Supporting Information

Sequence Isomeric Giant Surfactants with Distinct Self-Assembly Behaviors in Solution

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Methods and Characterizations

$^1$H NMR experiments were measured on a Varian Mercury 500 NMR spectrometer. The spectra were referenced to the residual solvent peak in CDCl$_3$ at $\delta$ 7.27 ppm.

Gel permeation chromatography (GPC) were measured in THF at 35 °C on Tosoh EcoSEC instrument with three columns [TSKgel SuperH3000 x 2, TSKgel SuperH5000] with a Guard Column (TSKgel SuperH1000-4000) and a UV detector.

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were measured on a Bruker Ultra flex III TOF/TOF mass spectrometer equipped with a Nd:YAG laser emitting at 355 nm. Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB, >98%, Sigma-Aldrich) was dissolved in THF (20.0 mg/mL) as the matrix solution. Sodium trifluoroacetate (NaTFA, 98%, Sigma-Aldrich), potassium trifluoroacetate (KTFA, 98%, Sigma-Aldrich), or silver trifluoroacetate (AgTFA, 98%, Sigma-Aldrich) was dissolved in MeOH/CHCl$_3$ (v/v = 1/3) at 10.0 mg/mL and used as the cationizing agent solution. The matrix and cationizing agent solutions were mixed in a 10/1 (v/v) ratio. Samples were typically dissolved in THF at 5.0 mg/mL. To prepare the samples, 0.5 $\mu$L of the matrix and cationizing agent mixture solution was deposited on the wells of a 384-well ground-steel sample plate and allowed to dry, followed by depositing 0.5 $\mu$L of the sample solution on a spot of the dried matrix and cationizing agent, and a second deposition of 0.5 $\mu$L of the matrix and cationizing agent mixture solution on top of the dried sample. The sample plate was loaded into the MALDI-TOF mass spectrometer and the spectra were measured in the reflection mode. Data analyses were conducted using the Bruker’s flexAnalysis software.
A typical preparation process for the solution assembled samples was to first completely dissolve the material in DMF with a certain initial concentration. Then, water was added dropwise at a rate of 20 μL/hour until the water content reached 50%. The solution was then dialyzed in water using a dialysis tube with molecular weight cutoff of 20k.

For the bulk state self-assembly studies, a piece of sample was thermal annealed for 1h at different temperatures (70-120 °C) to find the best condition and measured in small angle X-ray scattering (SAXS) experiments.

Dynamic light scattering (DLS) experiments were conducted on a commercial Brookhaven laser scattering spectrometer equipped with a 532 nm laser. An intensity-intensity BI-9000AT correlator was used to get the correlation function based on the particle movement. The diffusion coefficient $D$ could be obtained by $\Gamma=Dq^2$, which $\Gamma$ was calculated by CONTIN method. The hydrodynamic radius ($R_h$) can be calculated according to the Stokes-Einstein equation: $R_h=k_bT/6\pi\eta D$ in which $k_b$ is the Boltzmann constant and $\eta$ is the viscosity of the solution.

A JEOL JEM-2000 electron microscope operated at 200 kV was used for obtaining the images. The samples were prepared by dropping the solution on a copper grid coated with a thin carbon film. After about 30s, the excess solution was removed by a piece of filter paper, and the sample was dried at room temperature for overnight.

Cryo-TEM imaging was performed for the dialyzed solution of the nano-belt like structure. 6 μL of the sample solution was added onto a lacey carbon film supported TEM copper grid (Electron Microscopy Services, Hatfield, PA, USA), which was pre-treated
with plasma air. A thin ice layer of sample was produced using the Vitrobot (FEI). After dropping of the sample solution, the lacey carbon grid was blotted and plunged instantly into a liquid ethane reservoir precooled by liquid nitrogen. The vitrified samples were then transferred to a cryo-holder and cryo-transfer stage that was cooled by liquid nitrogen. During the imaging process, temperature of the cryo-holder was maintained below -170°C with liquid nitrogen to prevent sublimation of vitreous water. All images were recorded by a 16 bit 2K × 2K FEI Eagle bottom mount camera.

The samples were freeze dried before the wide angle X-ray diffraction (WAXD) experiments, which were performed on an instrument with a Rigaku 18 kW rotating anode generator and an image plate detector. The instrument was calibrated using silicon powders with 2θ of 28.4° under Cu Kα radiation. The air scattering was subtracted. The 1D WAXD curve was analyzed and integrated from the 2D image using a Rigaku software.

Synchrotron SAXS experiments were conducted at 12-ID-B, C station with X-ray energy of 12 keV at the Advanced Photon Source (APS) of Argonne National Laboratory. The sample-to-detector distance was adjusted to provide a detecting range for scattering vector \( q = \frac{4\pi\sin\theta}{\lambda} \) between 0.001 to 0.60 Å\(^{-1}\), calibrated using a silver behenate standard. A CCD area detector was used, and the typical exposure time was 0.1 s for each sample.

**Chemicals and Materials**

All the chemicals and solvents were used as received from Sigma-Aldrich, Acros Organic, or Fisher Scientific. PS-N\(_3\), DIBO-V-CHO, DIBO-B-CHO, the “click adaptor”, DIBO-V and DIBO-B were prepared as we previously reported.\(^1\)\(^-\)\(^3\)
Scheme S1. Chemical structures of building blocks: (a) the “click adaptor”; (b) DIBO-B-CHO; (c) DIBO-V-CHO; (d) DIBO-V; (e) DIBO-B.

**A typical procedure of SPAAC reactions:** The corresponding azido terminated giant molecule (1.0 eq.) and DIBO-V-CHO or DIBO-B-CHO or DIBO-V or DIBO-B (1.05 eq. per -N3) were fully dissolved in THF (3 mL). The mixture was stirred at ambient environment for 5 hours. Then, the solution was concentrated, followed by precipitation into cold methanol three times.

**A typical procedure of oxime ligations:** The corresponding aldehyde terminated giant molecules (1.0 eq.) was dissolved in THF (3mL), followed by the addition of the “click adaptor” (1.2 eq. per -CHO). The mixture was stirred for about 2 h to complete the reaction, as monitored by crude $^1$H NMR. Purification was performed by repeated precipitation in cold methanol.
A typical procedure of TECCs. The corresponding precursors containing VPOSS, 2 e.q. of thioglycolic acid to 1 e.q. vinyl group and 0.03 eq of photoinitiator 2-hydroxy-4’-(2-hydroxyethoxy)-2-methylpropiophenone (Irgacure 2959) were fully dissolved in THF (3mL). The solution was illuminated under 365 nm light in the UV reactor for 10 min. Then the solution was concentrated and precipitated into methanol/water 1:5. The products were collected by filtration.

Scheme S2. Synthetic route towards PS-BBA.
Scheme S3. Synthetic route towards PS-ABB.
Figure S1. (a) 1H NMR spectra and (b) GPC of PS-BBA and related intermediates; (c) MALDI-TOF spectrum of PS-BBV (The inset figure is zoomed in. The distance between each peak is 104, which corresponds to the molecular weight of one styrene unit.).
Figure S2. $^1$H NMR spectrum of PS-VBB.

Figure S3. $^1$H NMR spectrum of PS-ABB.
Figure S4. MALDI-TOF spectrum of PS-VBB

Figure S5. GPC curves of (a) PS-BBV and PS-VBB (b) PS-BBA and PS-ABB. Due to the same composition, the curve of PS-BBV almost overlap with that of PS-VBB, and the curve of PS-BBA almost overlap with that of PS-ABB.
Estimation of the Packing Parameters

For both PS-BBA and PS-ABB, due to their same composition, the volume of the hydrophobic part \( V \) is identical and can be estimated by the following calculation:

\[
V = V_B + V_{PS} = \frac{M_B}{N_A \rho_B} + \frac{M_{PS}}{N_A \rho_{PS}}
\]

\[
= \frac{1.6 \text{ kg/mol}}{6.02 \text{ mol}^{-1} \times 1.1 \text{ g/cm}^3} + \frac{2 \text{ kg/mol}}{6.02 \text{ mol}^{-1} \times 1.04 \text{ g/cm}^3} = 5.6 \text{ nm}^3
\]

where \( V_B \) and \( V_{PS} \) are the volume of the BPOSS and PS parts, respectively; \( M_B = 1.6 \text{ kg/mol} \) (for simplification we include the linker as well) and \( M_{PS} = 2 \text{ kg/mol} \) are the molecular masses of the BPOSS and PS parts, respectively; \( \rho_B = 1.1 \text{ g/cm}^3 \) and \( \rho_{PS} = 1.04 \text{ g/cm}^3 \) are their densities;\(^4\) and \( N_A \) is the Avogadro constant.

The contour length of polystyrene tail \( (l_{PS}) \) can be estimated about 5 nm by \( l = 0.154n \sin(109.5^\circ/2) \), where \( n = 40 \) (two carbons per repeat unit). The length of BPOSS part with the linkers \( (l_B) \) is also about 5 nm. When assuming no ionization of APOSS, according to its diameter of about 1.5 nm, the smallest cross section area of APOSS \( (a_A) \) can be estimated as:

\[
a_A = (d/2)^2 \pi = 1.8 \text{ nm}^2
\]

Since PS and BPOSS are “serially” linked in PS-BBA, by assuming no ionization of APOSS when the cross-section area of APOSS is the smallest, the maximum possible value of the packing parameter \( p \) for PS-BBA can be estimated as:
\[ p_{PS-BBA(max)} = \frac{V}{[a \times (l_{PS} + l_B)]} = \frac{5.6 \text{ nm}^3}{[1.8 \text{ nm}^2 \times (5 \text{ nm} + 5 \text{ nm})]} = 0.31 \]

Since PS and BPOSS are “parallelly” linked in PS-ABB, by assuming no ionization of APOSS when the cross-section area of APOSS is the smallest, similarly, the maximum possible value of the packing parameter \( p \) for PS-ABB can be estimated as:

\[ p_{PS-ABB(max)} = \frac{V}{(a \times l)} = \frac{5.6 \text{ nm}^3}{(1.8 \text{ nm}^2 \times 5 \text{ nm})} = 0.62 \]

Figure S6. CONTIN analysis of DLS data of PS-BBA in DMF/water with different initial concentrations (0.1 wt%, 0.4 wt% and 1 wt%).
Figure S7. CONTIN analysis of DLS data of PS-ABB in DMF/water with different initial concentrations (0.1 wt%, 0.4 wt% and 1 wt%).

Figure S8. SAXS profile of the freeze-dried “nano-belt” structure of PS-ABB.
Figure S9. WAXD spectra of PS-ABB from the freeze-dried assembled solution with initial concentration of (a) 0.1 wt% and (b) 0.4 wt%. Those data show no crystallization of BPOSS.
Figure S10. (a) SAXS profile of PS-ABB in the bulk state after annealing at 100 °C, which shows $q$ ratio of 1:2:3:4, indicating a lamellar structure. (b) SAXS profile of PS-BBA in the bulk state after thermal annealing at 100 °C, which shows no ordered structure. The results indicate that the two “sequence isomers” also show different assembly behavior in the bulk state.
References:


