Supporting Information to the Manuscript

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

Christian Hils,[a] *Joachim Schmelz,*[a] *Markus Drechsler*[b] *and Holger Schmalz**[a,c]

[a] Macromolecular Chemistry II, University of Bayreuth, Universitätsstraße 30, 95447 Bayreuth (Germany)

[b] Bavarian Polymer Institute, Keylab Electron and Optical Microscopy, Universitätsstraße 30, 95447 Bayreuth (Germany)

[c] Bavarian Polymer Institute, Keylab Synthesis and Molecular Characterization, Universitätsstraße 30, 95447 Bayreuth (Germany)

Experimental Procedures and Methods

Materials. All chemicals were used as received unless otherwise noted. Poly(ethylene oxide) (PEO, M_n = 10.000, Sigma-Aldrich), tris(triphenylphosphine)rhodium(I) chloride (Wilkinson's catalyst, 99.9% trace metals basis, Sigma-Aldrich), *iso*-propanol (*i*PrOH, p.a., ACS reagent, ≥99.8% (GC), Sigma-Aldrich), deuterated chloroform ($CDCl_3$, 99.8%, Deutero), hydrochloric acid (37 wt% in water, VWR), ruthenium(III) chloride hydrate (ReagentPlus®, Sigma-Aldrich), sodium hypochlorite solution (NaOCl, 10 – 15 wt% in water, Sigma-Aldrich), osmium tetraoxide (OsO_4, ReagentPlus®, 99.8%, Sigma-Aldrich), tetrahydrofuran (THF, ≥ 99.9%, Sigma-Aldrich), toluene (≥ 99.5%, AnalaR NORMAPUR® ACS, VWR), acetone (p.a., ACS reagent, ≥99.5% (GC), Sigma-Aldrich) and dialysis membrane (Spectra/Por® 3).

Synthesis of the SEEO triblock terpolymer. The polystyrene-*block*-polyethylene-*block*-poly(ethylene oxide) (SEEO) triblock terpolymer was synthesized by a combination of sequential living anionic polymerization to yield the corresponding polystyrene-*block*-poly(1,4-butadiene)-*block*-poly(ethylene oxide) (PS-*b*-PB-*b*-PEO) precursor, followed by catalytic hydrogenation. The sequential anionic polymerization of styrene, butadiene and ethylene oxide was conducted in toluene with *sec*-BuLi as initiator utilizing the phosphazene base *t*-BuP_4 to promote polymerization of ethylene oxide in the presence of Li^+ counter ions.[1] The polymerization of butadiene under the conditions employed led to a preferential 1,4-addition (88 mol% 1,4-units), which is essential to obtain the corresponding "pseudo-polyethylene" structure after hydrogenation. The hydrogenation of the obtained $S_{280}B_{630}EO_{640}$ triblock terpolymer (indices denote the average degrees of polymerization of the respective blocks) resulted in the corresponding $S_{280}E_{1250}EO_{670}$ triblock terpolymer. Homogeneous catalytic hydrogenation was carried out with Wilkinson's catalyst (1 mol% with respect to double bonds) in toluene at 60 °C and 60 bar H_2 pressure for 3 d. The used $S_{330}E_{1360}M_{760}$ triblock terpolymer was identical to that described in our previous work.[2]

Preparation of worm-like crystalline core micelles (wCCMs). The Janus and patchy wCCMs were prepared by crystallization-driven self-assembly (CDSA) of the triblock terpolymers $S_{280}E_{1250}EO_{670}$ and $S_{330}E_{1360}M_{760}$ in toluene, respectively.[3] To this end, the triblock terpolymers were dissolved in toluene (c = 10 g·L^{-1}) at 80 °C for 30 min and subsequently cooled to the crystallization temperature (T_c, Table S1) of the polyethylene (PE) middle block, using a thermostated shaker unit (HLC-MKR 13, Ditabis). The self-assembly process was allowed to proceed for 24 h at a shaking rate of 200 rpm. Afterwards, the PE core was annealed at T_a (Table

S1) for 5 min followed by cooling to 20 °C. In addition, micellar dispersions (c = 0.5 g·L^{-1} in toluene) were dialyzed for 6 d against acetone/*i*PrOH (4/1, v/v), followed by dilution to c = 0.1 g·L^{-1} by slowly adding the same solvent mixture over 2.5 h.

Table S1. Characteristics of the employed triblock terpolymers and micellar dispersions.

Triblock terpolymer[a]	**M_n / kg·mol^{-1} ($Đ$)**[b]	**T_c / °C**[c]	**T_a / °C**[c]	***l*(wCCMs) / nm**[d]
$S_{280}E_{1250}EO_{670}$	93.5 (1.03)	28.5	45.0	680 ± 280
$S_{330}E_{1360}M_{760}$	148 (1.03)	22.0	41.0	690 ± 270

[a] Indices denote the number average degree of polymerization. [b] Determined from the respective precursor triblock terpolymers with polybutadiene middle blocks using a combination of MALDI-ToF and ^{1}H-NMR for M_n calculation, dispersity ($Đ$) determined by $CHCl_3$-SEC employing a PS calibration. [c] Measured by μ-DSC (c = 10 g·L^{-1}). [d] Average micelle length ± standard deviation as determined by TEM image analyses of at least 100 micelles.

Nuclear Magnetic Resonance (NMR) Spectroscopy. The triblock terpolymers were characterized by ^{1}H NMR spectroscopy (Bruker Ultrashield 300 spectrometer) using $CDCl_3$ as solvent. $S_{280}E_{1250}EO_{670}$ was analyzed at 52 °C to ensure complete dissolution of the PE block. The signal assignment was supported by simulations with the NMR software MestReNova.

Size-Exclusion Chromatography (SEC). SEC measurements were performed on an instrument equipped with two PSS-SDV gel columns (particle size = 5 µm) with porosity range from 10^2 to 10^5 Å (PSS, Mainz, Germany). Chloroform (HPLC grade) was used as solvent (for dissolving polymer and as eluting solvent). The polymers were dissolved and filtered through a 0.22 µm PTFE filter before analysis. The samples were measured on a SEC 1260 Infinity system (Agilent Technologies) at a flow rate of 0.5 mL·min^{-1} at 23 °C, using a refractive index detector (Agilent Technologies). The calibration was done with narrowly distributed polystyrene standards (PSS calibration kit) and toluene (HPLC grade) was used as internal standard.

Micro Differential Scanning Calorimetry (μ-DSC). The measurements were performed on a SETARAM Micro DSC III using sealed measuring cells ("batch cells", V = 1 mL) filled with approx. 0.7 mL of the polymer dispersions (c = 10 g·L^{-1} in toluene). A scanning rate of 0.5 K·min^{-1} was employed and pure toluene was used as reference. The degrees of crystallinity were estimated employing the heat of fusions for 100% crystalline PEO[4] and PE[5] of ΔH_m^0 = 196.6 J·g^{-1} and ΔH_m^0 = 276.98 J·g^{-1}, respectively.

Transmission Electron Microscopy (TEM). The TEM measurements were carried out with a Zeiss CEM902, a ZEISS / LEO EM922 Omega and a JEOL JEM-2200FS field emission TEM. All microscopes are energy filtering transmission electron microscopes (EFTEMs), operated at an acceleration voltage of 80 kV and 200 kV, respectively. Zero-loss filtered micrographs ($\Delta E \approx 0$ eV) were taken with a side mounted CCD camera system (Orius, Gatan) in case of the Zeiss CEM902, a bottom mounted CCD camera (Ultrascan 1000, Gatan) in case of the ZEISS Omega and a bottom mounted CMOS camera system (OneView, Gatan) for the JEOL JEM-2200FS, respectively. The images were processed with a digital image processing software (Digital Micrograph DM 1.9, DM 2.3 and DM 3.3, Gatan). For TEM analysis of the triblock terpolymer micelle dispersions, the samples were diluted to a concentration of $c = 0.1$ g·L^{-1} and stirred for 30 min at room temperature. Subsequently, 10 µL of the respective dispersion was applied to a carbon-coated copper grid and residual solvent was removed by blotting with a filter paper followed by drying of the coated copper grid under vacuum (24 h, $1 \cdot 10^{-5}$ mbar, room temperature). For RuO_4 staining the samples were treated for 7 min with RuO_4 vapor, which was formed in situ from $RuCl_3$ hydrate and NaOCl. Staining with OsO_4 was conducted for 30 sec under vacuum (ca. 50 mbar). After staining, the samples were stored for at least 1 h in a fume hood to ensure that any not reacted staining agents were completely removed. The average lengths of the triblock terpolymer micelles were determined by measuring at least 100 micelles using the software ImageJ.[6] The greyscale analyses were performed with the Digital Micrograph software package (Gatan).

Interfacial Tension measurements were conducted employing a DS25 from Krüss. First, the interfacial tension of pure toluene in a cuvette (10 mm, QS) was determined with the software "Advanced Drop Shape Analysis" (version 1.3.1.0) and the method "Pendant Drop" using a droplet volume of $V = 35$ µL (deionized water). Micellar dispersions were measured at a concentration of $c = 0.1$ g·L^{-1}. The quasi-equilibrium interfacial tensions were determined as average over the last 30 min of the respective measurement, where the interfacial tension levels off. The interfacial tension of the pristine water/toluene interface was determined to $\gamma = 33.2$ mN·m^{-1}.

Supporting Figures

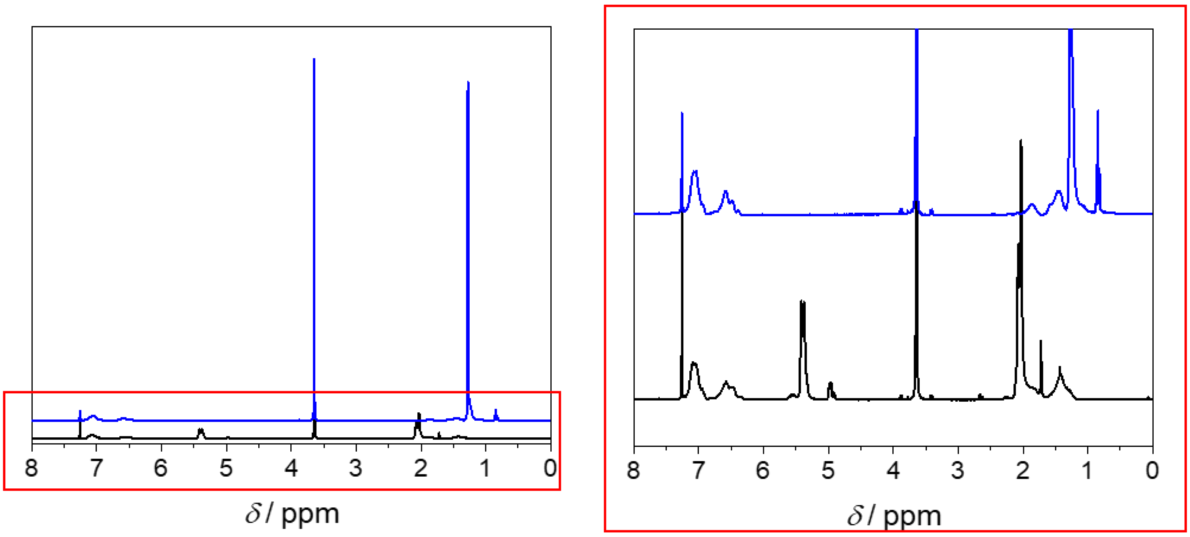

Figure S1. ^{1}H NMR in $CDCl_3$ of $S_{280}B_{630}EO_{640}$ (blue) and $S_{280}E_{1250}EO_{670}$ (black, T = 52 °C). Complete hydrogenation of the polybutadiene (PB) middle block to polyethylene is proven by the absence of PB related peaks between ca. 5 – 5.5 ppm in the ^{1}H NMR spectrum of $S_{280}E_{1250}EO_{670}$.

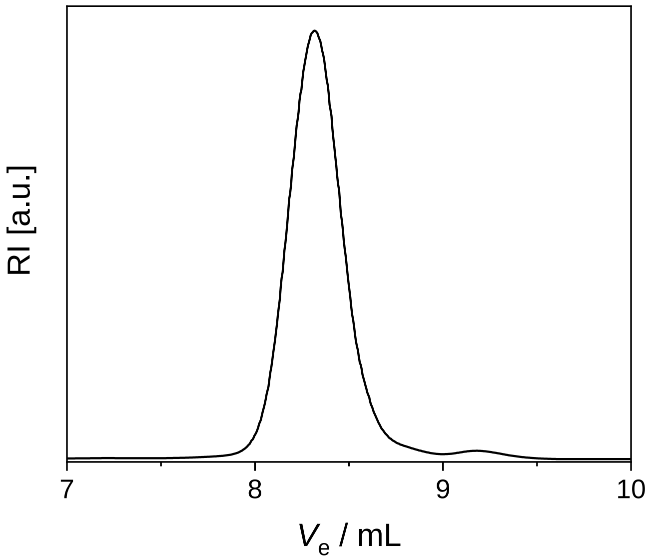

Figure S2. $CHCl_3$-SEC of the $S_{280}B_{630}EO_{640}$ triblock terpolymer.

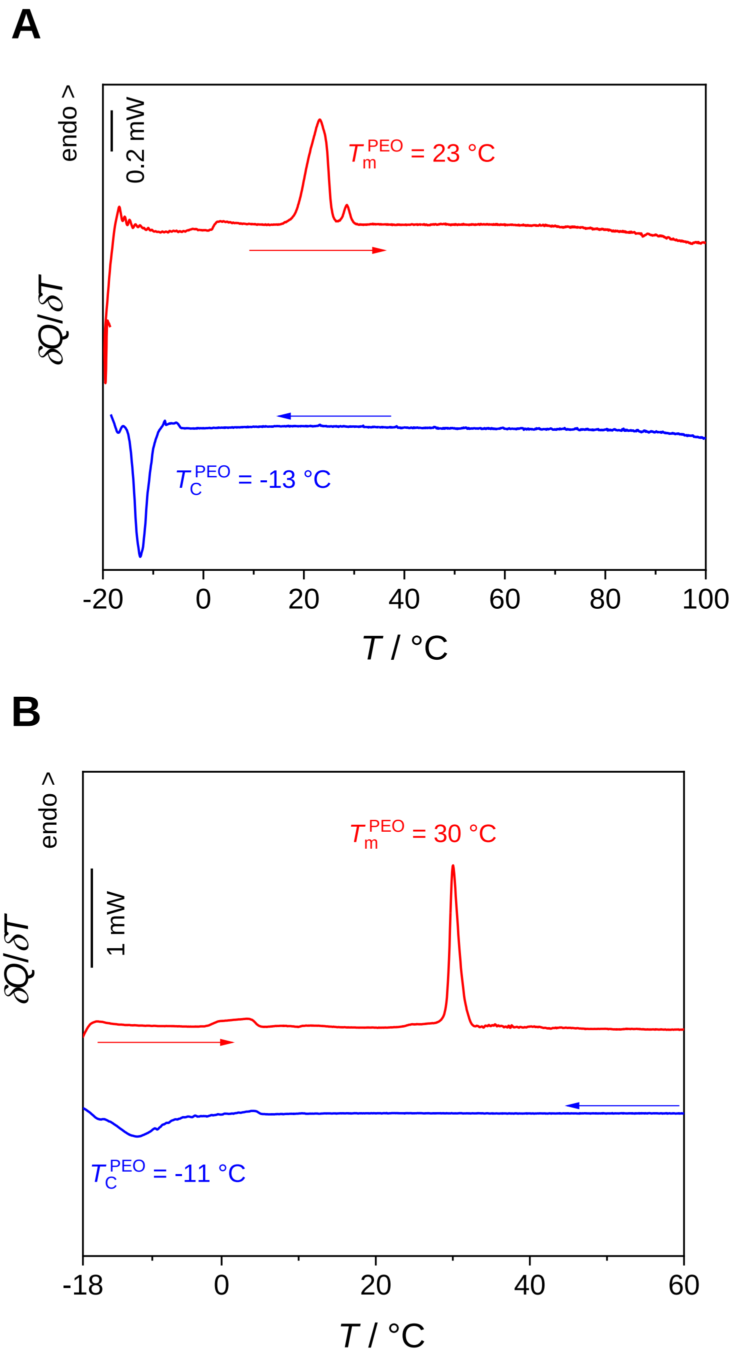

Figure S3. *μ*-DSC heating and cooling traces of A) $S_{280}B_{630}EO_{640}$ (c = 10 g·L^{-1}) and B) neat PEO homopolymer (c = 3 g·L^{-1}) in toluene.

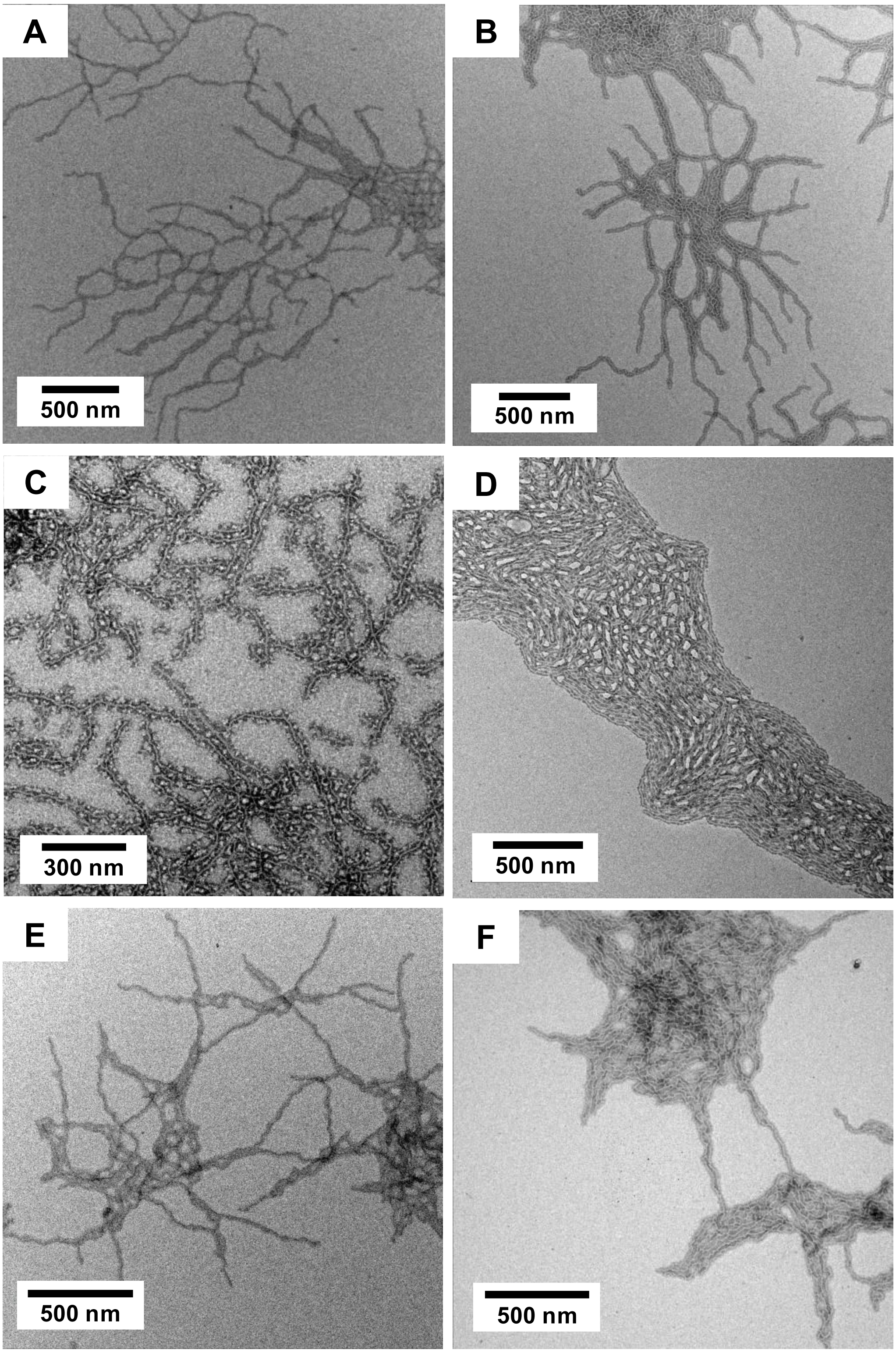

Figure S4. TEM measurements of worm-like crystalline-core micelles. A) $S_{280}E_{1250}EO_{670}$ (c = 0.1 g·L^{-1}, toluene), B) $S_{280}E_{1250}EO_{670}$ (c = 0.1 g·L^{-1}, toluene) stained with RuO_4, C) $S_{330}E_{1360}M_{760}$ (c = 0.1 g·L^{-1}, toluene) stained with RuO_4, D) $S_{330}E_{1360}M_{760}$ (c = 0.1 g·L^{-1}) dialyzed against acetone/*iso*-propanol (4/1 v/v) and stained with RuO_4, E) $S_{280}E_{1250}EO_{670}$ (c = 0.1 g·L^{-1}) dialyzed against acetone/*iso*-propanol (4/1 v/v) and stained with OsO_4, and F) $S_{280}E_{1250}EO_{670}$ (c = 0.1 g·L^{-1}) dialyzed against acetone/*iso*-propanol (4/1 v/v) and stained with RuO_4.

References

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