

Janus Discs: Preparation, Size-Tunability, Visualization, Self-Assembly

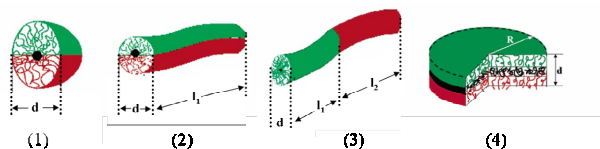
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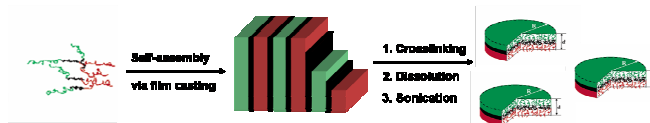
INTRODUCTION

In recent years, Janus particles have attracted much attention in nanoscience due to their interesting properties, both for academic as well as for technological reasons. In general, Janus structures have a compartmentalized surface and can be divided into three classes according to their architecture – spherical Janus micelles (3D)^{1, 2}, two types of Janus cylinders (1D)³ and Janus sheets or discs (2D), representing the intermediate case of dimensionality (see scheme 1). The synthesis of such non-centrosymmetric structures with compartmentalized coronas is a demanding task for the synthetic chemist. Hence, only a few real nanosized polymer-based Janus structures are known in literature.



Scheme 1. Possible Janus architectures with phase-segregated shells: (1) spherical Janus micelle, (2) & (3) two types of Janus cylinders, (4) Janus sheet/disc.

Here, we present for the first time the synthesis of novel disc-shaped Janus particles, having two different sides of polystyrene and poly(*tert*-butyl methacrylate), via a template-assisted pathway based on block terpolymer templates in the bulk (see scheme 2).



Scheme 2. Schematic synthesis of Janus discs, based on the selective crosslinking of PB domains of a SBT terpolymer with lamella-lamella (ll) morphology.

Using scattering and imaging techniques, we show that the particle size can be tuned, that the particles are of true Janus character and that they form supramolecular aggregates in good solvents.

EXPERIMENTAL SECTION

Crosslinking with AIBN / Thiol-Polyene Process. AIBN (5 wt%, relative to the mass of the SBT terpolymer), trimethylolpropane mercaptopropionate (TRIS, 0 - 5 wt%) and SBT terpolymer (synthesized by anionic polymerization) were dissolved in CHCl₃ and the film-casting process was allowed to take place in a solvent vapour-filled desiccator for about two weeks. Afterwards, the film was dried *in vacuo* at RT for 24 h and crosslinked at 80 °C for 48 h. Subsequently, the film was purified by Soxhlet extraction with THF for 24 h yielding a soluble and an insoluble fraction. The latter was subjected to a sonication.

Sonication. The product underwent ultrasonic treatment using a Branson model-250 digital sonifier, equipped with 1/8 in. diameter tapered microtip, at various amplitudes (200 watt at 100% amplitude). For this purpose, a dispersion of insoluble crosslinked material (c = 0.3 - 1 mg/ml) in THF was allowed to stand at room temperature for several hours to ensure good swelling of the material. Afterwards, it was subjected to the sonication treatment in a temperature controlled cell.

The on/off cycle times were typically in the range of 2s/2s and 2s/10s, depending on the amplitude used.

RESULTS AND DISCUSSION

Terpolymers and Microphase-Separated Structures. In the case of SBT terpolymers, it is known that the desired so-called lamella-lamella (ll) morphology is formed over a wide range of PB volume fractions as long as the end blocks are of similar volume fractions. Therefore two terpolymers (S₄₂B₁₀T₄₈¹³³ = SBT-1 and S₄₅B₅T₅₀¹³³ = SBT-2) with different fractions of polybutadiene were synthesized via sequential living anionic polymerization. The microphase separation was analyzed by transmission electron microscopy (TEM) and small angle x-ray scattering (SAXS) (see figure 1). Both terpolymers exhibit lamellar morphologies in the bulk state with alternating lamellae of PS (grey) and PtBMA (white), which are separated by a thin lamella of PB (black).

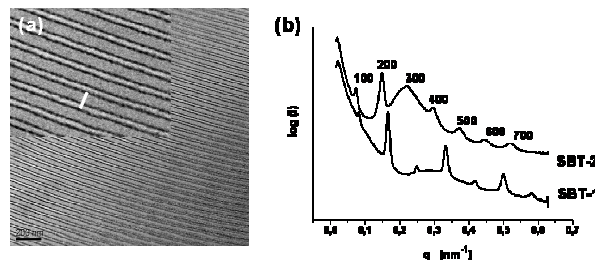


Figure 1. (a) Transmission electron micrograph of an ultrathin section of a SBT-1 film after staining with OsO₄. (b) SAXS diagrams after azimuthal integration of the intensity as a function of the scattering vector q for SBT-2 and SBT-1. The SAXS pattern of SBT-2 was multiplied by 15 to allow a better separation.

Both SAXS patterns exhibit the characteristic peak distributions for lamellar block copolymer structures, i.e., the reflections are integer multiples of the first order peak q^* ([100]). The positions of the reflections allow the calculation of the long period, d , of the structures via $d = 2\pi/q^*$. The deduced values are $d = 80$ and 86 nm for SBT-1 and SBT-2, respectively, corresponding to the ones which were determined by TEM investigations (SBT-1: $d = 78$ nm; SBT-2: $d = 86$ nm). By means of crosslinking the polybutadiene part, the preorientation of the two sides, PS and PtBMA, can be preserved.

Solution Properties. After successful crosslinking of the terpolymer templates, e.g. via radical crosslinking or “cold vulcanization” with S₂Cl₂, and subsequent purification with soxhlet extraction, the insoluble fractions were subjected to a sonication procedure in order to obtain soluble Janus discs. Thus, the solutions of swollen crosslinked gels were treated with high-energy ultrasound in a temperature-controlled cell until a semi-transparent solution was reached. After this procedure, dynamic light scattering measurements were conducted in order to investigate the sizes of the resultant flat Janus particles and their distribution.

Generally, a characteristic decay of the hydrodynamic radii can be observed with increasing sonication time for all homogenization procedures (see figure 2). The curves follow an exponential decay, indicating that in the beginning of the ultrasound treatment the large particles are fragmented into significantly smaller ones, causing the rapid decrease. After a certain time (20 - 30 min for SBT-1, 5 - 10 min for SBT-2) the curves show a more asymptotical behaviour. At this stage the particle size decays much more slowly.

Consequently, there is some higher resistance to the introduced sonication energy. This resistance is presumably due to the higher mobility of the smaller structures and an accompanying higher resistance and more flexible adaptation to the shock waves produced by the ultrasound. An increase in the sonication amplitude from 10 % to 70 % leads to a much faster disruption of the particles and the plateau is reached earlier. The plateau value is similar for all three sonication amplitudes, however, the lowest one is attained with the highest sonication amplitude.

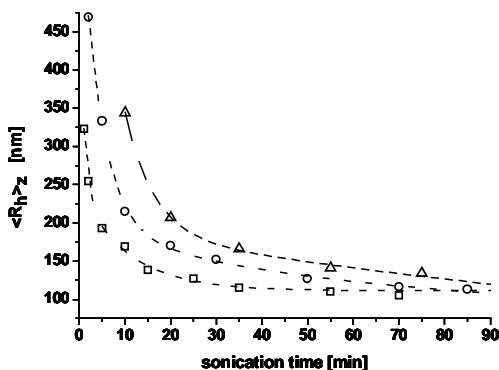


Figure 2. Dependence of the hydrodynamic radius obtained after extrapolating the angular dependent DLS data to $q^2 \rightarrow 0$, on the sonication power (\square : 70%, \circ : 30%, Δ : 10%) and duration for SBT-1 crosslinked with the thiol-polyene process (5 wt% AIBN in presence of 5 wt% TRIS).

Visualization. Several imaging techniques were used in order to visualize the resulting disc-like Janus structures. The focus of these investigations was to address the questions, whether the particles aggregate and how the actual shape looks like. In particular, one might expect a back-to-back stacking of the particles, i.e. an aggregation of two particles into dimeric superstructures. Furthermore, it is interesting to know, whether the particles possess a more sheet-like character with irregular edges or if they can reach a disc-like appearance.

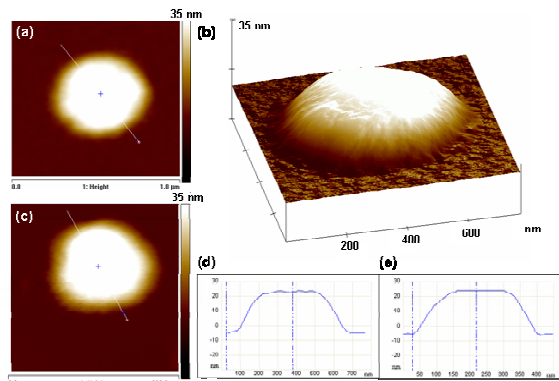


Figure 3. SFM height image obtained from a sample of Janus discs (SBT-2, 5 wt% AIBN, sonication for 1 min at 30% amplitude), dip-coated from a 0.1 mg/L CHCl_3 solution onto mica and annealed at 150 °C in vacuo (a) or at 90 °C in toluene vapour (c). (b): 3D surface plot of (a). (d) and (e): Section analyses of the lines shown in the height images (a) and (c), respectively.

The scanning force microscopy investigations revealed that the structures developed after adsorption of the Janus particles onto substrates is governed by a strong interplay between the interfacial tensions of the system and the brush-like behaviour of the flat Janus particles. A complete coverage of this behaviour is however beyond the scope of this contribution and will be published in a forthcoming article. Furthermore, it was found that the particles exhibit circular to ellipsoidal profiles with prolonged sonication. Really anisometric sheet-like Janus particles can only be found in the very beginning of the homogenization process. Figure 3 shows two Janus disc with very high aspect ratios and completely flat brush-like profile in the interior. The smooth height increase at the boarder of the Janus discs is typically in the region of 60 - 120 nm. However, considering the proportions of the polymer chains (e.g. contour length of P β BMA; $L_c \approx 115$ nm) and the strong adsorption tendency of the particles, it can be reasonably understood.

Self-Assembly. In Addition to SFM, cryo-TEM was chosen in order to explore the particle shape *in-situ* in solution and to investigate the samples towards the self-assembly into superstructures in more concentrated solution. Therefore, cryo-TEM investigations in a non-selective organic solvent, THF, were performed for a variety of different samples in the more concentrated regime, typically with concentrations higher than 1 mg/ml. Figure 4 shows a representative overview image with aggregated Janus discs.

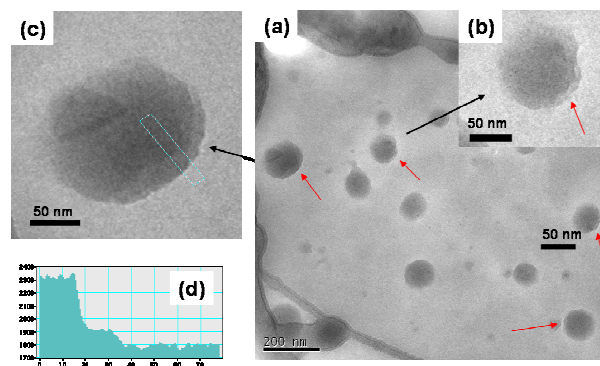


Figure 4. Cryogenic transmission electron microscopy images of a sample of Janus discs in tetrahydrofuran.

Despite the low contrast (mass density \times specimen thickness) between material and solvent, a layered superstructure can clearly be seen in the image. Several arrows highlight parts for which distinct layers can be seen most easily. The cross-section analysis (d) further elucidates the layered structures and additionally confirms a very flat profile of the particles in the centre.

CONCLUSION

We have been able to synthesize for the first time large sheet-like or disc-like Janus particles, consisting of a crosslinked inner polybutadiene layer and two phase-segregated sides of polystyrene and poly(*tert*-butyl methacrylate). The particles can be obtained via a simple template-assisted approach and their size can be tuned from the mesoscopic level to the nanometer scale, typically in the range of several micrometers to hundred nanometers. Due to the introduced ultrasound energy, the sheet-like particles get "shaved" and exhibit circular disc-like outer sides. By means of cryo-TEM, which was applied for the first time in THF, it was possible to visualize the aggregation behaviour of the Janus discs *in-situ*. The flat particles self-assemble into superstructures via back-to-back stacking even in good solvents. These particles show interesting surface-active properties.

ACKNOWLEDGMENTS

This work was supported by the ESF SONS-AMPHI Program and the Marie Curie RTN Polyamphi. We thank Astrid Gödel and Clarissa Abetz for numerous TEM and SEM images. A. W. thanks the Bavarian Graduate Support Program for a scholarship.

REFERENCES

- Erhardt, R.; Zhang, M.; Böker, A.; Zettl, H.; Abetz, C.; Frederik, P.; Krausch, G.; Abetz, V.; Müller, A. H. E., *Journal of the American Chemical Society* **2003**, 125, (11), 3260.
- Erhardt, R.; Böker, A.; Zettl, H.; Kaya, H.; Pyckhout-Hintzen, W.; Krausch, G.; Abetz, V.; Müller, A. H. E., *Macromolecules* **2001**, 34, (4), 1069.
- Liu, Y.; Abetz, V.; Müller, A. H. E., *Macromolecules* **2003**, 36, (21), 7894.