Supporting Information

Growth of Cylindrical Micelles and their Use to Prepare Porous Materials with Tailored Dimensions and Alignment

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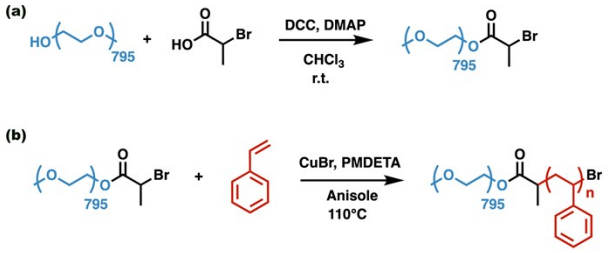


Figure S1. Synthesis scheme of (a) PEO-Br *via* Steglich esterification with 2-bromopropanoic acid to form an ATRP macroinitiator, followed by (b) ATRP chain extension to yield PEO-*b*-PS.

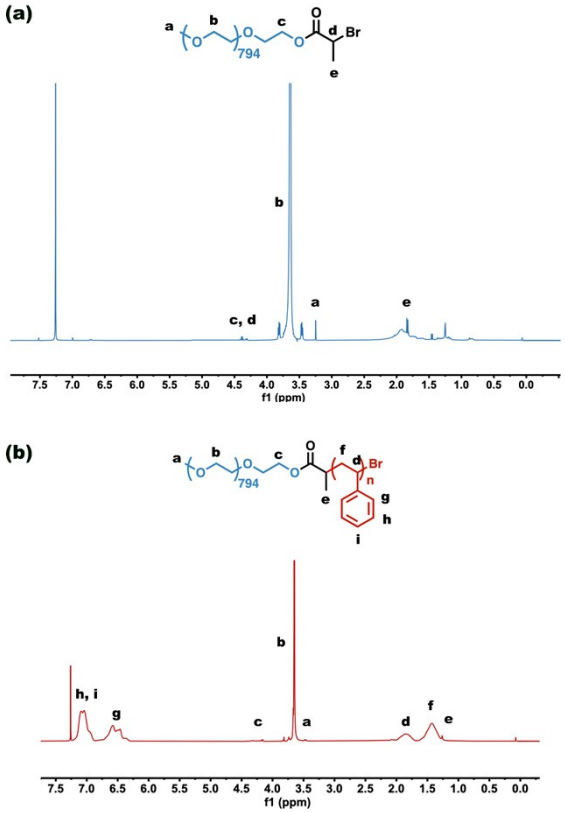


Figure S2. ^{1}H-NMR spectra of (a) the PEO_{795}-Br ATRP macroinitiator and (b) the $O_{795}S_{835}$ (OS1) diblock copolymer both measured within $CDCl_3$.

Table S1: Molecular weight (M_n), volume fraction of hydrophilic block (f_{PEO}) and molar mass dispersity index (Đ) analysis of OS diblock copolymers.

Name	Degree of Polymerization	Total M_n_NMR (g/mol)	f_{PEO} (wt%)	GPC Đ
OS1	PEO_{795}-*b*-PS_{835}	122,000	28.7	1.08
OS2	PEO_{795}-*b*-PS_{2381}	283,000	12.4	1.35
OS3	PEO_{113}-*b*-PS_{86}	14,000	35.7	1.07
OS4	PEO_{113}-*b*-PS_{144}	20,000	25.0	1.15
OS5	PEO_{113}-*b*-PS_{202}	26,000	19.2	1.05
OS6	PEO_{113}-*b*-PS_{298}	36,000	13.9	1.08
OS7	PEO_{113}-*b*-PS_{480}	55,000	9.1	1.05

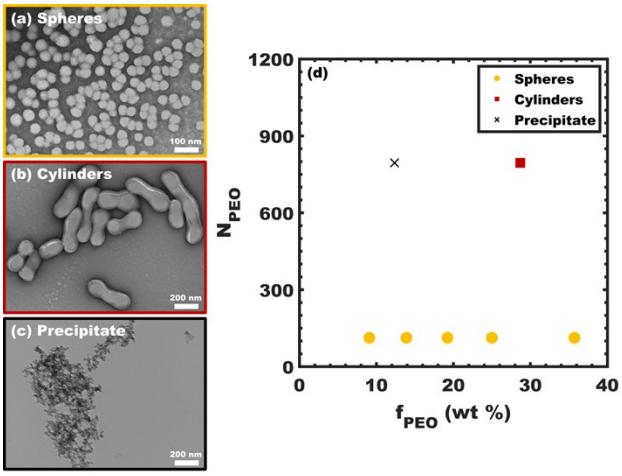


Figure S3. Micelle morphologies were mapped as a function of the polymer architecture using DCM/EtOH = 40/60 vol%. For each composition, an aliquot was quenched with 95 vol% EtOH, deposited on a TEM grid and stained with UrAc.

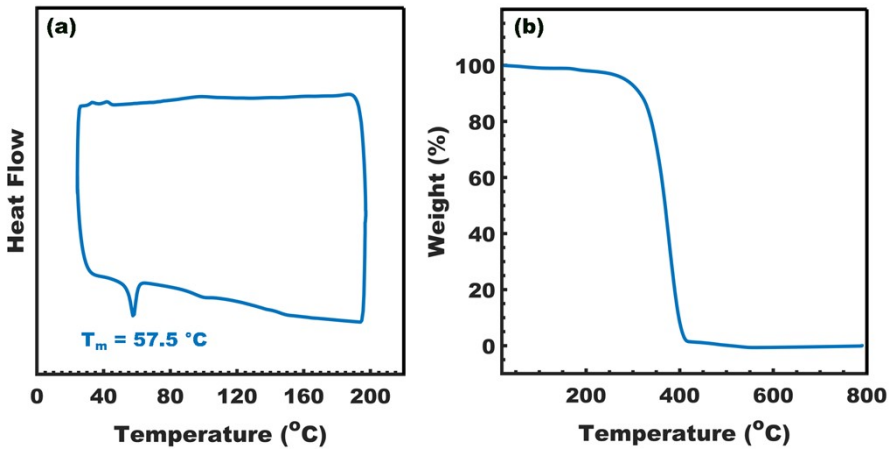


Figure S4. The thermal characteristics of OS were measured by (a) DSC and (b) TGA. The PEO melting was apparent at 57.5 °C and the PS T_g at ~100 °C. The polymer degraded at ~400 °C under N_2.

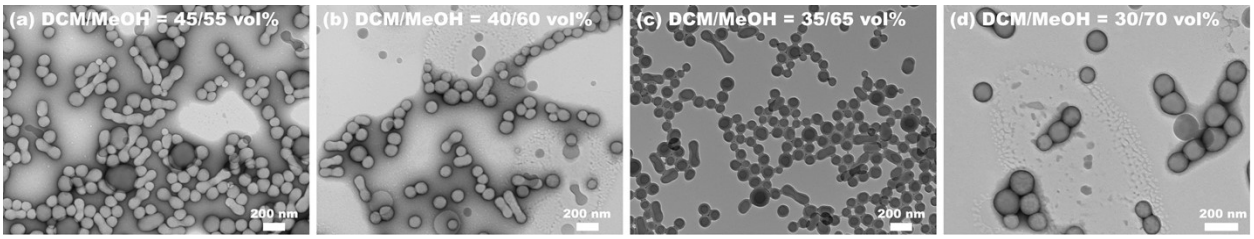


Figure S5. Micelle morphology trend for OS1 as a function of MeOH/DCM composition. Representative TEM images shown using UrAc stain (relative brightness of micelles depends on the local concentration of stain agent).

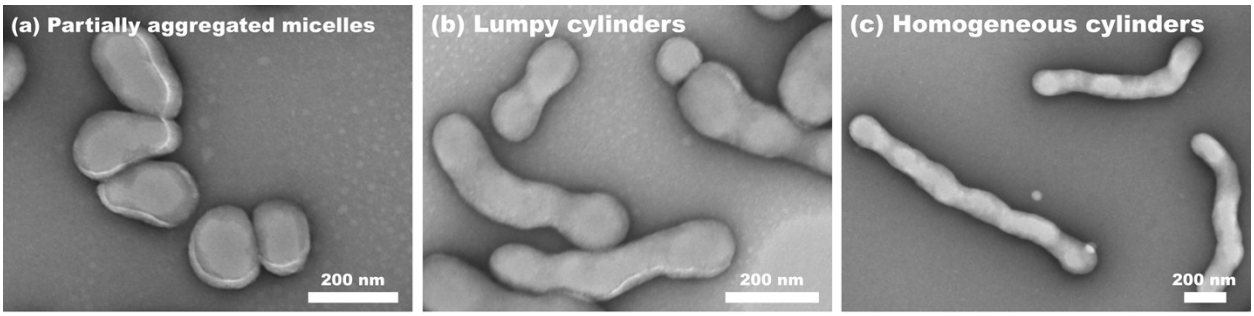
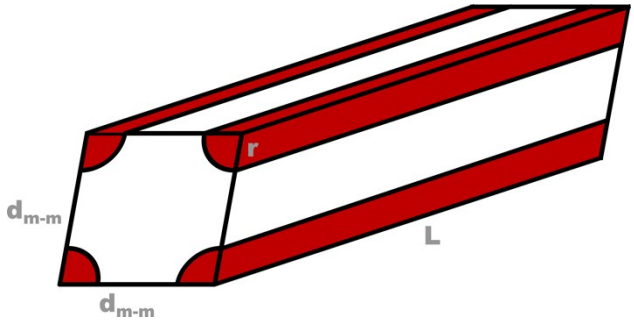


Figure S6. TEM images of (a) aggregated micelles, (b) lumpy cylinders and (c) homogeneous cylinders.

2D PMT Model for Aligned Cylinders



The parallelepiped has a total volume of:

$$V_{unitcell} = \gamma d_{m-m}^{2} L \quad \text{(Eq.S1)}$$

Where d_{m-m} is the micelle-to-micelle spacing, L is the cylinder length, and gamma is a scalar less than or equal to 1.0.

The template volume ($V_{template}$) depends on the cylinder radius, r:

$$V_{template} = V_{core} = \pi r^2 L \quad \text{(Eq.S2)}$$

The remaining volume is occupied by the matrix which is a combination of the material and the corona chains:

$$V_{matrix} = V_{material} + V_{corona} = d_{m-m}^{2} L\gamma - \pi r^2 L \quad \text{(Eq.S3)}$$

The corona volume can be calculated from the core volume using the corona volume fraction of the polymer:

$$V_{corona} = V_{core}\frac{f_{corona}}{1 - f_{corona}} = \pi r^2 L\frac{f_{corona}}{1 - f_{corona}} \quad \text{(Eq.S4)}$$

The combination of equations S1 – S4 can be used to solve for $V_{material}$:

$$V_{material} = V_{matrix} - V_{corona} = d_{m-m}^{2} L\gamma - \pi r^2 L\left(1 + \frac{f_{corona}}{1 - f_{corona}}\right) \quad \text{(Eq.S5)}$$

For use with experimentally convenient parameters we define X as the mass ratio of material:template using the material, core, and corona densities:

$$x \equiv \frac{m_{material}}{m_{template}} = \frac{V_{material}\rho_{material}}{V_{core}\rho_{core} + V_{corona}\rho_{corona}} \quad \text{(Eq.S6)}$$

The x could be calculated by combining equation S2, S4 and S5 into Eq.S6 to yield:

$$x = \frac{\rho_{material}}{\rho_{core} + \frac{f_{corona}}{1 - f_{corona}}\rho_{corona}} * \frac{d_{m-m}^{2}\gamma L - \pi r^2 L(1 + \frac{f_{corona}}{1 - f_{corona}})}{\pi r^2 L} \quad \text{(Eq.S7)}$$

When simplifying this expression, it becomes apparent that the cancelation of L reduces this to a two-dimensional problem (L-independent):

$$x = \frac{\rho_{material}}{\rho_{core} + \frac{f_{corona}}{1 - f_{corona}}\rho_{corona}} (\frac{d_{m-m}^{2}\gamma}{\pi r^2} - 1 - \frac{f_{corona}}{1 - f_{corona}}) \quad \text{(Eq.S8)}$$

For convenience, a convolved-density term is defined to simplify the pre-factor:

$$\beta = \frac{\rho_{core} + \frac{f_{corona}}{1 - f_{corona}}\rho_{corona}}{\rho_{material}} \quad \text{(Eq.S9)}$$

Using this pre-factor, equation S8 can be solved for the cylinder radius to yield:

$$r = d_{m-m}\sqrt{\frac{\gamma}{\pi}}(x\beta + 1 + \frac{f_{corona}}{1 - f_{corona}})^{-1/2} \quad \text{(Eq.S10)}$$

The $d_{m\text{-}m}$ value is derivable from the SAXS d-spacing when the structure factor scalar, S_{PMT}, is known such that:

$$S_{PMT} = \frac{d_{m-m}}{d_{spacing}} \quad \text{(Eq.S11)}$$

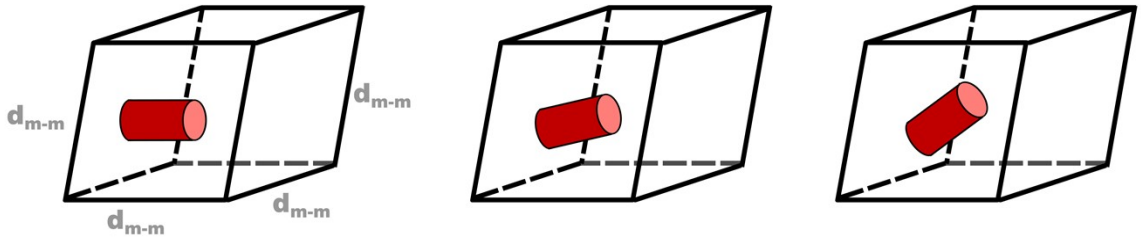
Equations S10 and S11 can be combined and expressed in terms of the micelle diameter (D=2r) to yield:

$$d_{spacing} = \frac{D}{2S}\sqrt{\frac{\pi}{\gamma}}(x\beta + 1 + \frac{f_{corona}}{1 - f_{corona}})^{1/2} \quad \text{(Eq.S12)}$$

Please note the power of ½ in equation S12 arises from the cancelation of cylinder length (equation S8) which reduces the dimensionality and corresponds to two-dimensional area conservation. This is distinct from the power of 1/3 that was found in all prior PMT models which were rather based on spheres and volume conservation.

3D PMT Model for Non-Aligned Cylinders

When the cylinders are not aligned, the geometry is more analogous to the original PMT model derivation.[1] Here, it will be shown that the lack of cylinder alignment prevents the geometric equations from reducing to two dimensions. Please note that the following derivation is in the spirit of crystallographic analogs, however, the rotational freedom makes this rather a descriptor of a "representative volume unit."



Here the representative parallelepiped has a total volume of:

$$V_{unitcell} = \gamma d_{m-m}^{3} \quad \text{(Eq.S13)}$$

$V_{template}$ remains the same as expressed by equation S2.

The remaining volume is occupied by the matrix which is a combination of the material and the corona chains:

$$V_{matrix} = V_{material} + V_{corona} = d_{m-m}^{3}\gamma - \pi r^2 L \quad \text{(Eq.S14)}$$

Please note that the full cylinder volume is considered, regardless of the size of the unit cell size. In this sense the geometry represents the average volume occupied by cylinders. The volume of corona remains the same as expressed by equation S4.

The combination of equations S13, S14, S2, and S4 allows one to solve for $V_{material}$:

$$V_{material} = V_{matrix} - V_{corona} = d_{m-m}^{3}\gamma - \pi r^2 L\left(1 + \frac{f_{corona}}{1 - f_{corona}}\right) \quad \text{(Eq.S15)}$$

The material:template mass ratio, X, remains the same as defined by equation S6.

X can be expressed by combining equation S6 with S2, S4 and S15 to yield:

$$x = \frac{\rho_{material}}{\rho_{core} + \frac{f_{corona}}{1 - f_{corona}}\rho_{corona}}\left(\frac{d_{m-m}^{3}\gamma}{\pi r^2 L} - 1 - \frac{f_{corona}}{1 - f_{corona}}\right) \quad \text{(Eq.S16)}$$

The same convolved-density term, β, is used as defined in S9.

The combination of equations S6 and S16 can be used to solve for the cylinder radius:

$$r = d_{m-m}^{3/2}\sqrt{\frac{\gamma}{\pi L}}(x\beta + 1 + \frac{f_{corona}}{1 - f_{corona}})^{-1/2} \quad \text{(Eq.S17)}$$

The same definition of S_{PMT} is used as specified in equation S11.

Combining equation S11 with S17 allows one to solve for $d_{spacing}$ as expressed in terms of the micelle diameter (D=2r) to yield:

$$d_{spacing} = \left(\frac{D^{2/3}}{S * \sqrt[3]{4}}\right) * \sqrt[3]{\frac{\pi L}{\gamma}}(x\beta + 1 + \frac{f_{corona}}{1 - f_{corona}})^{1/3} \quad \text{(Eq.S18)}$$

Please note that the final power of 1/3 on the last quantity arises from the 3D character of the representative volume since the L term did not cancel itself out in the case of non-aligned cylinders.

Table S2: 3D PMT fit parameters for OS ShortCyls.

	3D PMT model
α[1]	1.11
β[1]	0.91
γ[1]	1
L (nm)[3]	266
f_{PEO}[2]	0.260
S_{PMT}[1]	1.95
Pore/Template Diameter[3] (nm)	62.8

[1]Determined from the least squares fitting within the PMT window
[2]Determined from the ^{1}H-NMR and the densities of the polymer blocks
[3]Determined by SEM measurements

Table S3: 2D PMT fit parameters for OS LongCyls

	2D PMT model
α^1	1.40
β^1	0.486
γ^1	0.5610
f_{PEO}^2	0.260
S_{PMT}^1	1.64
Pore/Template Diameter[3] (nm)	60.4

[1]Determined from the least squares fitting within the PMT window
[2]Determined from the ^{1}H-NMR and the densities of the polymer blocks
[3]Determined by averaging the pore diameter measured by SEM

Reference

(1) Sarkar, A.; Stefik, M. How to make persistent micelle templates in 24 hours and know it using X-ray scattering. *J. Mater. Chem. A* **2017**, *5* (23), 11840-11853. DOI: 10.1039/C7TA01034F.