



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 ^1H NMR spectra were recorded on solutions in CD_2Cl_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 ^1H 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 $\text{H}_3\text{PO}_4 \cdot 12\text{WO}_4$, 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), pcohol 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 (R_f=0.55) to give the product as white solid. Yield 64 %. ¹H NMR (300 MHz, CD₂Cl₂/THF-*d*₈ (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 (R_f=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 (R_f=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-CH₂-CH₂-O-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), 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/CH₂Cl₂ as an eluent ($R_f=0.55$) to give **4** as a colorless liquid. Yield 98 %. ¹H NMR (300 MHz, CD₂Cl₂): δ 0.85 (br, 6H, CH₃ of *sec*-Bu), 1.5-1.3 (br, 10 H, CH₂ of 1,2-addition units), 2.2-1.9 (br, 67H, aliphatic CH₂ (both *cis*- and *trans*-) of 1,4-addition units), 4.32 (br, 2H, PB-CH₂-CH₂-O-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), 5.65-5.5 (br, 3H, vinyl -CH=CH₂ 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/CH₂Cl₂ 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 %. ¹H NMR (300 MHz, CD₂Cl₂): δ 1.18 (d, 18 H, $J = 8.2$ Hz, CH₃ of TIPS), 1.45 (m, 3H, CH from TIPS), 3.33 (s, 3H, terminal CH₃ of PEO), 3.75-3.45 (br, 170H, CH₂ of PEO), 3.82 (t, 2H, PEO-CH₂-CH₂-O-CO-), 4.49 (t, 2H, PEO-CH₂-CH₂-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 %. ¹H NMR (300 MHz, CD₂Cl₂): δ 3.33

(s, 3H, terminal CH_3 of PEO), 3.75-3.45 (br, 176H, CH_2 of PEO), 3.83 (t, 2H, PEO- CH_2 - CH_2 -O-CO-), 4.49 (t, 2H, PEO- CH_2 - CH_2 -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 CH_2Cl_2 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 CH_2Cl_2) to yield the product as a colorless liquid ($R_f = 0.4$). Yield: 75 %. 1H NMR (300 MHz, CD_2Cl_2): δ 1.13 (d, 18 H, $J = 8.2$ Hz, CH_3 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. % CH_2Cl_2 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 CH_2Cl_2 and washed with water 3 times. The product was purified by flash chromatography eluting with 3 % THF/ CH_2Cl_2 mixture ($R_f=0.6$) to give 7 as a colorless liquid. Yield: 77 %. 1H NMR (300 MHz, CD_2Cl_2): δ 0.88 (br, 6H, CH_3 of *sec*-Bu), 1.17 (d, 18 H, $J = 8.2$ Hz, CH_3 of TIPS), 1.55-1.3 (br, 12H, CH_2 of 1,2-addition units and CH from TIPS), 2.2-1.9 (br, 66H, aliphatic CH_2 (both *cis*- and *trans*-) of 1,4-addition units), 4.35 (br t, 2H, PB- CH_2 - CH_2 -O-CO-), 5.15-4.9 (br, 6H, vinyl $-CH=CH_2$ 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 $-CH=CH_2$ 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, Ar*H*, $J = 8.2$ Hz, biphenyl protons at positions 2' and 6'), 7.82 (d, 2H, Ar*H*, $J = 8.2$ Hz, biphenyl protons at positions 2 and 6), 8.17 (d, 2H, Ar*H*, $J = 8.3$ Hz, biphenyl protons at positions 3' and 5'), 8.31 (d, 2H, Ar*H*, $J = 8.4$ 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 CHCl₃ 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 %. ¹H NMR (300 MHz, CD₂Cl₂): δ 0.86 (br, 6H, CH₃ of *sec*-Bu of PB), 1.18 (d, 18 H, $J = 8.2$ Hz, CH₃ of TIPS), 1.5-1.3 (br, 13 H, CH₂ of PB 1,2-addition units and CH from TIPS), 2.2-1.9 (br, 72H, aliphatic CH₂ (both *cis*- and *trans*-) of PB 1,4-addition units), 3.34 (s, 3H, terminal CH₃ of PEO), 3.7-3.5 (br, 180H, CH₂ of PEO), 3.82 (t, 2H, PEO-CH₂-CH₂-O-), 4.35 (br, 2H, PB-CH₂-CH₂-O-), 4.51 (t, 2H, PEO-CH₂-CH₂-O-), 5.1-4.9 (br, 6H, vinyl -CH=CH₂ 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=CH₂ 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, Ar*H*, $J = 8.2$ 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, Ar*H*, $J = 8.4$ 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, Ar*H*, $J =$

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), $M_w = 6560$, 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 %. $^1\text{H NMR}$ (300 MHz, CD_2Cl_2): δ 0.87 (br, 6H, CH_3 of *sec*-Bu of PB), 1.55-1.25 (br, 11H, CH_2 of PB 1,2-addition units), 2.2-1.9 (br, 70H, aliphatic CH_2 (both *cis*- and *trans*-) of 1,4-addition units), 3.34 (s, 3H, terminal CH_3 of PEO), 3.7-3.5 (br, 181H, CH_2 from PEO), 3.84 (br t, 2H, PEO- CH_2 - CH_2 -O-), 4.33 (br, 2H, PB- CH_2 - CH_2 -O-), 4.50 (t, 2H, PEO- CH_2 - CH_2 -O-), 5.1-4.9 (br, 7H, vinyl - $\text{CH}=\text{CH}_2$ of PB 1,2-addition units), 5.5-5.3 (br, 31H, both *cis*- and *trans*- $\text{CH}=\text{CH}$ of PB 1,4-addition units), 5.7-5.5 (br, 3H, vinyl - $\text{CH}=\text{CH}_2$ of PB 1,2-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), $M_w = 6210$, PDI=1.13.

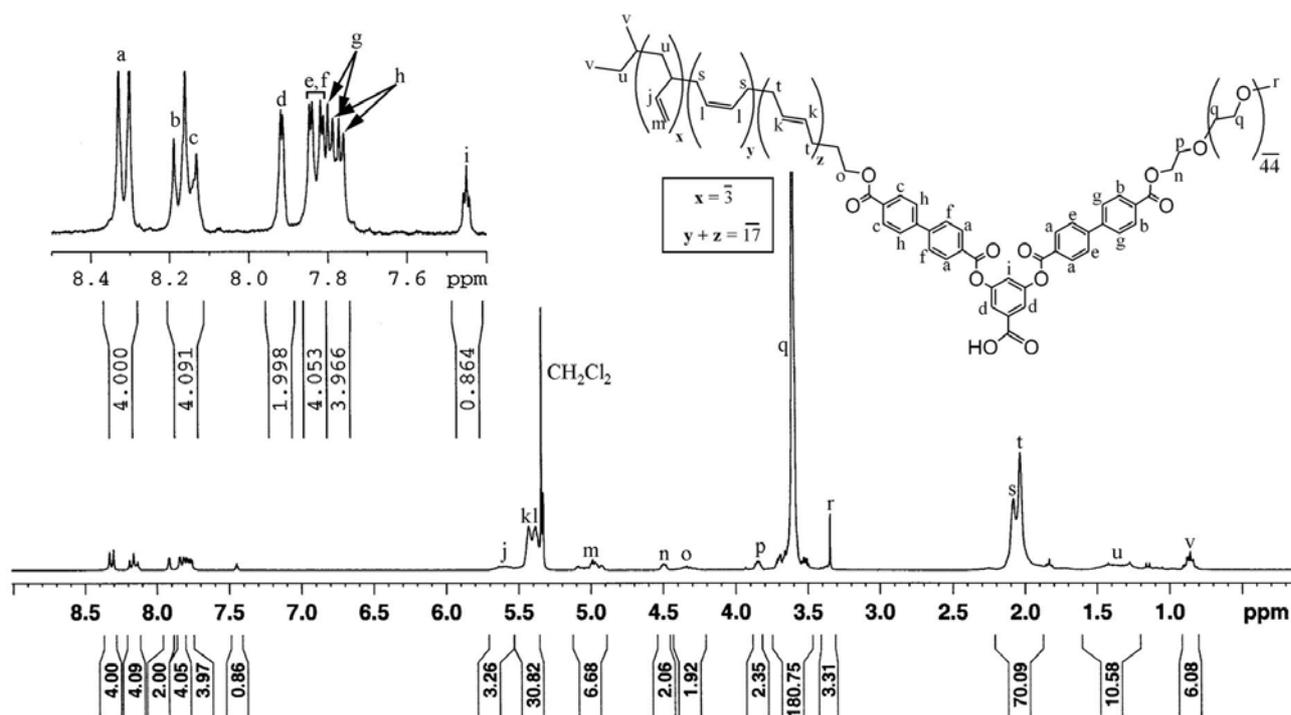


Fig. S1: ^1H NMR spectrum of Y-shaped PB-PEO amphiphile **9**.

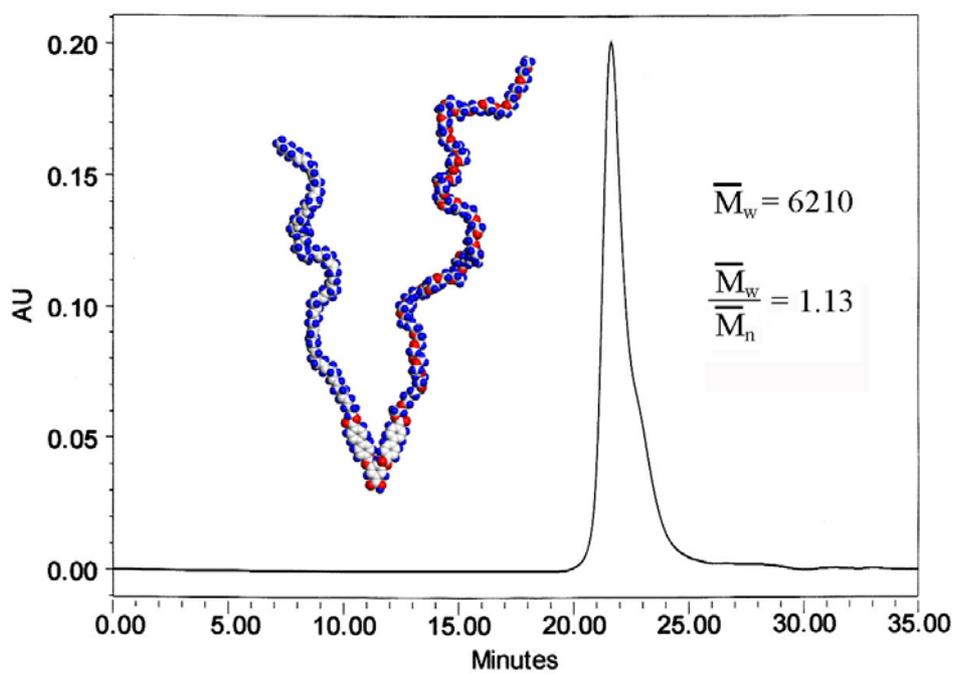


Fig. S2: GPC trace of V-shaped PB-PEO amphiphile **9**.

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 %. ^1H NMR (300 MHz, CD_2Cl_2): δ 0.25 (s, 36H, $\text{OSi}(\text{CH}_3)_2\text{C}(\text{CH}_3)_3$), 1.01 (s, 54H, $\text{OSi}(\text{CH}_3)_2\text{C}(\text{CH}_3)_3$), 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_2Cl_2 mixture as an eluent. Yield 90 %. ^1H NMR (300 MHz, $\text{DMSO-}d_6$): δ 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).

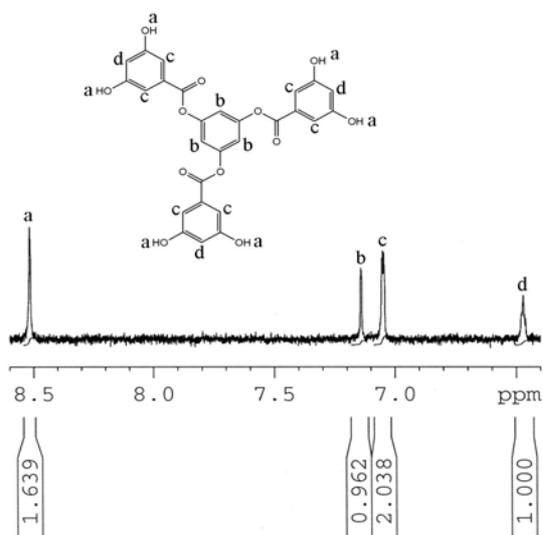


Fig. S3: ^1H NMR spectrum of hexahydroxyl dendrimer core.

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 %. $^1\text{H NMR}$ (300 MHz, CD_2Cl_2): δ 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, $\text{PEO-CH}_2\text{-CH}_2\text{-O-}$), 4.33 (br, 12H, $\text{PB-CH}_2\text{-CH}_2\text{-O-}$), 4.49 (br t, 12H, $\text{PEO-CH}_2\text{-CH}_2\text{-O-}$), 5.1-4.9 (br, 41H, vinyl $-\text{CH}=\text{CH}_2$ of PB 1,2-addition units), 5.5-5.3 (br, 188H, both *cis*- and *trans*- $\text{CH}=\text{CH}$ of PB 1,4-addition units), 5.7-5.5 (br, 18H, vinyl $-\text{CH}=\text{CH}_2$ of PB 1,2-addition units), 7.28 (s, 3H, protons of the central benzene ring of the core), 7.60 (br t, 9H, $\text{Ar}'\text{H}$, $J = 1.7$ Hz, protons at position 4 in DHBA), 7.77 (br, 24H, ArH , 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, ArH , $J = 8.4$ 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, $\text{Ar}'\text{H}$, $J = 1.6$ Hz, protons at position 2 and 6 in DHBA), 8.18 (t, 24H, ArH , $J = 8.5$ 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, ArH , $J = 8.4$ 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, $M_w=27,110$.

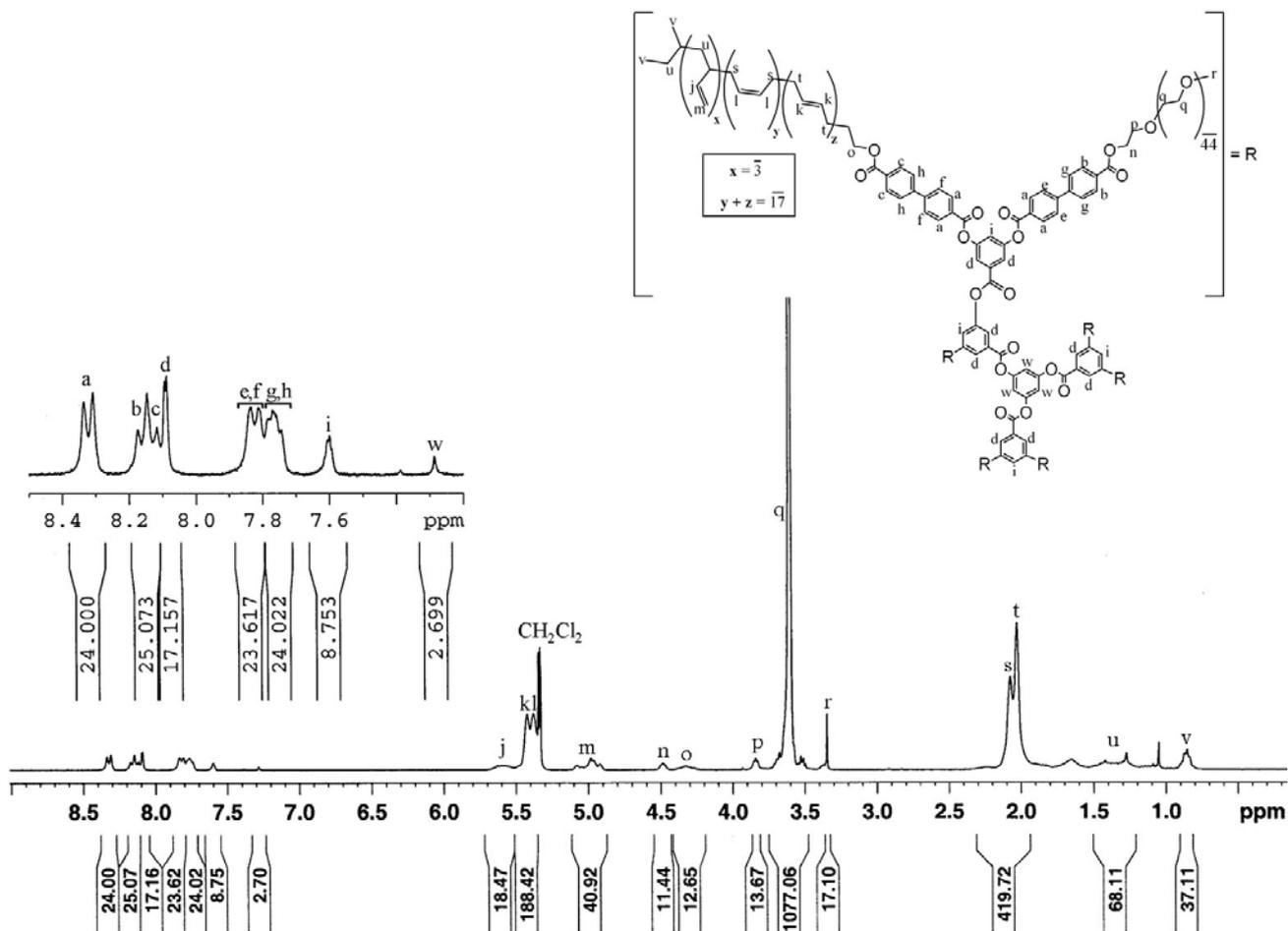


Fig. S4: ^1H NMR spectrum of star-shaped PB-PEO amphiphile 1.

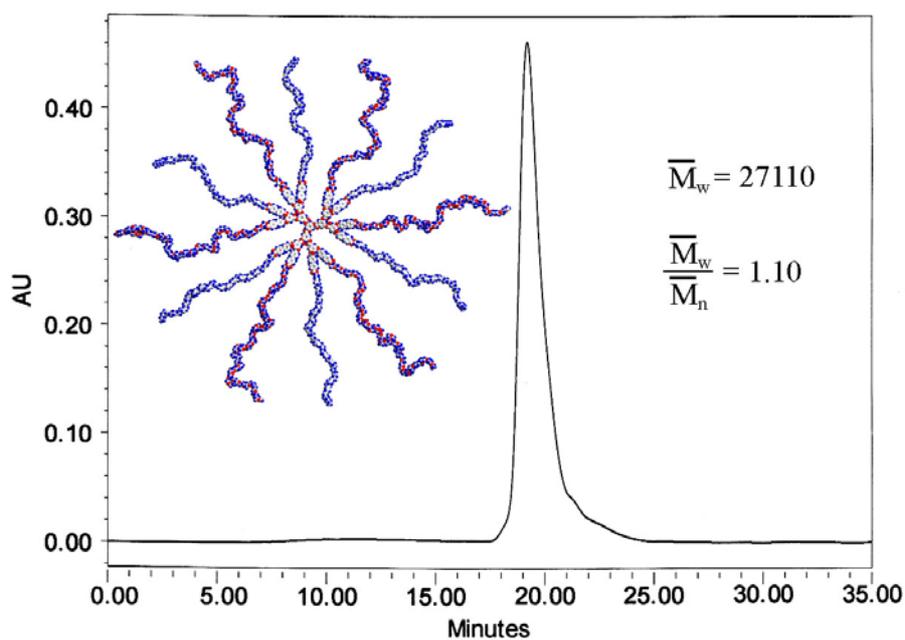


Fig. S5: GPC trace of star-shaped PB-PEO amphiphile 1.

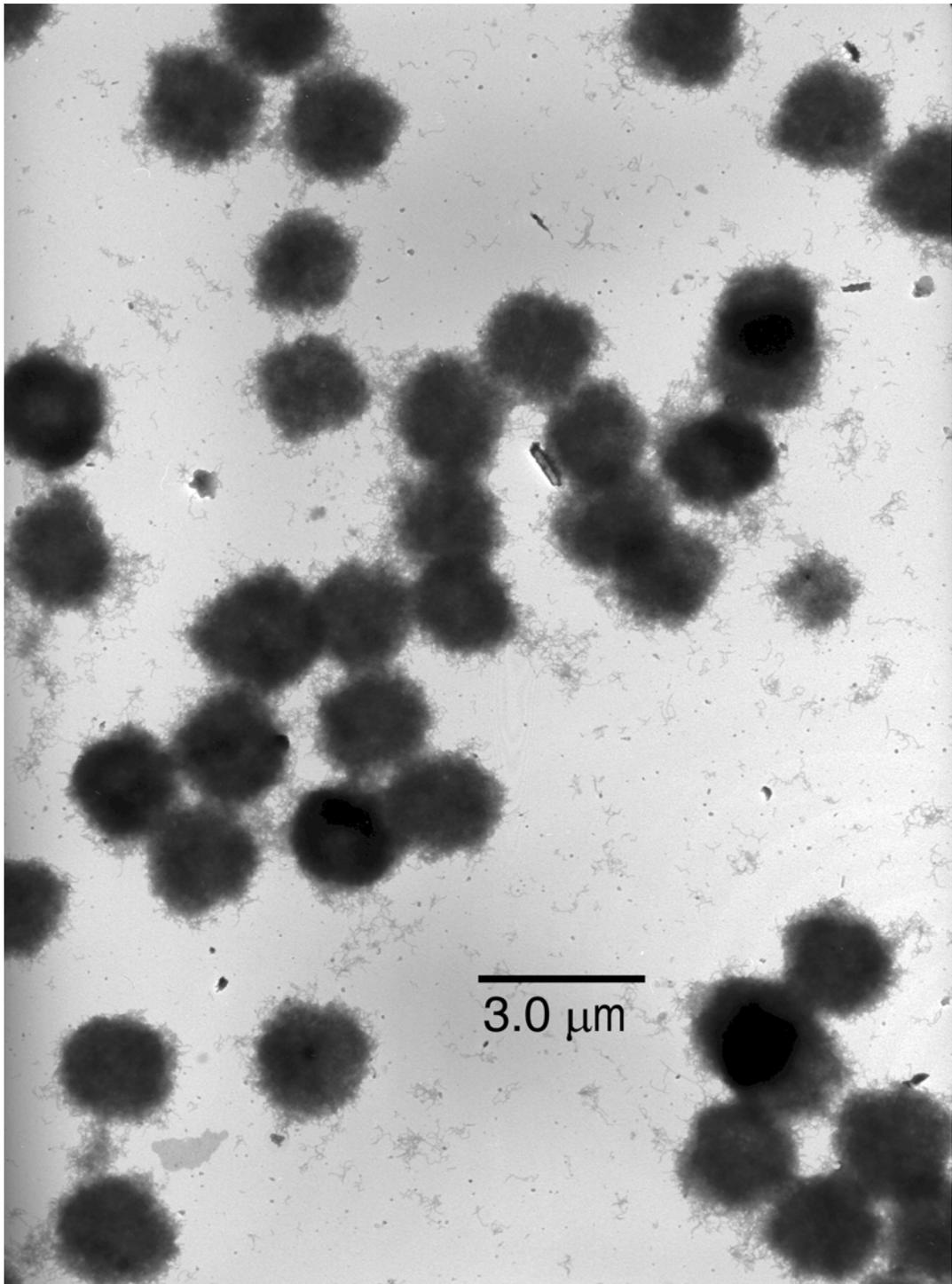


Fig. S6: TEM image of sample cast from 0.5 wt. % solution of amphiphile **1** in hexane.

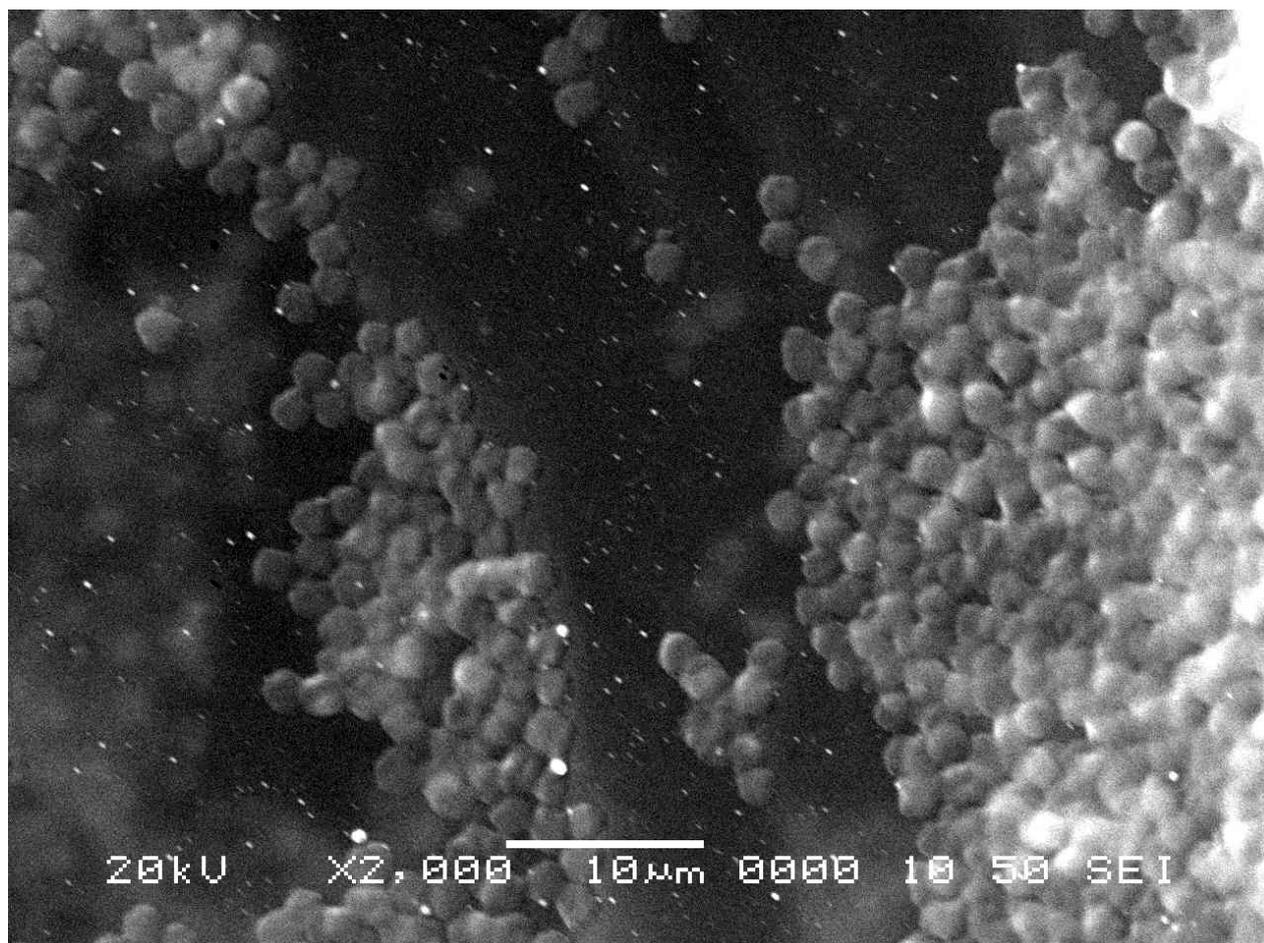


Fig. S7: SEM image of sample cast from 0.5 wt. % solution of **1** in hexane (coated with gold).

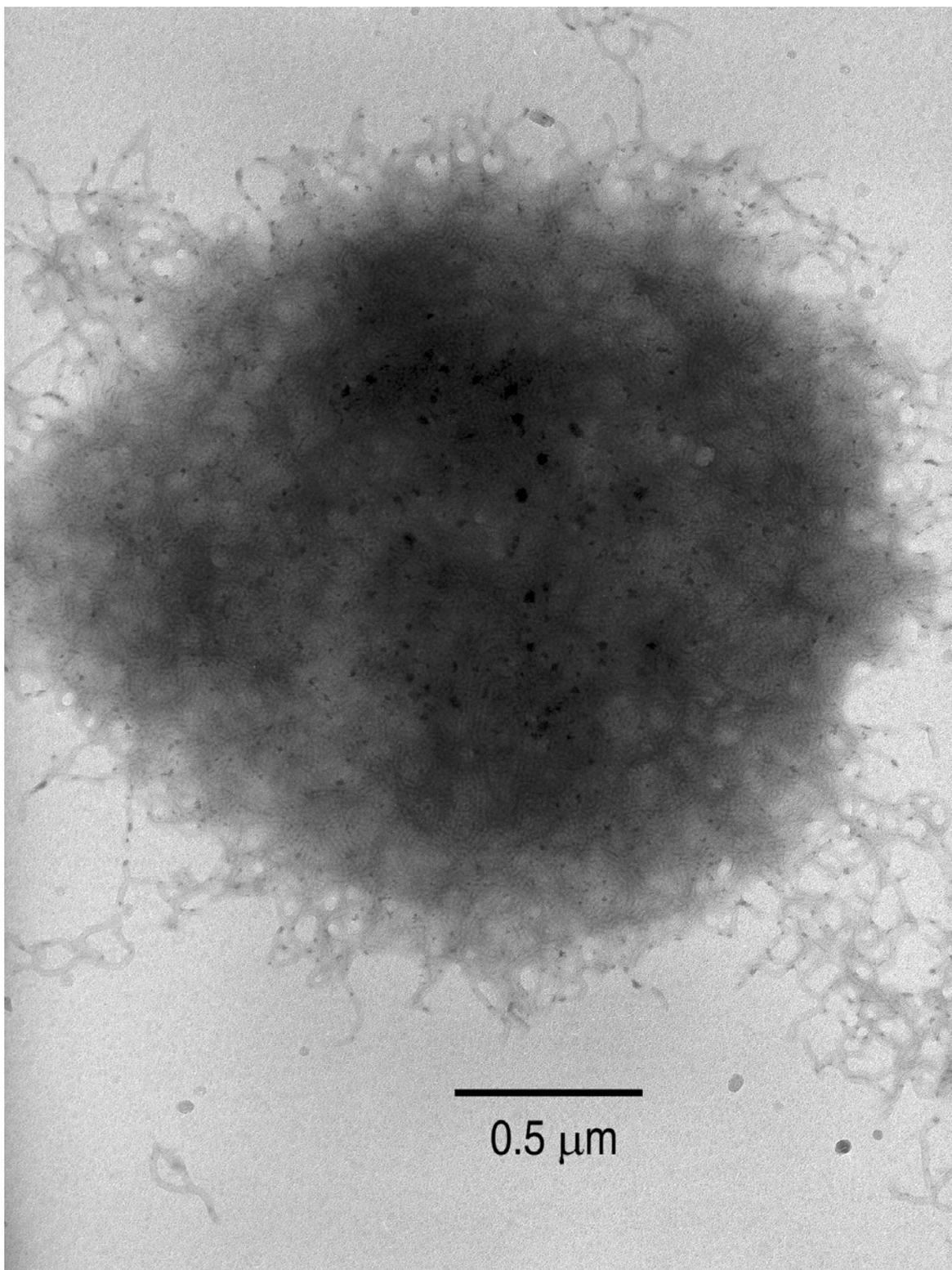


Fig. S8: TEM image of a “cottonball” after staining with osmium tetroxide.

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.

