Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Unimer Suppression Enables Supersaturated Homopolymer Swollen Micelles with Long-Term Stability after Glassy Entrapment

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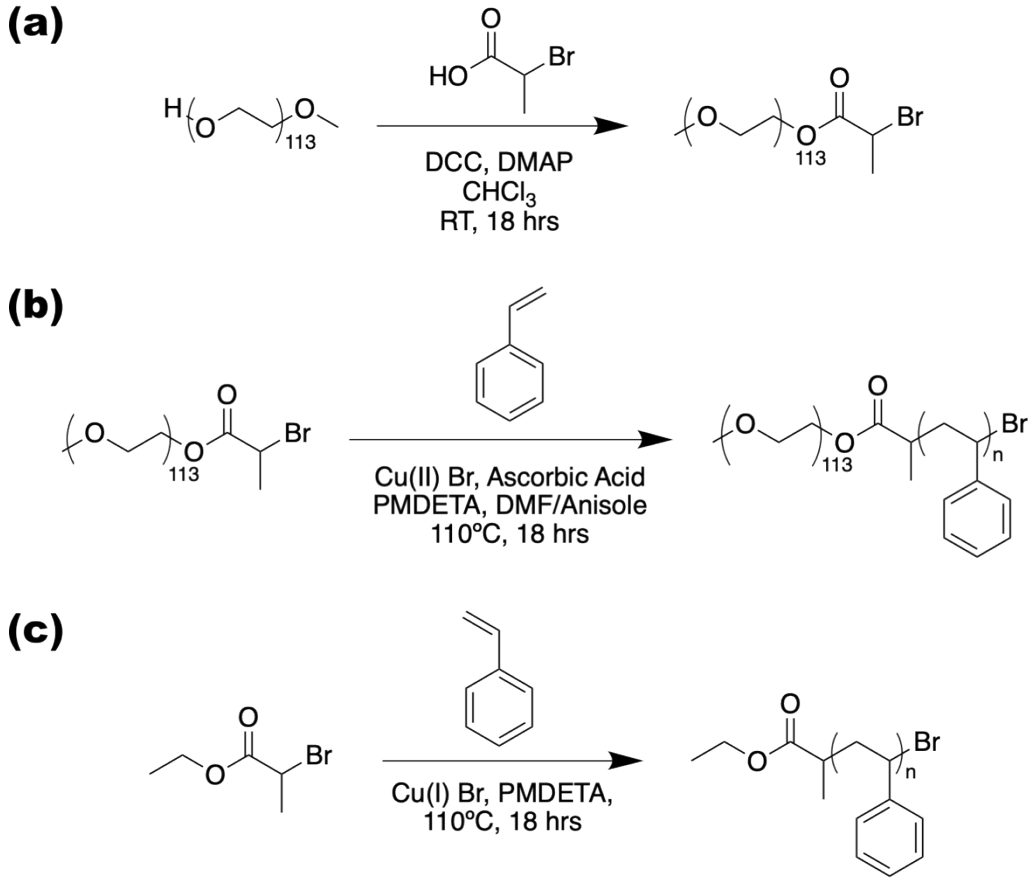

Figure S1. – Reaction schemes for the Steglich esterification of the (5k)PEO-OH to yield a macroinitiator for ATRP (a), followed by the synthesis of the PEO-*b*-PS (**OS**) diblock by AGET-ATRP (b). Homopolymerization of polystyrene (**hPS**) was carried out via normal ATRP (c).

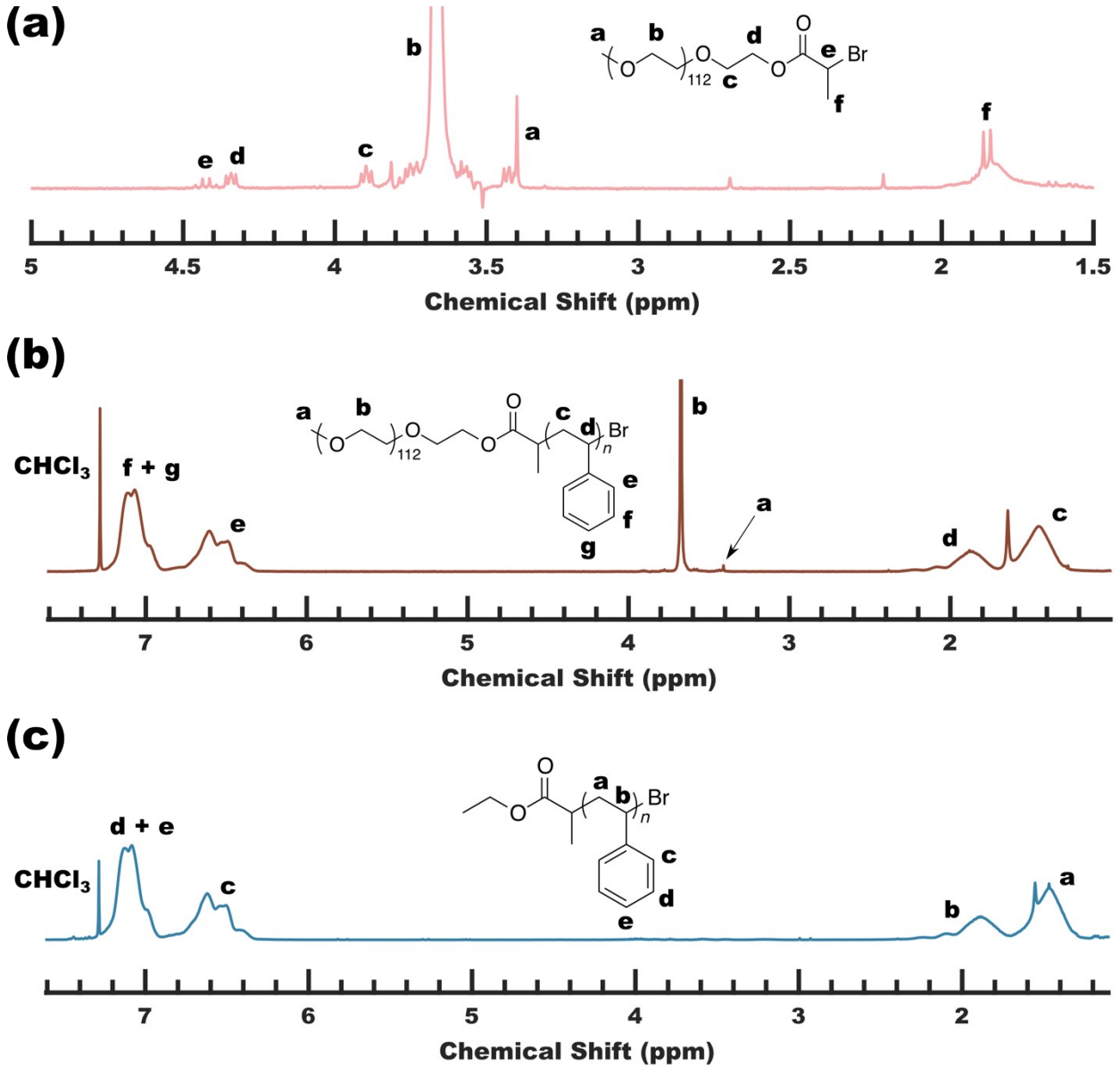

Figure S2. – ^{1}H-NMR spectra of the (5k)PEO-Br macroinitiator (a), **OS** diblock polymer (b), and the **hPS** homopolymer (c). All measurements performed in $CDCl_3$.

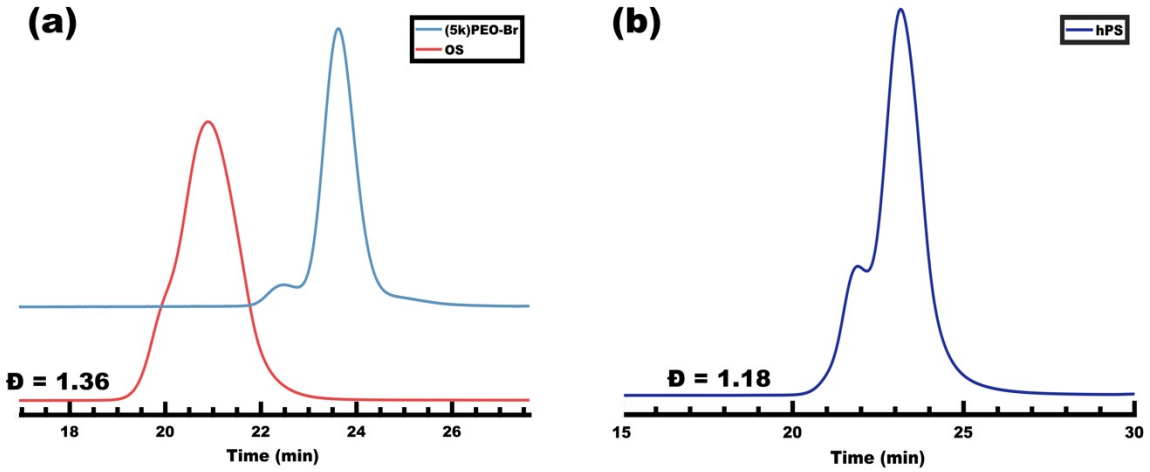

Figure S3. – GPC elugrams of the **OS** diblock polymer compared with the (5k)PEO-Br macroinitiator (a) and the **hPS** homopolymer (b).

Table S1. – Molecular characteristics of the **OS** diblock and **hPS** homopolymer.

Sample	M_n of PEO (g mol^{-1})	M_n of PS (g mol^{-1})	*Đ*
OS	5,000	40,091[a]	1.36[b]
hPS	N/A	9,998[b]	1.18[b]

[a]Determined by ^{1}H-NMR analysis.
[b]Determined by GPC analysis.

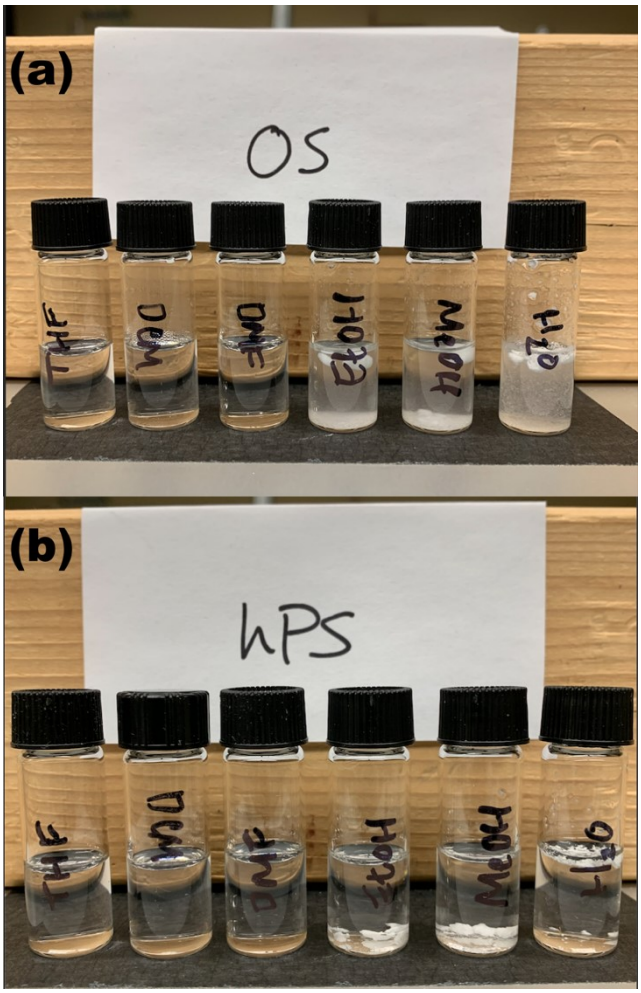

Figure S4. – Solubility characteristics of the **OS** (a) and **hPS** (b) polymers in a range of solvents. From left to right: THF, DCM, DMF, EtOH, MeOH, and H_2O. Note the direct dispersibility of both the **OS** and **hPS** polymers in PS solvents such as THF, DCM, and DMF while both polymers are completely insoluble in PS non-solvents such as EtOH, MeOH, and H_2O. Samples were prepared at a concentration of 10 mg mL^{-1} in their respective solvents.

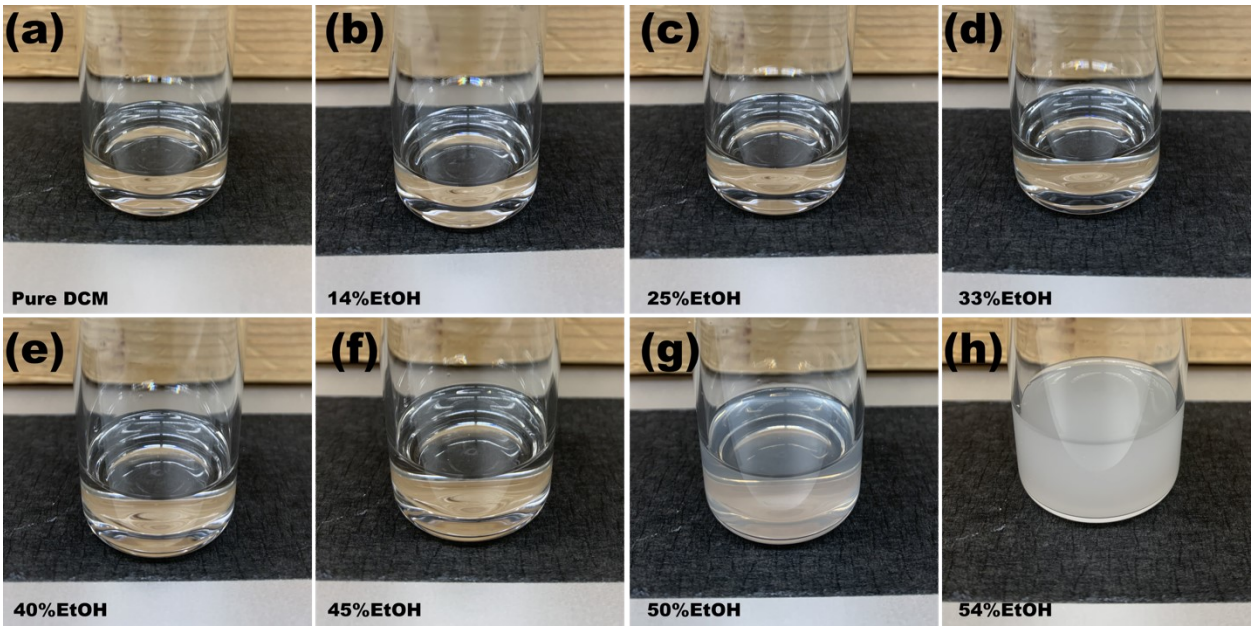

Figure S5 – Solubility characteristics of the **hPS** homopolymer at a concentration of 2 mg/mL in DCM following additions of EtOH (as vol%). The insolubility of the **hPS** becomes visually apparent around 50 vol% EtOH.

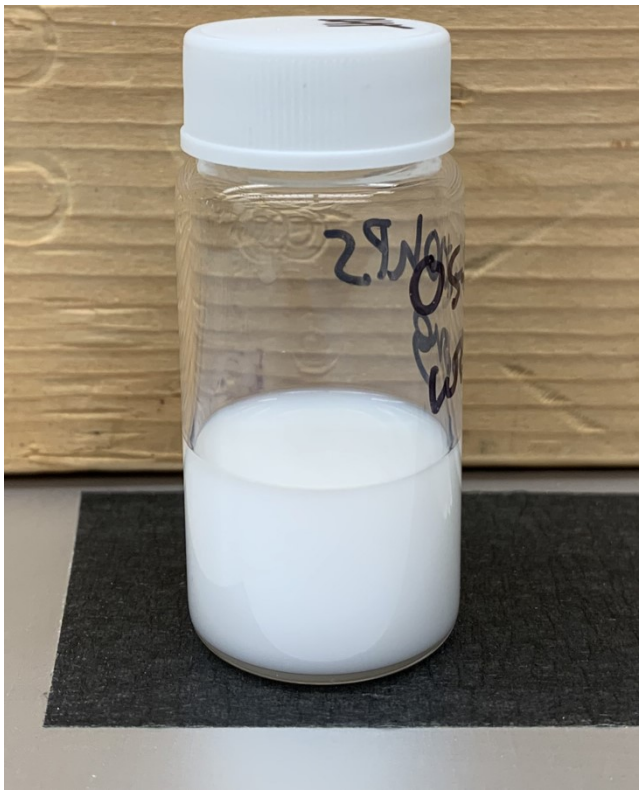

Figure S6 – Direct addition of EtOH to an **OS/hPS** solution in DCM results in large-scale precipitation of the homopolymer rather than the intended incorporation into the **OS** diblock.

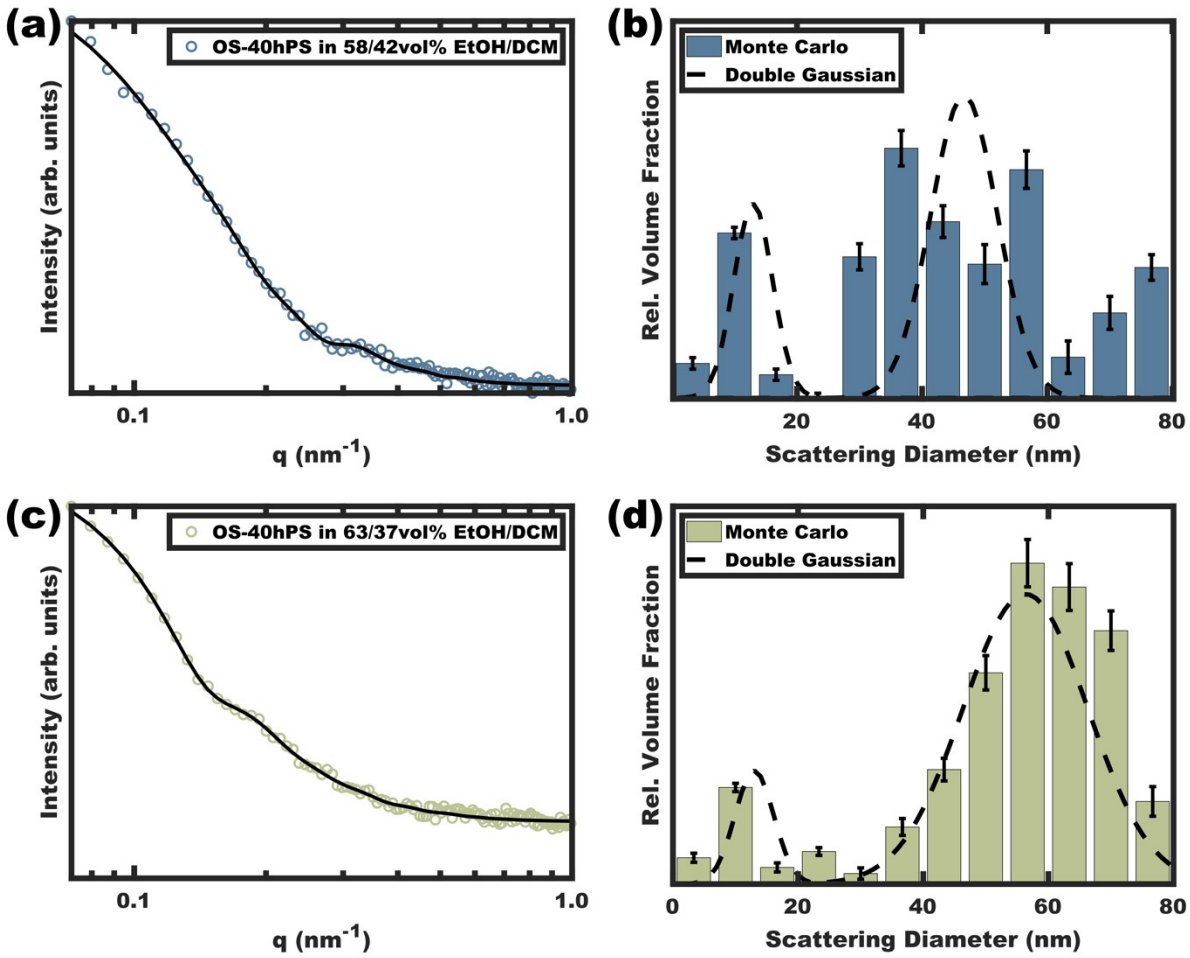

Figure S7. – SAXS scattering profiles for **OS-40hPS** micelles in 58/42 vol% EtOH/DCM (a) and 63/37 vol% EtOH/DCM (c). The scattering curves are well fitted with a micelle form factor model that used two Gaussian size distributions (b,d) which were similar to the results of McSAS fitting with a simpler hard sphere model. Here, the smaller size distributions correspond to the homopolymer-unimer aggregates also observed by TEM.

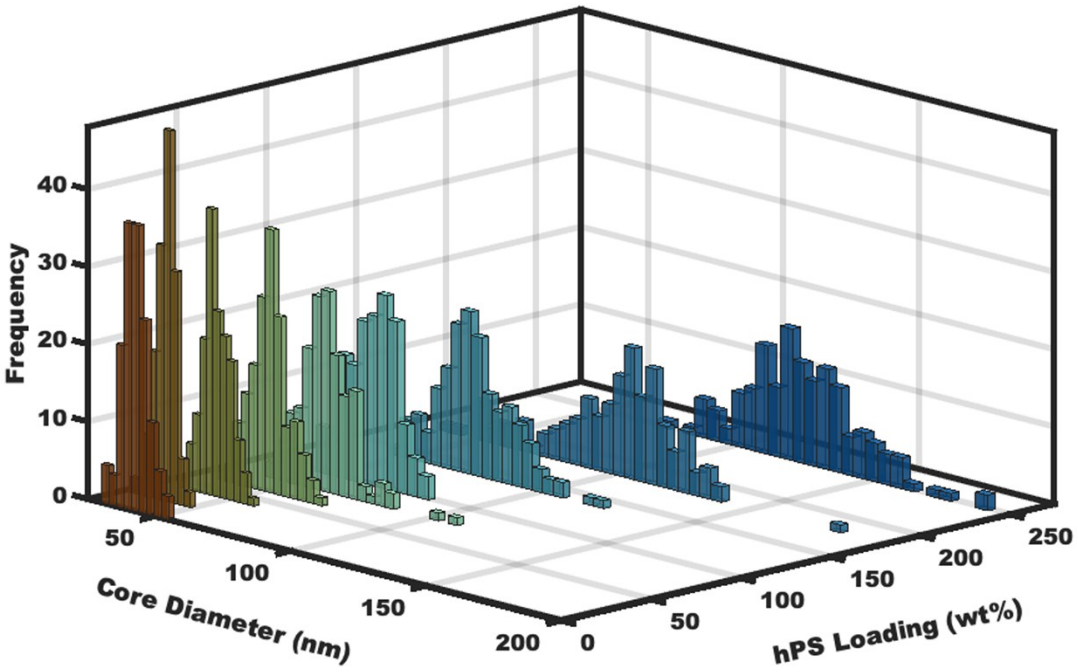

Figure S8. – Micelle diameter distributions from TEM data plotted as a function of homopolymer loading. The size distributions were determined from hundreds of measurements upon TEM images.

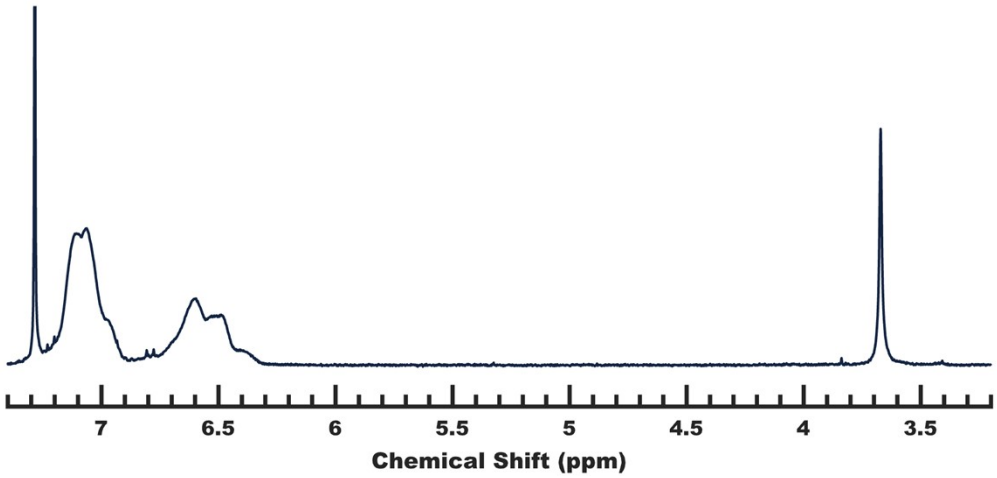

Figure S9. – ^{1}H-HMR analysis of the **hPS-OS** precipitants resulting from **hPS** additions to **OS** solutions that were not sufficiently selective (i.e., 50 and 58 vol% EtOH). The –O**C**$\mathbf{H_2}$**C**$\mathbf{H_2}$– signal of the (5k)PEO is apparent at δ ~3.66 ppm while the aromatic styrene –$\mathbf{C_6H_5}$ signal ranges from δ ~6.30–7.26 ppm. The solvent used was $CDCl_3$.

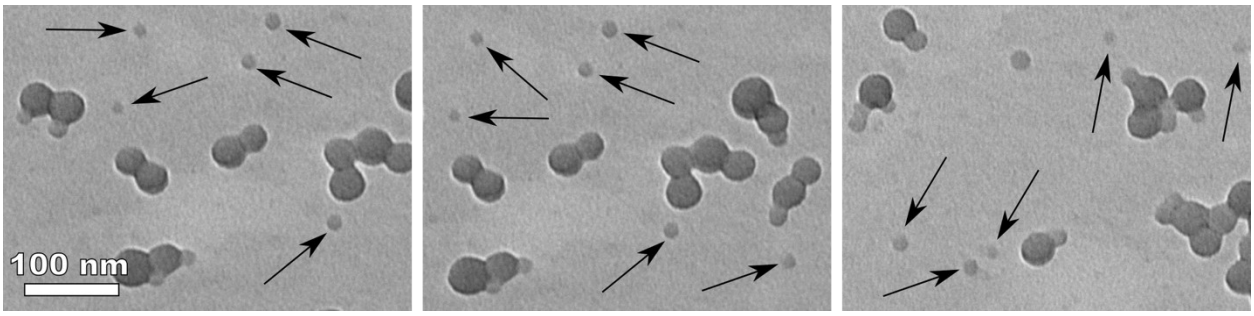

Figure S10. – TEM images of low aggregation number **OS-40hPS** unimer-homopolymer aggregates. The average diameter was determined to be 13.24 ± 2.76 nm, with the uncertainty corresponding to the standard deviation.

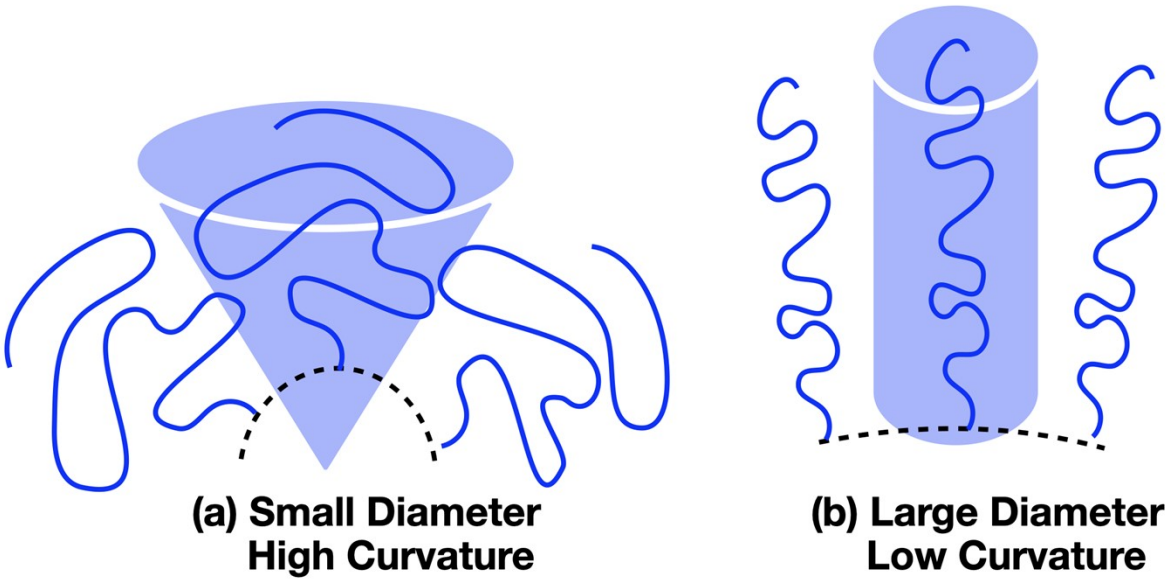

Figure S11. – Schematic showing how the curvature (diameter) of the micelle core (dashed line) influences the available volume for each corona block (shaded areas). Smaller diameter cores reduce steric crowding in 3D by provide additional volume for corona blocks to occupy away from the interface. In contrast, larger diameter cores (low curvature) limit the volume available to each corona block where crowding induces corona chain extension.

TEM Micelle Analysis based on Volume Conservation model:

Geometric aspects of the micelles were analyzed by assuming micelle core volume conservation. TEM analysis is carried out in vacuum which is of course free of any volatile solvents and thus provides model-free dimensions of the solid core. The aggregation number for homopolymer swollen micelles was calculated based upon three simple volume expressions corresponding to an average individual micelle:

$$V_{core} = V_{HP} + V_S \quad \text{(Eq. S1)}$$

$$V_{core} = \frac{4}{3}\pi\left(\frac{d_{core}}{2}\right)^3 \quad \text{(Eq. S2)}$$

$$V_{HP} = \xi V_{BCP} N_{agg} \quad \text{(Eq. S3)}$$

$$V_S = V_{BCP}\phi_S N_{agg} \quad \text{(Eq. S4)}$$

For S1, V_{core} refers to the total volume of the micelle core as well as V_{HP} and V_S referring to the sub-volumes occupied by the homopolymer and the PS block of the block polymer. For S2, d_{core} is the diameter of the micelle core. For S3, ξ is the homopolymer loading as a mass percent with respect to the mass of the **OS** diblock polymer, V_{BCP} is the volume of a single block polymer molecule, and N_{agg} is the number of block polymer chains within a micelle. For S4, furthermore ϕ_S is the PS core-content of the **OS** diblock polymer. The densities of the block polymer and the homopolymer are assumed to be equivalent ($\rho_{BCP} \approx \rho_{HP}$).

When equations S2-S4 are substituted into S1 and solved for the N_{agg}, the following expression is obtained:

$$N_{agg} = \frac{\pi {d_{core}}^3}{6V_{BCP}(\phi_S + \xi)} \quad \text{(Eq S5)}$$

For the **OS** used in this study, V_{BCP} was estimated to be 79.24 nm^3. This method of determining N_{agg} was used for TEM data alone. Please note that these equations were not needed to derive N_{agg} from the SAXS data as the used fitting model directly provides N_{agg}.

Analysis of Surface Area Per Chain

The surface area per chain was calculated simply as:

$$s = \frac{4\pi\left(\frac{d_{core}}{2}\right)^2}{N_{agg}} = \frac{\pi {d_{core}}^2}{N_{agg}} \quad \text{(Eq S6)}$$

N_{agg} values from both TEM analysis (Eq S5) and SAXS analysis (Eq S16) were directly employable into this expression.

Micelle swelling expectations with constant *s*:

Following the observation that swollen micelles tend towards a constant interfacial chain density (Fig. 6b), this trend was captured algebraically to yield quantitative expectations for the micelle swelling trajectory.

Solving Equation S6 for N_{agg} and substituting into Equation S5 yielded:

$$\frac{\pi {d_{core}}^2}{s} = \frac{\pi {d_{core}}^3}{6V_{BCP}(\phi_S + \xi)} \qquad \text{(Eq S7)}$$

Solving this expression for d_{core} yields a linear trajectory for swollen micelle size as a function of **hPS** loading ξ:

$$d_{core} = \frac{6V_{BCP}}{s}(\phi_S + \xi) \qquad \text{(Eq S8)}$$

Furthermore, solving Eq S6 for d_{core} and substituting into Eq S5 yielded:

$$N_{agg} = \frac{\pi}{6V_{BCP}(\phi_S + \xi)}\left(\frac{sN_{agg}}{\pi}\right)^{3/2} \qquad \text{(Eq S9)}$$

Solving this expression for N_{agg} yields a parabolic N_{agg} trajectory under the constraint of constant interfacial density:

$$N_{agg} = \frac{36\pi {V_{BCP}}^2(\phi_S + \xi)^2}{s^3} \qquad \text{(Eq S10)}$$

<u>SAXS Micelle Form Factor Fitting</u>

The micelle form factor simply assumes that the insoluble blocks of the block copolymer segregate to form a relatively compact core whereas the soluble blocks form a diffuse

corona surrounding the core. This form factor for the micelle contains four different terms: the self-correlation term of the core $N_{agg}^{2}\beta_{core}^{2}P_{core}(q)$, the self-correlation term of the chains $N_{agg}\beta_{brush}^{2}P_{brush}(q)$, the cross-term between the core and the corona chains $2N_{agg}^{2}\beta_{core}\beta_{brush}S_{brush-core}(q)$, and the cross term between different chains $N_{agg}(N_{agg}-1)\beta_{brush}^{2}S_{brush-brush}(q)$. This model was described by Pedersen and Gerstenberg[1,2] as:

$$I_{mic} = N_{agg}^{2}\beta_{core}^{2}P_{core}(q) + N_{agg}\beta_{brush}^{2}P_{brush}(q) + 2N_{agg}^{2}\beta_{core}\beta_{brush}S_{brush-core}(q) + N_{agg}(N_{agg}-1)\beta_{br}(q)$$

(Eq S11)

Here, N_{agg} is the aggregation number of diblock copolymers within the micelle. The contrast in scattering length density of a block in the corona or core were respectively addressed with $\beta_{brush} = V_{brush}(\eta_{brush} - \eta_{solv})$ and $\beta_{core} = V_{core}(\eta_{core} - \eta_{solv})$. The terms V_{brush} and V_{core} are the volume occupied by a single block in the corona/core (in nm^3), respectively. The fitting software implementing this model was not parameterized for homopolymer swelling so that additional volume was accounted for by varying V_{core} with respect to the extent of homopolymer added. The terms $\eta_{brush}$and η_{core} correspond to the scattering length densities for the brush and core segments, respectively, while η_{solv} is the scattering length density (SLD) of the solvent. These SLD values were determined using the SASFit. The functions $P_{core}(q), P_{brush}(q), S_{brush-core}(q)$, and $S_{brush-brush}(q)$ are all equal to unity for $q = 0$. The definitions of these four functions are repeated below, though they are thoroughly derived elsewhere.[1,2]

$$P_{core}(q,R_{core}) = \Phi^{2}(qR_{core}) \text{ where } \Phi(qR) = \frac{3\sin(qR) - qR\cos(qR)}{(qR)^{3}} \quad \text{(Eq S12)}$$

$$P_{brush}(q,R_g) = \frac{2e^{-x} - 1 + x}{x^{2}} \text{ where } x = R_g^{2}q^{2} \quad \text{(Eq S13)}$$

$$S_{brush-core}(q,R_{core},R_g,d) = \Phi(qR_{core})\psi(qR_g)\left(\frac{\sin\left(q[R_{core} + dR_g]\right)}{q[R_{core} + dR_g]}\right) \quad \text{(Eq S14)}$$

Here, $\psi(qR_g) = \frac{(1 - e^{-x})}{x}$ (form factor amplitude of the chain) with x being the same as noted above.

$$S_{brush-core}(q,R_{core},d,R_g) = \psi^{2}(qR_g)\left(\frac{\sin\left(q[R_{core} + dR_g]\right)}{q[R_{core} + dR_g]}\right)^{2} \quad \text{(Eq S15)}$$

Lastly, R_{core} refers to the core radius and can be related to the N_{agg} presented in Eq. S11 by:

$$N_{agg} = \frac{\frac{4}{3}\pi R_{core}^{3}(1 - x_{solv,core})}{V_{core}} \quad \text{(Eq S16)}$$

Here, $x_{solv,core}$ refers to the amount of solvent in the micelle core.

The fitting of this form factor model included either a single or a double Gaussian distribution of N_{agg} to account for micelle size dispersity. This distribution of aggregation numbers was also propagated to the presented distribution of R_{core}.

We note that SAXS analysis on an absolute intensity scale is necessary to determine the extent of solvent-core swelling from SAXS data alone. Here the combination of TEM and SAXS datasets allowed the comparison of N_{agg} from TEM to that from SAXS fitting. Statistically indistinguishable N_{agg} values resulted when assuming $x_{solv,core}$=0 during SAXS analysis (see Fig. 4b).

Table S2. Fit parameters for the **OS-hPS** swelling series after the removal of DCM, present in pure EtOH.

Sample	V_{core} (nm^3)	V_{brush} (nm^3)	η_{core} (cm^{-2})	η_{brush} (cm^{-2})	$\eta_{solvent}$ (cm^{-2})
OS	66.409	7.5313	9.144×10^{10}	1.029×10^{11}	7.580×10^{10}
OS_10hPS	73.049	7.5313	9.144×10^{10}	1.029×10^{11}	7.580×10^{10}
OS_20hPS	79.690	7.5313	9.144×10^{10}	1.029×10^{11}	7.580×10^{10}
OS_40hPS	92.972	7.5313	9.144×10^{10}	1.029×10^{11}	7.580×10^{10}
OS_60hPS	106.254	7.5313	9.144×10^{10}	1.029×10^{11}	7.580×10^{10}
OS_80hPS	119.536	7.5313	9.144×10^{10}	1.029×10^{11}	7.580×10^{10}
OS_100hPS	132.817	7.5313	9.144×10^{10}	1.029×10^{11}	7.580×10^{10}
OS_120hPS	146.099	7.5313	9.144×10^{10}	1.029×10^{11}	7.580×10^{10}

Sample	N	R_{core} (nm)	N_{agg}	R_g	c_0
OS	5.575×10^{-32}	19.9 ± 2.0	500 ± 49	5	0.0299

OS_10hPS	5.202×10^{-32}	21.6 ± 2.4	575 ± 63	5	0.0286
OS_20hPS	1.294×10^{-32}	21.5 ± 2.4	520 ± 58	5	0.0084
OS_40hPS	8.626×10^{-33}	24.7 ± 3.0	681 ± 82	5	0.0088
OS_60hPS	7.182×10^{-33}	25.6 ± 3.8	663 ± 98	5	0.0072
OS_80hPS	2.440×10^{-32}	31.8 ± 5.0	1120 ± 175	5	0.0345
OS_100hPS	3.362×10^{-32}	33.5 ± 5.8	1190 ± 206	5	0.0373
OS_120hPS	2.403×10^{-32}	36.8 ± 7.3	1430 ± 284	5	0.0544

Table S3. Double-Gaussian fit parameters for the **OS** and **OS_40hPS** samples with varying EtOH/DCM compositions of 52/48, and 63/37 vol% EtOH/DCM. Please note the 50/50 sample yielded equivocal fits and was thus omitted.

Sample:	**V_core (nm^3)**	**V_brush (nm^3)**	**η_{core}**	**η_{brush}**	**η_{solv}**	**$X_{solv,\ core}$**	**R_g (nm)**	**d**
OS-40hPS (58/42)	66.409	7.531	9.144×10^{10}	1.029×10^{11}	8.01×10^{10}	0.246	9.0	1
OS-40hPS (63/37)	80.344	7.531	9.144×10^{10}	1.029×10^{11}	8.01×10^{10}	0.247	8.7	1

Major Gaussian Parameters	***N***	**R_{core} (nm)**	**c_0**
OS-40hPS (58/42)	2.802×10^{-28}	23.4 ± 5.3	0.206
OS-40hPS (63/37)	3.266×10^{-28}	28.2 ± 5.0	0.250

Minor Gaussian Parameters	***N***	**R_{core} (nm)**	**c_0**
OS-40hPS (58/42)	2.191×10^{-36}	6.5 ± 1.6	0.206
OS-40hPS	$8.673\times$	6.5 ± 1.5	0.250

(63/37)	10^{-27}		

References:

1. Pedersen, J. S.; Gerstenberg, M. C. Scattering form factor of block copolymer micelles. *Macromol.* **1996**, *29*, 1363 – 1365.
2. Pedersen, J. S. Form factors of block copolymer micelles with spherical, ellipsoidal, and cylindrical cores. *J. Appl. Cryst.* **2000**, *33*, 637 – 640.