Supramolecular guests in solvent driven block copolymer assembly: From structured nanoparticles to micelles

Daniel Klinger,[1] Maxwell J. Robb,[2] Jason M. Spruell,[1] Nathaniel A. Lynd,[1] Craig J. Hawker[1,2] Luke A. Connal[3*]

1. Materials Research Laboratory and Materials Department, University of California, Santa Barbara, California USA 93106

2. Department of Chemistry and Biochemistry, University of California, Santa Barbara, California USA 93106

3. Department of Chemical and Biomolecular Engineering, the University of Melbourne, Victoria, Australia 3010

Supporting information

Experimental

Materials

All reagents were purchased from Sigma Aldrich unless otherwise specified. Dry THF was used directly from a solvent purification system.[1] Styrene was stirred over CaH_2 and degassed through three freeze-pump-thaw cycles, followed by distillation from dibutyl-magnesium to a flame-dried buret immediately prior to use. 2-vinyl-pyridine was stirred and degassed over triethylaluminum, and distilled to a flame-dried buret immediately prior to use. Water was purified using a millipore water purification system.

Polymer synthesis

Burets containing dry THF, purified styrene, and purified 2-vinyl-pyridine were attached to a flame-dried reactor under an argon atmosphere. The reactor assembly was again flame-dried and cycled between vacuum (5 mTorr) and a positive-pressure argon atmosphere five times. Under an argon atmosphere, THF was added and the reactor temperature was decreased to –70 °C. Styrene was added to the reactor followed by a predetermined amount of sec-butyllithium initiator (1.4M in hexane). Polymerization of styrene was allowed to proceed for 1.5h, 2-vinylpyridine was then added and polymerization continued for an additional 1.5h. The polymerization was terminated with degassed isopropanol. The PS-*b*-P2VP was precipitated in hexanes, filtered, and dried in vacuo. ^{1}H NMR spectroscopy: *M*n = 19 kDa, X_{P2VP} = 25%. Size-exclusion chromatography relative to PS-standards: PDI = 1.13

Self-assembly of BCP into nanoparticles

The block copolymer was dissolved in THF (4.5 mL, 0.1 wt %) and the solution was continuously stirred while water was added (9mL @ 1 mL/min). The solution was then allowed to stand under ambient conditions to evaporate THF (typically 3 days).

For supramolecular systems the BCP was dissolved in THF (10 mg/ml) and equimolar (relative to PVP block) addition of guest was added and stirred at room temperature for 12 hours. This solution was then diluted with THF (0.1 wt %) and the above self assembly procedure was followed. To remove PDP the particle dispersion was centrifuged (1000g, 15 min) and dispersed in methanol and stirred for 2 h. The dispersion was then isolated by multiple centrifugation dispersion cycles in methanol.

Characterization

Transmission electron microscopy was conducted on a FEI-T20 instrument, operating at 200 kV. Grids were prepared by casting a concentrated dispersion of particles onto the copper grids and the droplet was wicked through the grid using tissue paper. Particle dispersions were cast onto freshly cleaned silicon wafers, coated with a gold layer and visualized using Scanning electron microscopy (SEM) on a FEI XL30 Sirion FEG microscope.

Dynamic light scattering measurements were performed on a Wyatt DynaPro NanoStar instrument using Dynamics 7.0 software. Data were collected at 25 °C with an acquisition time of 5 sec. Hydrodynamic radii were averaged over 20 acquisitions. Solvent refractive index values were calculated based on volume composition from independent measurements on aqueous THF solutions performed on a Wyatt Optilab rEX instrument. Viscosities of the binary solvent mixtures were calculated from previously reported data.[2]

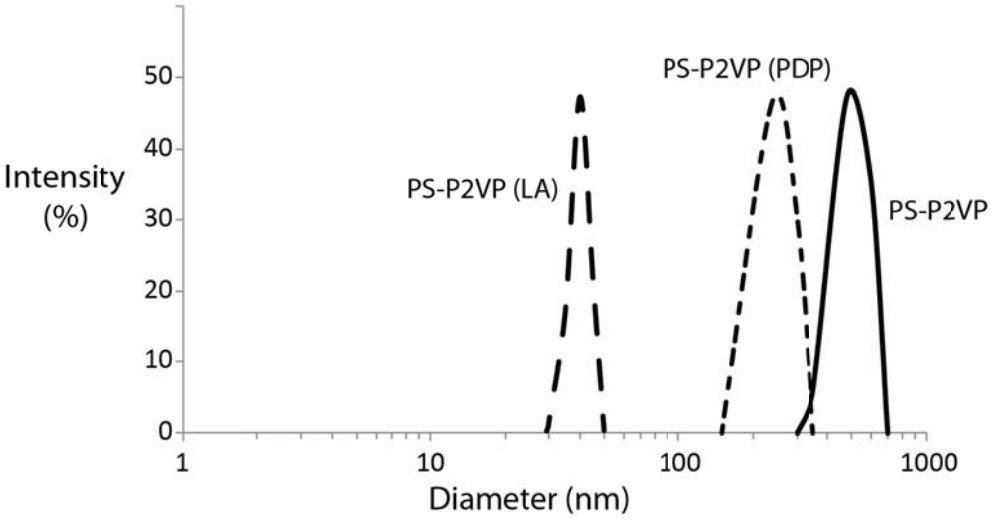

Figure S1 – Dynamic light scattering data for the different assemblies. **PS-P2VP** – the pure block copolymer assembled into water from THF, showing BCP particles of around 500nm diameters. **PS-P2VP (PDP)** – the supramolecular assembly of pentadecyl phenol and PS-P2VP assembled into water from THF, showing BCP supramolecular particles of around 250nm diameters. **PS-P2VP-(LA) -** the

supramolecular assembly of PS-P2VP with lactic acid assembled into water from THF, showing traditional micelles of 40nm diameters.

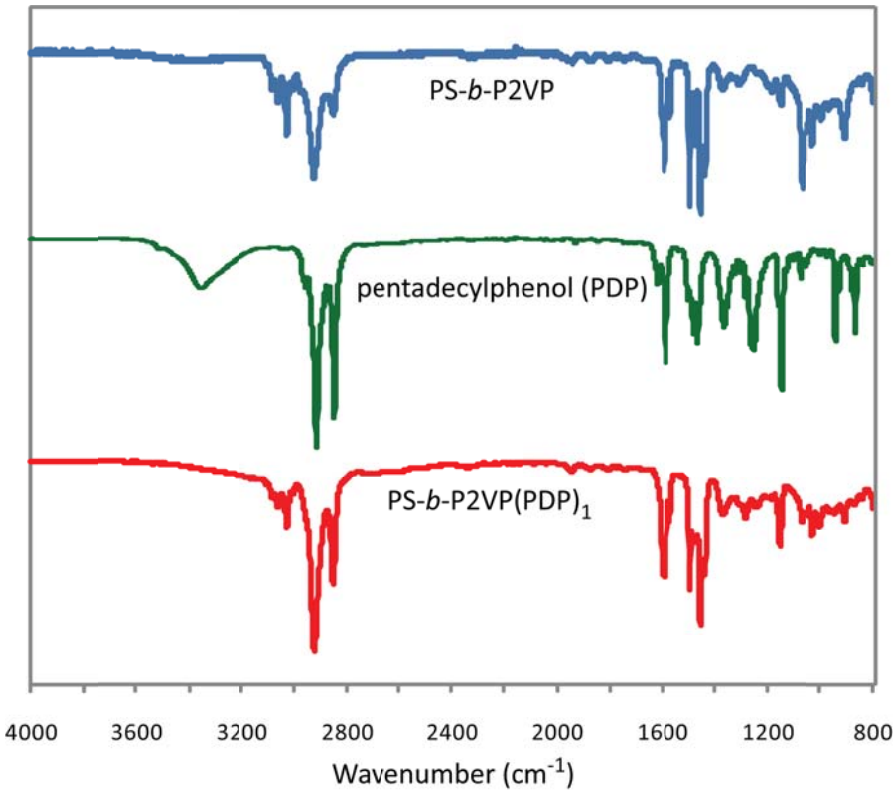

Figure S2 – full FTIR spectrum of (a) pure block copolymer, (b) pentadecyl phenol , and (c) supramolecular complex.

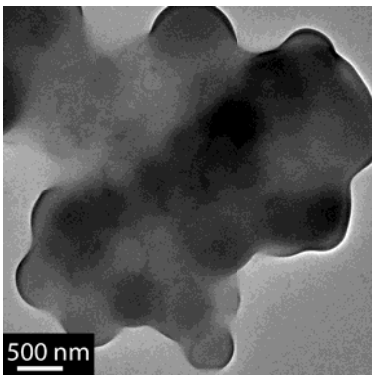

Figure S3 – TEM of control experiment, self-assembly of pentadecyl phenol without block copolymer.

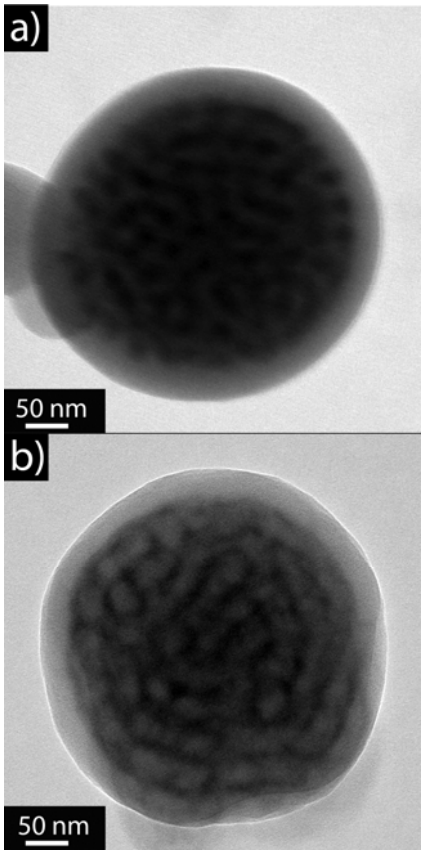

Figure S4. TEM micrographs of assemblies with varying incorporation of hydrophobic guests. a) PS-b-P2VP $(PDP)_{0.3}$. b) PS-b-P2VP $(PDP)_{0.4}$

[1] Pangborn, A. B.; Giardello, A. Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organomet.* **1996**, *15*, 1518.

[2] Aminabhavi, T. M.; Gopalakrishna, B. *J. Chem. Eng. Data,* **1995**, *40*, 856-861.