

Emulsion Polymerization Using Janus Particles as Stabilizers**

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Janus particles (JPs) are compartmentalized colloids that possess two sides of different chemistry or polarity. These particles have moved into the focus of various research groups in the fields of physics, chemistry, and biological science. One of the major challenging aspects in the synthesis of such particles is the production of larger quantities to allow investigations of their application possibilities. Several two-dimensional (2D) techniques, such as sputtering or micro-contact printing, only lead to a small amount of material.^[1,2] On the contrary, the template-assisted pathway using well-defined microphase-segregated block-terpolymer templates yields JPs of different architectures in considerable quantities.^[3–6] More recently, site-specific modification of Pickering emulsions, electrospinning, and upscaled microfluidic devices have been used to create larger amounts.^[7–12] Thus, major synthetic challenges in the production of JPs may be overcome in the near future.

JPs are interesting for a variety of reasons, one of them being their self-organization into complex and well-defined assemblies. Possible applications range from physics, biophysics, and medicine to display technology.^[9,13–20] However, the advanced surface-active properties of particles with a segregated corona over particles with a uniform wettability are most interesting. Binks et al. calculated that the surface activity of a JP is up to three times higher at an oil/water interface than that of a uniform particle, which leads to a strengthened adsorption at the interface.^[21] Recently, Glaser et al. found that bimetallic JPs lead to a significant reduction of the oil/water interfacial tension as compared to similar uniform particles.^[22] Thus, the predictions were verified, which rendered the surface-active properties highly interesting for industrial applications.

Herein, we report the first successful emulsion polymerization using JPs as stabilizers. This is the first time that JPs have been used in application studies that are very close to industrial requirements. In recent years, much work within the field of emulsion polymerization has been devoted to the

introduction of novel polymerization techniques, the generation of novel latex architectures, and the variation of the architecture of the polymeric stabilizer.^[23–35] Generally, electrosteric stabilization of polymers is superior to electrostatic stabilization alone, induced by classical low-molecular-weight surfactants, such as sodium dodecyl sulfate.^[36] However, particles with Janus character have not been used in these studies so far, mainly because of the difficult accessibility of these structures.

The application of JPs to emulsion stabilization is very interesting. These particles uniquely combine the so-called Pickering effect,^[37–39] known from particles, with amphiphilicity—similar to block copolymers—induced by the Janus character. As polymeric starlike JPs are used in this study, even the electrosteric stabilization effect is present. The adsorption energy at the interface is expected to be significantly higher than that for similar standard particles of uniform wettability or standard polymeric surfactants. Therefore, JPs are expected to suppress unwanted aggregation and coalescence more efficiently. This is certainly highly beneficial for long-term stability, as desorption of the stabilizer is minimized.

We prepared amphiphilic JPs by selectively cross-linking the spherical polybutadiene microdomains within the lamella–sphere morphology of a microphase-separated template of a polystyrene-*block*-polybutadiene-*block*-poly(methyl methacrylate) triblock terpolymer (PS-PB-PMMA) and subsequent hydrolysis of PMMA to poly(methacrylic acid) (see Figure 1).^[3,4]

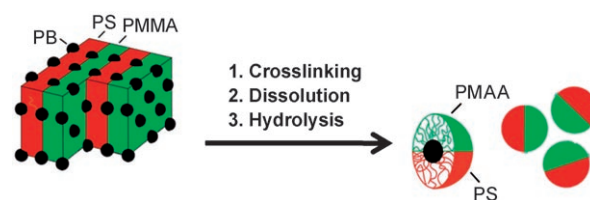


Figure 1. Template-assisted synthesis of spherical JPs and their aggregation into superstructures according to their compartmentalization. PB = polybutadiene, PS = polystyrene, PMMA = poly(methyl methacrylate), PMAA = poly(methacrylic acid).

Conventional emulsion polymerizations were carried out in a process adapted from Charleux et al.,^[35] with $K_2S_2O_8$ as thermal initiator in slightly basic solution (K_2CO_3). Styrene and *n*-butyl acrylate (*n*BuA) were selected as monomers, because of the possibility of studying the influence of the glass transition temperature (T_g) and the interaction between stabilizer and latex particle. Poly(*n*BuA) ($T_g \approx -46^\circ C$) has an unfavorable interaction with the PS part of the stabilizer. To allow a meaningful comparison, the amount of stabilizer

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was varied, whereas the concentrations of initiator and monomer were kept constant. Furthermore, all emulsion polymerizations were allowed to proceed to full conversion, as followed by gravimetry and the absence of monomer odor at the end of the reaction. Note that the JPs aggregate into micelle-like assemblies in aqueous solution in the concentration regime used here.^[3] The critical aggregation concentration is around 0.05 mg mL^{-1} and thus significantly higher than the critical micelle concentration of linear amphiphilic block copolymers.

After complete polymerization, the resulting latexes were characterized by transmission electron microscopy (TEM) and dynamic light scattering (DLS; see Table 1). All reactions

Table 1: Overview of latex characterization.

Entry	Monomer	JP [wt%] ^[a]	$\langle R_h \rangle_z$ (PDI) ^[b] [nm]	R_n (R_w/R_n) ^[c] [nm]	A_{JP} ^[d] [nm ²]	$N_{ad,JP}$ ^[e]
Ref.	Styrene	0	–	987 (1.15)	–	–
1	Styrene	0.51	147 (1.02)	129 (1.01)	16900	12
2	Styrene	1.96	112 (1.01)	95 (1.005)	6210	18
3	Styrene	3.88	91 (1.01)	81 (1.01)	3750	22
4	<i>n</i> BuA	0.51	198 (1.01)	–	–	–
5	<i>n</i> BuA	1.96	189 (1.01)	–	–	–
6	<i>n</i> BuA	3.97	163 (1.05)	–	–	–

[a] Relative percentage of JPs to monomer. [b] Polydispersity index, obtained by DLS. [c] Statistical calculation based on the TEM images. [d] Average surface area that is stabilized by one JP (see Experimental Section). [e] Number of JPs adsorbed onto one latex particle.

containing JPs are well controlled and lead to well-defined latexes with long-term stability. In comparison with soap-free emulsion polymerization (reference experiment; Ref.), a striking decrease of the particle size and polydispersity can be observed. The good control is also expressed by the decreasing particle size with increasing amount of stabilizer present in the system, as expected.

For instance, in the case of PS, the hydrodynamic radius decreases from approximately 147 nm for 0.5 wt % to 91 nm for 4 wt % of JP stabilizer (Figure 2). The hydrodynamic radii are smaller for the polymerization of styrene as compared to *n*BuA. This result indicates a better performance of the stabilizer for styrene as monomer, which is expected as PS is a

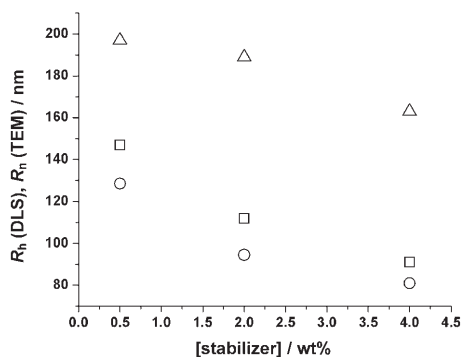


Figure 2. Dependence of the hydrodynamic radius (R_h ; DLS) and the number-average radius (R_n ; TEM) of the latex particles on the amount of stabilizer. □: DLS (styrene); ○: TEM (styrene); △: DLS (*n*BuA).

high- T_g material, thus enabling firm attachment of the PS part of the JP. Furthermore, the resulting PS latex particles do not have any unfavorable interaction with the PS side of the JP, as is the case for poly(*n*BuA). This also leads to a lower tendency for the JP to desorb from the interface. The difference in the radii obtained by DLS and TEM can be understood by considering the polyelectrolyte character of the stabilizer. The polyelectrolyte chains are partially extended under the conditions of the DLS measurements (high pH, moderate salinity), whereas they are collapsed in the dried state. Thus, the values obtained by TEM are closer to the real radius of an actual PS latex sphere.

The polydispersity of an emulsion system is another measure with which to estimate the efficiency of a stabilizer. Figure 3 displays the autocorrelation functions and CONTIN plots for the PS latexes obtained with three different amounts of JPs (0.5, 2, and 4 wt %). The CONTIN plots show very narrow unimodal peaks and the polydispersities of the samples can be estimated by cumulant analysis of the samples to yield very low values of 1.01–1.02, which indicate the generation of nearly monodisperse particles.

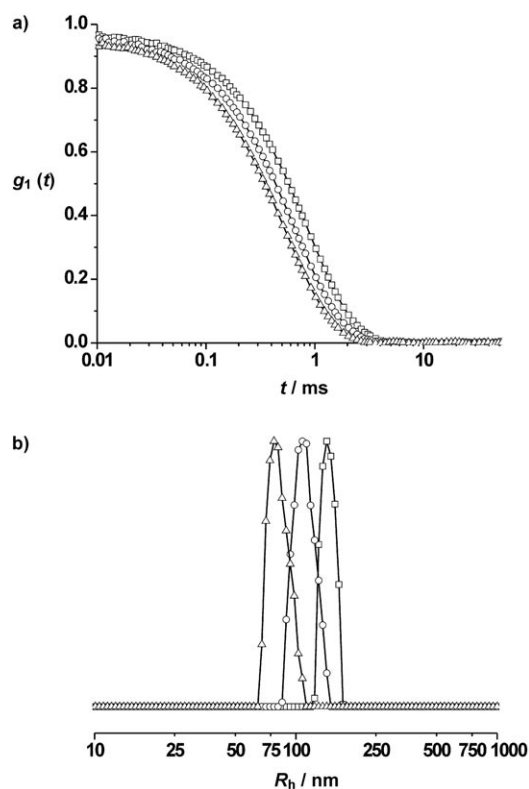


Figure 3. a) Normalized-field autocorrelation functions $g_1(t)$ and b) CONTIN plots obtained for the emulsion polymerization of styrene after full conversion. □: 0.5 wt %; ○: 2 wt %; △: 4 wt %.

Statistical TEM analysis of the PS latexes verifies the monodispersity with values of $R_w/R_n = 1.005$ – 1.01 ($R_w =$ weight-average radius). The poly(*n*BuA) latexes cannot be reliably analyzed by TEM because of their soft constitution. The results confirm an exceptionally good performance of the JPs in the emulsion polymerization of styrene and *n*BuA.

Strikingly, the particles assemble into regularly packed assemblies, although the liquid is blotted away fast and not evaporated slowly, as is usually done for the creation of 2D colloidal crystals. This observation confirms the high monodispersity of the latex particles (see Figure 4).

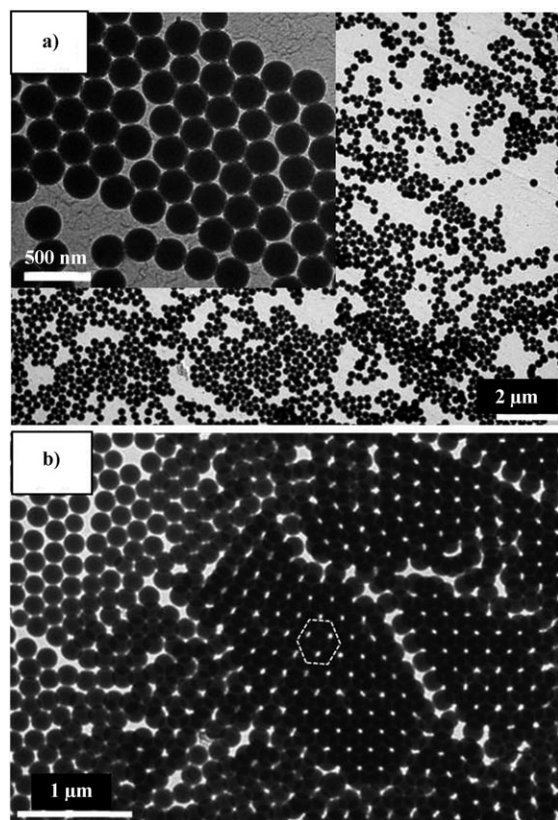


Figure 4. TEM images of PS latexes with a stabilizer content of a) 0.5 and b) 4 wt%. A double layer of particles can be seen in (b). The hexagon guides the eye for better recognition of the well-ordered pattern.

From the radii of the actual PS latex beads, we calculated the average surface area A_{JP} stabilized by one JP (Table 1 and Figure 5). Interestingly, A_{JP} decreases with increasing amount of stabilizer. The value obtained at very low stabilizer content ($1.7 \times 10^4 \text{ nm}^2$) is remarkably high, considering that the JPs possess a cross section of only about 1300 nm^2 ($R_h \approx 10 \text{ nm}$).^[3,4] Consequently, the area that is stabilized by one JP significantly exceeds the cross section, independent of the stabilizer concentration used. This leads to the conclusion that all JPs are adsorbed at the interface, which is not always the case for standard Pickering emulsions.^[40]

Certainly this positive effect of enhanced adsorption can be ascribed to the amphiphilic Janus character of the stabilizing particles and the accompanying high adsorption energy at the interface. The particle coverage on the latexes is loose with a reasonable amount of uncovered surface. A comparison of the latex particle size with the average surface area per particle A_{JP} shows that only 12 to 22 JPs per latex particle are necessary for stabilizing the dispersion at the

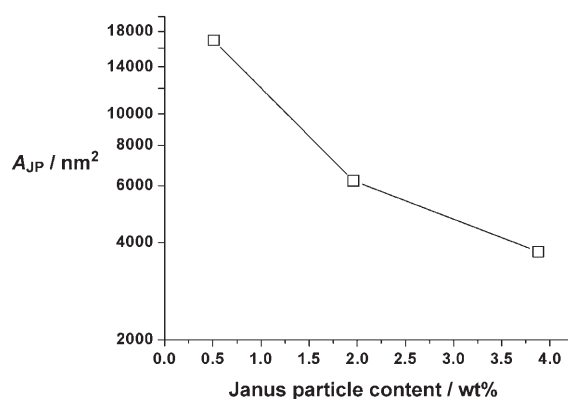


Figure 5. Dependence of the average surface area A_{JP} that is stabilized by one JP on the stabilizer content for PS latexes. The line serves to guide the eye.

lowest content of stabilizer. As stable dispersions can be obtained, the JPs act as excellent stabilizers.

The number of adsorbed JPs per latex particle, $N_{ad,JP}$, lies within the range of the number of JPs that form a micellar superstructure in water (28–38).^[3,4] Thus, the number of latex particles produced is similar to the number of supermicelles. Therefore, a first indication of the mechanism can be deduced. Most likely, in a first step, the superstructures act as a seed for the emulsion polymerization. As $N_{ad,JP}$ varies and is slightly lower than for the supermicelles, the system has a dynamic character as well.

A comparison of the good performance of the JPs with known systems is desired, but is not straightforward because of the novelty. Similar work on Pickering emulsion polymerization was performed, for instance, by Landfester et al.^[41] and Bon et al.,^[42] who employed silica particles or clay platelets with similar sizes to the JPs used. Their emulsion polymerizations suffered from coagulation and the mini-emulsion technique was required to obtain stable dispersions. In the case of silica, successful emulsion polymerizations were only possible in the presence of 4-vinylpyridine as comonomer to ensure some attractive interaction between polymerizing latex particles and silica beads. When JPs are used as stabilizers, stable dispersions can be obtained readily with simple conventional emulsion polymerization independently of the monomer used.

For a comparison with amphiphilic block copolymers, a scientifically correct and fair assessment of the performance can be made by comparing the molar concentrations of stabilizer used with the particle sizes obtained. As a result of the high molar mass of the polymeric JPs, the emulsion polymerizations were conducted at extremely low molar concentrations of stabilizer ($10^{-7} \text{ mol L}^{-1}$). In the field of block copolymers, such low concentrations are uncommon for emulsion polymerization and thus reference values hardly exist. The typical concentration range of standard stabilizers is in the region of $10^{-4} \text{ mol L}^{-1}$.^[30,35] Hence, it is highly doubtful that emulsion polymerizations with block-copolymer stabilizers might be able to yield comparable particle sizes and low polydispersities, even if similarly low concentrations of block-copolymer stabilizer were used and led to

stable dispersions. The development of a reference system for the JPs and investigations of their performance in emulsion polymerization, as well as of the complex mechanism of the Pickering emulsion polymerization using JPs, are under way.

In conclusion, JPs have been applied for the first time to the emulsion polymerization of different monomers, an industrially very relevant topic. The emulsion polymerizations can be conducted in a facile fashion and do not require additives or miniemulsion polymerization techniques, as do other Pickering emulsion polymerizations. The resulting latex dispersions show very well-controlled particle sizes with extremely low polydispersities. The particle size decreases with increasing content of stabilizer. A detailed analysis of the surface coverage of the latex particles reveals a loose coverage of the latex surface by the JPs. The surface area stabilized by one JP exceeds its cross section several times. A comparison with the literature strongly indicates a superior performance of the JPs in emulsion polymerization, and renders this material highly interesting for fundamental studies and future widespread industrial applications.

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- [1] O. J. Cayre, V. N. Paunov, O. D. Velev, *Chem. Commun.* **2003**, 2296.
- [2] V. N. Paunov, O. J. Cayre, *Adv. Mater.* **2004**, *16*, 788.
- [3] R. Erhardt, M. Zhang, A. Böker, H. Zettl, C. Abetz, P. Frederik, G. Krausch, V. Abetz, A. H. E. Müller, *J. Am. Chem. Soc.* **2003**, *125*, 3260.
- [4] R. Erhardt, A. Böker, H. Zettl, H. Kaya, W. Pyckhout-Hintzen, G. Krausch, V. Abetz, A. H. E. Müller, *Macromolecules* **2001**, *34*, 1069.
- [5] Y. Liu, V. Abetz, A. H. E. Müller, *Macromolecules* **2003**, *36*, 7894.
- [6] A. Walther, X. André, M. Drechsler, V. Abetz, A. H. E. Müller, *J. Am. Chem. Soc.* **2007**, *129*, 6187.
- [7] L. Hong, S. Jiang, S. Granick, *Langmuir* **2006**, *22*, 9495.
- [8] K.-H. Roh, D. C. Martin, J. Lahann, *Nat. Mater.* **2005**, *4*, 759.
- [9] K.-H. Roh, M. Yoshida, J. Lahann, *Langmuir* **2007**, *23*, 5683.
- [10] R. F. Shepherd, J. C. Conrad, S. K. Rhodes, D. R. Link, M. Marquez, D. A. Weitz, J. A. Lewis, *Langmuir* **2006**, *22*, 8618.
- [11] Z. Nie, W. Li, M. Seo, S. Xu, E. Kumacheva, *J. Am. Chem. Soc.* **2006**, *128*, 9408.
- [12] D. Dendukuri, D. C. Pregibon, J. Collins, A. T. Hatton, P. S. Doyle, *Nat. Mater.* **2006**, *5*, 365.
- [13] C. J. Behrend, J. N. Anker, B. H. McNaughton, R. Kopelman, *J. Magn. Magn. Mater.* **2005**, *293*, 663.
- [14] J. Choi, Y. Zhao, D. Zhang, S. Chien, Y.-H. Lo, *Nano Lett.* **2003**, *3*, 995.
- [15] J. N. Anker, C. Behrend, K. Raoul, *J. Appl. Phys.* **2003**, *93*, 6698.
- [16] J. N. Anker, R. Kopelman, *Appl. Phys. Lett.* **2003**, *82*, 1102.
- [17] C. J. Behrend, J. N. Anker, B. H. McNaughton, M. Brasuel, M. A. Philbert, R. Kopelman, *J. Phys. Chem. B* **2004**, *108*, 10408.
- [18] C. J. Behrend, J. N. Anker, R. Kopelman, *Appl. Phys. Lett.* **2004**, *84*, 154.
- [19] T. Nisisako, T. Torii, T. Takahashi, Y. Takizawa, *Adv. Mater.* **2006**, *18*, 1152.
- [20] R. Golestanian, T. B. Liverpool, A. Ajdari, *Phys. Rev. Lett.* **2005**, *94*, 220801.
- [21] B. P. Binks, P. D. I. Fletcher, *Langmuir* **2001**, *17*, 4708.
- [22] N. Glaser, D. J. Adams, A. Böker, G. Krausch, *Langmuir* **2006**, *22*, 5227.
- [23] S. Freal-Saison, M. Save, C. Bui, B. Charleux, S. Magnet, *Macromolecules* **2006**, *39*, 8632.
- [24] M. Manguian, M. Save, B. Charleux, *Macromol. Rapid Commun.* **2006**, *27*, 399.
- [25] E. B. Mock, H. D. Bruyn, B. S. Hawkett, R. G. Gilbert, C. F. Zukoski, *Langmuir* **2006**, *22*, 4037.
- [26] J. Nicolas, B. Charleux, O. Guerret, S. Magnet, *Macromolecules* **2005**, *38*, 9963.
- [27] J. Pusch, A. M. van Herk, *Macromolecules* **2005**, *38*, 6909.
- [28] C. J. Ferguson, R. J. Hughes, D. Nguyen, B. T. T. Pham, R. G. Gilbert, A. K. Serelis, C. H. Such, B. S. Hawkett, *Macromolecules* **2005**, *38*, 2191.
- [29] J. Nicolas, B. Charleux, O. Guerret, S. Magnet, *Angew. Chem.* **2004**, *116*, 6312; *Angew. Chem. Int. Ed.* **2004**, *43*, 6186.
- [30] M. Save, M. Manguian, C. Chassenieux, B. Charleux, *Macromolecules* **2005**, *38*, 280.
- [31] W. Smulders, M. J. Monteiro, *Macromolecules* **2004**, *37*, 4474.
- [32] S. Fujii, D. P. Randall, S. P. Armes, *Langmuir* **2004**, *20*, 11329.
- [33] C. Detrembleur, A. Debuigne, R. Bryaskova, B. Charleux, R. Jerome, *Macromol. Rapid Commun.* **2006**, *27*, 37.
- [34] L. Houillot, J. Nicolas, M. Save, B. Charleux, Y. Li, S. P. Armes, *Langmuir* **2005**, *21*, 6726.
- [35] C. Burguière, S. Pascual, C. Bui, J.-P. Vairon, B. Charleux, K. A. Davis, K. Matyjaszewski, I. Bétremieux, *Macromolecules* **2001**, *34*, 4439.
- [36] R. Gilbert, *Emulsion Polymerization: A Mechanistic Approach*, Academic Press, London, **1995**.
- [37] W. Wamsdon, *Proc. R. Soc. London* **1903**, *72*, 156.
- [38] S. U. Pickering, *J. Chem. Soc.* **1907**, *91*, 2001.
- [39] B. P. Binks, *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 21.
- [40] N. Saleh, T. Sarbu, K. Sirk, G. V. Lowry, K. Matyjaszewski, R. D. Tilton, *Langmuir* **2005**, *21*, 9873.
- [41] F. Tiarks, K. Landfester, M. Antonietti, *Langmuir* **2001**, *17*, 5775.
- [42] S. Cauvin, P. J. Colver, S. A. F. Bon, *Macromolecules* **2005**, *38*, 7887.