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Pickering Emulsion Polymerization Using Laponite Clay as Stabilizer To Prepare Armored "Soft" Polymer Latexes

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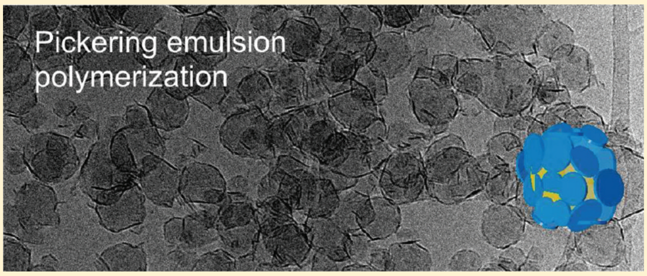
Supporting Information

ABSTRACT: The fabrication of "soft" nanocomposite clay armored polymer latexes is described. Laponite clay XLS is used as stabilizer in the Pickering emulsion polymerization of a variety of monomer mixtures, that is, methyl methacrylate and *n*-butyl acrylate, styrene and *n*-butyl acrylate, and styrene and 2-ethylhexyl acrylate. Overall solids contents of the hybrid latexes in complete absence of coagulation of up to 24 wt % are reported under batch conditions. Key mechanistic aspects of the Pickering emulsion polymerization process are discussed. The use of monomers that have high water solubility and are prone to hydrolyze under basic conditions, for example methyl methacrylate, should be restricted. The use of small amounts of methacrylic acid as auxiliary monomer promotes clay adhesion to the surface of the particles in the Pickering emulsion (co)polymerization of hydrophobic monomers. Detailed kinetic studies at both 60 and 80 °C of the Pickering emulsion copolymerization of styrene and *n*-butyl acrylate (Sty:BA = 0.67 w/w) are reported, with varying amounts of Pickering stabilizer. The Laponite clay discs play a crucial role in the particle formation (nucleation) stage of the Pickering emulsion polymerization process. Use of increasing amounts leads to smaller average particle sizes but inflicts longer nucleation periods, thereby broadening the particle size distributions. We report the occurrence of a catastrophic coagulation phenomenon for Pickering emulsion polymerizations carried out at a low initiator (ammonium persulfate) flux at 60 °C, for a small window of concentrations of Laponite clay discs.



Waterborne nanocomposite polymer colloid formulations are of increasing interest as a base for fabrication of hybrid materials with tailored features of nanoscale dimensional characteristics that enhance material properties and performance.[1−4] A straightforward way to such formulations is to blend colloidal components into a water-based dispersion in which the individuality of the premade colloidal particles is preserved. Orientation of the colloidal components takes place at a subsequent processing or application step, for example during film formation of a waterborne polymer latex coating.[5] A more exotic example following this approach is the fabrication of a nanocomposite open cellular conductive foam to be used as a gas sensor by freeze-drying a mixture of colloidal carbon black, nanoparticles of silica, and a "soft" polymer latex.[6] Whereas a certain extent of spatial control of colloidal components can be achieved in these cases, there is a clear need for better control of nanocomposite morphology. A clear and illustrative example is the impressive enhancement of tack adhesion energy of a waterborne pressure-sensitive adhesive upon addition of a small quantity of "soft" polymer latex particles which are armored with nanosized clay discs.[7] A simple blend of colloidal components did not lead to improvements, showing that the armored hybrid particle morphology was essential. Waterborne "soft" polymer latexes armored with silica or clay particles can form transparent nanocomposite polymer films, with a continuous honeycomb network of the inorganic nanoparticles.[8−10] When we restrict ourselves to binary colloidal systems, ways to achieve armored supracolloidal structures is the assembly of small particles onto a central larger colloidal object, a process traditionally referred to as heterocoagulation.[3]

An interesting strategy toward polymer latexes armored with inorganic nanoparticles is to synthesize the polymer particle *in situ*. Not only does this approach reduce product formulation steps, it also can potentially alleviate the issue of the necessary diluted conditions of traditional heterocoagulation processes. One attractive way to achieve this goal is to make use of Pickering stabilization, the phenomenon that solid particles can adhere to soft interfaces, hereby reducing the overall interfacial energy of the system. Pioneering work in the synthesis of armored polymer colloids through Pickering suspension polymerization was reported by Hohenstein and co-workers in the 1940s.[11,12] This concept was taken up and built upon in the past few years by us and others to fabricate a raft of armored micrometer-sized colloidal structures.[13−18] Miniaturization of this concept to polymerize Pickering stabilized emulsion droplets has led to the development of Pickering miniemulsion polymerization as a tool to fabricate armored nanocomposite polymer latexes of submicrometer

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Table 1. Pickering Emulsion Copolymerizations for Different Ratios of MMA:BA Stabilized by Laponite Clay XLS

sample	MMA/g	BA/g	MMA:*n*-(BA) ratio	Laponite clay/g	water/g	initiator/g	overall monomer content/wt %	clay:monomer/g × g^{-1}
RT-2-40	5.92	2.60	2.28	2.02	227.1	0.11	3.6	0.24
RT-2-41	2.52	5.95	0.42	1.99	221.8	0.11	3.6	0.24
RT-2-42	4.27	4.31	0.99	2.03	223.3	0.12	3.7	0.26
RT-2-43	3.41	5.12	0.67	2.02	224.2	0.11	3.6	0.24

particle size.[19−24] Drawbacks of this technology is that a high shear emulsification step is required to fabricate the small Pickering stabilized monomer droplets. An innovation therefore is to assemble the inorganic nanoparticles onto the forming polymer latex particles, employing a water-based emulsion polymerization process. Armes demonstrated the fabrication of poly(methyl methacrylate)−silica armored nanocomposite particles in aqueous alcoholic media in a single polymerization step without the need for pre-emulsification.[25] They extended their approach to a full waterborne system using a glycerol-modified silica sol as Pickering stabilizer.[26] Sacanna showed the spontaneous emulsification of methacryloxypropyltrimethoxysilane in the presence of silica nanoparticles in water[27] and reported seeded polymerization of methyl methacrylate onto the armored particles.[28] We reported on the Pickering emulsion polymerization using silica nanoparticles in water for a variety of monomers under batch emulsion polymerization conditions[29] and undertook a mechanistic study on the fate of the nanoparticles measuring their concentration in the water phase throughout the Pickering emulsion polymerization process.[30] Bourgeat-Lami and co-workers demonstrated that the use of poly(ethylene glycol) methacrylate as auxiliary comonomer promoted the adhesion of silica nanoparticles in the Pickering emulsion polymerization of styrene.[31] Dos Santos and co-workers used the same auxiliary approach in the Pickering emulsion copolymerization of styrene and *n*-butyl acrylate using Laponite clay discs as stabilizer.[32]

Herein, we report on our studies on the Pickering emulsion copolymerization of a variety of monomer mixtures stabilized by Laponite XLS clay discs. Our strategy was to focus on the preparation of “soft” polymer latexes armored with clay discs for potential use in the coatings, polymer films, and adhesive industries. We take a mechanistic approach to discuss our results in order to shine a further light on the mechanism of Pickering emulsion polymerization.

EXPERIMENTAL PART

Materials. All monomers, methyl methacrylate (MMA), *n*-butyl acrylate (BA), styrene (Sty), methacrylic acid (MA), and 2-ethylhexyl acrylate (2-EHA) were purchased from Aldrich at 99% or greater purity and used as received. Laponite Clay XLS, specific density of $\rho_{clay} = 2.57$ g cm^{-3}, was kindly donated by Rockwood Additives Ltd. Ammonium persulfate (APS, 99+% p.a) and potassium persulfate (KPS, 99+% p.a.) were obtained from Sigma-Aldrich. Deionized water was used in all experiments.

Equipment. Emulsion polymerizations were carried out in double-walled cylindrical glass reactors (250 mL, Asynt Ltd.) equipped with an external circulating heating bath (Julabo F-25 unit), a condenser, and a four-bladed Teflon or metal overhead turbine stirrer fitted at ∼2 cm from the bottom of the reactor vessel (Cowie Ltd.) typically running at 275 rpm. Average particle sizes and dispersities of the armored latexes were measured by dynamic light scattering using a Malvern Zetasizer Nano (data were analyzed using the CONTIN algorithm). Cryo-TEM analyses were performed on a JEOL 2011 TEM (200 KV LaB6) with a 2K Gatan Ultrascan camera or on a JEOL 2010F TEM (200 kV FEG) with a 4K Gatan Ultrascan camera using lacey carbon film grids (300 mesh Cu, Agar Sc. S166-3H). An analytical balance (Precisa XT 220A) was used for gravimetry.

Typical Solids-Stabilized Emulsion Polymerization (for Exact Quantities of All Polymerizations See Table 1−4). Accurately, 2.0 g of Laponite Clay XLS was dispersed in 200.0 g of deionized water in a 250 mL double-walled glass reactor and placed under a nitrogen atmosphere by purging for 15 min. Degassed monomer, 20.0 g (10.0 wt %), was added. After 5 min, the reaction mixture was heated to 60 °C, while stirring at 275 rpm. The emulsion polymerization was started upon addition of 0.13 g of APS dissolved in 2.0 g of water. Monomer conversion was monitored via gravimetry by taking samples of ∼2.0 g using a syringe.

Typical Solids-Stabilized Cryo-TEM Measurements. Cryo-TEM specimens were prepared by quench freezing one sample droplet on a lacey carbon film grid (300 mesh Cu, Agar Sc. S166-3H) in liquid ethane using a controlled humidity chamber.[33] The specimens were then mounted in dedicated cartridges for use in a JEOL 2011 TEM (200 kV LaB6) with a 2K Gatan Ultrascan camera or on a JEOL 2010F TEM (200 kV FEG) with a 4K Gatan Ultrascan. The specimens were observed in an environment cooled with liquid nitrogen.

RESULTS AND DISCUSSION

The aim of this study was to investigate the Pickering emulsion copolymerization of mixtures of monomers, that is, styrene/*n*-butyl acrylate, methyl methacrylate/*n*-butyl acrylate, and styrene/2-ethylhexyl methacrylate, using Laponite XLS clay discs as stabilizer. The reason for these combinations of monomers is to tailor the predicted glass transition temperature of the copolymer to be below room temperature to allow for film formation under ambient conditions (using the Fox equation to calculate a predictive value for T_g or an improved estimate taking into account hydroplastization as reported by Tsavalas and Sundberg[34]). This would allow for easy fabrication of waterborne nanocomposite polymer films with potentially interesting mechanical and physical properties.[9,10] In our previous studies on Pickering emulsion polymerization we used spherical nanoparticles of silica (Ludox). Conceptually, we were interested in replacing these spherical nanoparticles with Laponite, as the clay nanoparticles are of different geometry. Laponite clay XLS are disc-shaped crystals of specific density of $\rho_{clay} = 2.57$ g cm^{-3}, lateral diameter of ca. 25 nm, and ∼0.92 nm in thickness (h).[35,36] Laponite clay XLS is a synthetic layered silicate with low heavy metal content which contains a small quantity of blended tetrasodium pyrophosphate. The added tetrasodium pyrophosphate allows for easy sol formation, preserving a relatively low overall viscosity as the pyrophosphate anions associate onto the positively charged edges of the Laponite clay disc, inducing charge inversion. The difference in geometry of the Laponite clay discs with respect to spherical nanoparticles of silica (Ludox TM40 with $R = 12.03$ nm and $\rho_{silica} = 1.75$ g cm^{-3}),[21,30] and hence the difference in surface-to-volume ratio being $(3/R)$ for a

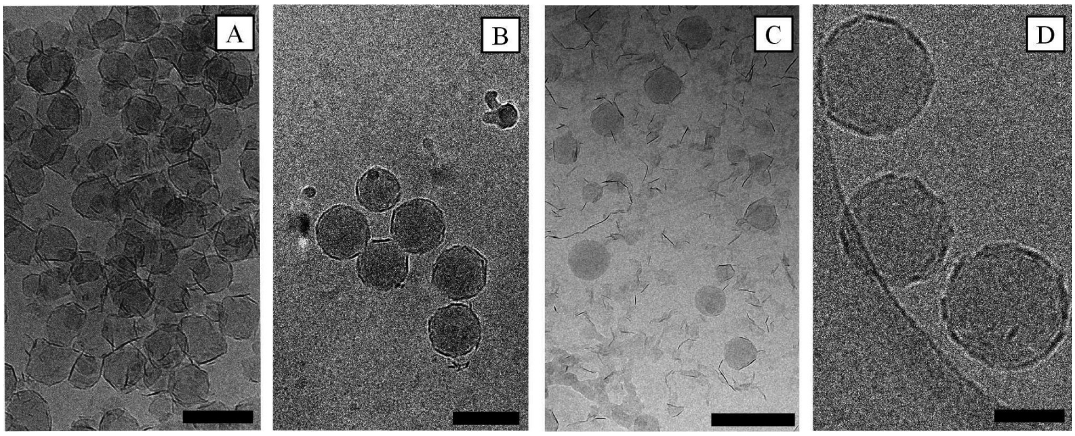

Figure 1. Cryo-TEM images of polymer latex particles: (A) poly(MMA-*co*-*n*-(BA)/Laponite, (B) poly(Sty-*co*-BA)/Laponite, (C) poly(Sty-*co*-2-EHA)/Laponite, (D) poly(Sty-*co*-2-EHA)/Laponite with methacrylic acid. Scales bars of 100, 100, 200, and 50 nm, respectively.

sphere and $(2/h)$ for a clay disc, allows for a marked reduction in the total amount required to fabricate armored hybrid polymer latex particles and nanocomposite coatings and films thereof (this despite the countereffect of the difference in densities between the two different inorganic nanoparticles).

In our previous works on Pickering emulsion polymerization using silica nanoparticles as stabilizer, we discussed that the mechanism for formation of the armored particles involved heterocoagulation between a growing latex particle and inorganic nanoparticles.[29,30] In this process the inorganic nanoparticle effectively adheres onto the surface of the growing polymer latex particle. The strength of this adhesion undoubtedly relies on the chemical nature of the polymer particle. We therefore wanted to establish first what polymer composition of the growing latex particles would warrant successful heterocoagulation throughout the Pickering emulsion polymerization process. In other words, to which particles would the Laponite clay discs adhere successfully? From our studies using Ludox silica nanoparticles in which we monitored the concentration of nanoparticles in the water phase throughout the Pickering emulsion polymerization process, we found that there had to be sufficient affinity between the hydrophilic silica-based surface of the nanoparticle and the surface composition of the latex particle. The surface of the latex particle had to be relatively hydrophilic. Pickering emulsion polymerizations of hydrophobic monomers such as vinyl pivalate,[30] *n*-butyl methacrylate, and styrene[29] resulted in stable effectively "bare" latexes, not having the targeted armored structure. In the Pickering emulsion polymerizations of more hydrophilic monomers, such as methyl or ethyl methacrylate and vinyl acetate, it was essential to lower the pH of the water phase. All Pickering emulsion polymerizations carried out with methyl methacrylate at pH 8−10 resulted in coagulation, the coagulum showing a mixture of "bare" latex particles and silica nanoparticles. Lowering the pH of Laponite sols to pH 5.5 or less unfortunately is not an option as the clay sol gels after about 20 min at room temperature. Pickering emulsion polymerizations in the presence of Laponite XLS without adjustment of the pH, and thus under basic conditions, of vinyl acetate and methyl methacrylate at a monomer-to-water ratio of 0.1 w/w, and a clay-to-monomer ratio of 0.1 w/w at 60 °C using 0.13 g of ammonium persulfate as initiator, resulted in complete microcoagulation. A potential reason is the substantial hydrolysis of the monomer throughout the polymerization process, as the water solubility of both these monomers is high in conjunction with the methyl and acetate moieties being good leaving groups for base-catalyzed hydrolysis. The logic of this is strengthened in that Pickering emulsion polymerization of ethyl methacrylate and *n*-butyl methacrylate using Laponite XLS clay discs as stabilizer under these conditions were successful. It therefore is important to restrict the use of monomers which have a relatively high water solubility and that can easily be hydrolyzed in water under basic conditions. This is further emphasized by our series of experiments in which we carried out the Pickering emulsion copolymerization of methyl methacrylate and *n*-butyl acrylate (Table 1). We had to reduce the monomer-to-water ratio to values of ∼0.038 w/w as all reactions carried out at higher ratios led to coagulation. Under these diluted conditions the ratio of MMA:BA was varied being 0.42, 0.67, 0.99, and 2.28 w/w. Only the two reactions with the lowest relative amount of MMA were successful, with MMA:BA of 0.42 and 0.67. Figure 1A shows a cryo-TEM image for the armored polymer latex obtained by Pickering emulsion copolymerization of an MMA:BA ratio of 0.67. It is clear from this image that the Laponite clay discs are adhered to the surface of the "soft" latex particles. The overall rate of polymerization was the highest for the reaction with the higher amount of MMA. Average values for the particle sizes are of the same order of magnitude (see Supporting Information for monomer conversion vs time plots and average particle diameter and dispersity vs monomer conversion). Initially, this result seems counterintuitive as the rate coefficient of propagation of BA is markedly higher than that of MMA. The reason for the lower rate of polymerization in the BA-rich Pickering emulsion polymerization is the result of diffusion limitation of monomer transport through the water phase and thus monomer entry into the latex particles.[37]

The issues and polymerization restrictions faced with using MMA led us to investigate alternative monomer combinations, replacing MMA with styrene. Pickering emulsion copolymerization of styrene and *n*-butyl acrylate (Sty:BA = 0.67 w/w) were successful up to 24 wt % overall solids under batch conditions at 80 °C (200.0 g of water, 60.0 g of monomer, 2.00 g of clay, 0.13 g of APS), all leading to the formation of the targeted Laponite clay armored "soft" polymer latex particles (see Figure 1B for a cryo-TEM image). Polymerizations at higher amounts of monomer at overall solids of 28, 33, and 40% keeping the quantities of water, clay, and initiator the same led to increasing amounts of coagulum, ca. 10%, 25%, and 50%, respectively.

Table 2. Pickering Emulsion Copolymerizations of Various Monomers Stabilized by Laponite Clay XLS[a]

sample	monomers	Mo_1	Mo_2	Laponite clay/g	water/g	initiator/g	overall monomer content/wt %	clay:monomer/g × g^{-1}
RT-2-44	Sty + BA	8.00	12.01	2.01	200.0	0.14	9.0	0.10
RT-2-25	MMA + BA	3.36	5.16	2.02	219.9	0.13	3.7	0.24
RT-2-21	Sty + 2-EHA	8.08	12.16	2.07	202.5	0.13	9.0	0.10

[a] The reaction RT-2-21, additional amounts of 0.21 of MA and 0.19 of β-cyclodextrin were added.

Table 3. Pickering Emulsion Copolymerizations of Sty:BA Using Different Amounts of Laponite Clay XLS at 80 °C

sample	Sty/g	BA/g	Sty:*n*-(BA) ratio	Laponite clay/g	water/g	initiator/g	overall monomer content/wt %	clay:monomer/g × g^{-1}	clay:water/mg/g
RT-2-50	8.41	13.65	0.61	2.08	207.1	0.14	9.5	0.0940	10.04
RT-2-52	8.16	13.18	0.62	1.04	204.9	0.14	9.4	0.0490	5.08
RT-2-51	8.37	12.59	0.66	0.52	201.7	0.14	9.4	0.0250	2.58
RT-2-54	8.34	12.5	0.67	0.22	204.0	0.14	9.3	0.0110	1.08
RT-2-56	8.12	12.13	0.67	0.14	204.3	0.14	9.0	0.0068	0.69
RT-2-55	8.27	12.06	0.69	0.078	202.8	0.13	9.1	0.0038	0.38
RT-2-57	8.55	12.65	0.68	0.046	207.8	0.13	9.2	0.0022	0.22
RT-2-53	8.29	12.35	0.67	0	206.3	0.14	9.1	0	0

The Pickering emulsion copolymerization of styrene and 2-ethylhexyl acrylate (Sty:EHA = 0.67 w/w) was briefly investigated at 60 °C. As observed also in the Pickering emulsion polymerizations stabilized with Ludox silica nanospheres,[29,30] these hydrophobic monomers did not lead to substantial adhesion of the clay platelets on the surface of the particles. This is clearly evident from the cryo-TEM analysis (Figure 1C), which shows that the majority of latex particles do not have any clay discs stuck onto their surface. To overcome this restriction and promote adhesion onto the surface of the latex particles, a small amount of methacrylic acid (1.04 wt % based on total amount of monomer) was added as functional hydrophilic comonomer, as part of the Pickering emulsion polymerization recipe. Cryo-TEM analysis now undoubtedly shows the desired clay armored supracolloidal morphology (see Figure 1D). This approach is in line with the one reported by Bourgeat-Lami, who employed poly(ethylene glycol) methacrylate as auxiliary monomer to promote the adhesion of Pickering stabilizers in the emulsion polymerization of styrene.[31] To facilitate transport of the hydrophobic monomers through the water phase during the Pickering emulsion polymerization process, β-cyclodextrin was used as a carrier.[38,39] Auxiliary monomers, such as poly(ethylene glycol) methacrylate and methacrylic acid, may promote adhesion of clays (and other silicates and metal oxides) through hydrogen bond interaction. On the other hand, the depth of the energy well as accomplished through minimization of the total interfacial free energy (following the classical description of Pickering stabilization) potentially is lowered as the interfacial tension between the latex particle and the water drops substantially when higher amounts of these hydrophilic monomers are used. Note that *in situ* hydrolysis of monomer (see before in case of Laponite clay stabilized Pickering emulsion polymerizations using MMA) or polymer during or after polymerization can also contribute in changing the chemical composition of the surface of the latex particles. The obvious unanswered question that remains is how much of these auxiliary monomers or better functional auxiliary surface functional groups is needed to optimize the fabrication of the armored nanocomposite latexes? This is something we would like to address in future studies.

Next we wanted to investigate whether the heterocoagulation process not only occurred during the growth stage of the polymer latex particles but also if it played a role in the nucleation phase of the Pickering emulsion polymerization process, as we suggested in our earlier work.[29] If affirmative, varying the amount of Laponite clay would have a pronounced effect on the particle size distribution of the hybrid latexes obtained by the Pickering emulsion polymerization process. We previously demonstrated that in the case of Pickering miniemulsion polymerizations indeed the particle size distribution was influenced by the total amount of Laponite clay used and that the average particle size could be predicted theoretically.[20] To probe the effect of the amount of Laponite clay discs used in Pickering emulsion polymerization, we carried out two series of copolymerizations of styrene and *n*-butyl acrylate, at Sty:BA ratio of ca. 0.67, at both 60 and 80 °C in which we varied the relative amounts of Laponite clay. For the clarity of the discussion of the results we will first address the reactions performed at 80 °C.

Figure 2 displays the results of overall monomer conversion, X_M, as a function of time as measured using gravimetry (for the data see Supporting Information). From a qualitative viewpoint the overall rate of polymerization (obtained from the first derivative of this plot) is increased when larger amounts of clay are employed as Pickering stabilizer, though the effect was not large. The enhancement in overall polymerization rate upon increasing amounts of clay suggests an increase in the total amount of particles, and hence smaller particles at the same value for X_M, as the rate in emulsion polymerization systems is proportional to the total amount of particles, as a direct result of compartmentalization.

The average particle diameter, d_z, and the corresponding dispersity of the particle size distribution, D, were measured by dynamic light scattering (DLS) as a function of monomer conversion (X_M) (see Figures 3 and 4, respectively). Substantial effects of varying the amount of Laponite XLS clay as Pickering stabilizer were found.

Use of relatively small amounts of clay already led to marked reductions in the particle diameters; in other words, addition of clay as Pickering stabilizer led to a greater number of latex

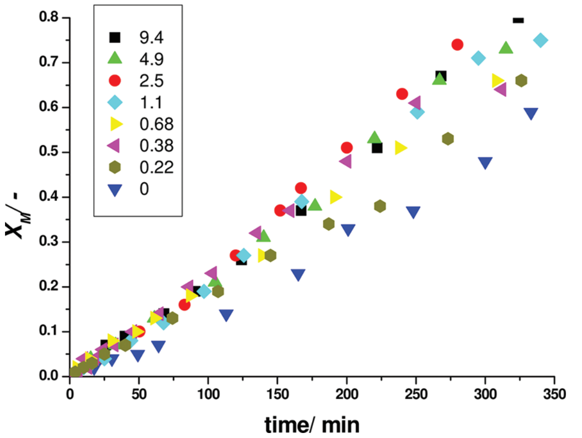

Figure 2. Overall monomer conversion, X_M, vs time for Pickering emulsion copolymerizations of styrene and *n*-butyl acrylate (at Sty:BA weight ratio of ca. 0.67) at 80 °C for varying amounts of Laponite XLS clay discs used as Pickering stabilizer (clay:monomer weight ratios ($\times 10^2$) of 9.4, 4.9, 2.5, 1.1, 0.68, 0.38, 0.22, and 0).

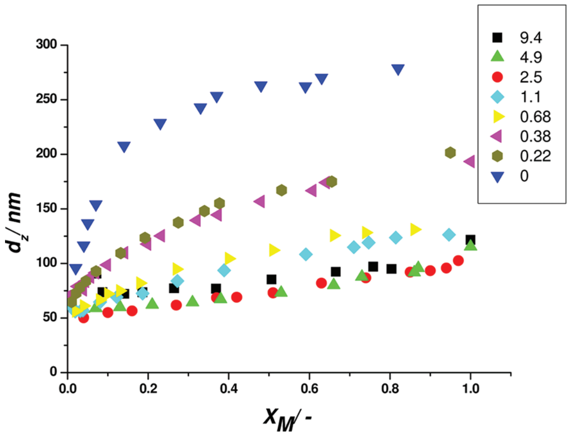

Figure 3. Average particle size diameter, d_z, vs overall monomer conversion, X_M, measured with dynamic light scattering (DLS) throughout the Pickering emulsion copolymerization of styrene and *n*-butyl acrylate (at Sty:BA weight ratio of ca. 0.67) at 80 °C for varying amounts of Laponite XLS clay discs used as Pickering stabilizer (clay:monomer weight ratios ($\times 10^2$) of 9.4, 4.9, 2.5, 1.1, 0.68, 0.38, 0.22, and 0).

particles. This not only supports the results found on the increase in overall polymerization rates upon increase of the amounts of Pickering stabilizer (see Figure 3), but also it is clear evidence that clay plays an important role in the particle formation stage of the Pickering emulsion polymerization process. Two important observations can be made from Figures 3 and 4. One is that reduction in particle size upon increase of the amounts of Laponite clay as Pickering stabilizer does not correlate in a straightforward manner. This becomes more evident when we plot the final average particle size of the polymer latexes as a function of the weight ratio of clay:monomer (see Figure 5). From this figure it is apparent that the influence of the amounts of clay used on the average particle size phases out rapidly to a approximate lower values of 120 nm (0.094 of clay:monomer weight ratio). From Figure 4 it can be observed that the dispersity of the particle size distributions increases upon greater amounts of clay as Pickering stabilizer used in the emulsion polymerizations.

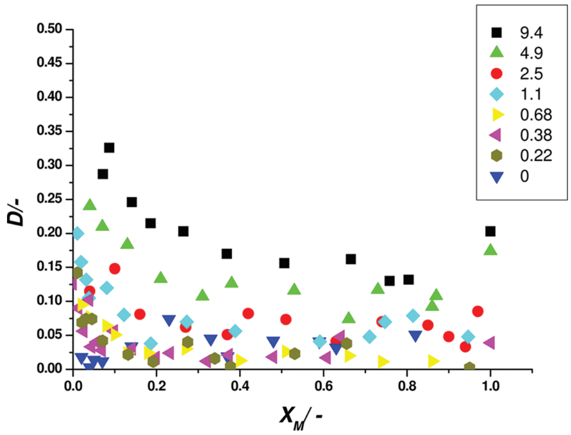

Figure 4. Dispersity of the particle size distributions, *D*, vs overall monomer conversion, X_M, measured with dynamic light scattering (DLS) throughout the Pickering emulsion copolymerization of styrene and *n*-butyl acrylate (at Sty:BA weight ratio of ca. 0.67) at 80 °C for varying amounts of Laponite XLS clay discs used as Pickering stabilizer (clay:monomer weight ratios ($\times 10^2$) of 9.4, 4.9, 2.5, 1.1, 0.68, 0.38, 0.22, and 0).

The values for *D* gradually decrease upon increase in X_M, which is logical. The increase in values for *D* upon increasing the amount of clay Pickering stabilizer suggests a prolongation of the nucleation period (particle formation) in these emulsion polymerization reactions. This is plausible as a greater number of Pickering nanoparticles in the water phase would lead to an increase in probability for the events of heterocoagulation of a clay disc with a precipitating oligomer of critical chain length from the water phase or with a colloidally unstable primary latex particle. If we would assume a short nucleation period leading to rapid formation of a stable and constant number of growing latex particles, plotting the data of Figure 3 as d_z^3 vs X_M must show a linear behavior. Figure 6 clearly shows this is the case (up to intermediate values for X_M) for the emulsion copolymerizations in the absence of clay and those with a weight ratio of clay: monomer of 0.0022 and 0.0038. Looking more closely at the data convex deviations are found for Pickering emulsion polymerizations operated at higher amounts of Laponite clay. Continuous generation of particles leads to a slower growth rate per particle. The particle formation process slows down and eventually ceases, which does explain the convex trend observed for d_z^3 vs X_M. From Figure 6 it can be seen that this behavior extends to higher values of X_M when more Laponite clay discs are used as Pickering stabilizer. This reaffirms that indeed longer nucleation periods occur in Pickering emulsion polymerizations using larger amounts of Laponite clay as stabilizer, with broader particle size distributions of the latexes as a consequence (as observed in Figure 4).

One question we could ask is, how much Laponite clay discs remain in the water phase after the armored polymer latexes have been fabricated? Whereas for Pickering stabilizers such as Ludox silica nanospheres this can be measured directly through quantitative disc centrifugation,[30] this technique was unfortunately not successful for clay nanodiscs because the clay discs did not have sufficient gravitational drag. Nevertheless, we can get an idea by taking the ratio of the total effective surface area provided by the laponite clay discs (assuming monodisperse discs and a square packing geometry) and the total surface area of the latex particles

Table 4. Pickering Emulsion Copolymerizations of Sty:BA Using Different Amounts of Laponite Clay XLS at 60 °C

sample	Sty/g	BA/g	Sty:*n*-(BA) ratio	Laponite clay/g	water/g	initiator/g	overall monomer content/wt %	clay:monomer/g × g^{-1}	clay:water/mg/g
HM-1	8.05	12.05	0.67	0	198.4	0.14	9.2	0	0
HM-2	8.05	12.07	0.67	0.10	199.0	0.14	9.2	0.0040	0.50
HM-3	8.02	12.09	0.66	0.20	199.0	0.14	9.2	0.0090	1.01
HM-4	8.05	12.00	0.67	0.50	198.5	0.14	9.1	0.0250	2.52
HM-5	8.05	12.01	0.67	0.70	198.2	0.14	9.2	0.0350	3.53
HM-6	8.06	12.01	0.67	1.00	198.4	0.14	9.1	0.0498	5.04
HM-7	8.00	12.10	0.66	2.00	199.0	0.14	9.1	0.0994	10.05

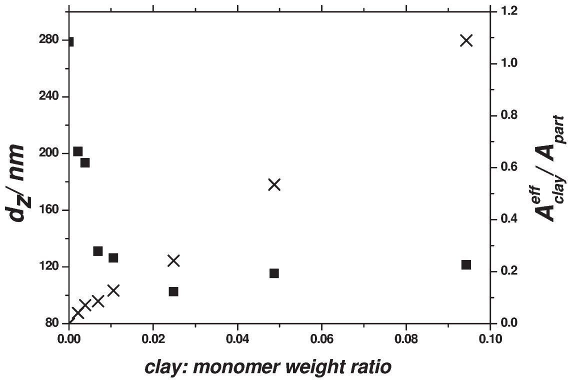

Figure 5. Average particle size d_z and ratio of the total effective surface area provided by the laponite clay discs and the total surface area of the polymer latexes vs the weight ratio of clay:monomer for the Pickering emulsion copolymerization of styrene and *n*-butyl acrylate (at Sty:BA weight ratio of ca. 0.67) at 80 °C for varying amounts of Laponite XLS clay discs used as Pickering stabilizer (clay:monomer weight ratios (×10^2) of 9.4, 4.9, 2.5, 1.1, 0.68, 0.38, 0.22, and 0).

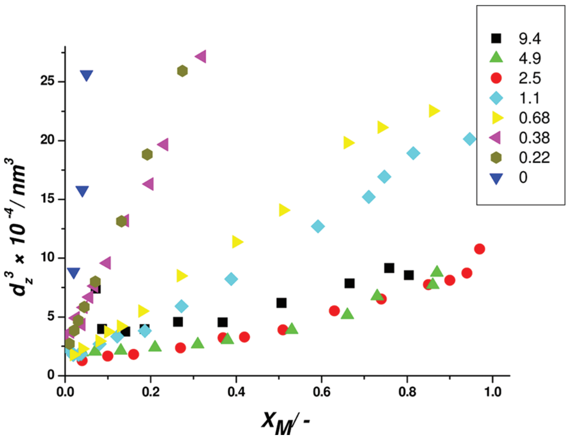

Figure 6. d_z^3 vs X_M measured with dynamic light scattering (DLS) throughout the Pickering emulsion copolymerization of styrene and *n*-butyl acrylate (at Sty:BA weight ratio of ca. 0.67) at 80 °C for varying amounts of Laponite XLS clay discs used as Pickering stabilizer (clay: monomer weight ratios (×10^2) of 9.4, 4.9, 2.5, 1.1, 0.68, 0.38, 0.22, and 0).

made (assuming monodisperse spherical particles). This ratio can be calculated from[20]

$$\frac{A_{clay}^{eff}}{A_{part}} = \frac{2}{3\pi}\left(\frac{d_z}{h}\right)\left(\frac{m_{clay}}{m_{pol}}\right)\left(\frac{\rho_{pol}}{\rho_{clay}}\right)$$

We further assume hereby complete conversion of monomer so that $m_{pol} = m_{Sty} + m_{BA}$ and use a value of 1.06 g cm^{-3} for the density of the copolymer. The values of the surface ratios are plotted in Figure 5. From this graph it can be seen that complete armored structure of the hybrid polymer "soft" latexes is achieved at a first approximate value of 0.08 for the clay:monomer weight ratio. Use of higher weight ratios will lead to excess of Laponite clay discs in the water phase. Substantial excess amounts of clay in the water phase are undesirable as it could have a detrimental effect on the properties of polymer films made from the armored latexes, such as lower transparency, increased brittleness, and cracking.

Pickering emulsion copolymerizations of styrene and *n*-butyl acrylate (at Sty:BA weight ratio of ca. 0.67) at 60 °C using various amounts of Laponite XLS clay discs used as Pickering stabilizer (clay:monomer weight ratios (×10^2) of 0.4, 0.9, 2.5, 3.5, 5.0, and 9.9) showed in general similar behavior in that faster polymerization rates were observed, with smaller particle sizes and broader dispersities in particle size distributions, upon increasing amounts of Laponite clay used (for X_M vs time data see Supporting Information). There was, however, one drastic difference. This becomes apparent from the average particle diameter, d_z, and the corresponding dispersity of the particle size distribution, *D*, data as measured measured by dynamic light scattering (DLS) as a function of monomer conversion (X_M) (see Figures 7 and 8, respectively).

When intermediate amounts of clay were used, that is, clay: monomer weight ratios of 0.009 and 0.025, colloidal instabilities during the emulsion polymerization process occurred. In the latter case this lead to full coagulation of the reaction at an onset of ∼40% overall monomer conversion. From Figure 7 this is seen as a rapid increase in the average measured values of d_z. The case of 0.009 is more interesting. Limited coagulation throughout the early stages of polymerization was observed up to ∼30% monomer conversion, after which the system regained colloidal stability. In Figure 7, this is reflected by the initial higher values for d_z than would be expected, on the basis of the data obtained for the experiment in the case the lower 0.004 value for the clay: monomer ratio. After regaining colloidal stability the particle growth proceeds as normal, with a final value of d_z in line with the other stable Pickering emulsion polymerizations. From the dispersity data of the particle size distributions as a function of monomer conversion (Figure 8) an increase in *D* can indeed be observed up to ∼30% monomer conversion which falls in line with partial coagulation of the growing latex particles. After colloidal stability is recuperated values for *D* drop, as expected.

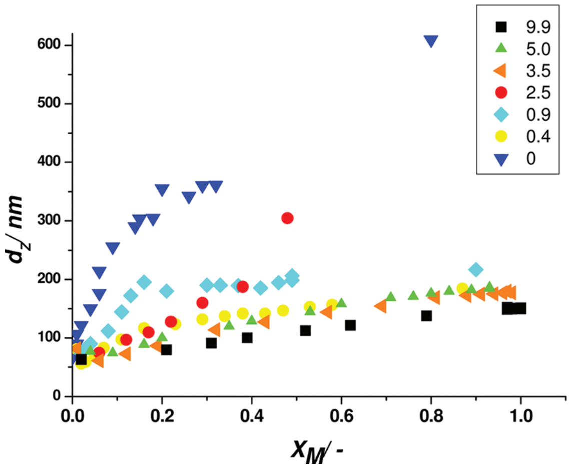

Figure 7. Average particle size diameter, d_z, vs overall monomer conversion, X_M, measured with dynamic light scattering (DLS) throughout the Pickering emulsion copolymerization of styrene and *n*-butyl acrylate (at Sty:BA weight ratio of ca. 0.67) at 60 °C for varying amounts of Laponite XLS clay discs used as Pickering stabilizer (clay:monomer weight ratios ($\times 10^2$) of 0.4, 0.9, 2.5, 3.5, 5.0, and 9.9).

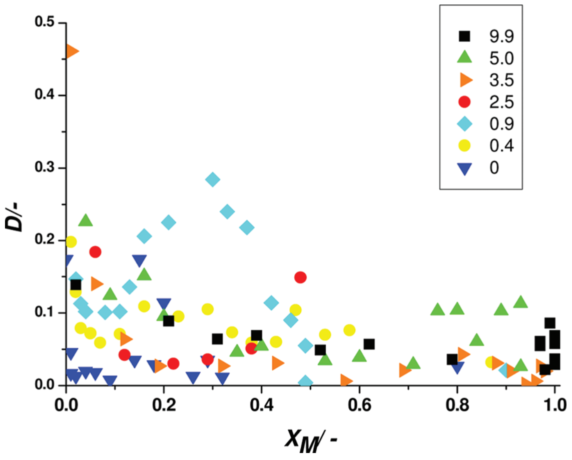

Figure 8. Dispersity of the particle size distributions, *D*, vs overall monomer conversion, X_M, measured with dynamic light scattering (DLS) throughout the Pickering emulsion copolymerization of styrene and *n*-butyl acrylate (at Sty:BA weight ratio of ca. 0.67) at 60 °C for varying amounts of Laponite XLS clay discs used as Pickering stabilizer (clay:monomer weight ratios ($\times 10^2$) of 0.4, 0.9, 2.5, 3.5, 5.0, and 9.9).

At the current stage we do not have a detailed explanation for the exact nature of this rather catastrophic colloidal instability in these Pickering emulsion polymerizations. What we do know is that the average particle sizes get influenced greatly by using Laponite clay, and not correlate clearly with the initiator concentration and decomposition, as known for traditional emulsion polymerizations. The flux of radicals generated at 60 °C is about 16−20 times smaller than that at 80 °C.[40,41] It could be that the number of initiator-derived hydrophilic end groups, that is, sulfate and hydroxy groups, linked to polymer chains plays a crucial role in providing sufficient colloidal stability. When a particle grows and creates additional hydrophobic surface, it can either gain stability through entry of such an end-capped growing oligomer, through heterocoagulation with a Laponite clay disc serving as Pickering stabilizer, or through coagulation with another growing latex particle. A fine balance exists between these events, and one can envisage that indeed for certain experiments with a low initiator flux and not high concentrations of Laponite clay discs colloidal instabilities can arise. This indeed falls in line with our observations from all our experiments. To test this hypothesis, we carried out two additional Pickering emulsion copolymerizations at clay:monomer weight ratio of 0.025 at increased initiator radical flux. In the first we used 5 times the amount of initiator; in the second we fed a 1 mol equiv of sodium metabisulfite in relation to the amount of ammonium persulfate during the first hour of polymerization. Both polymerizations lead to a reduction in the catastrophic coagulation phenomenon, both showing microcoagulation (the system remained liquid). This indicates that optimization of the initiator flux potentially may alleviate the problem.

■ CONCLUSION

In this paper, we have shown that hybrid "soft" polymer latexes armored with Laponite XLS clay discs can be prepared by Pickering emulsion polymerization using a variety of monomer mixtures. We highlighted that it was important to restrict the use of monomers which have a relatively high water solubility and which can easily be hydrolyzed in water under basic conditions, such as methyl methacrylate. We showed that when hydrophobic monomers are selected, such as in the case of the copolymerization of styrene and 2-ethylhexyl acrylate, the use of small amounts of methacrylic acid as auxiliary monomer promotes clay adhesion to the surface of the particles. In our detailed mechanistic studies of the pickering emulsion copolymerization of styrene and *n*-butyl acrylate (Sty:BA = 0.67 w/w) we showed that overall solids contents of 24 wt % could easily be achieved under batch conditions. We demonstrated that Laponite clay discs as Pickering stabilization played a crucial role in the particle formation (nucleation) stage of the Pickering emulsion polymerization process. Use of increasing amounts of Pickering stabilizer led to smaller average particle sizes but inflicted longer nucleation periods, hereby broadening the particle size distributions. Finally, we showed that the fine balance which exists between events occurring in the nucleation period could lead to catastrophic colloidal instabilities and thus coagulation for Pickering emulsion polymerizations for a small window of concentrations of Laponite clay discs when carried out at a low initiator flux.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Details on monomer conversion vs time and particle size distribution for the Pickering emulsion copolymerizations of methyl methacrylate and *n*-butyl acrylate; all kinetic raw data for the Pickering emulsion copolymerizations of styrene and *n*-butyl acrylate. This material is available free of charge via the Internet at http://pubs.acs.org.

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