Janus Micelles†

Rainer Erhardt, Alexander Boker, Heiko Zettl, Håkon Kaya, Wim Pyckhout-Hintzen, Georg Krausch, Volker Abetz, and Axel H. E. Müller‡,§

Makromolekulare Chemie II, Universität Bayreuth, D-95440 Bayreuth, Germany; Physikalische Chemie II, Universität Bayreuth, D-95440 Bayreuth, Germany; Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany; and Bayreuther Zentrum für Kolloide und Grenzflächen, D-95440 Bayreuth, Germany

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ABSTRACT: A novel strategy to synthesize amphiphilic surface-compartmentalized nanoparticles based on linear ABC triblock copolymers is presented. These so-called Janus micelles consist of a cross-linked core and a corona with a “northern” and a “southern” hemisphere. Selectively cross-linking spherical domains of the polybutadiene middle block in a well-ordered bulk morphology of a polystyrene-block-polybutadiene-block-poly(methyl methacrylate) triblock copolymer (SBM) leads to the conservation of the compartmentalization of the outer blocks after dissolution of the material. Multi-angle laser light scattering, light scattering gel permeation chromatography, fluorescence correlation spectroscopy, small-angle neutron scattering, and static and dynamic light scattering, as well as scanning force microscopy, indicate the existence of an equilibrium between molecularly dissolved Janus micelles (unimers) and aggregates (multimers), so-called supermicelles.

Figure 1. Schematic representation of the Janus micelles' synthesis (left-hand side: sketch of SBM Is-morphology).

Introduction

During the past few years a variety of novel bulk morphologies has been established for linear binary1−3 and ternary block copolymers4−7 as well as for block copolymers with nonlinear chain topologies.8−11 The amphiphilic nature of block copolymers composed of incompatible blocks has long been recognized, and a large number of studies have addressed the solution behavior of binary12−16 and, more recently, ternary block copolymers.17−20 In most of these investigations block copolymers were allowed to self-assemble or to dissolve on a molecular level in various solvents. Selective solvents often lead to the formation of micelles, where the less soluble parts of the block copolymers form core domains which are surrounded by a highly swollen corona of the more soluble blocks. Depending on the degree of swelling of the corona and the relative composition of the block copolymers, various shapes of micelles have been found, which in general show spherical or cylindrical symmetries. To our knowledge Liu and co-workers were the first who selectively cross-linked one component in block copolymers in order to obtain larger structures like spheres13 or cylinders.21 The term "Janus" used to describe the property of having two faces (a hydrophobic and a hydrophilic one) was first used in natural science by Veyssie et al. who created "Janus beads" by a partial hydrophobic modification of commercial glass spheres.22,23 Schlüter and co-workers reported on rodlike molecules with two different half-coronas based on polydendrons.24 Further cylindrical Janus-type structures were obtained by sequential ring-opening metathesis polymerization of poly(styrene and poly(ethylene oxide) macromonomers.25

However, noncentrosymmetric structures taking advantage of the inherently noncentrosymmetric nature of ABC triblock copolymers have not been reported on so far. While noncentrosymmetric lamellae were found in self-assembled blends of linear ABC triblock copolymers with AC26 or other ABC block copolymers,27 pure block copolymers typically form centrosymmetric structures in the bulk state. In the present contribution, the synthesis and characterization of noncentrosymmetric particles, so-called "Janus micelles", will be reported. Following an idea of Reimund Stadler, the particles are obtained via a three-step procedure (see Figure 1): (i) a film of an ABC triblock copolymer with lamellae of the outer blocks embedding spherical domains of the middle block (the so-called lamellae-sphere or Is-morphology)3 is prepared by solution casting, (ii) the spherical domains of the middle blocks are cross-linked in the bulk state, and (iii) the bulk phase is redissolved in a good solvent.

Experimental Section

Synthesis, SBM Precursor. The Janus micelles' precursor, a polystyrene-block-polybutadiene-block-poly(methyl methacrylate) (SBM) triblock copolymer, was synthesized via sequential anionic polymerization in tetrahydrofuran (THF), following procedures described elsewhere.28

Cross-Linking. The bulk cross-linking was performed in two ways. In the first approach, a film of SBM cast from chloroform (CHCl₃) solution was swollen in acetonitrile for 48 h (without destroying the morphology) and afterward cross-linked by adding 5% (w/v) disulfurdichloride (S₂Cl₂) and waiting for another 48 h.29−31 The product was purified in the following...
way: The film was rinsed three times with acetone and dried in a vacuum. Afterward it was redissolved in THF and reprecipitated in methanol twice and dried in a vacuum at room temperature. In the second approach a solution cast film of SBM containing 5% (w/w) \( \alpha,\alpha' \)-azoisobutyronitrile (AIBN) was annealed at \( 90^\circ\)C for 48 h in a vacuum for the radical cross-linking process. This product was also purified by reprecipitation and reprecipitated in a vacuum.

Transmission Electron Microscopy (TEM). The bulk morphology of the SBM block copolymer was examined using TEM. Films (around 1 mm thick) were cast from 10% (w/w) solutions in CHCl3 and allowed to evaporate slowly for 2 weeks.

The FCS experiments were carried out using a Zeiss DAWN DSP – F detector (Argon ion laser, \( \lambda_0 = 488 \) nm) and a Shodex-R1-71 detector. Further experimental conditions were tailored for the respective polymer. In the measurements of the SBM, three 30 cm 5 \( \mu \)m PSS SDV columns were used (10\(^3\), 10\(^4\), and 10\(^5\) \( \AA \)) with THF as eluent at a flow rate of 1 mL/min (c = 2 g/L; injection volume = 100 \( \mu \)L). In the case of the cross-linked SBMs one 30 cm 10 \( \mu \)m PSS SDV LINEAR ONE column was used with THF containing 0.25% tetrabutylammonium bromide as eluent at a flow rate of 0.25 mL/min (c = 0.2 – 0.4 g/L; injection volume = 50 \( \mu \)L). The sample was added to the solvent in order to prevent polymer adsorption on the columns.

Asymmetric Flow Field-Flow Fractionation (FFFF). The FFF experiments were performed at room temperature using a GPC equipped with a Wyatt Technology DAWN DSP – F detector (Argon ion laser, \( \lambda_0 = 488 \) nm) and a Shodex-R1-71 detector. Further experimental conditions were tailored for the respective polymer. In the measurements of the SBM, three 30 cm 5 \( \mu \)m PSS SDV columns were used (10\(^3\), 10\(^4\), and 10\(^5\) \( \AA \)) with THF as eluent at a flow rate of 1 mL/min (c = 2 g/L; injection volume = 100 \( \mu \)L). In the case of the cross-linked SBMs one 30 cm 10 \( \mu \)m PSS SDV LINEAR ONE column was used with THF containing 0.25% tetrabutylammonium bromide as eluent at a flow rate of 0.25 mL/min (c = 0.2 – 0.4 g/L; injection volume = 50 \( \mu \)L). The salt was added to the solvent in order to prevent polymer adsorption on the columns.

The measurement was done on a Postnova Analytics HRFFF-10000 system equipped with RI and UV detectors and a PD2000 light scattering detector with THF as eluent at a flow rate of 1 mL/min (c = 2 g/L; injection volume = 100 \( \mu \)L). In the case of the cross-linked SBMs one 30 cm 10 \( \mu \)m PSS SDV LINEAR ONE column was used with THF containing 0.25% tetrabutylammonium bromide as eluent at a flow rate of 0.25 mL/min (c = 0.2 – 0.4 g/L; injection volume = 50 \( \mu \)L). The sample was added to the solvent in order to prevent polymer adsorption on the columns.

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Asymmetric Flow Field-Flow Fractionation (FFFF). The setup is commonly used for measurements in water. Slight modifications were necessary to enable measurements in organic solvents.

Conical Fluorescence Correlation Spectroscopy (FCS). The FCS experiments were carried out using a Zeiss Confocor 2 spectrometer. This instrument consists of an Axiosvert microscope with a celsor corrected 40x water immersion objective, a He–Ne laser, and a variable excitation source.

For detection, an avalanche photodiode (APD) in single photon counting mode was used. This experimental setup allows FCS studies with confocal optics. Further details of FCS have already been described earlier.

The Unified Exponential/Power Law Equation. Starting with general expressions for the classical Porod correlation function \( f(r) \), Beaucage developed a universal equation which describes the entire scattering curve for a multitude of complex systems consisting of randomly distributed structures, or structures comprising several substructures. The equation is a combination of approximations, viz. Guinier-like exponential and generalized power laws, each describing different structural levels. These approximations are limited to the structural levels in which they are valid regarding size and morphology of the relevant structure. Transitions from one structural level to another is taken into account by error-function terms and exponential cutoffs.
curves obtained at different concentrations. This will only affect the prefactors in eq 3. From the shape of the scattering curves, it can be inferred that the scattering particles retain the same structure in the measured concentration range 0.025–3 g/L.

**Light Scattering.** Static light scattering experiments (SLS) were carried out on a SLS goniometer 1 (Sofica) using a He–Ne laser (λ₀ = 632.8 nm). The refractive index increment dn/dc, which is needed for the evaluation of the SLS data, was measured with a scanning Michaelson interferometer. Dynamic light scattering (DLS) was performed on an ALV 5000 correlator and a Kr ion laser (λ₀ = 647.1 nm). Prior to the light scattering experiments the Janus micelle solutions were filtered using Millipore filters (housing: polypropylene, membrane: poly(tetrafluoroethylene)) with a pore size of 3 μm (filters with smaller pore sizes were rapidly clogged).

**Scanning Force Microscopy.** The scanning force microscopy (SFM) images were taken on a Digital Instruments Dimension 3100 microscope operated in Tapping Mode. Reference (SFM) images were taken on a Digital Instruments Dimension 3100 microscope operated in Tapping Mode (free scanning velocities of around 6 µm/s). Phase images were recorded at scanning velocities of around 6 µm/s. Phase images can reveal lateral variations in the local elasticity (bright areas correspond to larger phase shifts than darker regions). For a correct evaluation of the mean radii of the micelles, one has to correct for the finite radius of curvature of the tip, which systematically enlarges the lateral dimensions (bright areas correspond to larger phase shifts than darker regions). For a correct evaluation of the mean radii of the micelles, one has to correct for the finite radius of curvature of the tip, which systematically enlarges the lateral dimensions of the tips. In this study tips were changed regularly in order to avoid contamination. We assume that all tips had a radius of curvature of about 10 nm, which was subtracted from the measured radii.

**Results and Discussion**

**Synthesis.** The starting material for the synthesis of the Janus micelles is a SBM triblock copolymer determined by 1H NMR). In the bulk, this polymer exhibits the so-called "is-morphology" with very narrowly distributed polybutadiene (PB) spheres located at the interface of the polystyrene (PS) and poly(methyl methacrylate) (PMMA) lamellae as shown in Figure 2 and schematically on the left-hand side of Figure 1. Please note that the PS/PMMA ratio (as determined by 1H NMR) is not reflected in the apparent volume fraction visible in the TEM image due to partial degradation of PMMA in the electron beam. Each PB sphere is potentially a core of a Janus micelle which has a compartmentalized shell consisting of a PS and a PMMA hemisphere. Cross-linking of these cores in bulk forces the system to retain such a noncentrosymmetric structure even after dissolution (Figure 1). On the basis of the diameter of the PB spheres (7.7 ± 1.0 nm) from the TEM image and the PB bulk density it is possible to estimate the average number of SBM chains participating in a single PB sphere to be 13 ± 5. As a consequence a single Janus micelle consists of approximately 13 SBM chains and therefore has an expected molecular weight M₁ ≈ 2.5 × 10⁶. The minimum diameter of the Janus micelles in solution can be roughly estimated to be half the long period L of the SBM in bulk (see Figure 2): L/2 = 22.9 ± 1.6 nm (radius R = 11.4 ± 0.8 nm).

To study the properties of the Janus micelles, a bulk specimen of S₂Cl₂ (M₄₃) was cross-linked and the purified product redissolved. Films of the cross-linking product cast from CHCl₃ solution also show a bulk is-morphology as the precursor SBM, thus confirming its noncentrosymmetric structure.

To determine the molecular weight, MALDI–GCP traces were recorded with THF as eluent. Using a combination of refractive index detector and MALDI detector, this method provides the true number-average molecular weight of block copolymers. Figure 3 shows the differential molecular weight distributions of both precursor SBM and SBM cross-linked with S₂Cl₂. The SBM shows a very narrow molecular weight distribution (M₄₃ ≈ 1.02) with M₁ = 1.63 × 10⁵. This M₁ value is about 14% smaller than the M₁ value mentioned above thus giving us an estimate of the error of these two methods. The SBM cross-linked with S₂Cl₂ shows a somewhat broader distribution (M₄₃ = 1.22). The obtained M₁ = 2.08 × 10⁷ is about 10 times higher than expected (see above).

The GPC results are confirmed by asymmetric flow field-flow fractionation in THF. Both cross-linking strategies lead to similar elugrams, thus indicating an effective cross-linking of the PB domains of the is-morphology. However, cross-linking with AIBN also leads to some degradation of the chains. In the following, we will only discuss results on the sample cross-linked with S₂Cl₂, since there are no degradation products to be separated from the material prior to further investigations.

The large difference of the expected molecular weight of the Janus micelles and the value obtained by MALDI–GCP...
GPC was seen as a motivation to further investigate SANS data for the Janus micelles in THF-polymer concentration (\(c = 0.515 \times 10^{-4}\) to 1 g/L). The critical aggregation concentration (cac) is taken as the concentration where the radius starts to increase (\(cac \approx 7 \pm 2\) mg/L).

**Fluorescence Correlation Spectroscopy.** FCS allows to investigate the aggregation behavior of particles at very low concentrations not accessible by other analytical methods. In the present work, we studied Janus micelles dissolved in THF in a concentration range of \(0.5 \times 10^{-4}\) to 1 g/L. The FCS results are shown in Figure 4. Below a critical concentration of about \(7 \pm 2\) mg/L particles of constant size are observed (\(R_h \approx 10\) nm), which may be identified as molecularly dissolved Janus micelles. At higher concentrations, an increase of the hydrodynamic radius to about 53 nm is observed, indicating an aggregation of single Janus micelles into multimers, which will be referred to as “supermicelles” in the following. The critical concentration of about \(7 \pm 2\) mg/L may therefore be taken as a critical aggregation concentration (cac) for the formation of supermicelles. The hydrodynamic radius, \(R_h\), of the Janus micelle unimers of about 10 nm correlates well with the size estimated from TEM (see above). We note, however, that the absolute values of \(R_h\) measured by FCS comprise the approximation made for the waist radius (see Experimental Section). All hydrodynamic radii determined by FCS are number-averaged.

**Small-Angle Neutron Scattering.** Figure 5 shows the results of SANS measurements performed in deuterated THF (THF-d\(_8\)). The intensity drop with the scattering vector \(q\) excludes simple models of spherical aggregate-like structures which should show a \(q^{-4}\) envelope in the low to intermediate \(q\) range. Instead, a clear \(q^{-3}\) dependence is found. In a first attempt, the data were fitted by a spherical core–shell structure; however, unphysical values for both the scattering length densities and the dimensions were obtained.

Lacking further information on the inner structure of the particles, a Beaucage fit was applied to the data. The Beaucage fit is based on the assumption of a homogeneous average scattering length density. This procedure should lead to acceptable dimensions at least at low to intermediate \(q\) values. High \(q\) values, however, which probe the internal length scales of the whole particle, are most affected by this assumption. Therefore, the power law for the primary particle (see above) is probably an artifact.

Applying eq 3, we are able to fit all scattering curves with the same set of five parameters: the prefactors \(G_0\), \(G_\infty\), and \(B_s\), and the structural dimensions \(R_g\) and \(R_s\). Fitting \(B\) gave negligibly small values, therefore the respective term was omitted in order to reduce the number of variables. As a consequence, lacking a value for the power law exponent \(P\), we are unable to infer any information on the shape of the superstructure. Likewise, we fixed the value of \(P_1\) to 1, as the fits yielded results close to this value. Regarding the range of large \(q\) values, an exponent \(P_6 = 1\) would indicate an extended internal structure possibly due to unfavorable interactions between PS and PMMA. However more detailed information about the structure of the particle is lacking and could only be obtained by further experiments of elaborate contrast-matching of components.

We emphasize that the presented Beaucage theory clearly indicated three regimes, corresponding to large aggregates, subunits, and a power law regime. The fit results are listed in Table 1. The first two regimes yield the sizes of the respective particles (\(R_g = 35.5\) nm, \(R_s = 9.9\) nm) whereas the power law term only concerns the internal structure, which is outside the scope of this publication. We note that convolution of eq 3 with the resolution function of Pedersen et al.\(^{41,42}\) did not significantly change the results on \(R_g\) and \(R_s\) (see Table 1).

**Light Scattering.** To further elucidate the solution properties of the Janus micelles, SLS experiments were performed in THF (0.025 g/L \(\leq c \leq 3\) g/L). The analysis of the scattering intensities using a Zimm plot\(^{43}\) (Figure 6) yields a molecular weight \(M_w = 3.45 \times 10^7\), a radius of gyration \(R_g = 69\) nm and a second virial coefficient (of the osmotic pressure) \(A_2 = 4.52 \times 10^{-6}\) mol·mL/g². These quantities are apparent quantities due to the well-known problem of static light scattering analysis of block copolymers especially in the case of PS-block-PMMA in THF (\(\Delta dn/dc \approx 0.1\))\(^{44,45}\). However, it has been shown that the chemical heterogeneity of aggregates (micelles) made from a considerable number of unimers is much smaller than the heterogeneity of the unimers and that in this case SLS yields the true

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**Table 1. SANS Fit Results from the Beaucage Model**

<table>
<thead>
<tr>
<th>(G) (cm(^{-1}))</th>
<th>(R_g) (nm)</th>
<th>(B_s)</th>
<th>(G_\infty) (cm(^{-1}))</th>
<th>(R_s) (nm)</th>
<th>(B_s)</th>
<th>(P_6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>34500 ± 330</td>
<td>35.5 ± 0.1</td>
<td>0</td>
<td>586 ± 15</td>
<td>9.9 ± 0.1</td>
<td>5.2 ± 0.2</td>
<td>1</td>
</tr>
<tr>
<td>35890 ± 331</td>
<td>36.2 ± 0.1</td>
<td>0</td>
<td>570 ± 15</td>
<td>9.9 ± 0.1</td>
<td>5.1 ± 0.2</td>
<td>1</td>
</tr>
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</table>

* Kept constant.
Consequently the measured M_w,app should at least be close to the true M_w, while the measured radius of gyration has to be treated as an apparent value without more detailed information about the shape of the aggregates.

It is interesting to note the linear dependence of Kc/\(R_ı\) on \(q^2\). In the case of spherical aggregates in solution, a distinct upward curvature in the Zimm plot is expected (also for coil-like structures at such high molecular weights). One may argue that the upward curvature is compensated by a downward curvature due to the polydispersity of the aggregates. However, without further supporting evidence these assumptions are purely speculative. A rod-like shape would cause a downward curvature which is also not observed. The interpretation is furthermore complicated by the fact that most of the scattering intensity is due to the PS part of the Janus micelles which has the predominant refractive index increment. The reason for the absence of the concentration dependence characteristic for aggregation phenomena in the Zimm plot is that the cac (as determined by FCS) is too small to be accessible to SLS.

In addition to SLS, DLS was performed on solutions of two different concentrations (0.005 and 0.5 g/L) in THF. The CONTIN analysis of the autocorrelation functions measured at four different angles (60, 90, 120, and 150°) (Figure 7) for both concentrations shows only one peak. The hydrodynamic radius of the corresponding species in solution was found to be \(R_h = 74\) nm (by extrapolating \(R_h(q^2)\) to \(q^2 \rightarrow 0\)). Because the experiments were done at concentrations \(c \geq cac\) and because the hydrodynamic radius determined by light scattering is z-averaged, only aggregates and no unimers were observed. It is obvious that the z-averaged hydrodynamic radius determined by DLS \((R_h^{-1})_{z-1} = 74\) nm is larger than the number-averaged hydrodynamic radius from FCS \((R_h)n = 53\) nm.

### Scanning Force Microscopy

To visualize the aggregates by SFM, the micelles were deposited onto polished silicon wafers by dip coating from very dilute solutions (c = 0.01 g/L). Figure 8 shows tapping mode topography and phase images of micelles obtained from THF. We observe both small particles and larger structures, the latter resembling the shape of a fried egg: They exhibit an elevated middle part which is surrounded by a corona that spreads on the surface. A cross section shown as inset in Figure 8A further underlines this shape. It is difficult to infer an inner structure from the SFM images of the smaller particles; however, in some of the cases a similar “fried egg”-like morphology can be seen (see, e.g., Figure 8D,E).

If we consider the well-known preference of PMMA for polar substrates like silicon oxide and keep in mind the Janus character of the micelles with a PS and a PMMA hemisphere, we may assume that the corona of the particles consists of the PMMA blocks whereas the elevated middle part is formed by PS. According to their sizes, the two objects in Figure 8, parts B and E, can be assigned as representative examples for the largest single aggregate (mean radius \(\approx 50\) ± 10 nm) and the smallest subunit, a unimer (mean radius \(\approx 7\) ± 2 nm). These dimensions agree well with values for

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**Figure 6.** Zimm plot of the Janus micelles in THF in a concentration range 0.025–3 g/L.

**Figure 7.** Field autocorrelation functions of the Janus micelles in THF at a concentration of 0.5 g/L.

**Figure 8.** Tapping mode SFM images of Janus micelles and their superstructures on a silicon wafer (dip coated from a 0.01 g/L solution in THF). A–C: topography (0–30 nm). D–F: phase (D and E, 0–10°; F, 0–30°).
supermicelles and single Janus micelles, respectively, as found in dilute solution (see above). At this point it is important to note that so far only little is known about the differences in size between the micelles in solution and deposited on a polar substrate. Swelling in solution and stretching of the polymer chains in contact with the substrate most certainly significantly influence the dimensions of the Janus particles. Although the concentration of the solutions used for the dip coating process is above the cac, a Beaucage fit of the scattering curves provides a critical aggregation concentration (from dilute to highly concentrated) before the solvent has evaporated completely. Obviously, the supermicelles already exhibit a certain critical size and therefore, instead of successively forming even larger aggregates, instead assemble on the surface to form a hexagonally packed array as shown in Figure 8, parts C and F. In summary, the Janus micelles were found to organize on different levels on the substrate surface: single micelles (unimers), supermicelles, and their hexagonal arrays.

Comparison of Results Obtained by Different Techniques and Conclusion. FCS experiments give an overview of the Janus micelles’ association behavior in THF and provide a critical aggregation concentration cac ≈ 7 ± 2 mg/L and approximate hydrodynamic radii of both unimer (R_{\text{h}} \approx 10 nm) and supermicelles (R_{\text{h}} \approx 53 nm). SANS confirms the existence of aggregates in a concentration range above the cac. A Beaucage fit of the scattering curves provides a R_h of the aggregates of 35.5 nm and a radius R_g of the substructures of 9.9 nm. Dynamic light scattering gives a hydrodynamic radius \( \langle R_g \rangle \approx 74 \text{ nm} \) of the supermicelles.

Using the true M_n values determined by MALLS–GPC of the precursor SBM and the supermicelles and the number of SBM chains in one Janus micelle from TEM (see Synthesis) and further taking into account the number of SBM chains in one Janus micelle from GPC and helpful discussions is possible to calculate an approximate aggregation number of 11 ± 4. The Janus micelles also exhibit a bulk morphology as the precursor SBM polymer confirming their noncentrosymmetric structure. However, so far there is no experimental evidence regarding the shape of the supermicelles in solution. Further SANS experiments with contrast-matching are necessary in order to clarify this issue.

SFM allows to visualize both unimers and aggregates precipitated on a silicon oxide surface and confirms the amphiphilic nature (surface activity) of the Janus micelles.

What has not been discussed so far is the important question why these Janus micelles show aggregation into supermicelles at all, because THF supposedly is a good solvent for both PS and PMMA. One may argue that the slight differences in solubility of individual PS and PMMA chains are amplified by bundling up several block copolymer chains into a Janus micelle. Slightly different degrees of swelling might induce a curvature of the PS/PMMA interface which may in turn lead to aggregation. Another suggestion is that chains in both hemispheres experience a loss in conformational entropy due to the cross-linking which can be diminished by forming larger phases (aggregates). However, the issue of supermicelle formation in THF is still open and further discussion is needed.

In summary, we have demonstrated a synthetic route for the formation of compartmentalized micellar objects by suitably preserving the molecular superstructure of a microphase separated ABC triblock copolymer (by cross-linking in the bulk phase and subsequent dissolution). Given the rich variety of morphologies known for this class of materials, this approach may well be utilized to create other complex supramolecular objects via the synthetic detour through the bulk phase.

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(50) To be more precise DLS provides the z-average of 1/hydrodynamic radius ($\langle R_h \rangle_z$).
(53) Numbers have been evaluated by measuring at least 20 unimers and supermicelles.

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