Supporting Information for

Phase Behavior and Structure of Supramolecules Formed by Poly(4-vinylpyridine) and Fan-Like Benzoic Acid Derivative with Long Hydrophobic Tails

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1. Synthesis and Characterization of 3,4,5-tris(hexadecyloxy) benzoic acid (THBA)[1]

A solution of gallic acid ethyl ester (5.01 g, 25.28 mmol), K_2CO_3 (17.43 g, 126.11 mmol) and KI (catalytic amount) in acetone (100 ml) was reflux at 60 ℃ for 0.5 h and then a solution of 1-bromohexadecane (25.43 g, 83.27 mmol) was added. The reaction mixture was stirred for 5 days. The solvent was removed under reduced pressure. The white solid was washed with ethyl acetate (3 × 100 ml) and dried under vacuum to give pure product (17.95 g, 90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.23 (s, 2H), 4.34 (q, 2H, J = 7.2 Hz), 3.97 (m, 6H), 1.78 (m, 6H), 1.48 (m, 6H), 1.36 (t, 3H, J = 7.1 Hz), 1.29 (m, 72H), 0.86 (t, 9H, J = 6.6 Hz). KOH (2.96 g, 52.74 mmol) was added to the solution of ethyl 3,4,5-tris(hexadecyloxy)benzoate (3.95 g, 4.46 mmol) in EtOH (70 ml) and the reaction

was reflux at 80 ℃ for 10h, and then the solution was cooled to room temperature and the precipitate was filtered. HCl (1 M, 10 ml) was added to the solution of precipitate in THF (50 ml) and the reaction was reflux at 80 ℃ for 2h. The THF/H2O solution was partitioned between ether and the organic extract was washed with brine (2 × 50 ml), dried over $MgSO_4$ and filtered, and the solvent was removed. The crude product was recrystallized twice from CH_2Cl_2/Ethanol, and a white solid was obtained (3.44 g, 90%). ^{1}H NMR(300 MHz, $CDCl_3$): δ = 7.29 (s, 2H), 4.00 (m, 6H), 1.76 (m, 6H), 1.46 (m, 6H), 1.29 (m, 72H), 0.86 (t, 9H, J = 6.7Hz). Anal. Calcd for $C_{55}H_{102}O_5$: C, 78.32; H, 12.19. Found: C, 78.36; H, 12.20.

Reference:

1. Serrette, A. G.; Lai, C. K.; Swager, T. M. *Chemistry of Materials* **1994,** 6, (12), 2252-2268.

2. Supporting Schematics and Figures

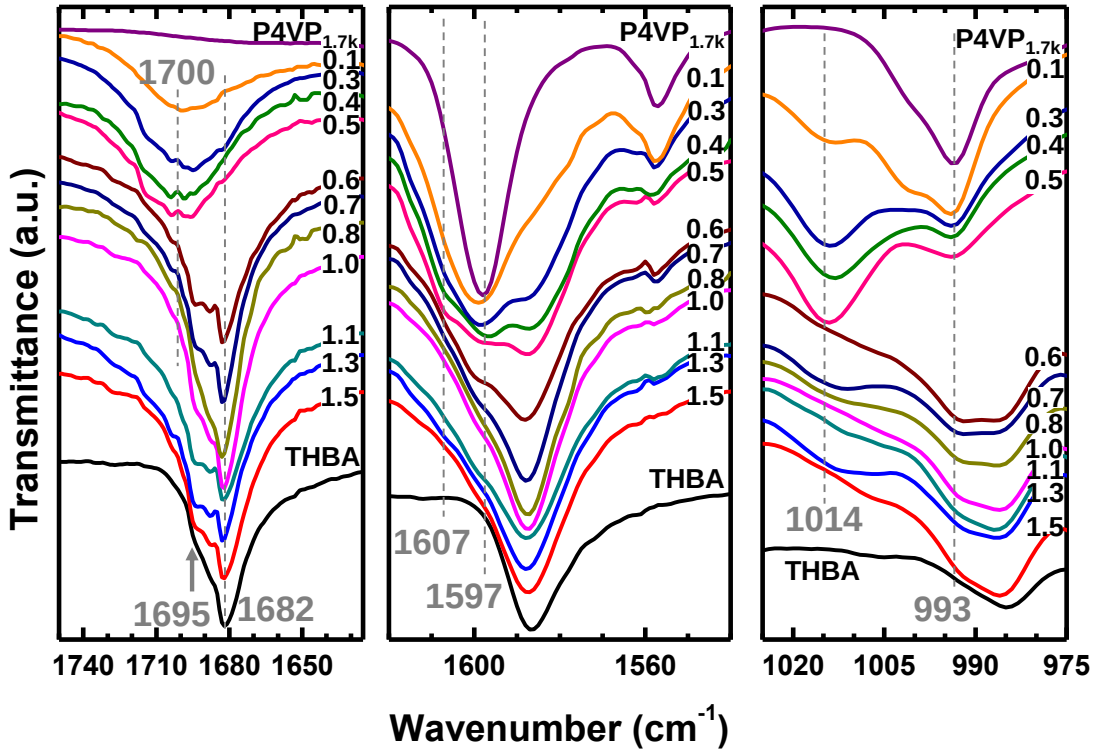

Figure S1. FTIR spectra of THBA, $P4VP_{1.7k}$ and $P4VP_{1.7k}(THBA)_x$ samples.

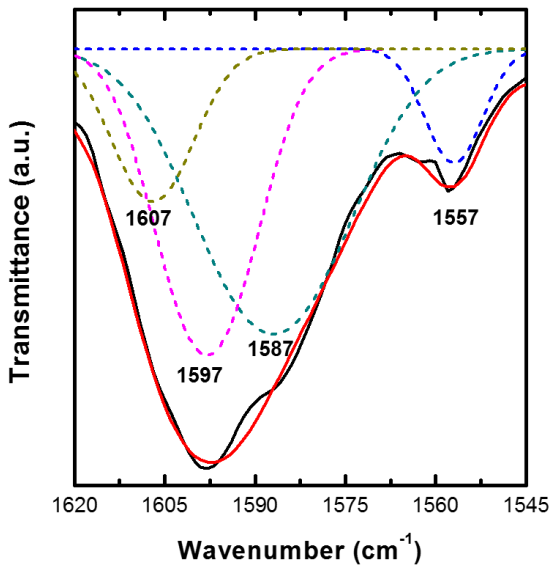

Figure S2. Peak deconvolution of the FTIR spectra for $P4VP_{15k}(THBA)_{0.3}$ in the range of 1545-1620 cm^{-1}. The original data are shown as the black curve and the red curve is the fitting result.

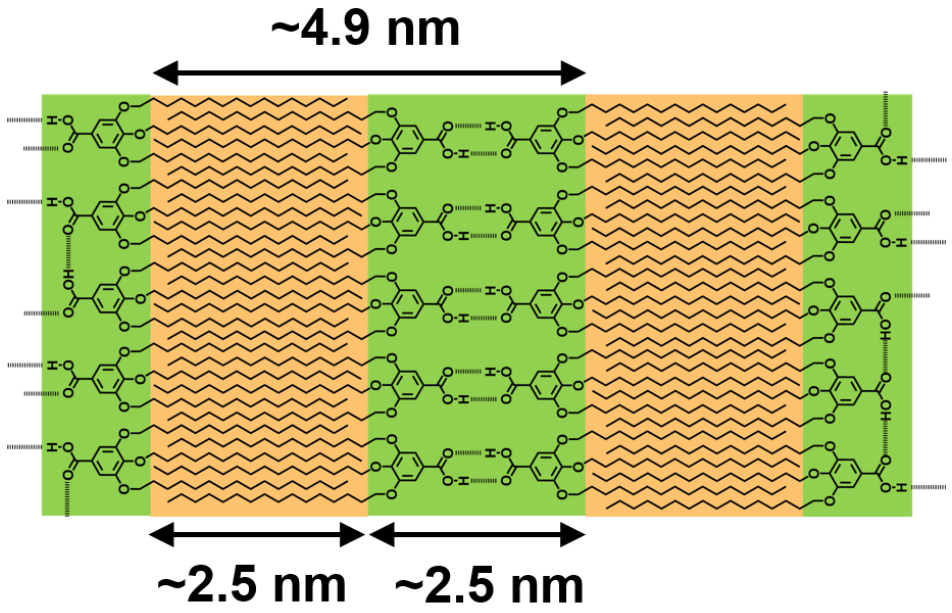

Figure S3. Schematic of THBA crystal structure. THBA crystallizes into lamellar structure and the thicknesses of the layers are approximately equal ~ 2.5 nm, inferred from the SAXS data in Figure 4a.

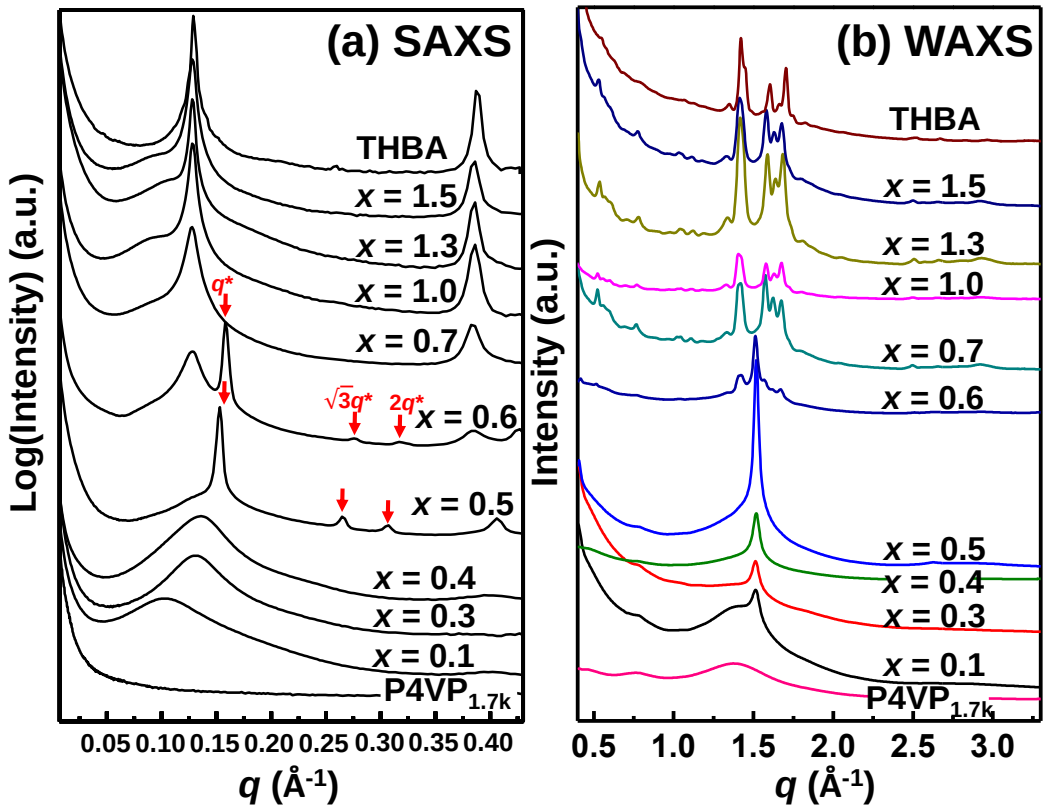

Figure S4. (a) SAXS and (b) WAXS profiles of THBA and P4VP$_{1.7k}$(THBA)$_x$ samples at room temperature.

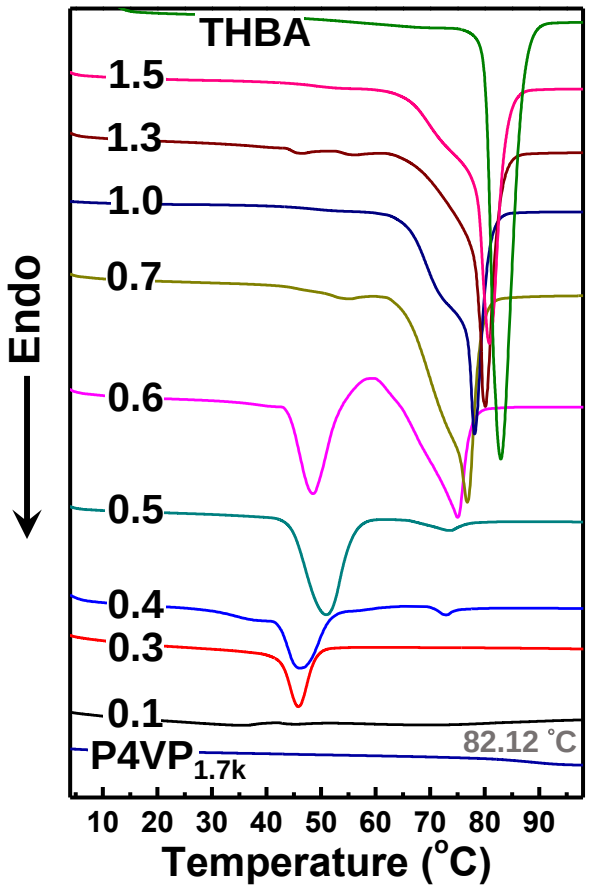

Figure S5. The DSC profiles of annealed $P4VP_{1.7k}(THBA)_x$ samples at a heating rate of 10 ℃/min.

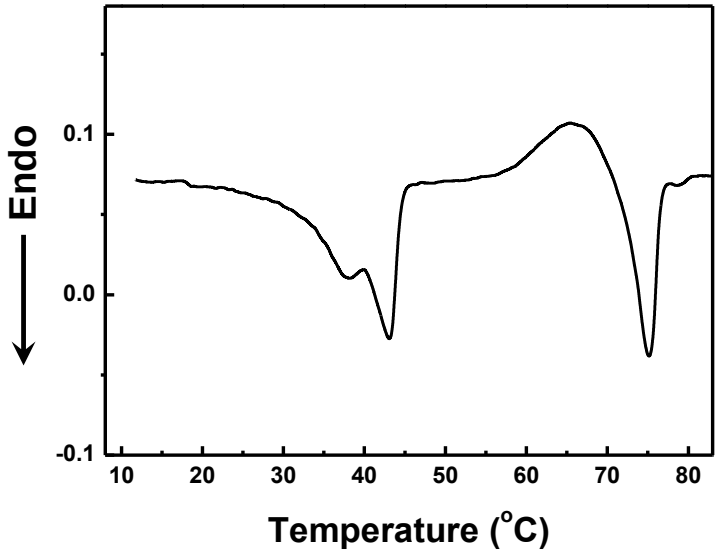

Figure S6. DSC profile of $P4VP_{15k}(THBA)_{0.5}$ at a heating rate 1 ℃/min after the sample is slowly cooled down from melt.

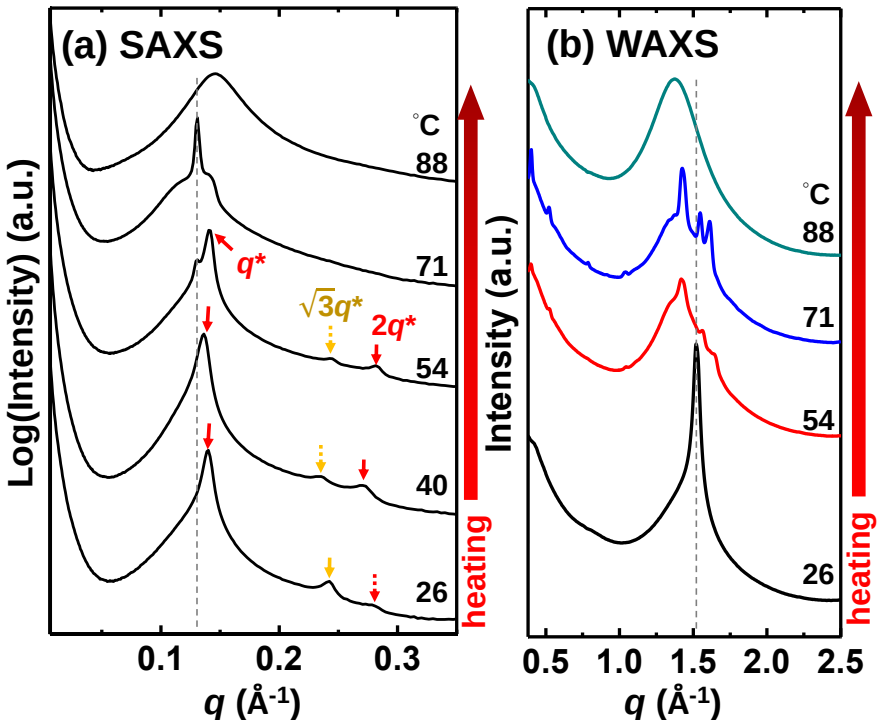

Figure S7. *In-situ* (a) SAXS and (b) WAXS data of P4VP$_{15k}$(THBA)$_{0.5}$ at a heating rate ~ 1 °C/min. The dashed arrows for $\sqrt{3}q^*$ peaks indicate the intensities of the peaks are weaker than those of the corresponding $2q^*$ peaks.

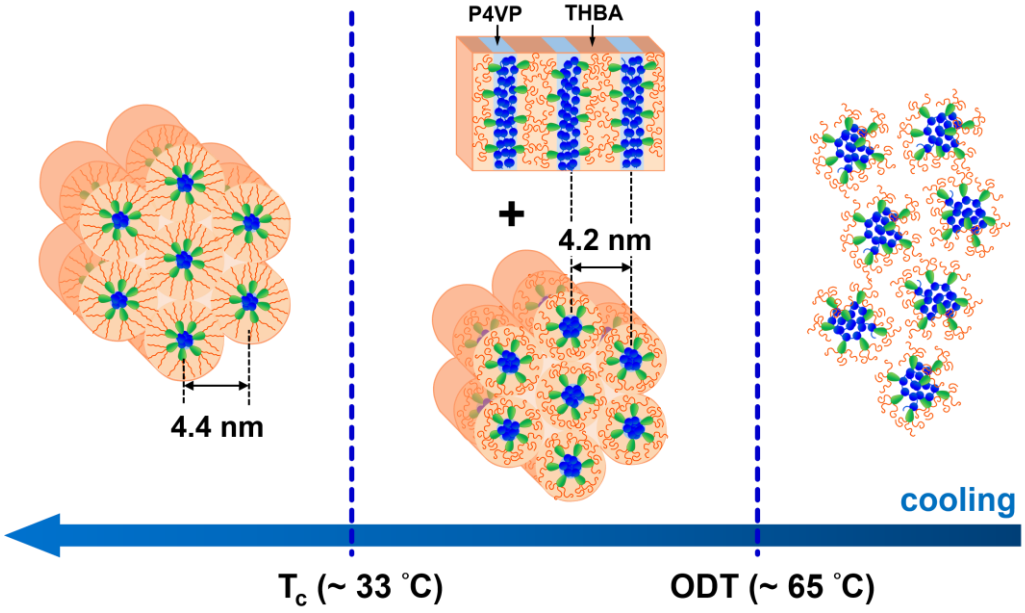

Figure S8. The phase transition of P4VP$_{15k}$(THBA)$_{0.5}$ in the cooling process. Between the order-disorder transition (ODT) and the crystallization temperature of associated THBA (T_c), lamellae coexist with HPC structure. Below T_c, only HPC is formed and the d-spacing is increased from ~ 4.2 to 4.4 nm.

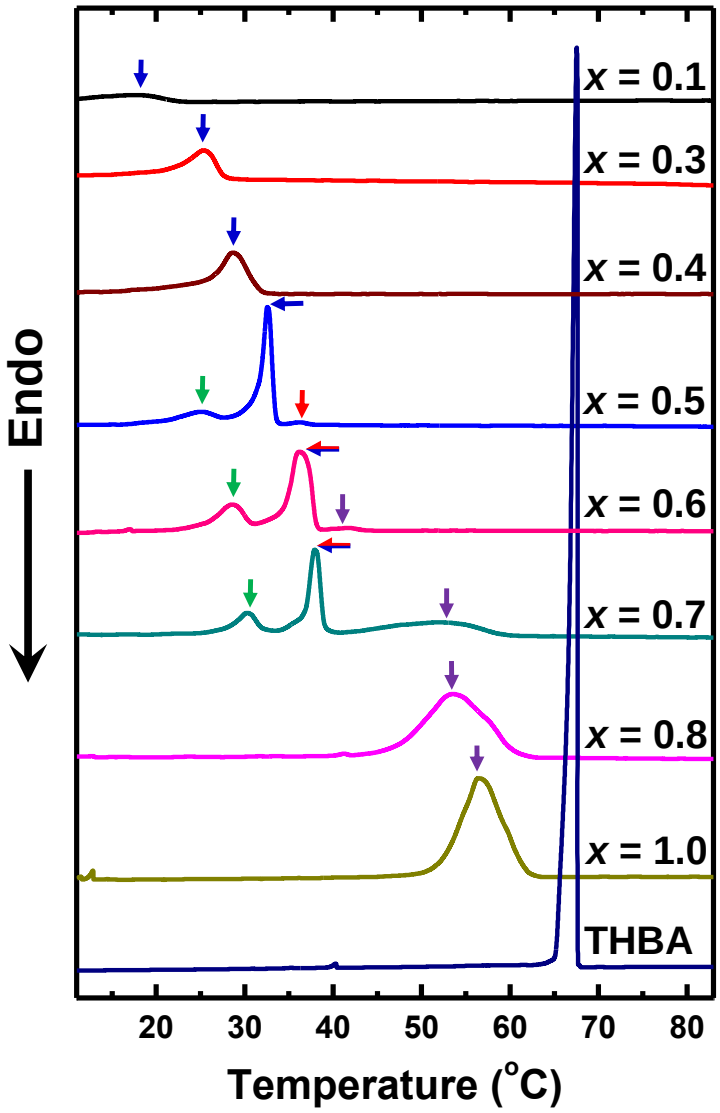

Figure S9. DSC profiles of $P4VP_{1.7k}(THBA)_x$ at a cooling rate 1 ℃/min. The peaks of the self-crystallization of free THBA molecules, the order-disorder transition, the crystallization of associated THBA, and the crystal reorganization are marked with the purple, red, blue and green arrows, respectively.

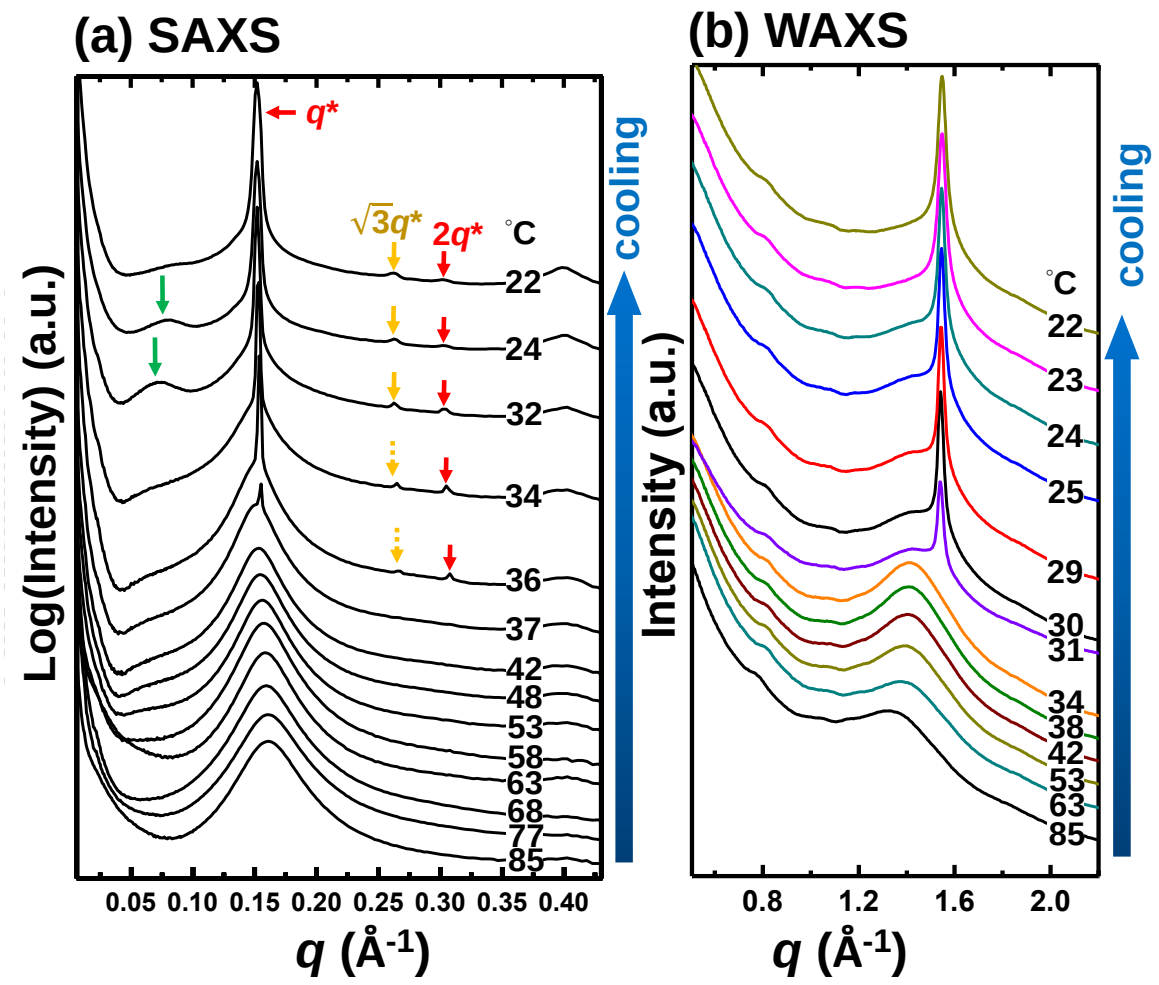

Figure S10. *In-situ* (a) SAXS and (b) WAXS profiles of P4VP$_{1.7k}$(THBA)$_{0.5}$ at a cooling rate ~1 ℃/min. The dashed arrows for √3*q** peaks indicate the intensities of the peaks are weaker than those of the corresponding 2*q** peaks. The green arrows label the diffraction peaks from the co-crystals composed of associated and free THBA.

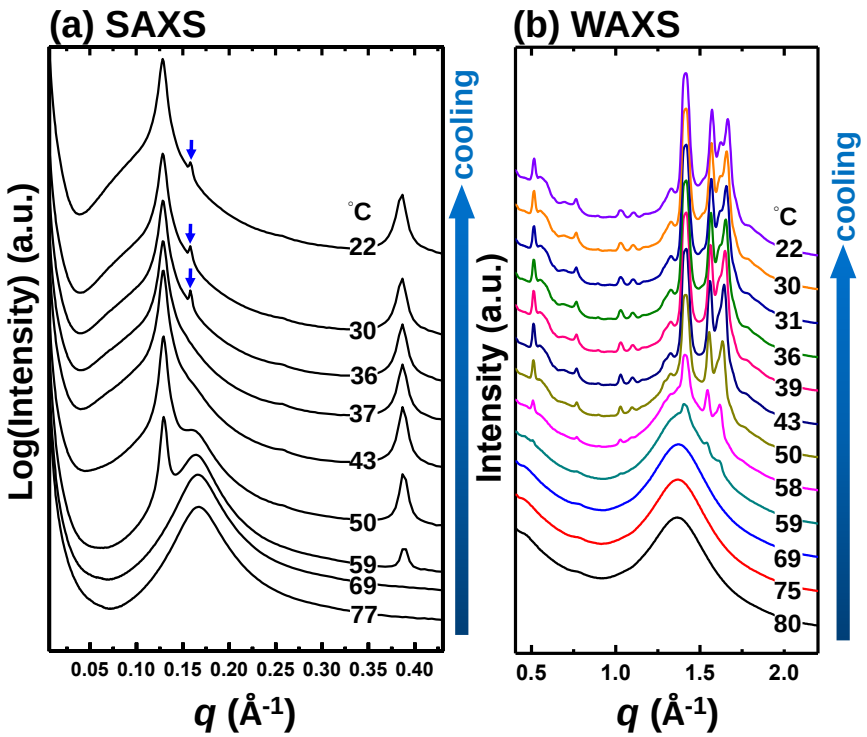

Figure S11. *In-situ* (a) SAXS and (b) WAXS profiles of P4VP$_{1.7k}$(THBA)$_{0.7}$ at a cooling rate ~1 ℃/min.

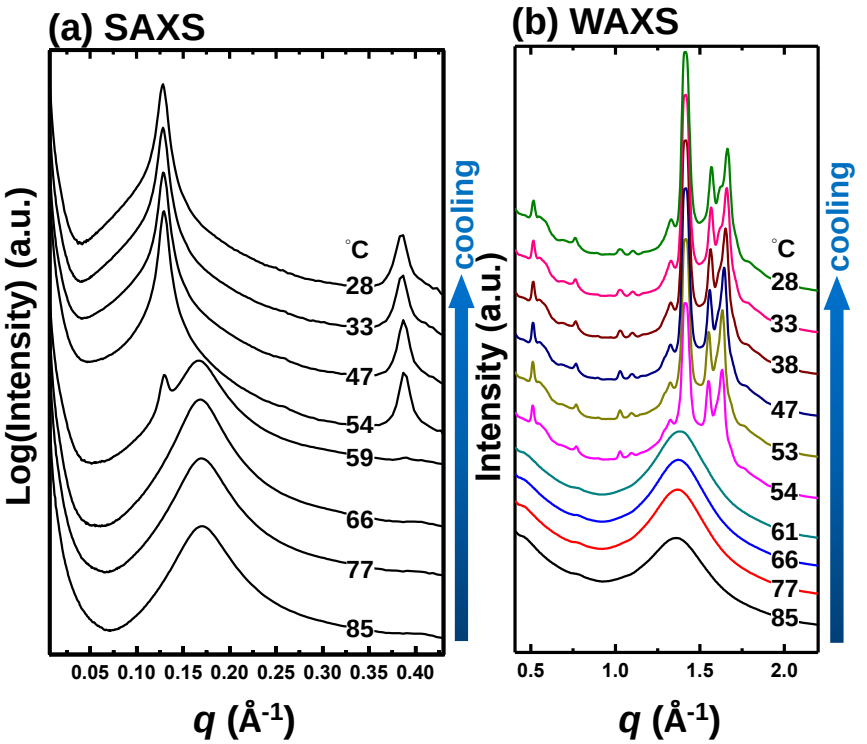

Figure S12. *In-situ* (a) SAXS and (b) WAXS profiles of P4VP$_{1.7k}$(THBA)$_{0.8}$ at a cooling rate ~1 ℃/min.

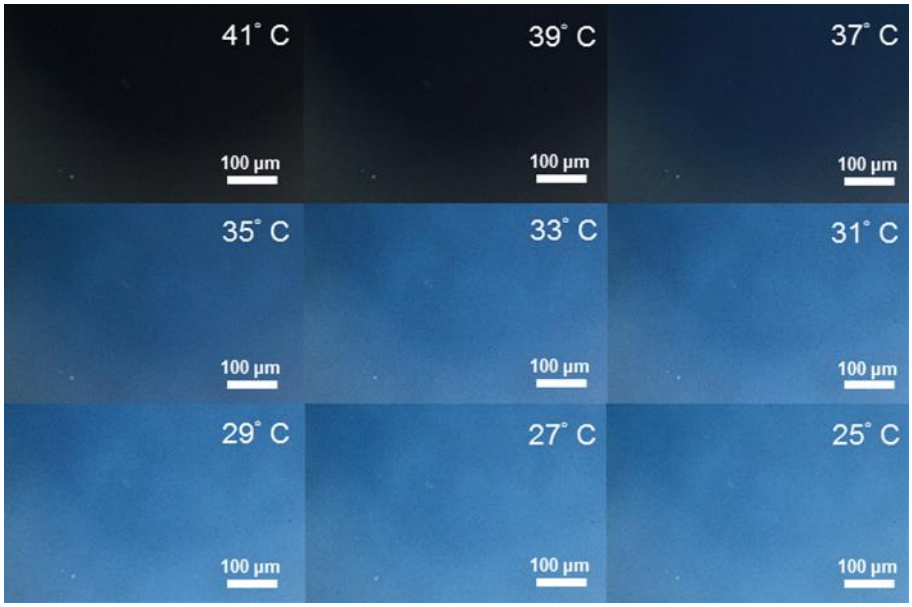

Figure S13. Complete *in-situ* POM images of $P4VP_{1.7k}(THBA)_{0.5}$ at a cooling rate of 1 ℃/min.

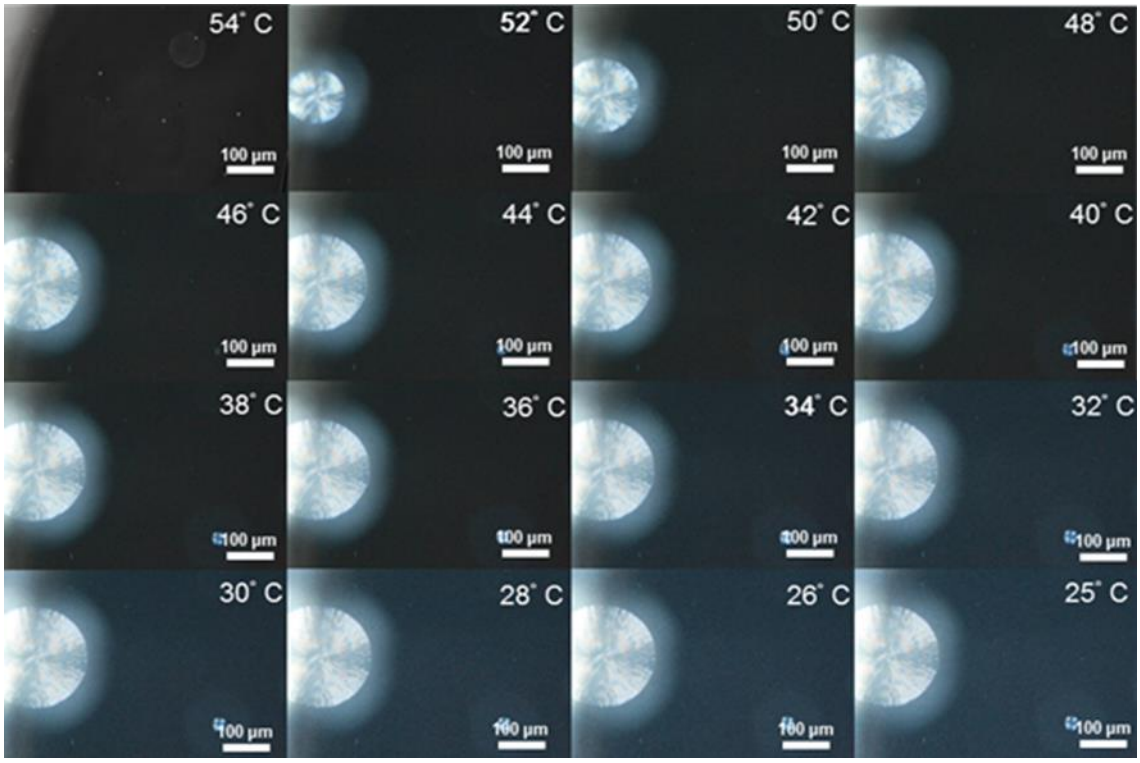

Figure S14. Complete *in-situ* POM images of $P4VP_{1.7k}(THBA)_{0.7}$ at a cooling rate of 1 ℃/min.