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Supporting Information

Hierarchical Layer Engineering Using Supramolecular Double-Comb Diblock Copolymers

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Experimental

Materials

Five symmetric (i.e. $f_{\mathrm{P4VP}} \approx f_{\mathrm{PAPI}} \approx 0.5$) P4VP-*b*-PAPI diblock copolymers with molecular weights ranging from 31 up to 272 kg·mol^{-1} were prepared by RAFT polymerization.[1] Exact reaction conditions are provided in Tables S1 and S2, for the preparation of P4VP macro-CTAs and P4VP-*b*-PAPI diblock copolymers, respectively. 3-NDP amphiphiles were synthesized according to the route described in ref. 2. All solvents were of analytical grade.

Sample Preparation

Neat block copolymer (BCP) bulk films were obtained by slow evaporation of chloroform (room temperature, P4PA272k-51) or *N,N*-dimethylformamide (45 °C, other four BCPs) based solutions (150 mg, 2 wt%) in a saturated solvent atmosphere. Complete evaporation was achieved in 4 days up to one week. Equilibrium structures of the films were checked by thermal annealing at 200 °C in vacuum for at least 5 days.

P4PA(3-NDP)$_{0.5}$ complexes were prepared by dissolving the parent BCP together with the calculated amount of 3-NDP (150 mg material) in analytical grade DMF, and casting these solutions into 4 cm diameter Petri dishes. Similar to the diblock copolymers, full evaporation of the solvent was achieved in roughly 5 days. Complexes were subsequently annealed at 130 °C for 1 h.

Ultrathin sections (80 nm) for transmission electron microscopy (TEM) were acquired by microtoming in epoxy (Epofix, Electron Microscopy Sciences) embedded pieces of the bulk films using a Leica Ultracut UCT ultramicrotome equipped with a 35° DiATOME diamond knife. Enhanced contrast was realized by staining the sections with iodine for 1 to 3 h (BCPs) or 10 min up to 1 h (complexes).

Characterization

Molecular weights of the P4VP homopolymers and molecular weight distributions (BCPs) were determined by gel permeation chromatography (GPC). It 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 Viscotec Omnisec software. A predetermined refractive index

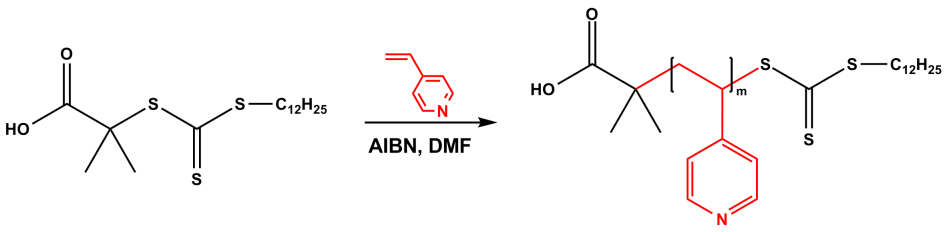
increment (dn/dc) of 0.153 ml·g^{-1} was used for P4VP homopolymers.[3] Molecular weights of the P4PA diblock copolymers were determined by using their composition (^{1}H-NMR) and the molecular weight of the applied P4VP macro-CTA.

Differential scanning calorimetry (DSC) was performed on a TA Instruments DSC Q1000 by heating the samples to 150 °C and cooling to −20 °C at a rate of 10 °C·min^{-1}. The second heating cycle was used for analysis.

Small-angle X-ray scattering (SAXS) measurements were carried out at the Dutch-Belgian Beamline (DUBBLE) station BM26B of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France.[4,5] The sample-to-detector distance (Dectris Pilatus 1M) of the setup was ca. 5.0 m. 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). The acquisition time was 3 to 5 min per sample (room temperature) or 30 s per frame (temperature-resolved measurements).

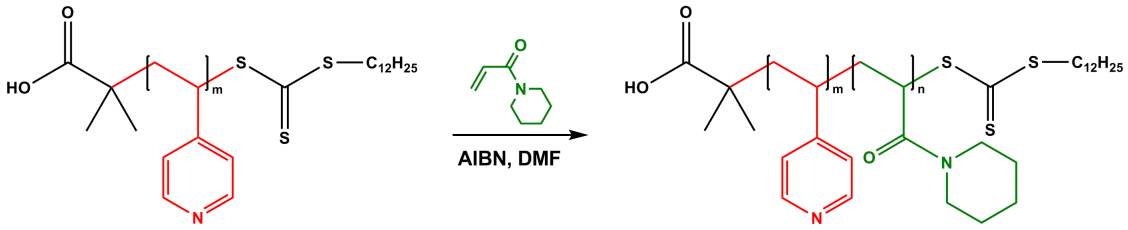
Sections of both iodine stained diblock copolymers and complexes were analyzed on a Philips CM12 electron microscope operating at an accelerating voltage of 120 kV. Images were recorded on a Gatan slow-scan CCD camera. Unstained complexes were measured at the Nanomicroscopy Center (Aalto University, Espoo, Finland) using a 300 kV JEOL JEM-3200FSC cryo-TEM. Micrographs collected on this instrument were taken in bright field mode using a zero-loss energy filter (omega type) with a slit width of 20 eV and were recorded on a Gatan Ultrascan 4000 CCD camera. The samples were kept at liquid helium temperature for enhanced stability.

Polymer synthesis



Macro-CTA	[DIBTTC]	[AIBN]	[AIBN]/[DIBTTC]	[4VP] (M)	T	t_R	Conv.	$M_{n,\text{theory}}$	$M_{n,\text{GPC}}$	M_w/M_n
P4VP-14k	19	1.0	1/18	3.8	70	21	57	12.8	14.2	1.13
P4VP-29k	9.8	1.0	1/10	3.7	70	20	66	26.5	28.8	1.05
P4VP-52k	6.5	0.63	1/10	6.1	70	18	50	49.3	52.0	1.11
P4VP-93k	4.6	0.55	1/8.4	7.6	70	21	48	83.9	93.4	1.09
P4VP-137k	4.3	0.51	1/8.4	8.0	80	22	64	125	137	1.09

Table S1: Reaction conditions and analysis of RAFT-synthesized P4VP macro-CTAs. Concentrations [DIBTTC] and [AIBN] are in mM, temperatures T in °C, reaction times t_R in h, conversions (Conv.) in % and molecular weights in kg·mol^{-1}.



BCP	[P4VP]	[AIBN]	[AIBN]/[P4VP]	[API] (M)	t_R	Conv.
P4PA31k-47	14	1.2	1/12	1.7	19	90
P4PA57k-47	7.1	0.76	1/9.4	1.8	17	83
P4PA109k-48	4.2	0.42	1/10	2.2	19	76
P4PA189k-50	2.1	0.24	1/8.4	1.9	22	68
P4PA272k-51	1.1	0.12	1/8.7	1.9	18	56

Table S2: Reaction conditions for the preparation of P4VP-*b*-PAPI diblock copolymers by RAFT. Concentrations [P4VP] and [AIBN] are in mM, reaction times t_R in h and conversions (Conv.) in %.

P4VP-*b*-PAPI self-assembly

BCP	M_n (kg·mol^{-1})	M_w/M_n	f_{P4VP}	d_{SAXS}	χN
P4PA31k-47	30.5	1.12	0.47	22.6	9
P4PA57k-47	56.5	1.06	0.47	37.2	17
P4PA109k-48	109	1.19	0.48	60.2	33
P4PA189k-50	189	1.29	0.50	93.4	57
P4PA272k-51	272	1.29	0.51	146	82

Table S3: Overview of the RAFT-synthesized symmetric P4PA diblock copolymers. Fractions represent weight fractions, d_{SAXS} is in nm, $\chi = 0.03$ and $N = M_n/100$ g·mol^{-1}.[1]

P4PA(3-NDP)$_{0.5}$ self-assembly

BCP	$d_{L,\,\mathrm{TEM}}$ (nm)	d_L (nm)	d_S (nm)	n_{SAXS}	n_{TEM}	$n_{\mathrm{TEM,\,P4VP}}$	$n_{\mathrm{TEM,\,PAPI}}$
P4PA31k-47	17	17.5	4.4	4	4	2	2
P4PA57k-47	28	26.9	4.5	6	6	3	3
P4PA109k-48	36	36.8	4.4	8	8	4	4
P4PA189k-50	54	49.2	4.4	11	~ 11	5 to 6	5 to 6
P4PA272k-51	76	77.0	4.5	17	~ 17	8	9 to 10

Table S4: Overview of the characteristics of each P4PA(3-NDP)$_{0.5}$ double parallel lamellar-*in*-lamellar structure. n_i is the number of internal structures (d_S) and domain spacings d_i were obtained from SAXS. $d_{L,\,\mathrm{TEM}}$ was determined using the Fourier transformations illustrated in Figure S3.

BCP	T (°C)	d_L (nm)	Δq (nm^{-1})	L (nm)	$\overline{N}$
P4PA31k-47	57.5	18.9	0.023	257	14
P4PA57k-47	65.0	28.6	0.028	211	7.4
P4PA109k-48	57.5	42.5	0.018	328	7.7
P4PA189k-50	57.5	53.8	0.011	537	10
P4PA272k-51	57.5	90.6	0.0095	621	6.9

Table S5: Scherrer correlation length (L) analysis of P4PA(3-NDP)$_{0.5}$ supramolecular complexes, with Δq being the full width at half-maximum of the primary scattering peak. $L = 2\pi K/\Delta q$, with $K = 2\sqrt{\ln(2)/\pi} \approx 0.9394$. $\overline{N}$ is the average number of Bragg planes (i.e. $\overline{N} = L/d_L$).[6] Analysis was performed in the melt state (Figure S2), due to its stronger scattering compared to the crystalline state.

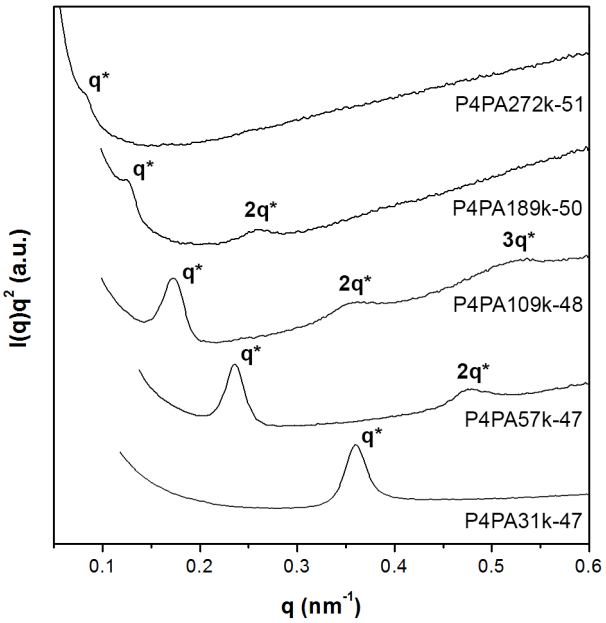


Figure S1: Room temperature Lorentz-corrected SAXS profiles of P4PA(3-NDP)$_{0.5}$. First order scattering maxima (q^*) are clearly visible.

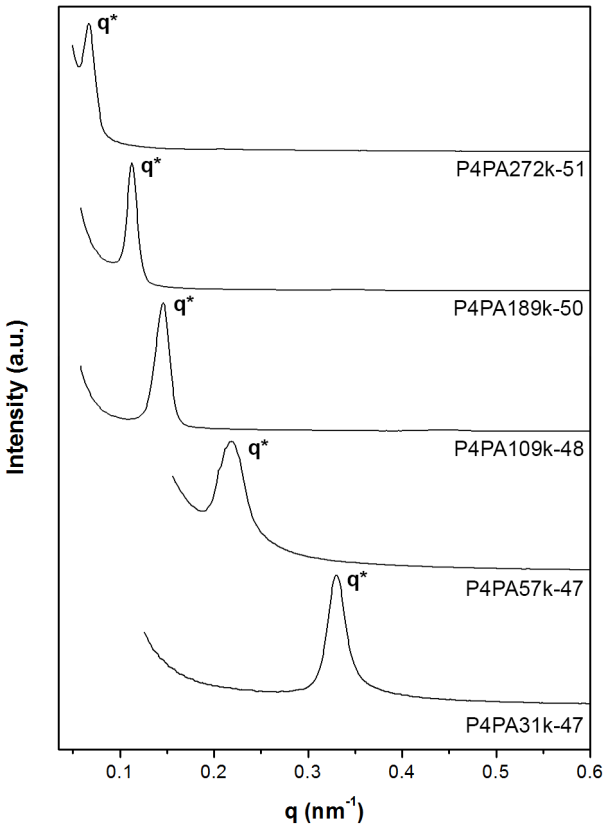


Figure S2: SAXS profiles of P4PA(3-NDP)$_{0.5}$ recorded at $T > T_m$ ($T = 55 - 65\,^{\circ}\mathrm{C}$) used for the Scherrer grain size analysis (Table S5).

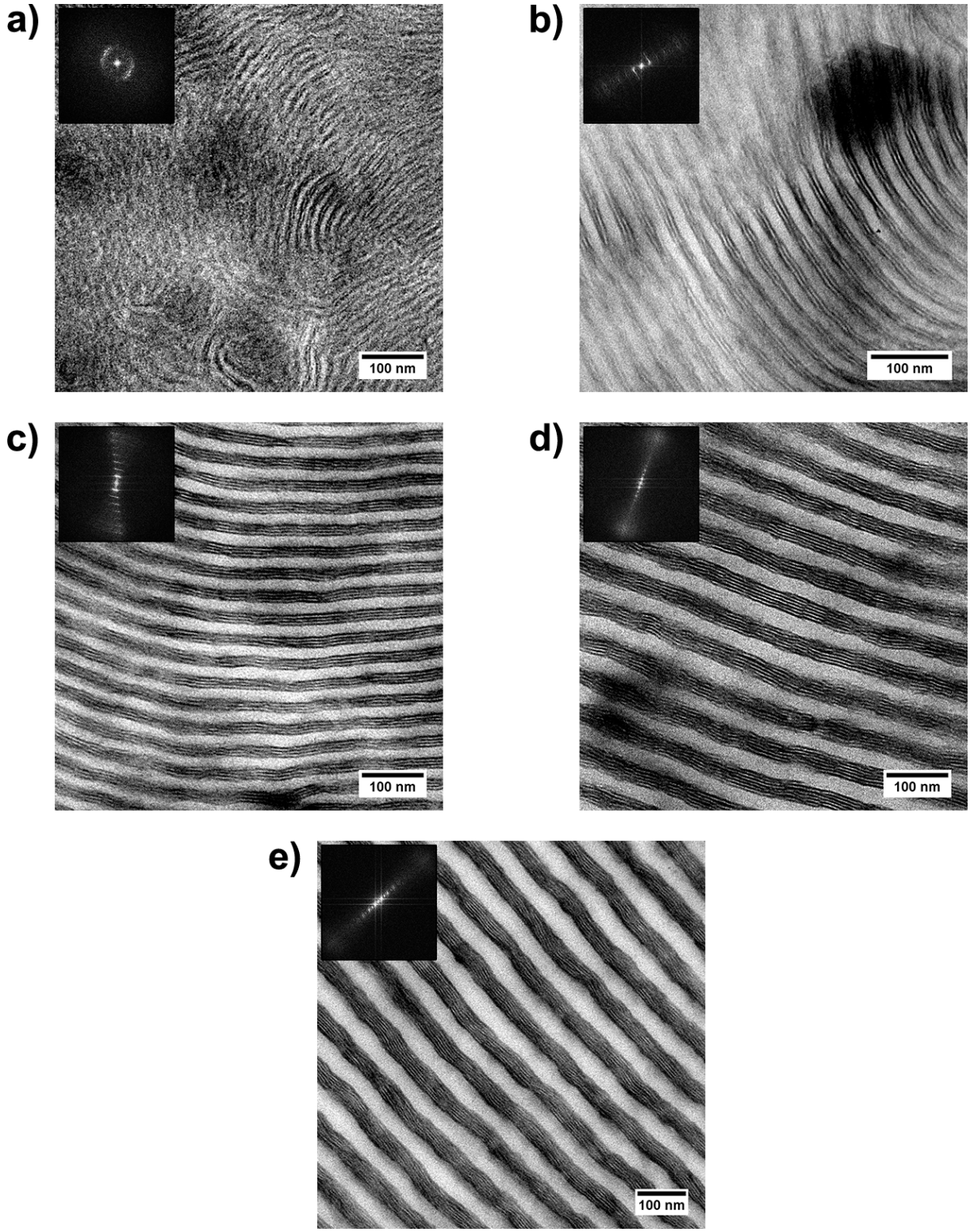


Figure S3: Electron micrographs of iodine stained P4PA(3-NDP)$_{0.5}$ supramolecular complexes recorded at a lower magnification. Insets show their corresponding Fourier transformation. P4PA31k-47 (a), P4PA57k-47 (b), P4PA109k-48 (c), P4PA189k-50 (d) and P4PA272k-51 (e).

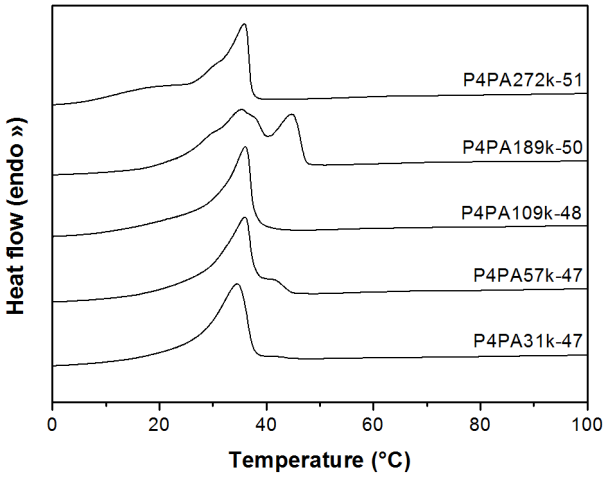


Figure S4: DSC thermograms of P4PA(3-NDP)$_{0.5}$ supramolecular double-comb diblock copolymers.

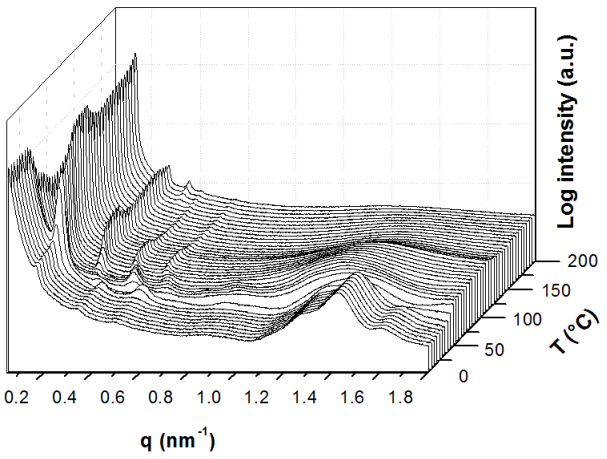


Figure S5: Temperature-resolved SAXS intensity profiles of P4PA109k-48(3-NDP)$_{0.5}$ (heating scan, 10 °C·min^{-1}).

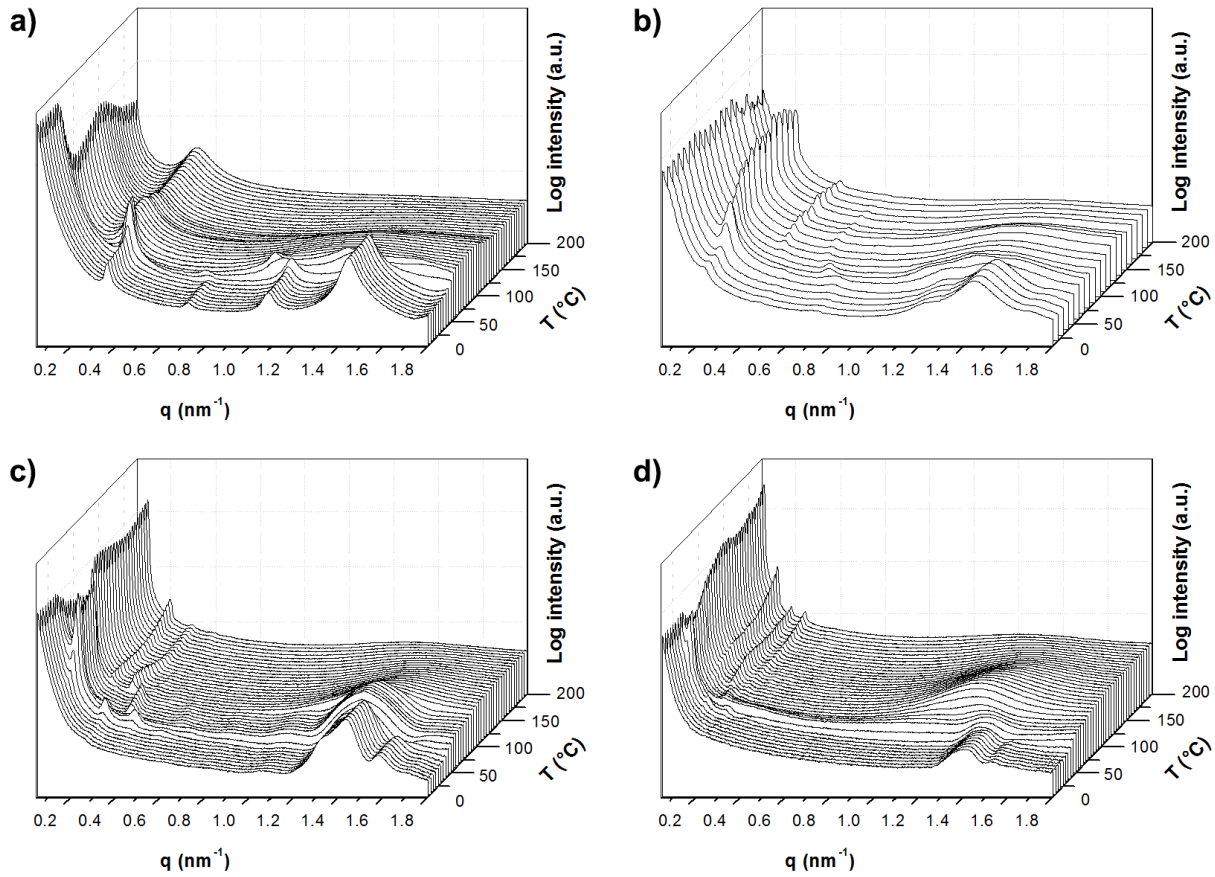


Figure S6: Temperature-resolved SAXS intensity profiles of P4PA(3-NDP)$_{0.5}$: P4PA31k-47 (a), P4PA57k-47 (b), P4PA189k-50 (c) and P4PA272k-51 (d). Heating scans were peformed at 10 °C·min^{-1} (P4PA31k-47, P4PA189k-50 and P4PA272k-51) or 20 °C·min^{-1} (P4PA57k-47).

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