## **Supplemental Information for**

## Tailored Porous Carbons Enabled by Persistent Micelles with Glassy Cores

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**Figure S1.** <sup>1</sup>H NMR (a) and GPC (b) of OS1 along with the GPC (c) of OS2 demonstrate the controlled chain extension with polystyrene and the resulting narrow molar mass dispersity. The GPC elugrams were offset vertically for clarity.



**Figure S2.** DSC data illustrating the thermal characteristics of the diblock polymer OS1 (a). The midpoint of the  $T_g$  feature is 99.1°C. Plot of the Flory-Fox prediction of PS  $T_g$  as a function of molecular mass (b). This relationship predicts a  $T_g$  value of ~ -20°C for the ~800 g mol<sup>-1</sup> PS in OS2.



Figure S3. DLS data of OS1 micelles at each processing stage.



**Figure S4.** Multiple SAXS measurements demonstrate narrow variation with as-made OS1-EtOH sample series. Samples are offset vertically for clarity.

M:T Ratio	d-spacing (nm)	Average	Standard	Average	Standard	Percent
		Template	Deviation of	Wall	Deviation of	change
		Diameter	Template	Thickness	Wall	in Wall
		(nm) <sup>a</sup>	Diameter	(nm) <sup>b</sup>	Thickness	Thickness
			(nm) <sup>b</sup>		(nm) <sup>b</sup>	(%)
0	N/A	18.68±0.22	3.06	N/A	N/A	N/A
0.50	25.03	17.11±0.31	3.12	8.34±0.34	3.42	N/A
0.85	24.01	17.51±0.26	2.61	8.00±0.15	1.53	N/A
0.95	24.29	17.60±0.27	2.70	8.40±0.17	1.70	5.00
1.00	23.99	17.45±0.28	2.83	9.18±0.18	1.75	14.75
1.05	24.34	17.30±0.27	2.68	9.74±0.18	1.81	21.75
1.10	25.21	17.68±0.25	2.50	10.24±0.20	2.05	28.00
1.20	25.71	17.50±0.23	2.31	10.74±0.20	2.00	34.25
1.40	25.41	17.16±0.22	2.21	11.81±0.31	1.81	47.63

## Table S1. Measurements from series OS1-EtOH as-made

<sup>a</sup>Average values are reported ± the standard error of the mean to indicate the uncertainty in the reported average value. <sup>b</sup>The standard deviation of the measured metric are presented to indicate the statistical distribution of the measured values.



**Figure S5.** Simulated SAXS pattern for randomly packed hard spheres at 70 vol% and a gaussian size distribution having 6% standard deviation. The structure factor peaks have a q-spacing ratio of  $q/q_0=1$ , 1.7, 2.4, 3.1, 3.9 where q0 is the first structure factor peak.



**Figure S6.** TEM image of OS1-EtOH-1.15 showing the wall  $(d_{wall})$  and pore  $(d_{pore})$  dimensions used for statistical analysis.



**Figure S7.** Porous PMT carbon (center) and non-templated carbon carbon (edges) were both found with M:T values exceeding 1.3 and were attributed to partial phase separation of some carbon precursors from the micelle templates. The sample has an M:T of 2.15 and was processed from EtOH.



**Figure S8.** Mass analysis identified that the material precursors partition between the solvent-rich phase and the precipitated micelle-rich phase. The yield of material precursors to each phase varied with M:T ratio. These data are from the sample series OS1-EtOH.



**Figure S9.** Relative d-spacing contraction for carbonized samples as compared to the as-made samples from series OS1-EtOH.



**Figure S10.** Nitrogen physisorption isotherms for samples of the series OS1-EtOH which fell outside of the fitted window (a) along with the associated BJH pore diameter analysis from the adsorption branch of the isotherm (b).

**Table S2.** Polydispersity Index (PDI) values for DLS data from intensity weighted distributions.

Sample	Average PDI
OS1 in THF	0.273
OS1 in THF-H₂O	0.398
OS1 in THF-H <sub>2</sub> O-EtOH	0.499
OS1 in EtOH	0.824