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Pickering Stabilized Miniemulsion Polymerization: Preparation of Clay Armored Latexes

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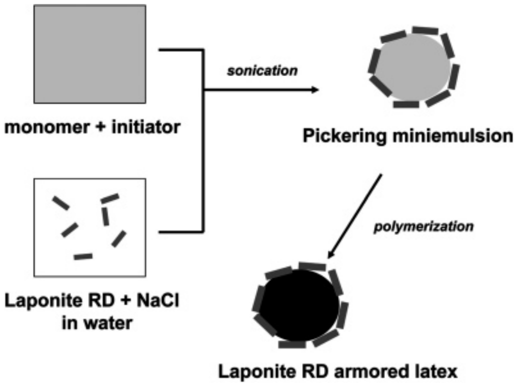
When particles, instead of surfactant molecules, are used to stabilize an emulsion, one speaks of a Pickering emulsion.[1,2] Important applications can be found for example in the food, cosmetics, and oil-recovery industries. Pickering stabilized colloidal systems are currently going through a renaissance. For example, vast arrays of supracolloidal self-assembled structures can be built. Pioneering work by Velev showed that latex particles could be used to self-assemble into supracolloidal structures at the liquid−liquid interface of emulsion droplets.[3,4] Weitz reported the fabrication of similar structures, naming them colloidosomes.[5] Paunov showed that polymeric rods could be used to prepare "hairy" colloidosomes.[6] Recently, responsive magnetic Pickering emulsions were reported which allowed reversible emulsification on application of an external magnetic field.[7] The majority of these self-assembled structures have micron-sized dimensions, as their building blocks have dimensions on the scale of 100−3000 nm. However, Lin reported on Pickering emulsions stabilized by CdSe nanoparticles.[8] The use of smaller nanosized building blocks would allow the preparation of Pickering miniemulsions, with typical droplet sizes of ca. 50−700 nm.

Our general interest lies in the use of colloidosomes as polymerization vessels as a versatile strategy toward novel supracolloidal structures. In this work we report the preparation of Laponite clay armored latex particles of polystyrene made via a Pickering stabilized miniemulsion polymerization of monomer filled Laponite colloidosomes of submicron dimensions (see Scheme 1).

Scheme 1. Synthesis of Laponite RD Armored Polystyrene Latex via Pickering Miniemulsion Polymerization



Laponite clay−polymer nanocomposites are of great interest, as the inorganic fillers—by addition of relatively low quantities in percentage—are known to enhance for example the mechanical and thermal properties of polymeric materials. Preparation of such composites via emulsion/suspension polymerization systems include heterocoagulation of the clay minerals onto the polymer particles,[9] complexation of cationic monomers/surfactants[10] or covalent modification of the Laponite to facilitate dispersion into the polymer matrix,[11] and use as Pickering stabilizer in conjunction with ordinary surfactant stabilization.[12] To our knowledge, our approach to clay armored latexes is novel, with Pickering stabilization as the exclusive tool to provide colloidal stability.

Laponite RD is a synthetic trioctahedric hectorite clay, composed of two tetrahedral silica sheets and a central octahedral magnesia sheet. Its chemical formula can be expressed as $[Si_8(Mg_{5.45}Li_{0.4})O_{20}(OH)_4]Na_{0.7}$, and it has a density of 2570 kg m^{-3}. The disks have an overall negative charge with the rim being amphoteric. In water Laponite RD can be dispersed as individual disk-shaped colloids with a lateral diameter of ca. 25−35 nm and ~1 nm in thickness.[13] These dimensions are of the right order to provide Pickering stabilization for miniemulsions, having droplet diameters of submicron sizes.

In order for the nanosized clay building blocks to adsorb at the monomer−water interface and to provide Pickering stabilization, they have to possess surface characteristics which allow for favorable partitioning on the interface in competition with the two bulk phases. A measure often used for particles to adsorb at the oil−water interface of oil droplets dispersed in water is their three-phase contact angle,[14,15] which ideally has a value of "slightly" less than 90° for an oil-in-water emulsion. A value too low would favor the particles to be dispersed in the water phase, whereas values a bit higher than 90° would favor oil as the continuous phase. Much higher values would give preference for the particles to be dispersed in the oil phase. A complementary measure which we use is the average value of the zeta potential of the building blocks measured when they are dispersed in water of low electrolyte concentration. High positive or negative values would keep them colloidally stable in the continuous water phase but would not favor the adsorption process to the liquid−liquid interface.

As indicated above, Laponite RD clay disks can form stable colloidal systems when dispersed in water.[16,17] Addition of sodium chloride would induce slight colloidal instability, leading to clay particle flocculation, but more importantly would greatly enhance the capacity of the clay to allow Pickering stabilization of oils in water.[16] In other words, the addition of salt compresses the double layer,[18] lowers the zeta potential, thereby reducing electrostatic repulsion, inducing possible clay flocculation, and thus increasing its partitioning to the oil−water interface. In our experiments we operate at approximate clay concentrations of 0.5 wt % and sodium chloride concentrations of 0.1 mol L^{-1}.

To make the targeted clay armored latex particles of polystyrene, it is important to ask oneself whether the oil droplets of the Pickering miniemulsion have full surface coverage. Only then we can talk of the supraparticle structure referred to as colloidosome. In other words, how many clay particles are required to fully

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cover a monomer droplet? As a very crude estimate, the coverage can be expressed as a ratio of effective area covered by the clay, $A_{\mathrm{part}}^{\mathrm{cov}}$, and the total area of the oil droplet, A_{oil}. We assume 2D square lateral packing, uniform clay and droplet sizes, clay particle dimensions negligible with respect to size of monomer droplets, and infinite interfacial partitioning coefficient. This then results in

$$\text{coverage} = \frac{A_{\mathrm{part}}^{\mathrm{cov}}}{A_{\mathrm{oil}}} = \frac{4}{3\pi}\left(\frac{w_{\mathrm{part}}}{w_{\mathrm{oil}}}\right)\left(\frac{\rho_{\mathrm{oil}}}{\rho_{\mathrm{part}}}\right)\left(\frac{R_{\mathrm{oil}}}{h}\right) = \frac{4}{3\pi}\left(\frac{0.5}{5.4}\right)\left(\frac{0.909}{2.57}\right)\left(\frac{75}{1}\right) = 1.04$$

with w_{part} and w_{oil} being the amounts of clay and monomer used in g, ρ_{oil} and ρ_{part} being the densities of styrene and Laponite RD in g cm^{-3}, R_{oil} being the radius of the oil droplet in nm, and h being the rim height of the clay pellet in nm. The above estimate indicates that full coverage, and thus an armored or colloidosome structure, is possible under the chosen experimental conditions.

In a typical experiment 0.5 g of Laponite RD was dispersed in 100 mL of a 0.1 M aqueous solution of NaCl using sonication. The pH of the resulting colloidal system had a value in the region of 10. 0.43 g of hexadecane (hydrophobe) and 0.12 g of dimethyl-2,2-azobis(isobutyrate) (V-601: oil-soluble radical initiator) were dissolved in 5.0 g of styrene, and subsequently this was mixed with the clay dispersion. A stable Pickering miniemulsion of submicron Laponite colloidosomes was generated via sonication. The system was degassed by purging with nitrogen gas for 20 min and was subsequently polymerized at 65 °C overnight.

Near quantitative conversion of styrene was achieved. The result was a latex of polystyrene purely stabilized via Pickering stabilization, in other words, armored with Laponite RD clay disks. Upon storage the armored particles would sedimentate within days but could easily be redispersed via agitation. This seems plausible because of the high density of the Laponite clay.

We found that the use of the oil-soluble and nonionic initiator V-601 was essential to obtain stable polymer–clay nanocomposite latexes. The use of both potassium persulfate and 2,2′-azobis(2-amidinopropane) dihydrochloride (V-50) resulted in incomplete conversion and coagulation. Possible explanations could be that initiation from the aqueous phase with an ionic initiator would create surface active oligomers which would interfere and compete with the Pickering stabilization process. Oil phase initiation is preferred as the clay particles at the interface could complicate radical entry and exit events. Furthermore, potential secondary nucleation could be fatal with the restricted adsorption dynamics of the clay Pickering system.

Relatively stable Pickering emulsions were obtained when styrene was replaced by methyl or ethyl methacrylate and when 16.7% of 4-vinylpyridine was added as cationic comonomer. The latter idea was based on the reported synthesis of stable armored latexes with silica particles by Landfester et al.[19] In their case the 4-vinylpyridine promoted partitioning of the silica particles onto/into the polymer and was essential to obtain stable hybrid latexes. However, in our case none of the above systems generated stable latexes after polymerization. All suffered from (partial) coagulation, indicating that aqueous phase polymerization events, which depend on the water solubilities of the respective monomers, should be minimized.

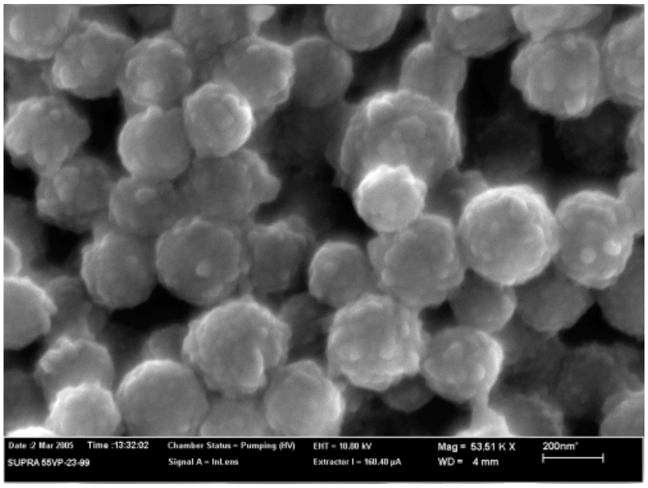

Figure 1. FE-SEM image of Laponite RD armored polystyrene latex. Scale bar indicates 200 nm.

We analyzed the particle morphology and particle size distribution of our Laponite RD armored latexes via FE-SEM and dynamic light scattering (DLS). It should be noted that upon prolonged storage the armored latexes should be kept at pH values of around 10, by storage under an inert atmosphere. The reason is that at lower pH the clay will release cations and decompose.[20] This complicates characterization of the polystyrene-filled colloidosomes. For FE-SEM characterization the NaCl needs to be removed, whereas care must be taken that the clay will not decompose. The best results were obtained when NaCl was removed by dialysis over a short period of time. From Figure 1 the armored structure of the polystyrene–clay composite latex can clearly be observed. Dynamic light scattering measurements performed in a 0.1 M NaCl solution at pH 10 confirmed an average particle size of ca.145 nm with polydispersity indices between 0.08 and 0.12, indicating relatively narrow particle size distributions.

In conclusion, we have successfully prepared polystyrene latex particles with an approximate average diameter of 145 nm, armored with Laponite RD clay particles. They were made via a miniemulsion polymerization process solely using Pickering stabilization. It was shown that aqueous phase polymerization events should be kept to a minimum, since both the use of water-soluble initiators and more polar monomers resulted in partial conversion and coagulation.

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Supporting Information Available: Detailed experimental procedures and an additional FE-SEM image of the Laponite RD clay armored polystyrene latex. This material is available free of charge via the Internet at http://pubs.acs.org.

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