Supramolecular Chemistry

Supramolecular Assemblies of Starlike and V-Shaped PB–PEO Amphiphiles**

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Self-assembly of linear amphiphiles is a well-known phenomenon,[1–5] and the number of different structures observed both in the solid-state and in selective solvents is exceedingly large.[6–10] It is difficult to envision a diblock amphiphile that would not undergo self-assembly, and in this context, the terms “linear amphiphilic” and “self-assembling” are nearly synonymous. Branched amphiphiles such as dendrimers[11] and stars[12] also undergo self-organization in selective solvents.[13–18] However, there are examples in which they do not aggregate,[19–23] but rather behave as unimolecular micelles.[24–26] Furthermore, the morphological diversity of aggregates formed by branched structures is significantly lower than that of linear counterparts. For example, most self-assembling star-shaped amphiphiles only form spherical micelles,[27–31] whereas linear diblocks can organize into at least 30 different morphologies.[9] This creates the impression that a branched architecture somewhat precludes morphological diversity and that star-shaped amphiphiles cannot compete with linear analogues. In contrast, we document here that the multiarm PB_6–PEO_6 (PB = polybutadiene, PEO = poly(ethylene oxide)) molecule **1** self-assembles into non-spherical structures in water and generates unique “cotton-ball” morphology in hexane. Such hierarchical structures have not been observed in PB–PEO diblocks or any other linear system.

Starlike amphiphiles[32–38] are generally difficult to synthesize owing to the limitations of many synthetic techniques,[39]

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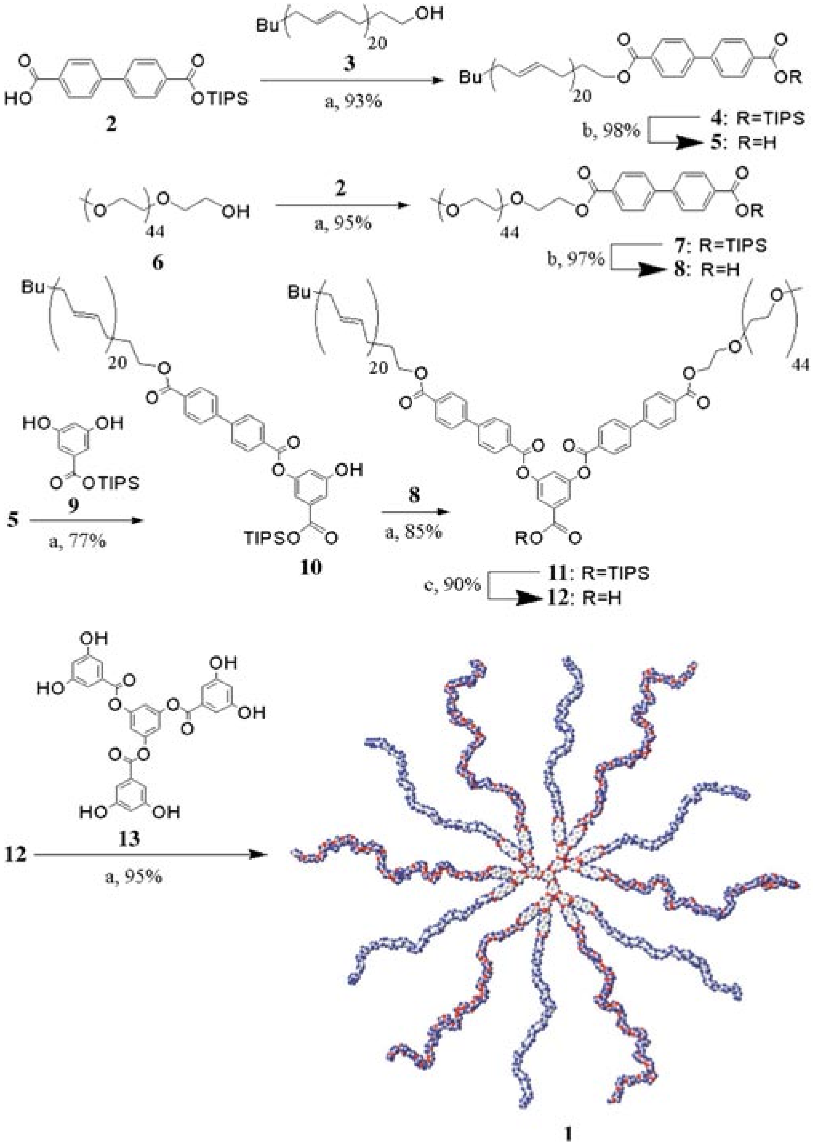
and most of such structures are based on styrenic and acrylic monomers. These limitations may also explain one seemingly surprising fact: linear PB–PEO diblocks have been known and studied extensively for many decades,[40] whereas the synthesis of star-shaped PB–PEO molecules has not been reported to date. Herein, we describe a modular approach to produce a 12-arm PB–PEO star with V-shaped chains directly connected to an aryl ester dendrimer.



Scheme 1. Stepwise synthesis of amphiphile **1**. Reagents: a) DPTS/DIPC, CH_2Cl_2, room temperature, 1–3 h; b) TBAF, −78 °C, 2 h; c) HF, THF, room temperature, 12 h. DPTS = 4-(*N*,*N*-dimethylamino)pyridinium-4-*p*-toluenesulfonate, DIPC = 1,3-diisopropylcarbodiimide, TBAF = tetra-*n*-butylammonium fluoride.

Commercially available hydroxyl-terminated polybutadiene (**3**; $M_n = 1000$, $M_w/M_n = 1.12$) and poly(ethylene oxide) (**6**; $M_n = 2200$, $M_w/M_n = 1.15$) were both coupled with mono(silyl)-protected biphenyl dicarboxylic acid, **2**, under mild esterification conditions. The TIPS (triisopropylsilyl) group of the respective products, **4** and **7**, were subsequently removed to afford the carboxyl-terminated linear precursors **5** and **8**, respectively (Scheme 1). Biphenyl groups were specifically introduced to have reliable NMR references in order to analyze and confirm unambiguously the purity of all the intermediate compounds. The linear precursors **5** and **8** were then coupled sequentially to TIPS-protected 3,5-dihydroxybenzoic acid (DHBA), **9**, under the same esterification conditions to give **11**. Deprotection of the TIPS-protected carboxylate group produced the V-shaped PB–PEO amphiphile **12** in high yield and purity ($M_w = 6210$, $M_w/M_n = 1.13$). All intermediate compounds were isolated and purified by conventional column chromatography. The hexafunctional aryl ester dendrimer (generation 1) was then prepared by using standard procedures.[41] The key coupling reaction between the amphiphile **12** and the dendrimer core **13** was found to proceed very rapidly and in near-quantitative yield (by GPC and NMR spectroscopy). The final product **1** was further purified by dialysis against deionized water through a membrane with a molecular-weight cut-off at 30000 g mol^{-1} to remove low-molecular-weight components.

Figure 1 shows the aromatic regions of the ^{1}H NMR spectra of the V- and star-shaped amphiphiles. In the spectrum of **12** (Figure 1 a), the doublet signal at 7.92 ppm and the triplet signal at 7.45 ppm correspond to protons at C-2 and C-6, and C-4, respectively, of the DHBA hinge. Upon coupling with the dendrimer core, these signals are shifted downfield to 8.09 and 7.6 ppm, respectively, whereas the signals for the protons from the biphenyl system are almost unaffected (Figure 1 b). Most importantly, the doublet at 8.09 ppm in the NMR spectrum of the star-shaped product represents 18 protons, and therefore includes not only 12 protons from the DHBA moieties of six V-shaped substituents, but also an additional 6 protons from DHBA fragments of the dendrimer core (see Supporting Information for the fully assigned spectra).[41] The area of the triplet at 7.6 ppm is also increased by a factor of 1.5 (9 protons; 6 H from V-shaped fragments and 3 H from the core) with respect to the biphenyl signals. The appearance of the singlet at 7.28 ppm (3 protons) also confirms the presence of the fully substituted dendritic core. All these features suggest that the product, **1**, is a defect-free 12-arm starlike molecule that does not contain ten-, eight-, six-, or four-arm byproducts. The presence of such impurities would otherwise have been observed as residual peaks and by unsymmetrical shapes of the signals. The observed 1.5-fold increase in the areas of the doublet and triplet signals is the highest value possible and can only be attained if all the molecules are fully substituted. The GPC trace of **1** also suggests complete substitution as the peak

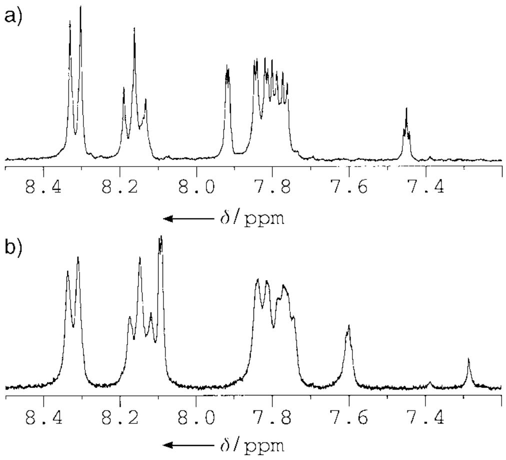


Figure 1. Aromatic regions of ^{1}H NMR spectra of a) the V-shaped amphiphile **12** and b) the star-shaped amphiphile **1**.

becomes even sharper than that of the V-shaped precursor **12** (polydispersity index, PDI = 1.10 versus 1.13, respectively).[41]

To investigate the self-assembly properties, we studied aqueous solutions of V- and star-shaped amphiphiles at room temperature. Figure 2, a and b, show representative TEM micrographs of samples cast from 3-wt % solutions of compounds **12** and **1**, respectively. In the V-shaped precursor, only densely packed spherical micelles that measure ≈18 nm in diameter were observed. This size is in good agreement with numbers predicted by molecular modeling calculations (Materials Studio Program) and suggests that the self-assembly proceeds by a closed association mechanism.[41,42] In contrast, the majority of the star-shaped amphiphile, **1**, exists in the form of one-dimensional structures that measure ≈20 nm in diameter and up to 300 nm in length. Such morphology is typically referred to as short-rod micelles. Furthermore, some spherical micelles as well as toroidal structures are present. All these objects are composed of many starlike unimers **1** and can be regarded as supermicelles rather than unimolecular micelles.[24–26]

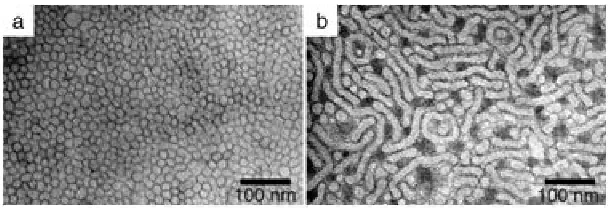


Figure 2. TEM images of samples cast from 3-wt.% aqueous solutions of a) the V-shaped amphiphile **12** and b) the star-shaped amphiphile **1**. An aqueous solution of PTA (phosphotungstic acid) was used as a negative staining agent.

Figure 2 demonstrates a significant influence of molecular architecture on the self-assembly process. Interestingly, the volume fraction of the hydrophile PEO is nearly the same (≈ 0.65) in the V- and star-shaped compounds, and according to theoretical predictions, they both should form spherical micelles.[1,2] The observed difference can be related to a topological restriction imposed by the rigid aromatic core on the packing of the flexible arms in the amphiphile **1**. It is important to emphasize that the arms are not emanating from one specific point, but from six equidistant peripheral points of a fairly large disklike core (see Scheme 1). Thus, the presence of an aromatic core in **1** prevents the dense packing of the PEO chains located in the corona of the supermicelles. To minimize the interfacial energy and to increase the shielding of the hydrophobic PB core from water molecules, the curvature of the micelle surface has to decrease, and this would favor a sphere-to-cylinder morphological transition.

It is still unclear if the presence of the biphenyl moieties facilitates the self-assembly process. However, it is reasonable to assume that aromatic π–π interactions do not play a significant role in this process as heteroarm amphiphiles can form supermicelles even with a poorly defined divinyl benzene (DVB) core.[13] We believe that the main influence of the biphenyls on the self-organization of **1** arises from their rigidity, which prevents the dense packing of the arms. As a result of this loose distribution of arms on the surface of the supermicelle, a cylindrical morphology is preferred over the spherical one. In other words, the biphenyls promote the formation of cylinders, whereas the self-assembly process itself is mainly promoted by the heteroarm molecular architecture. This is consistent with the fact that heteroarm amphiphiles without biphenyl groups undergo self-assembly,[13] but only into spheres, whereas the cylindrical morphology has never been observed for such systems. Furthermore, even the V-shaped amphiphile exclusively forms spheres, although it has the same volume ratio of hydrophilic and hydrophobic blocks.

Because water is a selective solvent for PEO, the central core of the cylindrical micelles should be composed of PB chains. However, such an arrangement would first require a spatial separation of multiple hydrophobic and hydrophilic arms on the scale of one unimer. It can be envisioned that prior to aggregation the starlike amphiphile **1** adopts a conformation where six water-insoluble PB arms are positioned below the plane of the aromatic disklike core and the hydrophilic PEO arms segregate on the opposite side as represented schematically in Figure 3. However, the collapse of six hydrophobic PB arms that belong to a given molecule of **1** may not be enough to avoid unfavorable interactions with water. This is again because of the presence of the rigid core that spatially separates the arms and prevents their dense packing. As a result, the unimers **1** would be driven to aggregate to further minimize the unfavorable contacts by placing the PB chains of all the aggregating molecules into the central core of a supermicelle.

The amphiphile **1** can also be dissolved in solvents that are selective for PB arms. TEM images of samples cast from 0.5-wt % solutions in hexane revealed giant spherical objects that can be seen at very low magnification (Figure 4a). These structures measure ≈2 μm in diameter and have a narrow size distribution with a standard deviation of about 90 nm, which is less than 5 % of the mean diameter value.[41] These microstructures represent discrete objects that do not form a continuous network. At higher magnification, the image clearly shows that the microstructures are composed of

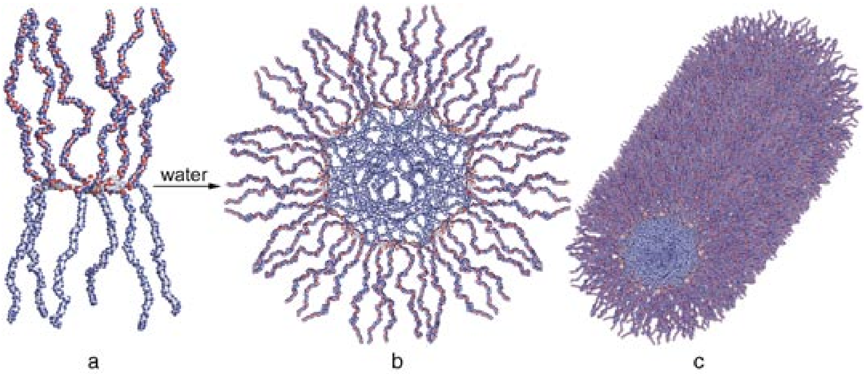


Figure 3. A schematic molecular-graphics representation of the self-assembly of amphiphile **1** in water. a) The image shows a unimer with the 6 arms of PEO (top) and the 6 arms of PB (bottom) spatially separated; b) and c) the images show the cross-section and the side view, respectively, of a cylindrical supermicelle with a PB core and a PEO corona.

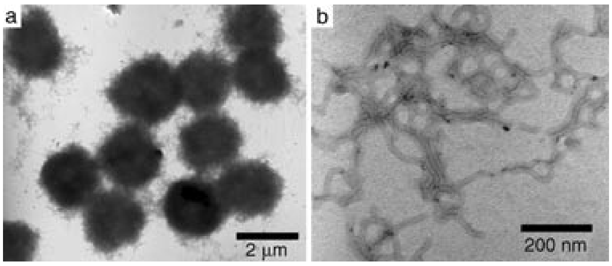


Figure 4. a) Low-magnification TEM image of a sample cast from a 0.5-wt.% solution of **1** in hexane; b) high-magnification TEM image of the same sample taken from an area near the edge of a microsphere. Osmium tetroxide was used as a staining agent to improve the contrast.

numerous one-dimensional structures that are ≈20 nm in diameter (Figure 4b). Thus, the observed microspheres have internal structural constituents in the form of nanosized cylindrical supermicelles.

Selective staining of the samples with osmium tetroxide, which reacts only with the PB chains, generated a characteristic contrast with two thin, dark lines located on the opposite sides of the cylinders (Figure 4b). These images confirmed that the PB chains constitute the corona of the cylindrical supermicelles formed in hexane. Hence, the large spherical microstructures (Figure 4a) are composed of *reverse* cylindrical micelles (Figure 4b). Interestingly, linear PB–PEO diblocks can easily form *regular* micelles in water (PB core/PEO corona),[43] whereas their reverse analogues (PEO core/PB corona) have not been reported to date. Therefore, the star-shaped amphiphile **1** forms both regular and reverse cylindrical micelles in water and hexane, respectively. Most importantly, the self-assembly process in hexane proceeds through two hierarchical levels of self-organization: First, the unimers **1** form cylinders, and then these cylinders self-assemble into finite spherical microstructures. Owing to obvious similarities, we refer to this novel morphology as "cottonballs". These structures are very stable, and images taken from samples cast from hexane solutions that were aged for nearly 3 months showed that they remained intact. Their formation is highly reproducible as confirmed by multiple control experiments.

However, it still remains unknown how the formation of a continuous 3D network is prevented and why nearly monodisperse cottonballs form instead. This is a particularly remarkable observation given the fact that their structural constituents (reverse cylindrical micelles) are highly flexible objects as revealed by TEM. It is important to note that dissolution of **1** in hexane proceeds at elevated temperatures (≈60 °C), above the melting point of PEO. The cottonballs only form after cooling the solutions to room temperature and subsequent aging for several hours. In a control experiment, we cast a sample directly from a hot solution of **1** in hexane and did not observe any microspheres; this suggests that the formation of these structures is a thermoreversible process. It is reasonable to assume that either partial crystallization of PEO or a reduction in the solubility of the PB arms upon cooling to room temperature drives the association of reverse cylindrical micelles into well-defined spheres.

Furthermore, we investigated hexane solutions of the V-shaped precursor **12** under the same conditions and found completely different structures. Figure 5 shows a representative TEM image of square-shaped platelets formed by **12** in hexane. The structures possess a two-dimensional morphology; they measure ≈1 micron in lateral dimensions and only 22 nm in thickness (determined by AFM). The square shape and the presence of faceted edges are indicative of a single-crystalline structure. However, in the V-shaped amphiphile **12**, there is only one crystallizable block (PEO) because polybutadiene is composed of both 1,4- and 1,2-addition monomer units randomly distributed along the chains. The square platelets form in a solvent that is selective for PB, therefore PEO arms must be located in the midsection of such structures. In essence, they can be viewed as sandwichlike structures with a single-crystalline layer of PEO coated with amorphous PB layers on both sides. If the sample is rinsed with water, the square platelets are completely destroyed. However, after staining with osmium tetroxide vapor for only 5 mins, the structures remain intact and retain their original shape upon multiple rinsings with water. The contrasting

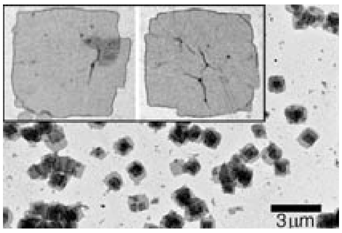


Figure 5. TEM micrograph of a sample cast from a 0.5-wt.% solution of the V-shaped PB–PEO amphiphile **12** in hexane . Inset: Two isolated square platelets that do not have a screw dislocation. Osmium tetroxide was used as a staining agent to enhance the contrast.

effect also increases very rapidly as the squares become much darker upon staining with OsO_4. These results support the idea that PB chains are located on the surface of the platelets and that their cross-linking with OsO_4 stabilizes the morphology and converts 2D supramolecular ensembles into macromolecular objects.

Similar single-crystalline sandwich structures were observed in solutions of PS–PEO diblocks in toluene,[44] but not for PB–PEO linear amphiphiles, which typically form large 2D layers.[45] We specifically synthesized a linear PB–PEO molecule with the same volume ratio of blocks[41] but similar structures were not observed in hexane. Figure 5 also reveals that whereas some of the squares are isolated structures (see inset), the majority of them have a screw dislocation in the center and a helical ramp is created by several interconnected layers. The formation of discrete 2D objects with a narrow size distribution, rather than large layers, suggests that the crystalline growth is terminated when the size approaches some critical value (≈1 micron). The exact mechanism that leads to such limited growth of the observed 2D microstructures is not known. However, we conclude that a simple change from a V-shaped to a starlike molecular architecture profoundly influences the morphology of the self-assembled structures formed by PB–PEO amphiphiles in selective solvents, namely hexane and water (see also Figure 2). The starlike architecture seems to disturb the crystallization process which may also be related to an inability of the arms to pack densely owing to the presence of a disklike core. This may be the driving force of an alternative assembly into reverse cylindrical micelles with little or no crystalline order in the PEO core as suggested by the highly flexible and winding shape of the supermicelles (Figure 4b).

In summary, this study brings a simple, yet unexpected, conclusion: Starlike molecular architecture does not always have a detrimental influence on self-assembly processes and it provides a rare opportunity for novel hierarchical ensembles, which may not be possible even in their linear analogues, to be generated. The presence of a rigid disklike core in a starlike amphiphile promotes the formation of cylindrical micelles in the selective solvents, water and hexane. A comparison of the self-assembled structures formed by V-shaped and starlike amphiphiles clearly demonstrates that the molecular architecture itself is a very powerful morphogenic factor. Thus, synthetic manipulation of the architecture of amphiphiles can be an efficient way to generate complex and yet unseen morphologies.

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