## Supporting Information

## Topochemical polymerization of hierarchically ordered diacetylene monomers within the block copolymer domains

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Figure S1. SAXS patterns of (a) PS-b-P4VP, (b) PCDA and WAXS patterns of (c) PS-b-P4VP, (d) PCDA.

PS-b-P4VP(PCDA) $x_{x}$ supramolecular complexes were prepared in 1,4-dioxane, where $x$ denotes the molar ratio between PCDA monomer and 4VP unit. The stoichiometric ratio (x) of PCDA to 4VP unit was varied from $0.25,0.5,0.75$, and 1 . The SAXS patterns shown in Fig. S2(a) were obtained for the solvent-vapor annealed samples, whereas the SAXS patterns in Fig. S2(b) were obtained after thermal annealing of the samples at $90{ }^{\circ} \mathrm{C}$. Solvent-vapor annealed PS-b-P4VP(PCDA) complexes show only one peak corresponding to the domain spacing of the block copolymer supramolecules. It is clear from the SAXS patterns that in solvent-vapor annealed samples the domain spacing corresponding to the block copolymer self-assembly decreases with the increase in the molar ratio of PCDA. As higher order peaks are absent, it is not possible to identify the morphology of the block copolymer in these samples. At higher q , a peak at $\mathrm{q}=1.36 \mathrm{~nm}^{-1}$ is observed in all the samples, which is corresponding to the molecular packing of PCDA within the block copolymer microdomains. As discussed in the original manuscript, the solvent-vapor annealed samples showed poor block copolymer morphology, however, PCDA monomers packing is better within the block copolymer microdomains as evident from the intensity of the peak at $q=1.36 \mathrm{~nm}^{-1}$. On the other hand, thermally annealed samples show well-defined block copolymer morphology and the morphology was dependent on the molar ratio of PCDA relative to the 4 VP units. PS-b-P4VP(PCDA) $)_{0.25}$ sample shows peaks with a ratio of $1: \sqrt{3}: 2$ indicating the formation of hexagonally packed cylinders, whereas PS-b-P4VP(PCDA) 0.5 sample shows the mixed morphology of hexagonally packed cylinders and lamellae. The samples with higher molar ratio PS-b-P4VP(PCDA) $)_{0.75}$ and $\operatorname{PS}-b-\mathrm{P} 4 \mathrm{VP}(\mathrm{PCDA})_{1}$ shows a well-defined lamellar morphology as evident from the peak ratios (1:2:3). These results are in good agreement with the literature where authors demonstrated that the molar ratio of small molecules play a key role in determining the morphology of the block copolymer supramolecules (Macromolecules, 2010, 43, 2463-2473; ACS nano, 2013, 7, 5514-5521; and Macromolecules, 2016, $49,2639-2645)$. At the same time, the peak at $\mathrm{q}=1.36 \mathrm{~nm}^{-1}$, which is corresponding to the molecular packing of PCDA within the block copolymer microdomains shows intense peak in the case of PS-bP4VP(PCDA) ${ }_{1}$ and other samples with lower molar ratios show less intense peak indicating that the molecular packing of PCDA monomer is not well organized within the block copolymer microdomains. Up on the UV-irradiation, SAXS patterns of the solvent-vapor annealed samples (Fig. S2(c)) show a broad peak at around $q=1.03 \mathrm{~nm}^{-1}$ corresponding to the polymerized PDA. On the other hand, thermally annealed samples Fig. S2(d) did not show this peak indicating that the molecular packing of PCDA is not appropriate for the polymerization.


Figure S2: SAXS patterns of PS-b-P4VP(PCDA) $x_{x}$ supramolecular complexes for (a) solvent-vapor annealed samples and (b) thermally annealed samples and SAXS patterns of PS-b-P4VP(PDA) ${ }_{x}$ supramolecular complexes after polymerization (UV-irradiation) for (c) solvent-vapor annealed samples and (d) thermally annealed samples.


Figure S3: TEM image of solution casted PS-b-P4VP(PCDA).


Figure S4. DSC thermogram of pure PCDA measured during first heating.


Figure S5. Comparison of FTIR spectra of PS-b-P4VP, thermally annealed PS-b-P4VP(PCDA), and solvent vapor annealed PS-b-P4VP(PCDA) in the region of 1030-980 $\mathrm{cm}^{-1}$.


Figure S6. Emission spectra ( $\lambda_{\mathrm{ex}}=500 \mathrm{~nm}$ ) of pure PCDA and PS-b-P4VP(PCDA) complex.


Figure S7. The $d$-spacings corresponding to the phase separated morphology and the hierarchically ordered PDA estimated from Figure 6 during the heating process.


Figure S8. DSC thermogram of melt-cooled PS-b-P4VP(PDA) measured during first heating.

