

SUPPORTING Information

Janus Micelles by Crystallization-Driven Self-Assembly of an Amphiphilic, Double-Crystalline Triblock Terpolymer

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ABSTRACT: Surface-compartmentalized micellar nanostructures (Janus and patchy micelles) have gained increasing interest due to their unique properties opening highly relevant applications, e.g., as efficient particulate surfactants, compatibilizers in polymer blends, or templates for catalytically active nanoparticles. We present a facile method for the production of worm-like Janus micelles based on crystallization-driven self-assembly of a double-crystalline triblock terpolymer with a crystallizable polyethylene middle block and two highly incompatible corona blocks, polystyrene and poly(ethylene oxide). This approach enables the production of amphiphilic Janus micelles with excellent interfacial activity by a comparably simple heating and cooling protocol directly in solution.

urface-compartmentalized polymeric nanostructures are of Substantial interest, as their unique corona structure paves the way to a multitude of highly relevant applications.¹⁻⁶ In general, they can be divided in Janus and patch-like (patchy) particles. Janus particles (or micelles) exhibit two opposing faces with different chemistry and/or polarity, whereas patchy micelles are characterized by a patch-like microphase-separated corona, consisting of several compartments. Janus particles and micelles have been intensively studied in the past with a strong focus on spherical structures, which is owed to the fact that cylindrical (1D) or platelet-like (2D) Janus structures are more difficult to realize.^{7–13} Janus particles can be applied in a broad range of applications, for example, as highly efficient particulate surfactants for emulsion stabilization or compatibilization of polymer blends, as optical nanoprobes and biosensors, for selfpropulsion, interfacial catalysis, and superhydrophobic and anti-ice coatings, and many more. 1D (cylindrical or wormlike) patchy micelles can be produced in an efficient manner employing crystallization-driven self-assembly (CDSA) and living CDSA, which allows control over length, length distribution, and corona chemistries.¹⁴⁻¹⁹ There are two main concepts for the fabrication of 1D patchy micelles: (i) CDSA of linear triblock terpolymers with a crystallizable middle block,^{19–21} or of μ -ABC miktoarm star terpolymers,² and (ii) CDSA of a mixture of diblock copolymers bearing a common crystallizable block.²³⁻²⁶ The patchy structure of the micellar corona gives rise to specific applications, for example, as templates for the regioselective incorporation of different nanoparticle types,¹⁹ in heterogeneous catalysis,^{27,28} as compatibilizers in polymer blends or as highly efficient particulate surfactants,^{29,30} and for the construction of hierarchical superstructures.³¹ So far, CDSA of triblock terpolymers with crystallizable middle blocks has always resulted in 1D micelles with a patchy corona. Nevertheless, a Janus-type structure of the corona might also be feasible when the two soluble corona blocks have a sufficiently high incompatibility or if there is another driving force promoting microphase separation in the corona. This has been predicted

theoretically and observed experimentally for two-component bottle brush copolymers, featuring a polymer backbone that is densely grafted with two strongly immiscible amorphous polymer segments.^{32–36} Interestingly, introducing crystallizable grafts has been shown to facilitate the formation of Janus structures for two-component bottle brushes as well as amphiphilic, double-grafted hyperbranched polymers.^{37–41} Thus, we speculated whether increasing the incompatibility between the corona-forming blocks by introducing a hydrophilic and crystallizable poly(ethylene oxide) (PEO) block can guide the formation of Janus-type worm-like micelles in the CDSA of triblock terpolymers with a polyethylene middle block. In this context, CDSA of double-crystalline block copolymers has yet only rarely been studied.^{42–44}

In this Communication, we report the formation of amphiphilic, worm-like Janus micelles by CDSA of a doublecrystalline polystyrene-*block*-polyethylene-*block*-poly(ethylene oxide) (PS-*b*-PE-*b*-PEO: $S_{280}E_{1350}EO_{670}$, where indices denote number-average degrees of polymerization of the respective blocks) triblock terpolymer in toluene (Scheme 1). The $S_{280}E_{1250}EO_{670}$ triblock terpolymer ($M_n = 93.5 \text{ kg} \cdot \text{mol}^{-1}$) was synthesized by catalytic hydrogenation of a polystyrene-*block*-poly(1,4-butadiene)-*block*-poly(ethylene oxide) precursor ($S_{280}B_{630}EO_{640}$, $M_n = 92.5 \text{ kg} \cdot \text{mol}^{-1}$, D = 1.03, 88 mol% 1,4-butadiene units), prepared by sequential anionic polymerization (for details please see Supporting Information: Table S1, Figures S1 and S2).⁴⁵ CDSA was conducted in toluene, being a good solvent for the triblock terpolymer above the melting point of the PE middle block, resulting in the formation of worm-like micelles with a crystalline PE core.^{14,20}

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Scheme 1. CDSA of an Amphiphilic, Double-Crystalline PS*b*-PE-*b*-PEO Triblock Terpolymer in Toluene Favors Formation of Janus Micelles with a Crystalline PE Core



Microdifferential scanning calorimetry (μ -DSC) measurements reveal a melting point for the PE block at $T_{\rm m}$ = 46 °C and crystallization at $T_{\rm c}$ = 28 °C, respectively (Figure 1A). This is in line with the behavior of other triblock terpolymers with crystalline PE middle blocks.^{19,20} Interestingly, the crystallization temperatures ($T_{\rm c}$) of the PEO block ($T_{\rm c1}$ = 11 °C and



Figure 1. (A) μ -DSC traces for S₂₈₀E₁₂₅₀EO₆₇₀ in toluene ($c = 10 \text{ g} \cdot \text{L}^{-1}$) with melting and crystallization temperatures as well as degrees of crystallization (α). (B) TEM image of worm-like Janus micelles formed at $T_c = 28.5 \text{ °C}$ (OsO₄ staining).

 $T_{c2} = 0$ °C) are significantly higher compared to those observed for the $S_{280}B_{630}EO_{640}$ precursor ($T_c = -13$ °C, Figure S3A) and neat PEO in toluene at identical PEO concentration $(T_c = -11 \ ^{\circ}C, Figure \ S3B)$. Besides, only one melting endotherm at $T_{\rm m}$ = 25 °C was observed. Thus, the potentially microphase-separated corona of the formed worm-like crystalline-core micelles (wCCMs) seems to facilitate PEO crystallization in the corona. As for a patch-like microphaseseparated corona with patches in the nanometer range, a strong confinement effect on PEO crystallization is expected (significant decrease in T_c compared to molecularly dissolved $S_{280}B_{630}EO_{640}$ or PEO homopolymer),⁴⁶ the observed increase in T_c might be taken as a first hint for a more "continuous" (Janus-type) corona structure. The transmission electron microscopy (TEM) image of the wCCMs formed by CDSA in toluene at $T_c = 28.5$ °C (average micelle length: $l_{wCCM} = 680$ ± 280 nm; for details please see Supporting Information) confirms this assumption, as in contrast to the usually observed patchy corona a Janus-type corona segregation is formed (Figure 1B). Here, staining with OsO₄ was employed in order to weakly stain the PEO domains in the corona.⁴⁷ The PE core appears dark due to the dense chain packing in the PE crystallites, and only one half of the corona (the PEO face) is discernible as light gray regions predominantly located on one side of the micelles.

Janus and patchy micelles exhibit comparable interfacial activities, and also in 2D 1 H nuclear Overhauser effect spectroscopy (NOESY), a NMR technique probing internuclear distances, cross peaks are absent for both structures.^{29,48} Thus, differentiation between the two corona structures is only feasible using imaging techniques. A systematic study on the influence of staining on the observed corona structure was conducted to unambiguously differentiate between a Janus-type and patchy structure. From Figure 2A,B it can be clearly deduced that the pristine micelles (no staining, overview TEM image in Figure S4A) and the micelles after staining with OsO₄ show an identical corona structure, where



Figure 2. TEM images (left) and corresponding grayscale analyses of the indicated regions (right) for $S_{280}E_{1250}EO_{670}$ Janus micelles: (A) not stained, (B) stained with OsO₄ vapor for 30 s (under vacuum, ca. 50 mbar), and (C) stained with RuO₄ vapor for 7 min (ambient conditions).

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Figure 3. TEM images (top) and corresponding grayscale analyses of the indicated regions (bottom) for (A) patchy $S_{330}E_{1360}M_{760}$ micelles stained with RuO₄ for 7 min, and $S_{280}E_{1250}EO_{670}$ Janus micelles stained with (B) OsO₄ for 30 s and (C) RuO₄ for 7 min. Staining with OsO₄ vapor was conducted under vacuum (ca. 50 mbar) and with RuO₄ vapor under ambient conditions, respectively.

only one half of the corona, that is, the PEO hemicorona, is visible.

In contrast, staining with RuO_4 , which stains both the PEO and PS parts of the corona, resulted in micelles with a homogeneously dark corona with the bright-appearing PE core (thickness $d = 6.3 \pm 1.0$ nm) being located in the center of the micelles (Figures 2C and S4B). This is supported by grayscale analyses over selected cross-sectional areas (Figure 2, right panels), revealing an almost double micelle width in the case of RuO₄ staining compared to the widths obtained for OsO₄ staining or without staining. Thus, a Janus-type microphaseseparated corona seems to be preferred over the entropically more favored patchy structure when two highly incompatible corona blocks, PS and PEO, are combined.

In addition, the presence of a Janus-type corona structure can be verified by comparing the behavior with that of an $S_{330}E_{1360}M_{760}$ (M = poly(methyl methacrylate)) triblock terpolymer, which features weakly incompatible PS and PMMA end blocks and, thus, forms patchy wCCMs in toluene (Figure S4C).⁴⁹ Upon dialysis in a solvent mixture, here acetone/isopropanol (4/1 v/v), being selective for the PEO and PMMA corona blocks, respectively, is expected to result in different corona structures. Moreover, as the structure of the corona is additionally fixed by the collapse of the insoluble PS domains, any impact of drying effects during sample preparation for TEM on the corona structure can be ruled out. For $S_{330}E_{1360}M_{760}\text{,}$ the patchy structure of the corona should remain upon collapse of the insoluble PS patches, whereas for $S_{280}E_{1350}EO_{670}$, the corona should exhibit a continuous structure consisting of two hemicylinders, PEO and the collapsed PS phase. This is confirmed by the TEM images and grayscale analyses shown in Figure 3, where for $S_{330}E_{1360}M_{760}$ (Figure 3A) the patchy structure of the corona is clearly visible (PS patches were selectively stained with RuO₄ and appear dark, overview TEM in Figure S4D), whereas for $S_{280}E_{1350}EO_{670}$ (Figure 3B,C) a homogeneous corona is observed for both OsO4 and RuO4 staining. As OsO4 is only a weak staining agent for PEO, the darker hemicylinder corresponds to the PE core plus the collapsed PS hemicorona and the light gray part to PEO (Figures 3B and S4E). Consequently, for RuO₄ staining (stains PS and PEO), both hemicylinders appear dark and the PE core bright (Figures 3C

and S4F). The width of the Janus wCCMs is significantly smaller (ca. 40 nm, Figure 3C, bottom) compared to that observed for $S_{280}E_{1350}EO_{670}$ Janus wCCMs in toluene (ca. 50 nm, Figure 2C, right panel). This can be attributed to the collapse of the insoluble PS chains in acetone/isopropanol, resulting in a shrinkage of the PS hemicylinder.

The excellent interfacial activity of Janus and patchy micelles is attributed to the synergy between their particulate nature ("Pickering effect") and the amphiphilicity of the microphaseseparated corona.^{29,50,51} 1D Janus and patchy micelles with PS and PMMA corona compartments have been shown to exhibit identical interfacial activities, owing to the ability of the patchy corona to adapt to the interface by selective collapse/swelling of the respective insoluble/soluble corona block, forming an "in situ Janus" structure at the interface.²⁹ Hence, for $S_{280}E_{1250}EO_{670}$ Janus micelles, the stronger amphiphilic character of the PS/PEO corona might result in an even higher interfacial activity.

Figure 4 displays the results from pendant drop tensiometer measurements at the water/toluene interface for worm-like, patchy $S_{330}E_{1360}M_{760}$ and Janus-type $S_{280}E_{1250}EO_{670}$ micelles. Both have comparable lengths ($l \approx 700$ nm, Table S1) and degrees of polymerization of the corona blocks to rule out any effect of micelle length or corona width on the interfacial properties.^{29,51} Already at a concentration of c = 0.1 g·L⁻¹, the



Figure 4. Interfacial tension isotherms of worm-like $S_{280}E_{1250}EO_{670}$ Janus micelles compared with patchy $S_{330}E_{1360}M_{760}$ micelles at the water/toluene interface ($c = 0.1 \text{ g-L}^{-1}$).

S₂₈₀E₁₂₅₀EO₆₇₀ Janus micelles. In conclusion, this work shows that amphiphilic, worm-like Janus micelles with a crystalline PE core are accessible via CDSA of a double-crystalline triblock terpolymer, polystyreneblock-polyethylene-block-poly(ethylene oxide) (PS-b-PE-b-PEO). The combination of two highly incompatible corona blocks (PS and PEO) seems to be decisive for the formation of a Janus-type microphase-separated corona. Hence, enthalpy (in terms of incompatibility) wins over entropy, which would instead favor a patch-like microphase separation. The excellent interfacial activity of these amphiphilic Janus micelles could be applied in the stabilization of emulsions or compatibilization of polymer blends. This approach allows the production of 1D Janus micelles by a comparably easy heating and cooling protocol and, thus, might stimulate further research on CDSA of triblock terpolymers with strongly incompatible coronaforming blocks. This, in turn, can open new routes to hierarchical self-assemblies based on 1D Janus micelles.

nature of the PS/PEO corona on the interfacial activity of

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c08076.

Materials, experimental procedures, methods, ¹H NMR spectra and SEC traces of triblock terpolymers, and additional TEM images (PDF)

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Notes

The authors declare no competing financial interest.

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