because of the high ionic strength in the aqueous phase, the electrostatic interactions are not so strong (no phase separation), but are strong enough to increase the stability of the surfactant film. However, the incorporation of the polyelectrolytes often leads to a partial decrease of the area of the L2 phase, e.g., by adding Na-PAA or Na-CMC. In other cases PELs can be solubilized in the water droplets much better. For example, PDADMAC can be incorporated up to higher polymer concentrations without a significant change of the L2 area in the SDS/pentanol/xylol/water system. When the SDS is substituted by an amphoteric surfactant (SB), the added PDADMAC leads to a significant increase of the L2 area, as is shown in Fig. 3.8 [217]. Similar effects, meaning an expansion of the isotropic phase area in direction to

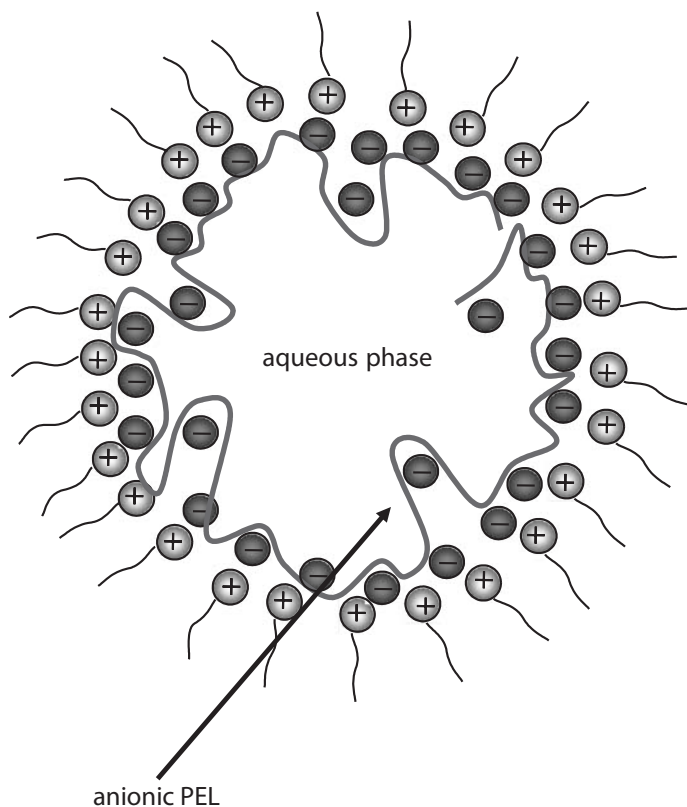


Fig. 3.9. Low-molecular-weight polyelectrolytes incorporated into individual w/o microemulsion droplets

the water corner, can be observed when the oil component is substituted by a long chain alcohol, e.g., pentanol, hexanol or heptanol [218]. Vice versa, amphoteric polyelectrolytes, added to the SDS-based microemulsion, can lead to an increase of the L2-phase, too [219]. Furthermore, it is well known that amphiphilic block copolymers can be used as efficiency boosters for microemulsions [220]. In addition, the molar mass of the polyelectrolyte is of high relevance. When the molar mass of the polyelectrolyte is low, an incorporation into individual microemulsion droplets is possible (cf. Fig. 3.9). Exemplary, we are able to visualize such polymer-filled individual microemulsion droplets by means of freeze-fracture electron microscopy (Fig. 3.10). However, when the radius of gyration of the polymer exceeds the droplet size, a polymer-induced cluster formation is observed [221], as is schematized in Fig. 3.11.

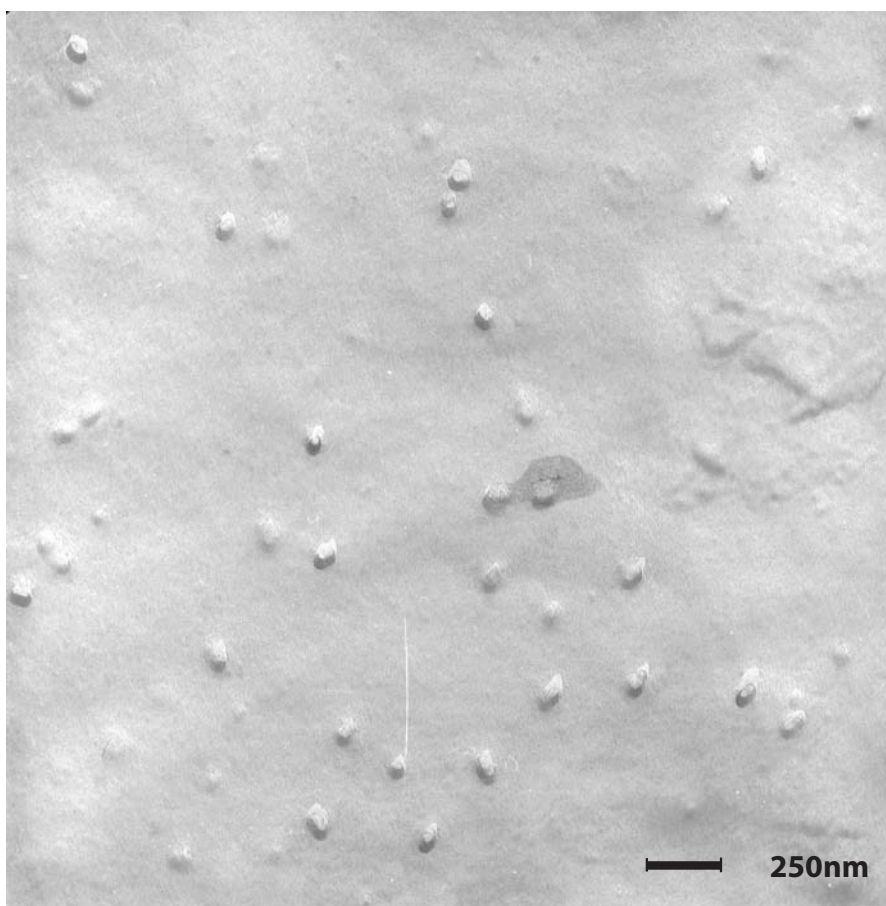


Fig. 3.10. Freeze fracture electron micrograph of a polymer-modified w/o microemulsion

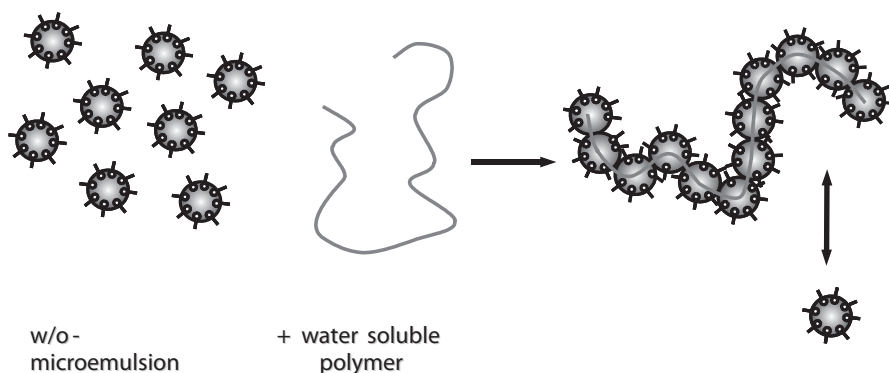


Fig. 3.11. Polymer-induced cluster formation by adding high molecular weight polymers

Thus, these polyelectrolyte-modified microemulsions can be used as special templates for the nanoparticle formation. Our own experiments show that polyelectrolytes are indeed able to control the size of the nanoparticles. For example, well-defined BaSO_4 nanocrystallites can be formed in the inverse microemulsion droplets. The role of the PEL can be explained by PEL-surfactant interactions (increase of the stiffness of the surfactant film) in combination to PEL-nanoparticle interactions during the particle growth process.

Furthermore, the adsorption of the polyelectrolytes onto the surface of the individual nanoparticles is of primary importance in the following solvent evaporation and redispersion process according to the procedure described in [222]. Only when the nanoparticles are electrosterically stabilized by the polyelectrolyte adsorption layer is the recovery of the individual small nanoparticles possible. Our own experiments show that polyelectrolyte-stabilized spherical nanoparticles with diameter below 10 nm can be redispersed from different types of microemulsion after solvent evaporation [223,224]. However, the size of the redispersed nanoparticles strongly depends on the molar mass of the polyelectrolyte. Only when the molar mass of the polyelectrolyte is small (for example by using a PDADMAC with $M_n = 7000$ g/mol, $M_w = 11\,500$ g/mol) polyelectrolyte-stabilized spherical nanoparticles with an average particle size of 6 nm can be redispersed after solvent evaporation [223,224]. In absence of the polyelectrolyte or by using a polymer with higher molar mass, aggregation phenomena lead to the formation of significant larger aggregate structures. It has to be mentioned here that these aggregation processes of primary spherical particles can also be used to produce ordered structures on the supramolecular level, e.g., cubes with an edge length of 20 nm (Fig. 3.12) [225] or triangular structures as well as nanotubes (Fig. 3.13) [226].

The effect of stabilization due to the adsorption of polyelectrolytes onto nanoparticles is not restricted to the formation of barite nanoparticles. Recently we were able to show that gold nanoparticles can also be redispersed from

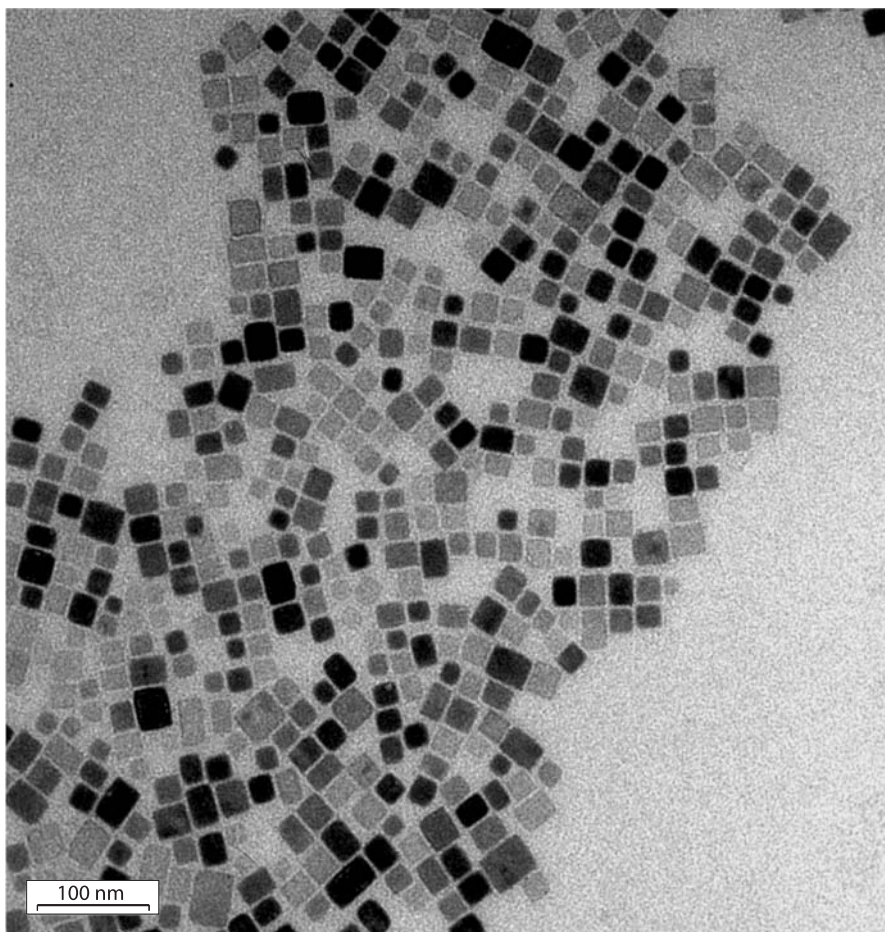


Fig. 3.12. TEM micrograph of BaSO₄ nanocubes

polyethylenimine-modified microemulsions by preventing phenomena of aggregation during the process of solvent evaporation and redispersion.

The results clearly show that polyelectrolytes can play a dominant role during the particle formation process in the microemulsion droplets, due to:

- the control of the particle growth (PEL-nanoparticle interactions)
- the restriction of the particle growth (PEL-surfactant interactions)

as well as in the redispersion process, due to:

- the stabilization of the nanoparticles (PEL-nanoparticle interactions)
- the control of the nanoparticle aggregation (PEL-nanoparticle interactions)

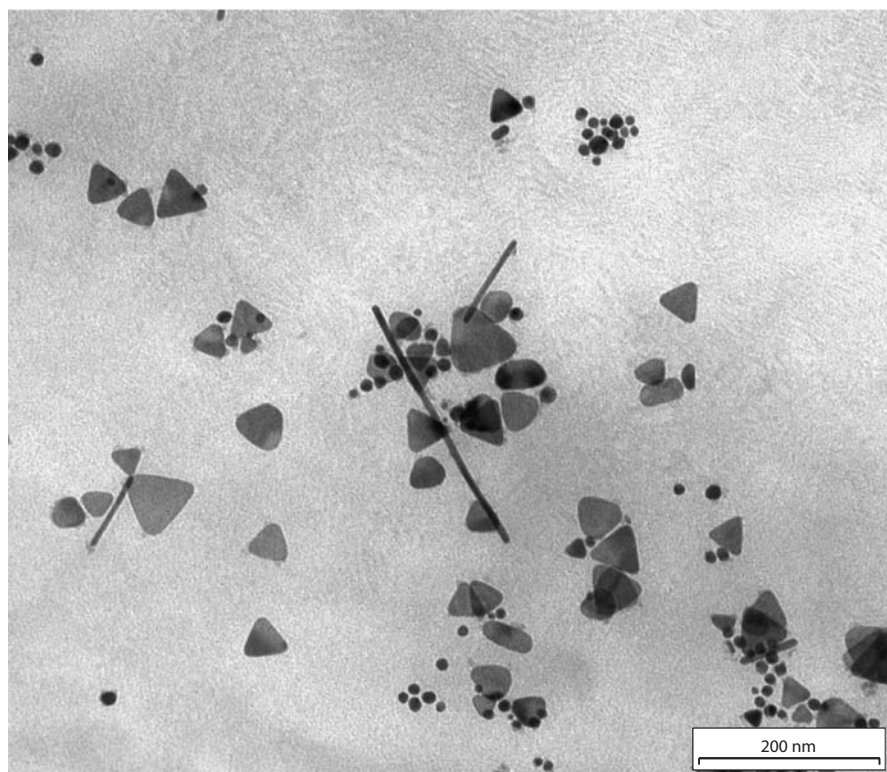


Fig. 3.13. TEM micrograph of BaSO₄ nanotubes and triangular structures

However, for each nanoparticle system the type of polyelectrolyte and microemulsion have to be optimized according to the PEL-nanoparticle as well as the PEL-surfactant interactions.

3.2.3 Block Copolymers as Templates

Amphiphilic block copolymers represent a new class of functional polymers, consisting of at least two parts, a lyophilic and a lyophobic one. In most cases, one block is water-soluble (hydrophilic block) in contrast to the other one (hydrophobic block) fulfilling the requirements of amphiphily. However, the control of the block length is essential with regard to the special features of the block copolymers. Living anionic polymerization has been known for a long time as the classical route to come to block copolymers with well-defined block length [227]. In addition to the classical diblock (AB) copolymers, ternary (ABC) triblock copolymers have also been in the center of research during the last decades [228–230].

Other types of living polymerization include group-transfer, ring-opening metathesis, cationic, and free-radical polymerization [231]. In dependence on

these different types of polymerization, only a limited number of monomers can be copolymerized. For the preparation of ionic block copolymers [232] especially the polymerization of methacrylates, acrylates (AA), and vinylpyridines (VP) is of special interest. These monomers can be polymerized by an anionic polymerization, and recently by special techniques of radical polymerization, i.e., atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer polymerization (RAFT).

For example, block PEL with cationic VP-, and anionic AA-blocks, respectively, were synthesized and investigated in more detail by Eisenberg et al. [233, 234]. Cationic PEL-based ionic diblock copolymers can also be synthesized by copolymerization of ethylene glycol with diallyldimethylammonium chloride [235].

Another route starts with the synthesis of block copolymers of vinylbenzyl chloride (VBC) with a narrow molecular weight distribution by (2,2,6,6-tetramethyl-piperidine-N-oxyl)-mediated controlled free radical polymerization, followed by a modification of the VBC-block to cationic structures [236]. Recently, Laschewsky et al. [237] were able to show that butyl acrylate is easily polymerizable in a controlled manner by means of RAFT-polymerization with a series of hydrophilic monomers, including anionic, i.e., (2-acrylamido-2-methylpropanesulphonic acid), and cationic, i.e., (3-acrylamidopropyl-trimethylammonium chloride) monomers. Their self-assembly in aqueous solution was investigated in more detail in [238]. Near-monodisperse anionic or zwitterionic methacrylate-based PEL block copolymers can be prepared by a group-transfer polymerization [239].

It is well known that the self-assembly of block copolymers leads to a broad variety of morphologies, e.g., micelles of various shapes, lamellae, ordered cylinders, or bicontinuous structures. Most of the block copolymers that have been investigated form micelles in solvents that selectively dissolve only one of the blocks. What makes the PEL block copolymers unique is the ability to control the different micellar morphologies by regulating the hydrophilic/hydrophobic balance via the salt concentration and/or the pH of the solution. The morphologies present in diblock copolymers are rather well defined with a long range order, and their characteristic size can be controlled in the range between 10 and 250 nm. Common morphologies of micro-phase separated block copolymers are:

- body-centered cubic packed spheres
- hexagonally ordered cylinders
- hexagonally performed layers
- lamellae
- cylindrical or spherical micelles

In order to use block copolymers as templates for the nanoparticle formation, the inorganic precursors are first loaded into the template, meaning into the micellar cores or the bulk block copolymer microphases. For a size-controlled synthesis of nanoparticles it is necessary to control the size of the microcompartment. Since loading of an inorganic precursor can change the size and shape of the micelles, the solubilization process has to be studied for a given system in more detail.

For example, HAuCl_4 precursor solutions can be homogeneously distributed within the micellar core of poly(styrene-*b*-4-vinylpyridine) block copolymer micelles, and nanoscale Au particles can be obtained by a fast reduction with LiAlH_4 at high supersaturation. The slow reduction with Et_3SiH (low supersaturation) leads to significantly larger single gold colloids, and the reduction with aqueous hydrazine to anisometric gold aggregates [240].

This example shows that the block copolymer micelles are often not stiff enough to fix the size of the nanoparticles. The colloids are generally quite stable, and precipitation, redispersion, or heating does not affect the size distribution [241].

A list of inorganic precursors and colloids, including different metal, metal sulfide, and metal oxide nanoparticles that have been prepared in block copolymers is presented in [240]. It has to be noted here that block copolymer micelles can be used especially for the preparation of quantum size semiconductor particles (e.g., ZnO).

Polyelectrolytes and Nanoparticles

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