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Platelet Self-Assembly of an Amphiphilic A−B−C−A Tetrablock Copolymer in Pure Water

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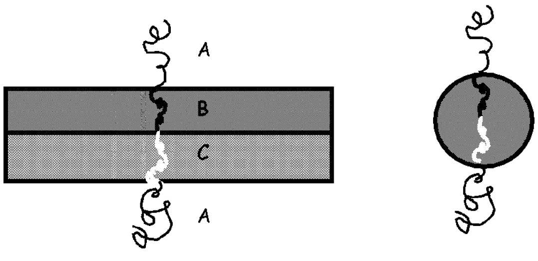
The ability of amphiphilic molecules to spontaneously aggregate into well-defined spherical, cylindrical, and planar geometries is well-established.[1−3] However, control over the size and shape of self-assembled structures by tuning the chemical details of the molecular building blocks remains a challenging and unresolved issue. In particular, comprehensive strategies for obtaining planar (or nearly planar) assemblies such as platelets and vesicles in arbitrary solvents do not exist. Vesicles are usually produced in a multistep process wherein the amphiphile is first dissolved in a common solvent (e.g., tetrahydrofuran (THF) or chloroform) and then exposed to water. This is followed by extrusion, sonication, or electroformation.[3−7] Discher and Eisenberg start with solutions of poly(styrene-*block*-acrylic acid) in a common solvent, such as dioxane, and then add increasing amounts of water, a selective solvent for the poly(acrylic acid) block.[6] With increasing water content, they find transitions from micelles to vesicles. Kukula and coworkers have shown that poly(butadiene-*block*-L-glutamate) copolymers form vesicles in acidic aqueous solutions containing NaCl.[8] A common theme in the systems discussed above is that vesicle formation requires precise control over the composition of the solvent (e.g., THF/water, brine, etc.). Many applications would benefit if planar aggregates with controlled sizes could be obtained by directly dissolving the amphiphilic molecules in a solvent of one's choosing (e.g., pure water). The purpose of this paper is to explore the possibility of designing such amphiphilic molecules.

Our approach uses an ABCA tetrablock copolymer with hydrophilic A blocks and hydrophobic B and C blocks. The molecular weights of the B and C blocks were chosen so that a B−C diblock copolymer would be lamellar in the temperature range of interest, a necessary condition to promote the formation of quasi-planar aggregates (Figure 1a) and prevent the formation of spherical micelles (Figure 1b). A noteworthy feature of our design is the fact that the planar assemblies are composed of a monolayer of amphiphilic molecules (Figure 1a). In contrast, the planar assemblies obtained by previous approaches[1−20] are composed of a bilayer.[21]



(a) (b)

Figure 1. Schematic representation of the aggregates formed by self-assembly of ABCA tetrablock copolymers in water: (a) planar aggregates and (b) spherical micelles.

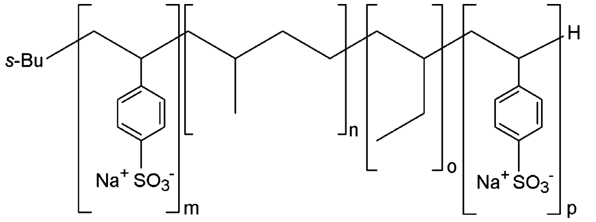


Figure 2. Chemical structure of poly(sulfonated styrene-*block*-methylbutylene-*block*-ethylethylene-*block*-sulfonated styrene), the ABCA tetrablock copolymer studied in this paper.

A poly(styrene-*block*-isoprene-*block*-butadiene-*block*-styrene) copolymer (S_1IBS_2) was synthesized by sequential anionic polymerization.[22,23] The molecular weights of the S_1, I, B, and S_2 blocks were 38, 42, 35, and 31 kg/mol, respectively, determined through GPC and ^1H NMR. The polydispersity of the final tetrablock was calculated to be 1.07, and a small amount ($<3\%$ by GPC) of (S_1I) diblock copolymer was present due to early termination. The diene blocks were hydrogenated using a Ni−Al catalyst,[24] while the polystyrene outer blocks were sulfonated and neutralized with NaOH.[25] The (simplified) chemical structure of the poly(styrenesulfonate-*block*-methylbutylene-*block*-ethylethylene-*block*-styrenesulfonate) tetrablock copolymer thus obtained is shown in Figure 2, and we will refer to this polymer as an ABCA copolymer. Solutions were made at various weight fractions (w) using filtered 18.2 MΩ·cm Millipore water and were analyzed using dynamic light scattering (DLS) and cryogenic transmission electron microscopy (cryo-TEM).

DLS studies were performed using an ALV-5000 instrument with a 100 mW solid-state frequency-doubled Nd:YAG laser ($\lambda = 532$ nm) as the source. Data were obtained at several scattering angles between 30° and 150°. The time autocorrelation function of the scattered intensity $g(\tau)$ was accumulated in the homodyne mode and used to obtain the intensity-weighed distribution of mobilities $G(\Gamma)$[26,27] using CONTIN.[28] Typical $G(\Gamma)$ distributions obtained from the ABCA/water mixtures are shown in Figure 3, where data from a $w = 0.0058$ solution at 45 and 21 °C at a scattering angle of 30° are shown. At 45 °C we obtain a single, sharply defined peak in the mobility distribution with a characteristic decay rate $\Gamma_c = 83$ s^{-1}. At 21 °C we obtain a broad distribution of mobilities with charac-

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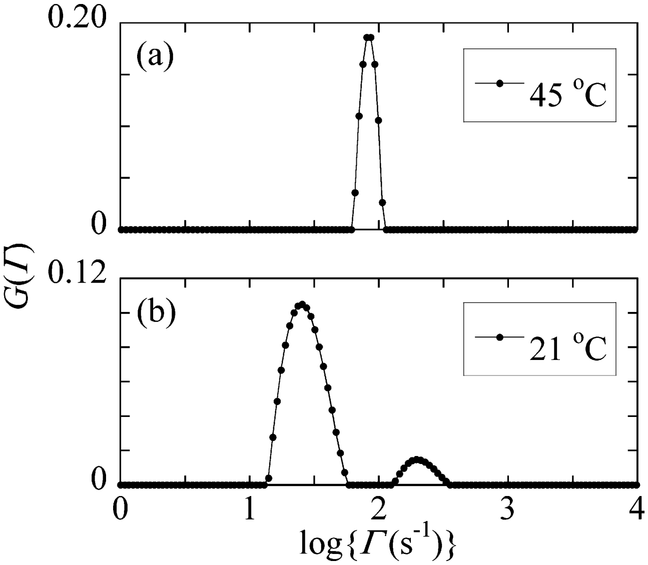

Figure 3. Distribution of decay rates $G(\Gamma)$ for an ABCA/water solution ($w = 0.0058$) at (a) 45 and (b) 21 °C at a scattering angle of 30°.

teristic relaxation rates that are both faster and slower than the Γ_c value at 45 °C. The broad distribution of relaxation times was seen at all temperatures between 11 and 38 °C. We thus conclude that the aggregation state of the ABCA/water solution changes dramatically when the temperature is changed from 45 to 38 °C. The DLS data obtained from solutions with w from 0.0016 through 0.0058 were similar to that shown in Figure 3 and omitted for brevity.

The structure of the aggregates in our ABCA/water solutions was determined by cryo-TEM. A 2−5 μL drop of a $w = 0.0053$ sample is placed on a R2/2 (circular holes of 2 μm, separated by 2 μm) Quantifoil grid. Two kinds of samples were made, one at 25 °C and the other at 45 °C. Both samples were prepared in a controlled environment chamber, where the temperature was maintained and the humidity was greater than 95% to suppress any water evaporation during sample preparation. Excess liquid on the grid was blotted, leaving sample liquid films of thicknesses below 200 nm spanning the grid holes. The grid was then plunged into liquid ethane maintained close to its freezing point in a liquid nitrogen bath, which rapidly vitrifies the sample, thus preserving the microstructure. The sample is withdrawn, excess ethane blotted, transferred to a cold stage (Oxford Instruments CT 3500J), and viewed on a JEOL1200EX S/TEM. The sample temperature is maintained at −170 °C during imaging to prevent the amorphous to crystalline transformation and to minimize sublimation and beam damage. Images were captured on a TVIPS F-224 slow-scan CCD (2048 × 2048 resolution) camera.

In Figure 4a we show a cryo-TEM image of a $w = 0.0053$ solution vitrified from 45 °C, and for clarity we show an isolated aggregate in the inset of Figure 4a.

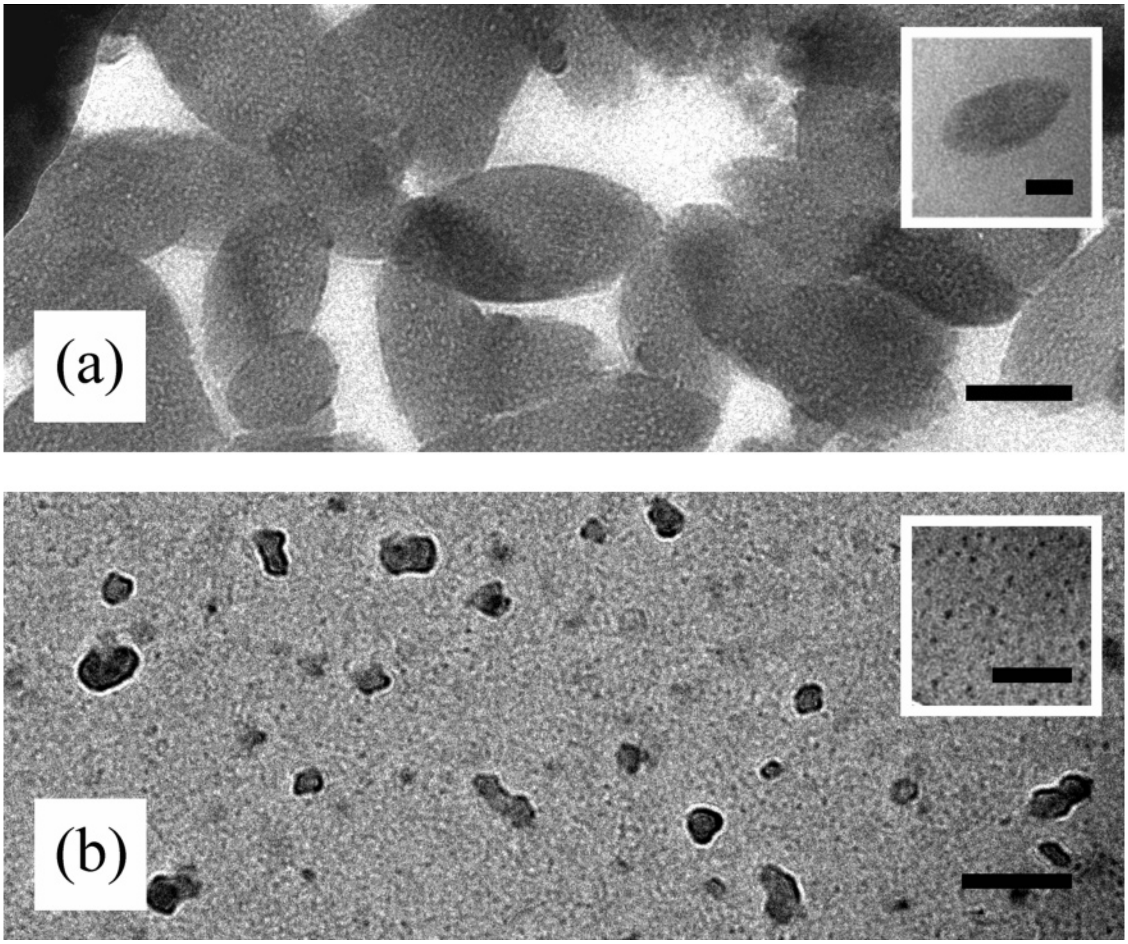

Figure 4. Cryo-TEM images of the ABCA copolymer in water ($w = 0.0053$) vitrified from (a) 45 and (b) 25 °C. At 45 °C only platelets are present, and at 25 °C large aggregates coexist with micelles. Insets show (a) an isolated platelet at 45 °C, and (b) isolated micelles at 25 °C. All scale bars represent 100 nm.

One sees clear evidence for the formation of planar platelets. The two-dimensional aggregates visible in Figure 4a lack the variability in electron density expected of three-dimensional spheres or vesicles. The few darker regions can be attributed to overlapping aggregates. The platelets appear to have an elliptical cross section with major axes ranging from 100 to 300 nm. It is clear that our ABCA copolymer has formed the planar aggregates that we had anticipated in Figure 1.

Figure 4b shows a cryo-TEM image of the $w = 0.0053$ sample vitrified from 25 °C. Comparing parts a and b of Figure 4 indicates a dramatic change in the structure of the aggregates with temperature. At 25 °C, micelles with diameters of about 15 nm in size (inset, Figure 4b) are seen to coexist with larger aggregates that are 50−100 nm in diameter (Figure 4b). Although the large aggregates appear to be platelets, our imaging results are inconclusive due to the high structural variability between pictures (additional images are presented in the Supporting Information).

We now consider possible reasons for the dissolution of platelets with decreasing temperature. The three main driving forces that govern aggregation of ABCA copolymers in water are (1) the repulsion between the B and C blocks, (2) the hydrophobic interactions between the B and C blocks in water, and (3) the hydrophilic interactions between the A blocks and water. The interactions between the B and C blocks have been studied extensively[29] and characterized in terms of χ, the Flory−Huggins interaction parameter.[30] The product χN (where N is the number of monomers in the B and C blocks based on the same reference volume as χ) ranges from 20 to 23 in our temperature window, and it decreases with increasing temperature. Thus, driving force 1 cannot account for the dissolution of the platelets. The aggregation number of micelles increases rapidly as the interactions between the poorly solvated block and the solvent become more repulsive.[31] One thus expects a micelle-to-platelet transition in ABCA/water mixtures as the hydrophobic interactions (driving force 2) increase in strength. It is known, however, that the solubility of hydrocarbons in water increases with increasing temperature.[32−34] Thus, driving force 2 cannot account for the dissolution of the platelets. We are thus forced to conclude that driving force 3, i.e., the changes in the solubility of the coronal chains, must be responsible for our observation. Soo and Eisenberg have noted that decreasing solvent selectivity leads to a micelle-to-vesicle transition.[10] A possible reason for this is that the outer blobs of the well-solvated chains attached to the cores of spherical micelles are larger due to geometric reasons while the blob sizes of chains attached to flat interfaces are independent of position.[6] Similarly, we conclude that the micelle-to-platelet transition that we have observed is probably driven by the decreasing solubility of the PSS blocks in water with increasing temperature. Cohen and Priel found that the peak in the concentration dependence of the specific viscosity in PSS/water mixtures moved to higher concentrations with increasing temperature.[35] Since the position of the peak in the intrinsic viscosity is an indication of the range of intermolecular interactions, an increase in the peak concentration indicates a decrease in the range of polymer−polymer interactions. This may be caused by a decrease in chain size, which, in turn, signifies a lowering of solvent quality with increasing temperature. We note, however, that Cohen and Priel did not make this conclusion in their paper. Despite an extensive literature search, we were unable to find a definitive statement about the temperature dependence of the interactions between poly(styrenesulfonate) and water.

In conclusion, we have demonstrated a new principle for controlling the self-assembly of amphiphilic molecules. An ABCA tetrablock copolymer was designed and synthesized so that it would form locally planar aggregates in pure water. The molecular weight of each of the blocks was about 35 kg/mol. The two end blocks, which were hydrophilic, enabled dispersion of the molecule in water. The planarity of the aggregates was enforced by the mutual incompatibility of the inner B and C blocks. Experiments showed that platelets with lateral dimensions in the 100−300 nm range formed spontaneously in dilute ABCA/water mixtures at 45 °C. At temperatures ≤38 °C, the platelets gave way to a broad distribution of aggregates. This transition was attributed to the temperature dependence of the interactions between the hydrophilic blocks and water. We believe that our work provides the motivation for a systematic study of the aggregation of amphiphilic ABCA tetrablock copolymers as a function of molecular architecture and solvent quality.

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Supporting Information Available: Supplemental cryo-TEM images. This material is available free of charge via the Internet at http://pubs.acs.org.

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