Self-assembly of linear amphiphiles is a well-known phenomenon, and the number of different structures observed both in the solid-state and in selective solvents is exceedingly large. 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 and stars also undergo self-organization in selective solvents. However, there are examples in which they do not aggregate but rather behave as unimolecular micelles. 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 whereas linear diblocks can organize into at least 30 different morphologies. 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 PB₆–PEO₆ (PB = polybutadiene, PEO = poly(ethylene oxide)) molecule self-assembles into nonspherical 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 are generally difficult to synthesize owing to the limitations of many synthetic techniques.
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.

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 1a), 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 1b). 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

Scheme 1. Stepwise synthesis of amphiphile 1. Reagents: a) DPTS/DIPC, CH$_2$Cl$_2$, 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.
In contrast, the majority of the star-shaped amphiphile, negative staining agent. An aqueous solution of PTA (phosphotungstic acid) was used as a

Figure 2.

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 \(\approx 18\) 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 \(\approx 20\) 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 demonstrates a significant influence of molecular architecture on the self-assembly process. Interestingly, the volume fraction of the hydrophile PEO is nearly the same (\(\approx 65\)) in the V- and star-shaped compounds, and according to theoretical predictions, they both should form spherical micelles.\(^{[11-13]}\) 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 moiety facilitates the self-assembly process. However, it is reasonable to assume that aromatic \(\pi-\pi\) 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.\(^{[23]}\) 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 \(\approx 2\) \(\mu\)m 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

\[
\begin{align*}
\text{Figure 1. Aromatic regions of } ^1\text{H NMR spectra of a) the V-shaped amphiphile 12 and b) the star-shaped amphiphile 1.}
\end{align*}
\]

\[
\begin{align*}
\text{Figure 2. TEM images of samples cast from 3-wt.% aqueous solutions of a) the V-shaped amphiphile 12 and b) the star-shaped amphiphile 1. An aqueous solution of PTA (phosphotungstic acid) was used as a negative staining agent.}
\end{align*}
\]
numerous one-dimensional structures that are \( \approx 20 \text{ nm} \) in diameter (Figure 4 b). 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 4 b). These images confirmed that the PB chains constitute the corona of the cylindrical supermicelles formed in hexane. Hence, the large spherical microstructures (Figure 4 a) are composed of reverse cylindrical micelles (Figure 4 b). 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 TEM image of square-shaped platelets formed by 12 in hexane. The structures possess a two-dimensional morphology; they measure \( \approx 1 \text{ micron} \) in lateral dimensions and only \( 22 \text{ nm} \) 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 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 (\( \approx 60^\circ C \)), 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 representa-
effect also increases very rapidly as the squares become much darker upon staining with OsO₄. These results support the idea that PB chains are located on the surface of the platelets and that their cross-linking with OsO₄ 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, but not for PB–PEO linear amphiphiles, which typically form large 2D layers.

The size approaches some critical value (≈ 1 micron). The crystallinity process which may also be related to an inability of the arms to pack densely owing to the presence of a rigid disklike core in a starlike molecular architecture does not always provide a rare opportunity for novel hierarchical ensembles, rather than large objects with a narrow size distribution, rather than large layers, suggests that the crystalline growth is terminated when the size approach 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).

In summary, this study brings a simple, yet unexpected, conclusion: Starlike molecular architecture does not always provide 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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Supporting Information

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

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General. Unless otherwise stated, all starting materials were obtained from commercial suppliers and used without further purification. The $^1$H NMR spectra were recorded on solutions in CD$_2$Cl$_2$ on a Varian Unity 300 (300 MHz) spectrometer. $^{13}$C NMR spectra were recorded at 75 MHz on a Varian Unity 300 spectrometer using the solvent carbon signals as internal references. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were obtained on a Thermo BioAnalysis Dynamo mass analyser using dithranol as a matrix and lithium trifluoroacetate as a cationizing salt. GPC analysis was conducted on a Waters Breeze 1515 series liquid chromatograph equipped with a dual λ absorbance detector (Waters 2487) and three styrogel columns (HR1, HR3, HR4) using linear polystyrene as calibration standards and THF as an eluent. Hydroxyl-terminated polybutadiene containing 90 % of 1,4-addition monomeric units as determined by NMR ($M_n=1000$, $M_w/M_n=1.12$) was purchased from Polymer Source, Inc. Hydroxyl-terminated poly(ethylene oxide) (monomethyl ether) with molecular weight $M_n=2200$ ($M_w/M_n=1.15$) was also purchased from Polymer Source, Inc. and was used as received. 4-(N,N-dimethylamino)pyridinium-4-$p$-toluenesulfonate (DPTS) was prepared by mixing saturated THF solutions of DMAP (1 equiv) and $p$-toluenesulfonic acid monohydrate (1 equiv) at room temperature. The precipitate was filtered, washed several times with THF, and dried under vacuum. The structure of DPTS was confirmed by $^1$H NMR. Materials Studio Program (version 2.1.5) was used to estimate the contour length of the arms, and the size of micelles upon force field energy minimization in the absence of solvent.

Transmission Electron Microscopy (TEM). TEM images were obtained on a JEOL 1200EX scanning/transmission electron microscope operating at 100 kV accelerating voltage. Samples were
prepared by casting one droplet of a micellar solution onto carbon-coated TEM grids followed by immediate blotting of the droplet with filter paper. After drying for 5 minutes the samples were stained by H_3PO_4·12WO_4, by depositing a drop of 2 wt % phosphotungstic acid (PTA) aqueous solution onto the surface of the sample-loaded grid. One minute later the solution was blotted with a filter paper, and the sample was dried in air for several hours. Positive staining with osmium tetroxide was performed by placing TEM grids 3 mm above the surface of 3 wt. % aqueous solution of OsO_4 for 2 h in a closed chamber. Complete dissolution of 1 in hexane requires heating the suspension to ~60 °C. Samples were cast after cooling to room temperature and aging for at least 3 h. The average size of the cottonballs and the standard deviation were calculated from TEM images (~100 microspheres) using Photoshop 7.0.1. Program.

**General procedure for esterification coupling reactions.** The acid (1.1 equiv), phenol or hydroxyl-terminated core (1 equiv), DPTS (1.6 equiv), and CH_2Cl_2 were combined in a round-bottom flask with a stir bar at room temperature. 1,3-Diisopropyl carbodiimide (DIPC, 2.5 equiv) was added after 2 minutes and the solution was allowed to stir for several hours. The coupling reactions were monitored by TLC, GPC, and NMR. Most of the esterification reactions reported here were found to proceed very rapidly at room temperature and nearly complete disappearance of starting materials was typically observed within 1-3 h. The reaction mixture was then diluted by dichloromethane and 2-4 extractions with DI water were used to quench the reaction and to remove DPTS. The crude product was purified by column chromatography on silica gel and/or dialysis against DI water for several days as outlined below.

**General procedure for the deprotection reactions using tetrabutyl ammonium fluoride (TBAF).** Triisopropylsilyl (TIPS) protected compound (1 equiv) was dissolved in THF and cooled to -78 °C using dry ice-acetone bath. The solution was allowed to stir for 5 min and 5 equiv of TBAF (1.0 M solution in THF) was slowly added via syringe upon rigorous stirring. Addition of TBAF immediately resulted in appearance of a characteristic yellow-greenish color which remained unchanged throughout
the entire reaction. Acetic acid (6 equiv) was added to reaction mixture after 2 h and the stirring proceeded for additional 5 min to ensure that all residual TBAF was quenched before the mixture was allowed to warm to room temperature. The mixture was then diluted with CH₂Cl₂ and washed several times with DI water. The organic layer was collected and concentrated in vacuo. The crude product was purified by column chromatography as outlined in the following text.

**Biphenyl-4,4'-dicarboxylic acid 4'-triisopropylsilyl ester (2).** Biphenyl-4,4'-dicarboxylic acid (1 equiv) was dissolved in DMSO and 0.3 equiv. of triisopropylsilyl chloride (TIPSCl) was added via syringe. The mixture was stirred for 5 min and 0.33 equiv. of triethyl amine was added dropwise. The reaction was monitored by TLC and was complete after 2 h. The reaction mixture was diluted with 5 fold volume of dichloromethane/THF mixture (70:30 vol.) and DMSO was removed upon several extractions with DI water. The product was purified by flash chromatography on silica gel eluting with THF/CH₂Cl₂ (7:93 vol.) mixture (Rf=0.55) to give the product as white solid. Yield 64 %. ¹H NMR (300 MHz, CD₂Cl₂/THF-d₈ (9:1 vol.)): δ 1.16 (d, 18 H, J = 8.3 Hz), 7.74 (dd, 4H, J = 8.3 Hz), 8.13 (d, 2H, J = 8.4 Hz), 8.16 (d, 2H, J = 8.4 Hz).

**Compound 3.** Hydroxyl-terminated 1,4-polybutadiene (1 equiv), biphenyl-4,4'-dicarboxylic acid 4'-triisopropylsilyl ester 2 (1.4 equiv), and DPTS (1.6 equiv) were dissolved in CH₂Cl₂ and the mixture was allowed to stir for 5 min before 2.5 equiv of DIPC was added dropwise. The reaction was monitored by TLC using CH₂Cl₂ as an eluent. Complete disappearance of polybutadiene spot (Rf=0.3) occurred after 3 h and the reaction mixture was evaporated and the product was isolated by column chromatography eluting with a mixture of hexane and dichloromethane (30:70 vol.) to give the product as a colorless liquid (Rf=0.7). Yield 93 %. ¹H NMR (300 MHz, CD₂Cl₂): δ 0.85 (br, 6H, CH₃ of sec-Bu), 1.17 (d, 18 H, J = 8.2 Hz, CH₃ of TIPS), 1.5-1.2 (br, 14 H, CH₂ of 1,2-addition units and CH from TIPS), 2.2-1.9 (br, 70H, aliphatic CH₂ (both cis- and trans-) of 1,4-addition units), 4.33 (br t, 2H, PB-CH₂CH₂O-CO-), 5.1-4.8 (br, 6H, vinyl -CH=CH₂ of 1,2-addition units), 5.5-5.3 (br, 32H, both cis- and trans-CH=CH of 1,4-addition units), 5.7-5.5 (br, 3H, vinyl -CH=CH₂ of 1,2-addition units).
units), 7.71 (d, 4H, ArH, $J = 8.2$ Hz, protons at positions 2', 6', 2, and 6), 8.08 (d, 2H, ArH, $J = 8.3$ Hz, protons at position 3' and 5'), 8.12 (d, 2H, ArH, $J = 8.1$ Hz, protons at position 3 and 5).

**Compound 4.** This compound was prepared from 3 following the standard TBAF deprotection procedure described above. The crude product was purified by column chromatography on silica gel eluting with 5 % THF/CH$_2$Cl$_2$ as an eluent ($R_f=0.55$) to give 4 as a colorless liquid. Yield 98 %. $^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ 0.85 (br, 6H, CH$_3$ of sec-Bu), 1.5-1.3 (br, 10 H, CH$_2$ of 1,2-addition units), 2.2-1.9 (br, 67H, aliphatic CH$_2$ (both cis- and trans-) of 1,4-addition units), 4.32 (br, 2H, PB-CH$_2$-CH$_2$-O-CO-), 5.1-4.8 (br, 6H, vinyl -CH=CH$_2$ of 1,2-addition units), 5.5-5.3 (br, 32H, both cis- and trans-CH=CH$_2$ of 1,4-addition units), 5.65-5.5 (br, 3H, vinyl -CH=CH$_2$ of 1,2-addition units), 7.73 (d, 4H, ArH, $J = 8.2$ Hz, protons at positions 2', 6', 2, and 6), 8.10 (d, 2H, ArH, $J = 8.2$ Hz, protons at position 3' and 5'), 8.15 (d, 2H, ArH, $J = 8.3$ Hz, protons at position 3 and 5).

**Compound 5.** Compound 2 (4 equiv), hydroxyl-terminated PEO (1.0 equiv), and DPTS (1.6 equiv) were dissolved in dichloromethane. DIPC (2.5 equiv) was added after 5 min and the reaction was stirred for 4 h. The reaction mixture was washed 3 times with DI water and the product was purified by column chromatography using 12 % MeOH/CH$_2$Cl$_2$ mixture as an eluent. The product can also be purified from excess 2 by several precipitations from THF solution upon addition of 30 % (vol.) hexanes. Yield 95 %. $^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ 1.18 (d, 18 H, $J = 8.2$ Hz, CH$_3$ of TIPS), 1.45 (m, 3H, CH from TIPS), 3.33 (s, 3H, terminal CH$_3$ of PEO), 3.75-3.45 (br, 170H, CH$_2$ of PEO), 3.82 (t, 2H, PEO-CH$_2$-CH$_2$-O-CO-), 4.49 (t, 2H, PEO-CH$_2$-CH$_2$-O-CO-), 7.75 (d, 4H, ArH, $J = 8.2$ Hz, biphenyl protons at positions 2', 6', 2, and 6), 8.14 (d, 2H, ArH, $J = 8.3$ Hz, biphenyl protons at positions 3' and 5'), 8.17 (d, 2H, ArH, $J = 8.3$ Hz, biphenyl protons at positions 3 and 5). GPC (254 nm, THF), $M_w=3170$, PDI=1.1.

**Compound 6.** This compound was prepared from 5 following the standard TBAF deprotection procedure described above. The crude product was purified by precipitation from THF solution by adding 30 % (vol.) hexane to give 6 as tacky solid. Yield 97 %. $^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ 3.33
(s, 3H, terminal CH₃ of PEO), 3.75-3.45 (br, 176H, CH₂ of PEO), 3.83 (t, 2H, PEO-CH₂-CH₂-O-CO-), 4.49 (t, 2H, PEO-CH₂-CH₂-O-CO-), 7.72 (d, 2H, ArH, J = 8.2 Hz, biphenyl protons at positions 2’ and 6’), 7.75 (d, 2H, ArH, J = 8.2 Hz, biphenyl protons at positions 2 and 6), 8.14 (d, 2H, ArH, J = 8.3 Hz, biphenyl protons at positions 3’ and 5’), 8.17 (d, 2H, ArH, J = 8.3 Hz, biphenyl protons at positions 3 and 5). GPC (254 nm, THF), M_w=2950, PDI=1.08.

3,5-Dihydroxy-triisopropylsilyl benzoate. Morpholine (1.3 equiv) was added to a homogeneous solution of 3,5-dihydroxybenzoic acid (1 equiv) in DMF. Triisopropylsilyl chloride (1.1 equiv) was added via syringe upon rigorous stirring. The reaction mixture was allowed to stir for 5 minutes at room temperature and then diluted with CH₂Cl₂ and washed several times with DI water. The organic layer was evaporated and the crude product was purified by column chromatography on silica gel (5% THF in CH₂Cl₂) to yield the product as a colorless liquid (R_f = 0.4). Yield: 75 %. ¹H NMR (300 MHz, CD₂Cl₂): δ 1.13 (d, 18 H, J = 8.2 Hz, CH₃ of TIPS), 1.41 (m, 3H, CH of TIPS), 6.59 (t, 1H, Ar’H, J = 2.0 Hz, DHBA proton at position 4), 7.16 (d, 2H, Ar’H, J = 2.2 Hz, DHBA protons at positions 2 and 6).

Compound 7. Compound 4 (1 equiv), was added to a 10 wt. % CH₂Cl₂ solution of 3,5-dihydroxy-triisopropylsilyl benzoate (10 equiv). DPTS (1.2 equiv) was added to the resulting solution and the mixture was stirred for 5 minutes before DIPC (1.5 equiv) was added via pipette. The reaction proceeded for 2 h. The mixture was diluted with CH₂Cl₂ and washed with water 3 times. The product was purified by flash chromatography eluting with 3 % THF/CH₂Cl₂ mixture (R_f=0.6) to give 7 as a colorless liquid. Yield: 77 %. ¹H NMR (300 MHz, CD₂Cl₂): δ 0.88 (br, 6H, CH₃ of sec-Bu), 1.17 (d, 18 H, J = 8.2 Hz, CH₃ of TIPS), 1.55-1.3 (br, 12H, CH₂ of 1,2-addition units and CH from TIPS), 2.2-1.9 (br, 66H, aliphatic CH₂ (both cis- and trans-) of 1,4-addition units), 4.35 (br t, 2H, PB-CH₂-CH₂-O-CO-), 5.15-4.9 (br, 6H, vinyl -CH=CH₂ of 1,2-addition units), 5.55-5.3 (br, 32H, both cis- and trans-CH=CH- of 1,4-addition units), 5.65-5.55 (br, 3H, vinyl -CH=CH₂ of 1,2-addition units), 7.02 (t, 1H, Ar’H, J = 1.8 Hz, proton at position 4 in DHBA), 7.49 (br t, 1H, Ar’H, protons at position 2 in
DHBA), 7.52 (br t, 1H, Ar’H, protons at position 6 in DHBA), 7.78 (d, 2H, ArH, $J = 8.2$ Hz, biphenyl protons at positions 2’ and 6’), 7.82 (d, 2H, ArH, $J = 8.2$ Hz, biphenyl protons at positions 2 and 6), 8.17 (d, 2H, ArH, $J = 8.3$ Hz, biphenyl protons at positions 3’ and 5’), 8.31 (d, 2H, ArH, $J = 8.4$ Hz, biphenyl protons at positions 3 and 5). GPC (254 nm, THF), $M_w = 2650$, PDI = 1.08.

**Compound 8.** Compound 7 (1.1 equiv), compound 6 (1.0 equiv), and DPTS (1.6 equiv) were dissolved in dichloromethane. DIPC was added after 5 min and the reaction was stirred for 3 h. The reaction was monitored by TLC and GPC since the molecular weight of the product is much higher than that of both starting materials. The reaction mixture was directly placed onto silica gel column running in 11:89 (vol.) mixture of chloroform and methanol. Collected solution of the product was dried by blowing air through the flask at room temperature. Please note that if solution is heated under reduced pressure to remove MeOH and CHCl$_3$ partial reesterification of silyl ester occurs. This is highly undesirable side reaction which must be avoided since selective deblocking of methyl ester cannot be carried out in the presence of other esters (i.e. esters connecting the arms and biphenyls).

After removal of methanol by blowing air the product was put on vacuum line and dried for additional 2 h. Yield 85 %. $^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ 0.86 (br, 6H, CH$_3$ of sec-Bu of PB), 1.18 (d, 18 H, $J = 8.2$ Hz, CH$_3$ of TIPS), 1.5-1.3 (br, 13 H, CH$_2$ of PB 1,2-addition units and CH from TIPS), 2.2-1.9 (br, 72H, aliphatic CH$_2$ (both cis- and trans-) of PB 1,4-addition units), 3.34 (s, 3H, terminal CH$_3$ of PEO), 3.7-3.5 (br, 180H, CH$_2$ of PEO), 3.82 (t, 2H, PEO-CH$_2$-CH$_2$-O-), 4.35 (br, 2H, PB-CH$_2$-CH$_2$-O-), 4.51 (t, 2H, PEO-CH$_2$-CH$_2$-O-), 5.1-4.9 (br, 6H, vinyl -CH=CH$_2$ of PB 1,2-addition units), 5.5-5.3 (br, 34H, both cis- and trans-CH=CH of PB 1,4-addition units), 5.68-5.52 (br, 3H, vinyl -CH=CH$_2$ of PB 1,2-addition units), 7.49 (t, 1H, Ar’H, $J = 1.6$ Hz, proton at position 4 in DHBA), 7.79 (dd, 4H, ArH, $J = 8.2$ Hz, two protons at positions 2’ and 6’ of biphenyl attached to PB, and two protons at position 2’ and 6’ of biphenyl attached to PEO), 7.85 (dd, 4H, ArH, $J = 8.4$ Hz, two protons at positions 2 and 6 of biphenyl attached to PB, and two protons at position 2 and 6 of biphenyl attached to PEO), 7.88 (d, 2H, Ar’H, $J = 1.5$ Hz, protons at position 2 and 6 in DHBA), 8.18 (t, 4H, ArH, $J =$
8.3 Hz, two protons at positions 3’ and 5’ of biphenyl attached to PB, and two protons at positions 3’ and 5’ of biphenyl attached to PEO), 8.32 (d, 4H, ArH, J = 8.3 Hz, two protons at positions 3 and 5 of biphenyl attached to PB, and two protons at positions 3 and 5 of biphenyl attached to PEO). GPC (254 nm, THF), M_n=6560, PDI=1.14.

**Compound 9 (PB-PEO V-shaped amphiphile).** 10 wt. % solution of 8 in THF was placed into a plastic container and excess (~50 equiv) hydrofluoric acid (49 % aq. solution of HF) was added via syringe upon rigorous stirring. The reaction was allowed to stir for 12 h at room temperature. The mixture was then diluted with dichloromethane and quenched with aqueous saturated solution of sodium bicarbonate while in the plastic bottle. The organic layer was additionally washed 3 times with water and the product was purified by precipitation from THF solution by adding 30 % (vol.) hexane to give 6 as a colorless tacky solid. Yield 90 %. 1H NMR (300 MHz, CD2Cl2): δ 0.87 (br, 6H, CH₃ of sec-Bu of PB), 1.55-1.25 (br, 11H, CH₂ of PB 1,2-addition units), 2.2-1.9 (br, 70H, aliphatic CH₂ (both cis- and trans-) of 1,4-addition units), 3.34 (s, 3H, terminal CH₃ of PEO), 3.7-3.5 (br, 181H, CH₂ from PEO), 3.84 (br t, 2H, PEO-CH₂-CH₂-O-), 4.33 (br, 2H, PB-CH₂-CH₂-O-), 4.50 (t, 2H, PEO-CH₂-CH₂-O-), 5.1-4.9 (br, 7H, vinyl -CH=CH₂ of PB 1,2-addition units), 5.5-5.3 (br, 31H, both cis- and trans-CH=CH of PB 1,4-addition units), 7.45 (t, 1H, Ar’H, J = 1.6 Hz, proton at position 4 in DHBA), 7.78 (dd, 4H, ArH, J = 8.2 Hz, two protons at positions 2’ and 6’ of biphenyl attached to PB, and two protons at position 2’ and 6’ of biphenyl attached to PEO), 7.82 (dd, 4H, ArH, J = 8.4 Hz, two protons at positions 2 and 6 of biphenyl attached to PB, and two protons at position 2 and 6 of biphenyl attached to PEO), 7.92 (d, 2H, Ar’H, J = 1.5 Hz, protons at position 2 and 6 in DHBA), 8.18 (t, 4H, ArH, J = 8.3 Hz, two protons at positions 3’ and 5’ of biphenyl attached to PB, and two protons at positions 3’ and 5’ of biphenyl attached to PEO), 8.32 (d, 4H, ArH, J = 8.4 Hz, two protons at positions 3 and 5 of biphenyl attached to PB, and two protons at positions 3 and 5 of biphenyl attached to PEO). GPC (254 nm, THF), M_n=6210, PDI=1.13.
Fig. S1: $^1$H NMR spectrum of Y-shaped PB-PEO amphiphile 9.

Fig. S2: GPC trace of V-shaped PB-PEO amphiphile 9.
Silyl-protected hexafunctional core. 1,3,5-trihydroxybenzene (1 equiv), 3,5-di(tert-butyl dimethylsilyloxy) benzoic acid (4.5 equiv), and DPTS (4.5 equiv) were dissolved in dichloromethane at room temperature. DIPC (6 equiv) was added after 2 minutes and the solution was allowed to stir for 2 hours. The crude product was purified by column chromatography using 50:50 (vol.) mixture of hexane and dichloromethane as an eluent to give the product as a colorless liquid. Yield 85 %. $^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ 0.25 (s, 36H, OSi(CH$_3$)$_2$C(CH$_3$)$_3$), 1.01 (s, 54H, OSi(CH$_3$)$_2$C(CH$_3$)$_3$), 6.65 (t, 3H, $J = 1.8$ Hz, DHBA protons at position 4), 7.12 (s, 3H, protons of the central benzene ring at positions 2, 4, and 6), 7.29 (d, 6H, $J = 1.9$ Hz, DHBA protons at positions 2 and 6).

Aryl-ester dendrimer core. The silyl-protected compound was dissolved in THF (~10 wt. %) and excess (~50 equiv) of hydrofluoric acid (49 % aq. solution of HF) was added via syringe upon rigorous stirring. The reaction was allowed to stir for 24 h and was monitored by TLC. The mixture was diluted by dichloromethane and after 4 extractions with DI water the crude product was purified by column chromatography using 10 % THF/CH$_2$Cl$_2$ mixture as an eluent. Yield 90 %. $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ 6.47 (t, 3H, $J = 1.6$ Hz, DHBA protons at position 4), 7.05 (d, 6H, $J = 1.7$ Hz, DHBA protons at positions 2 and 6), 7.14 (s, 3H, protons of the central benzene ring at positions 2, 4, and 6), 8.52 (s, 6H, terminal OH groups).

Fig. S3: $^1$H NMR spectrum of hexahydroxyl dendrimer core.
**Compound 1.** V-shaped copolymer 9 (6.1 equiv) and DPTS (8 equiv) were added to a suspension of hexahydroxyl core in dichloromethane. After 5 min, DIPC (12 equiv) was added and the reaction mixture was allowed to stir at room temperature for 3 h. The completion of the coupling reaction was observed by GPC as the new sharp peak of a high molar mass product ($M_w=37544$) appeared in the GPC trace, whereas the peak of the starting material ($M_w=6480$) gradually disappeared. The reaction mixture was diluted with dichloromethane and washed 3 times with water. The crude product was purified by dialysis of DMF solution against DI water for 3 days using a membrane with a cut-off molecular weight of 30,000. The water was evaporated by blowing air through the flask. The polymer was then dried on vacuum line at 50 °C for 3 h. Yield: 95 %. $^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ 0.87 (br, 36H, $CH_3$ of sec-Bu of PB), 1.55-1.25 (br, 68H, $CH_2$ of PB 1,2-addition units), 2.2-1.9 (br, 420H, aliphatic $CH_2$ (both cis- and trans-) of 1,4-addition units), 3.34 (s, 18H, terminal $CH_3$ of PEO), 3.7-3.5 (br, 1077H, $CH_2$ from PEO), 3.84 (br t, 12H, PEO-$CH_2$-$CH_2$-O-), 4.33 (br, 12H, PB-$CH_2$-$CH_2$-O-), 4.49 (br t, 12H, PEO-$CH_2$-$CH_2$-O-), 5.1-4.9 (br, 41H, vinyl $-CH=CH_2$ of PB 1,2-addition units), 5.5-5.3 (br, 188H, both cis- and trans-$CH=CH$ of PB 1,4-addition units), 5.7-5.5 (br, 18H, vinyl $-CH=CH_2$ of PB 1,2-addition units), 7.28 (s, 3H, protons of the central benzene ring of the core), 7.60 (br t, 9H, Ar$^r H$, $J = 1.7$ Hz, protons at position 4 in DHBA), 7.77 (br, 24H, Ar$H$, protons at positions 2’ and 6’ of biphenyls attached to PB (12H), and protons at position 2’ and 6’ of biphenyls attached to PEO (12H)), 7.83 (d, 24H, Ar$H$, $J = 8.4$ Hz, protons at positions 2 and 6 of biphenyls attached to PB (12H), and protons at position 2 and 6 of biphenyls attached to PEO (12H)), 8.09 (d, 18H, Ar$^r H$, $J = 1.6$ Hz, protons at position 2 and 6 in DHBA), 8.18 (t, 24H, Ar$H$, $J = 8.5$ Hz, protons at positions 3’ and 5’ of biphenyls attached to PB (12H), and protons at positions 3’ and 5’ of biphenyls attached to PEO (12H)), 8.32 (d, 24H, Ar$H$, $J = 8.4$ Hz, protons at positions 3 and 5 of biphenyls attached to PB (12H), and protons at positions 3 and 5 of biphenyls attached to PEO (12H)). GPC (254 nm, THF) PDI=1.10, $M_w$=27,110.
Fig. S4: $^1$H NMR spectrum of star-shaped PB-PEO amphiphile 1.

Fig. S5: GPC trace of star-shaped PB-PEO amphiphile 1.
Fig. S6: TEM image of sample cast from 0.5 wt. % solution of amphiphile 1 in hexane.
Fig. S7: SEM image of sample cast from 0.5 wt. % solution of 1 in hexane (coated with gold).
Fig. S8: TEM image of a “cottonball” after staining with osmium tetroxide.
Linear analogue PB-biphenyl-PEO was prepared via coupling of 6 with hydroxyl-terminated polybutadiene as shown below. Standard procedures described above were used to purify the product.