SELF-ASSEMBLED STRUCTURES IN DIBLOCK COPOLYMERS WITH HYDROGEN BONDED AMPHIPHILIC PLASTICIZING COMPOUNDS

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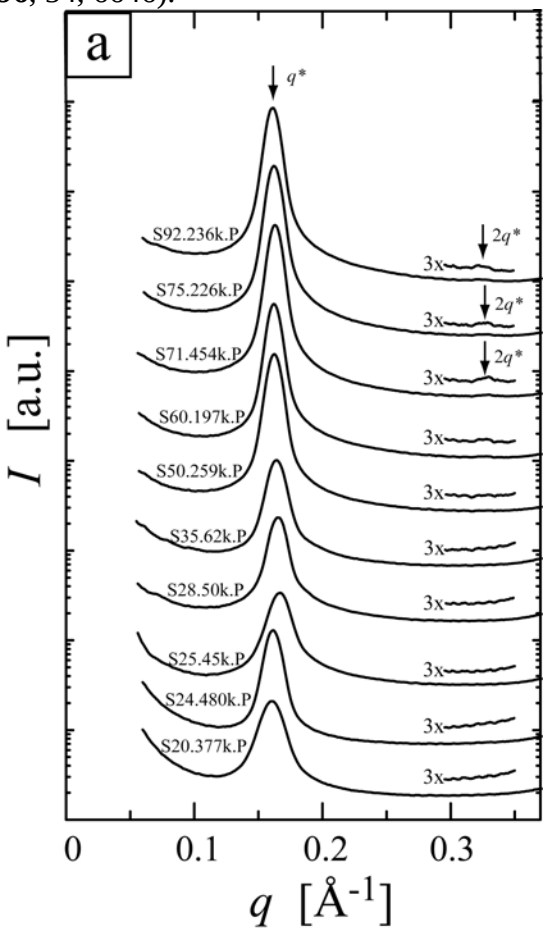
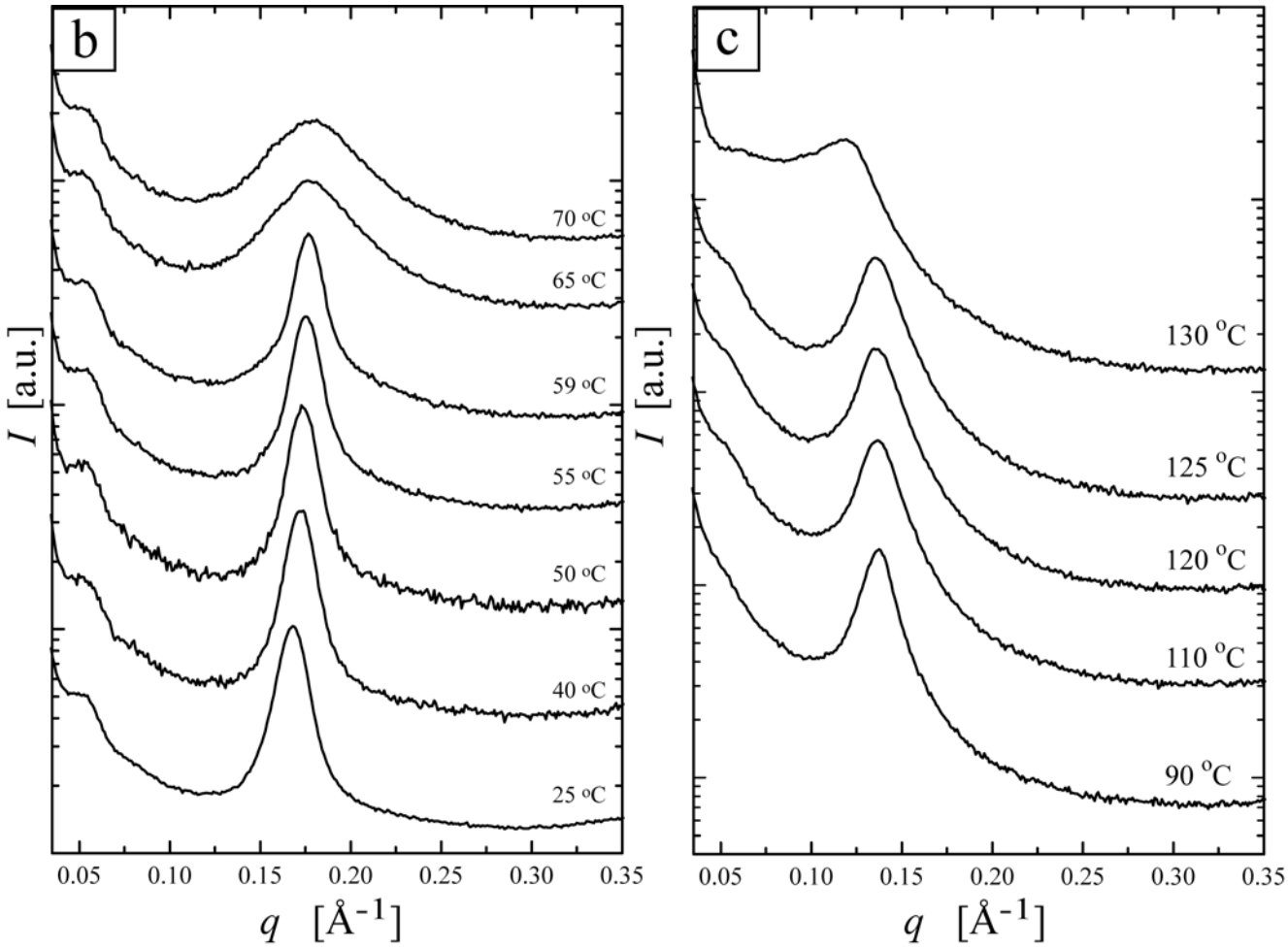
Supporting information

PS-*block*-P4VP(PDP)$_{1.0}$ and PS-*block*-P4VP(MSA)$_{1.0}$(PDP)$_{1.0}$: Order-disorder transition of the smaller length scale structure within the supramolecular comb blocks:

Supporting Figures S1a-c represent the order-disorder transition (ODT) of the smaller length scale *lam* structure within the P4VP(PDP)$_{1.0}$ or P4VP(MSA)$_{1.0}$(PDP)$_{1.0}$ domains of PS-*block*-P4VP(PDP)$_{1.0}$ or PS-*block*-P4VP(MSA)$_{1.0}$(PDP)$_{1.0}$, respectively. For P4VP(PDP)$_{1.0}$, the intensity maximum is observed at q^* = 0.17 Å^{-1} (corresponding to a long period of L_p = 37 Å). A faint evidence of higher order reflection at $2q^*$ corresponding to lamellar structure is observed for the block copolymers where P4VP is the majority domain, see Fig. S1a. and ODT can be seen as broadening of the intensity maximum at ca. T = 60 ^{o}C (Fig. S1b). For P4VP(MSA)$_{1.0}$(PDP)$_{1.0}$ system the intensity maximum is located at q^* = 0.13 Å^{-1} (corresponding to a long period of L_p = 48 Å) and in this case ODT temperature is at ca. T = 125 ^{o}C (Supporting Fig. S1c). The second order reflections are weakly observed probably due to roughly equal thicknesses of the polar and non-polar domains. Upon side chain crystallization, however, it becomes observable (see Phys Rev E **1996**, 54, 6646).



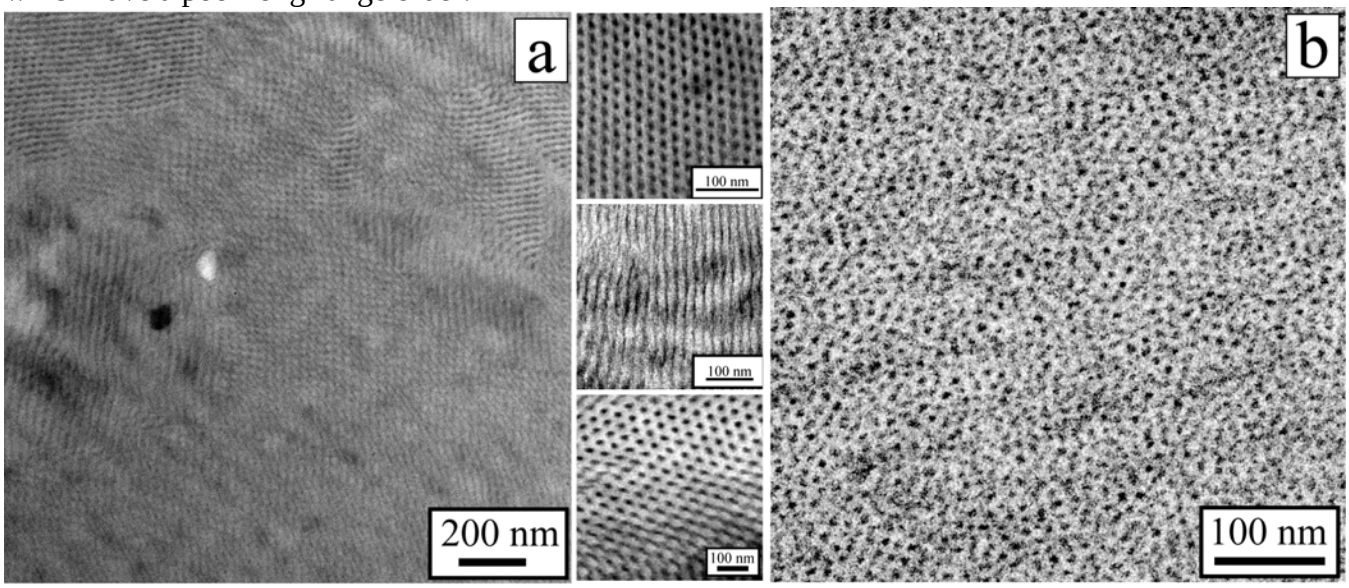


Supporting Figure S1. a) SAXS curves for various PS-*block*-P4VP(PDP)$_{1.0}$ at room temperature, showing a faint evidence of second order reflection at 2*q****.** b) SAXS intensity patterns of PS-*block*-P4VP(PDP)$_{1.0}$ with the P4VP(PDP)$_{1.0}$ weight fraction 0.62 (S62.83k.P), at different temperatures showing the order-disorder transition of short length scale structure within P4VP(PDP)$_{1.0}$ domains at ca. T = 60 °C. c) The order-disorder transition of the short length scale structure within P4VP(MSA)$_{1.0}$(PDP)$_{1.0}$ occurs at ca. T = 125 °C (S88.161k.MP with the weight fraction 0.88 of the supramolecular comb block P4VP(MSA)$_{1.0}$(PDP)$_{1.0}$).

Order-order transitions in PS-*block*-P4VP(PDP)$_{1.0}$ system:

PS-*block*-P4VP(PDP)$_{1.0}$ with $f_{comb,1}$ = 0.28 (Sample S28.50k.P)

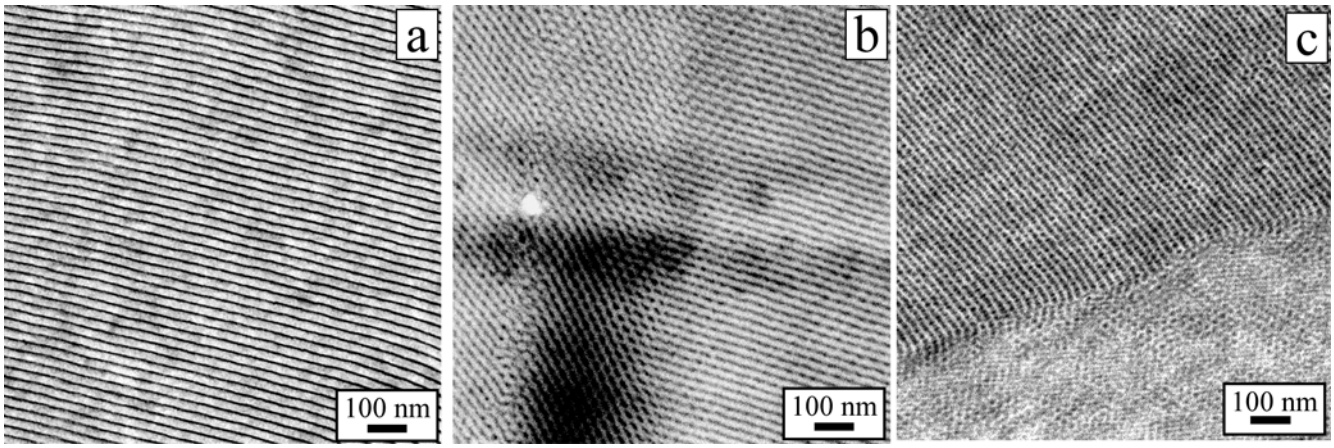
Phase transitions from lamellar-in-hexagonally perforated layer to hexagonally perforated layer to spherical structures (lam-in-HPL´ to HPL´ to SPH´): S28.50k.P forms a lamellar-*in*-hexagonally perforated layer (*lam-in-HPL´*) morphology at room temperature, which is manifested in the TEM image showing projections both parallel and normal to the perforated layer structure (Supporting Fig. S2a and insets). Upon heating the *lam-in-HPL´* morphology has an order-disorder transition of the smaller length scale structure and finally it is transformed to P4VP spheres (Supporting Figs. S2b), which have a poor long-range order.



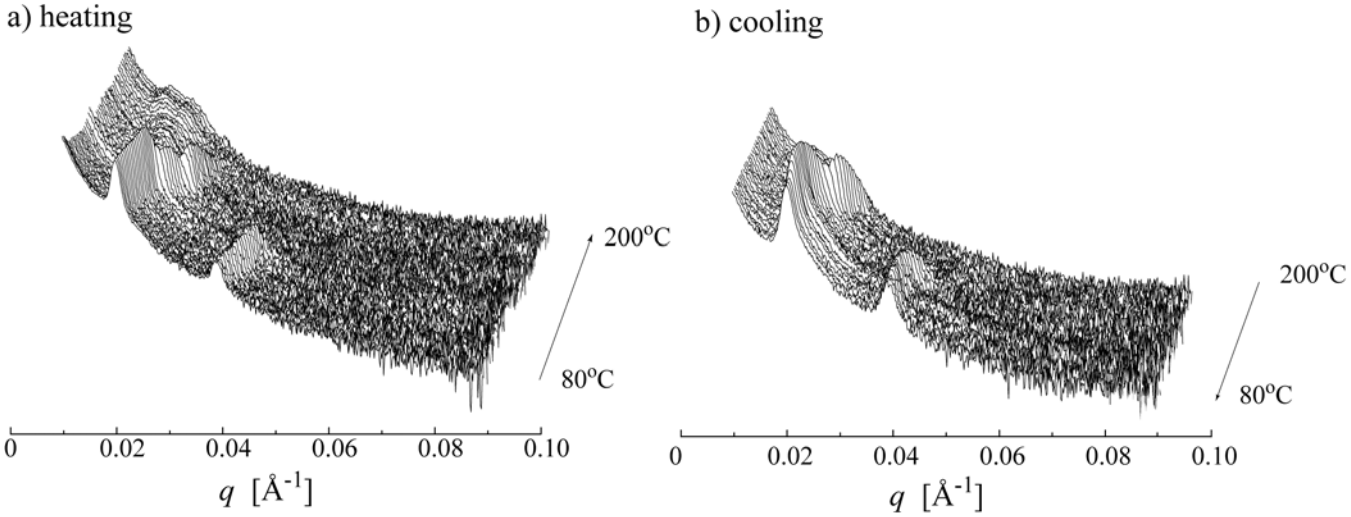
Supporting Figure S2. TEM micrographs of PS-*block*-P4VP(PDP)$_{1.0}$ with $f_{comb,1}$ = 0.28 (S28.50k.P) a) at room temperature a *lam-in-HPL´* structure is formed and the insets illustrates the characteristic features of *HPL´* structure. b) At T = 170 ^{o}C S28.50k.P forms P4VP spheres. P4VP regions appear dark in the images due to the I_2 staining.

PS-*block*-P4VP(PDP)$_{1.0}$ with $f_{comb,1}$ = 0.35 (Sample S35.62k.P)

Phase transitions from lamellar-in-lamellar to lamellar to hexagonally perforated layer structures (lam-in-LAM to LAM to HPL´): A lamellar-*in*-lamellar to hexagonally perforated layer transition was observed for S35.62k.P sample (see Supporting Fig. S3a-c and Fig. S4a-b).



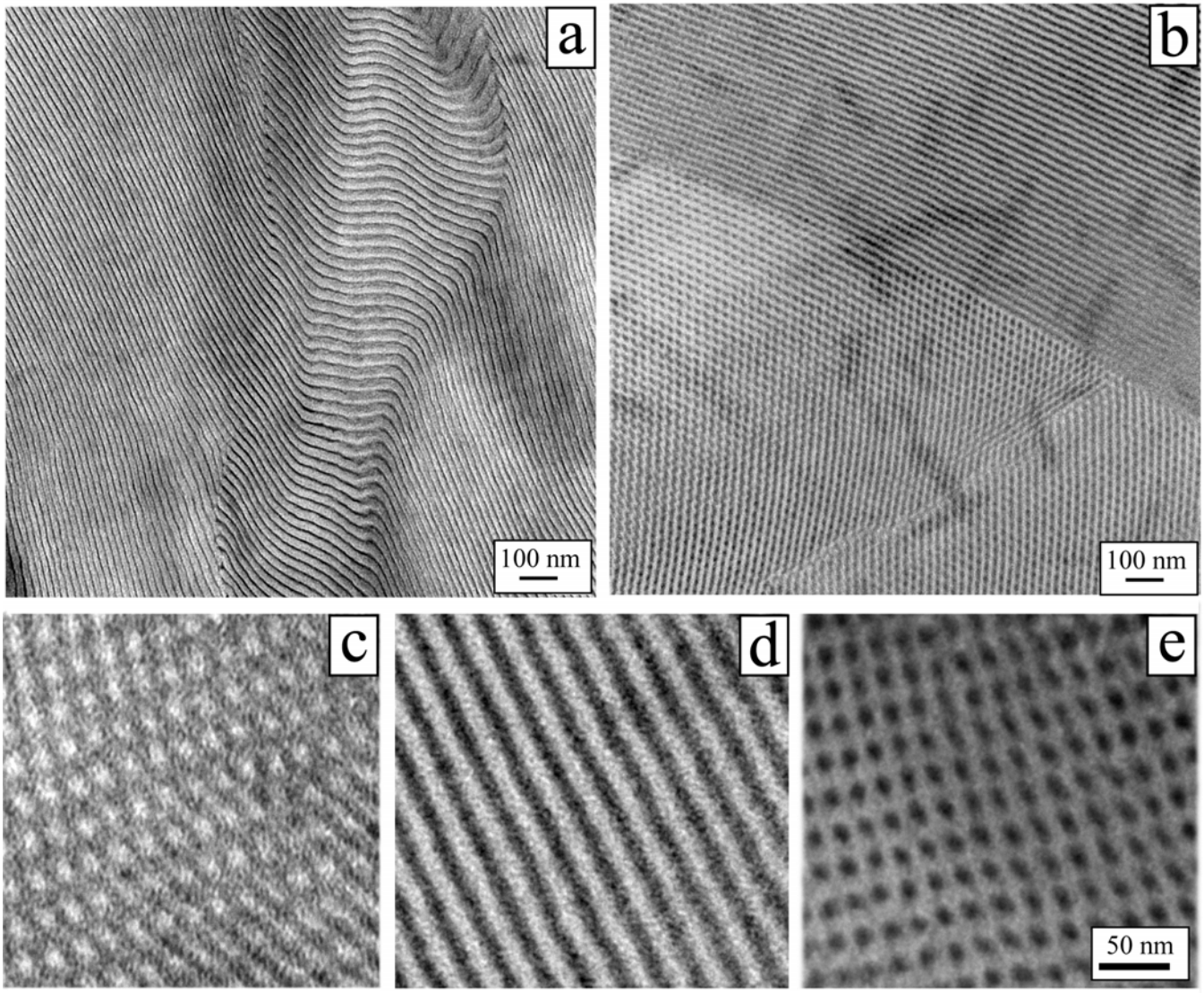
Supporting Figure S3. TEM micrographs of PS-*block*-P4VP(PDP)$_{1.0}$ with $f_{comb,1}$ = 0.35 (S35.62k.P) a) at room temperature showing a *lam-in-LAM* structure, and b-c) at T = 170 °C and T = 210 °C a hexagonally perforated layer morphology. P4VP shows dark in the images due to the I_2 staining.



Supporting Figure S4. SAXS intensity patterns of PS-*block*-P4VP(PDP)$_{1.0}$ with $f_{comb,1}$ = 0.35 (S35.62k.P) as a function of temperature. Curves upon a) heating from 80 °C to 200 °C (heating rate 5 °C/min) and b) cooling from 200 °C to 80 °C (cooling rate 10 °C/min) indicating reversibility of the transitions.

PS-*block*-P4VP(PDP)$_{1.0}$ with $f_{comb,1}$ = 0.43 (Sample S43.74k.P)

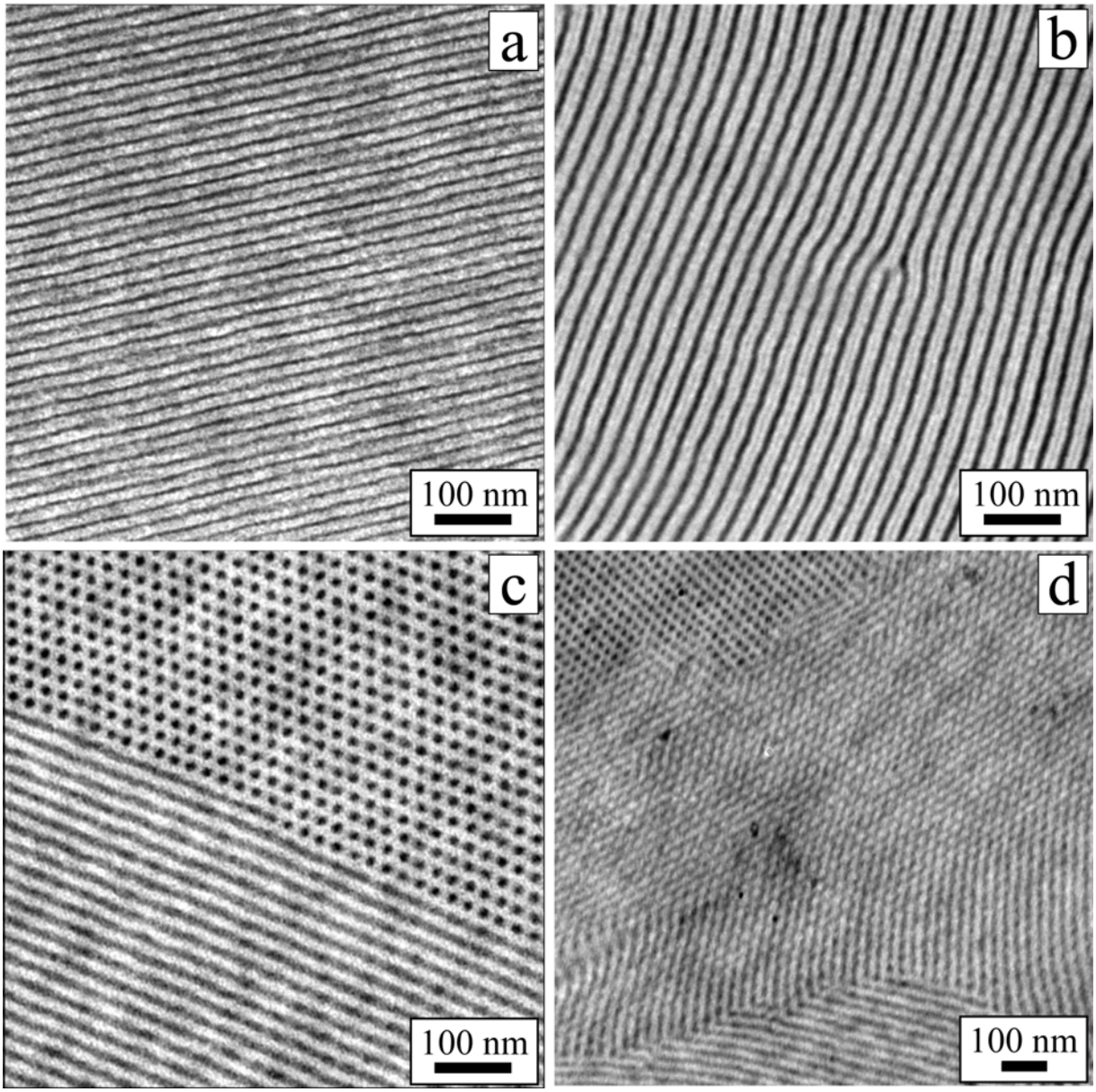
Phase transitions from lamellar-in-lamellar to lamellar to hexagonally perforated layer structures (lam-in-LAM to LAM to HPL´): A *lam-in-LAM* structure was observed for S43.74k.P at room temperature (Supporting Fig. S5a). Heating causes an order-disorder transition of the smaller length scale structure within P4VP(PDP)$_{1.0}$ domains and upon further heating an order-order transition to hexagonally perforated layer morphology is observed (see Supporting Fig. S5b-e). This sample has only two order-order transition indicating that it is not near the phase boundary at room temperature and therefore minor changes in the volume fractions are not enough to cause several consecutive order-order transitions.



Supporting Figure S5. TEM micrographs of PS-*block*-P4VP(PDP)$_{1.0}$ with $f_{comb,1}$ = 0.43 (S43.74k.P). a) At room temperature it forms a *lam-in-LAM* structure and b) *HPL´* at T = 210 ^{o}C. The characteristic features of *HPL´* structure are shown in Figs. c-e). P4VP regions appear dark in the images due to the I_2 staining.

PS-*block*-P4VP(PDP)$_{1.0}$ with $f_{comb,1}$ = 0.49 (Sample S49.64k.P)

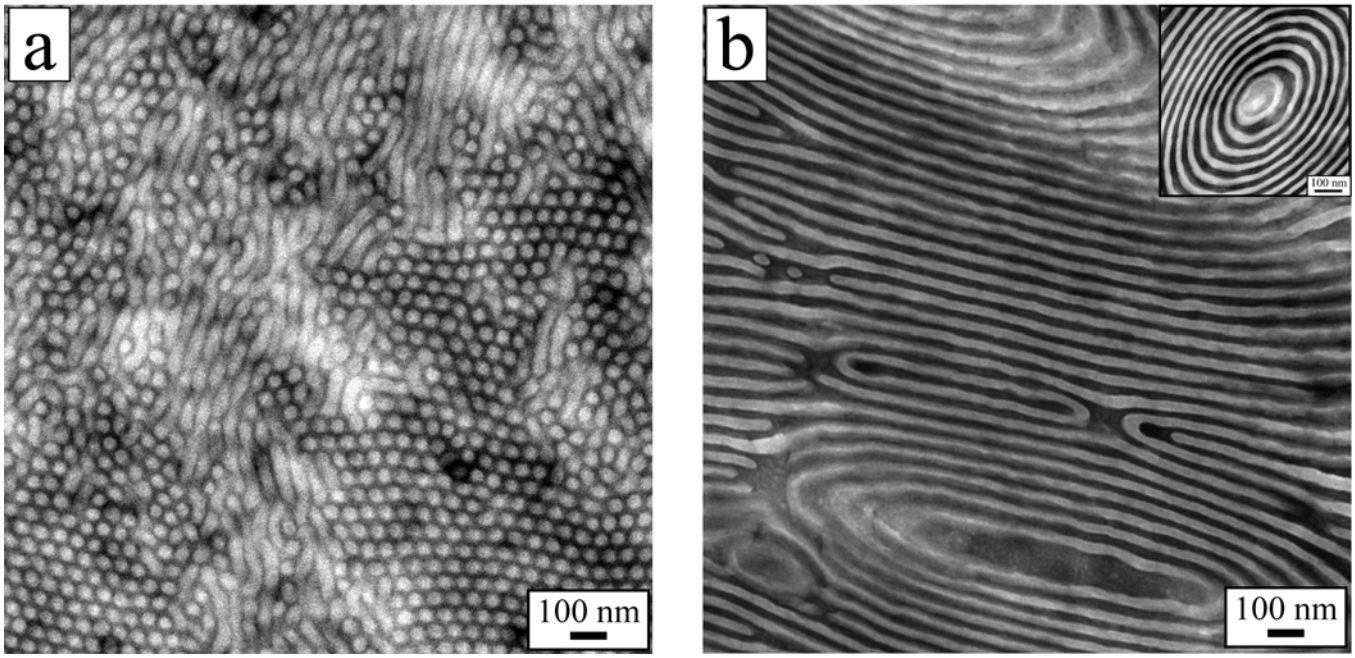
Phase transitions from lamellar-in-lamellar to lamellar to hexagonally perforated layer structures (lam-in-LAM to LAM to HPL´): S49.64k.P forms a *lam-in-LAM* structure at room temperature (Supporting Fig. S6a). Upon heating an order-disorder transition of the smaller length scale structure occurs at ca. T = 60 ^{o}C and thereafter the sample remains lamellar at ca. T = 170 ^{o}C (see Supporting Fig. S6b), thereafter it undergoes an order-order transition to hexagonally perforated layer morphology (Supporting Fig. S6c-d). This sample has only two order-order transitions indicating that it is not near the phase boundary at room temperature and therefore minor changes in the volume fractions are not enough to cause several consecutive phase transitions.



Supporting Figure S6. TEM micrographs of PS-*block*-P4VP(PDP)$_{1.0}$ with $f_{comb,1}$ = 0.49 (S49.64k.P) a) at room temperature it forms a *lam-in-LAM* structure, b) at T = 170 ^{o}C a *LAM* structure, and c-d) at T = 210 ^{o}C a *HPL´* . P4VP regions appear dark in the images due to the I_2 staining.

PS-*block*-P4VP(PDP)$_{1.0}$ with $f_{comb,1}$ = 0.75 (Sample S75.226k.P)

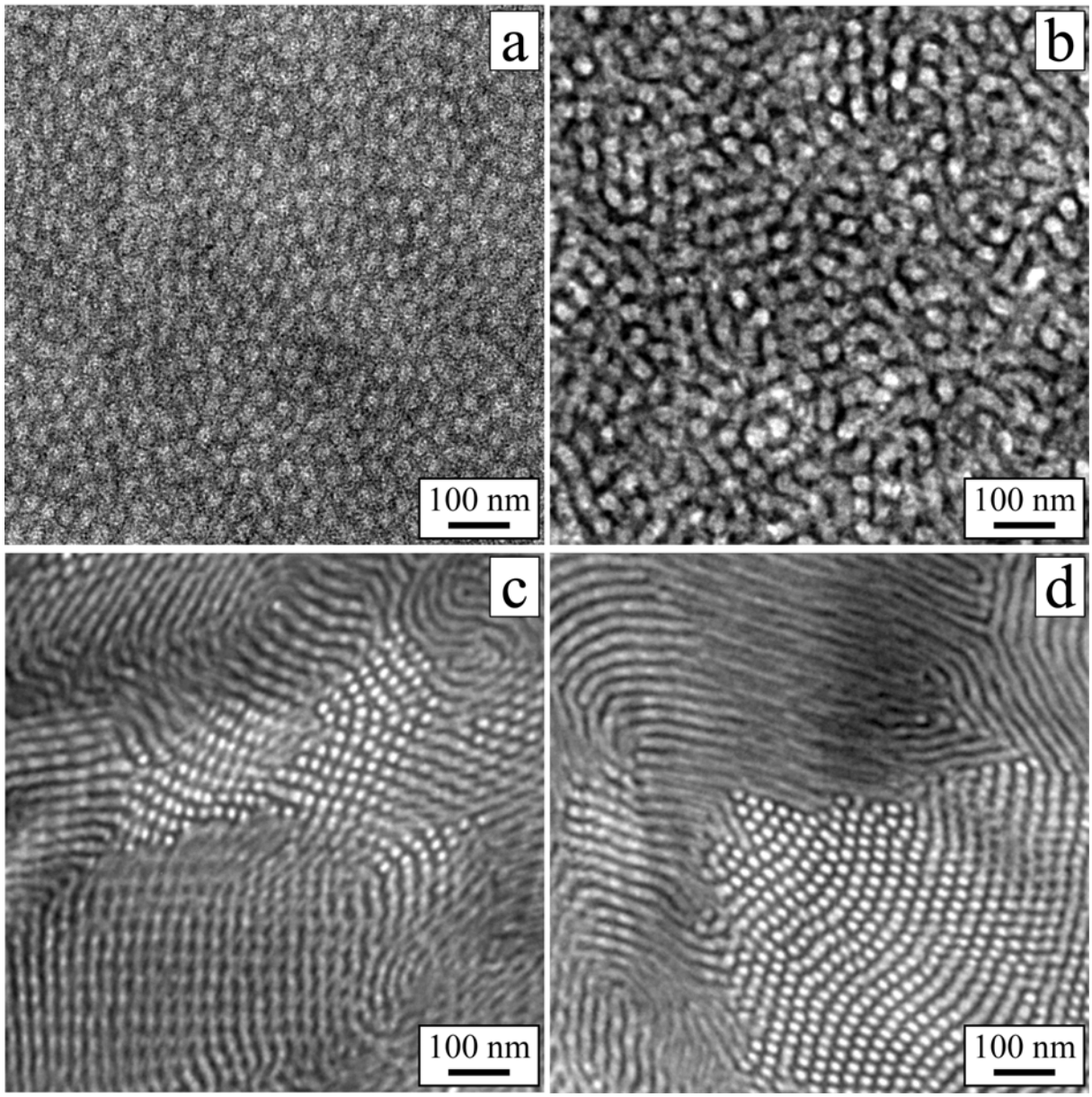
Phase transitions from cylindrical-in-lamellar to cylindrical to lamellar structures (CYL-in-lam to CYL to LAM): CYL-in-lam morphology was observed at room temperature for S75.226k.P (Supporting Fig. S7a). Upon heating, an order-disorder transition of the smaller length scale structure takes place at ca. T = 60 °C and thereafter it undergoes a order-order transition to a lamellar structure, as can be seen in the TEM image, which is taken after quenching from T = 170 °C (Supporting Fig. S7b). The *LAM* structure has onion shaped defects, which are more clearly illustrated in the inset.



Supporting Figure S7. TEM micrographs of PS-*block*-P4VP(PDP)$_{1.0}$ with $f_{comb,1}$ = 0.75 (S75.226k.P) forming a) *CYL-in-lam* morphology at room temperature and b) a *LAM* structure with onion shaped defects at T = 170 °C. Characteristic example of the defect is illustrated in the inset. P4VP regions appear dark in the images due to the I_2 staining.

PS-*block*-P4VP(PDP)$_{1.0}$ with $f_{comb,1}$ = 0.85 (Sample S85.135k.P)

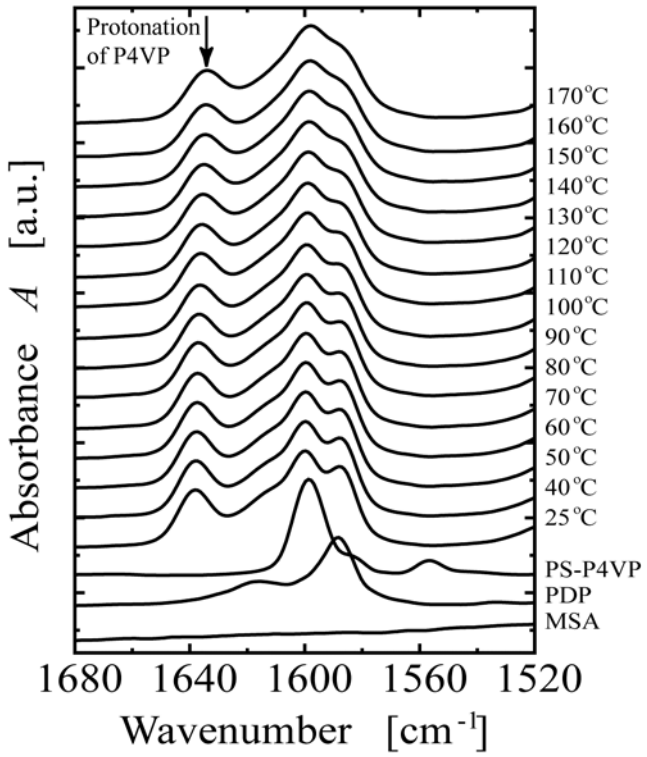
Phase transitions from spherical-in-lamellar to spherical to cylindrical to hexagonally perforated layer structures (SPH-in-lam to SPH to CYL to HPL): Sample S85.135k.P forms a *SPH-in-lam* structure at room temperature (Supporting Fig. S8a) as expected based on the weight fractions. Upon heating an order-disorder transition of the smaller length scale structure occurs at T = 60 ^{o}C. PS worm-like cylindrical structure (Supporting Fig. S8b) was obtained at T = 170 ^{o}C and *HPL* morphology at T = 210 ^{o}C (Supporting Fig. S8c-d) due to the increase in volume fraction of PS domains. TEM images of the *HPL´* structure consist of bright spots, which result from the parallel projection to the PS layers. PS layers are perforated by P4VP(PDP)$_{1.0}$ domains appearing as dark spots in the normal projection. Note that polystyrene is the minority component in this HPL structure and the scheme in Fig. 2c shows the projections for transverse *HPL´* structure.



Supporting Figure S8. TEM micrographs of PS-*block*-P4VP(PDP)$_{1.0}$ with $f_{comb,1}$ = 0.85 (S85.135k.P). a) At room temperature it forms a *SPH-in-lam* structure, b) at T = 170 ^{o}C a PS worm-like cylindrical structure, and c-d) at T = 210 ^{o}C a *HPL* morphology. P4VP regions appear dark in the images due to the I_2 staining.

Ionic bonding between MSA and P4VP

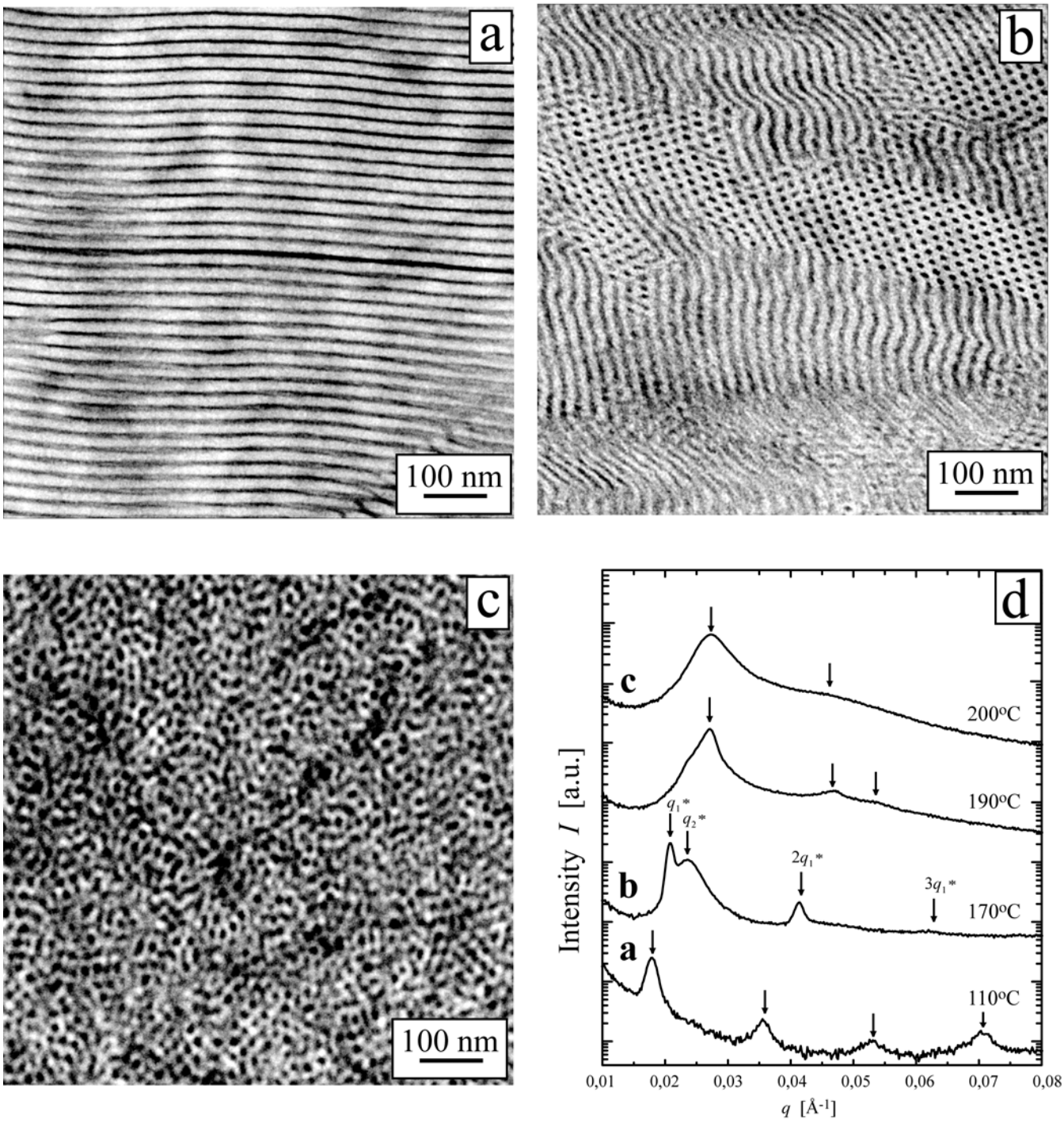
Pure PS-*block*-P4VP has absorption band at 1600 cm^{-1} and 1596-1597 cm^{-1} resulting from the aromatic carbon-carbon stretching of the phenyl groups and carbon-nitrogen stretching of the unprotonated pyridine rings, respectively. After the protonation of pyridine the carbon-nitrogen stretching band of PS-*block*-P4VP(MSA)$_{1.0}$(PDP)$_{1.0}$ is shifted to 1639 cm^{-1}. The ionic interaction between P4VP and MSA remains unchanged upon heating.



Supporting Figure S9. FTIR measurements of PS-*block*-P4VP(MSA)$_{1.0}$(PDP)$_{1.0}$ as a the function of temperature. Also FTIR spectrum of the pure PS-*block*-P4VP, MSA, and PDP are shown at room temperature for reference. Absorption peak at 1639 cm^{-1} remains unchanged upon heating to high temperatures indicating the ionic interaction between pyridine of P4VP and MSA.

PS-*block*-P4VP(MSA)$_{1.0}$(PDP)$_{1.0}$ with $f_{comb,2}$ = 0.48 (Sample S48.81k.MP)

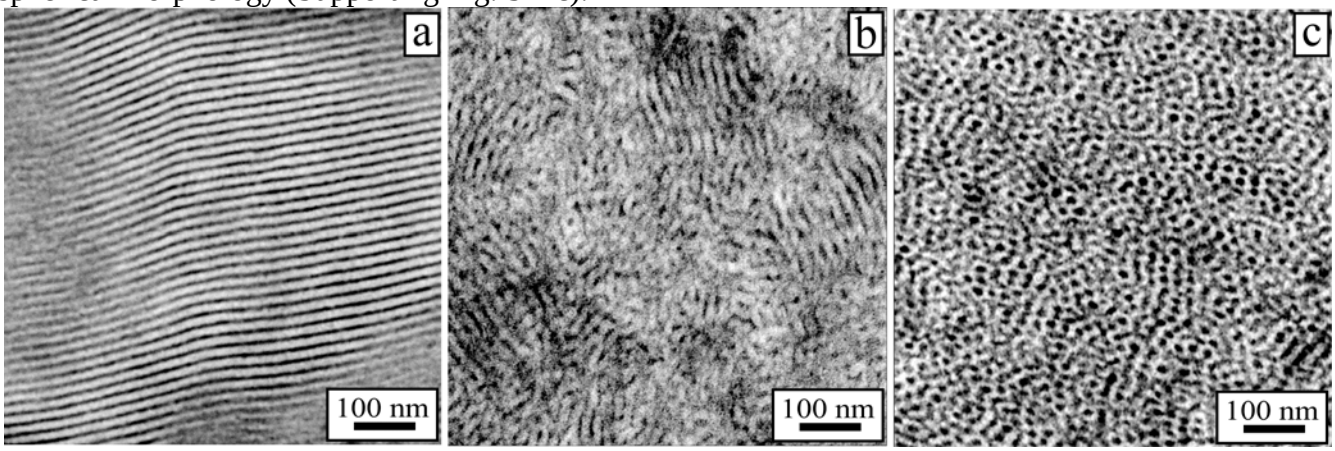
Phase transitions from lamellar-in-lamellar to lamellar to hexagonally perforated layer to cylindrical to spherical structures (lam-in-LAM to LAM to HPL´ to CYL´ to SPH´): When $f_{comb,2}$ = 0.48 (S48.81k.MP), a *lam-in-LAM* morphology was observed at room temperature (Supporting Fig. S10a). Upon heating an order-disorder transition of the smaller length scale structure within the P4VP(MSA)$_{1.0}$(PDP)$_{1.0}$ domains occurs at ca. T = 125 ^{o}C. *HPL´* structure was observed at ca. T = 170 ^{o}C, which can be seen both in TEM and SAXS (Supporting Fig. S10b and S10d). The SAXS pattern for *HPL´* shows a peak from a layer-like structure at q_1* = 0.0209 Å^{-1}, and its higher order reflections at 2q_1* and 3q_1*, and a reflection at q_2* = 0.0235 Å^{-1} (corresponding to 1.12q_1*) resulting from the hexagonal perforations (Supporting Fig. S10b). *CYL´* was obtained at ca. T = 190 ^{o}C, which can be seen in the SAXS intensity patterns (Supporting Fig. S10d) showing the characteristic cylindrical reflections at q*, √3q*, and 2q* (indicated with arrows). The cylindrical structure, in turn, was observed only at a narrow temperature range and already at ca. T = 200 ^{o}C a *SPH´* morphology was obtained (Supporting Fig. S10c-d). The spherical structure has a poor long-range order and the SAXS reflection at q* = 0.028 Å^{-1} and the shoulder at ca. q* = 0.045 Å^{-1} are broadened. Similar order-order transitions (*lam-in-LAM* to *LAM* to *HPL´* to *CYL´* to *SPH´*) were also observed for S67.95k.MP and S54.71k.MP samples. This is expected as they are more close to the phase boundary and smaller changes in $f_{comb,2}$ are enough to lead to order-order transitions.



Supporting Figure S10. TEM micrographs of PS-*block*-P4VP(MSA)$_{1.0}$(PDP)$_{1.0}$ with $f_{comb,2}$ = 0.48 (S48.81k.MP) a) at room temperature showing a *lam-in-LAM* structure, b) at T = 170 ^{o}C *HPL´*, and c) at T = 210 ^{o}C a *SPH´* structure. P4VP regions appear dark in the images due to the I_2 staining. d) SAXS intensity patterns at different temperatures. Letters refer to TEM images.

PS-*block*-P4VP(MSA)$_{1.0}$(PDP)$_{1.0}$ with $f_{comb,2}$ = 0.54 (Sample S54.71k.MP)

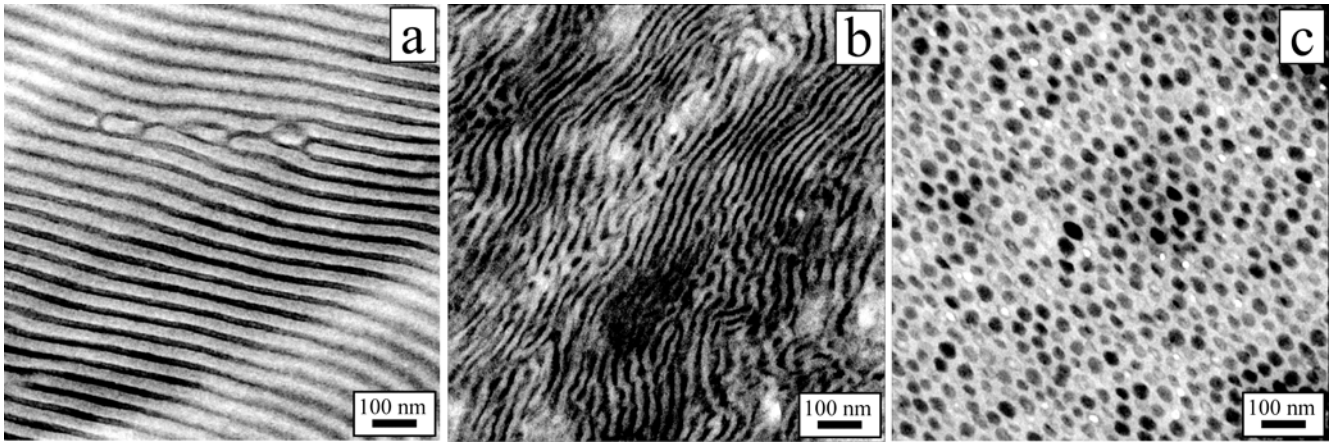
Phase transitions from lamellar-in-lamellar to lamellar to cylindrical to spherical structures (lam-in-LAM to LAM to CYL´ to SPH´): S54.71k.MP formed a *lam-in-LAM* structure at room temperature (Supporting Fig. S11a). Heating induces an order-disorder transition of the smaller length scale structure at ca. T = 125 ^{o}C and an order-order transition to P4VP cylinder (Supporting Fig. S11b) and finally to a spherical morphology (Supporting Fig. S11c).



Supporting Figure S11. TEM micrographs of PS-*block*-P4VP(MSA)$_{1.0}$(PDP)$_{1.0}$ with $f_{comb,2}$ = 0.54 (S54.71k.MP). a) At room temperature it forms a *lam-in-LAM* structure, b) at T = 170 ^{o}C *CYL´*, and c) T = 210 ^{o}C *SPH´*. P4VP shows dark in the images due to the I_2 staining.

PS-*block*-P4VP(MSA)$_{1.0}$(PDP)$_{1.0}$ with $f_{comb,2}$ = 0.67 (Sample S67.176k.MP)

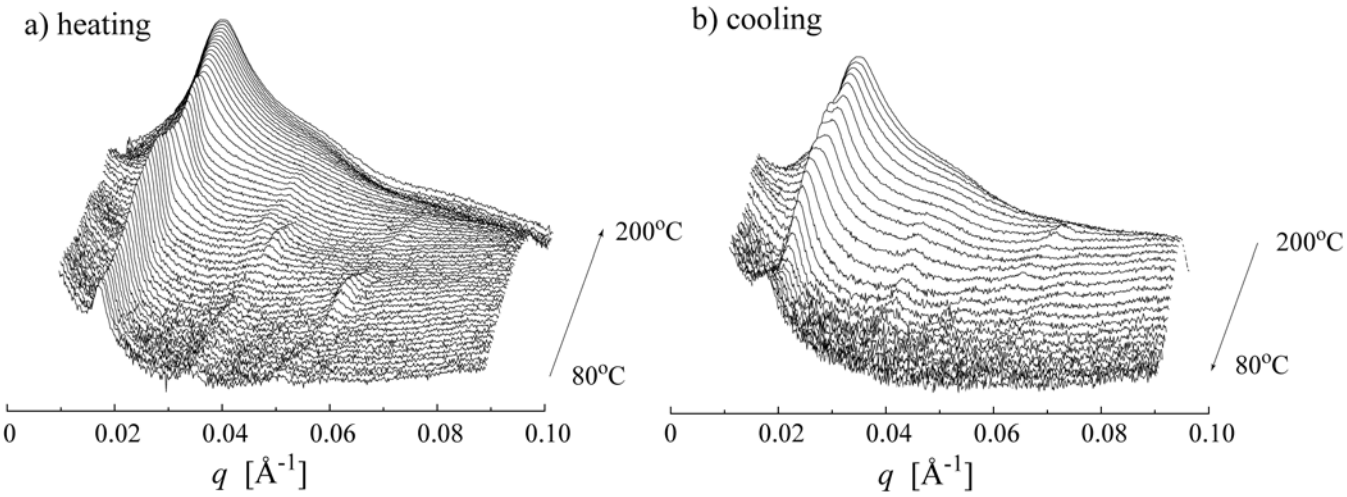
Phase transitions from lamellar-in-lamellar to lamellar to cylindrical to spherical structures (lam-in-LAM to LAM to Cyl´ to Sph´): Sample S67.176k.MP forms a *lam-in-LAM* structure at room temperature (Supporting Fig. S12a). Heating induces first an order-disorder transition of the smaller length scale structure at ca. T = 125 ^{o}C followed by an order-order transition to *CYL´* (Supporting Fig. S12b). When temperature was further increased to ca. T = 210 ^{o}C *SPH´* morphology was observed (Supporting Fig. S12c). This is supported by the fact that when PDP becomes a selective solvent for PS, the weight fraction of polystyrene domain changes from 0.33 to 0.73 (calculated values).



Supporting Figure S12. TEM micrographs of PS-*block*-P4VP(MSA)$_{1.0}$(PDP)$_{1.0}$ with $f_{comb,2}$ = 0.67 (S67.176k.MP) a) at room temperature showing a *lam-in-LAM* structure, b) at T = 170 ^{o}C *CYL*, and c) at T = 210 ^{o}C a *SPH*. P4VP regions appear dark in the images due to the I_2 staining.

PS-*block*-P4VP(MSA)$_{1.0}$(PDP)$_{1.0}$ with $f_{comb,2}$ = 0.67 (Sample S67.95k.MP)

Phase transitions from lamellar-in-lamellar to lamellar to cylindrical to spherical structures (lam-in-LAM to LAM to CYL´ to SPH´): Sample S67.95k.MP has similar transitions as sample S67.176k.MP, which can be followed in SAXS intensity patterns (Supporting Fig. S13a-b) upon heating and cooling cycles.



Supporting Figure S13. SAXS intensity patterns of PS-*block*-P4VP(MSA)$_{1.0}$(PDP)$_{1.0}$ with $f_{comb,1}$ = 0.67 (S67.95k.MP) as a function of temperature. a) Heating cycle from 80 °C to 200 °C (heating rate 5 °C/min) and b) cooling cycle from 200 °C to 80 °C (cooling rate 10 °C/min) indicating reversibility of transitions.