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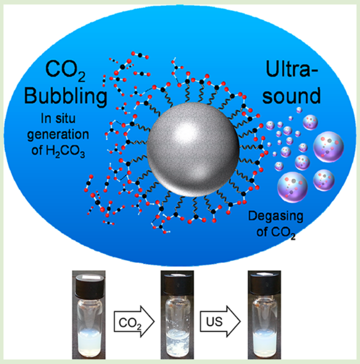
Molecularly Controlled Coagulation of Carboxyl-Functionalized Nanoparticles Prepared by Surfactant-Free Miniemulsion Polymerization

Viktor Fischer, Katharina Landfester, and Rafael Muñoz-Espí*

Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

Supporting Information

ABSTRACT: We present the synthesis of molecularly controlled "CO_2-switchable" polystyrene nanoparticles by surfactant-free miniemulsion polymerization using a carboxyl-functionalized surface-active monomer, which acts as comonomer and stabilizer at the same time. The obtained nanoparticles are about 100 nm in size and show a small size distribution, confirmed by dynamic light scattering (DLS) and electron microscopy. Under ambient conditions, the latex particles form a stable suspension that can be coagulated by bubbling CO_2. The redispersion of the coagulated particles can be easily achieved by ultrasonication. The reversibility of the coagulation is confirmed after several coagulation/redispersion cycles (CO_2 bubbling and ultrasonification) from DLS and zeta potential measurements.



The technique of miniemulsion polymerization is a powerful tool to produce colloids of nanometric size for a wide range of applications, such as drug delivery systems, coatings, support mineralization processes, and formation of hybrid particles.[1,2] Miniemulsions have even been extended to the synthesis of nanoparticles by controlled living polymerization processes.[3] Unfortunately, the purification of the particles takes often days of conventional dialysis in which the dispersion gets more diluted and becomes often less stable. The creation of a particle system with the ability to be easily coagulated and redispersed would allow the recovery of the nanoparticles at high concentrations, or even the storage of the particles in powder form to redisperse them in a later step if needed. Coagulated particle systems can also help in saving energy and transportation cost, since water can be added to the coagulated system at the destination.

A coagulation mechanism based on the addition of CO_2 would be perfectly suited to avoid the purification needed in other coagulation techniques. Carbon dioxide-switchable systems have been recently studied for emulsion polymerization in the presence of tertiary amines. Zhu et al. reported the preparation of amidine-containing styrene derivatives, which can be destabilized by addition of NaOH, needed because of the presence of amidine dihydrochloride species resulting from the decomposition of the initiator.[4] Cunningham et al. reported the application of a CO_2-switchable monomer, (dimethylamino)ethyl methacrylate (DMAEMA), and a CO_2-switchable initiator, 2,2′-azobis(2-(2-imid-azolin-2-yl)propane), inducing the coagulation of the particle system by argon and heating.[5,6] Polymerizable (*N*-amidino)dodecyl acrylamide synthesized in a four-step reaction has also been applied.[7] Other approaches show the application of CO_2-switchable surfactants like long-chain alkyl *N*,*N*-dimethylacetamidinium bicarbonates.[8,9] Zhao et al. have reported reversible aggregation of nanoparticles prepared with *N*,*N*-dimethylalkylamines.[10] Furthermore, the possibility of triggering the hydrophobicity of tertiary amines by the addition of CO_2 has been studied, and monomers like DMAEMA were applied to synthesize so-called CO_2-responsive polymers.[11−13]

All these works on CO_2-responsive colloids, synthesized by an emulsion polymerization process, imply water-soluble hydrogen carbonate species that become hydrophobic and coagulate when CO_2 is removed. However, CO_2 can also be used to coagulate colloidal suspensions. Moore and Lefevre[14] demonstrated in a patent that butadiente/styrene emulsions stabilized with carboxylic-containing surfactants (sodium oleate) could be coagulated by addition of CO_2. Usually, the functionalization of colloids with carboxylic groups can introduce a pH responsivity.

Here, we present for the first time, to the best of our knowledge, the preparation of CO_2-switchable COOH-functionalized polymer nanoparticles by application of a reactive surfactant, a so-called surfmer. No high-shear is needed for the coagulation, which represents a very significant difference with previous works.[14] The particles can be coagulated by the addition (i.e., bubbling with) carbon dioxide and redispersed by ultrasound. In most cases, miniemulsions are stabilized by commercially available sufactants, including anionic (e.g., sodium lauryl sulfate), cationic (e.g., cetyl

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ammonium chloride, with a quaternary amine), or nonionic (e.g., PEGylated surfactants, such as Lutensol AT50) molecules.[1] Those surfactants are stabilizing either sterically, or electrostatically. Steric stabilizing surfactants are not affected by the dissolution of CO_2 due to the lack of responsive functional groups. Quaternary amines or sulfates are also not affected by the pH change caused by dissolving carbon dioxide in water, because quaternary amines cannot be protonated and sulfates are very weak bases (HSO_4^-; $pK_{a2} = 1.99$). A surfactant-free approach would be, therefore, of great interest for the emulsion community. The application of surface-active monomers has already been proven as a convenient strategy for the preparation of functional hybrid particles and as additive for mineralization processes.[15−17]

Previously reported systems based on tertiary amines should be stored under a CO_2 atmosphere to maintain colloidal stability so that a lack of CO_2 or handling of the dispersion under ambient conditions can cause aggregation and destabilization of the particle system. In the case of carboxyl-based systems, no special gas atmosphere is needed for handling, and latex dispersions may be processed under normal atmosphere.

In this work, we show the synthesis of functionalized polystyrene latex particles by a surfactant-free miniemulsion polymerization in the presence of the surfmer *N*-methacryloyl-11-aminoundecanoic acid (treated equimolarly with NaOH), which has a polymerizable methacrylic acid group and a carboxylate functionality (see Figure 1), and it serves simultaneously as stabilizer and monomer. Styrene, hexadecane (acting as an osmotic reagent in order to guarantee stability of the droplets), and the oil-soluble initiator 2,2′-azobis(2-methylbutyronitrile) were mixed with a second phase comprised of a small amount of the surfmer in water. The resulting mixture was pre-emulsified by stirring (1400 rpm) at room temperature for 45 min, homogenized by ultrasonication, and subsequently polymerized at 72 °C, as schematically depicted in Figure 1.

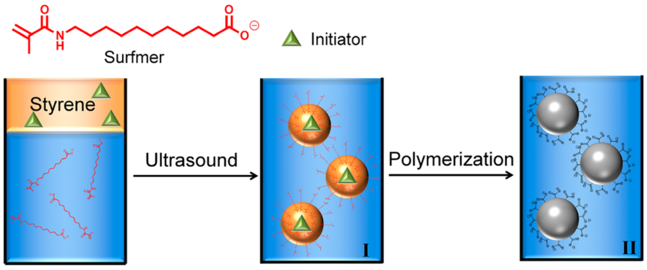

Figure 1. Synthesis of COOH-functionalized latex particles.

After homogenization, the surfmer molecules are arranged at the droplet (oil−water) interface. The hydrophobic tail containing the polymerizable group (methacrylate) points to the oil phase (Figure 1, I). This provides a well-defined, "non-hairy" surface functionality, because all surface-active molecules are distributed at the droplets and no free surfmer is floating in the continuous phase. The possibility of buried functionalities inside the particle, common with conventional monomers,[18] is heavily suppressed when surfmers containing a methacrylic group are used, because this group is polymerized at a conversion of styrene of 90%.[19] Thus, the surfmer stays mobile at the oil−water interface during the polymerization, warranting a complete stabilization of the droplets during the entire reaction time. Unpolymerized surfmer or water-soluble by-products can be easily removed at the end of the reaction from the dispersion because the surfmer is bound covalently to the particle and cannot be detached by dialysis or centrifugation processes, as it happens with ordinary surfactants.

The dispersion was purified by three cycles of a quick (only 10 min) centrifugation dialysis with a 100 kDa membrane filter. The efficiency of the dialysis was investigated by NMR spectroscopy with H_2O signal suppression, which showed that after only three runs all nonpolymerized surfmer or small water-soluble polymer chains were removed (Supporting Information, Figure S1). The purified dispersion showed a better performance during the coagulation and redispersion experiments. After dialysis, the dispersion was treated with an aqueous NaOH solution (1 M, 1.5 equiv with respect to COOH content) to ensure complete deprotonation. The solid content of the dispersion was 19.5 wt %, with a surface charge density of 1.2 groups nm^{-2} with a mean particle size of 106 nm (±21%).

In a first set of experiments, the dispersion was diluted to 0.1 wt % for the aggregation and redispersion experiments to provide the typical dilution needed for DLS measurements. The coagulation was initiated by bubbling CO_2 through the dispersion under gentle stirring (300 rpm) in a closed vessel. The pH changed from an initial value of 8.9 to 4.1 when the particles start to aggregate. The deprotonated carboxylate groups are protonated by the carbonic acid generated in situ during dissolution of CO_2 (Figure 2). The subsequent coagulation of the protonated particles is analogue to the solubility of protonated long-chained alkyl acids. For redispersion, the coagulated suspension was sonified for 10 s with an ultrasound microtip using an amplitude of 65% (see Supporting Information for details). The temperature of the dispersion was 57−62 °C after the ultrasonication steps. Ultrasound is known to be used for solution degassing and it generates high local heat due to the formation/deformation of cavity bulbs.[20,21] The heat generation and the "degassing effect" promote the decomposition of the dissolved carbonic acid CO_2 and H_2O according to the equilibrium

$$H_2CO_3(aq) \rightleftharpoons CO_2(aq) + H_2O \qquad (1)$$

which allows a fast homogenization of the coagulated latex dispersion within seconds.

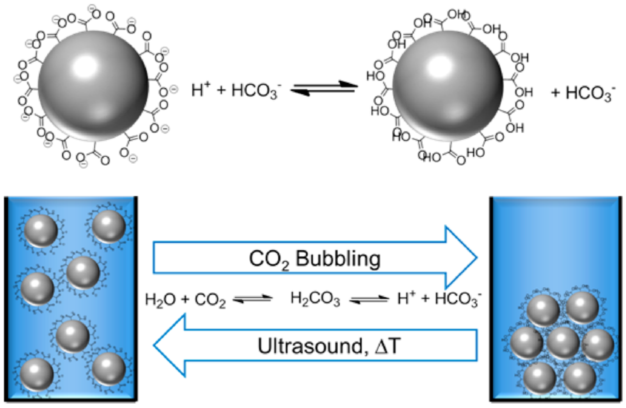

Figure 2. Mechanism of coagulation and redispersion of COOH functionalized latex nanoparticles.

The aggregation/redispersion experiments were followed by dynamic light scattering (DLS). Figure 3a shows the reversibility of the coagulation and redispersion steps. The same mean particle size was reached even after three cycles of destabilization/stabilization. Particle size distributions of the initial latex dispersion and the dispersions after each step of redispersion are comparable within the limits of error (Figure S2a). Size distributions of aggregated systems confirm the particle coagulation. Broad size distributions with mean aggregates of 1.5 μm are measured (Figure S2b).

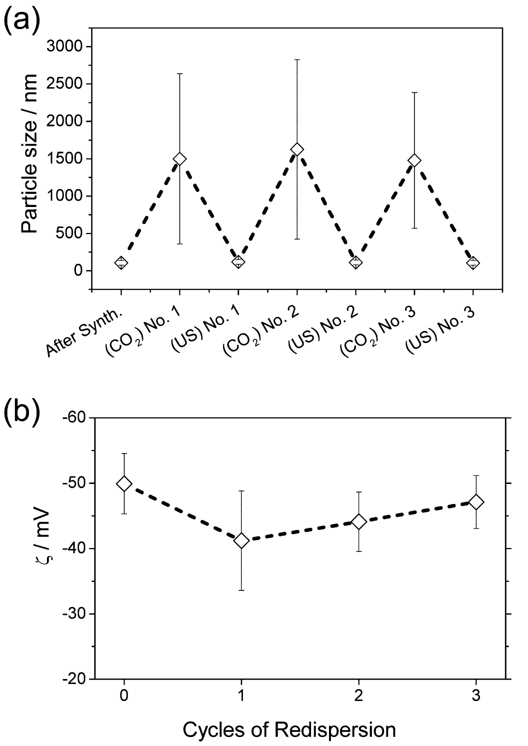

Figure 3. (a) Size determined by DLS for different cycles of coagulation/redispersion of the latex suspensions. (b) Zeta potential of the latex particles after synthesis and redispersion.

As a further control experiment, we conducted zeta potential measurements after each restabilization step. Figure 3b demonstrates that the zeta potential remains nearly constant after each step of redispersion. The small decrease in the zeta potential from the initial value to the one shown by the restabilized dispersion (cycles 1−3) can be explained by considering the measured pH values because zeta potential correlates with the amount of deprotonated-COOH functions. The initial pH value of 8.9 could not be achieved after sonication. After redispersion, pH values of 7.9 (first cycle), 8.1 (second cycle), and 8.3 (third cycle) were measured. The equilibrium state of dissolved CO_2 after ultrasonication is reached at an average pH of 8.1. Figure 4 shows photographs of the dispersion as initially prepared, after coagulation, and after redispersion. A well-dispersed colloidal system is obtained after ultrasonication. SEM images of the nanoparticles before and after the third restabilization can be observed in Figure 4a,b. No morphology change, coagulation, or film formation could be observed after the different restabilization steps (Figure S3).

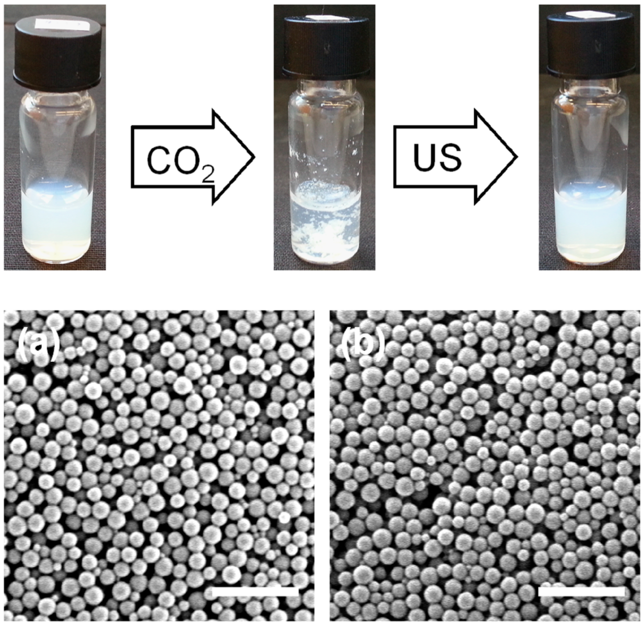

Figure 4. Photograph of the latex dispersion before coagulation with CO_2 (left), after coagulation (middle), and after three redispersion cycles (right). SEM images of COOH-functionalized polystyrene nanoparticles (a) before and (b) after redispersion (scale bar: 500 nm).

For the preparation of high solid content dispersions, the initial dispersion was bubbled with CO_2 for 45 min and the coagulated gel-like latex was isolated and dried in vacuum, as shown in Figure 5a. Afterward, the desired amount of dried particles was mixed with water, and the pH was adjusted to 9.0 with ammonia. For redispersion, the mixture was treated with ultrasound by means of an ultrasound bath for 15 min. The kinetic of redispersion was followed by DLS measurements. For that aim, aliquots were taken after certain time periods and diluted to DLS conditions. Kinetic measurements, depicted in Figure 5b, demonstrated that complete redispersion can be achieved after 10 min. By using this method, we could obtain emulsions up to a solid content of about 30 wt % (see Table S1 for characterization and details). When ammonia is added, the particles (R−COOH) are stabilized by direct deprotonation:

$$\mathrm{R{-}COOH + NH_3 \rightleftharpoons R{-}COO^- + NH_4^+} \qquad (2)$$

The formed ammonium ions can decompose in the presence of bicarbonate and heat:

$$\mathrm{NH_4^+ + HCO_3^- \rightleftharpoons NH_3\uparrow + H_2CO_3 \rightleftharpoons CO_2\uparrow + H_2O} \qquad (3)$$

The obtained dispersions were purified by a fast (2 × 10 min) centrifugation−filtration method using membrane filter tubes (100 kDa, Figure S4). The colloidal stability was also confirmed by zeta potential measurements and SEM.

Observation of the particles after coagulation by SEM showed their aggregation and a film formation. After treatment with ammonia and mild homogenization in an ultrasound bath, the particles were well dispersed and show no aggregates or film formation, situation that remains after purification (Figure S5).

In summary, we have reported the preparation of carboxyl-functionalized, CO_2-switchable nanoparticles by a surfmer-assisted miniemulsion polymerization. The obtained latex dispersion had a high solid content and could be easily purified by centrifugation dialysis with membrane filters. The particles had a diameter of about 100 nm. The coagulation of a colloidally stable particle system could be induced at molecular

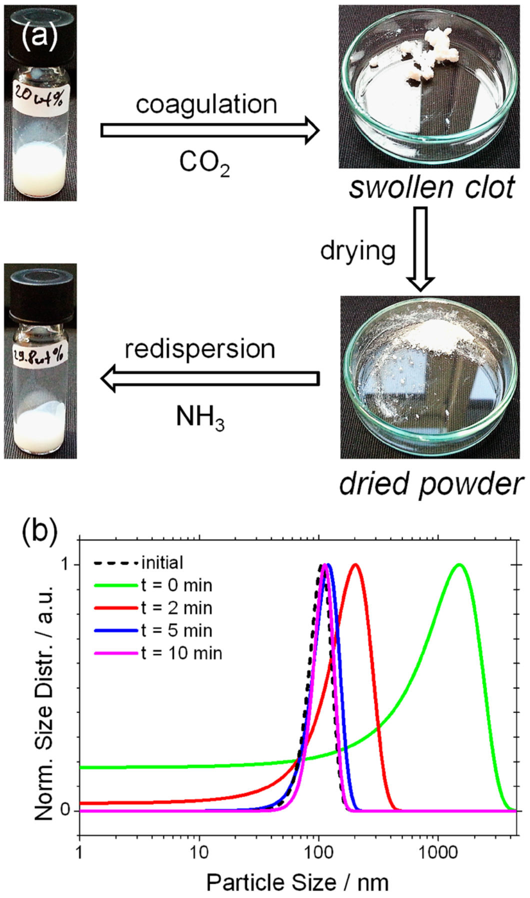

Figure 5. (a) Steps of coagulation, isolation of particles, drying, and redispersion. (b) Redispersion kinetics of high solid content (30 wt %) method.

level by bubbling CO_2 to form in situ carbonic acid, which protonates the $-COO^-$ groups covalently bound to the surface. The process could be reversed by ultrasonic treatment with an ultrasound tip (low solid contents) or by the addition of ammonia and subsequent homogenization in an ultrasound bath (high solid contents). The reversibility of the coagulation/redispersion was demonstrated by DLS and zeta potential measurements.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedure and characterization results of NMR, DLS, and SEM measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: munoz@mpip-mainz.mpg.de.

Notes

The authors declare no competing financial interest.

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