Preparation of Polymerizable Miniemulsions by Ultrasonication

Katharina Landfester, Jördis Eisenblätter, and Regina Rothe—*Max Planck Institute of Colloids and Interfaces**

Styrene miniemulsions are prepared by ultrasonicating a system at different amplitudes until an equilibrium is reached. It is shown by turbidity measurements that the efficiency of the dispersion process is strongly dependent upon the ultrasonication time at the different amplitudes. In addition, the influence of monomer type on the homogenization process is also shown. The sizes of the droplets (before and after polymerization of the particles) are mainly determined by the type of monomer as well as the type and amount of the surfactant, as is shown for methyl methacrylate and butyl acrylate as monomers.

Keywords: Polymerization, acrylics, latexes, colloids, emulsions, latex, water-based, emulsification

The formulation of polymer latex particles for application in paints, adhesives, and coatings is popular in both academia and industry. Usually, the technique of emulsion polymerization[1] is used for the preparation of polymer particles. However, this technique is based on a kinetic control during the 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 in the accessible composition have to be accepted. With the concept of "nanoreactors" where the essential ingredients for the formation of the nanoparticles are in the preformed droplets, one can take advantage of a potential thermodynamic control for the design of nanoparticles. It is understood 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.

The idea of polymerization in a nanoreactor is technically realized in high perfection in suspension polymerization, where droplets in the micrometer range are created and can be polymerized without change of particle identity.[2] The suspension principle was transferred to obtain smaller droplet sizes by Ugelstad[3] who scaled down the droplet size to several hundred nanometers by shearing the system to obtain "miniemulsions." Miniemulsions are classically defined as aqueous dispersions of relatively stable oil droplets within a size range of 50-500 nm that are prepared by shearing a system containing oil, water, a surfactant, and a hydrophobic agent, which efficiently prevents the droplets from Ostwald ripening.[4,5] A mechanical emulsification starts with a premix of the fluid phases containing surface active agents and further additives. The emulsification includes two mechanistic steps: (1) deformation and disruption of droplets, which increase the specific surface area of the emulsion, and (2) the stabilization of this newly formed interface 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 ultra-turrax is also described in early articles. However, the energy transferred by these techniques is not sufficient to obtain small and homogeneously distributed droplets.[6] A much higher energy for the conversion of large droplets into smaller ones is required, significantly higher than the difference in surface energy $\gamma \Delta A$ (with γ = surface/interfacial tension and ΔA = the newly formed interface), since the viscous resistance during agitation absorbs most of the energy and creates heat.[7,8] 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 are favorable for the emulsification of higher quantities. One goal of this article is to characterize the efficiency of the dispersion process by measuring the turbidity in dependence of ultrasonication time at different amplitudes.

If the small, homogeneous, and stable droplets consist of monomer or polymer precursors they can then be transferred by polymer reactions to the final polymer latexes, retaining their particular identity without serious exchange kinetics involved. In addition, the influence of the type of the monomer on the homogenization process by ultrasonication is shown.

EXPERIMENTAL

Chemicals

Styrene, methyl methacrylate (MMA), acrylonitrile, and butyl acrylate (BA) (Aldrich) were distilled under reduced pressure prior to use. Lauryl methacrylate was purified by using a column of aluminum oxide. Sodium dodecylsulfate (SDS) and potassium peroxodisulfate (KPS) were purchased from Fluka and used as received.

Synthesis

The monomer phase composed of 6 g of a styrene and 250 mg of hexadecane as hydrophobe was added to 24 g of water containing 72 mg of SDS. After stirring at room temperature for one hour, miniemulsification was ob-

(a)

(b)

Figure 1—(a) Homogenization process for 90 ml of styrene/ water miniemulsions (20 wt% styrene, 1.2 wt% SDS, and 4.2 wt% hexadecane based on styrene) followed turbidity measurements at different amplitudes. Note that for all samples of 20% or more amplitude, the absolute value of turbidity was the same, however, for clarity, the graphs have been separated; (b) The ultrasonication time after reaching the steady state (where the change of the absolute turbidity is less than 1%) is plotted vs the amplitude.

tained by ultrasonicating (Branson sonifier W450 digital) at 0°C. One hundred milligrams of KPS were then added to the water phase. For polymerization, the temperature was increased to 72°C.

Sonifier

For the experiments, a Branson Sonifier W450 Digital with a frequency of 20 kHz was used. The amplitude can be regulated between 10 and 100%.
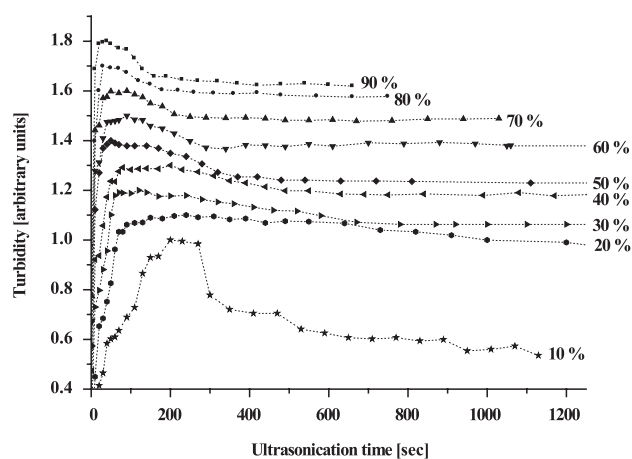
Analytical Instruments

The particles sizes were measured using a Nicomp particle sizer (model 370, PSS Santa Barbara, U.S.) at a fixed scattering angle of 90°.

The turbidity measurements were carried out by a Process Turbiditymeter (FSC 402, Mettler Toledo, Switzerland) with a sensor for high turbidity values which is sensitive to the backscattered light. The wavelength of the light was 880 nm.
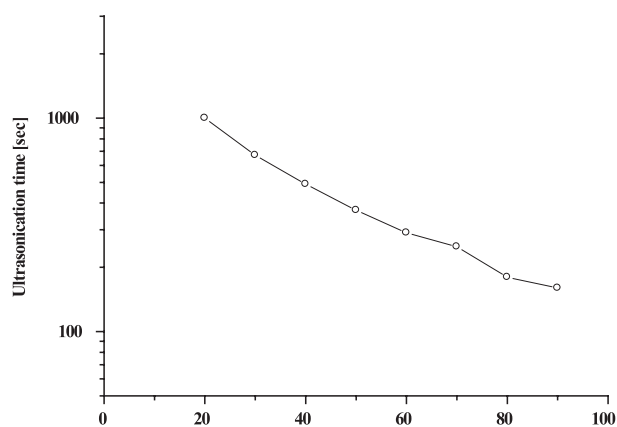
The surface tension measurements were performed with the K12 processor-tensiometer from Krüss employing the DuNoüy-Ring method. The radius of the Pt-Ir-ring RI12 was 9.545 mm and the wire had a radius of 0.185 mm. Each measurement was repeated 10 times.

INFLUENCE OF AMPLITUDE

A key step in preparing a miniemulsion is the homogenization step. The process of homogenization can be followed by different methods, e.g., by turbidity and by surface tension measurements. By increasing the time of ultrasonication, the droplet size decreases and, therefore, the number of droplets increases. Since a constant amount of surfactant has to be distributed onto a larger interface, the interfacial tension as well as the surface tension at the air/emulsion interface increases since the droplets are not fully covered by surfactant molecules. Turbidity measurements are sensitive to the size and size distribution of the droplets. In *Figure* 1, the turbidity during ultrasonication at different amplitudes is shown. At an amplitude of 10%, no stable state during miniemulsification can be reached. A minimum amplitude of at least 20% is necessary to reach an equilibrium state of the miniemulsion. In the case of 30 ml of a 20 wt% styrene in water miniemulsion, the equilibrium was reached after 1000 sec. It was seen that the time for obtaining a equilibrium value decreases significantly with increasing amplitude (see *Figure* 1b). At 90% amplitude, the equilibrium for the same miniemulsion was already reached after 200 sec. It is important to note that these absolute times are strongly dependent upon the volume. To obtain an equilibrium at 90% amplitude in 300 ml of a 20 wt% styrene miniemulsions, about 1000 sec of ultrasonication were required to obtain the same equilibrium state. However, the absolute turbidity value after reaching the equilibrium was always the same, showing that indeed the same miniemulsions were obtained. As expected, the particle size of the polymerized droplets is independent of the amplitude during sonication, always about 85 nm. It should be noted that the same particle size was also obtained if a high-pressure ho-

mogenizer was used. Here several passes may be required for reaching the equilibrium state.

All the experimental details we found support 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 are much smaller directly after sonication, but colloidally unstable, whereas larger droplets are broken up with higher probability. (Note that the Fokker-Planck equation is a linear partial differential equation of second order, and is applied to analyses of stochastic dynamics in a large number of different fields, i.e., quantum physics, chemical physics, and theoretical biology.[9]) This also means that miniemulsions reach the minimal droplet sizes under the applied conditions (surfactant load, volume fraction, temperature, salinity, etc.), and, therefore, the resulting nanodroplets are at the critical borderline between stability and instability. This borderline is reached with any homogenization method above a certain minimum energy. This is why we call miniemulsions directly after homogenization "critically stabilized."[10,11] Practically speaking, miniemulsions potentially make use of the surfactant in the most efficient way possible.

INFLUENCE OF THE MONOMER ON THE HOMOGENIZATION PROCESS

The type of monomer also has a significant influence on the homogenization process. For the next experiments, miniemulsions consisting of different monomers (20 wt%), but otherwise identical compositions of ingredients (1.2 wt% SDS, 4.2 wt% hexadecane), were used. For a better comparison of the ultrasonication times, 300 ml of the systems were used, the sonication amplitude was chosen to be constant at 90%. As expected, the time of sonication strongly depended upon the hydrophilicity of the monomer. As can be seen in *Figure* 2, in the case of the hydrophilic monomers methyl methacrylate and acrylonitrile, an equilibrium was reached after approximately 500 sec of ultrasonication, whereas the hydrophobic lauryl methacrylate required more than 2000 sec to reach the equilibrium state. In between these times butyl acrylate required about 600 sec and styrene about 1000 sec of ultrasonication.

After polymerization of the miniemulsions, similar particle sizes were found (about 80-90 nm) in the MMA and styrene systems; the particles in the butyl acrylate system were about 100 nm larger. The hydrophobic monomer LMA led to significantly larger particles (about 200 nm). This was due to the larger interfacial tension between the monomer and the water phase, which has to be compensated for by a higher coverage with surfactant molecules. Also, the hydrophilic acrylonitrile led to larger particles (180 nm), which show a crystallinity of about 30%.[12]

Colloidal stability is usually controlled by the type and amount of the employed surfactant. In miniemulsions, the fusion-fission rate equilibrium during sonication and, therefore, the size of the droplets directly after primary equilibration depends on the amount of surfactant. For sodium dodecylsulfate and butyl acrylate at 20% dispersed phase, it spans a range from 180 nm (0.33 wt% SDS based on BA) down to 50 nm (33 wt% SDS based on BA), for
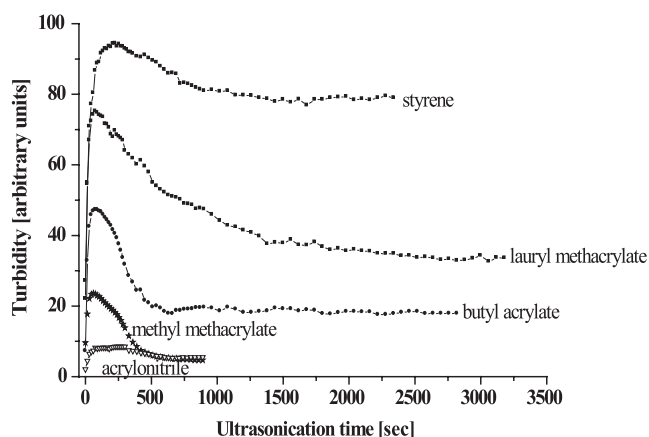

Figure 2—Homogenization process by ultrasonication for 300 ml of styrene/water miniemulsions (20% monomer, 1.2% SDS, and 4.2% hexadecane compared to styrene). The amplitude was kept constant at 90%.

methyl methacrylate from 125 nm (0.33 % SDS based on MMA) to 55 nm (33 wt% SDS based on MMA), as seen in *Figure* 3.

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 for the droplets. The A_{surf} values show a strong dependence on the particle size (see *Figure* 4). It is seen for BA and MMA that the entire range of a dense surfactant monolayer from small particles to very incompletely covered particles 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 remember: certain effects and reactivities might depend on the droplet size and work better for larger particles, which is somewhat counterintuitive.
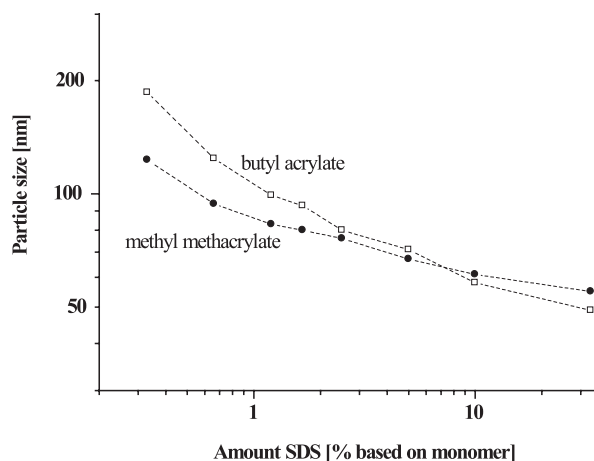

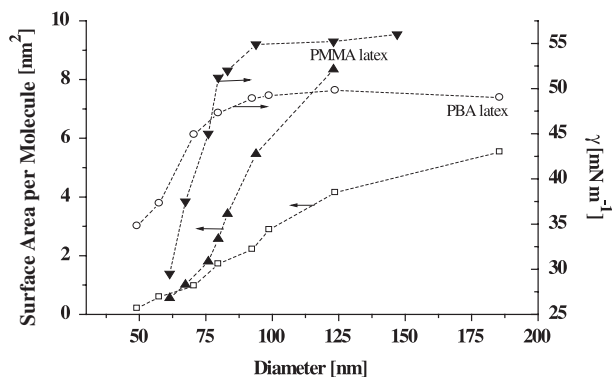Figure 3—Dependence of the particle size vs the amount of SDS for BA and MMA as monomers.

Figure 4—Surface tension and the surface area per surfactant molecule vs the diameter of PBA and PMMA particles.

A_{surf} values of less than 0.2 nm² calculated at high surfactant loads indicate the presence of free micelles or multilayer adsorption, which is not considered in these simplified area calculations. Here, we clearly leave the region of well-defined ("clean") miniemulsions. It is a matter of course that the different surfactant coverages are also reflected in the corresponding surface tensions γ of the latexes (see *Figure* 4). An increase of the surface tension with increasing diameter is observed. The miniemulsions based on polystyrene particles exceeding 100 nm have a surface tension close to that of pure water (72 mN·m⁻¹). This is due to the fact that the bare particle surface is so large that adsorption equilibrium ensures a very low surfactant solution concentration. In the case of PBA and PMMA, the surface tensions are lower, as seen in *Figure* 4. Independent of the monomer, it is true that smaller particles with their higher surface coverage also have a higher equilibrium concentration of free surfactant, but the concentration usually stays well below the critical micelle concentration value. This means that in miniemulsions, there are no free micelles present. This is very important for the chemical reactivity and the polymerization kinetics in such systems. As in the case of the highest surfactant load, a dense surface layer and a γ value typical for a micellar phase are observed. Here, we leave the composition region for well-defined miniemulsions.

CONCLUSION

The key step in the process of miniemulsions is the homogenization step. Here, ultrasonication is a very efficient tool to obtain miniemulsions in an equilibrium state. It was shown by turbidity measurements that the efficiency of the dispersion process is strongly dependent upon the ultrasonication time at different amplitudes. It was also shown that the hydrophilicity of the monomer has a strong influence on the sonication time until an equilibrium is reached: the more hydrophobic the monomer is, the longer sonication was required. The size of the droplets (before and after polymerization of the particles) is mainly determined by the type of monomer as well as the type and amount of the surfactant as it was shown for methyl methacrylate and butyl acrylate as monomers.

References

(1) Blackley, D.C., *Polymer Latices*, Chapman & Hill, London, 1997.
(2) Dawkins, J.V., *Comprehensive Polymer Science*, Allan, G. and Bevington, J. (Eds.), Pergamon Press, Oxford, pp. 231-241, 1989.
(3) Ugelstad, J., El-Aasser, M.S., and Vanderhoff, J.W., *J. Polym. Sci., Polym. Lett. Ed.*, 11, 503-513 (1973).
(4) Sudol, E.D. and El-Aasser, M.S., *Emulsion Polymerization and Emulsion Polymers*, Lovell, P.A. and El-Aasser, M.S. (Eds.), John Wiley & Sons Ltd., Chichester, pp. 699-722, 1997.
(5) Landfester, K., *Macromol. Rapid Comm.*, 22, 896-936, 2001.
(6) Abismail, B., Canselier, J.P., Wilhelm, A.M., Delmas, H., and Gourdon, C., *Ultrasonics Sonochemistry*, 6, 75-83, 1999.
(7) Walstra, P., *Chem. Eng. Sci.*, 48, 333-349, 1993.
(8) Friberg, S.E. and Jones, S., in *Kirk-Othmer Encyclopedia of Chemical Technology*, Kroschwith, J.I. (Ed.), Vol. 9, Wiley, New York, pp. 393-413, 1994.
(9) Risken, H., *The Fokker-Planck Equation: Methods of Solution and Applications*, Springer Verlag, Berlin, Heidelberg, 1989.
(10) Landfester, K., Bechthold, N., Tiarks, F., and Antonietti, M., *Macromolecules*, 32, 5222-5228 (1999).
(11) Landfester, K., *Macromol. Symp.*, 150, 171-178, 2000.
(12) Landfester, K. and Antonietti, M., *Macromol. Rapid Comm.*, 21, 820-824, 2000.