Engineering Nanostructured Polymer Blends with Controlled Nanoparticle Location using Janus Particles

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The combination of polymer properties by blending is one of the most attractive ways for obtaining new products with superior material properties, such as for tailoring the electronic, mechanical, or optical properties. This does not only hold for large-scale industrial applications, but also for scientific problems as for instance in the case of polymer blend solar cells. In both fields, there is a constant search for novel and better ways of compatibilization [1,2] The major challenging difficulty is to overcome the inherent immiscibility of polymers by using compatibilizing agents to allow for a sufficient mixing into nanoscopically sized domains of the dispersed phase. In industry, most commonly reactive blending or, similarly, the addition of block copolymers is used for compatibilizing the two components. One of the major drawbacks of this approach is that much of the block copolymer stabilizer does not adsorb at the interface and is lost during the high shear extrusion process, thus significantly increasing the cost of the polymer blend.[3–6]

In analogy to colloid science, we conceived of a novel concept of compatibilizing polymer blends and for controlling the location of the particles within the blend structure. In recent years, several publications have appeared discussing the superior surface-active properties of so-called Janus particles (JPs).[7] Janus particles are compartmentalized colloidal particles, which show segregation into two hemispheres. These particles uniquely combine the so-called Pickering effect with amphiphilicity and are thus known as surfactant particles.[8] It has been calculated and experimentally shown for liquid−liquid interfaces that these particles adsorb strongly at interfaces, in particular stronger than standard surfactants or homogeneous particles.[7,9−11] Triggered by these stimulating results, we applied Janus particles, having one PS and one PMMA side, for the blend compatibilization of PS and PMMA.
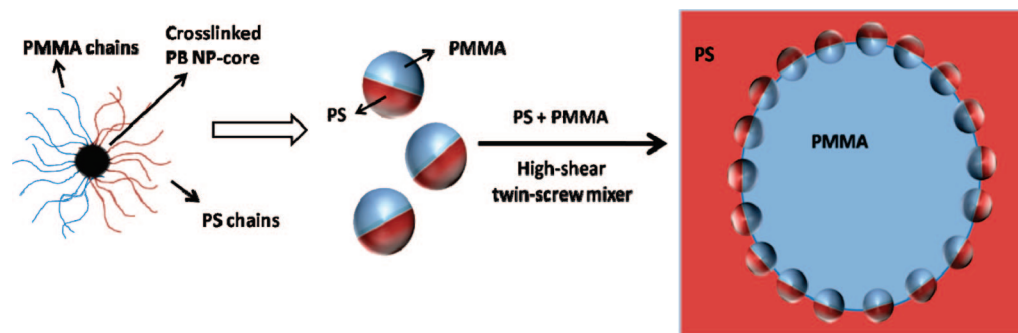
Generally, nanocomposites, that is, nanoparticle-filled block copolymers and homopolymers have been attracting increasing interest in the past years, which was triggered by several interesting theoretical and experimental contributions. Very important contributions for a fundamental understanding of nanocomposites were for instance published by Mackay and co-workers,[12] who analyzed the miscibility of polymers with nanoparticles in dependence of their relative sizes, meaning radii of gyration. In essence, they found that polymeric nanoparticles are completely miscible with a matrix material as long as the particle radius is smaller than the radius of gyration of the polymer used as matrix. They proposed an enthalpic gain due to an increase in

ABSTRACT Janus particles are used on a multigram scale for the blend compatibilization of two polymers in a twin screw mini-mixer. It is shown that the Janus particles can be located exclusively at the interface of the two polymer phases despite the high temperature and shear conditions. The domain sizes of the dispersed phase decrease with increasing content of Janus particles. The decrease is yet ongoing for high contents of Janus particles. Furthermore, the biphasic particles exhibit an ordered arrangement at the interface. Thus, the approach demonstrates that a nanoscopic structuring of the interface can be achieved under macroscopic processing conditions. The structural order occurs on two levels. The first is the complete adsorption at the interface and the second is the lateral ordering at the interface. The strong adsorption at the interface is explained in terms of the increased desorption energy of Janus particles. Secondly, the compatibilization efficiency is critically compared to state-of-the-art compatibilizers. The efficiency of the Janus particles is found to be superior as compared to block copolymer-based compatibilizers. The efficiency gap between Janus particles and block copolymer compatibilizers widens for larger amounts added.

KEYWORDS: Janus particles · nanoparticles · nano-composites · polymer blends · Pickering effect · interface · polymer engineering

Scheme 1. Schematic representation of Janus particles and their adsorption at the blend interface of a PS/PMMA blend.

molecular contacts at the dispersed nanoparticle surfaces as compared with the surface of phase-segregated nanoparticles. With increasing the nanoparticle size above the coil dimensions of the polymeric materials, the particles are expelled from the matrix and large-scale phase separation occurs. In terms of block-copolymer nanoparticle composite materials, it was shown by Thompson *et al.* that in the absence of any specific (enthalpic) interactions, larger particles are expelled from the bulk phase.[13] This is caused by a loss of conformational entropy, because the polymer chains must stretch around the solid particles. This penalty increases with rising particles size. In the case of binary polymer blends containing polymers A and B, it should first be distinguished between blends containing particles, which are preferentially attracted by one component (*e.g.*, polymer A) and particles which are attracted similarly to both components. For the first system, Ginzburg and co-workers stated that a decrease of the particle size, smaller than the radius of gyration would have a beneficial effect on compatibilizing a mixture.[14,15] However, in the latter case, when the interfacial tension between the polymers A and B, γ_{AB}, exceeds the difference of the interfacial tension of a colloid C with the two components, $\gamma_{AB} > \gamma_{CA} - \gamma_{BC}$, the situation is different. The system is then largely dominated by the interfacial tension between the two blend components. Hore *et al.*[16] found that large-scale phase separation is favored for low interfacial tensions between the two mixture components, simply because of an insufficient adsorption of the nanoparticles. The tendency of a particle to migrate and stick to an interface scales with the interfacial tension of A and B, γ_{AB}, and with the square of the particle radius. Consequently, the compatibilization of the system is better for larger particles as they cannot be removed so easily from the interface once they are adsorbed.

In conclusion, a complex interplay between enthalpic and entropic contributions governs the dispersion and location of particles in polymers, block copolymers, and polymer blends.

With respect to materials science, nanocomposites represent a very promising and also in some cases cost-effective way of structuring hybrid materials and ob-

taining high-performance properties.[17–19] For instance, nanoparticles can be used to positively alter processing conditions,[20] mechanical properties such as toughness[21] or crack characteristics,[22,23] or to change the electronic[24–26] and optical properties.[27,28] To achieve better materials, control in the precise location of the nanoparticles is essential.

Recently, Kramer and co-workers[29–35] showed that a control of the location and spatial distribution of homogeneously coated gold nanoparticles (polystyrene or poly(2-vinylpyridine) chains as corona) within one phase of a polystyrene-*block*-poly(2-vinylpyridine) (PS-*b*-PVP) diblock copolymer can be achieved by changing the grafting density, the added volume fraction of particles as well as the block copolymer molecular weight. For small grafting densities of PS or in case of particles grafted with a mixture of PVP and PS polymers, the particles are predominantly located at the interface. The results suggested a redistribution of the coronal chains into a surfactant-like particle. However, in order to obtain these results, very mild film casting processes were required that would allow for a suggested redistribution of the corona chains. Moreover, the process is limited to a small scale, both caused by the relatively limited film casting process and secondly by the complex nanoparticle synthesis.

Herein, we will demonstrate two major results. First, a superior performance of Janus particles for compatibilizing polymer blends under high-shear conditions in a twin-screw miniature mixer, utilizing Janus particles on a *multigram* scale. Secondly, we will show how to overcome problems in the precise positioning of particles in polymer blends. So far, success in the controlled and exclusive location of particles at interfaces under aggressive conditions remains limited. However, with this approach, we will illustrate that the location of the Janus particles can be effectively controlled on the nanoscale, whereas the processing parameters are applicable to macroscopic production constraints.

RESULTS AND DISCUSSION

Janus Particles and Their Behavior in a Homopolymer. The Janus particles in this study were prepared by crosslinking the well-defined lamella-sphere bulk structure of a
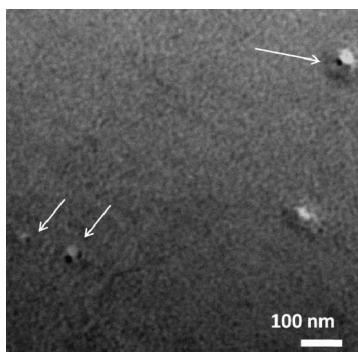
Figure 1. TEM of Janus particles blended into a PS matrix (2 wt % of Janus particles). The arrows highlight Janus particles.

polystyrene-*block*-polybutadiene-*block*-poly(methyl methacrylate) triblock terpolymer (SBM), having symmetric end blocks and a very small fraction of polybutadiene. Details of this procedure were published earlier.[36] These Janus particles consist of a tightly crosslinked polybutadiene nanoparticle core with *ca.* 13 chains each of PMMA and PS protruding out of it. The two polymers are microphase-segregated into two hemispheres, leading to a biphasic particle as shown in Scheme 1.

In organic solution, these particles have a number-average hydrodynamic radius of around 10 nm, as found by fluorescence correlation spectroscopy, and are thus of comparable dimensions as the polymers used in this study, PMMA (M_w = 120 kg/mol, PDI = 1.8, $R_g \approx 9.5$ nm) and PS (M_w = 230 kg/mol, PDI = 1.6, $R_g \approx 14.4$ nm). To allow drawing meaningful conclusions from the following blend results and from the influence of the Janus character onto their location in the blend, a sufficient mixing of the particles with the matrix component PS has to be assured. In particular, it needs to be shown that large-scale phase separation does not occur, as otherwise, the particles might be preferentially segregated to the blend interface because of their size, and therefore less influence of the biphasic Janus character would dominate the results.

Figure 1 shows a representative nonstained TEM micrograph of Janus particles blended into the PS matrix. At low magnification the TEM images appear completely homogeneous and only for higher magnifications the well-dispersed Janus particles become distinguishable. Large-scale phase separation cannot be detected; in contrast, the Janus particles are predominantly unimolecularly dispersed. Note that also the formation of dimers, trimers, or micelle-like aggregates is very limited. The Janus particles are thus well dispersed. The small black dots correspond to the polybutadiene nanoparticle core, which has the highest
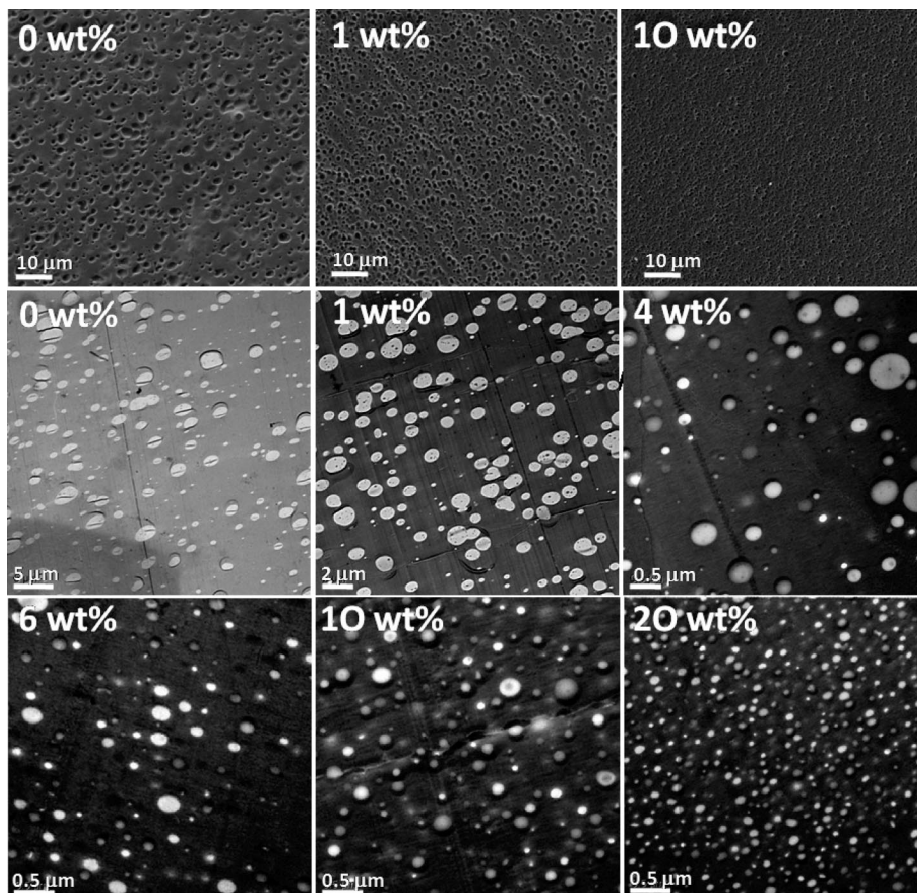

Figure 2. SEM images obtained for blends at a PS/PMMA ratio of 6/4 (top row). Nonstained TEM images obtained for blends at a PS/PMMA ratio of 8/2 (center and lower row). The amount of compatibilizer is indicated in each image.
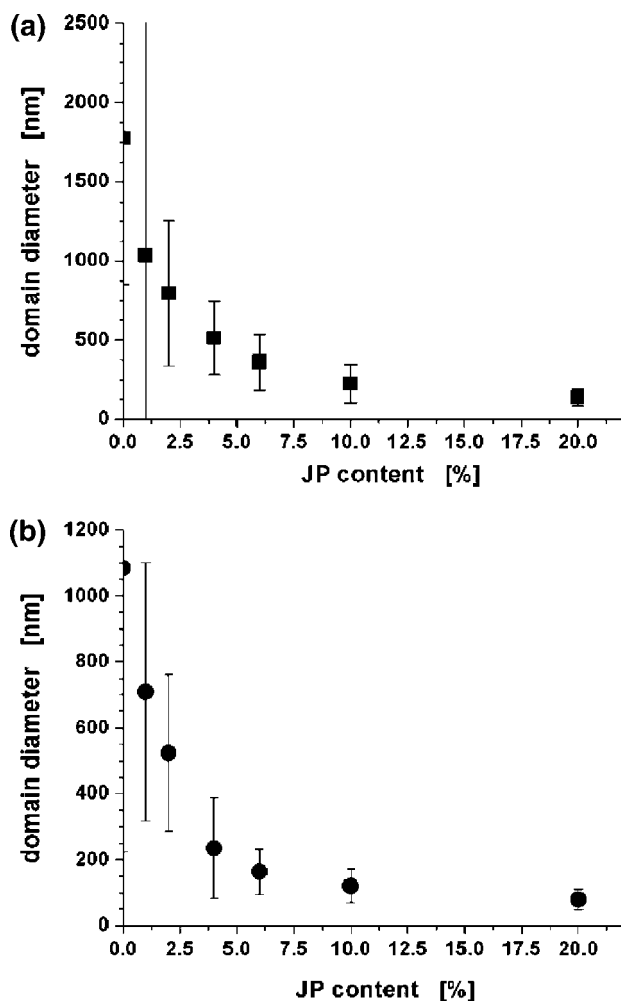
(a)

(b)

Figure 3. Decrease of the number-average PMMA domain diameter as a function of the content of Janus particles at PS/PMMA ratios of 6/4 (a) and 8/2 (b). The vertical bars show the standard deviation of the size distribution of the PMMA domains.

contrast in TEM, due to its crosslinking with S_2Cl_2. The white shadow on one side is caused by the PMMA side, which is degraded upon e-beam exposure. Apart from allowing a conclusion of the miscibility of the Janus particles with the homopolymer, these images also unambiguously confirm the non-centrosymmetric Janus character of these particles. An analysis of the dimensions of the structures yields a radius of the polybutadiene nanoparticle core of 3−5 nm and a total radius, as judged from the white PMMA shadow, of 20−25 nm.

Although the total visible radius is larger than the radius of gyration of the PS matrix, the particles stay well dispersed. Apart from the applied shear, which certainly assists the dispersion, this can be rationalized considering several factors. First, the radius of gyration of the Janus particles is significantly smaller than the visible radius, deduced by TEM. Additionally, only one side is immiscible with the PS phase, which can be seen as a reduction of the radius to almost half of its total dimension. This goes along with a reduction of unfavorable contacts as compared to a homogeneous particle of similar size and different composition as the matrix ma-

terial. Secondly, only the polybutadiene core is a densely crosslinked impenetrable nanoparticle core, having a radius smaller than the coil dimensions of the PS phase. Furthermore, a penetration of the PS side of the Janus particle by the PS chains of the matrix material is possible, thus further limiting an entropic penalty by chain conformational entropy loss. Another factor in this context, which might play a role, is the fact that the PS matrix material exhibits a high polydispersity, which presumably favors the miscibility.

In conclusion, the Janus particles are well dispersed in the matrix material and hence the influence of the Janus character on the location of the particles in a polymer blend and the compatibilization efficiency can be rationally investigated.

Janus Particles in PS/PMMA Polymer Blends. Due to the unique combination of amphiphilicity with the particle character, Janus particles are expected to strongly adsorb and orient at the interface. The adsorption energy at the interface is significantly enhanced as compared to standard block copolymers, which are commonly used as stabilizers in polymer alloys. To the best of our knowledge, none of the theoretical studies has included Janus particles into their considerations. Janus particles impose another significant enthalpic contribution to the free energy of the system. The interfacial tension between the sides and the respective polymers is negligibly small, whereas the interfacial tensions of the two sides with the unlike blend component is in the region of the interfacial tension of the mixture.

To apply this new concept and to study the effect of the Janus particles on the compatibilization of polymer blends, we prepared PS/PMMA blends at weight ratios of 6/4 and 8/2 with various amounts of Janus particles. To allow a meaningful estimation of the performance of the beadlike stabilizer, several polymer blends using linear block copolymers were prepared for comparison.

In a first step, the weight fraction of Janus particles was changed from one to 20 wt % to allow a monitoring of the morphological changes. The mixing parameters like temperature, shear rate, and mixing period were kept constant for all mixtures to minimize the experimental errors during the blending and to allow a reliable comparison. Note that the statistical analysis of polymer blends with 8/2 blending ratio leads to more accurate values, as a thermal relaxation of the droplets after blending can be done in order to reduce the shear-induced asymmetry of the dispersed droplets. In the case of a blend ratio of 6/4 this is not possible, because the morphology may relax into a co-continuous one after prolonged annealing,[37] for which a straightforward droplet analysis cannot be applied anymore. The symmetric blend ratio was however additionally chosen for its significance in terms of tailoring mechanical properties or, for example, in polymer solar cells, which would in the best sense require co-continuous morphologies.
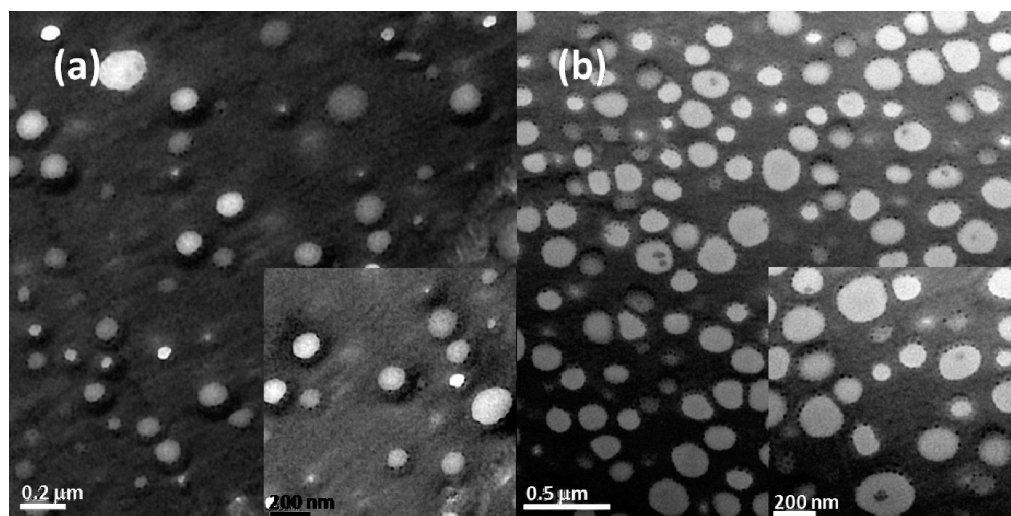
Figure 4. TEM images obtained for (a) 10 wt % JP in a 8-2 PS/PMMA blend and for (b) 20 wt % JP in a 6/4 PS/PMMA blend.

Furthermore, it was theoretically shown that for different mixing ratios of polymers, the compatibilization efficiency of a given particle can be different.[14]

The SEM and TEM images shown in Figure 2 give a first overview of the development of the domain sizes of the dispersed phase. The SEM images (PS/PMMA = 6/4) are shown at the same magnification to allow a straightforward overview of the changes occurring with increasing Janus particle content. The magnification of the TEM images (PS/PMMA = 8/2) is changed progressively to allow a good display of the domain sizes. Clearly, the PMMA domains, appearing as dips or white domains in the PS matrix in the SEM and TEM images, respectively, show a distinct and rapid decrease in size. Initially, the number-average domain diameter, D_n, of the reference sample without addition of any stabilizer is in the micrometer range ($D_n = 1.8$ μm for 6/4 and $D_n = 1.1$ μm for 8/2). Upon addition of only one percent of Janus particles, a rapid decrease of the domain diameter to an average PMMA domain diameter of $D_n = 1.2$ μm (6/4) and $D_n = 710$ nm (8/2) can be observed. This decay steadily continues with increasing amount of compatibilizer and truly nanoscopically sized domains can be obtained. With a further increase of the Janus bead content, a continuous decrease of the domain sizes even below $D_n = 140$ nm (6/4) and $D_n = 80$ nm (8/2) for 20 wt % Janus particle content can be observed. Importantly, this nanostructuring of the polymer blend can be achieved without special high-shear processing units or complex chemical reactions within the blend mixture. Moreover, no optimization of the blending conditions was done, demonstrating furthermore the efficiency of the stabilizer used.

The decay of the number-average domain diameters of the PMMA droplets ($D_{n,PMMA}$), is shown in Figure 3.

A strong and strikingly rapid decay of the PMMA domain sizes can be observed. The decrease is yet ongoing for high concentrations, indicating an only insignificant loss of stabilizer in one of the blend components. The rapid decay itself is an indication for the presence of a compatibilizer of very high interfacial activity.

In conclusion of the observed decrease of the domain diameter with the increased addition of Janus particles, it is evident that the Janus particles act as stabilizers at the interface of the PS/PMMA blends. Figure 4 shows a representative overview of two selected TEM images at higher magnification for two different Janus particle contents and two different blending ratios of PS and PMMA. In both images, small black dots can be observed at the interface of the PMMA and PS phases. These small black particles can be identified, in terms of their size, as the cores of the Janus particles. Those cores consist of polybutadiene, which was crosslinked with S_2Cl_2, thus explaining the contrast in TEM. Furthermore, both domains, PS and PMMA, appear homogeneous and hardly any single or aggregated Janus particles within one phase can be found. Note that Janus particles can be clearly identified within the PS or PMMA phase (see e.g., Figure 1).

These observations give a first explanation of the excellent performance of Janus particles as stabilizers in polymer blends. Obviously, the Janus particles are almost exclusively located at the interface and only a negligibly small fraction is "lost" as unimers or micellar aggregates in one of the components, also representing a significant improvement as compared to block copolymer compatibilizers.[3–6] This is a direct consequence of the high interfacial activity and increased adsorption energy at interfaces of Janus particles.

The strong adsorption of Janus particles can be elucidated with an energetic consideration of the system. The surface activity of a particle can be expressed in terms of the desorption energy of the particle from an interface. Binks et al. derived an expression for the calculation of the desorption energy of an amphiphilic particle, adsorbed at an interface of two immiscible liquids, on the basis of its surface free energy, $E(\beta)$.[7]

$$E(\beta) = 2\pi R^2 \Big[\gamma(S_{jp}S)(1 + \cos\alpha) + \gamma(M_{jp}S)(\cos\beta - \cos\alpha)$$
$$+ \gamma(M_{jp}M)(1 - \cos\beta) - \frac{1}{2}\gamma(SM)(\sin^2\beta) \Big] \quad (1)$$

for $\beta \leq \alpha$.

The surface free energy (equation 1) depends on the immersion depth of the particle at the interface, β, the asymmetry of the biphasic particle, α, and the radius, R, of the particle. A particle is completely immersed into one of the phases for $\beta = 0°$ and $\beta = 180°$ and adsorbed along its equator for $\beta = 90°$. For completely symmetric hemispheres, α approaches 90°. Furthermore, the equation depends on the various interfacial tensions between the PMMA (M_{JP}) and PS (S_{JP}) side of the Janus particle with the two bulk phases PS (S) and PMMA (M) ($\gamma(S_{JP}S)$, $\gamma(M_{JP}M)$, $\gamma(M_{JP}S)$), as well as on the interfacial tension of the blend components ($\gamma(MS)$). Note that this equation is valid under the condition that the Janus particles are sufficiently smaller than the stabilized domains, allowing the assumption of quasi-planar interfaces. The desorption energy, which is a measure for the interfacial activity of a particle, can be calculated from the energy which is necessary to transfer a particle from the interface to one of the bulk phases ($E_{PS} - E_{interface}$ or $E_{PMMA} - E_{interface}$). Assuming negligible interfacial tensions ($\gamma(S_{JP}S)$, $\gamma(M_{JP}M)$) for the sides of the Janus particle with their respective blend phases and an equatorial adsorption ($\beta = 90°$) of the indeed completely symmetric Janus particle ($\alpha = 90°$), the desorption energy for a Janus particle ($E_{JP,des}$) reads as:

$$E_{jp,des} = 2\pi R^2 \gamma(SM) + \pi R^2 \gamma(SM) = 3\pi R^2 \gamma(SM) \quad (2)$$

Similarly, Pieranski derived an expression for the desorption energy of a homogeneous particle, P,[7,38] ($\alpha = 0°$, $E_{hom,des}$). Herein $\gamma(PS)$, $\gamma(PM)$, and $\gamma(SM)$ are the interfacial tensions of the particle with PS and PMMA, and between the two polymers (PS & PMMA), respectively.

$$E_{hom,des} = \pi R^2 \gamma(SM)(1 - |\cos\beta|)^2$$

$$\text{with} \quad \cos\beta = \frac{|\gamma(PS) - \gamma(PM)|}{\gamma(SM)} \quad (3)$$

The maximum of the desorption energy, $E_{hom,des}$, can be reached if $|\gamma(PS) - \gamma(PM)| \ll \gamma(SM)$ and reads as $\pi R^2 \gamma(SM)$.

Clearly, these considerations show the stronger adsorption of the Janus particles as compared to homogeneous particles of similar size. The desorption energy of an ideal Janus particle is three times higher than for a standard particle. This gap widens for asymmetrically (non-equatorially) adsorbed homogeneous particles, which are preferentially wetted by one blend component. In particular for small nanoparticles and higher temperatures, the energetic difference between biphasic and normal particles matters most. Note that the probability of the displacement of a particle from the interface scales with $p \approx \exp(-E/kT)$. Therefore, the probability of a Janus particle to desorb from the interface is lower by a factor of $e^3 \approx 20$. Consequently, the biphasic nature of the Janus particles is the origin of a crucial additional energetic contribution and is the reason for a complete adsorption in combination with a firm attachment of the particles at the interface.

In terms of a general applicability of this approach for other polymer blend systems, the Flory-Huggins interaction parameter, χ, can be used to rationalize the effect of changing the polymer blend components. This interaction parameter is related to the interfacial tension, γ, of a binary blend system via $\gamma \sim \chi^{1/2}$.[39,40] Thus, the Flory-Huggins parameter can be directly related to the desorption energies in equations 2 and 3. Following these considerations, the adsorption is favored and simplified for polymer systems with larger unfavorable interaction, χ. Herein, we used a PS/PMMA polymer blend model system with a relatively low incompatibility ($\chi(SM) \approx 0.036$ at 210 °C,[41] $\gamma(SM) \approx 1.12$ mN/m at 210 °C[42]). Note that a complete particle adsorption at the interface could even be achieved for such a system with relatively low incompatibility for which the location of the particles at the interface is less favored. Most polymer blend systems show a higher incompatibility and would thus lead to a strengthened adsorption at the interface.

In this context, a comparison with previous results in literature is appropriate. Kramer and co-workers[29–35] could show a control of the location of homogeneous particles and mixed (possibly biphasic) particles in block copolymers in one of the phases or predominantly at the interface, respectively. However, they required extremely mild film casting processes in their preparation of the composite materials, which is thus not representative of the conditions used here. Concerning high shear blending, this is the first time that Janus particles are used and so any comparison with literature can be made. For homogeneous particles, it is known that the exclusive location of particles at the interface remains challenging. Often only a fraction of the particles can be located at the interface or there is an incomplete coverage of the interface.[43,44] Therefore, the order at the interface is low as well and a significant fraction of particles is "lost" in one of the phases and may contaminate the properties of a nanocomposite material. For instance, Vermont et al.[44] demonstrated that they could obtain some compatibilization of polyisobutylene /polydimethylsiloxane (PIB/PDMS) blends with silica particles. However, the particles were also located in both phases, particularly in the PDMS phase, thus altering the properties of all phases and resulting in ill-defined nanocomposites. Additionally, the particles did not exhibit any order at the interface. An inversion

of the weight fractions of the polymer blend resulted in an unsatisfying compatibilization, demonstrating the need of tailoring the surface chemistry of the particles. Some further success was recently reported by Chung *et al.*,[45] who showed that nanoparticles with specifically tailored surface chemistry assembled to a large extent at a polymer blend interface after a soft annealing step in a thin film. After casting of the film, the particles were located in all components. Whether the interfacial adsorption would persist during high shear blending could not be shown, but is at least uncertain.

Aside the strong adsorption of the Janus particles, even an ordering of the particles could be observed. Owing to the yet finite thickness of 70−90 nm of the ultrathin sections used for the TEM investigations, several circular endcaps of the PMMA droplets can be identified at closer observation of the TEM images. Two of those caps are shown in Figure 5.

Ordered Arrangement of the Janus Particles at the Interface. The section analysis in Figure 5a shows a core diameter of around 8−10 nm, which confirms the black points as the diameter of individual Janus particles. The particles adsorb strongly at the interfaces, but are yet separated from each other by the repellence of their polymer brush-like corona. Both TEM images exhibit an ordered arrangement of the Janus particles (dark dots) at the interface. All Janus particles are separated from each other by a similar centre-to-centre distance of around 30−35 nm and are closely packed. The efficient repellence of the Janus particles along the PS/PMMA interface also goes along with a strong reduction of the coalescence of Janus particle stabilized PMMA droplets during the blending process. The exhibited order at the interface is a very interesting observation that would allow a lateral two-dimensional nanoscopic structuring of the interface

These results additionally demonstrate that desired functionalities based on modified Janus particles (*e.g.,* bimetallic Janus particles[46]) could be precisely and exclusively located at the blend interface even under the strong shear and high temperature conditions of the twin-screw mini-mixer. In a next step, this implies that particles can be selectively located in the two phases or at the interface, just depending on the fact whether they are homogeneous in their corona or phase-segregated into two hemispheres. This offers a high control for engineering nanocomposite polymer blends of desired compositions and properties.

Comparison with State-of-the-Art Compatibilizers. Apart from the structuring of the interface, a comparison with existing polymer blend stabilizers is very desirable. In the competitive field of polymer engineering and in particular in polymer blend processing, a novel type of stabilizer will only be of scientific and economic interest if a considerable improvement in the compatibilization can be achieved. Currently,
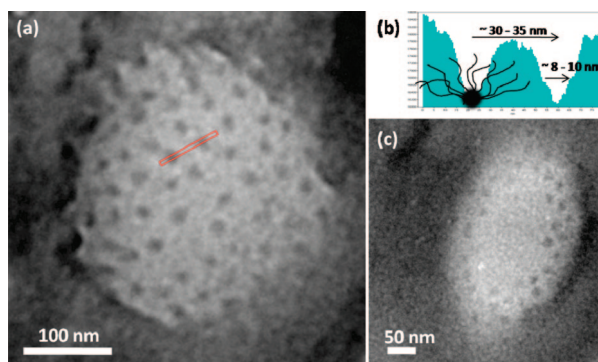

Figure 5. Endcaps of PMMA droplets with Janus particles located at the interface. Panels a and c are representative examples at 10 wt % and 6 wt % of JP content in a 6/4 PS/PMMA blend. (b) Section analysis of the red bar shown in image a. One side of a Janus particle is schematically sketched to show its brush-like character and the location of the polybutadiene core.

block and graft copolymers are state of the art compatibilizers for polymer blends. The effectiveness of a block copolymer to adsorb and stabilize a polymer blend interface against coalescence depends mainly on its molecular weight, the block ratios, and the molecular weights of the blend components. The tendency of migrating to an interface is highest for low-molecular weight polymers, whereas the suppression of coalescence is often best for high molecular weight polymers. Additionally, low molecular weight polymers have a high solubility in the blend components and high molecular weight polymers tend to form micelles, thus representing an obstacle for the compatibilization. This controversy is also expressed in the fact that self-consistent field modeling suggested on the one hand that the interfacial tension of an A/B blend is best reduced for high molecular weight diblocks, thus leading to a strong emulsification.[47] On the other hand, experimental studies find that high molecular weight block copolymers do not give the best results, simply because they are not able to diffuse to the interface in an appropriate time and are trapped in micelles.[5,48] Therefore, these counteracting forces always need to be balanced carefully for the development of efficient stabilizers.

Generally, the PS/PMMA blend system is a well explored system and thus would, in principal, allow a comparison with the literature.[3,47,49−51] However, because of the different experimental conditions for the preparation and the different compatibilizers used, we decided to establish our own reference system, for which we can apply exactly the same blending conditions as for the Janus particles. Therefore, we prepared two series of PS/PMMA blends using a linear SBM (polystyrene-*block*-polybutadiene-*block*-poly(methyl methacrylate)) block terpolymer as stabilizer. Note that SBM triblock terpolymers are very efficient blend compatibilizer.[52−55] The linear triblock terpolymer used is exactly the same polymer,
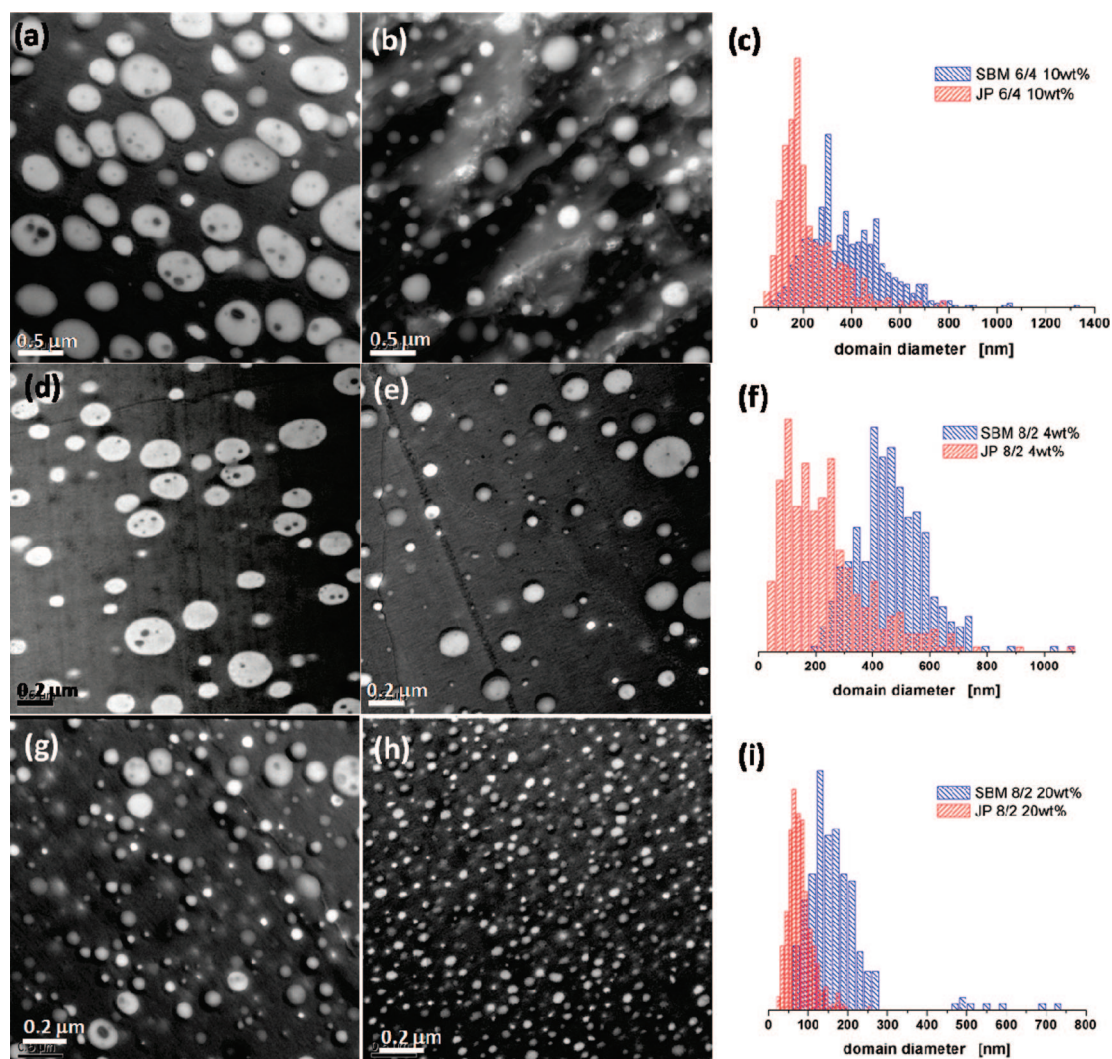
Figure 6. TEM images for polymer blends stabilized with SBM (a, d, g) and Janus particles (b, e, h) for different PS/PMMA ratios of 6/4 (first row) and 8/2 (second and third row). The concentration of the compatibilizer is 10 wt % (a), 4 wt % (b) and 20 wt %. The right side shows histograms of the statistical analysis of the PMMA domains.

which is employed for the preparation of the Janus particles. It is of the same composition and has a similar radius of gyration as compared to the Janus particles. Thus, partitioning effects because of different radii of gyration are similar. Therefore, it can be considered as a scientifically correct and fair assessment of the compatibilization efficiency. Similarly to the polymer blends prepared with the Janus particles, the amount of SBM stabilizer was varied for the polymer blends to follow the decay of the domain size of the dispersed PMMA phase in dependence of the compatibilizer content. The fraction of added SBM terpolymer was corrected for the slight mass increase, caused by the cold vulcanization, during the crosslinking reaction yielding the Janus particles. Hence, the blends were prepared at exactly the same molar amount of SBM, either in the form of linear polymer or crosslinked in a Janus particle and thus allow a scientifically correct assessment of the stabilizer performance. A first overview can be

obtained by comparing the TEM images and the frequency distributions of the dispersed PMMA droplets at a given concentration of stabilizer. Figure 6 displays data for PS/PMMA blends at 4 wt %, 10 wt % and 20 wt % of compatibilizer and blending ratios of 8/2 and 6/4, respectively.

A striking difference can be observed from the images straightaway. At any given concentration, the addition of Janus particles leads to significantly smaller domain diameters, indicating a superior stabilization of the polymer blend system. A more detailed conclusion can be drawn by analyzing the frequency distribution of the domain sizes as shown on the right-hand side in Figure 6. The maximum of the size distribution of the PMMA domains is shifted towards higher diameter when using the block copolymer instead of the Janus particles. The effect is present independently of the stabilizer content and blend ratios used. Consequently, the Janus particles outperform the standard block copolymer tremendously.

A completely quantitative picture can be obtained by comparing the number-average PMMA domain sizes for both compatibilizers over the full range of stabilizer content and the different blending ratios. Figure 7a shows the evolution of the domain diameters as a function of the stabilizer content.

Comparing the filled (Janus particles) with the open symbols (SBM) leads to the conclusion that under any blending ratio, the Janus particles lead to smaller domain sizes. Additionally, the Janus particles lead to a more rapid decay than the block copolymer, which is also a typical feature of a compatibilizer with a higher efficiency. Moreover, the SBM block copolymer shows a leveling off for higher concentrations and the addition of more block copolymer does not further decrease the domain sizes. Domain sizes in the region below 100 or 250 nm for the different blending ratios of 8/2 and 6/4, respectively, may not be reached. The block copolymer stabilizer loses its efficiency, a phenomenon seen for other systems already.[3,6] In accordance with the TEM images, a significant fraction of the block copolymer stabilizer is lost as micellar aggregates. Those aggregates can be found at most of the concentrations and appear to be increasingly dominant for higher concentrations. Figure 8 shows some of these aggregates after selectively staining the remaining olefinic polybutadiene bonds with OsO_4. The structures embedded into the PMMA droplets are very small and often darker than the matrix phase composed of PS. Bearing in mind that the contrast in TEM evolves from thickness in combination with mass density, it is evident that these structures are significantly stained with OsO_4, thus confirming the presence of polybutadiene and henceforth of SBM block terpolymer micelles. A dark ring can be seen surrounding the PMMA domain at the interface to the PS matrix. This ring originates from the SBM block terpolymer acting as stabilizer of the phase boundary. The micellar aggregates are too small to contain significant amounts of polystyrene homopolymer. Consequently, they do not participate in the compatibilization process and thus the limited compatibilization efficiency of the SBM block copolymer can be reasonably understood. Note that micelles within the PS matrix cannot be identified easily as the micelles cannot be unambiguously distinguished from small dispersed and stabilized PMMA domains. Therefore, in order to not underestimate the performance of the block copolymer, those small structures were counted as domains. Presumably, a fair amount of those might be micelles though, which would increase the number average domain size, $D_{n,SBM}$.

Concerning the blends compatibilized with Janus particles, the domain sizes continue to decrease even for high contents of stabilizer. This is a direct consequence of the Janus character of the particles. Due to the unique combination of the Pickering effect with amphiphilicity, the biphasic particles adsorb strongly at the interface and
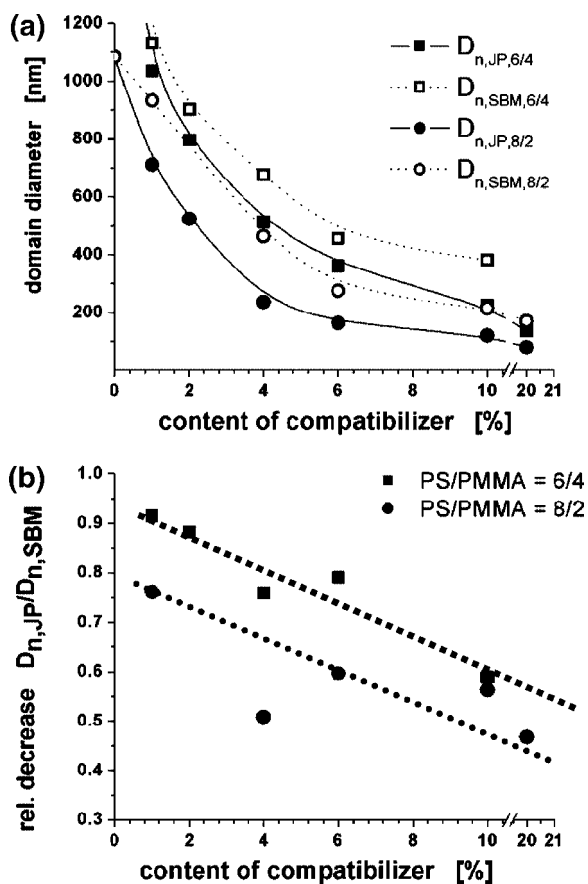

Figure 7. (a) Evolution of the PMMA domain diameter as a function of the content of compatibilizer for different types of stabilizers, SBM and Janus particles, and varying blending ratios as indicated in the graph. (b) Relation between the number average PMMA domain sizes of polymer blends compatibilized with SBM and Janus particles. Both blend ratios are shown as indicated in the graph. The lines serve to guide the eye.

do not lose their efficiency for higher concentrations. This is also the reason why with increasing content of stabilizer, the relative gap between the domain sizes for blends stabilized with block copolymers or Janus particles, respectively, widens. Figure 7b displays the ratio of the two values $D_{n,JP}$ over $D_{n,SBM}$, which can be best used to demonstrate this behavior. A decrease of this ratio can be observed. This means that the SBM block copolymer is outperformed at all times, but the effect and the efficiency gap becomes more and more pronounced for increasing compatibilizer content. Already at moderate compatibilizer concentrations at a blending ratio of 8/2, the Janus particles lead to domains of half the size as when using the block copolymer. This is a tremendous boost in the performance and nicely demonstrates the powerful capabilities of Janus particles for stabilizing block copolymer interfaces and homogenizing polymer blends.

Depending on the targeted or desired diameter of the dispersed phase, the mass fraction of the stabilizer can be cut back by even fifty percent. All of this can be realized in this case by a relatively simple synthetic transformation of the block terpolymer into a Janus particle. The
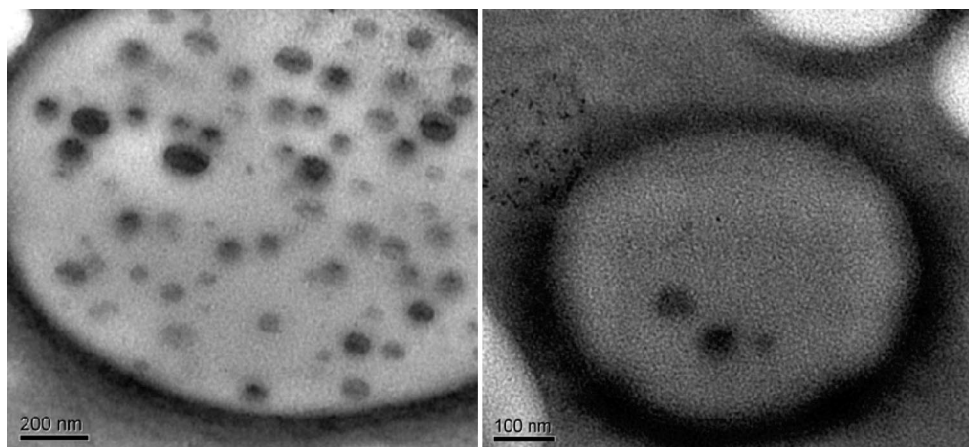
Figure 8. TEM micrographs for a polymer blend (PS/PMMA = 8/2) stabilized with 10 wt % SBM, after staining of the polybutadiene double bonds with OsO_4.

large size range at the interface, in particular those particles, which, if they were homogeneous, would not adsorb at the interface due their size. Additionally, with our results, we also hope to promote some theoretical work, treating the behavior of Janus particles in polymer blends and homopolymers in order to gain further insights into the system.

CONCLUSION

resulting physical characteristics of the Janus particles, that is, the strengthened adsorption based on the combination of Pickering effect with amphiphilicity, lead to the superior performance observed here. Note that in this first study of the PS/PMMA model system, no further optimization of the blending conditions or special high shear blending apparatuses were used,[56] and we could nonetheless obtain very promising results.

Looking out to the future, with the growing number of preparation pathways to Janus particles in the chemists' and material scientists' hand (electrospinning, microfluidic devices, Pickering particle route, bimetallic nanoparticles, triblock terpolymer based route[57]), it appears likely to increasingly obtain tailor-made Janus particles. With these particles, it would be possible to blend a large variety of different polymers. Although Janus particles may not find widespread application for blending standard commodity plastics, they are very promising candidates for the nanostructuring of high performance materials of strongly immiscible components, for self-healing composites, increased thermo-conductivity, or for optoelectronic devices. It appears possible, for instance, that adequately functionalized inorganic nanoparticles may do light harvesting in combination with compatibilizing polymer blend solar cells.

Additionally, due to the strong adsorption, Janus particles can overcome energetic boundaries, which were theoretically calculated for homogeneous particles and are thus another efficient mean in the nanoparticle toolbox for the controlled positioning of nanoparticles in polymer blends and block copolymers. Therefore, it may be possible to locate particles of a

We present the first application study using Janus particles on a *multigram* scale, which can be seen as a demonstration of the capabilities of the synthesis of complex nanoparticles. It is shown that Janus particles can be used to efficiently compatibilize polymer blends under high shear conditions. A constant decay of the domain size of the dispersed phase can be observed, independent of the blend composition used. The performance of the Janus particles in compatibilizing the polymer blend is significantly superior to other state-of-the-art compatibilizers, such as linear block copolymers. Common problems like micellization of the stabilizer and insufficient adsorption at the interface can be overcome to a major extent. The origin of this continuous decrease is the strengthened adsorption of the Janus particles at the interface, which is in turn caused by their biphasic particle character. In contrast to block copolymers or homogeneous particles, the Janus particles are located at the interface, even at high temperature and shear. The adsorption energy of a Janus particle at an interface at processing conditions is almost as high as for a homogeneous particle at room temperature. This can be explained by an additional enthalpic contribution to the adsorption energy. The Janus particles, adsorbed to the polymer blend interface, exhibit an ordered arrangement. Consequently, the structural order occurs on two levels. The first is the complete adsorption at the interface and the second is the lateral ordering at the interface. This renders them an interesting tool for the nanostructuring of blend and block copolymer interfaces. Therefore, Janus particle provide a mean for the nanoscopic engineering of polymer blend systems, while matching some macroscopic processing constraints.

METHODS

Materials. Poly(methyl methacrylate) (PMMA, M_w = 120000, PDI = 1.8) and polystyrene (PS, M_w = 230000, PDI = 1.6) were purchased from Aldrich. The SBM polymer used for blending and for the preparation of the Janus particles is a polystyrene-*block*-polybutadiene-*block*-poly(methyl methacrylate) (SBM) triblock ter-

polymer, which was prepared by anionic polymerization. The Janus particles were obtained by crosslinking the lamella-sphere morphology of the SBM triblock terpolymer in the bulk state *via* cold vulcanization with sulphur monochloride (S_2Cl_2). The two sides consist each of *ca.* 13 chains, which are attached to a central crosslinked particular polybutadiene core. They core is surrounded

by about 13 chains each of PS (DP = 800) and PMMA (DP = 700), which are phase-separated.

Blend Preparation. To prepare a homogenous polymer powder, the calculated amounts of PS, PMMA, and Janus particles were dissolved in THF, precipitated into methanol, and dried in vacuo for 2 days. The blends were prepared in a Haake MiniLab Twin Screw extruder at 210 °C and 40 rpm. The duration of melt blending was 3 min. After blending the material was extruded and the center of the released strand was microtomed at half of its length. The microtom cut sections were imaged with TEM, whereas the cut material area was exposed to deep UV for etching away the PMMA domains. The latter one was used for SEM imaging after covering with a thin layer of platinum.

Scanning Electron Microscopy (SEM). SEM was performed using a LEO 1530 Gemini instrument equipped with a field emission cathode with a lateral resolution of approximately 2 nm. The acceleration voltage was chosen between 0.5 and 3 kV.

Transmission Electron Microscopy (TEM). For TEM, thin sections were cut at room temperature using a Reichert-Jung Ultracut E microtome equipped with a diamond knife. Bright-field TEM was performed on Zeiss CEM 902 and LEO 922 OMEGA electron microscopes operated at 80 and 200 kV, respectively.

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