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Janus Cylinders

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Introduction. Currently, amphiphilic copolymers with nonlinear and noncentrosymmetric architectures start to attract much interest due to the synthetic challenges and their unprecedented properties.[1−3] The particular asymmetric character of amphiphilic particles having two faces was termed as "Janus".[4−6]

Depending on their shape, Janus particles can be divided into Janus spheres, cylinders, and sheets (Figure 1). These amphiphilic nanoparticles should have novel properties in solution, at interfaces, or in the bulk. Because of their amphiphilic nature, the formation of structures of higher hierarchical order is expected. Proteins in the shape of "amphiphilic helices" are observed in nature, and they form oligomeric superstructures.[7]

Various strategies can be designed to construct the structures in Figure 1. One strategy is based on the self-assembly of block terpolymers (i.e., ABC triblock copolymers) in the bulk.[8−10] Depending on their composition, they can form, for example, lamellae−sphere, lamellae−cylinder, or lamellae−lamellar morphologies in the bulk. Selective cross-linking of the central block and redissolution leads to nanoscopic particles where the corona is forced to be compartmentalized. This approach was used by Erhardt et al. in order to synthesize spherical Janus micelles with polystyrene (PS) and poly(methyl methacrylate) (PMMA) hemicoronas.[3] These micelles form larger aggregates in nonselective organic solvents, on a silicon surface, and at the air/water interface.[3,11] Hydrolysis of the PMMA ester groups led to amphiphilic Janus micelles with PS and poly(methacrylic acid) hemicoronas which again lead to superstructures and giant particles.[12]

Another strategy to form Janus micelles is based on the self-assembly of block copolymers in solution.[13] In one approach, block terpolymers can form micellar solutions in a solvent that dissolves the outer blocks but is a nonsolvent for the middle block. Cross-linking of the core again should form Janus micelles.[14] However, phase separation of the outer blocks may not be as pronounced as in the bulk approach. Another self-assembly approach is based on the electrostatic interactions of AB and CD diblock copolymers where B and C form insoluble complexes, e.g., inter-polyelectrolyte complexes, in a solvent for blocks A and D. The first reported approach has led to nonsymmetric vesicles rather than to Janus spheres.[15]

Alternatively, great efforts have been taken into the synthesis of Janus-like particles through pure organic synthetic approaches in recent years. Hadjichristidis et al. and other groups investigated the synthesis of miktoarm star copolymers through living anionic polymerization,[1,2] controlled radical polymerization,[16] or ring-opening metathesis polymerization.[17] Schmidt and co-workers obtained wormlike cylinders through radical copolymerization of macromonomers poly(4-vinylpyridine) and poly(methyl methacrylate).[18] Ishizu and co-workers also prepared alternate heteroarm copolymer brushes by free radical copolymerization of macromonomers, ω-vinylbenzylpolystyrene and a ω-methacryloylpoly(ethylene oxide), and afterward studied their dilute solution properties and aggregation behavior.[19,20] Schlüter and co-workers synthesized poly(p-phenylene)s with hydrophilic and hydrophobic dendrons through polycondensation.[21] Laschewsky and co-workers reported the partial modification of cyclodextrins and obtained amphiphilic cylinders.[22] In all these works, the synthetic routes are complicated or not easy to be operated. Moreover, because of the steric effects and the reactivity of functional groups, in many cases, both the density and the length of side chains are rather low; it is difficult to reach high overall molecular weights. Also, spontaneous phase separation of the chemically different chains may not always occur easily in these systems.[23] In conclusion, the synthesis of Janus structures through chemical design is still a challenge to chemists.

In the present paper, we report first results on the synthesis and characterization of Janus cylinders where the separation plane is parallel to the cylinder axis. These particles were obtained in a similar way as the Janus spheres by using a polystyrene-*block*-polybutadiene-*block*-poly(methyl methacrylate) (SBM) block terpolymer forming the lamellae−cylinder morphology (Scheme 1).

Experimental Section. a. SBM Precursors. SBM block terpolymers were synthesized via sequential anionic polymerization in tetrahydrofuran (THF), following procedures described earlier.[24] In this paper $S_{44}B_{20}M_{36}^{250}$ is represented as SBM-1 ($M_w/M_n = 1.03$) and $S_{41}B_{14}M_{45}^{110}$ is represented as SBM-2 ($M_w/M_n = 1.01$). The subscript numbers denote the mass fraction in percent, and the superscripts give the number-average molecular weight in kg/mol.

b. Selective Bulk Cross-Linking. The films of precursors (0.15 g, 1.0 mm thickness) were first cast from $CHCl_3$ (10% w/w) at ambient temperature for 3 weeks. After annealing at 60−90 °C in a vacuum, films were swollen in 50 mL of acetonitrile at room temperature for 24 h. Then 5% (v/v) disulfur dichloride (S_2Cl_2) were added to the system, and it was kept at room temperature for 24 h. Afterward, the film was taken out and rinsed several times with acetonitrile and then purified by Soxhlet extraction in THF/$CHCl_3$ (1:1) for another 24 h.

The product underwent ultrasonic treatment using a Branson model-250 digital sonifier, equipped with $^1/_8$ in. diameter tapered microtip, at 50% amplitude under 1.0 s/1.0 s pulse on/off mode in THF at room temperature for 30−60 min. This treatment lead to semitransparent solutions, which were further purified by precipitation in methanol and finally dried in a vacuum.

c. Elemental Analysis (EA). The elemental analyses were performed by Ilse Beetz Mikroanalytisches Laboratorium (Kulmbach).

d. Transmission Electron Microscopy (TEM). The bulk morphologies of the SBM films before and after cross-linking were examined by TEM. Thin sections

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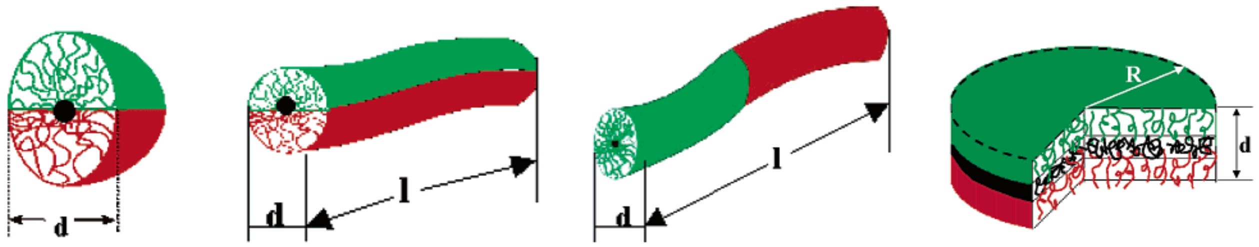

(1) Janus micelle (2) Janus cylinder (3) Janus cylinder (4) Janus sheet

Figure 1. Various possible Janus structures.

Scheme 1. Representation of the Janus Cylinders' Synthesis, Center: Sketch of Lamella–Cylinder Morphology

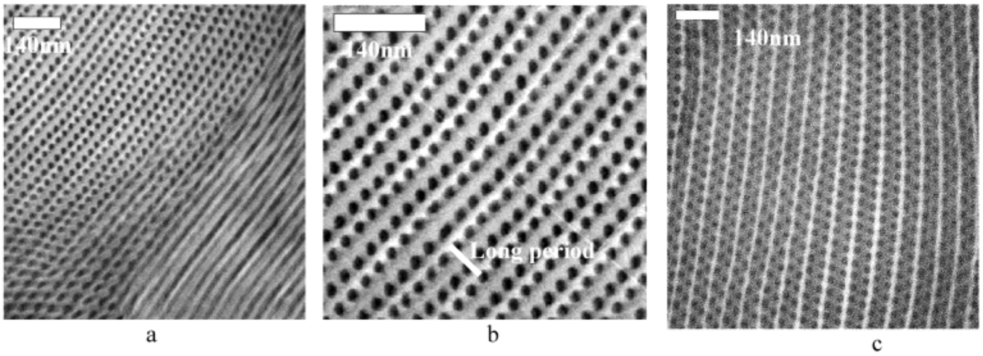

Figure 2. TEM micrographs of SBM-1 before (a, b) and after cross-linking (c).

of the films were cut at room temperature using a Reichert-Jung Ultracut E microtome equipped with a diamond knife. To enhance the electron density contrast between the three blocks, the sections were exposed to OsO_4 vapor for 60 s, which lead to a preferential staining of the PB block (appears black). Bright field TEM was performed using a Zeiss CEM 902 electron microscope operated at 80 kV.

e. Scanning Electron Microscopy (SEM). SEM was performed on a LEO 1530 field emission microscope using secondary electron detection. The samples were obtained by dip coating the silicon wafer into a dilute solution of products with 0.1 g/L concentration.

f. Scanning Force Microscopy (SFM). The products after sonification were dissolved in various solvents at a concentration of 0.01 g/L and dip-coated onto mica sheets or silicon wafers. The scanning force micrographs were taken on a Digital Instruments Dimension 3100 microscope operated in Tapping Mode (free amplitude of the cantilever ~20 nm, set point ratio ~ 0.98). The standard silicon nitride cantilevers were driven at a frequency about 3% below resonance. Height and phase images were recorded at a scanning velocity of approximately 5.0 μm/s.

Results and Discussion. a. Morphology of SBM Precursors by Transmission Electron Microscopy. Block terpolymers SBM-1 ($S_{44}B_{20}M_{36}^{250}$) and SBM-2 ($S_{41}B_{14}M_{45}^{119}$) were used as precursors for Janus cylinders. They form a lamellae–cylinder (lc) morphology in the bulk,[9] as shown in Figure 2a,b. PB core cylinders (black) are embedded at the interface of PS (gray) and PMMA (white) lamellae. After cross-linking the PB core this morphology was retained (Figure 2c). Thus, each PB cylinder is potentially the core of a Janus cylinder which has a compartmentalized shell consisting of a PS and a PMMA hemicylinder (Scheme 1).

The TEM images of the samples after cross-linking in bulk show that the lengths of PS and PMMA domains remained constant (the approximate average data of SBM-1 are $l_M = 8.4 \pm 1.3$ nm, $l_S = 27.8 \pm 3.8$ nm; that of SBM-2: $l_M = 6.0 \pm 1.1$ nm, $l_S = 16.9 \pm 0.7$ nm). However, the diameters of the PB cylinders are considerably increased after cross-linking (see Table 2), and as a consequence, the diameter of an SBM cylinder (taken as half of the long period) is also increased. The expansion is caused by the incorporation of S_2Cl_2 molecules during cross-linking. The covalent bond radii of S and Cl are 0.104 and 0.099 nm, respectively, which is considerably larger than the corresponding covalent bond radius of C, which is 0.077 nm. Both heteroatoms have large atomic volumes, and thus their occupation of a certain volume inside the PB core cannot be ignored. Furthermore, elemental analysis of the precursor and cross-linked SBMs was performed; the results are shown in Table 1. The molar ratios of S and Cl to C were calculated. Comparison with the theoretical value (assuming that the cross-linking efficiency of S_2Cl_2 to the PB core is 100%) leads to the conclusion that this reaction in fact is quantitative. Therefore, the weight fraction of each polymer composition changed after cross-linking, and the new compositions are $S_{35}B'_{36}M_{29}$ for Janus cylinder-SBM-1 and $S_{35}B'_{24}M_{41}$ for Janus

Table 1. Elemental Analysis of SBM Precursors and Janus Cylinders

	elemental analysis (wt %)							theoretical value[a]		
sample	C	H	O	S	Cl	S:C[b]	Cl:C[b]	S:C = Cl:C[b]	B, wt %	representation
SBM-1	79.59	8.80	11.60						20	$S_{44}B_{20}M_{36}{}^{250}$
Janus-1	60.96	6.74	11.05	11.96	9.62	0.07	0.05	0.06	36	$S_{35}B'_{36}M_{29}$
SBM-2	75.84	8.16	10.16						14	$S_{41}B_{14}M_{45}{}^{110}$
Janus-2	63.90	6.88	11.98	10.37	6.90	0.06	0.04	0.04	24	$S_{35}B'_{24}M_{41}$

[a] Calculation was performed by assuming the cross-linking efficiency of S_2Cl_2 agent to the double bond in PB core is 100%. [b] Molar ratio.

Table 2. TEM Characterizations of SBM Precursors in Bulk

precursor		$d_B{}^{a}$/nm	$d_{cyl}{}^{b}$/nm	$10^{-3}A_{cyl,1}{}^{c}$/nm^2	$10^{-3}A_{cy,-2}{}^{d}$/nm^2
SBM-1 = $S_{44}B_{20}M_{36}{}^{250}$	before cross-linking	17.3 ± 1.8	34.6±2.7	1.20 ± 0.25	1.00 ± 0.15
	after cross-linking	27.1 ± 3.1	40.0 ± 3.8	1.60 ± 0.36	1.30 ± 0.24
SBM-2 = $S_{41}B_{14}M_{45}{}^{110}$	before cross-linking	9.0 ± 0.8	21.2 ± 0.8	0.46 ± 0.08	0.35 ± 0.26
	after cross-linking	15.5 ± 0.4	33.7 ± 5.2	0.80 ± 0.40	0.90 ± 0.30

[a] Diameter of PB core cylinder. [b] Diameter of SBM cylinder. [c] SBM cylinder cross section according to eq 1. [d] According to eq 2.

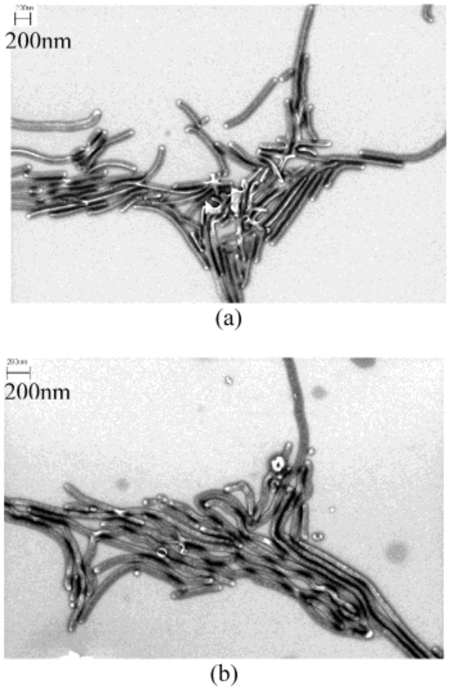

Figure 3. SEM images of Janus cylinders SBM-1 (a) and SBM-2 (b), dip-coated from THF on a silicon wafer.

cylinder-SBM-2, where B′ indicates the cross-linked B domains.

Furthermore, with the weight fraction of the PB (B% in Table 1), the cross section of an SBM cylinder can be estimated as

$$A_{cyl,1} = \pi d_B{}^2/4w_B \qquad (1)$$

or can be estimated from the diameter of a cylinder (taken as half of a long period):

$$A_{cyl,2} = \pi d_{cyl}{}^2/4 \qquad (2)$$

The corresponding data are summarized in Table 2.

b. Characterization of Single Janus Cylinders by SEM and SFM. Because of the extremely long cylinders in the bulk morphology and morphological defects connecting different PB cylinders to a loose network after cross-linking, the cross-linked films were dissociated and disrupted by sonification before being measured by SFM and SEM.

c. Scanning Electron Microscopy (SEM). The SEM images (Figure 3) clearly show that the products are single, long (ca. 100 nm up to many micrometers), rodlike cylinders with a very high persistence length. This shape should be related to the intrinsically stiff, cross-linked PB core and the high grafting density of side chains (PS and PMMA hemicylinders), which demonstrate that our cross-linking approach is very effective. A certain curvature can be observed in some cylinders, possibly stemming from imperfections in the precursor morphology or from a nonequilibrium conformation on the substrate. Some cylinders show branch points, which either reflect morphological defects of the previous bulk structure or result from the deposition on the substrate.

The average diameters of Janus cylinders-SBM-1 and -SBM-2 are 100 ± 10 and 70 ± 10 nm, respectively.

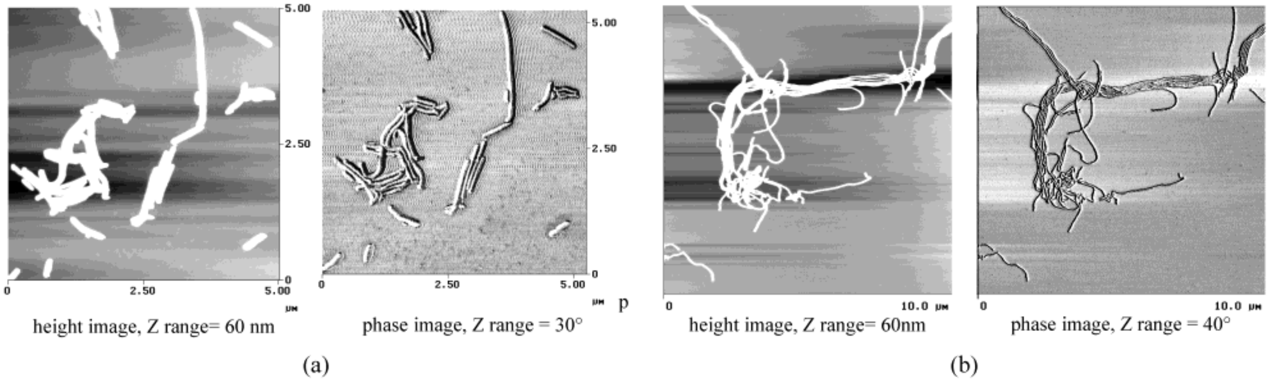

Figure 4. SFM images of Janus cylinders SBM-1 (a) and SBM-2 (b), dip-coated from THF on a silicon wafer.

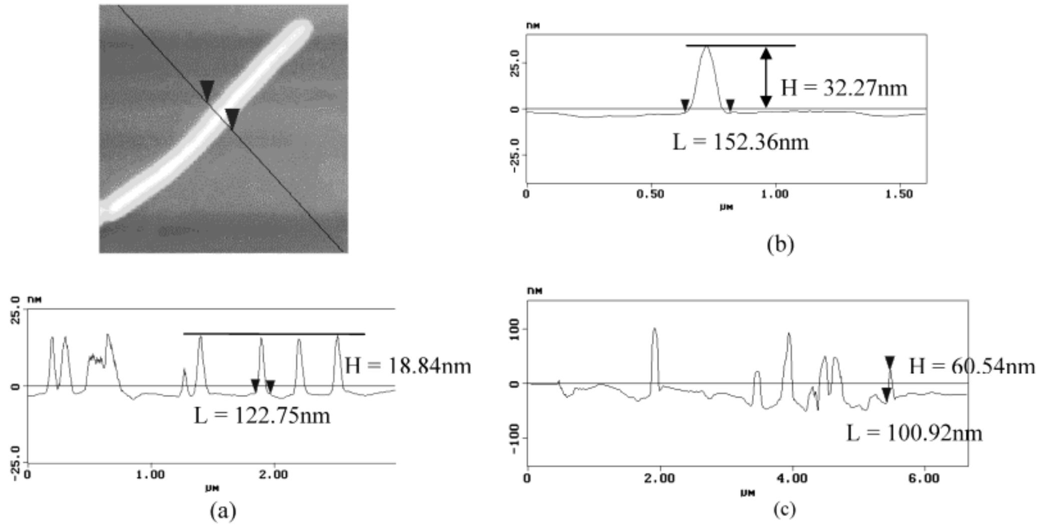

Figure 5. SFM analysis of single Janus cylinders: (a) SBM-2, $CHCl_3$/mica, Z range = 50 nm; (b) SBM-1, THF/silicon wafer, Z range = 70 nm; (c) SBM-1, acetone/mica, Z range = 200 nm.

Table 3. Dimensions and Cross Sections of Janus Cylinders from SFM Images (Dip-Coated from $CHCl_3$ on Mica)

sample	H/nm	L/nm	$10^{-3}A_{cyl-3}{}^{a}$/nm^2	$10^{-3}A_{cyl,1}{}^{b}$/nm^2	$10^{-3}A_{cy,-2}{}^{c}$/nm^2
SBM-1	34.50 ± 10.0	114 ± 37	1.50 ± 0.10	1.60 ± 0.36	1.30 ± 0.24
SBM-2	18.51 ± 2.2	88 ± 11	1.00 ± 0.26	0.80 ± 0.40	0.90 ± 0.30

[a] From SFM, ellipse model. [b] From TEM, eq 1. [c] From TEM, eq 2.

These diameters are about 2.5 times larger than in the bulk state but 3−4 times smaller than the contour lengths of the PS and PMMA chains (estimated as around 400 nm for Janus cylinder-SBM-1 and around 250 nm for Janus SBM-2).

d. Scanning Force Microscopy (SFM). Separated cylinders (Figure 4) are also visualized by SFM, on both silicon and mica. The shape of randomly selected cylinders was analyzed by using the Nanoscope III V4.43r8 software. The height, H, and the diameter, L, of the cylinders were measured (Figure 5), indicating a collapsed structure on the surface, typical for cylindrical polymer brushes. The values are given in Table 3. Assuming an ellipsoid shape, the average cross-section area was calculated from the H and L values as $A_{cyl,3} = \pi HL/4$.

To correct for the finite tip size, 20 nm was subtracted from the measured value of L. Table 3 shows that all the calculated data are in good agreement with those of the precursors in the bulk state. Thus, in contrast to the spherical Janus micelles, these Janus cylinders apparently are not forming supermicelles in THF or chloroform.

e. Effect of Solvent and Substrate. Different aggregation behaviors of the obtained particles affected by the substrates and solvents were observed by AFM and SEM measurements. On silicon wafers, Janus cylinders show a strong tendency for lateral aggregation for both THF or $CHCl_3$ as dip-coating solvents. A similar aggregation was observed on mica surface when the sample was dip-coated from THF or cyclohexanone; however, from $CHCl_3$ and ethyl acetate the particles are well-dispersed.

In contrast, when acetone was used for dip-coating onto mica, the Janus cylinders show 2 times larger heights as compared to the cylinders obtained from THF and $CHCl_3$. For example, the averaged data of Janus cylinder-SBM-1 are $H = 58.3 \pm 3.8$ nm, $L = 104 \pm 12$ nm, and the cross section $A_{cyl} = (3.89 \pm 0.70) \times 10^{-3}$ nm^2 (Figure 5c), which corresponds to more than one cylinder. Since acetone is a nonsolvent for PS, the PS hemicylinders are expected to collapse and aggregate, with PMMA forming the outside. Further detailed investigations are being conducted in order to elucidate the structure of SBM Janus cylinders as a function of solvent and substrate nature. Moreover, hydrolysis of the PMMA arms to form amphiphilic Janus cylinders will be investigated in the future.

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