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Electronic Supplementary Information

How to Make Persistent Micelle Templates in 24 Hours and Know It using X-ray Scattering

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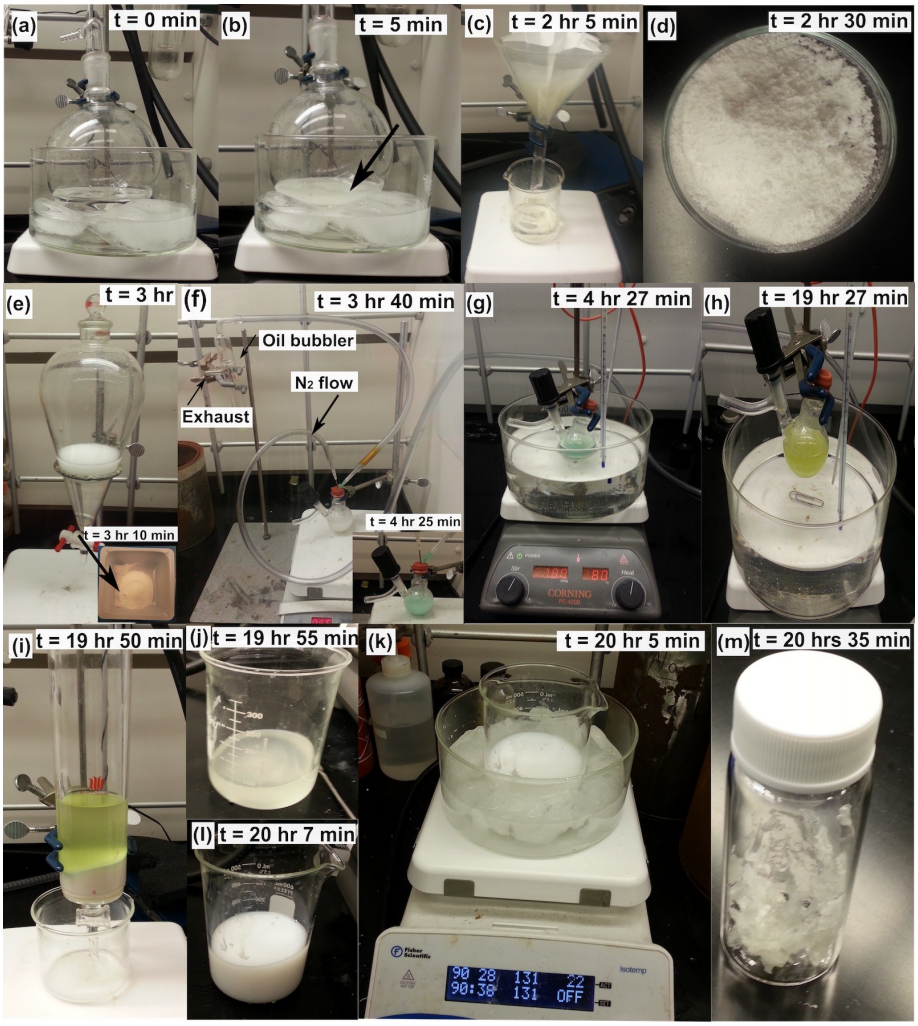


Fig. S1. Photographs of each step of the PEO-*b*-PHA synthesis, dissolution of PEO-OH (a) followed by the addition of DCC and DMAP (b), filtration (c), recovery of crude PEO-Br (d), purification of PEO-Br (e), sparging the polymerization solution (f), ATRP reaction (g-h), removal of copper salts (i-j), precipitation (k-l) and recovery of pure PEO-*b*-PHA after solvent evaporation (m).

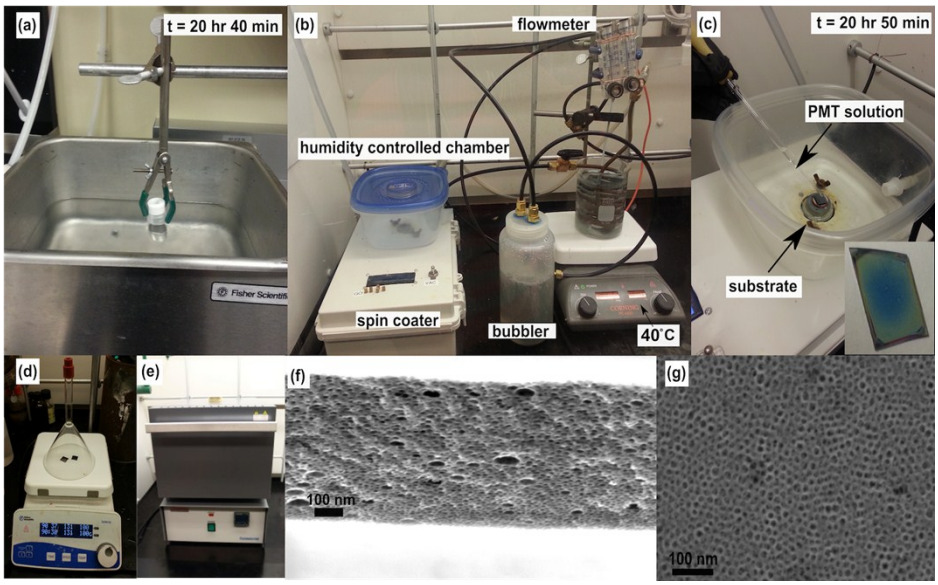


Fig. S2. Photographs of micelle templating steps, including sonication induced exchange of micelle solution (a), home-made spin coater with humidity control (b), application of solution to substrate (normally performed through a hole in the lid) (c), prompt sample aging (d). Some samples were calcined (e), for SEM imaging in cross-section (f), and top-view (g).

Table S1. Change of PEO-*b*-PHA micelles with sonication induced exchange as measured by DLS.

Sample	Average Hydrodynamic Diameter (nm)	Standard deviation (nm)	Standard Deviation/Average (%)
As micellized	**33.5**	**7.31**	**21.8%**
Sonicated 5 min	**21.4**	**3.12**	**14.6%**

Table S2. PEO-*b*-PHA synthesis conditions

Trials	[M]:[I]:[Cu(I)]:[L]	Temp (˚C)	Reaction Time (hr)	Đ[a]	% monomer conversion[b]
1	100:1:0.25:0.25[c]	70	15	1.36	70
2	100:1:0.50:0.50[c]	70	10	1.11	28
3	100:1:0.50:0.50[c]	80	15	1.10	49
4	100:1:0.50:0.50[c]	100	18	1.53	71
5	100:1:1:1[c]	70	15	1.89	87
6	100:1:1:1[d]	70	15	1.13	20
7	100:1:1:1[d]	70	24	1.15	50

[a] obtained from GPC analysis, [b] calculated using ^{1}H NMR, [c] Me6TREN and [d] HMTETA were used as ligands

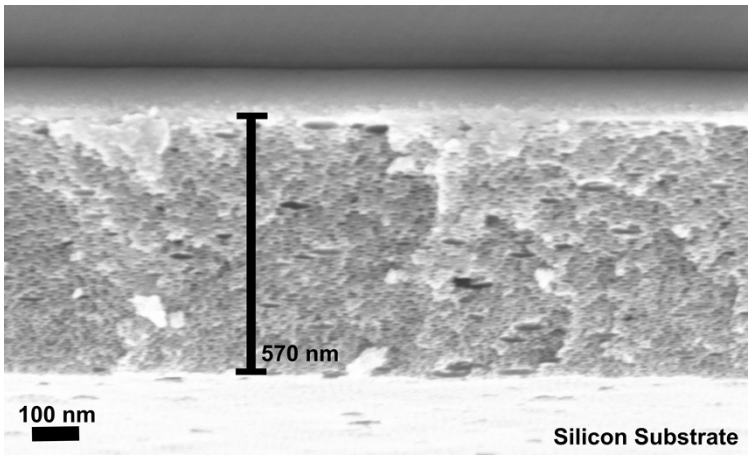


Fig. S3 Cross-sectional SEM image of micelle template sample from series W7.5 where the nominal film thickness was 570 nm.

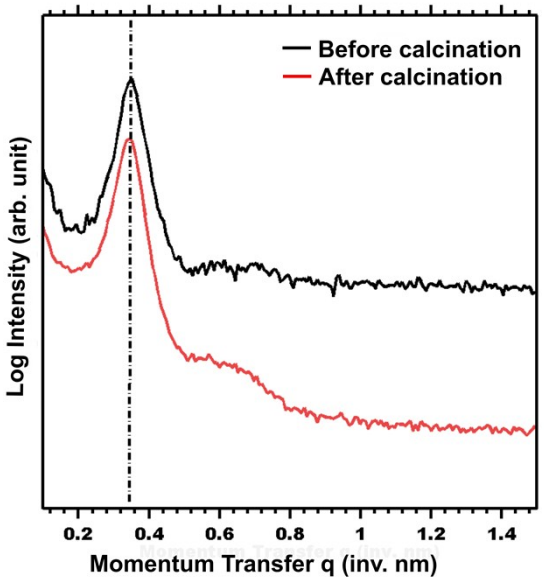


Fig. S4 Azimuthally integrated SAXS data from sample **W7.5-1.21** before and after calcination. The dashed line indicates that the primary peak position was preserved, suggesting preservation of the in-plane lattice constant.

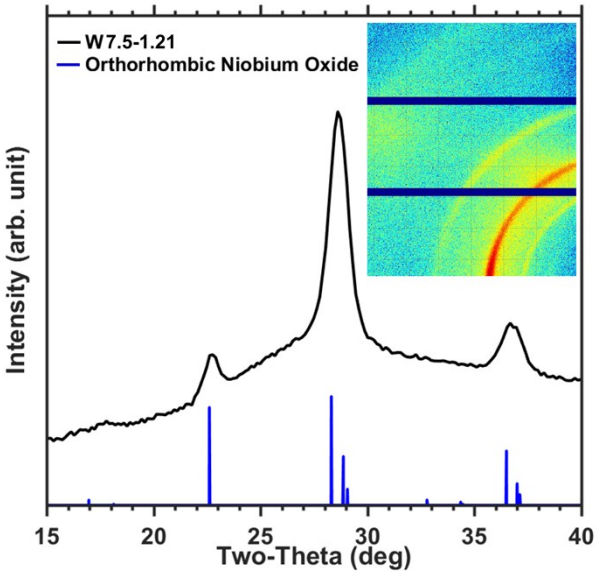


Fig. S5. GIWAXS of sample **W7.5-1.21** after calcination to 500˚C demonstrating crystalline Nb_2O_5 consistent with PDF#27-1003. The 2D image was inset where the color scale corresponds to the log of X-ray intensity.

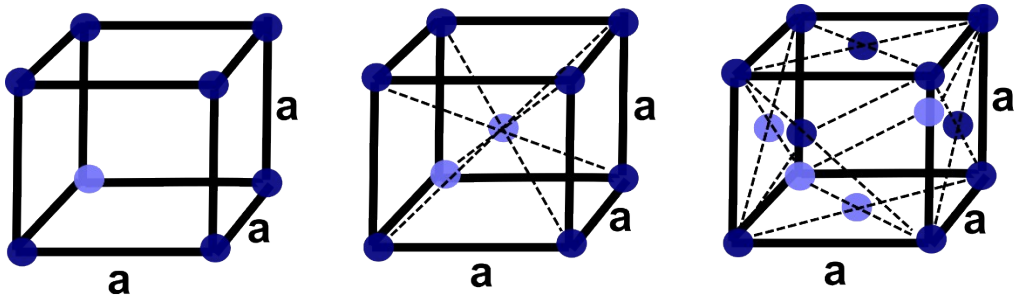
Derivation of SAXS based Geometric Models

Calculations based on SAXS measurements provide the fundamental micelle-to-micelle spacing. First, we will start with simple cubic structures and consider two configurations of the micelles relative to the material. Then we will show an extension to a general case. The general case uses a simple correlation of SAXS and real-space measurements to enable modeling without identification of the specific space group. This extension to generic primitive lattices accommodates paracrystalline arrangements containing disorder.

The sample preparation conditions define an anticipated volume fraction for each component based upon the amount of material added relative to the amount of template. The use of density terms allows conversion of these volume fractions to the internal morphology separation of template and material. Thus knowledge of the micelle-to-micelle spacing enables deconvolution of template and material dimensions based on a density term and the material:template (M:T) ratio. Two models are considered, differing based upon the interaction of the corona block with the material being templated.

Whole Micelle Template (WMT) Model:

Consider a simple cubic (SC), body-centered cubic (BCC), or face-centered cubic (FCC) lattice:



The WMT model assumes that the material being templated is excluded from the entire volume of the micelle (manuscript **Scheme 1** top). Thus the template volume ($V_{template}$) per unit cell is a function of the sphere radius, r, and the number of spheres per unit cell, n:

$$V_{template} = \frac{4n\pi r^3}{3} \quad \text{(eq 1)}$$

Here, n = 1 for a simple cubic lattice, n = 2 for a body-centered cubic lattice, and n = 3 for a face-centered cubic lattice.

The matrix volume is occupied solely by the material being templated. Since the total volume of the unit cell is a^3, the volume of matrix per unit cell is:

$$V_{material} = a^3 - \frac{4n\pi r^3}{3} \quad \text{(eq 2)}$$

where the lattice constant is a. The material:template mass ratio (M:T=x) is used as a convenient handle to quantify titration of material into a micelle template solution. The definition of x is thus:

$$x \equiv \frac{m_{material}}{m_{template}} = \frac{V_{material}\rho_{material}}{V_{template}\rho_{template}} \quad \text{(eq 3)}$$

where ρ terms correspond to component densities. Combining equations (1) and (2) into (3) yields:

$$x = \frac{\rho_{material}\left(a^3 - \frac{4n\pi r^3}{3}\right)}{\frac{4n\pi r^3}{3}\rho_{template}} \quad \text{(eq 4)}$$

This equation may be reorganized after solving for template sphere radius, r, to yield:

$$r = a\sqrt[3]{\frac{3}{4n\pi\left(1 + x\frac{\rho_{template}}{\rho_{material}}\right)}} \quad \text{(eq 5)}$$

The density terms are combined for fitting a single convolved density term β defined as:

$$\beta_{wmt} \equiv \frac{\rho_{template}}{\rho_{material}} \quad \text{(eq 6)}$$

The template or pore radius may thus be predicted based upon a lattice measurement by SAXS (a), the M:T ratio (x), and a single fit parameter for relative densities, β:

$$r = a\sqrt[3]{\frac{3}{4n\pi\left(1 + x\beta_{wmt}\right)}} \quad \text{(eq 7)}$$

The micelle or pore diameter, D, is found simply by multiplying this radius by 2. This cubic form of the WMT model will later be extended to non-cubic or disordered systems by accounting for the specific relationship of micelle-to-micelle spacing to the observed by SAXS peak.

Micelle Core Template (MCT) Model:

The MCT model assumes that the material being templated is excluded from the core of the micelle (manuscript **Scheme 1** bottom). Thus the template volume per unit cell ($V_{template}$) is a function of the sphere radius, r, and the number of spheres per unit cell, n:

$$V_{template} = V_{core} = \frac{4n\pi r^3}{3} \quad \text{(eq 8)}$$

Here we address a few cubic lattices where n = 1 for a simple cubic, n = 2 for a body-centered cubic, and n = 3 for a face-centered cubic. The matrix volume is occupied by a combination of the material being template and the corona chains, in this case PEO. Since the total volume of the unit cell is a^3, the volume of matrix per unit cell is:

$$V_{matrix} = a^3 - \frac{4n\pi r^3}{3} = V_{material} + V_{corona} \quad \text{(eq 9)}$$

Again, the material:template mass ratio (M:T=x) is used as a convenient handle to quantify the titration of materials into a micelle template solution. Please note that for experimental convenience, we define the template mass as the total polymer mass, including both core are corona. The definition of x is the same as before, however the expression of x in terms of material volumes and densities changes somewhat:

$$x \equiv \frac{material}{template} = \frac{V_{material}\rho_{material}}{V_{core}\rho_{core} + V_{corona}\rho_{corona}} \quad \text{(eq 10)}$$

where volume terms V are for each component per unit cell and density terms are for each component. The corona volume per unit cell may be found based on the volume fractions of the block copolymer where:

$$V_{corona} = V_{template}\frac{f_{corona}}{1 - f_{corona}} \quad \text{(eq 11)}$$

In this manuscript, PEO is the corona block and PHA is the core/template block. Substituting equation 8, 9, and 11 into equation 10 yields an equation that may be simplified to:

$$x = \frac{\rho_{material}}{\rho_{core} + \frac{f_{corona}}{1-f_{corona}}\rho_{corona}} \left(\frac{3a^3}{4n\pi r^3} - 1 - \frac{f_{corona}}{1 - f_{corona}} \right) \quad \text{(eq 12)}$$

Solving (12) for radius yields the following expression:

$$r = a\sqrt[3]{\frac{3}{4n\pi}} \left(\frac{x}{\left(\frac{\rho_{material}}{\rho_{core} + \frac{f_{corona}}{1-f_{corona}}\rho_{corona}} \right)} + 1 + \frac{f_{corona}}{1 - f_{corona}} \right)^{-1/3} \quad \text{(eq 13)}$$

that may be simplified by defining a relative density parameter as:

$$\beta_{mct} \equiv \frac{\rho_{core} + \frac{f_{corona}}{1-f_{corona}}\rho_{corona}}{\rho_{material}} \quad \text{(eq 14)}$$

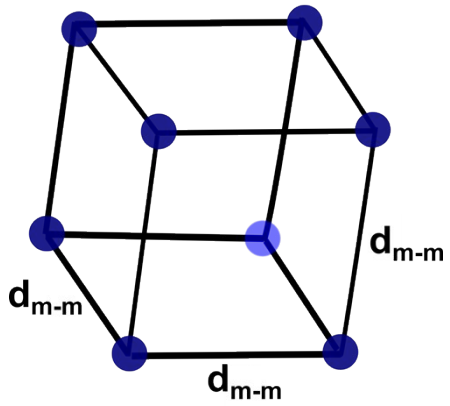
Substituting (14) into (15) yields the simplified expression:

$$r = a\sqrt[3]{\frac{3}{4n\pi}} \left(x\beta_{mct} + 1 + \frac{f_{corona}}{1 - f_{corona}} \right)^{-1/3} \quad (15)$$

Again, the template or pore diameter, D, is found simply by multiplying this radius by 2. This cubic form of the MCT model will next be extended to non-cubic or paracrystalline systems.

Triclinic and Paracrystalline Systems

Consider a primitive cell that is equilateral and triclinic:



This parallelepiped imposes a geometric constraint similar to the cubic cases above based upon the relative volume fractions of each component. For the non-cubic MCT case, equation 8 remains unchanged with n=1. However, the unit cell volume scales with the micelle-to-micelle spacing as:

$$V_{unitcell} = \gamma d_{m-m}^3 \quad (16)$$

where γ is a scalar less than or equal to 1.0 and d_{m-m} is the micelle-to-micelle spacing. The d_{m-m} may be found from SAXS measurements after establishing a correlation with real-space data, using a scalar conversion, S:

$$S = \frac{d_{m-m}}{d_{spacing}} = \frac{q d_{m-m}}{2\pi} \quad (17)$$

where q is an easily tracked structure factor feature such as a maximum or minimum in SAXS. Here we used the first SAXS maxima for the presented data in the manuscript. The MCT matrix volume may then be expressed as:

$$V_{matrix} = V_{material} + V_{corona} = \gamma d_{m-m}^3 - \frac{4\pi r^3}{3} \quad (18)$$

Substituting equations 8, 11, and 18 into equation 10 may be simplified to yield:

$$x = \frac{\rho_{material}}{\rho_{core} + \frac{f_{corona}}{1-f_{corona}}\rho_{corona}} \left(\frac{3\gamma d_{m-m}^3}{4\pi r^3} - 1 - \frac{f_{corona}}{1-f_{corona}} \right) \quad (19)$$

This may be solved for radius, yielding:

$$r = d_{m-m}\sqrt[3]{\frac{3\gamma}{4\pi}}\left(x\beta_{mct} + 1 + \frac{f_{corona}}{1 - f_{corona}}\right)^{-1/3} \quad (20)$$

Again, the template or pore diameter, D, is found simply by multiplying this radius by 2. This generic form of the MCT model may be used to extract pore dimensions from SAXS data using directly measured values (S and f) and two fit paramters (ϒ and β). Please note the similarity to equation 15, the MCT model for cubic systems. In the context of micelle templates, we expect typical ϒ values to be ~1, with limited distortion.

A similar derivation for the non-cubic WMT model yields a result closely related to equation 7:

$$r = d_{m-m}\sqrt[3]{\frac{3\gamma}{4\pi\left(1 + x\beta_{wmt}\right)}} \quad (21)$$

The Material Wall-Thickness Derivation

The WMT and MCT models provide the template/pore dimensions. The material wall-thickness is a natural outcome from identifying component geometries, independent of which model was used. One added complexity is that material wall-thickness varies with crystallographic direction. For example, the wall-thicknesses in major directions of a BCC lattice are:

$$w_{100} = a - D$$

$$w_{110} = \sqrt{2}a - D$$

$$w_{111} = \frac{\sqrt{3}}{2}a - D \quad \text{(eq 22-24)}$$

Considering the convoluted distribution wall-thicknesses, we propose an expression for the nominal wall-thickness using an additional fit term, α to accommodate the variable distribution of wall-thickness contributions for any candidate lattice:

$$w = (\alpha a - D) \quad \text{(eq 25)}$$

For cubic crystal systems, we anticipate that alpha values ~1±0.5 to be typical.

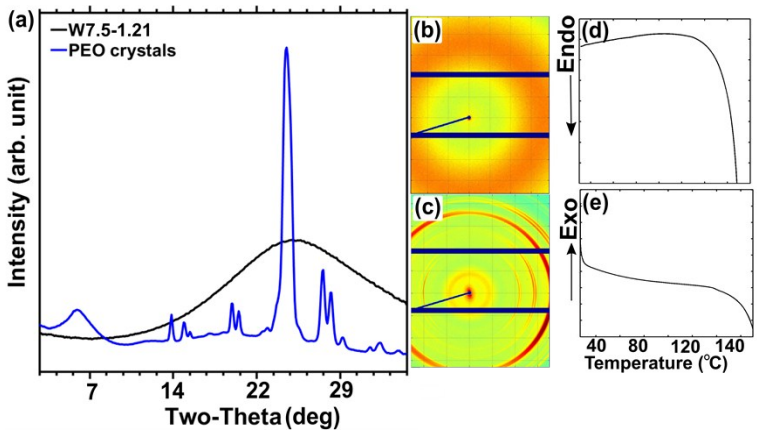


Fig. S6 WAXS of sample **W7.5-1.21** (a,b) and PEO crystals (a,c). The lack of PEO crystallites in templated films suggests that the PEO corona are mixed with the material**.** DSC data of **W7.5-1.21** also lacked any observable PEO crystallization, also suggesting PEO corona mixing with the material being template (d-e).

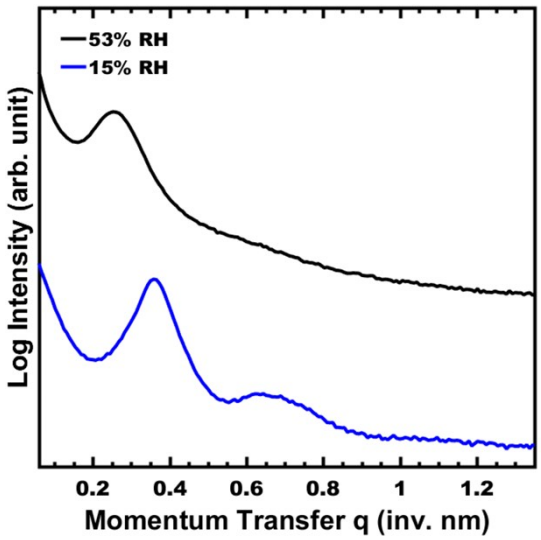


Fig. S7 1D SAXS plot of micelle template samples prepared under different relative humidity conditions.

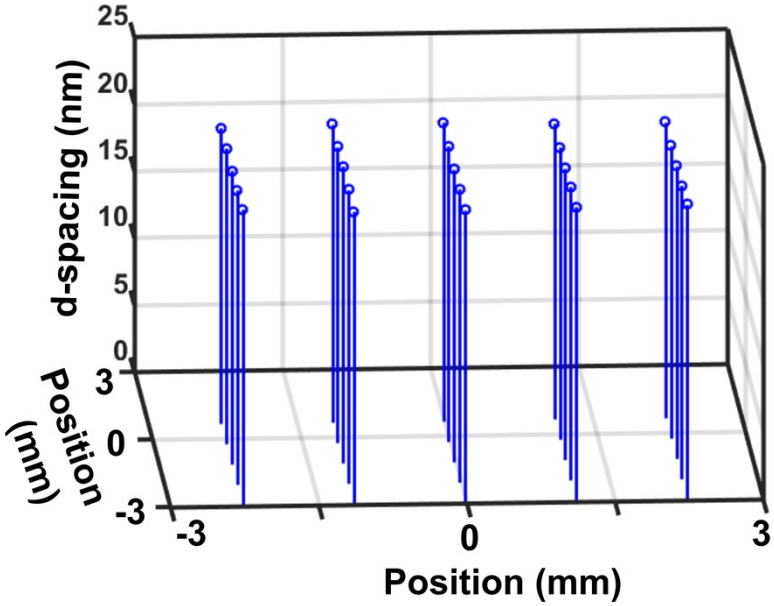


Fig. S8 Map of SAXS d-spacing uniformity across a 6x6 mm^2 area of a sample **W-7.5-1.19**. The X and Y axis correspond to sample position and the d-spacing was calculated was the best-fit of the first SAXS peak. A total of 25 measurements were taken. The average d-spacing was 21.95 nm with a standard deviation of 0.145 nm, corresponding to <1% variation.

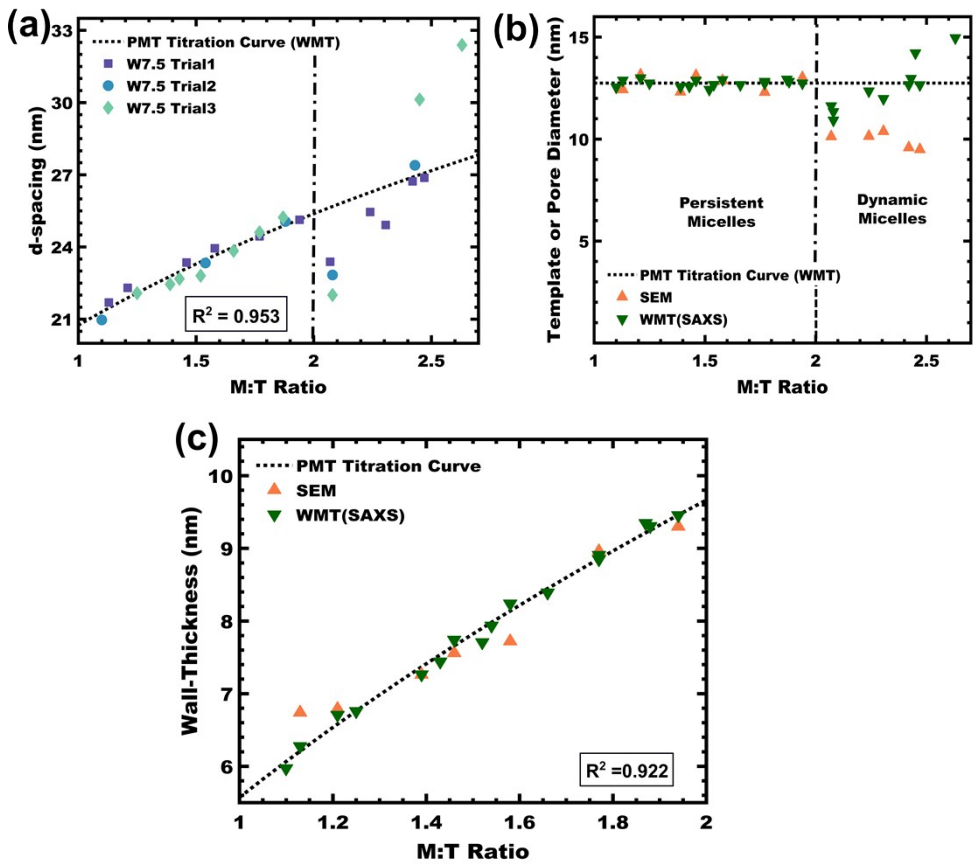


Figure S9. Best fit results for the combined 3 trial runs of sample series **W7.5** using the WMT model for d-spacing (a), pore diameter (b), and wall-thickness (c). PMT titration curves are shown as dotted lines and feature sizes were separately calculated based on each SAXS pattern as compared to SEM data.

Table S3. Calculations resulting from the best fit evaluation of the WMT model with sample series **W7.5**. **.**

Sample Name	PMT Titration Curve (WMT model)			WMT Interpretation of SAXS Data	
	d-spacing (nm)	Pore Size (nm)	Wall-Thickness (nm)	Pore Size (nm)	Wall-Thickness (nm)
W7.5-1.13	21.46	12.74	6.21	12.88	6.27
W7.5-1.21	21.88	12.74	6.58	12.99	6.71
W7.5-1.39	22.78	12.74	7.37	12.56	7.26
W7.5-1.46	23.11	12.74	7.66	12.88	7.74

W7.5-1.58	**23.65**	**12.74**	**8.14**	**12.90**	**8.24**
W7.5-1.77	**24.46**	**12.74**	**8.85**	**12.73**	**8.85**
W7.5-1.94	**25.14**	**12.74**	**9.46**	**12.74**	**9.45**
W7.5-2.07	**25.64**	**12.74**	**9.90**	**11.62**	**9.03**
W7.5-2.24	**26.27**	**12.74**	**10.45**	**12.35**	**10.13**
W7.5-2.30	**26.50**	**12.74**	**10.66**	**11.98**	**10.02**
W7.5-2.42	**26.90**	**12.74**	**11.01**	**12.66**	**10.93**
W7.5-2.47	**27.07**	**12.74**	**11.16**	**12.65**	**11.08**

Table S4. Best fit parameters for the WMT model

α	**0.99**[a]
β density	**4.9316**[a]
PEO volume fraction	**38%**[b]
S	**0.8963**[c]
ϒ	**1.00**[a]
[g] **Pore size (nm)**	**12.74**[d]

[a] determined by least squares fitting within PMT window
[b] determined by NMR analysis of polymer
[c] average S value for all samples within PMT window determine by SEM and SAXS
[d] average pore data for all samples within PMT window.

Table S5. MCT model calculations for series **W7.5** based upon fit values established from a limited dataset that included SEM measurements from a single sample **W7.5-1.13** and all SAXS data

Sample Name	**PMT Titration Curve (MCT Model)**			**MCT Interpretation of SAXS Data**	
	d-spacing (nm)	**Pore Size (nm)**	**Wall-Thickness (nm)**	**Pore Size (nm)**	**Wall-Thickness (nm)**
W7.5-1.13	**21.63**	**12.43**	**6.74**	**12.21**	**7.01**

W7.5-1.21	**22.01**	**12.43**	**7.08**	**12.35**	**7.41**
W7.5-1.39	**22.83**	**12.43**	**7.80**	**12.01**	**7.88**
W7.5-1.46	**23.13**	**12.43**	**8.07**	**12.34**	**8.35**
W7.5-1.58	**23.63**	**12.43**	**8.51**	**12.40**	**8.82**
W7.5-1.77	**24.38**	**12.43**	**9.18**	**12.28**	**9.38**
W7.5-1.94	**25.02**	**12.43**	**9.74**	**12.32**	**9.95**
W7.5-2.07	**25.48**	**12.43**	**10.15**	**11.26**	**9.46**
W7.5-2.24	**26.06**	**12.43**	**10.67**	**12.00**	**10.56**
W7.5-2.30	**26.28**	**12.43**	**10.86**	**11.65**	**10.43**
W7.5-2.42	**26.65**	**12.43**	**11.19**	**12.33**	**11.36**
W7.5-2.47	**26.81**	**12.43**	**11.33**	**12.32**	**11.49**

Table S6. Fit parameters for series **W7.5** established from a limited dataset that included SEM measurements from a single sample **W7.5-1.13** and all SAXS data

α	**1.09**[a]
β density	**3.6281**[a]
PEO volume fraction	**38%**[b]
S	**0.8113**[c]
ϒ	**1.00**[a]
[h]**Pore size (nm)**	**12.43**[d]

[a] determined by least squares fitting within PMT window
[b] determined by NMR analysis of polymer
[c] S value for samples **W7.5-1.13** determined by SEM and SAXS
[d] average of pore size of sample **W7.5-1.13**