Supplementary Information

Fabrication and 3D Tomographic Characterization of Nanowire Arrays and Meshes with Tunable Dimensions from Shear-Aligned Block Copolymers

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Quantification of alignment quality

To characterize the quality of metal nanowire arrays fabricated by shear alignment, we chose to image samples by AFM after polymer removal, which made any discontinuities in the nanowires more evident than when imaging prior to polymer removal (see Figure S1 for example). To quantify the alignment quality of the arrays from the AFM images, we utilized an image analysis program by Murphy *et al.* called Automated Defect Analysis of Block Copolymers (ADAblock).[1] The program was written to identify and quantify the types and number of defects (primarily terminations and junctions) present in SEM images of lamellar and cylindrical BCPs, but the same analysis can be applied to AFM images of ordered nanowires. ADAblock also computes Hermans orientation parameter, *f*, which is a mathematical construct commonly used to quantify the orientation of fibers relative to a fixed direction and is calculated for a 2D system as:[2]

$$f = 2\langle \cos^2(\theta - \theta_r) \rangle - 1$$

$\frac{3\langle \cos(\theta\text{-}\theta_r) \rangle\text{-}1}{2}$where θ is the angle of a fiber -- or in our case nanowire -- and θ_r is a specified reference angle, which was the average orientation over the entire image. This value can range from 0 to 1, where a value of 1 indicates that all the fibers are perfectly straight and parallel with the specified angle and a value of 0 indicates that all the fibers are randomly oriented.

Defect analysis was performed on 1x1 μm AFM images for the 48.5-14.5 kg/mol, 68.5-26 kg/mol, and 79-36.5 kg/mol PS-P2VP and 1.5x1.5 μm images for the 110-52 kg/mol PS-P2VP since the higher molecular weight block copolymer had less wires per unit area. Nanowire heights and periodicities were measured from AFM images, averaged across nine 1 μm lineouts from a minimum of eight samples. Nanowire widths were measured with SEM across a representative sample.

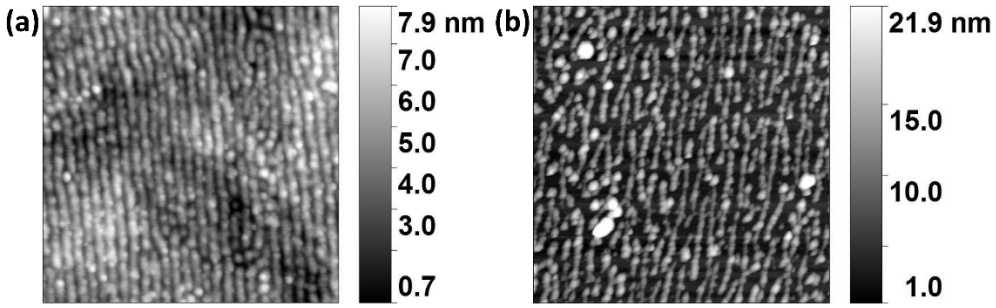

Figure S1. AFM height images of a shear-aligned and Pt-infiltrated PS-P2VP film **(a)** before and **(b)** after removal of the block copolymer – an illustrative example of how the true quality of the metal nanowires may not be apparent until after polymer removal. Images are of 1 μm x 1 μm areas.

Optimization experiments

To reduce our experimental parameter space, we kept the shear stress at which we aligned our polymers constant at 33kPa for 48-14 PS-P2VP and 45 kPa for all other molecular weight PS-P2VPs. We also kept the temperature at which the polymer film was aligned at 150°C, which is above the glass transition temperature (which is at least 102.7°C),[3] but significantly lower than the order-disorder transition temperature (ODT).[4]

We explored the effect of film thickness by creating series of samples with increasing film thickness for each molecular weight of PS-P2VP. We kept the shearing time constant at 2, 2, 2.5, and 3.5 hrs for all samples in the 48-14, 68-26, 79-36, and 110-52 PS-P2VP series, respectively, as these times were long enough to observe significant (though not necessarily optimal) alignment. Figure S2 shows the defect density (left y-axis, black open squares) and orientation parameter (right y-axis, blue filled squares) versus the film thickness for each PS-P2VP molecular weight. To compare the defect densities across the different molecular weights of block copolymers, which have varying wire densities, we normalize the measured defect densities (defects/area) by multiplying them by the square of the periodicity of that particular PS-P2VP.[5] Figure S3 shows representative progressive wire morphology as the film thickness increases.

The 68-26, 79-36, and 110-52 PS-P2VPs show a clearly defined and broad optimal thickness window, as represented by minima and maxima in defect densities and orientation parameters, respectively. However, this window is not as readily apparent in the lowest molecular weight PS-P2VP, 48-14, which has an initial defect minimum and orientation maximum at 40 nm but shows additional local minima and maxima at higher thicknesses (ca. 56 and 62 nm). Past the initial optimum at 40 nm, the wire morphology appears to consist of well aligned nanowires with clusters of defects, shown in Figure S4.

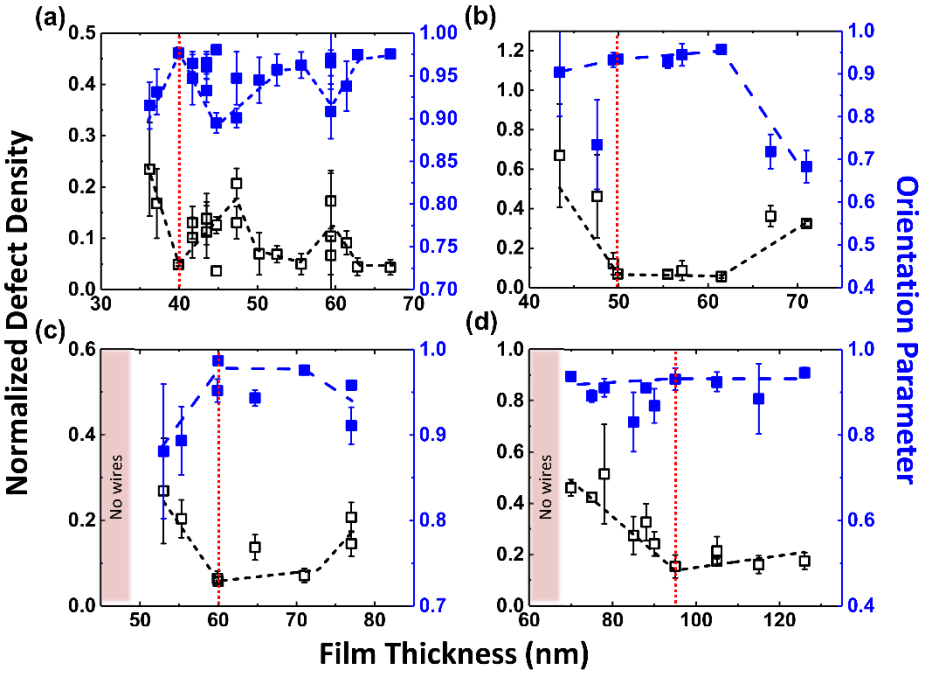

Figure S2. The normalized defect density (left axis, black open squares) and orientation parameter (right axis, blue filled squares) of nanowire arrays as a function of the polymer film thickness for each molecular weight PS-P2VP: **(a)** 48-14, **(b)** 68-26, **(c)** 79-36, and **(d)** 110-52 kg/mol. Each data point represents a separate sample on which multiple measurements were made. Dashed lines are provided as a guide for the eye. The minimum thicknesses for good alignment, defined as a maximization in orientation and concurrent minimization in defect density, are marked with red vertical dashed lines.

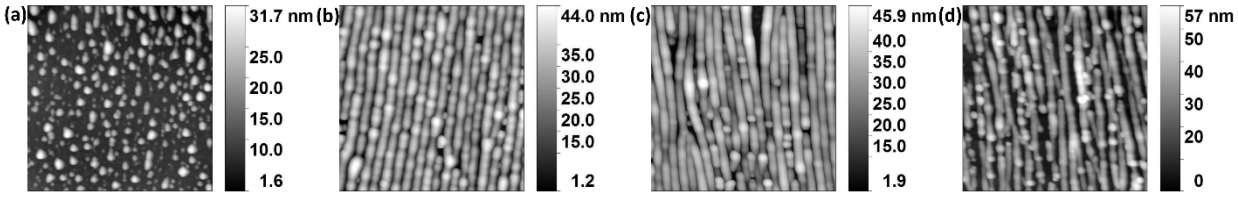

Figure S3. AFM height images showing the representative nanowire morphologies of shear-aligned films of 79-36 PS-P2VP that are **(a)** thinner (42.5 nm) than the minimum optimal thickness, resulting in sparse Pt features; **(b)** at the minimum optimal thickness (59.9 nm), resulting in well-aligned nanowires; and **(c, d)** thicker than the optimal film thickness (71 and 77 nm, respectively), resulting in increased nanowire roughness and branching. Images are of 1 μm x 1 μm areas.

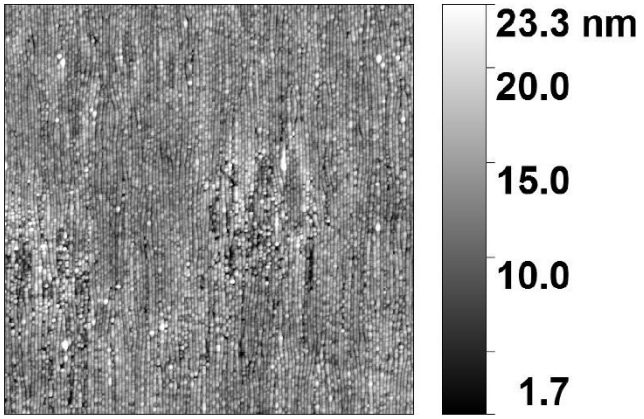

Figure S4. AFM height image showing the representative nanowire morphology of a shear-aligned 48-14 PS-P2VP film that is thicker than the optimum (63 nm instead of 40 nm). Image is of a 5 μm x 5 μm area.

Once the optimal film thickness was determined for each molecular weight PS-P2VP, we next kept film thickness constant and varied the amount of time the shear stresses were applied to further optimize Pt nanowire quality. We chose to maintain the film thicknesses at 40, 55, 60, and 95 nm for the 48-14, 68-26, 79-36, and 110-52 PS-P2VPs, respectively, as these thicknesses yielded maxima in alignment quality. Figure S5 depicts the normalized defect density (left y-axis, black open squares) and orientation parameter (right y-axis, blue filled squares) as a function of the shearing time for thin films of each molecular weight PS-P2VP. Figure S6 shows progressive representative wire morphology as shearing time is increased.

Optimal shearing conditions for each PS-P2VP are listed in Table S1 along with periodicities with and without shearing. Unsheared samples were solvent vapor annealed with toluene for 3.75 hr. Periodicity, defined here as the spacing between lines of spheres, was calculated with the equation $a\sqrt{3}/2$, where a is the average distance between sphere centers.[6]

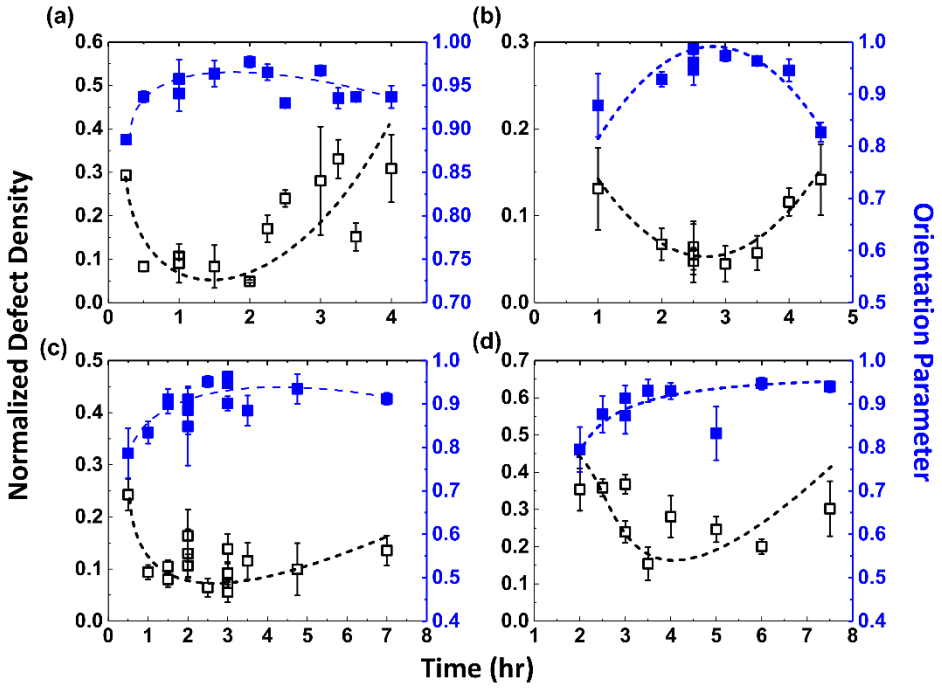

Figure S5. Normalized defect density (left axis, black open squares) and orientation parameter (right axis, blue filled squares) of nanowire arrays as a function of the duration of shear alignment for each molecular weight PS-P2VP: **(a)** 48-14, **(b)** 68-26, **(c)** 79-36, and **(d)** 110-52 kg/mol. Each data point represents a separate sample on which multiple measurements were made. Dashed lines are provided as a guide for the eye.

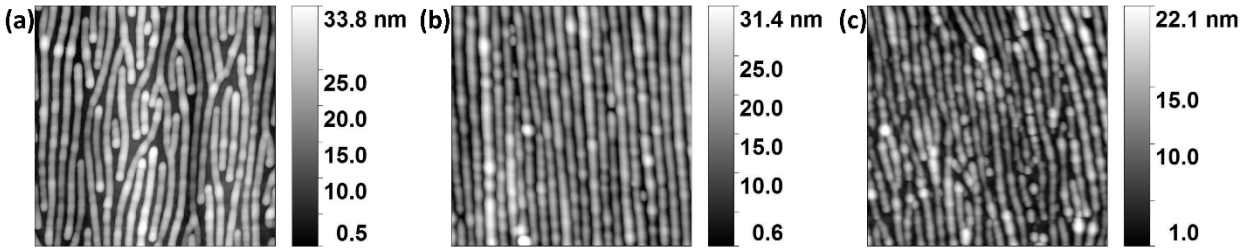

Figure S6. AFM height image showing the representative nanowire morphologies of 68.5-26 PS-P2VP that are **(a)** below the optimal shearing time (1 hr), resulting in poor alignment; **(b)** at the optimal shearing time (3 hrs), resulting in well aligned nanowires; and **(c)** above the optimal shearing time (4 hrs), resulting in a lower alignment quality. Images are of 1 μm x 1 μm areas.

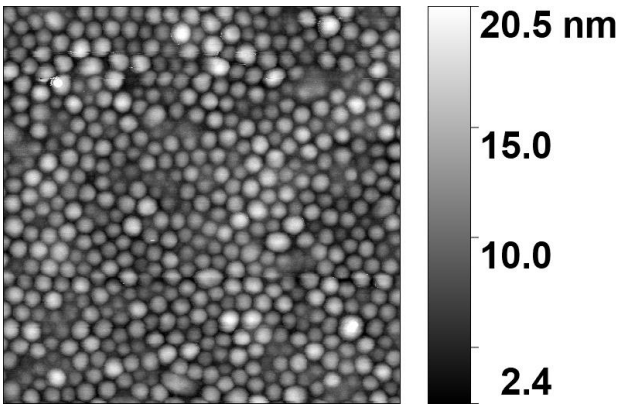

Figure S7. AFM height image of the 68-26k PS-P2VP film (55 nm) after thermally annealing for 3 hr at 150°C in the absence of shear forces. Image is of a 1 x 1 μm area. The P2VP phase was Pt infiltrated to improve contrast between polymer domains.

Table S1. Optimal shearing conditions and periodicity for each PS-P2VP studied.

PS-*b*-P2VP	Shear stress (kPa)	Film thickness (nm)	Shearing time (hr)	Periodicity (unsheared, nm)	Periodicity (sheared, nm)
48-14	33	40	2	36±6	37±3
68-26	45	55	3	41±6	43±2
79-36	45	60	3	44±8	47±3
110-52	45	95	3.5	59±10	63±4

Supplementary References

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2. U. Gedde, *Polymer Physics*, Springer Netherlands, 1 edn., 1999.
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6. Y.-R. Hong, D. H. Adamson, P. M. Chaikin and R. A. Register, *Soft Matter*, 2009, **5**, 1687-1691.