

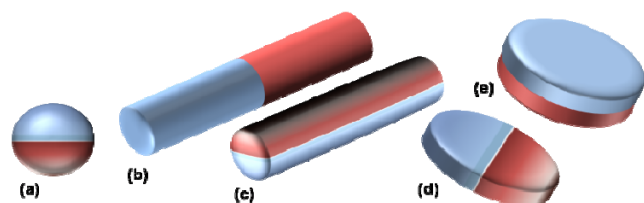
Janus Particles at Interfaces

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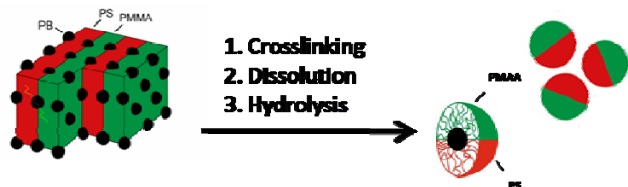
INTRODUCTION

Janus particles are compartmentalized colloids which possess two sides of different chemistry or polarity. These particles have moved into the focus of various research groups ranging from physics, chemistry to biological science. In general, Janus particles can be divided into several classes according to their architecture and dimensionality (see Scheme 1). Most commonly, spherical Janus particles can be imagined. In addition, two types of Janus cylinders (1D) and two types of disc-like particles (2D) are conceivable. The lack of centrosymmetry is inherent to all of these particles and is the major challenging aspect in their preparation.



Scheme 1. Overview of possible Janus particle architectures. (a) spherical Janus particle, (b+c) two types of Janus cylinder and (d+e) two types of Janus discs.

Janus particles are interesting for a variety of reasons, one of them being the self-organization into complex and well-defined assemblies. From a scientific, as well as from an industrial point of view, the advanced surface-active properties of particles with a segregated corona over particles with a uniform wettability are very interesting. Binks et al. calculated that the surface activity of a Janus particle is up to three times higher at an oil/water interface than that of a uniform particle, leading to an enhanced adsorption at the interface.¹ Recently, Glaser et al. found that bimetallic Janus particles lead to a significant reduction of the oil/water interfacial tension as compared to similar uniform particles.² Thus, the predictions were verified, rendering the surface active properties highly interesting for industrial application. Janus particles uniquely combine the so-called Pickering effect³⁻⁵, known from particles, with amphiphilicity - similar to block copolymers - induced by the Janus character. This combination enables a firm attachment at interfaces and may lead to advanced stabilizing properties in dispersions. Unwanted coalescence of domains of the dispersed phase is thus expected to be diminished using these highly surface-active particles.



Scheme 2. Schematic representation of the template-assisted synthesis of spherical Janus particles and their aggregation into superstructures according to their compartmentalization. PB = polybutadiene, PS = polystyrene, PMMA = poly(methyl methacrylate), PMAA = poly(methacrylic acid). Microphases in the bulk morphology of a PS-PB-PMMA triblock terpolymer with 6% PB content and symmetrical outer blocks.

Herein, we report on the application of spherical Janus particles as stabilizers for two types of dispersions of high scientific and

industrial relevance. Firstly, emulsion polymerization of standard monomers towards the preparation of well-defined latexes and secondly the compatibilization of polymer blends. In both cases spherical Janus micelles are used, which are prepared with the template-assisted pathway based on a microphase separated template of a polystyrene-*block*-polybutadiene-*block*-poly(methyl methacrylate) triblock terpolymer (PS-PB-PMMA) (see Scheme 2). Details of the synthesis of Janus particles via the template assisted pathway can be found elsewhere.⁶⁻⁸ A hydrolysis of the PMMA hemisphere to polymethacrylic acid is required to obtain water soluble Janus particles for the emulsion polymerization studies.

EXPERIMENTAL

Emulsion Polymerization. For the preparation of the solutions, the Janus particles (PS-PMAA) at the desired concentration were dissolved in an aqueous solution, containing K_2CO_3 (0.02 mol/L), degassed by N_2 bubbling and stirred for at least 12 hours at 70 °C in 10 – 15 ml glass bottles. Afterwards, styrene or n-butyl acrylate (10 wt%) as a monomer was added with a syringe and the system was allowed to equilibrate for 2 hours. Adding of $K_2S_2O_8$ solution to give a final concentration of $c = 0.01$ mol/L initiated the reaction, which was stopped no sooner than 24 hours to get full conversion.

Polymer Blend Preparation. PS/PMMA blends (ca. 5g) were prepared in a small high-shear twin screw mixer at 220 °C, by co-mixing PS, PMMA and PS-PMMA Janus micelles. The weight ratio of PS to PMMA was kept constant at 60:40 and the amount of Janus micelles was varied.

RESULTS AND DISCUSSION

Emulsion Polymerization. Conventional emulsion polymerizations were carried out using $K_2S_2O_8$ as thermal initiator in slightly basic solution (K_2CO_3) and styrene and n-butyl acrylate as monomers. To allow a meaningful comparison, the amount of stabilizer was varied, whereas the initiator and monomer concentrations were kept constant. Furthermore, all emulsion polymerizations were allowed to proceed to full conversion which could be followed by gravimetry and the absence of monomer odor at the end of the polymerization. After complete polymerization, the resulting latexes were characterized by transmission electron microscopy (TEM) and dynamic light scattering (DLS). The results are summarized in Table 1.

Table 1. Overview of Latex Characterization

Entry	Monomer	JP content [wt%] ^[a]	$\langle R_n \rangle_z$ (PDI) ^[b] [nm]	R_n R_w/R_n ^[c] [nm]
1	Styrene	0.51	147 (1.02)	129 (1.010)
2	Styrene	1.96	112 (1.01)	95 (1.005)
3	Styrene	3.88	91 (1.01)	81 (1.010)
Ref.	Styrene	0	-	987 (1.15)
4	n-BuA	0.51	198 (1.01)	-
5	n-BuA	1.96	189 (1.01)	-
6	n-BuA	3.97	163 (1.05)	-

[a] Relative percentage of Janus particles to monomer. [b] Obtained by Dynamic Light Scattering measurements. [c] Statistical calculation based on the TEM micrographs.

All reactions containing Janus particles are well controlled and lead to well-defined latexes with long-term stability. Additionally, they can be conducted in a facile fashion and no prehomogenization or miniemulsion polymerization route is necessary. In comparison with the soap-free emulsion polymerization (Ref.), a striking decrease of the particle size and polydispersity can be observed. The good control is also expressed by the fact that the particle size decreases with increasing amount of stabilizer present in the system, as it is expected. The polydispersity of an emulsion system is another measure to estimate the efficiency of a stabilizer. The polydispersities of the samples, as estimated by DLS using the cumulant analysis, yield very low values of 1.01 – 1.02. Some values are even fairly below 1.01, thus indicating the generation of nearly monodisperse particles. Statistical TEM analysis of the PS latexes verifies the monodispersity with values

of $R_w/R_n = 1.005 - 1.01$. The results confirm an exceptionally good performance of the Janus beads in the emulsion polymerization of styrene and n-butyl acrylate. The resulting PS latexes easily form colloidal crystal-like packing when deposited onto surfaces (see Figure 1).

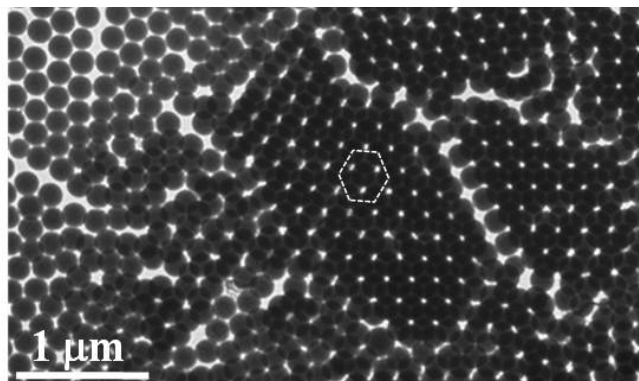


Figure 1. TEM micrograph of a polystyrene latex with a stabilizer content of 4 wt%. A double layer of particles can be seen in the lower micrograph. The hexagon guides the eye for a better recognition of the well ordered pattern.

Polymer Blends. Polymer blends are widely used in industry to conveniently combine desired properties of commodity plastics. Due to the inherent immiscibility of most polymers, compatibilizing agents and strong shear are necessary to allow for a sufficient microscopic mixing of the two components. Random or diblock copolymers are frequently added to enhance the dispersion of the minor component and to stabilize the dispersed droplets against coalescence. One of the major problems is the insufficient adsorption of the block copolymers at the interfaces under the strong shear and high temperature conditions during the polymer processing, e.g. via extrusion. Thus, a significant percentage of the compatibilizer is not located at the interface, but dispersed in one of the phases. Therefore, high weight fractions of block copolymer are necessary to compensate the loss of the dispersed amount. In order to overcome this challenging problem, Janus particles may serve as alternative. Due to the particular character, combined with amphiphilicity, Janus particles adsorb strongly at interfaces and are less likely to desorb from interfaces during shearing at elevated temperatures.

In order to investigate the performance of Janus particles in polymer blends, we blended high molecular weight PS and PMMA using PS-PB-PMMA Janus particles under high shear conditions in a miniature twin-screw mixer at 220 °C. The amount of Janus particles in the mixture was varied to study the effect systematically. Figure 2 depicts TEM images obtained after microtome cutting the PS/PMMA blends. When no Janus particles are present as compatibilizer, the blend has PMMA domain sizes considerably larger than 2 μm (Figure 2a). Upon addition of only 1 wt% of Janus particles a significant decrease of the PMMA droplet sizes can be observed. The average domain sizes reach values of around 2 μm and lower (Figure 2b). A further increase of the content of Janus particles leads to a further reduction of the domain sizes of the dispersed phase to diameters of only 500 nm and less (Figure 2c). Consequently, the domain size of the minor component can be controlled by the amount of Janus particles added. The TEM images also reveal that the Janus particles are located at the interface of the polymer blend. They are well visible as black dots in the magnified image in Figure 2d. The strong contrast in TEM arises from the content of sulfur and chlorine inside the core of the Janus particles, crosslinked by disulfur dichloride. The size corresponds to the core size of a single Janus particle. The interface exhibits a dense coverage of Janus particles, which is the reason for the excellent compatibilization of the two immiscible phases. A careful inspection of the bulk phases does hardly show any Janus particles dispersed in the polymers. Thus, the Janus particles are almost exclusively adsorbed at the blend interface, representing a major

advantage compared to standard block copolymer compatibilizers or reactive blending. The enhanced adsorption originates from the amphiphilic character of the particles.

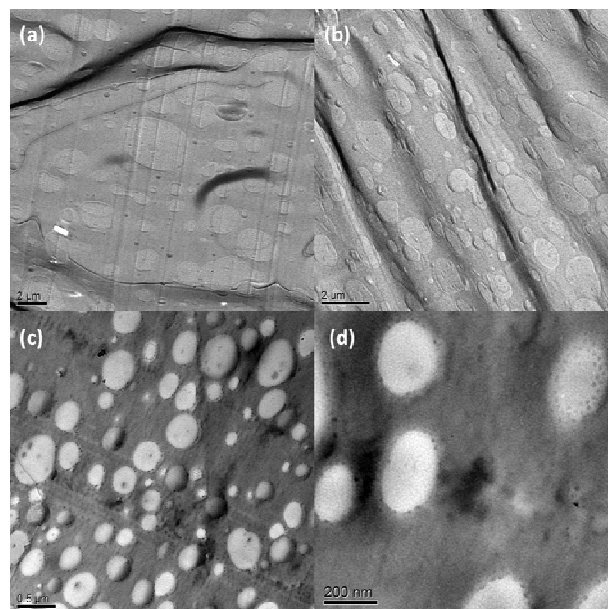


Figure 2. TEM images of PS/PMMA blends at various content of PS-PMMA Janus particles. (a = 0 wt%, b = 1 wt%, c = 6 wt%). Image (d) shows a magnified image of a blend with 6 wt% Janus particles.

CONCLUSION

The application of spherical Janus particles for the stabilization of different interfaces was studied. In the emulsion polymerization, the Janus particles can be used as stabilizer and the polymerization can be conducted via a simple conventional emulsion polymerization route. In the end, the latex particles are covered with amphiphilic Pickering particles, exhibiting excellent size distributions and long-term stability.

Secondly, the addition of PS-PMMA Janus particles to a blend of PS and PMMA homopolymer results in a considerable reduction of the domain sizes of the minor component. The Janus particles are predominantly located at the interface of the two blend components and form a densely packed layer.

In summary, the unique combination of amphiphilicity with the Pickering effect of particles leads to enhanced surface active properties and to excellent stabilizing properties.

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