Supporting information for

Hierarchical Self-Assembly of Supramolecular Double-Comb Triblock Terpolymers

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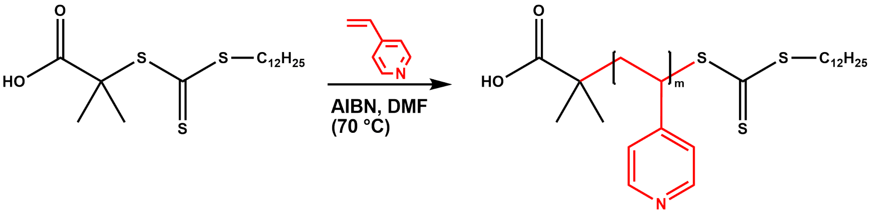
1 Experimental section

1.1 Materials

All chemicals were obtained from Sigma-Aldrich, TCI or Acros Organics in the highest purity available. Solvents were of analytical grade and were used as received, unless stated otherwise. Anhydrous *N,N*-dimethylformamide (DMF, 99.8%) that was used for the polymer synthesis was obtained from Sigma-Aldrich. 4-vinylpyridine (4VP) and styrene were vacuum distilled twice from finely ground calcium hydride. α,α'-azobis(isobutyronitrile) (AIBN) was recrystallized twice from methanol. The RAFT agent *S*-dodecyl-*S*'-(isobutyric acid) trithiocarbonate (DIBTTC) was prepared according to literature procedure.[1] *N*-acryloylpiperidine (API) was synthesized via the route described by Kobayashi et al.,[2] purified by silica column chromatography (acetone as an eluent) and finally vacuum distilled from finely ground calcium hydride. 3-nonadecylphenol (3-NDP) was synthesized as reported in Ref. 3.

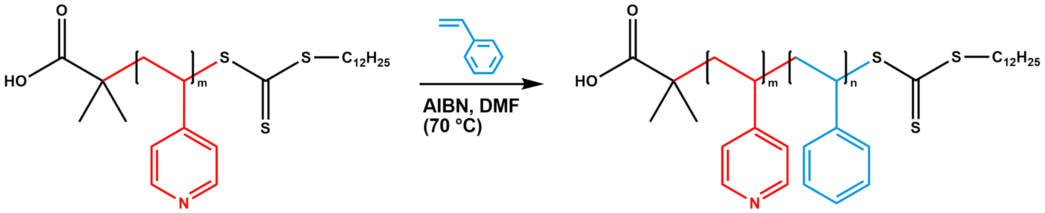
1.2 Synthesis

1. Synthesis of P4VP



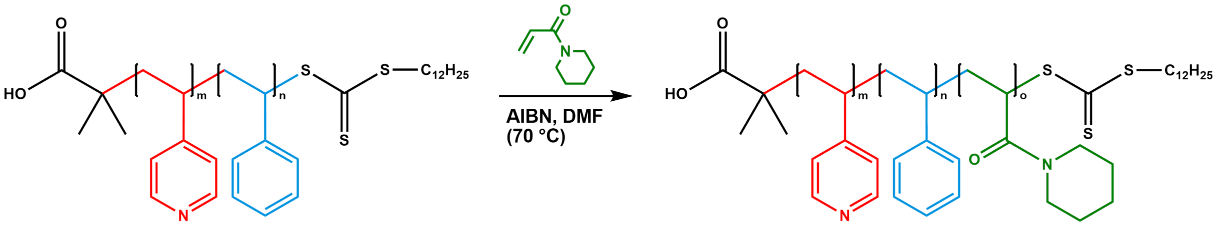
The P4VP macro-CTA was synthesized by RAFT polymerization according to a previously reported procedure.[4] In a 100 ml round-bottom flask, 4VP (16.0 g; 153 mmol) and DIBTTC (137 mg; 0.375 mmol) were dissolved in 15.0 ml anhydrous DMF. AIBN was added by using a 5.50 mg ml^{-1} DMF-based stock solution (1.0 ml; 5.50 mg; 0.0335 mmol). The flask was connected to a high-vacuum Schlenk line (10^{-5} mbar), the bright yellow solution was subjected to five freeze-pump-thaw cycles and it was finally backfilled with argon. The polymerization was started by submerging the closed flask in a thermostated oil bath at 70 °C. The reaction mixture turned orange within an hour and the reaction was stopped after 22 h by rapid cooling using liquid nitrogen. After that the conversion had been determined by ^{1}H-NMR (58.1 %), the orange solution was diluted with 16 ml DMF and precipitated into 800 ml toluene. The fine powder was dried in a vacuum oven overnight (40 °C), redissolved in 35 ml DMF and reprecipitated into 700 ml toluene. 8.1 g orange powder was obtained after drying overnight in vacuo (yield: 87 %). $M_{n,\text{calc}} = 25.2$ kg mol^{-1}; $M_{n,\text{GPC}}$ (dn/dc = 0.153 ml g^{-1}) = 28.7 kg mol^{-1}; Đ = 1.07 (Figure S1).

2. Synthesis of P4VP-*b*-PS



A similar procedure was used for the preparation of the P4VP-*b*-PS diblock copolymer. In a 50 ml round-bottom flask P4VP macro-CTA (2.03 g; 0.0707 mmol) was dissolved in 1.8 ml anhydrous DMF. A calculated amount (0.5 ml) of freshly prepared 3.23 mg ml^{-1} AIBN stock solution in DMF was added (1.62 mg; 9.85 μmol), and the clear yellow solution was diluted with 5.05 g styrene (48.5 mmol). After being subjected to 5 freeze-pump-thaw cycles and refilled with argon, the polymerization was started by submerging the closed flask in a thermostated oil bath at 70 °C. The reaction was stopped after 44 h (^{1}H-NMR: conversion = 38.1 %). The dark yellow viscous solution was diluted with 20 ml chloroform and precipitated into 400 ml toluene/hexane (1/3). The dried powder was redissolved in 30 ml chloroform and reprecipitated into 500 ml hexane, resulting in 2.9 g off-white powder after drying in a vacuum oven overnight (yield: 73 %). $M_{n,\mathrm{calc}} = 55.9$ kg mol^{-1}; $M_{n,\mathrm{GPC+NMR}} = 53.6$ kg mol^{-1}; Đ = 1.05; $f_{\mathrm{P4VP}} = 0.54$; $f_{\mathrm{PS}} = 0.46$ (Figure S1).

3. Synthesis of P4VP-*b*-PS-*b*-PAPI



For the triblock terpolymer, 1.52 g (0.0284 mmol) P4VP-*b*-PS was dissolved in 3.8 ml anhydrous DMF. Subsequently 0.2 ml of a 2.53 mg ml^{-1} AIBN stock solution (0.505 mg; 3.08 μmol) and 1.0 ml API (1.05 g; 7.54 mmol) were added. The yellow solution was subjected to 5 freeze-pump-thaw cycles, backfilled with argon and the reaction was started by submerging the 50 ml flask into a thermostated oil bath at 70 °C. After 20 h the polymerization was quenched by using liquid nitrogen (conversion = 83.5 % from ^{1}H-NMR). The very viscous yellow solution was diluted with 15 ml chloroform and precipitated into 375 ml hexane/diethyl ether (2/1). The dried off-white powder was redissolved in 22 ml chloroform and reprecipitated into 350 ml hexane, giving 1.91 g off-white powder after being dried in a vacuum oven overnight (yield: 80 %). $M_{n,\mathrm{calc}} = 84.5$ kg mol^{-1}; $M_{n,\mathrm{GPC+NMR}} =$ 84.1 kg mol^{-1}; Đ = 1.08; $f_{\mathrm{P4VP}} = 0.34$; $f_{\mathrm{PS}} = 0.28$; $f_{\mathrm{PAPI}} = 0.38$ (Figure S1).

1.3 Sample preparation

A bulk film of the neat P4VP-*b*-PS-*b*-PAPI triblock terpolymer was obtained by slow evaporation of a 2 wt% chloroform-based solution in a saturated solvent atmosphere (glass Petri dish, $\varnothing = 4$ cm, 150 mg material). Complete evaporation was achieved in a few days and the film was further dried in an oven afterwards (130 °C for 1 h).

Supramolecular complexes were prepared by dissolving the terpolymer together with a calculated amount of 3-NDP (150 mg total) in either chloroform ($x = 0.5$) or analytical grade DMF ($x = 0.1$, 0.3 and 1.0). The homogeneous solutions were subsequently cast into glass Petri dishes ($\varnothing = 4$ cm) and the solvent was allowed to evaporate slowly in a saturated solvent atmosphere at room temperature (chloroform) or 45 °C (DMF). After that the solvent had been completely removed (approximately 5 days), the complexes were finally annealed at 130 °C for 1 h.

Ultrathin sections (80 nm) for transmission electron microscopy (TEM) were obtained by microtoming in epoxy (Epofix, Electron Microscopy Sciences) embedded pieces of the bulk films using a Leica Ultracut UCT ultramicrotome that was equipped with a 35° DiATOME diamond knife. Sections for the unstained analysis were collected on Formvar/carbon-coated copper grids in order to reduce sample drift, while sections for the stained analysis were transferred to untreated copper grids. Enhanced contrast was realized by staining the sections with iodine for 15 min (supramolecular complexes) or 3 h (neat triblock terpolymer).

1.4 Characterization

Nuclear magnetic resonance (NMR) spectra were recorded on a 400 MHz Varian VXR operating at room temperature using deuterated chloroform ($CDCl_3$) as a solvent.

Gel permeation chromatography (GPC) was performed in DMF (containing 0.01 M LiBr) on a Viscotek GPCmax equipped with model 302 TDA detectors, using a guard column (PSS-GRAM, 10 μm, 5 cm) and two analytical columns (PSS-GRAM-1000/30 Å, 10 μm, 30 cm) at a flow rate of 1.0 ml min^{-1}. Both the columns and detectors were held at 50 °C. Narrow PMMA standards were used for calibration of the system and samples were filtered over a 0.45 μm PTFE filter prior to injection. Molecular weights were calculated by applying a triple detection method (refractive index, viscosity and light scattering) using Viscotek OmniSEC software. A predetermined refractive index increment ($\mathrm{d}n/\mathrm{d}c$) of 0.153 ml g^{-1} was used for the P4VP homopolymer.[5] Molecular weights ($M_{n,\mathrm{GPC+NMR}}$) of the diblock and triblock copolymers were determined by combining the molecular weight of the P4VP macro-CTA (GPC) and the composition of the copolymer (^{1}H-NMR). $M_{n,\mathrm{calc}}$ is the calculated molecular weight based on the conversion (^{1}H-NMR) and the theoretical maximum molecular weight (DIBTTC or macro-CTA concentration, and monomer concentration).

Differential scanning calorimetry (DSC) was performed on a TA Instruments DSC Q1000 by heating the complexes to 180 °C and cooling to −50 °C at a rate of 10 °C min^{-1}. The second heating cycle was used for analysis.

Small-angle X-ray scattering (SAXS) diffraction patterns were acquired at the Dutch-Belgian Beamline (DUBBLE) station BM26B of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France.[6,7] The sample-to-detector distance of the setup measured 5.0 m (Dectris Pilatus 1M). The scattering vector q is defined as $q = 4\pi/\lambda \sin\theta$ with 2θ being the scattering angle and λ the wavelength of the X-rays (1.03 Å). For room temperature measurements the acquisition time was 3 min per sample, while for the temperature scans (10 °C min^{-1}) a 30 s frame time was applied.

Iodine-stained sections (neat triblock terpolymer and supramolecular complexes) were analyzed on a Philips CM12 transmission electron microscope operating at an accelerating voltage of 120 kV. Images were recorded on a Gatan slow-scan CCD camera. Micrographs of the unstained sections were obtained by using a FEI Tecnai T20 electron microscope operating at 200 kV that was equipped with a Gatan model 626 cryo stage and a Gatan US4000 ultrascan CCD camera. To avoid sample damage the images were recorded under low-dose conditions at −180 °C.

2 Results and discussion

2.1 P4VP-*b*-PS-*b*-PAPI triblock terpolymer

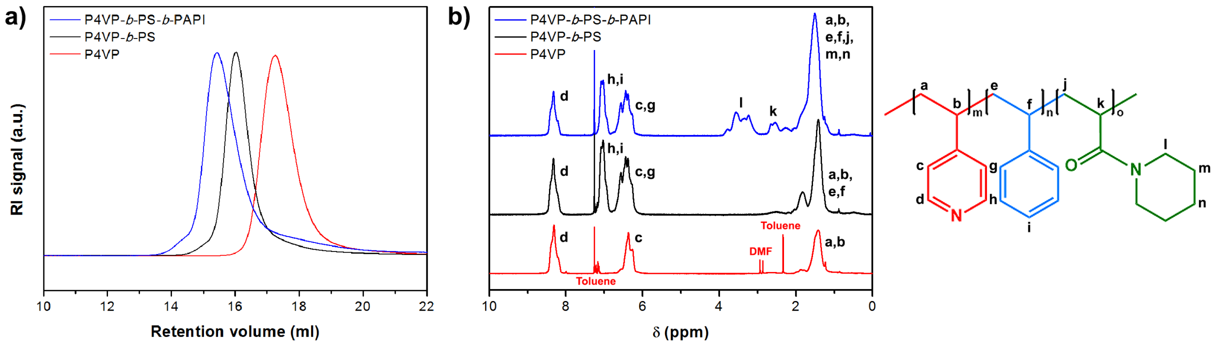


Figure S1: (a) GPC elugrams and (b) ^{1}H-NMR spectra of the P4VP-*b*-PS-*b*-PAPI triblock terpolymer and its P4VP and P4VP-*b*-PS precursors.

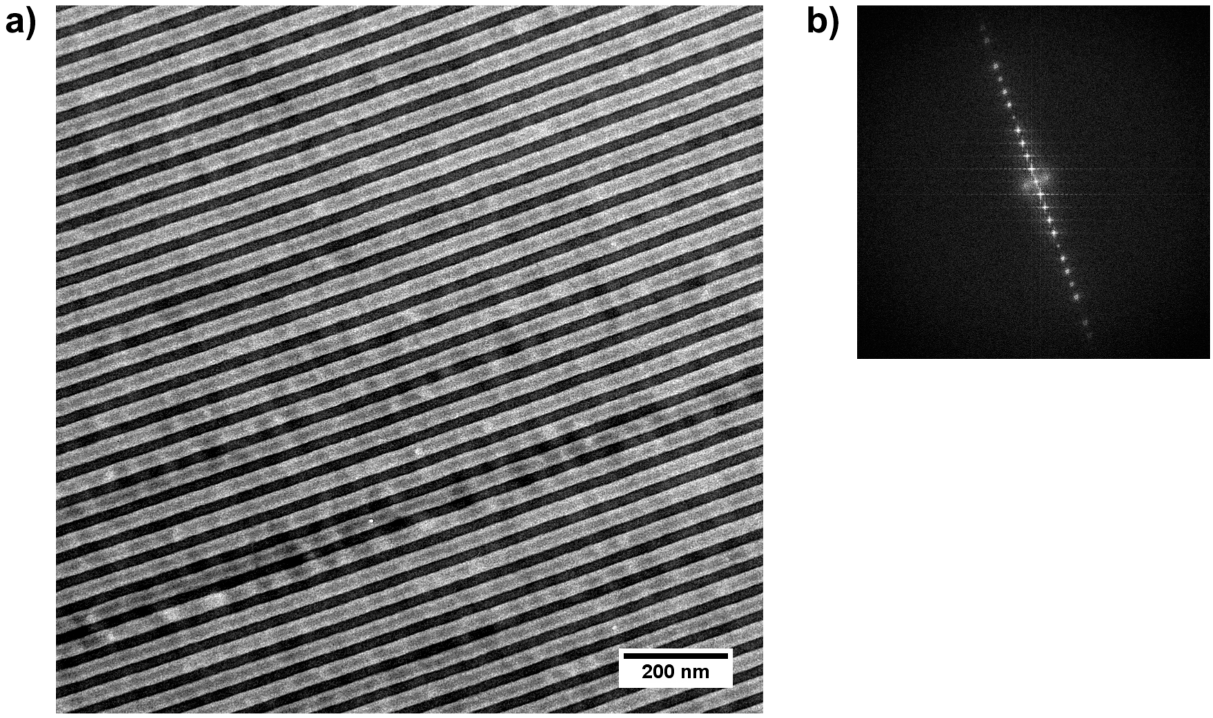


Figure S2: (a) Transmission electron micrograph of the neat P4PSPA84k triblock terpolymer recorded at a lower magnification. P4VP appears dark (stained by I_2), PAPI grey and PS white. (b) The fast Fourier transform (FFT) of this image indicates a highly ordered structure.

2.2 [P4VP-*b*-PS-*b*-PAPI](3-NDP)$_x$ supramolecular complexes

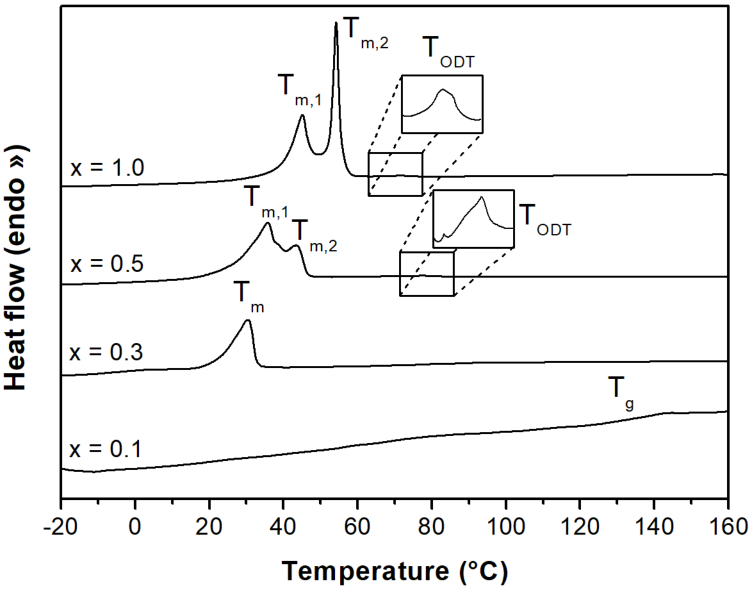


Figure S3: DSC thermograms of the P4PSPA84k(3-NDP)$_x$ supramolecular terpolymer complexes ($x = 0.1 - 1.0$) recorded at $10\,^\circ\mathrm{C}\ \mathrm{min}^{-1}$.

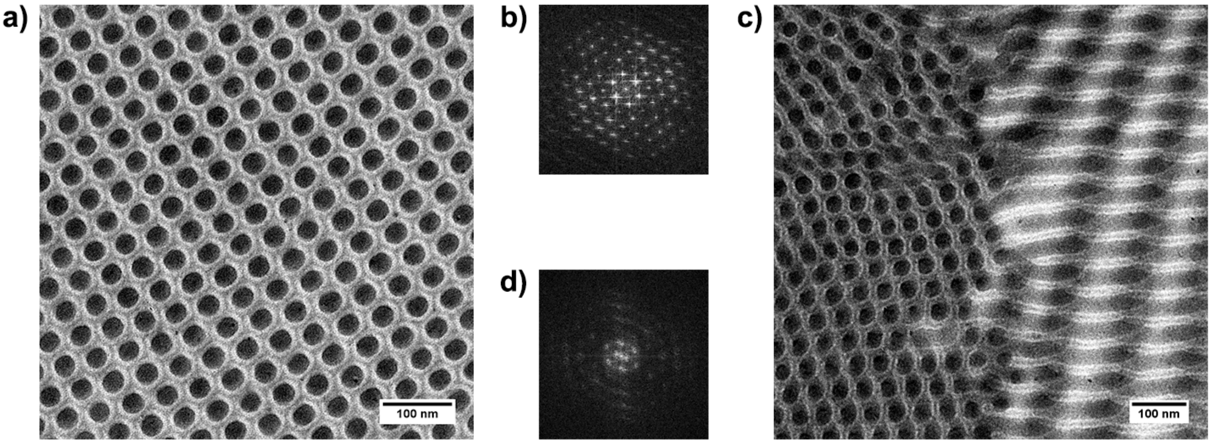


Figure S4: (a) TEM image of P4PSPA84k(3-NDP)$_{0.1}$ recorded at a lower magnification and (b) its FFT. (c) Micrograph demonstrating parallel alignment of the core-shell cylindrical morphology and (d) its corresponding FFT. P4VP appears dark (stained by I_2), PAPI grey and PS white.

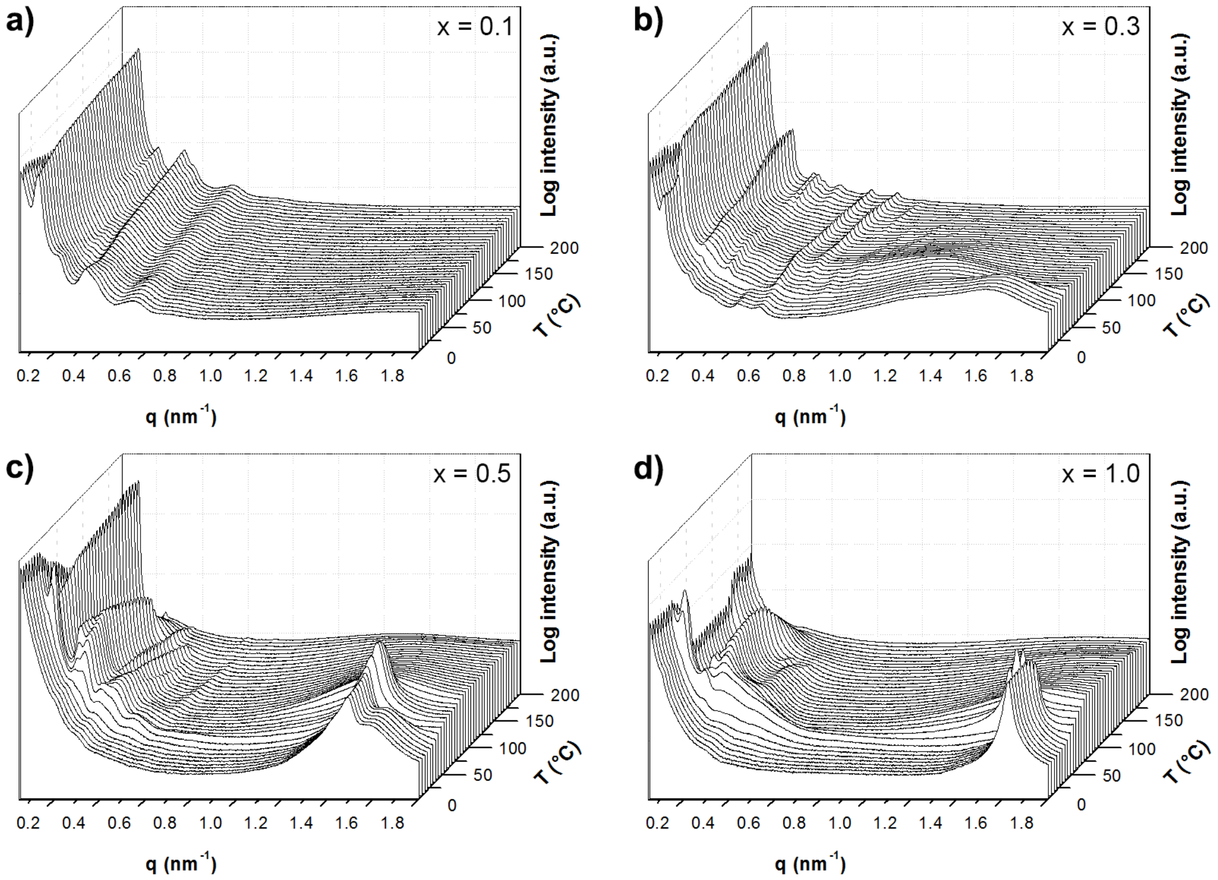


Figure S5: Temperature-resolved SAXS profiles of P4PSPA84k(3-NDP)$_x$ supramolecular complexes: $x = 0.1$ (a), $x = 0.3$ (b), $x = 0.5$ (c) and $x = 1.0$ (d). Data was recorded at 10 °C min^{-1}.

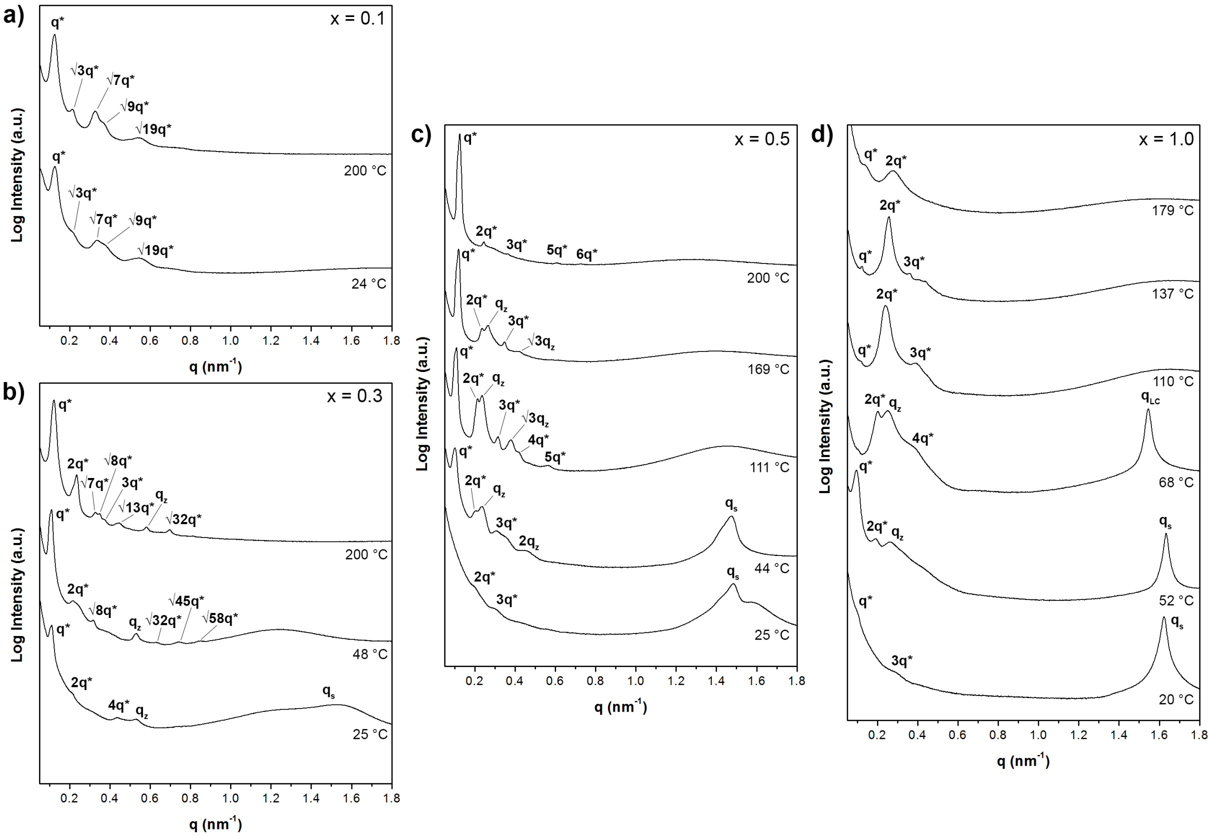


Figure S6: SAXS patterns that highlight the most important phase transitions observed in the P4PSPA84k(3-NDP)$_x$ supramolecular complexes: x = 0.1 (a), x = 0.3 (b), x = 0.5 (c) and x = 1.0 (d). q* is the first-order reflection of the large length scale morphology, q_z corresponds to a spherical PS substructure and q_s a surfactant-based structure.

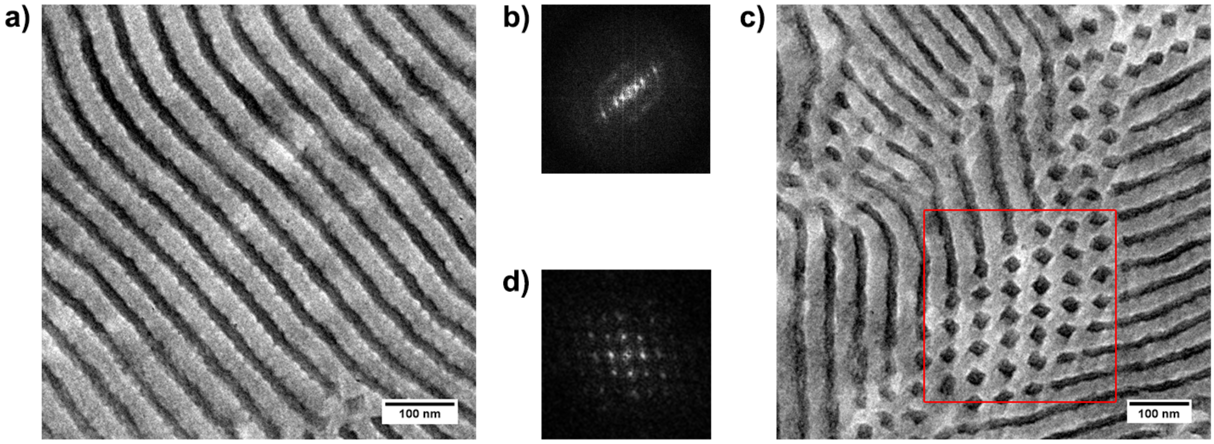


Figure S7: (a) TEM image of P4PSPA84k(3-NDP)$_{0.3}$ showing parallel orientation of the cylinders and clearly demonstrates the formation of spherical PS domains. (b) The FFT of this micrograph was used to calculate the interspherical distance ($d_z \approx 16$ nm). (c) TEM image recorded at a lower magnification. (d) The FFT of the area highlighted in (c) supports the tetragonal packing that was observed in SAXS.

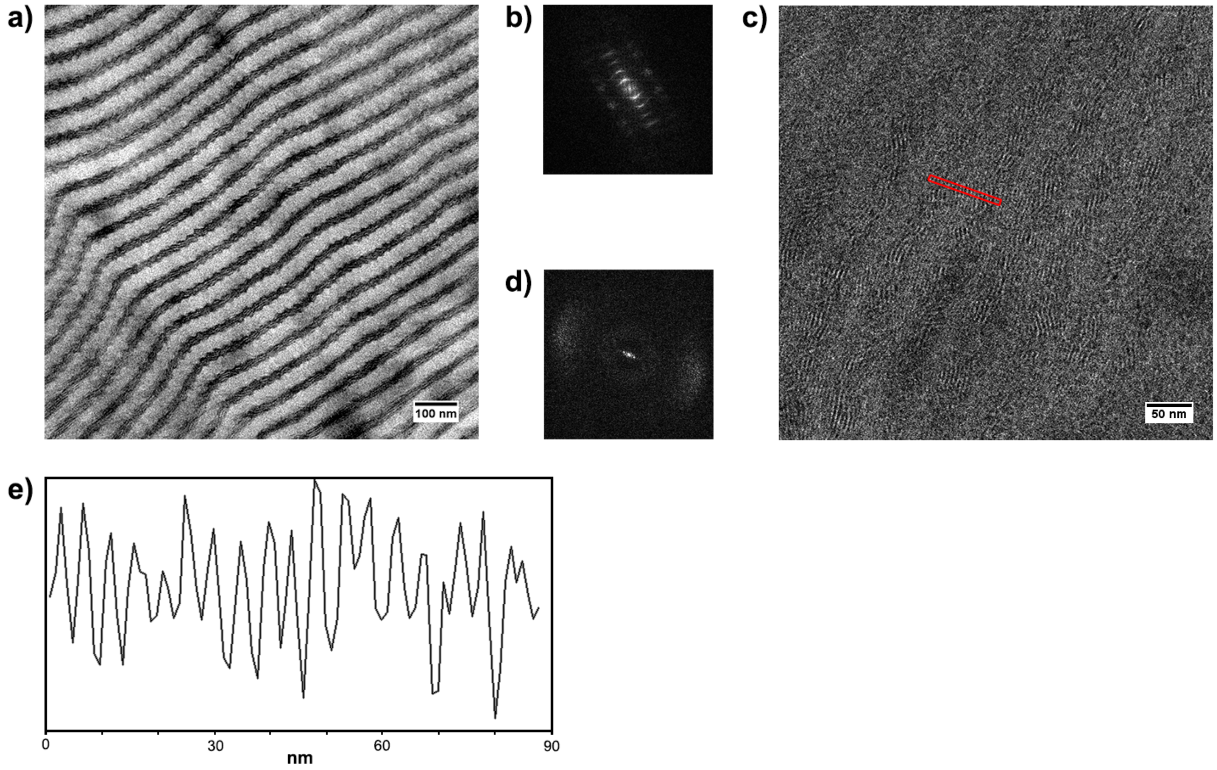


Figure S8: (a) Low-magnification TEM micrographs of the stained and (c) unstained P4PSPA84k(3-NDP)$_{0.5}$ complex. (b) The FFT of the stained image demonstrates the bright PS spheres to be evenly distributed along the large lamellae, while (d) the FFT of the unstained image indicates the small structure to be ordered over the full area. (e) Integration of the highlighted area in (c) proves the small lamellae to cover both P4VP and PAPI layers with a periodicity of approximately $4-5$ nm.

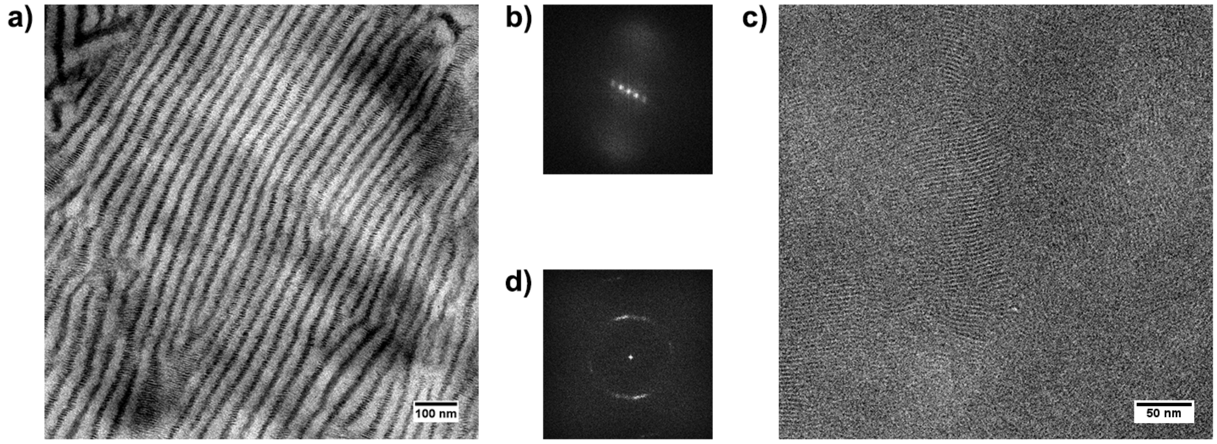


Figure S9: (a) Stained and (c) unstained TEM micrographs of P4PSPA84k(3-NDP)$_{1.0}$ recorded at a lower magnification and (b, d) their corresponding FFTs. PS domains are not visible due to the low concentration and low contrast.

References

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