

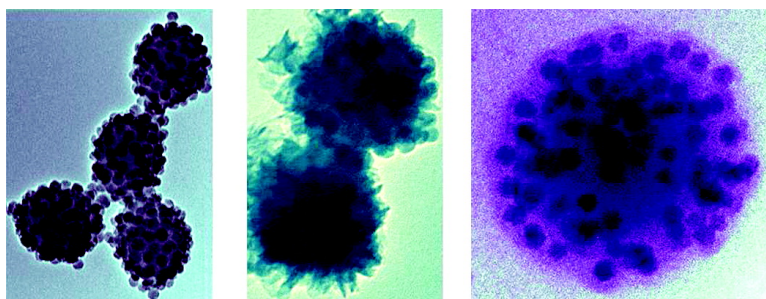
Communication

Multilayered Nanocomposite Polymer Colloids Using Emulsion Polymerization Stabilized by Solid Particles

Patrick J. Colver, Catheline A. L. Colard, and Stefan A. F. Bon

J. Am. Chem. Soc., **2008**, 130 (50), 16850-16851 • DOI: 10.1021/ja807242k • Publication Date (Web): 20 November 2008

Downloaded from <http://pubs.acs.org> on February 8, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



ACS Publications
High quality. High impact.

Multilayered Nanocomposite Polymer Colloids Using Emulsion Polymerization Stabilized by Solid Particles

Patrick J. Colver, Catheline A. L. Colard, and Stefan A. F. Bon*

Department of Chemistry, University of Warwick, Coventry, CV4 7AL, U.K.

Received September 12, 2008; E-mail: S.Bon@warwick.ac.uk

We report an emulsion polymerization process in which colloidal stability is provided by nanosized solid particles that adhere to the surface of the polymer colloids, thereby replacing the role of surfactants. This results in polymer latexes which are armored with a layer of nanoparticles. We show the easy transformation into multilayered nanocomposite polymer colloids by using a conventional second emulsion polymerization step.

Emulsion polymerizations have led to fascinating colloidal structures, such as core-shell¹ and hollow latexes,² or peanut³ and multilobbed particles.⁴ Miniemulsion polymerization, a variant in which monomer droplets play a key role in particle nucleation, has led to a vast array of composite latexes encapsulating materials, such as semiconducting polymers.⁵

One interesting class of nanocomposite polymer latexes is those with morphologies that are armored or multilayered in nature. These potentially have great performance benefits when applied in waterborne coatings and adhesives, for example on scratch resistance. These complex composite colloids, however, are not easily made. Vogt et al.⁶ and later Caruso et al.⁷ reported the fabrication of hollow multilayered capsules using a layer-by-layer approach, an extension of the heterocoagulation method to create armored structures.⁸ Disadvantages are that these methods are time-consuming and require dilute conditions. Armes et al. described the synthesis of poly(methyl methacrylate)-silica nanocomposite particles in aqueous alcoholic media using silica nanoparticles as stabilizer,⁹ recently extending this method to operate in water using a glycerol-modified silica sol.¹⁰ Sacanna showed that methacryloxypropyltrimethoxysilane, in the presence of nanosized silica led to spontaneous emulsification in water,¹¹ which upon a two-step polymerization procedure afforded armored particles with an outer shell of poly(methyl methacrylate).¹² Müller reported the use of Janus-type polymer particles as stabilizers in emulsion polymerization.¹³

We previously showed that when we replaced conventional surfactants with nanosized Laponite clay discs we could fabricate clay-armored polymer latexes via a Pickering miniemulsion polymerization method.^{14,15} Pickering stabilization, the process by which solid particles stabilize the interface between two immiscible liquids or the surface of bubbles, has been known for over a century.^{16,17} A recent surge in interest has led to the production of a vast range of supracolloidal materials.^{11,18–22} While versatile, our Pickering miniemulsion polymerizations do show some limitations. First a high shear emulsification step is required to generate the emulsion droplets, a step undesirable for industrial scale-up. Second, an excess of solid stabilizers remains in the continuous phase after polymerization, which in combination with the restriction to use oil-soluble initiators, will invoke colloidal stability issues in multistep polymerization procedures needed to manufacture multilayered particles. Our newly reported solids-stabilized, or Pickering, emulsion polymerization process overcomes these problems.

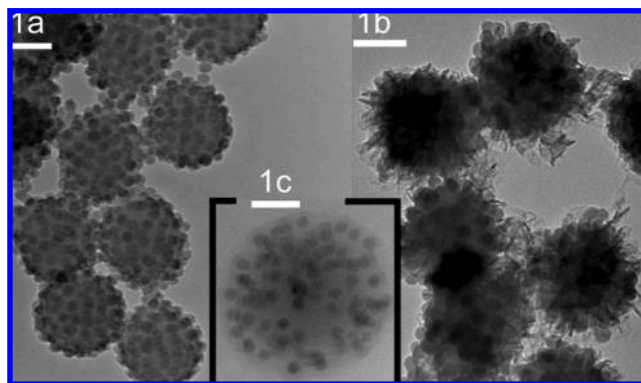


Figure 1. TEM images (scale bar = 100 nm) of (a) poly(methyl methacrylate) latex armored with silica nanoparticles obtained by Pickering emulsion polymerization. Multilayered nanocomposite polymer colloids with (b) a “hairy” outer-layer of poly(acrylonitrile) and (c) a soft shell of poly(*n*-butyl acrylate).

We performed various series of soap-free emulsion polymerizations in the presence of silica nanoparticles of approximately 25 nm in diameter (Ludox TM-40). All reactions were carried out at 65 °C using 1.85 mM potassium persulfate as initiator, thereby providing a low and steady flux of radicals (see Supporting Information). In our first series we used methyl methacrylate as monomer at a monomer-to-water ratio (*v:v*) of 0.13 and we varied the pH of the water, that is, 10.0, 5.5, and 3.0, to influence the surface charge densities of the growing latex particles and the silica nanoparticles. Emulsion polymerizations carried out at pH 10.0 led to full coagulation. SEM analysis of the coagulum showed bare polymer latex particles, thereby indicating that no adhesion had taken place (Figure S3). At pH 3.0 a seemingly stable latex was obtained. Dynamic light scattering, however, showed a broad particle size distribution with micrometer-sized averages, indicating that some coagulation on a microscopic scale had occurred. This is plausible as electrostatic stabilization through charge repulsion at this low pH is insufficient. Nevertheless, SEM analysis showed a closely packed armored layer of silica particles present on the polymer latex particles (Figure S2). At pH 5.5 stable armored polymer latexes with narrow particle size distributions were obtained (Figures 1a and S4). Noteworthy is that the silica nanoparticles are slightly separated on the surface as a direct result of electrostatic repulsion. All further experiments were performed at pH 5.5.

We varied the amount of silica nanoparticles, using Ludox sol-to-monomer volumetric ratios of 0.67, 0.83, 1.00, and 1.25, to investigate if we could control the particle size of the latexes obtained. All emulsion polymerizations led to stable armored latexes with narrow particle-size distributions (PDI (DLS) < 0.074), but with limited control of the average particle diameter (see Table S1). At Ludox sol-to-monomer volumetric ratios of 0.5 and less, all experiments failed and led to full coagulation.

We also tried to maximize the overall solids content of our Pickering emulsion polymerizations carried out under batch conditions. We used monomer-to-water ratios of 0.14, 0.33, and 0.97 with fixed Ludox sol-to-monomer volumetric ratios of 1.0. Stable armored latexes were obtained in all cases, the latter conditions reaching an overall solids content of 45 wt %.

In our final series we employed different monomers: ethyl methacrylate, *n*-butyl methacrylate, and styrene. This was done to investigate if the interfacial tension between monomer and water played a role. Reactions were performed at a monomer-to-water (v:v) ratio of 0.05, with a fixed Ludox sol-to-monomer volumetric ratio of 1.0. All emulsion polymerizations were successful. However, SEM analysis showed that in the case of *n*-butyl methacrylate and styrene no particles were present at the surface of the latex spheres (Figures S5–S7), and that the obtained particle sizes were substantially larger (Table S1).

On the basis of our results we would like to propose the following mechanistic events for emulsion polymerizations stabilized by solid particles. In conventional soap-free emulsion polymerization the particle nucleation process goes via coagulative homogeneous nucleation. Primary particles are created by collapse of a single growing polymer chain. Growth of these primary loci through polymerization leads to a colloidal instability which causes them to coalesce with one another, until a decreasing surface-to-volume ratio of the formed clusters warrants colloidal stability through charge repulsion, creating a set of mature growing particles. A constant number of mature particles is achieved when new aqueous-phase radical species can have no other fate but to terminate or to enter existing particles, and when newly formed primary particles and clusters thereof heterocoagulate with existing mature particles. When this nucleation process is fast with respect to the overall polymerization time narrow particle size distributions are obtained. When we add nanoparticles to our emulsion polymerization system they potentially can participate in this nucleation step. Growing polymer chains in the water phase can now precipitate onto a nanoparticle, under the conditions that wetting of the nanoparticle with the polymer chain is favorable. This leads to a higher number of latex particles and thus smaller particle sizes. The second stage in emulsion polymerization is particle growth, a process which enhances interfacial area between latex particles and water. Growing particles need to be stabilized with sufficient surface charge or by other means, such as steric stabilization, to prevent coagulation. In case of our solids-stabilized emulsion polymerizations the nanoparticles play herein a crucial role. We suggest that when a latex particle grows and thus increases its interfacial area, thereby reducing its surface charge density, it can heterocoagulate with a nanoparticle. Upon collision the nanoparticle can adhere to the interface acting as a Pickering stabilizer and, additionally, will provide extra charge to secure sufficient electrostatic repulsion between growing polymer latex particles, the latter to avoid full coagulation of the system. Indeed emulsion polymerizations of methyl methacrylate in absence or low amounts of Ludox particles fully coagulated at early stages of reaction. To avoid coagulation in Pickering emulsion polymerizations the time scale of the heterocoagulation process should be short in order to cope with the expansion of the total interfacial area, which is directly linked to the overall rate of polymerization. A simple model estimate puts this time scale in the order of ms (see Supporting Information). Moreover TEM analysis carried out at different times throughout our solids-stabilized emulsion polymerization process shows a gradual increase in the number of nanoparticles on the surface of growing latex particles, in support of our theory (Figures S8–S10).

The elegance of our solids-stabilized emulsion polymerization process provides opportunity for a straightforward second step extension that allows for the fabrication of multilayered core–shell nanocomposite polymer latex particles. We used our stable silica nanoparticle armored poly(methyl methacrylate) latexes as a seed and carried out a conventional monomer starved-fed emulsion polymerization, now in the presence of sodium dodecyl sulfate as surfactant. For the outer-polymeric shell we used acrylonitrile, ethyl methacrylate, and *n*-butyl acrylate as monomers. Seeded emulsion polymerization of acrylonitrile afforded composite multilayered latex particles of complex “hairy” morphology, as poly(acrylonitrile) is semicrystalline (see Figure 1b). Use of ethyl methacrylate provided multilayered nanocomposite colloids with a hard outer polymeric shell and encapsulation of the silica nanoparticles. Use of *n*-butyl acrylate created a soft outer shell. Intriguingly, slow migration of the nanoparticles through the soft polymer matrix to the outer surface occurred minimizing overall surface energy and potentially gaining entropy,²³ spacing them further apart (Figures 1c and S11).

In conclusion we demonstrated a versatile emulsion polymerization process in which solid nanoparticles are used as stabilizer, thereby replacing the role of surfactants, allowing the simple fabrication of armored nanocomposite polymer latexes. Use of a second conventional seeded emulsion polymerization step provided a straightforward route to more complex multilayered nanocomposite polymer colloids.

Acknowledgment. We thank Stefan Schumann and Steve York for help with TEM, and Wacker Chemie AG for funding (C.A.L.C.).

Supporting Information Available: Experimental procedures, a derivation for the time scale of heterocoagulation, and additional SEM and TEM images. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Hergeth, W. D.; Schmutzler, K.; Wartewig, S. *Makromol. Chem., Macromol. Symp.* **1990**, *31*, 123–142.
- (2) McDonald, C. J.; Devon, M. J. *Adv. Colloid Interface Sci.* **2002**, *99*, 181–213.
- (3) Mock, E. B.; Bruyn, H. D.; Hawket, B. S.; Gilbert, R. G.; Zukoski, C. F. *Langmuir* **2006**, *22*, 4037–4043.
- (4) Okubo, M.; Kanaida, K.; Matsumoto, T. *Colloid Polym. Sci.* **1987**, *265*, 876–881.
- (5) Kietzke, T.; Neher, D.; Landfester, K.; Montenegro, R.; Guentner, R.; Scherf, U. *Nat. Mater.* **2003**, *2*, 408–412.
- (6) Pommersheim, R.; Schrezenmeier, J.; Vogt, W. *Macromol. Chem. Phys.* **1994**, *195*, 1557–1567.
- (7) Caruso, F.; Caruso, R. A.; Möhwald, H. *Science* **1998**, *282*, 1111–1114.
- (8) Vincent, B.; Young, C. A.; Tadros, T. F. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 665–673.
- (9) Percy, M. J.; Amalvy, J. I.; Randall, D. P.; Armes, S. P.; Greaves, S. J.; Watts, J. F. *Langmuir* **2004**, *20*, 2184–2190.
- (10) Schmid, A.; Tonnar, J.; Armes, S. P. *Adv. Mater.* **2008**, *20*, 3331–3336.
- (11) Sacanna, S.; Kegel, W. K.; Philipse, A. P. *Phys. Rev. Lett.* **2007**, *98*, 158301.
- (12) Sacanna, S.; Philipse, A. P. *Adv. Mater.* **2007**, *19*, 3824–3826.
- (13) Walther, A.; Hoffmann, M.; Müller, A. H. E. *Angew. Chem., Int. Ed.* **2008**, *47*, 711–714.
- (14) Cauvin, S.; Colver, P. J.; Bon, S. A. F. *Macromolecules* **2005**, *38*, 7887–7889.
- (15) Bon, S. A. F.; Colver, P. J. *Langmuir* **2007**, *23*, 8316–8322.
- (16) Ramsden, W. *Proc. R. Soc.* **1903**, *72*, 156–164.
- (17) Pickering, S. U. *J. Chem. Soc., Trans.* **1907**, *91*, 2001–2021.
- (18) Dinsmore, A. D.; F., H. M.; Nikolaidis, M. G.; Marquez, M.; Bausch, A. R.; Weitz, D. A. *Science* **2002**, *298*, 1006–1009.
- (19) Colver, P. J.; Bon, S. A. F. *Chem. Mater.* **2007**, *19*, 1537–1539.
- (20) Melle, S.; Lask, M.; Fuller, G. G. *Langmuir* **2005**, *21*, 2158–2162.
- (21) Lin, Y.; Skaff, H.; Boeker, A.; Dinsmore, A. D.; Emrick, T.; Russell, T. P. *J. Am. Chem. Soc.* **2003**, *125*, 12690–12691.
- (22) Arumugam, P.; Patra, D.; Samanta, B.; Agasti, S. S.; Subramani, C.; Rotello, V. M. *J. Am. Chem. Soc.* **2008**, *130*, 10046–10047.
- (23) Gupta, S.; Zhang, Q.; Emrick, T.; Balazs, A. C.; Russell, T. P. *Nat. Mater.* **2006**, *5*, 229–233.

JA807242K