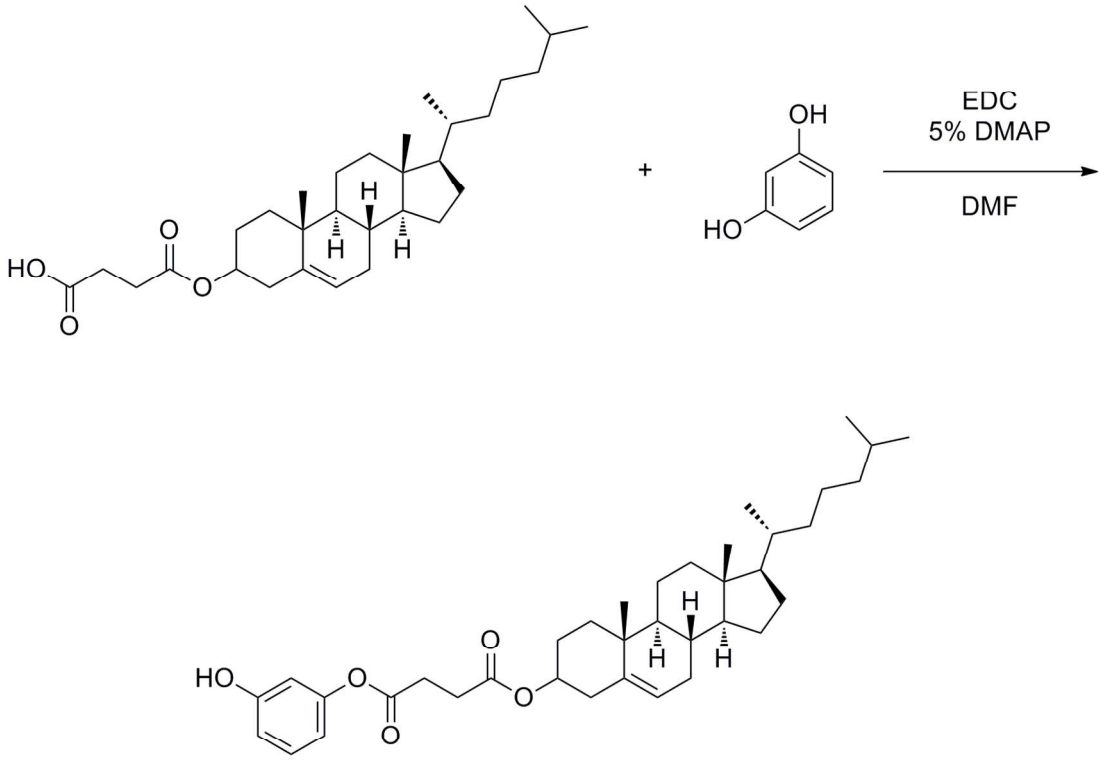
Supporting Information

S1. ChHP Small Molecule Synthesis

All chemicals were purchased from Aldrich and used without further purification unless otherwise noted. All reactions were performed under dry N_2 unless otherwise noted. All extracts were dried over $MgSO_4$ and solvents were removed by rotary evaporation with aspirator pressure. Flash chromatography was performed using Merck Kieselgel 60 (230-400 mesh) silica. DMF was purchased from Fisher and vigorously purged with nitrogen for 1h. The solvent was further purified by passing it under nitrogen pressure through two packed columns (Glass Contour) of activated molecular sieves. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AV-600 instrument using $CDCl_3$ as the solvent. High Resolution Mass Spectometry (HRMS) using Fast Atom Bombardment (FAB) was done with a Micromass ZAB2-EZ double focusing mass spectrometer (BE geometry). Elemental analyses were performed at the UC Berkeley Microanalysis Laboratory.



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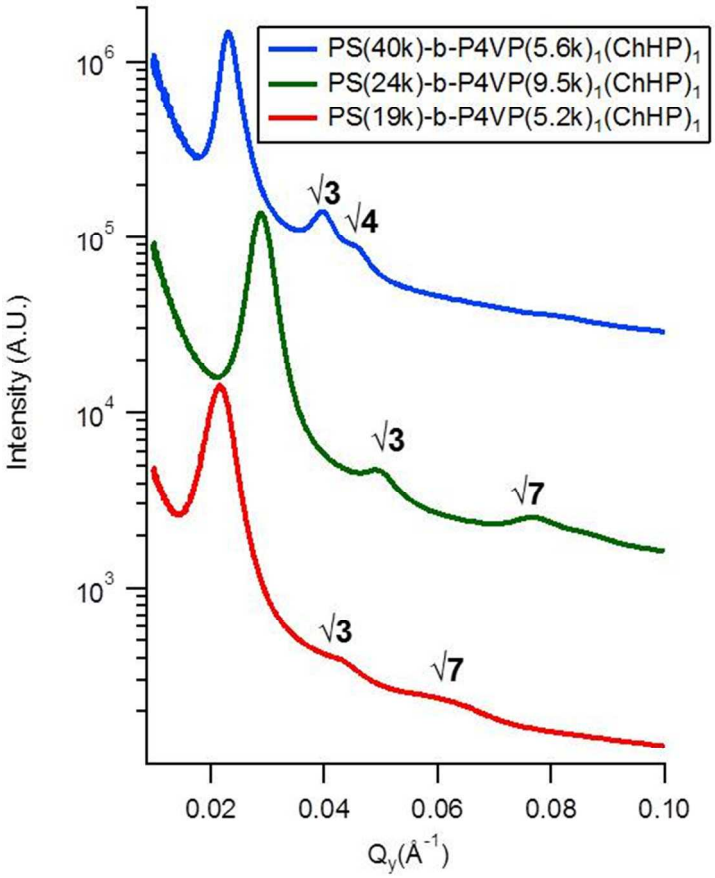
A flask was charged with 3.45 g (7.1 mmol) cholesteryl hemisuccinate, 7.8 g (71 mmol) resorcinol, 43 mg (5%) DMAP, and 60 mL DMF. The mixture was cooled to 0 °C and 1.36 g (7.1) EDC was added. The mixture was allowed to warm to room temperature and was stirred for 6 h. The mixture was then poured into 300 mL water and the product was then extracted 3x with 100 mL DCM. The organic fractions were combined and dried with MgSO4. The solvent was evaporated and the crude product was purified via flash chromatography, eluting with 30% ethyl acetate in hexanes to yield 2.75 g (67%) of a white solid. 1H NMR (600 MHz): δ 0.67 (s, 3H), 0.85-0.87 (m, 6H), 0.91-1.63 (m, 28H), 1.83-1.87 (m, 3H), 1.95-2.01 (m, 2H), 2.32-2.35 (m, 2H), 2.71 (t, J = 6.6 Hz, 2H), 2.86 (t, J = 6.6 Hz, 2H) 4.63-4.68 (m, 1H), 5.37 (d, J = 4.8 Hz, 1H), 6.59-6.60 (m, 1H), 6.65-6.70 (m, 2H), 7.20-7.22 (m, 1H). 13C NMR (150 MHz): δ 11.84, 18.72, 19.27, 21.02, 22.56, 22.81, 23.85, 24.27, 27.69, 27.98, 28.22, 29.35, 29.44, 31.82, 31.87, 35.78, 36.18, 36.53, 36.90, 38.00, 39.51, 39.71, 42.29, 49.97, 56.15, 56.66, 74.87, 76.84, 77.06, 77.27,

109.06, 113.09, 113.09, 113.31, 122.81, 129.95, 139.38, 151.31, 157.10, 171.44, 172.01. HRMS (FAB) m/z calc for (C37H54O5, M-1) 577.3898; found 577.3884. Anal. Calcd for C37H54O5: C, 76.78; H, 9.40. Found C, 76.73; H, 9.56.

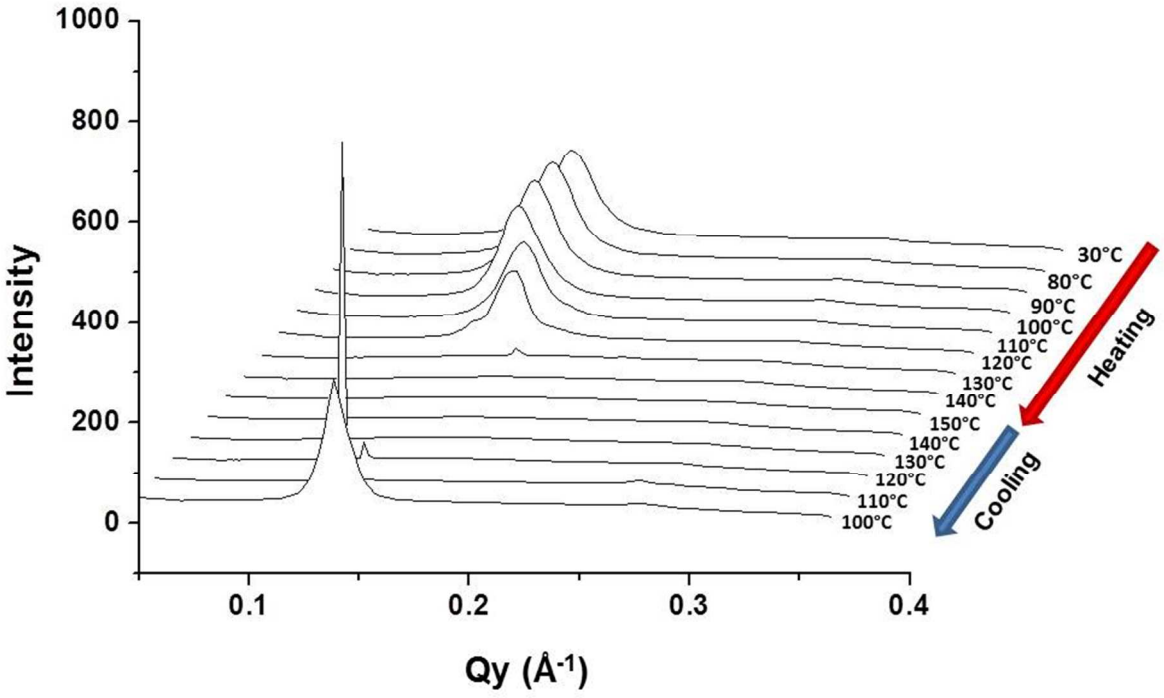
S2 Post Thermal Annealing Morphology of PS-*b*-P4VP(ChHP) via Transmission Small Angle X-ray Scattering (SAXS)

The post thermal annealing morphology of the supramolecule is characterized by transmission SAXS to corroborate with the TEM data presented in Figure 2. The supramolecule samples, which have been annealed at 150°C for 12 hours, are exposed to X-ray for 60s and the resulting 2D scattering plot was circularly integrated to generate 1-D intensity vs. *q* plots. All three plots exhibit scattering peaks indicative of long range hexagonally packed cylinder morphology. (1:√3:√7 for PS(24k)-*b*-P4VP(9.5k)$_1$(ChHP)$_1$ and PS(19k)-*b*-P4VP(5.2k)$_1$(ChHP)$_1$ and 1:√3:√4 for PS(40k)-*b*-P4VP(5.6k)$_1$(ChHP)$_1$).



S3. PS/ChHP miscibility

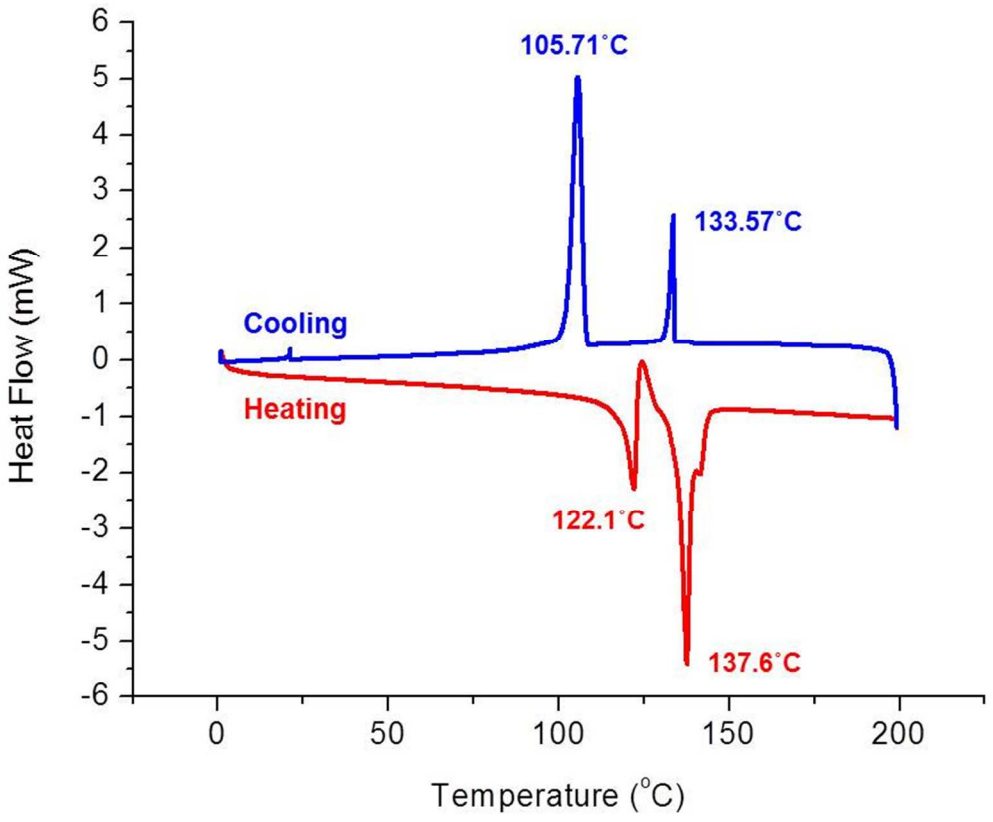
S3.1 Small Angle X-ray Scattering (SAXS)



Small angle X-ray scattering (SAXS) was performed on ChHP *in-situ* during heating at a rate of 10°C/min from 30°C to 150°C and subsequently cooled back down to room temperature to analyze its crystal structure. The ChHP sample has a characteristic scattering peak at q = 0.14 $Å^{-1}$, corresponding to a crystal structure with a periodicity of 4.5 nm. Upon heating to above 120°C, the periodicity of the crystal structure begins to decrease, reaching 3.8 nm at 130°C. Above 130°C, the characteristic scattering peak disappears as the ChHP becomes isotropic. As the sample is gradually cooled back to room temperature, the 4.5 nm peak reappears around 120°C, indicating recrysallization of the small molecules.

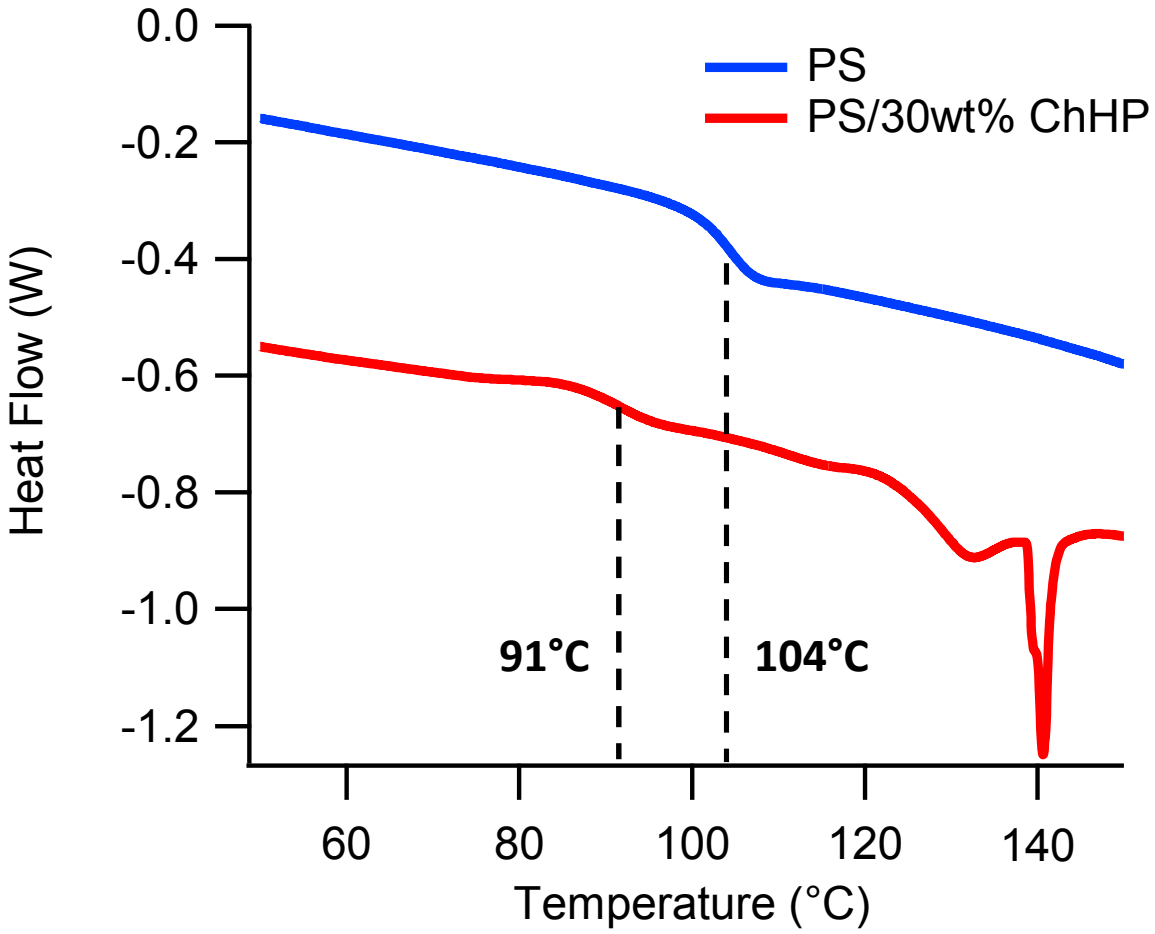
S3.2 Differential Scanning Calorimetry (DSC) of ChHP

DSC was performed on pure ChHP to characterize its melting and phase transitions. The temperature was ramped from 0°C to 200°C at a rate of 10°C/min and subsequently cooled to 0°C for three cycles to eliminate the thermal history of the ChHP sample. The DSC scan of the third heating and cooling cycles is shown below. Upon heating, ChHP undergoes a crystalline to liquid crystalline (LC) phase transition at 122°C and a LC to isotropic transition at 138°C. Upon cooling, an isotropic to LC transition occurs at 134°C and a LC to crystalline transition occurs at 106°C.



S3.3 DSC of PS/ChHP Blend

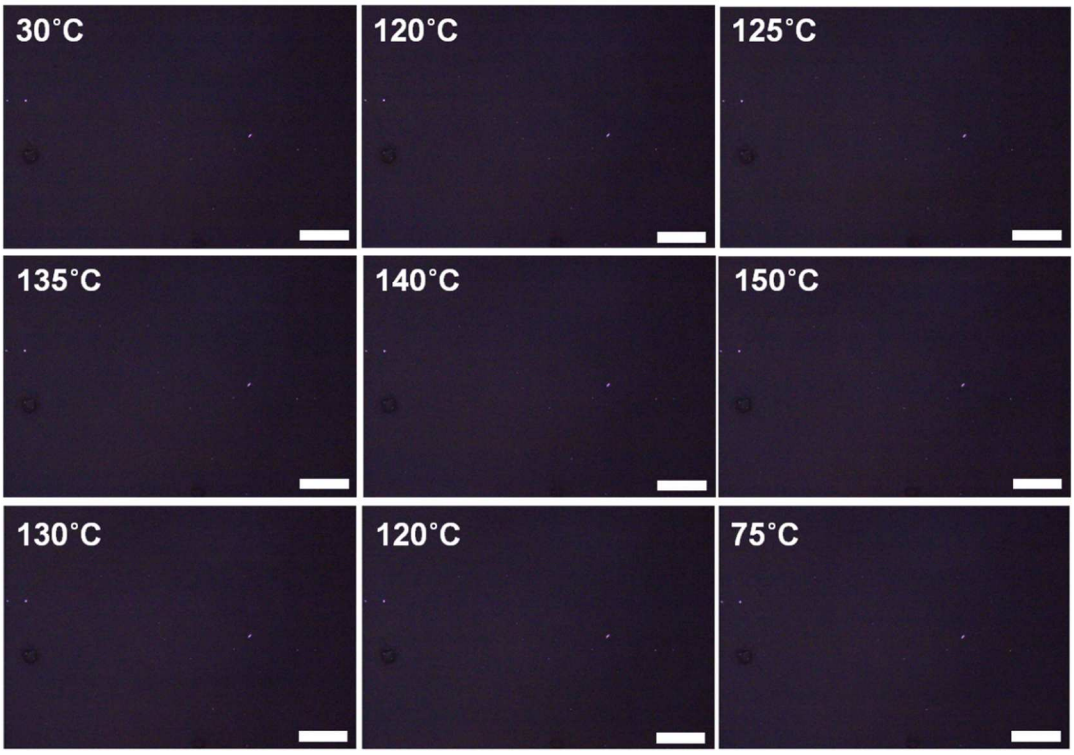
DSC was performed on a pure 22k PS sample and a 30wt% ChHP in 22k PS mixture to characterize the miscibility of ChHP in PS. The temperature was ramped from 0°C to 200°C at a rate of 10°C/min and subsequently cooled to 0°C for three cycles to eliminate the thermal history of the ChHP sample. The DSC scan of the third heating cycle is shown below. The scan of pure PS shows a T_g of 104°C, while the T_g of the PS/ChHP mixture decreases to 91°C, suggesting miscibility of ChHP in PS.



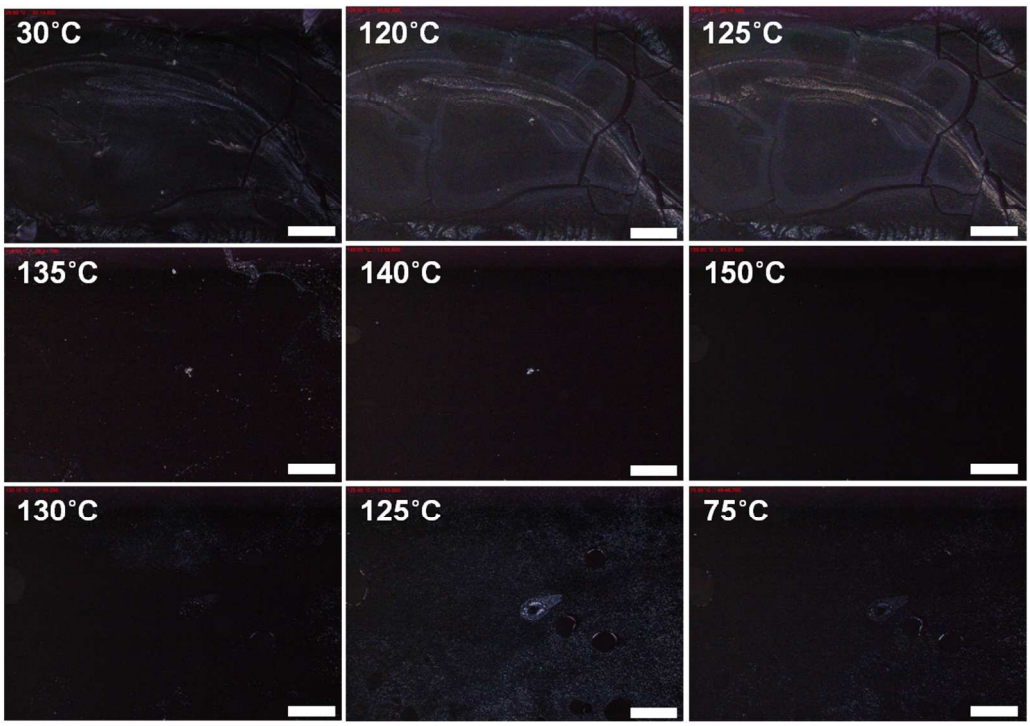
S3.4 Polarized Optical Microscopy (POM)

POM was conducted on PS(22k)/ChHP mixtures with a) 10wt%, b) 30wt% and c) 50wt% ChHP loading during heating from room temperature to 150°C under a heating rate of 10°C/min and subsequent cooling to room temperature to confirm miscibility of ChHP in PS. At 10wt% ChHP loading, no birefringence is detected at any temperature, suggesting miscibility of ChHP in PS at small loadings. For 30wt% and 50wt% ChHP loaded samples, birefrigent ChHP crystals are visible from 30°C to 135°C. Between 135°C and 140°C, the crystallites promptly disappear, indicating that ChHP has become miscible and all anisotropy has been lost. During cooling to 130°C, birefringence reappears, suggesting crystallization of ChHP at temperatures below 130°C. Scale bars are 2mm.

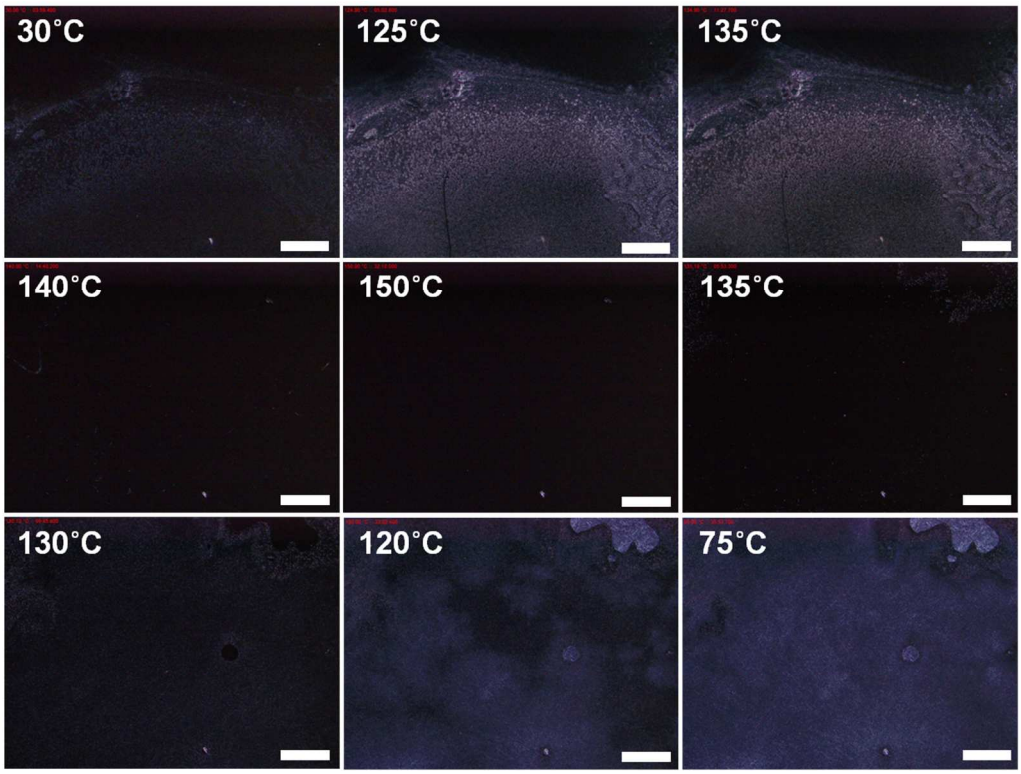
a)



b)


30°C
120°C
125°C
135°C
140°C
150°C
130°C
125°C
75°C

c)


30°C
125°C
135°C
140°C
150°C
135°C
130°C
120°C
75°C

S4. TEM of PS-*b*-P4VP(ChHP) Supramolecule with Slow Cooling Rate

a) high magnification and b) low magnification images of PS(19k)-*b*-P4VP(5.2k)$_1$(ChHP)$_1$, PS(24k)-*b*-P4VP(9.5k)$_1$(ChHP)$_1$, and PS(40k)-*b*-P4VP(5.6k)$_1$(ChHP)$_1$ supramolecule samples annealed at 150°C for 12 hours and subsequently cooled slowly from 150°C to 100°C over 4 hours. The resulting morphologies are cylindrical with P4VP(ChHP) as the minority microdomain, similar to samples cooled over 1 hour.