Electronic Supplementary Information

Block Copolymer Supramolecular Assemblies Hierarchically Structured by Three-Beam Interference Laser Ablation

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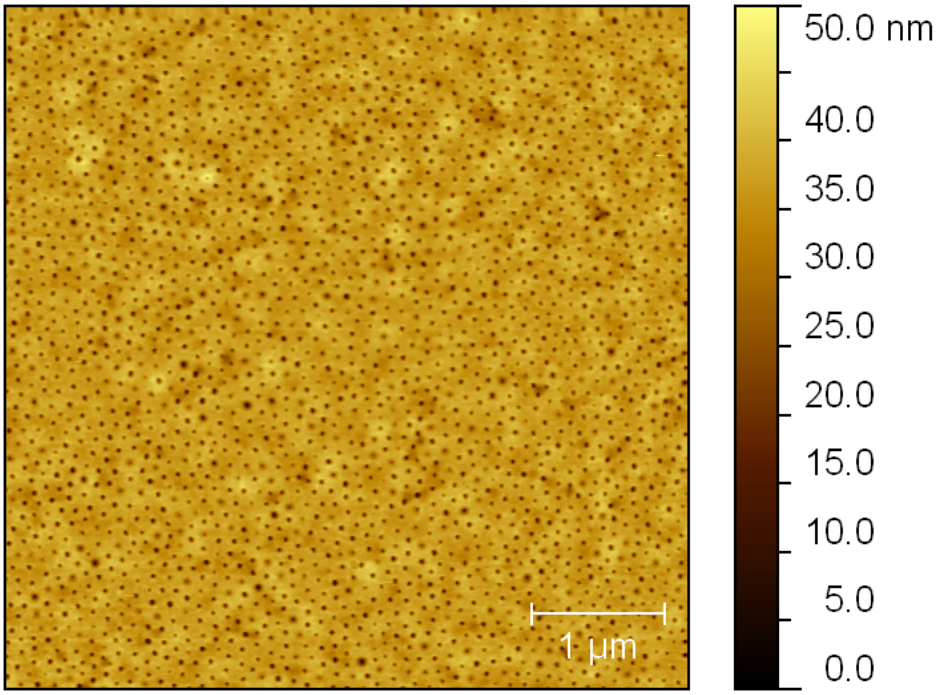

Figure S1. AFM height image of PS-b-P4VP(AzoCH$_3$)$_{0.5}$ film after rinsing in ethanol for 30 min. This shows that phase separation nanostructures retain after AzoCH$_3$ is selectively washed away.

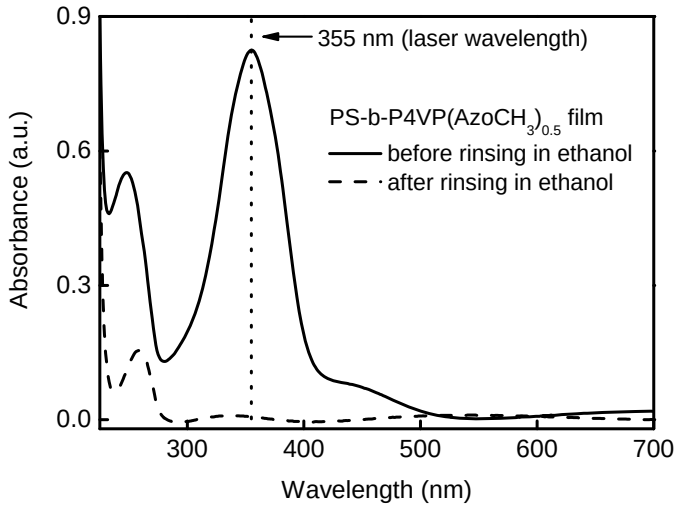

Figure S2. UV-vis absorption spectra of a PS-b-P4VP(AzoCH$_3$)$_{0.5}$ film on a fused silica substrate before and after rinsing in ethanol for 30 min, which show that AzoCH$_3$ can be washed away selectively. The dotted line indicates the laser wavelength at 355 nm.

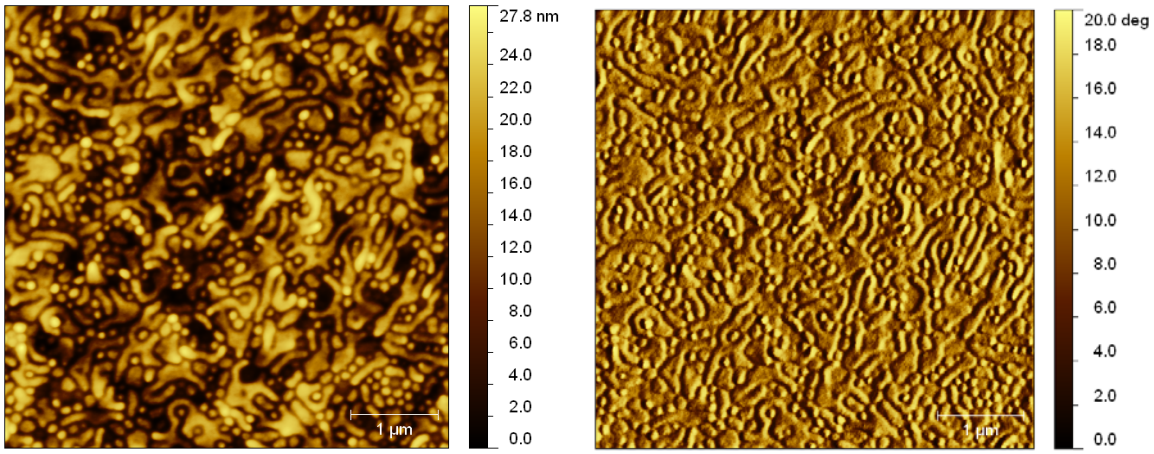

Figure S3. AFM height (left) and phase (right) images of PS-b-P2VP(AzoCN)$_{0.3}$. These images show the phase separation nanostructure of the sample in Figure 4(d) before laser ablation.

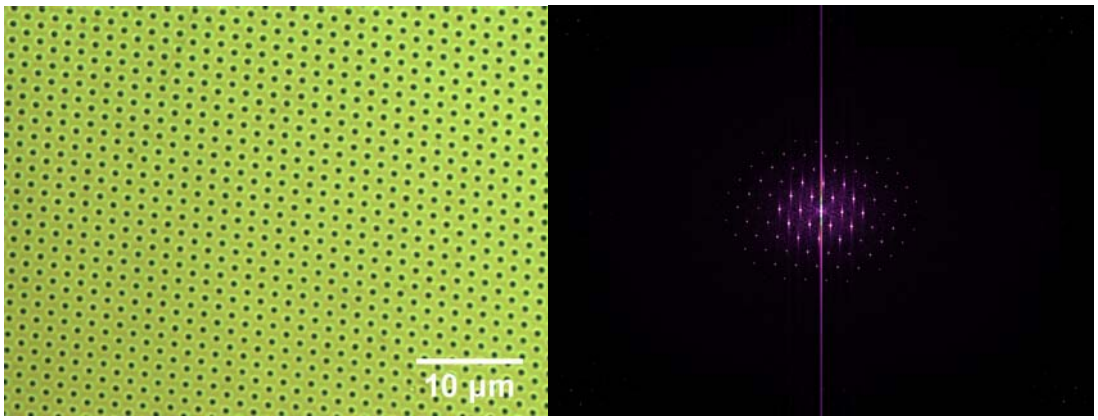

Figure S4. Optical microscopy image (left) and fast Fourier transform image (right) of hexagonally packed holes in a film of PS-b-P4VP(AzoCH$_3$)$_{0.5}$. The AFM image of the same sample is shown in Figure 4(a). This optical microscopy image shows that hierarchical structures can be obtained on large areas.

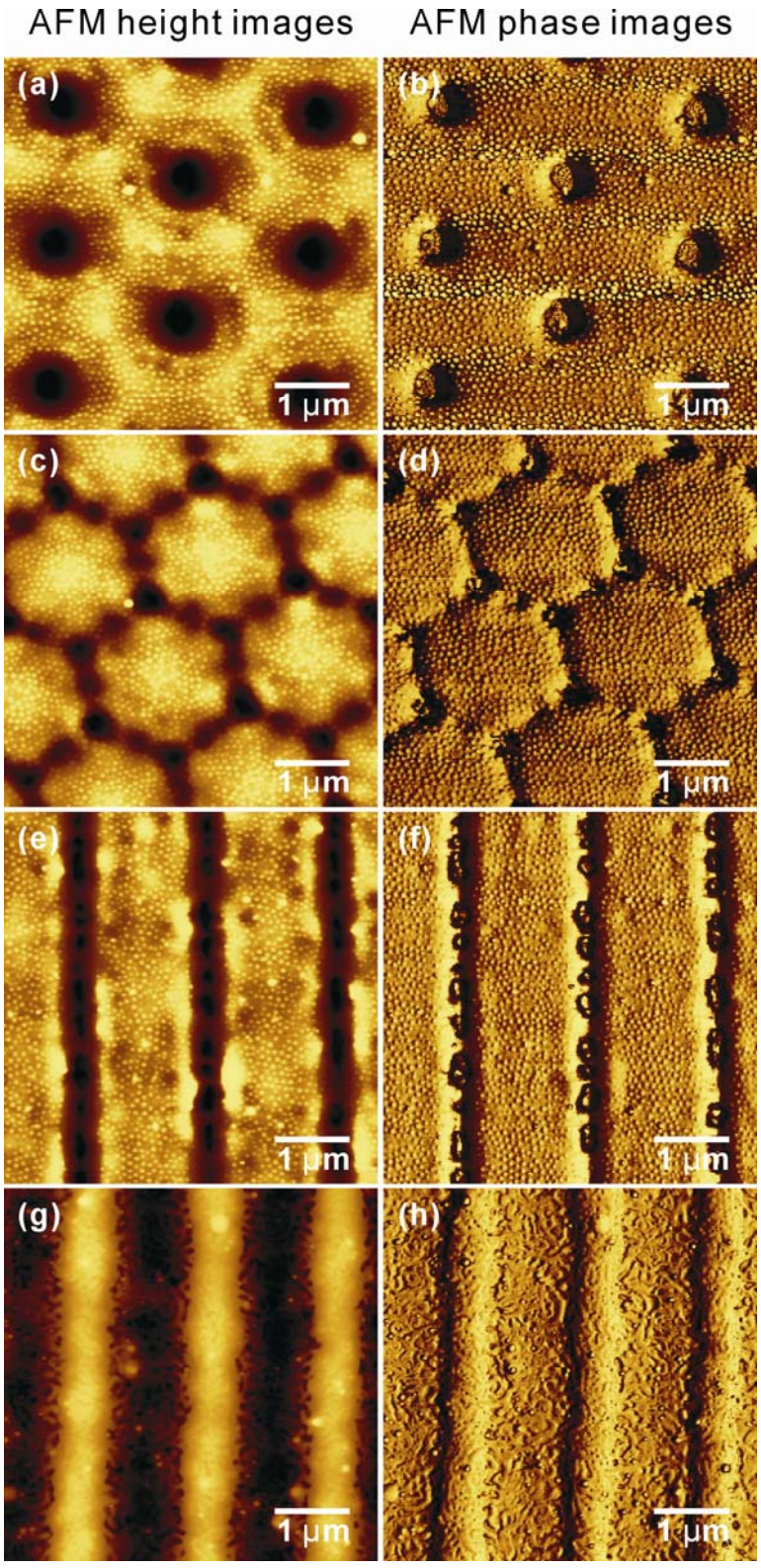

Figure S5. AFM height (left) and phase (right) images of PS-b-P4VP(AzoCH$_3$)$_{0.5}$ and PS-b-P2VP(AzoCN)$_{0.3}$ after exposure to interference beams. The AFM height images of the same samples are also shown in Figure 4 in the manuscript. The contrast of AFM phase images is due to different mechanical properties of PS phases and PVP-Azo phases, which provides further evidence that the phase separation nanostructures in the low intensity regions of the interference pattern are retained after laser ablation.

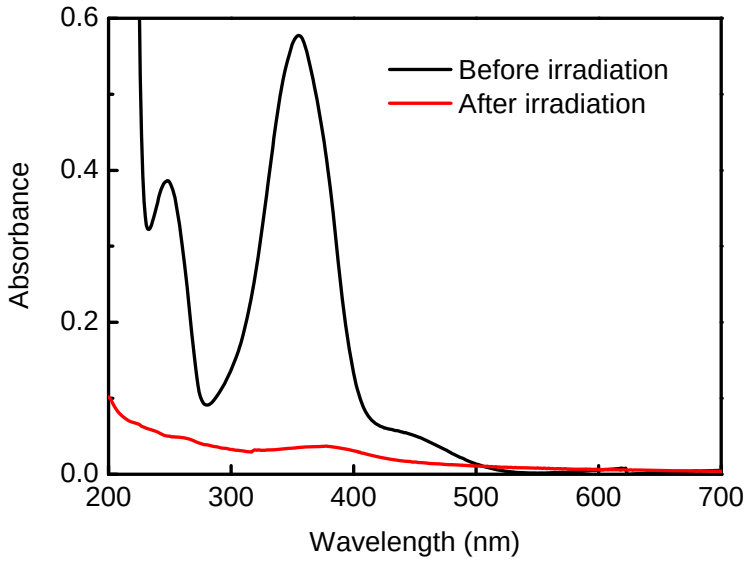

Figure S6. UV-vis absorption spectra of a PS-b-P4VP($AzoCH_3$)$_{0.5}$ film on a fused silica substrate before and after single beam irradiation with a single pulse using the same laser as for interference experiments. The peak intensity of the laser is in the order of ~10^6 W/cm^2. The absorptions of cis azobenzene at ~450 nm, trans azobenzene at ~355 nm, and benzene and pyridine rings at ~250 nm are decreased, indicating that laser irradiation ablates both, the azo dyes and the block copolymers.

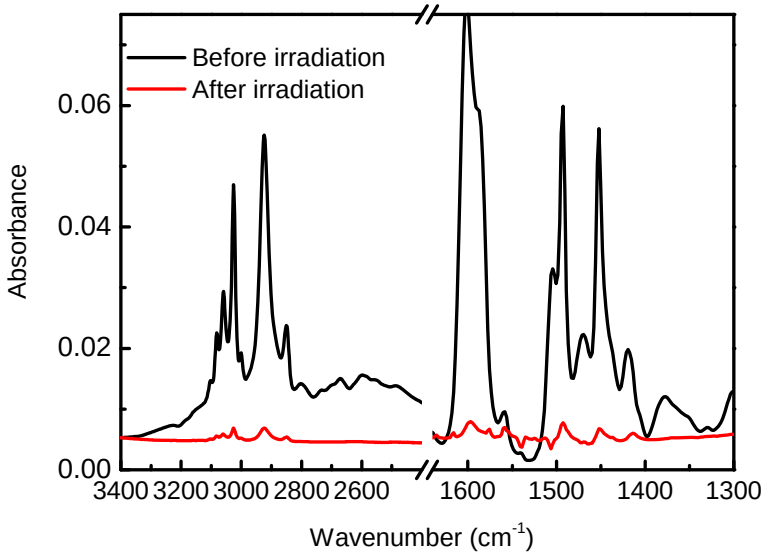

Figure S7. FTIR spectra of a PS-b-P4VP($AzoCH_3$)$_{0.5}$ film on a silicon wafer before and after single beam irradiation with a single pulse using the same laser as for interference experiments. The peak intensity of the laser is in the order of ~10^6 W/cm^2. The C-H stretchings (C-H on polymer backbone, C-H on pyridine and benzene rings) in the range of 3200-2800 cm^{-1} are decreased. The C=C, C=N and N=N bands in the range of 1640-1300 cm^{-1} are also decreased. These results indicate that azo dyes and block copolymers are both ablated by laser irradiation.