

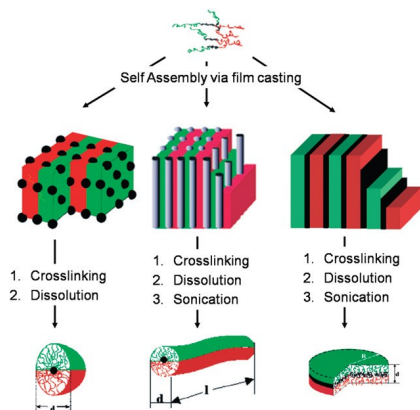
PREPARATION OF A VARIETY OF JANUS PARTICLES FROM A NEW VERSATILE BLOCK TERPOLYMER

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Introduction

Mentioned for the first time in 1985¹ Janus particles have attracted a lot of attention during the last decade. They were named after the two-faced Roman god Janus. In a similar way Janus particles feature two sides or surfaces of different chemistry or polarity. This distinctive feature gives Janus particles a non-centrosymmetric architecture, making them a unique kind among micron- or nanosized colloids. Several review articles have already been dedicated to this interesting field of research.^{2,3} Recently a review covering exclusively polymeric Janus particles was published.⁴ The synthesis approach of our group is based on converting block terpolymer bulk structures via selective crosslinking of the middle block, resulting in very well-defined polymeric Janus particles of different architectures (Scheme 1). So far, polystyrene-*block*-polybutadiene-*block*-poly(methyl methacrylate) (SBM) and polystyrene-*block*-polybutadiene-*block*-poly(*tert*-butyl methacrylate) (SBT) block terpolymers have been used as polymeric material. Now we have synthesized a new block terpolymer, poly(*p*-*tert*-butoxystyrene)-*block*-polybutadiene-*block*-poly(*tert*-butyl methacrylate) (tSBT), via living anionic polymerization to render more versatile Janus particles.



Scheme 1. Preparation of Janus particles with different architectures based on crosslinking the polybutadiene segments of various block terpolymers in the bulk.³

Experimental

Materials. Monomers *p*-*tert*-butoxystyrene and *tert*-butyl methacrylate (both Aldrich) were degassed, treated with dibutyl magnesium (*p*-*tert*-butoxystyrene) or trialkyl aluminium (*tert*-butyl methacrylate) and distilled or condensed, respectively.³ Acetonitrile (anhydrous 99.8%, Aldrich), chloroform (p.a. grade, Fisher Scientific), dioxane (p.a. grade, Fisher Scientific and Riedel de Haën), THF (technical grade for Soxhlet extraction, p.a. grade, VWR), sulphur monochloride (98% Aldrich), Lucirin TPO (BASF) and trimethylsilyl iodide (purum \geq 98%, Fluka) were used as received.

Water was purified with a Milli-Q water purification system by Millipore.

Instrumentation. Photo-crosslinking was induced with a HONLE UVAHAND 250 lamp, equipped with water cooling for the sample holder.

Sonication treatment was performed with a Branson model-250 digital sonifier with a 1/8 in. diameter tapered microtip (200 watt at 100% amplitude).

Transmission electron microscopy (TEM) images were recorded in bright field mode with a Zeiss CEM 902 electron microscope operated at 80 kV and a LEO 922 OMEGA electron microscope operated at 200 kV. Polymer films were cut into thin sections at room temperature using a Reichert-Jung Ultracut E microtome equipped with a diamond knife.

Synthesis of poly(*p*-*tert*-butoxystyrene)-*block*-polybutadiene-*block*-poly(*tert*-butyl methacrylate). tSBT was synthesized via living anionic polymerization. Having become a standard method by now, the general procedure of this polymerization technique is described elsewhere.⁵ *P*-*tert*-butoxystyrene was added to the initiator at -78 °C, butadiene was added to the mixture at -78 °C and tBMA at -60 °C. Before the addition of the tBMA, the reaction mixture

was treated with a five-fold excess of DPE related to the number of expected chain ends.

Film casting. The respective amount of tSBT or tSBT with Lucirin TPO was dissolved in CHCl₃ in a crystallization dish. After that, evaporation of the solvent was led to take place for two weeks at room temperature and the films were dried in vacuum for 24h at room temperature.

Photo-crosslinking with Lucirin TPO. Polymer films, co-casted with 30 wt% of Lucirin TPO, were exposed to the radiation of a UV-lamp (cut off < 350 nm) for 3.5 hours. Subsequently, films were either left without further treatment or Soxhlet extracted for several days with THF.

Crosslinking with sulphur monochloride (S₂Cl₂). A piece of polymer film was swollen in acetonitrile for one day. 5-10 vol% of S₂Cl₂ were added via a syringe and the crosslinking took place at room temperature overnight. In the case of Janus ribbons, films were swollen in an acetonitrile/decane emulsion that needed constant, not too strong stirring to avoid large-scale demixing of the two solvents. Crosslinking time was 7 hours.

After the reaction, the films were washed several times with aprotic solvents acetonitrile and dioxane and purified via Soxhlet extraction with THF for several days if desired.

Sonication. Crosslinked material was dispersed in dioxane to give dispersions of an approximate concentration of 1 mg/mL. Portions of about 20 mL were then treated with an ultrasound sonication tip under water cooling. The typical settings were a pulse of 2 seconds, 5 to 10 seconds of pause (according to particle size), sonication time of 30 to 90 seconds and amplitude of 30%. Afterwards, the solutions were filtrated using a 5µm PTFE filter and freeze dried.

Hydrolysis of Janus cylinders. Janus cylinders were dissolved in CHCl₃ to give a solution in the range of 1.23 to 1.96 wt%. After degassing for approximately 20 minutes, a 1.3-fold excess of trimethylsilyl iodide regarding the amount of *tert*-butoxy groups was introduced to the solution with a syringe under N₂. Afterwards, the mixture was stirred for 1h either at room temperature (partial hydrolysis) or 60 °C (full hydrolysis) and then treated with few mL of basic MilliQ-water (pH 12-14). Subsequent dialysis against dioxane, water/dioxane (1/1) and water of different pH values was used for subsequent work up. A regenerated cellulose Spectra/Por dialysis membrane with molecular weight cut off of 50000 was used.

Preparation of TEM samples. Cut film sections were exposed to OsO₄ vapour for 60 seconds for preferential staining of the polybutadiene block (appears black) in order to increase the electron density contrast between the three terpolymer blocks. Liquid TEM samples have been solvent evaporated from solutions with a concentration of 1mg/mL on carbon-coated copper grids. For aqueous solutions, grids were turned hydrophilic via a plasma treatment and the sample was blotted after 30 sec. Cryo-TEM samples on lacey carbon-coated copper grids were frozen in liquid nitrogen.

Results and Discussion

Preparation of Janus particles. All Janus particles in this work were synthesized from the block terpolymer tS₄₆B₁₆T₃₈¹⁶³ (Poly(*tert*-butoxystyrene)-*block*-polybutadiene-*block*-poly(*tert*-butyl methacrylate) (the subscripts denote the weight fractions of the individual blocks and the superscript corresponds to the molecular weight in kg/mol). The bulk structure of this block terpolymer is a lamella-cylinder morphology. **Figure 1a** shows a TEM-micrograph of a OsO₄-stained ultrathin section of tSBT. The polybutadiene cylinders (appearing black) are surrounded by alternating lamellae of poly(*p*-*tert*-butoxystyrene) (PtBS) and poly(*tert*-butyl methacrylate) (PtBMA). As was expected, photo-crosslinking of the polybutadiene (PB) microdomains in this bulk structure and subsequent dissolution of the material resulted in well-defined Janus cylinders (**Figure 1b**).

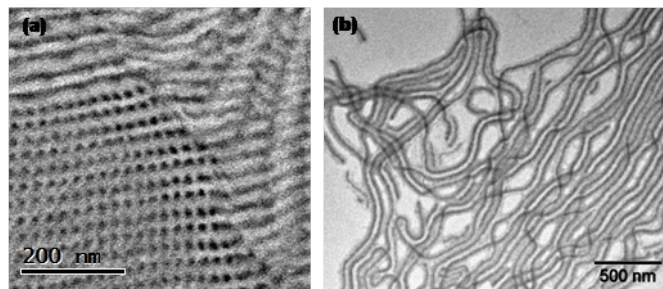


Figure 1. TEM images of an ultrathin section of a tSBT film stained with OsO₄ (PB appears black, PtBS grey and PtBMA white) (a) and Janus cylinders (b).

In contrast to this photo-crosslinking method, using S_2Cl_2 as crosslinker involves some preceding swelling of the polymer film in acetonitrile. Interestingly, after crosslinking with S_2Cl_2 followed by sonication Janus sheets instead of cylinders were obtained. Therefore, a transition in the morphology has occurred during swelling or crosslinking. The structure developing during the cold vulcanization is best described as an undulated lamellar morphology (Figure 2).

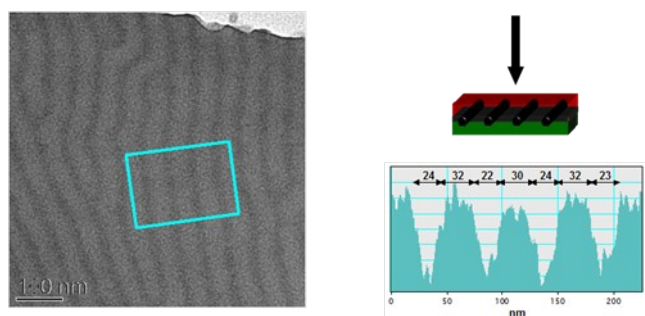


Figure 2. TEM image of a Janus sheet with density profile of the cross section indicated in the micrograph. The schematic drawing indicates the line of sight onto the Janus sheet.

However, swelling in an acetonitrile/decane emulsion resulted in yet another morphology change, leading to the formation of a connecting PB-layer between the original Ic-cylinders only in every second interspace. This way, after crosslinking and sonication, we could find a completely new Janus structure, Janus ribbons (Figure 3).

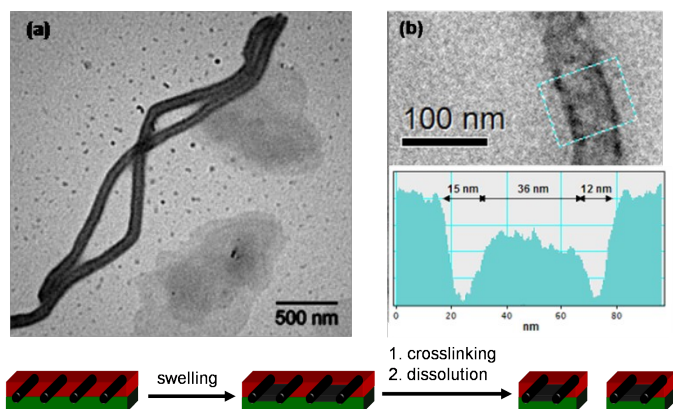
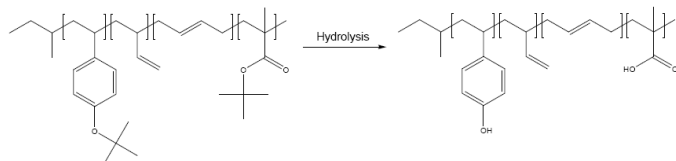


Figure 3. TEM (a) and cryo-TEM (b) images of Janus ribbons from tSBT block terpolymers with density profile of the cross section indicated in the micrograph and a scheme illustrating the actual formation of ribbons.

Hydrolysis of Janus cylinders. Poly(*tert*-butoxy styrene) was chosen as a first block of tSBT because it can be hydrolyzed to poly(*p*-hydroxystyrene) (PHS), which renders the block water-soluble at $pH \geq 10.5$ (Scheme 2).



Scheme 2. Hydrolysis of tSBT.

Full hydrolysis of Janus cylinders results in particles with two water-soluble hemispheres. Apart from hydrolysing both PtBS and PtBMA, PtBMA can be also exclusively hydrolyzed to water-soluble poly(methacrylic acid) (PMAA), resulting in amphiphilic particles. Figure 5 shows a partially hydrolyzed Janus cylinder at pH 11, where only PMAA is soluble whereas PtBS collapses onto the PB-core. The Janus character can clearly be seen.

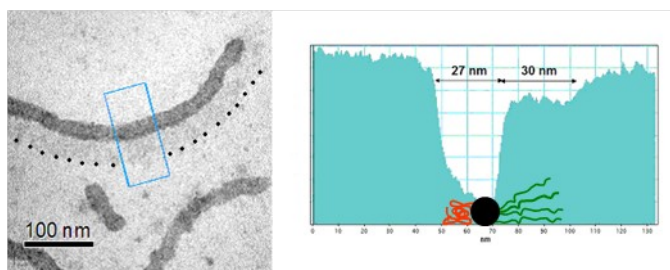


Figure 5. Cryo-TEM image and density profile of tBS-B-MAA Janus cylinders in water at pH 11. The PMAA hemisphere (dotted line) is expanded whereas the PtBS hemisphere is collapsed.

Conclusions

For the preparation of polymeric Janus particles we crosslinked the polybutadiene microdomains within the bulk phase of the poly(*p*-*tert*-butoxystyrene)-*block*-polybutadiene-*block*-poly(*tert*-butyl methacrylate) terpolymer, tSBT, via different methods. A careful adjustment of synthesis conditions allows the synthesis of three different kinds of Janus particles from one single block terpolymer. Janus cylinders, Janus sheets and an intermediate, completely new structure, Janus ribbons, could be obtained. Depending on the hydrolysis conditions, Janus particles with two hydrolyzed sides or with just one hydrolyzed side can be produced. In Cryo-TEM images of partially hydrolyzed Janus cylinders the corona phase-segregation can be nicely visualized and presents one of the best real space proofs of the biphasic character of nanosized polymeric Janus particles obtained so far.

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References

- (1) Cho, I.; Lee, K.W. *J. Appl. Polym. Sci.* **1985**, *30*, 1903.
- (2) Perro, A.; Reculosa, S.; Ravaine, S.; Bourgeat-Lami, E.; Duguet, E. *J. Mater. Chem.* **2005**, *15*, 3745.
- (3) Walther, A.; Müller, A.H.E. *Soft Matter* **2008**, *4*, 663.
- (4) Wurm, F.; Kilbinger A.F.M. *Angew. Chem. Int. Ed.* **2009**, Early View.
- (5) Goldacker, T.; PhD Thesis, Universität Bayreuth, Bayreuth, 1999.