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Supplementary Information

Polyphthalaldehyde-*block*-Polystyrene as a Nanochannel Template

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Contents

S-1 Chemicals and Reagents

Styrene (Acros) was purified by passing through a column of basic alumina (Merck) prior to use. Copper(I) bromide (Sigma Aldrich) was purified by stirring in concentrated glacial acetic acid overnight at ambient conditions, then filtered off, dried under high vacuum and stored under argon. *N,N*-dimethylformamide (DMF, Fisher) was stored over activated molecular sieves and under argon prior to use. Methyl-2-bromopropionate (MBP, abcr), *N,N,N',N",N"*-pentamethyldiethylenetriamine (PMDETA, Acros), toluene (Acros), sodium azide (Acros), chloroform (VWR), glacial acetic acid (Roth), sulfuric acid (96%, Roth), hydrogen peroxide (35%, Roth), HPLC grade tetrahydrofuran (THF, Roth), ethanol (technical grade, VWR), and trifluoroacetic acid (TFA, Fluka) were used as received.

Silicon wafers (orientation <100>, B-doped, resistivity 5-20 Ω cm) with 50 nm thermal silicon dioxide (SiO_2) over-layer were purchased from Siegert Consulting e. K., Germany.

S-2 Instrumentation Methods

Size Exclusion Chromatography (SEC). Molecular weight determination was performed on a SEC system (PL-GPC 50 Plus, Polymer Laboratories) consisting of an auto injector, a guard column (PLgel Mixed C, 50 × 7.5 mm), three linear columns (PLgel Mixed C, 300 × 7.5 mm, 5 µm bead-size) and a differential refractive index detector using THF as the eluent at 35 °C and a flow rate of 1 $mL \cdot min^{-1}$. The system was calibrated using narrow polystyrene (PS) standards (Polymer Standards Service) ranging from 2000 to 2×10^6 $g \cdot mol^{-1}$. Samples were injected from solutions in THF (2 $mg \cdot mL^{-1}$) and molecular weights were deduced via the Mark–Houwink–Sakurada (MHS) parameters for polystyrene ($K = 14.1 \times 10^{-5}$ $dL \cdot g^{-1}$, $\alpha = 0.7$).

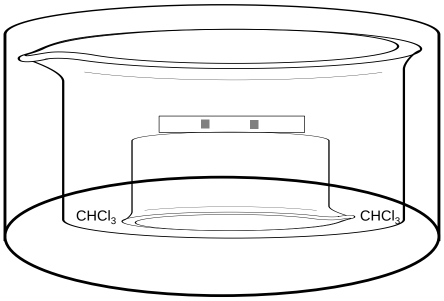
^{1}H NMR Spectroscopy. NMR spectroscopy was performed using a Bruker Avance III Microbay 400 spectrometer operating at 400 MHz. The samples were dissolved in $CDCl_3$, and the δ-scale was referenced to tetramethylsilane ($\delta = 0.00$ ppm) as internal standard.

Atomic Force Microscopy (AFM).

Sample Preparation:

<u>Spin-Coating</u>: One side polished silicon wafers (1 cm x 1 cm) with a 50 nm thermal silicon dioxide (SiO2) over-layer were subjected to fresh piranha solution (20 mL H_2SO_4, 10 mL H_2O_2) for 30 min. then rinsed with excess deionized water followed by a small amount of ethanol and dried under a stream of argon prior to spin coating. Spin-coating was performed at 1 wt% and 2 wt% of the block copolymer in both THF and chloroform using a Semiconductor Production Systems Spin 150 single wafer spin coater equipped with a diaphragm pump. The best AFM results were obtained from spin-coating at 1 wt% in THF at 2000 rpm while increasing to 3000 rpm, then allowed to spin at 3000 rpm for 60 seconds.

<u>Solvent Annealing</u>: Solvent annealing was performed in a chloroform rich environment by placing the sample surfaces on a glass slide atop an inverted pyrex dish (7 cm diameter × 4 cm height) in the middle of an upright second pyrex dish (11.5 cm diameter × 6.5 cm height) containing 30 mL chloroform which was subsequently covered by an inverted third pyrex dish (14 cm diameter × 7.5 cm height) for 30 min. at ambient temperature (21 °C).



Polyphthalaldehyde Block Removal: The polyphthalaldehyde block was removed by dripping eight 50 µL drops of concentrated TFA onto the sample surface and allowing for a 60 second incubation time followed by drying under a stream of compressed air for 60 seconds. The samples were then stored in a desiccator overnight before imaging.

Sample Measurements: Atomic force microscopy for surface morphology analysis was performed on a Multi Mode (Bruker) with an "E" scanner at a scan speed of 0.5 Hz, with a resolution of 512 lines and point, at a scan angle of 0°. The cantilever type was a Mikromasch HQ:NSC35/No Al (no metal coating), cantilever "C" with a spring constant of approximately 5.4 N/m. Scan sizes were made of 1 µm and 250 nm. The shown 3D images are a combination of the topography information (height) and the overlaid phase image.

Scratch-Analysis: Initially the film is scratched (90 µm scratch) in contact mode with force using an MFP-3D (Asylum Research) AFM equipped with a Mikromasch HQ:NSC18/No Al (no metal coating) cantilever and then reimaged with a 10 µm scan sized region in AC mode at a scan speed of 0.75 Hz, with a resolution of 512 lines and points, at a scan angle of 0°.

Scanning Electron Microscopy (SEM). The polystyrene nanochannel surface was analyzed on a Zeiss Supra 55. The surface was sputter-coated with approximately 4 nm of gold-palladium prior to imaging.

S-3 Synthesis

Synthesis of Azide Terminated Polystyrene. The azide terminated polystyrene was synthesized according to the literature.[1] Briefly, PS was prepared by ATRP ([Sty]/[MBP]/[CuBr]/[PMDETA]) 500:1:1:1, 40 vol % toluene, 77 °C). The polymerization was stopped after 24 hours by cooling in liquid nitrogen while exposing the reaction mixture to air. The mixture was diluted with THF and passed through a neutral alumina column to remove the catalyst. The bromine terminated PS polymer was then isolated by precipitation into methanol, filtered off and dried under high vacuum. The bromo-terminated polymer was subsequently reacted with NaN_3 (1.1 equiv) at ambient temperature in DMF (0.05 M-Br) for 24 hours to yield an azido-terminated polymers (PS-N3). The polymer was isolated by precipitation into methanol, filtered off and dried under high vacuum.

Synthesis of Alkyne Terminated Polyphthalaldehyde. The alkyne terminated polyphthalaldehyde was synthesized using a slightly modified procedure than previously reported.[2] In a glovebox, 10 mg of 9-anthracenemethanol and 500 mg of *ortho*-phthalaldehyde were added into a screw top vial and dissolved in 8 mL of dichloromethane (DCM). In two separate GPC vials, 1 equivalent of catalyst (*tert*-Butylimino-tris(dimethylamino)phosphorane; P_1-*t*-Bu, ~10mg) and 1 equivalent of pentynoic anhydride were dissolved in a small amount of DCM. Out of the glove box, the monomer/initiator solution was cooled to -90°C. Subsequently, the catalyst mixture is rapidly added to the monomer solution by the use of a syringe. After 10 minutes of reaction time, the quenching agent is added to the polymer solution and kept at -90°C for 15 minutes before the precipitation of PPA in cold methanol. The polymer is recovered by centrifugation and dried in a vacuum oven at ambient temperature (recovering yield ~70%).

Pentynoic anhydride is not commercially available and has been synthesized following a procedure reported in the literature.[3]

Synthesis of Polyphthalaldehyde-*b*-Polystyrene. The azido-terminated PS (1.0 equiv) and alkyne terminated PPA (1.0 equiv) were dissolved in DMF (0.05 M), purged with argon to remove oxygen, and subsequently transferred via cannula to a vial containing CuBr (0.5 equiv) and PMDETA (0.5 equiv) under an argon environment. The reaction was allowed to proceed at ambient temperature for 24 h. Next, the reaction mixture was exposed to air and the solution was passed through a column of neutral alumina and flushed with a small amount of THF. The PPA-*b*-PS was isolated by precipitating one time into methanol, filtered off and dried under high vacuum.

S-3 Supporting Figures

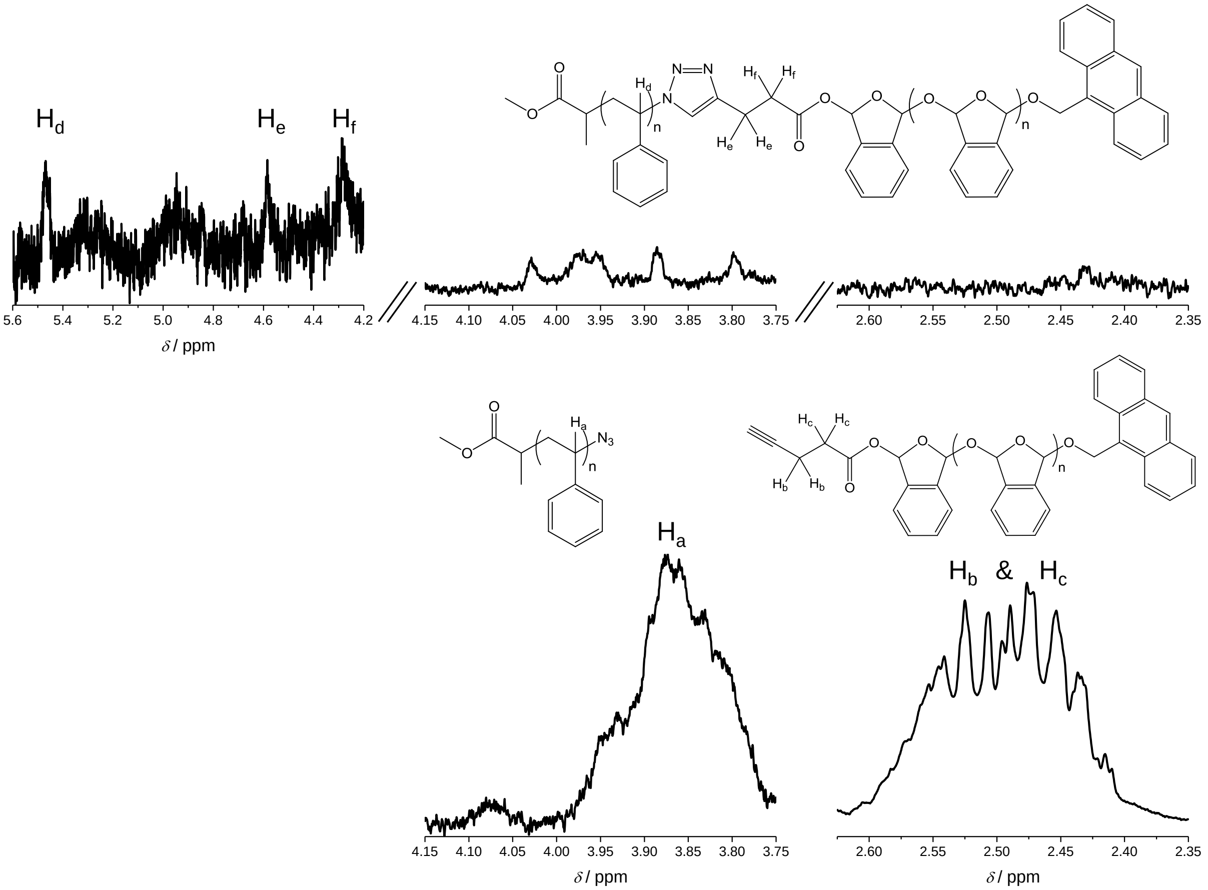
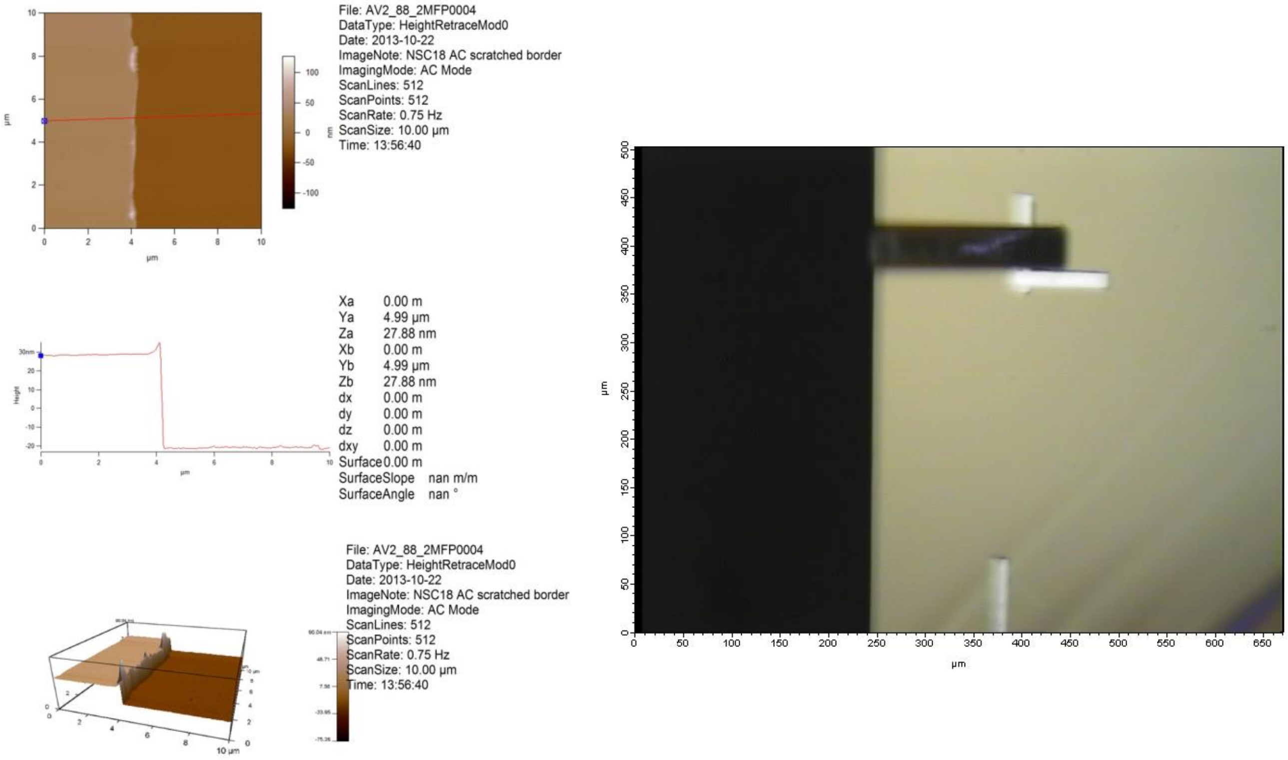


Figure S1. ^{1}H NMR spectra in the key regions of alkyne terminated PPA, azide terminated PS, and triazole containing PPA-*b*-PS.



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Za      27.88 nm
Xb      0.00 m
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Zb      27.88 nm
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dz      0.00 m
dxy     0.00 m
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SurfaceSlope   nan m/m
SurfaceAngle   nan °
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Figure S2. AFM scratch analysis to determine PPA-*b*-PS film thickness. It can be seen in the left middle image that the height changes from 30 to -20 nm indicating a film thickness of approximately 50 nm.

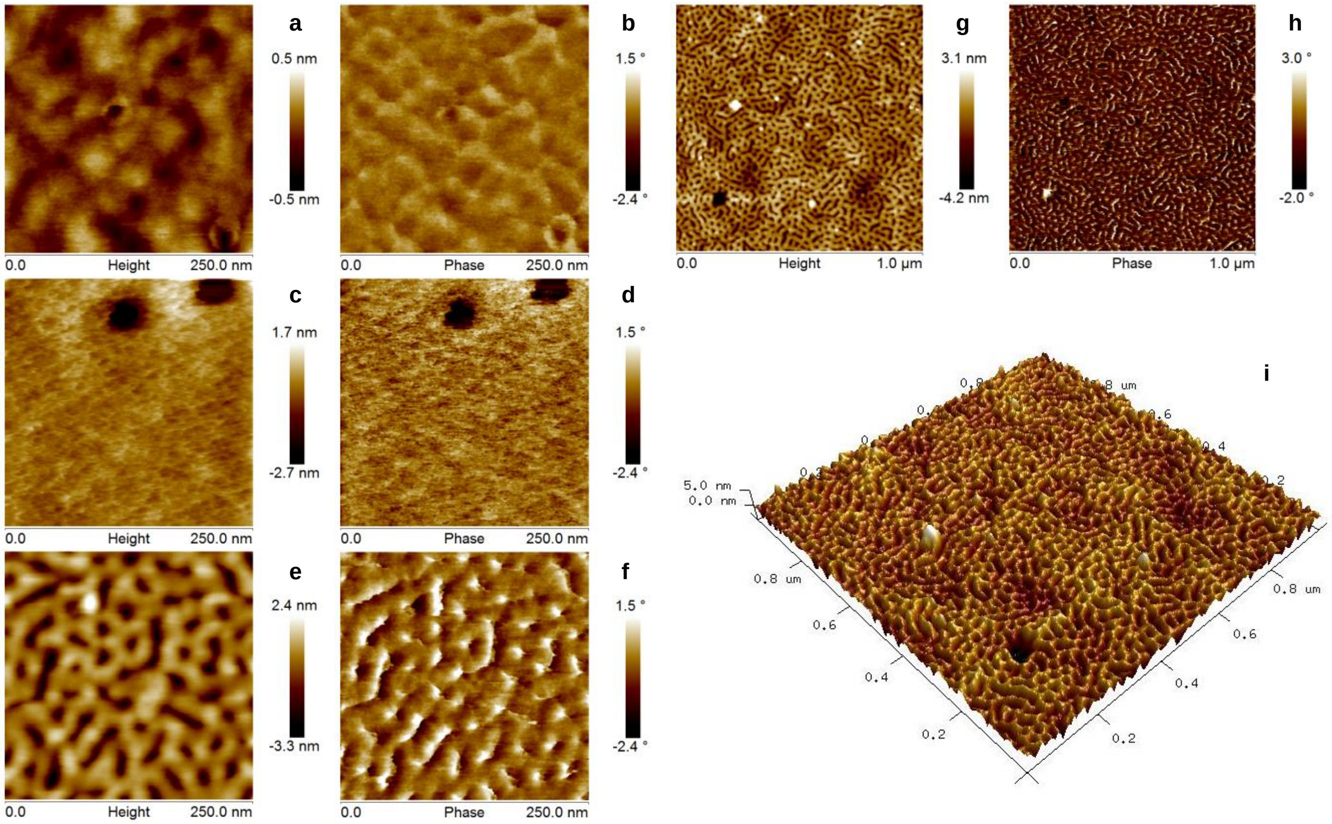

Figure S3. AFM 2D images (height image and phase image) of PPA-b-PS (a and b) as spin-coated, (c and d) solvent annealed in chloroform vapour for 30 min, and (e and f) after PPA removal which generated the 3D images of Figure 2 in the main text. All images are 250 nm x 250 nm scan size with additional 1 μm x 1 μm scale images of the nanochannel surface after PPA removal to exhibit the extent of the nanochannel network (g-i).

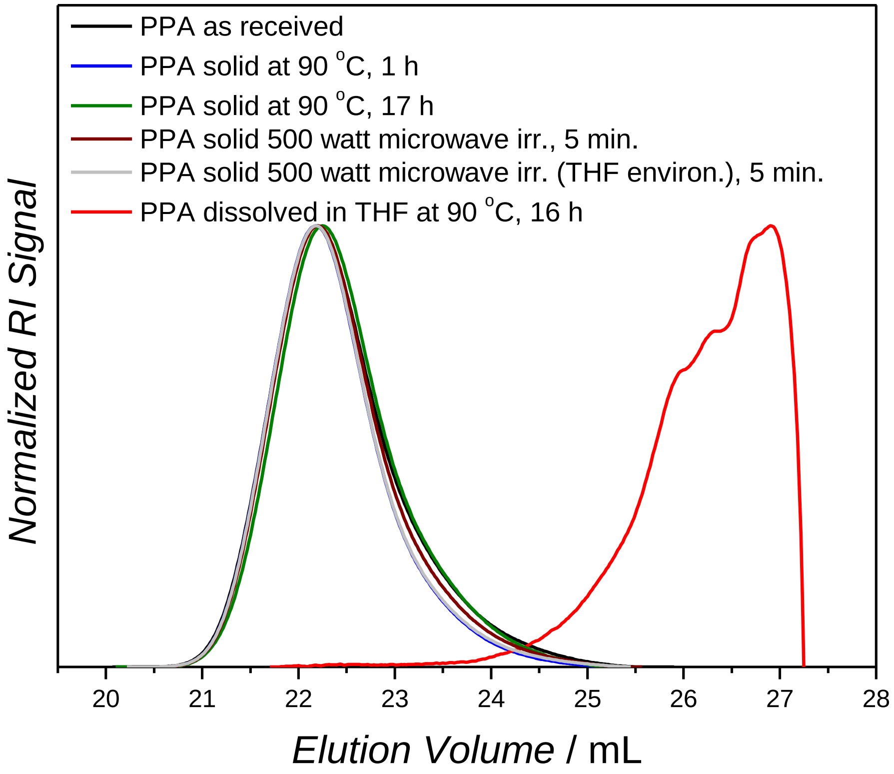

Figure S4. SEC analyses of PPA depolymerization trials under variable conditions.

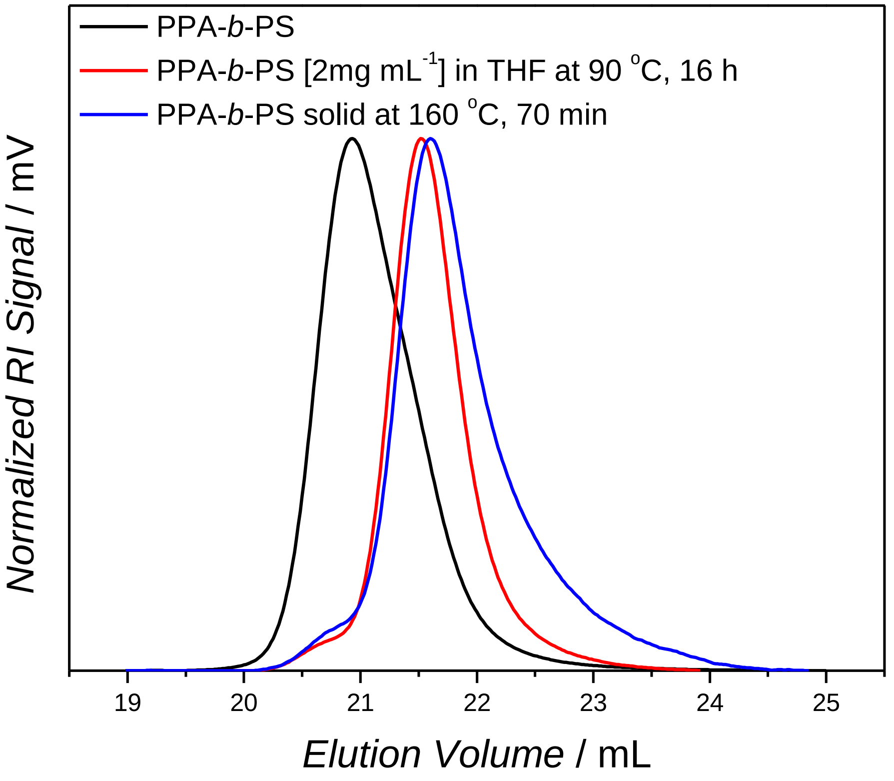

Figure S5. SEC analyses of PPA-*b*-PS recorded before and after depolymerization under thermal conditions.

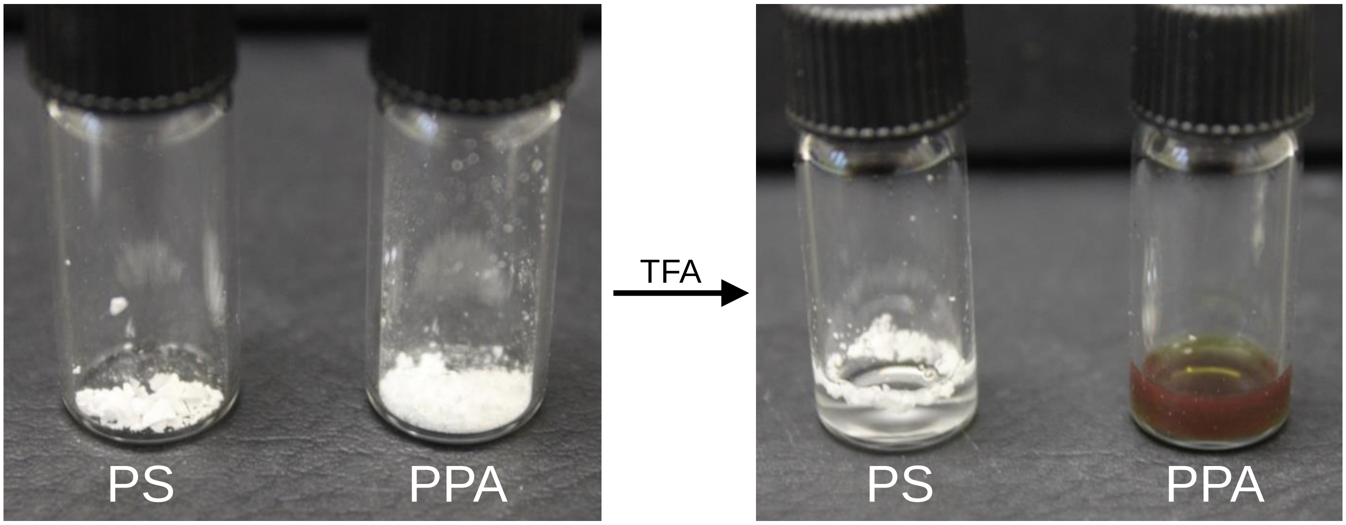

Figure S6. Photographs of azide terminated PS (left vial, 5 mg) and alkyne terminated PPA (right vial, 5 mg) before (left photo) and after (right photo) addition of 0.2 mL concentrated TFA. It can clearly be observed that the PS does not dissolve or depolymerize in TFA, whereas PPA immediately depolymerized and changed from a white powder to the brown/green solution with no PPA left.

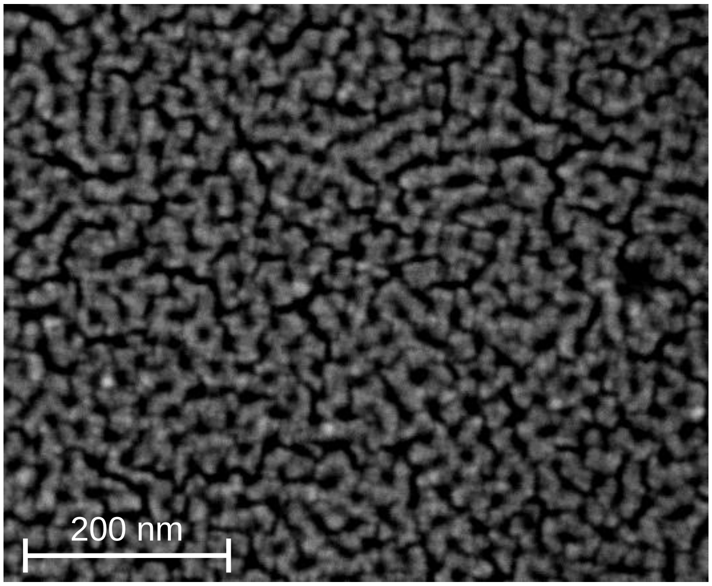

Figure S7. SEM image of PS matrix/nanochannel surface after PPA depolymerization.

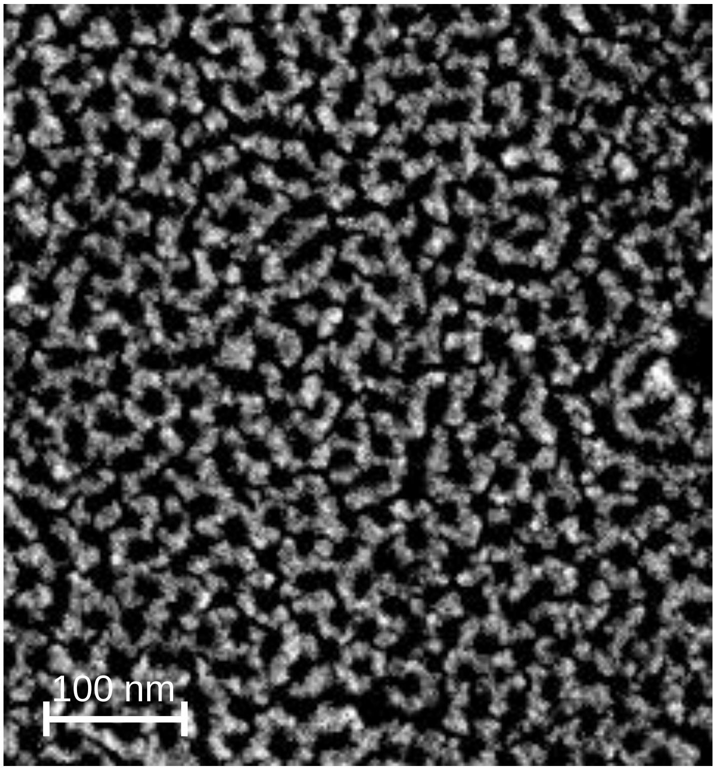

Figure S8. SEM image of PS matrix/nanochannel surface after PPA depolymerization.

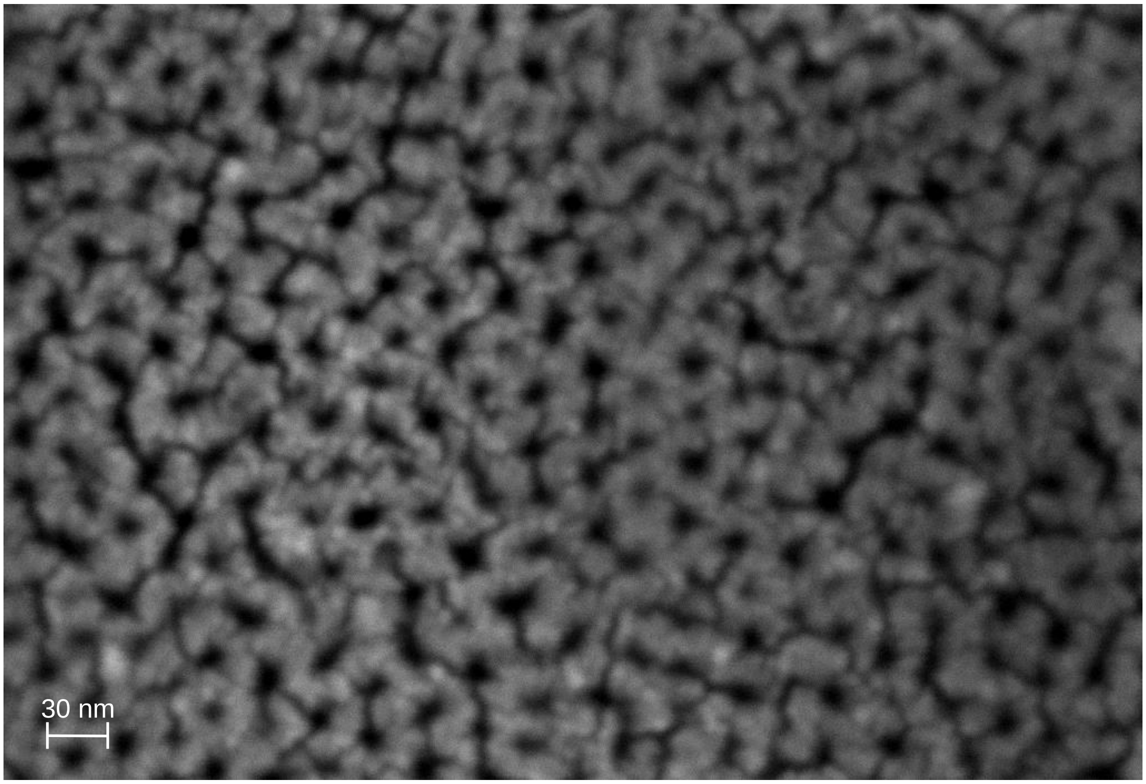

Figure S9. SEM image of PS matrix/nanochannel surface after PPA depolymerization.

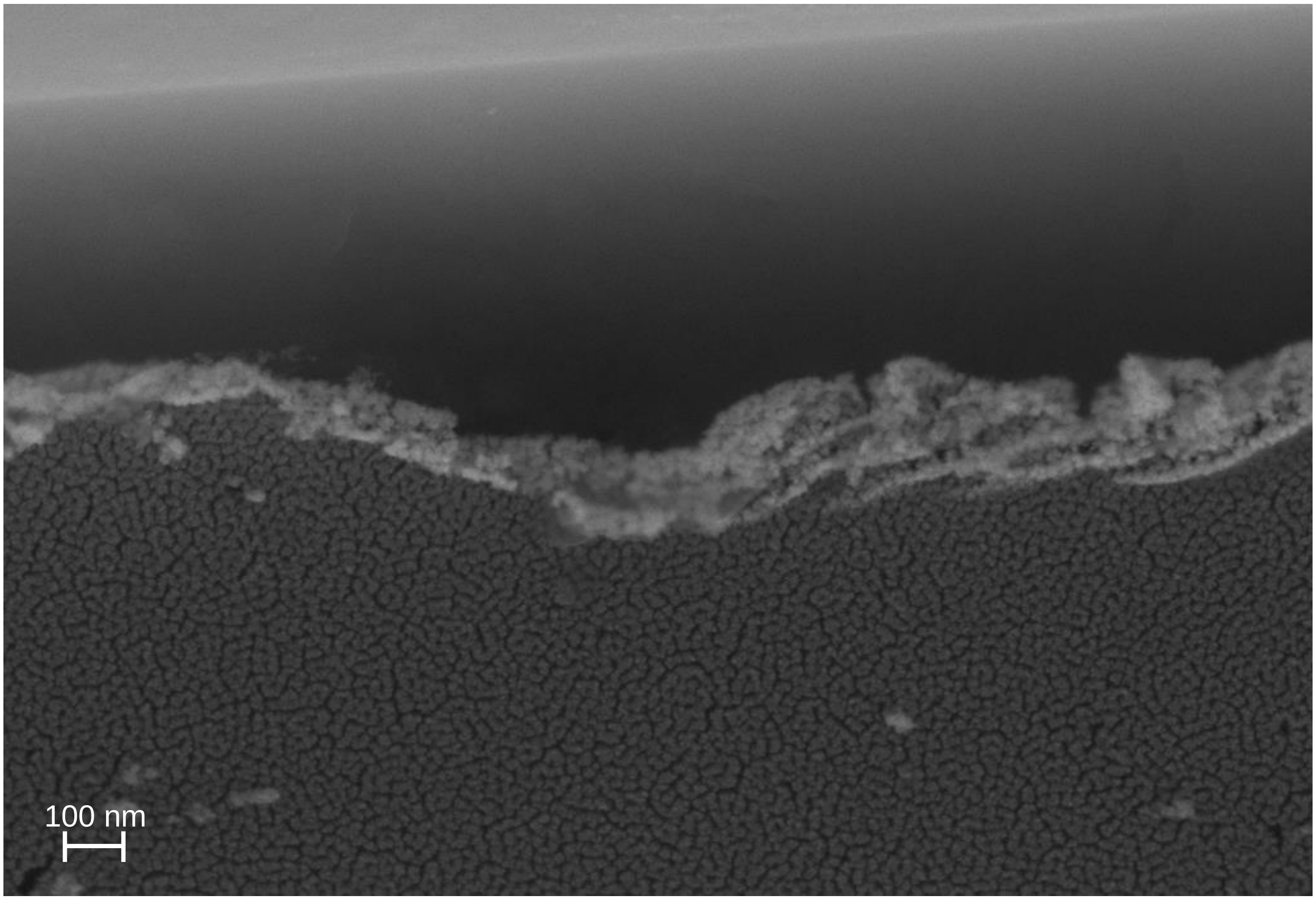

Figure S10. SEM image of PS matrix/nanochannel film after PPA depolymerization and snapping the surface. The nanochannel matrix is observed on the bottom of the film that has curled on itself similar to the top of the film which exhibits PPA depolymerization through the entire film and not merely on the top surface.

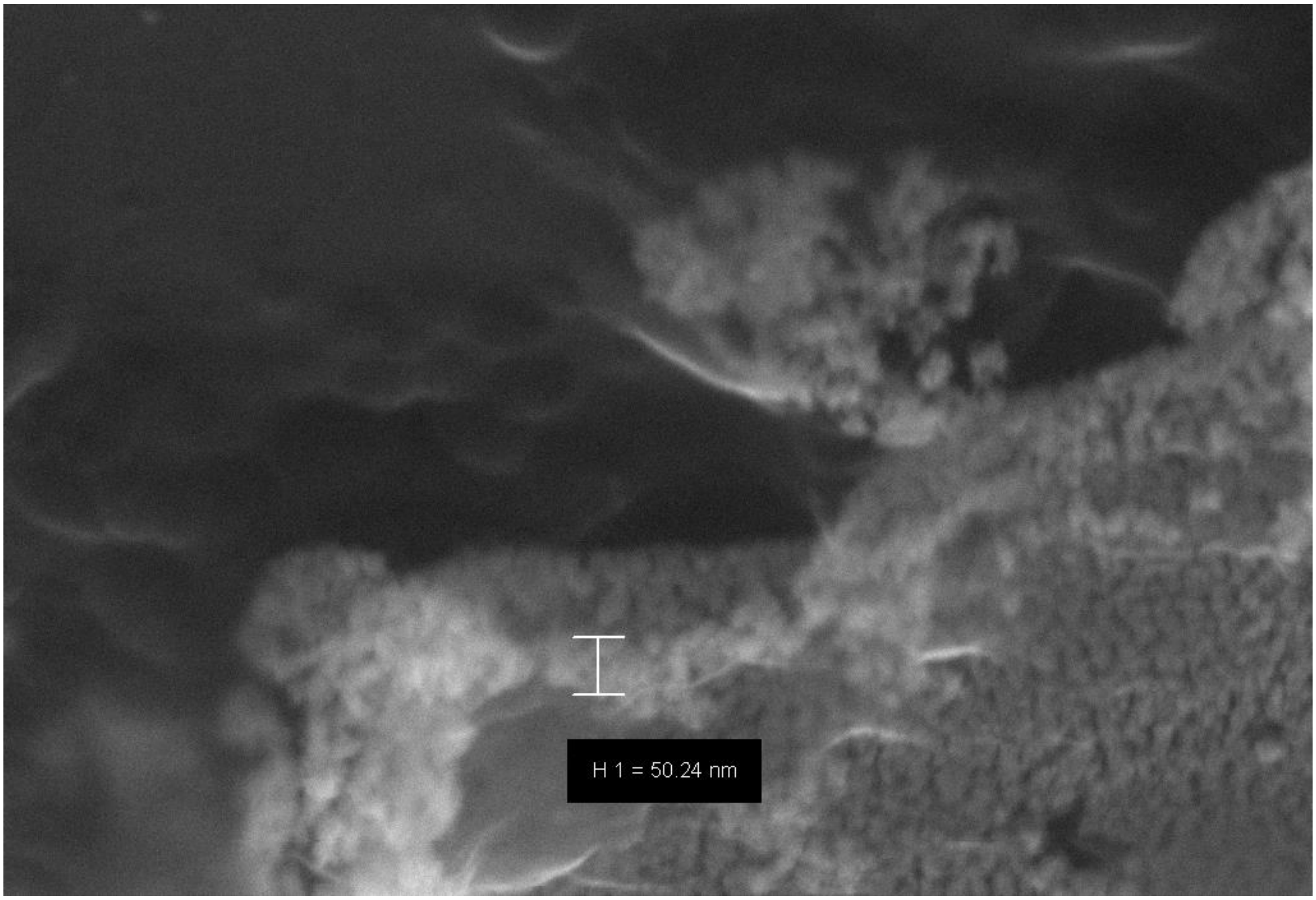

Figure S11. SEM image of PS matrix/nanochannel film after PPA depolymerization and snapping the surface. The nanochannel matrix is observed on the bottom of the film that has curled on itself similar to the top of the film which exhibits PPA depolymerization through the entire film and not just on the top surface. The edge of the film is measured to be 50 nm which coincides with the AFM analysis.

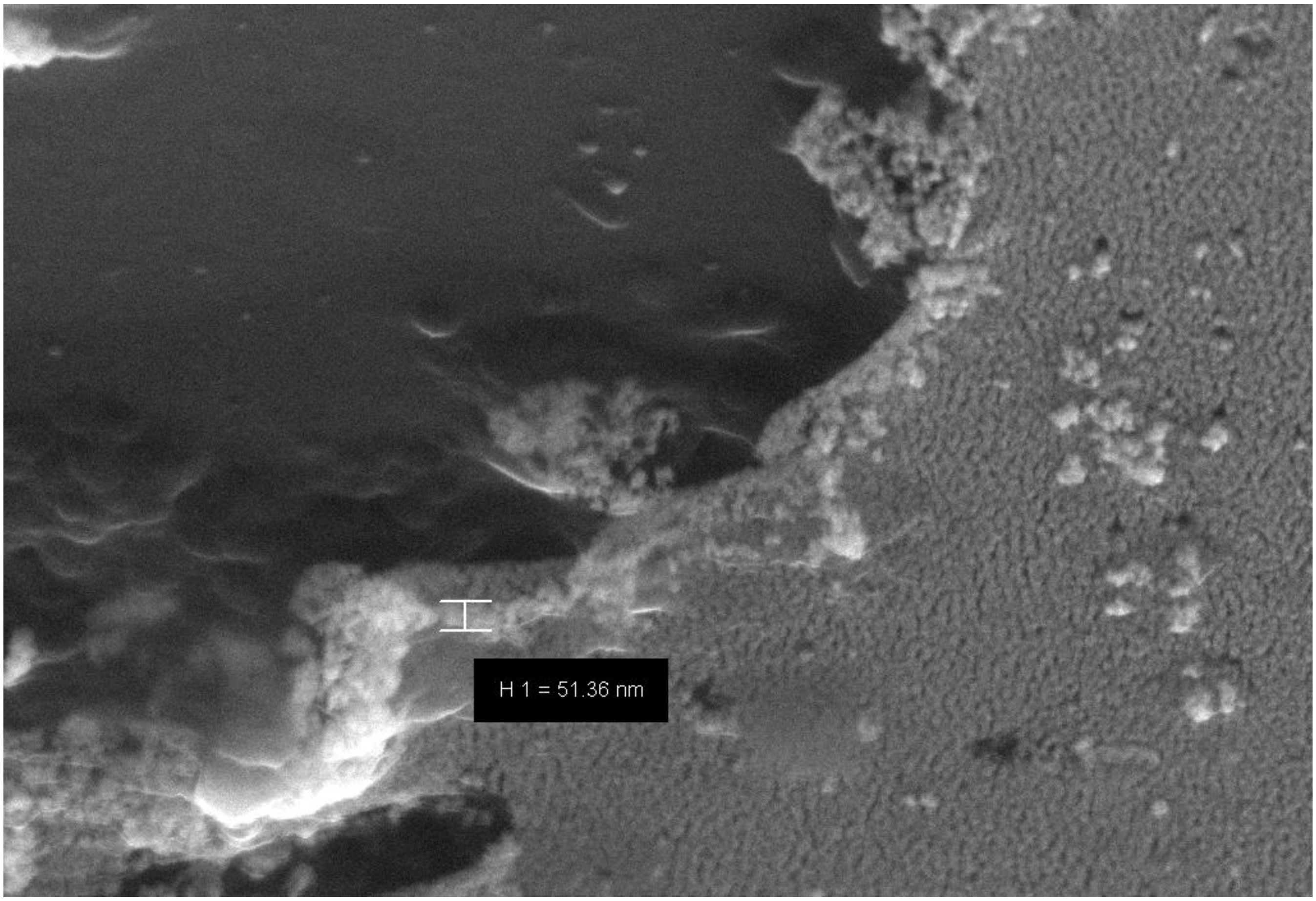

Figure S11. SEM image of PS matrix/nanochannel film after PPA depolymerization and snapping the surface. The nanochannel matrix is observed on the bottom of the film that has curled on itself similar to the top of the film which exhibits PPA depolymerization through the entire film and not merely on the top surface. The edge of the film is measured to be 50 nm which coincides with the AFM analysis.

References

1. A. P. Vogt and B. S. Sumerlin, *Macromolecules*, 2006, **39**, 5286-5292.
2. J. De Winter, A. P. Dove, A. Knoll, P. Gerbaux, P. Dubois and O. Coulembier, *Polymer Chemistry*, 2014, **5**, 706-711.
3. M. Malkoch, K. Schleicher, E. Drockenmuller, C. J. Hawker, T. P. Russell, P. Wu and V. V. Fokin, *Macromolecules*, 2005, **38**, 3663-3678.