Supporting Information

Experiments and Simulations of Complex Sugar-Based Coil-Brush Block Polymer Nanoassemblies in Aqueous Solution

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Figure S1. $^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of NB-NHS, 1, in CDCl$_3$. 
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<th>$M_{n, \text{SEC}}^b$ (kDa)</th>
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$^a$ Calculated from the monomer to initiator ratio based on $^1$H NMR spectroscopy

$^b$ Measured by THF SEC calibrated using polystyrene standards
Figure S2. Normalized SEC (THF eluent) traces of the (a) macromonomers NB-PGC<sub>a</sub>, 2, and (b, c, d) coil-brush block polymers P(NB-NHS)<sub>m</sub>-b-P(NB-g-PGC<sub>a</sub>)<sub>n</sub>, 3, compared to the corresponding macromonomers with different degrees of polymerization (DP<sub>a</sub>).
Figure S3. MALDI-TOF MS spectra of macromonomer NB-PGC$_{\text{a}}$, 2. DCTB and KTFA were used as a matrix and cationization reagent, respectively.
Figure S4. TGA traces obtained under Ar atmosphere with a heating rate of 10 °C/min for macromonomers NB-PGC₆, 2.
Figure S5. DSC traces obtained under N₂ atmosphere with a heating and cooling rate of 10 °C/min of selected macromonomer NB-PGC₁₇, and coil-brush block polymers, J P(NB-COOH)₁₅₉-b-P(NB-PGC₁₈)₇, F P(NB-COOH)₁₁₄-b-P(NB-PGC₁₇)₇, and B P(NB-COOH)₈₉-b-P(NB-PGC₃₃)₅. Glass transition temperatures ($T_g$) are labeled on the thermograms. Arrows indicate the direction of temperature ramping.
Figure S6. (a) $^1$H NMR (CDCl$_3$, 500 MHz) and (b) $^1$H NMR (DMSO-d$_6$, 400 MHz) spectra, as well as (c) FT-IR spectra of coil-brush block polymers before (red line) and after hydrolysis (blue line), showing the proton NMR resonance at 2.82 ppm in CDCl$_3$ and at 12.04 ppm in DMSO-d$_6$ disappeared and appeared, respectively, as well as the appearance of a broad O-H stretch from 3745 to 2756 cm$^{-1}$. 
Figure S7. Coarse grained representations of the coil-brush chemistry (left) for coil-brush block polymer E P(NB-COOH)$_{29}$-b-P(NB-g-PGC$_{17}$)$_{3}$ (right column). Different coarse-grained representations (center column) and representative simulation snapshots (right column) of the (solvophilic) linear norbornene-based coils with every 4 repeat units represented by a bead of 1.00$d$ diameter (top row), every 2 repeat units represented by a bead of 0.50$d$ diameter (middle row) and every repeat unit represented by a bead of 0.25$d$ diameter (bottom row).
Figure S8. Schematic illustration of the assembly procedure. To mimic the gradual solvent exchange in experiments, in the simulations the solvent quality was altered by changing $\varepsilon_{BB}$. The simulation volume was kept constant and the effect of the changing volume on the assembly was tested with separate simulations at the initial and final concentrations (1.0 and 0.3 mg/mL, respectively).
Figure S9. AFM micrographs (a), (b), height profile (c), 3D image (d) of collapsed vesicles in dry state, and CryoTEM images (e), (f) of vesicles in a frozen-hydrated state obtained from an aqueous solution of coil-brush block polymer B, P(NB-COOH)$_{89}$-b-P(NB-g-PGC$_{33}$)$_{5}$. For AFM characterization, the sample solution was deposited on to freshly cleaved mica, spin coated, and then dried in vacuo. The height profiles were measured along the red line shown on the micrographs. For CryoTEM characterization, a droplet of polymer solution was deposited onto a plasma-treated lacey carbon grid, and then quickly plunged into a liquid ethane reservoir. The grids were then transferred to liquid nitrogen until the imaging. The temperature was maintained at -176 °C during the imaging to prevent ice crystallization. Scale bars = 200 nm.
Figure S10. AFM micrographs (a), height profile (b), 3D image (c) of nanoassemblies obtained from coil-brush block polymers $\text{I, } \text{P(NB-COOH)}_{143-} \text{-} \text{b-P(NB-g-PGC}_{33})_2$. For AFM characterization, the sample solution was drop cast onto the freshly cleaved mica and then dried in air. The height profiles were measured along the red line shown on the micrographs.
Figure S11. Histograms of the diameters of nanoassemblies obtained from coil-brush block polymers A, P(NB-COOH)$_{54}$-b-P(NB-g-PGC$_{33}$)$_{5}$, and I, P(NB-COOH)$_{143}$-b-P(NB-g-PGC$_{33}$)$_{2}$, as determined by TEM analysis (a, b) and DLS characterization (c, d) respectively.
**Figure S12.** Additional TEM analysis of assemblies obtained from coil-brush block polymer E, P(NB-COOH\textsubscript{29})-b-P(NB-g-\textsubscript{17}PGC\textsubscript{3}3). TEM samples were negatively stained by 1 wt\% phosphotungstic acid aqueous solution (20 µL).
Figure S13. AFM micrographs (a), height profile (b), 3D image (c) of nanoassemblies obtained from coil-brush block polymers E, P(NB-COOH_{29})-b-P(NB-g-PGC_{17})_3. For AFM characterization, the sample solution was drop cast onto the freshly cleaved mica and then dried in air. The height profiles were measured along the red line shown on the micrographs.
Figure S14. AFM micrographs (a), height profile (b), 3D image (c) of nanoassemblies obtained from coil-brush block polymers F, P(NB-COOH)$_{114}$-b-P(NB-g-PGC$_{17}$)$_{7}$, analyzed after 3 days. For AFM characterization, the sample solution was drop cast onto the freshly cleaved mica and then dried in air. The height profiles were measured along the colored lines shown on the micrographs.
Figure S15. Additional TEM analysis of assemblies obtained from coil-brush block polymers $F$, $P(NB-COOH)_{114-b-P(NB-g-PGC)_{17}}$: (a-c) different regions of a TEM grid for a sample analyzed after 3 days; (d) a TEM image collected for the same sample allowed to incubate for 5 days. TEM samples were negatively stained by 1 wt% phosphotungstic acid aqueous solution (20 µL).
Figure S16. Characterization of nanoassemblies obtained from coil-brush block polymers F, P(NB-COOH)$_{114}$-$b$-P(NB-$g$-PGC$_{17}$)$_7$ by tomographic TEM (a) still images taken at 0°, 20°, and 50°; (b) x-y tilt series of images consolidated as a quicktime video. TEM samples were negatively stained by 1 wt% phosphotungstic acid aqueous solution (20 µL).
Figure S17. Phase diagram of assembled morphologies from simulations of coil-brush block polymers A, E, F, J, I at 0.3 mg/mL (a, b and c) and 1.0 mg/mL (d, e and f). The models used to produce the phase diagrams are shown at the top of the column.
Figure S18. Phase diagram of assembled morphologies from simulations of coil-brush block polymers (A-L) at a polymer concentration of 0.3 mg/mL. The assembled states including cylinders (orange triangles), disc-like structures (orange stars), bilayers (purple diamonds), and spheres (green spheres) are shown as a function of the side chain length and hydrophobic-hydrophilic ratio. In addition to representative assembled states (boxes with solid borders), one representative assembled micelle for each state is also shown (boxes with dashed borders) at different scales for visual clarity.
Additional discussion of chain conformations during assembly.

We investigated the conformations of the polymer chains during assembly, and the results are shown in Figure S19. As the results follow a similar qualitative trend for all coil-brush block polymers, we show the results for one of each of the assembled morphologies as an example, where a representative micelle and chain are shown in Figure S19a. We determined the chain conformations as a function of solvophobicity (Figure S19b) by considering the average and the probability distribution of the squared radius of gyration, $R_g^2$, at low and high solvophobicity, as indicated in (Figure S19b), for each solvophobic (Figure S19c) and solvophilic block (Figure S19d), and for each chain (Figure S19e).

The average $R_{g,B}^2$ of the solvophobic block decreases with increasing solvophobicity, (Figure S19b), as chains collapse with worsening solvent quality. This is also reflected in the $R_{g,B}^2$ probability distribution (Figure S19c). The average and the probability distribution of $R_{g,A}^2$ of the solvophilic block do not change significantly with increasing solvophobicity (Figure S19b and d).

The average $R_g^2$ of the chains decreases with increasing solvophobicity as chains collapse with worsening solvent quality, until clusters start to form (Figure S19b). After clusters start to form, the average $R_g^2$ of the chains increases with increasing solvophobicity (Figure S19b), as the solvophobic and solvophilic block separate to the micelle core and corona, respectively.
Figure S19. Chain conformations during micellization for coil-brush block polymers J, E, C and A. Part (a) shows representative simulation snapshots of a micelle and a chain within the micelle core. The radius of gyration as a function of solvophobicity for different components of the polymer chain (b) as shown in (c), (d) and (e). The radius of gyration probability distribution at low and high solvophobicity for the whole molecule (c), the solvophobic B-block (d), and the solvophilic A-block (e). The low and high solvophobicity values, $\varepsilon_{BB}$, are indicated with dashed lines on (b).
Figure S20. Schematic of the chain packing parameter ($p$) calculation. Values of $p < 1/3$ indicate spherical morphologies, values between $1/3$ and $1/2$ indicate cylindrical morphologies, values between $1/2$ and 1 indicate vesicle morphologies and values around 1 indicate bilayers.
Figure S21. Comparison of micelle sizes and core sizes for spherical micelle forming coil-brush polymers H, I, J, K and L. From simulations, the ensemble average radius of gyration, $<R^2_g>^{1/2}$, and the ensemble average value of the distance from the micelle center of mass at which the concentration profile of the micelle from its center of mass reaches 50% of its maximum value, $<R_C>$, were calculated for the core and total micelle dimensions. The micelle core and total dimensions were also determined from TEM images (larger images coinciding with the zoomed in regions shown in Figure 5 for H, I, J, K, and L), by measuring the core and entire micelle radii for ca. 50 particles. Due to complications with visualization of the outer micelle surface, the entire micelle radii were estimated by measuring the center-to-center distances for contact pairs of micelles and dividing by 2. Error bars indicate the standard deviation. The standard deviations from the simulation results were determined from multiple uncorrelated configurations from one trial.