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Self-assembled polymeric solid films with temperature-induced large and reversible photonic-bandgap switching

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In aqueous solutions the response of polymers and biological matter to external conditions, such as temperature and pH, is typically based on the hydrophobic/hydrophilic balance and its effects on the polymer conformation^{1,2}. In the solid state, related concepts using competing interactions could allow novel functions. In this work we demonstrate that polymeric self-assembly, reversibility of hydrogen bonding, and polymer-additive phase behaviour allow temperature response in the solid state with large and reversible switching of an optical bandgap. A complex of polystyrene-*block*-poly(4-vinylpyridinium methanesulphonate) and 3-*n*-pentadecylphenol leads to the supramolecular comb-shaped architecture with a particularly long lamellar period. The sample is green at room temperature, as an incomplete photonic bandgap due to a dielectric reflector is formed. On heating, hydrogen bonds are broken and 3-*n*-pentadecylphenol additionally becomes soluble in polystyrene, leading to a sharp and reversible transition at ~125 °C to uncoloured material due to collapse of the long period. This encourages further developments, for example, for functional coatings or sensors in the solid state.

Stimuli- and condition-responsive smart and functional polymeric materials have been extensively pursued and a particular emphasis has been paid to water-soluble polymers and biomacromolecules as they easily allow detailed control of the chain conformations, using, for example, temperature, pH and even light^{1,2}. Poly(*N*-isopropylacrylamide) and elastin-like polypeptides are classic examples used to prepare responsive polymeric materials such as selective membranes and controlled-drug-release materials^{1–3}, not to forget proteins with their biochemical activity in living organisms. In these systems, the responsivity specifically requires interplay between the hydrophobic and hydrophilic interactions and they take place typically in a 'dilute' aqueous environment. Small changes in solvent properties or concentrations may suppress or prevent the response and, most importantly, they do not work in the

solid state, which can be a problem for many device applications. Therefore, in the solid state, corresponding design principles might require other types of interactions and combinations of attractions and repulsions (beyond hydrophilic/hydrophobic interactions). This may naturally lead to self-assembly and could allow use of phase transitions, such as order–disorder or order–order transitions within the self-assembled structures. For various aspects of polymeric self-assembly, see refs 4–7.

The functionality that we want to address here concerns photonic bandgaps where the transport of visible light is totally or partly suppressed due to periodic dielectric structures^{8,9}. Many methods have been demonstrated to form photonic bandgaps, such as lithographic and etching techniques¹⁰, spontaneous self-assembly of colloids¹¹, synthetic opals^{12–14}, inverted opals^{15,16} and block copolymers^{17–21}, each having their own characteristic advantages and drawbacks. The aim of this work is to demonstrate responsive photonic bandgaps in the solid state based on self-assembly of block copolymers, where temperature changes cause pronounced and reversible switching, which manifests itself, for example, as distinct colour changes.

Block copolymers consisting of mutually repulsive blocks form a variety of self-assembled phases, such as the lamellar (1D), cylindrical (2D), spherical and gyroid (3D) phases, typically at a length scale of 10–100 nm (ref. 5). Long periods with well-defined macroscopic order approaching the optical wavelength $\lambda/2n$ (where n is the refractive index) as required for photonic bandgaps are not straightforward to achieve. Using pure block copolymers, this would require very high molecular weights, where the structure formation is slow. Usually, this has been overcome by swelling the block-copolymer domains with narrow molecular weight homopolymers or oligomeric plasticizers^{18,19}. In this way, incomplete photonic bandgaps have been constructed where the dielectric contrast has in some cases been increased by incorporating high-refractive-index inorganic additives^{17,21}.

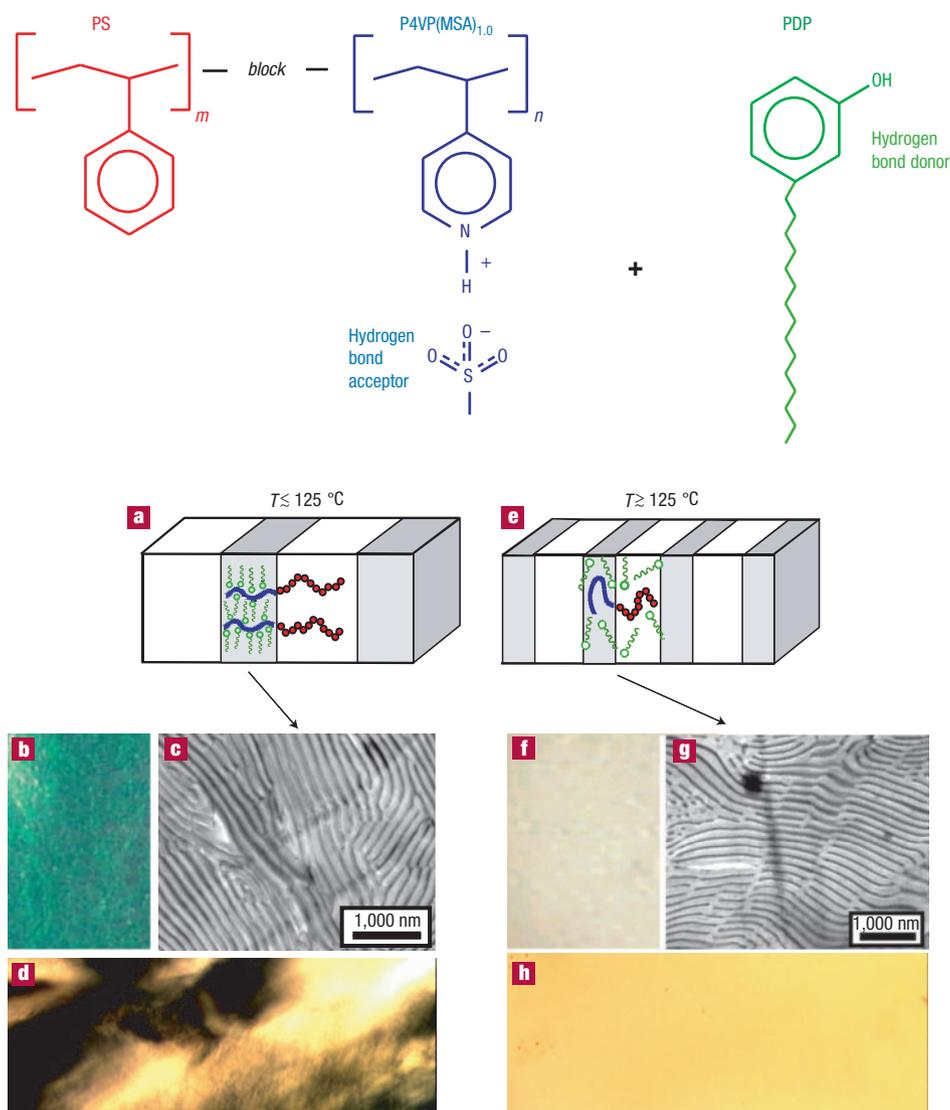


Figure 1 PS-*block*-P4VP(MSA)_{1.0}(PDP)_{1.5} at room temperature and at $T \geq 125$ °C. **a**, At room temperature, PDP is a selective solvent for the P4VP(MSA)_{1.0} and the sample has structural hierarchy. **b**, At room temperature the sample is green. **c**, The TEM image shows the lamellar structure, with the long period of ~160 nm due to stretching of the chains. The smaller structure is not resolved. **d**, An optically anisotropic, that is, birefringent, texture is observed below ~125 °C with crossed polarizers suggesting an internal self-assembly within P4VP(MSA)_{1.0}(PDP)_{1.5} domains. **e**, At $T \geq 125$ °C, PDP becomes a non-specific solvent for PS and P4VP(MSA)_{1.0} and there is no internal structure within the P4VP(MSA)_{1.0}-containing domains²⁷. **f**, At $T \geq 125$ °C the sample is uncoloured. **g**, Rapid quenching of the sample from 170 °C shows a lamellar structure, as confirmed by SAXS. **h**, Above 125 °C the sample becomes non-birefringent in agreement with an internal phase transition to a disordered phase within the P4VP(MSA)_{1.0}-containing domains.

Previously we have shown that comb-shaped polymeric supramolecules can be used to prepare one-dimensional optical reflectors in a facile way²⁰. Such systems did not show optically responsive or switching behaviour, but it can be expected that phase transitions of self-assembled block copolymers could lead to a useful platform for switchable bandgaps in the solid state. Concepts for switching bandgaps have so far been based, for example, on liquid crystals^{22,23}, hydrogels and colloids^{14,24–26}, mechanical tuning of plastic opals¹³, and thermochromism¹². Within the context of the present work, the block-copolymer/liquid-crystal systems are particularly interesting, and reversible changes in optical properties have been demonstrated²². However, large and reversible thermal switching still seems to remain a challenge in the solid state.

The poly(4-vinylpyridine) (P4VP) block of polystyrene-*block*-poly(4-vinylpyridine) can selectively bond amphiphilic molecules by hydrogen bonding, coordination or ionic interaction allowing hierarchical structures and phase transitions^{7,27,28}. Previously, it was observed that the comb-shaped architecture, formed by bonding dodecylbenzenesulphonic acid (DBSA) to the P4VP-block of PS-*block*-P4VP (where PS is polystyrene) caused large stretching of the chains thus leading to a visible bandgap²⁰. In the present work, the additional temperature responsivity is based on the hypothesis that the alkyl combs should not be bonded by strong ionic interaction, but rather by weaker hydrogen bonding, still keeping the protonation of P4VP. Therefore, the P4VP-block has first been stoichiometrically protonated with methanesulphonic acid (MSA) which leads to poly(4-vinylpyridinium methanesulphonate).

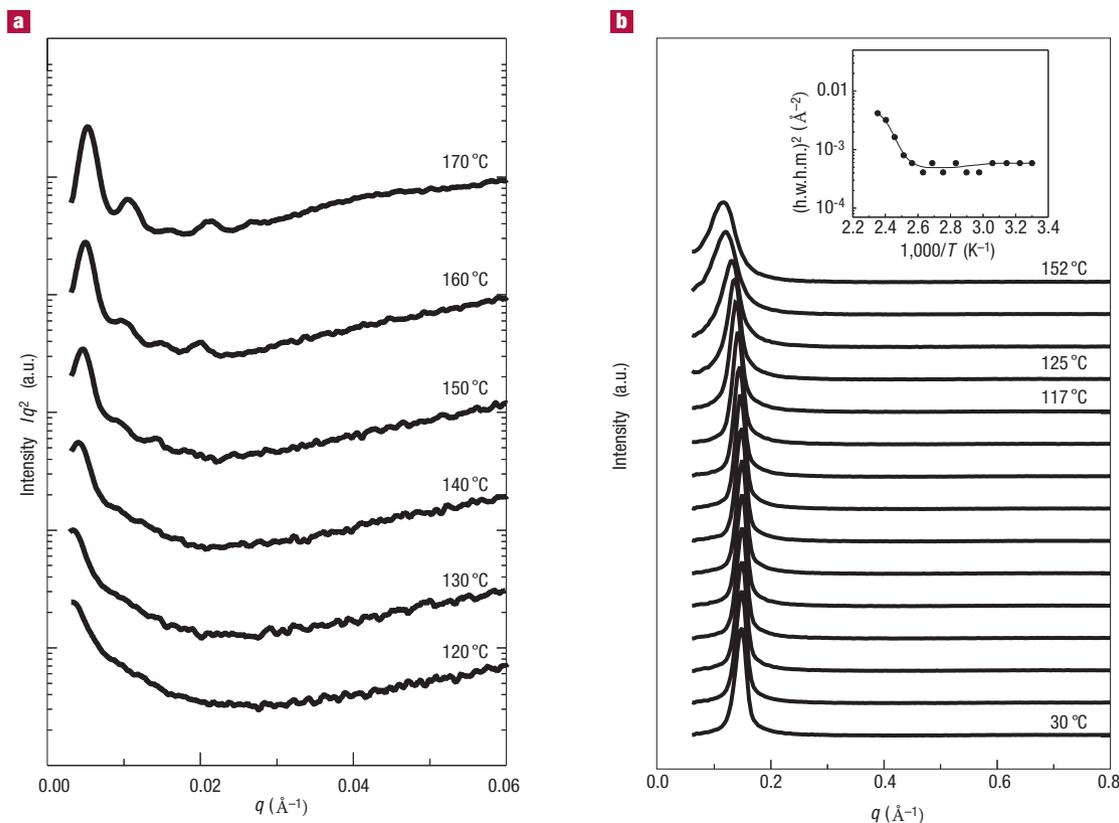


Figure 2 SAXS curves of PS-*block*-P4VP(MSA)_{1.0}(PDP)_{1.5} at different temperatures. **a**, At ~170 °C five equally spaced intensity maxima were observed indicating a lamellar structure. The long period gradually increases with decreasing temperature and stepwise shifts to beyond the SAXS range at the transition temperature at ~125 °C. **b**, The internal phase transition within the P4VP(MSA)_{1.0}(PDP)_{1.5}-domains is observed at ~125 °C seen as a broadening of the peak. The internal phase transition within the P4VP(MSA)_{1.0}(PDP)_{1.5}-domains is observed at ~125 °C seen as a broadening of the peak. The internal phase transition is also seen as a sudden change in the square of half-width at half-maximum, (h.w.h.m.)², as a function of 1,000/T (K⁻¹), as represented in the inset. The magnitude of the scattering vector is given by $q = (4\pi/\lambda) \sin \theta$, where 2θ is the scattering angle and $\lambda = 1.54 \text{ \AA}$.

Then 3-*n*-pentadecylphenol (PDP) is hydrogen bonded to this polymer salt leading to a comb-shaped supramolecular block P4VP(MSA)_{1.0}(PDP)_{1.5} (ref. 27).

The structures were examined using transmission electron microscopy (TEM) (Fig. 1) and small-angle X-ray scattering (SAXS) (Fig. 2). Figure 1c shows a lamellar self-assembled structure having a long period of ~160 nm and the sample is green in reflection (Fig. 1b). Below ~130 °C, the periodicity was larger than the available q -range of the synchrotron SAXS (Fig. 2a) and no intensity maxima were observed. A faint indication of the first intensity maximum starts to appear at ~130 °C and the sample turns uncoloured (Fig. 1f). Five equally spaced intensity maxima are observed at 170 °C, indicating a lamellar structure with a long period of ~117 nm. To confirm the structure at high temperature, the sample was rapidly quenched from $T = 170 \text{ °C}$ to liquid propane, and the TEM micrograph showed lamellar structure (Fig. 1g).

The material contains a self-assembled structure-within-structure hierarchy (Fig. 1a), see refs 7, 20 and 27 for arguments in related materials: Fig. 2b shows a relatively narrow SAXS reflection at $q = 0.147 \text{ \AA}^{-1}$ corresponding to a long period of 43 Å of the inner structure within the P4VP(MSA)_{1.0}(PDP)_{1.5} domains, and the material is birefringent in polarized optical microscopy (see Fig. 1d). Figure 1h shows that on passing 125 °C the material becomes non-birefringent and simultaneously the SAXS reflections

(Fig. 2b) become broadened stepwise. These results indicate that the ordered structure within the P4VP(MSA)_{1.0}(PDP)_{1.5} domains has been suppressed but it will be reversibly recovered on cooling.

Optical properties were determined using ultraviolet–visible (UV-vis) transmission and reflection measurements as a function of temperature (Fig. 3). At room temperature, the UV-vis transmission curve indicates a bandgap located at ~500 nm. On heating, the position of the bandgap remained approximately constant up to 117 °C and further heating caused a large shift of the bandgap position to smaller wavelengths within a narrow temperature range (Fig. 3a). Note that the shift is particularly large—that is, more than 100 nm—to values below 400 nm, where further changes in the transmission spectra were difficult to observe due to the optical absorption of the materials. Figure 3b shows the UV-vis transmission curves for the complex on cooling indicating a reversible behaviour. The small difference between the position of the bandgap (~15 nm) at room temperature before and after the heating ramp is due to the different cooling rates in the annealing procedure and optical measurement. The reflection spectra of PS-*block*-P4VP(MSA)_{1.0}(PDP)_{1.5} are represented in Fig. 3c. Increasing the temperature from room temperature to ~80 °C decreases the intensity of reflection, while the position remained at ~530 nm. Further increase of temperature shifts the peak position to 420 nm and 370 nm corresponding to 120 °C and 134 °C, respectively. This was manifested as a major

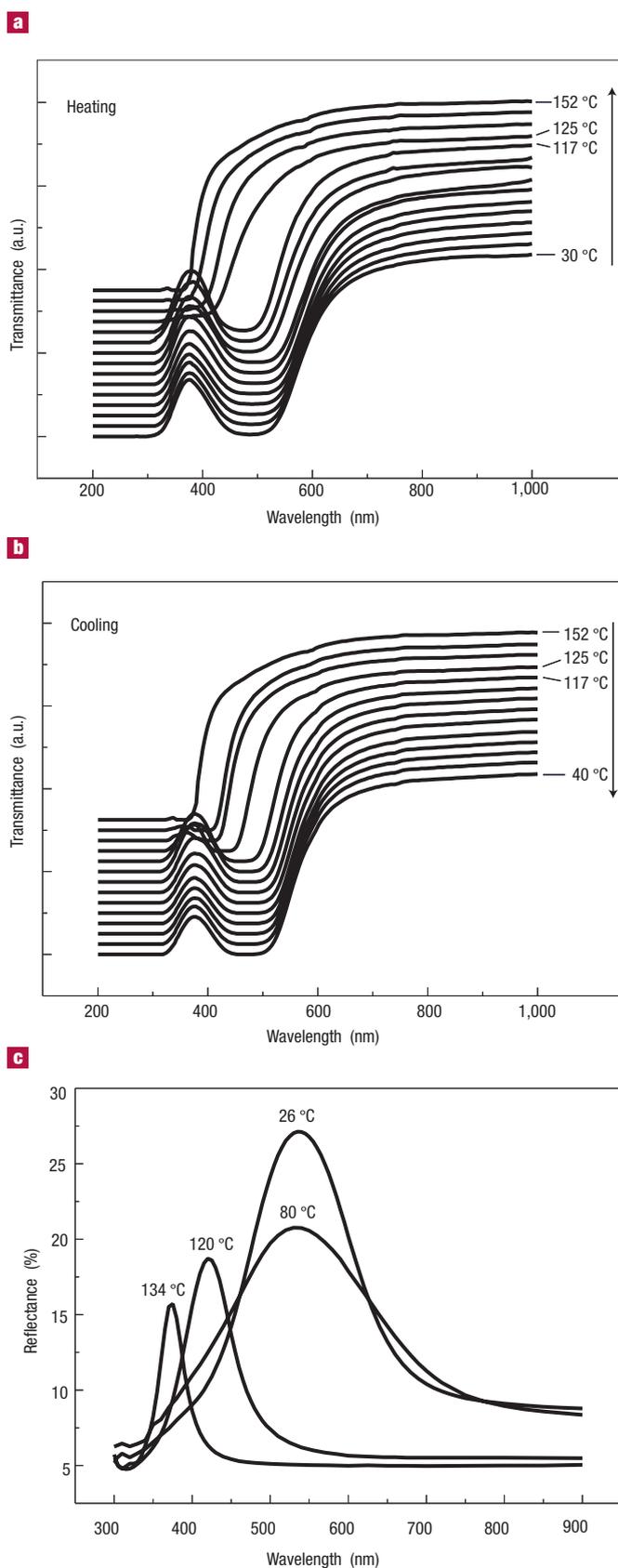


Figure 3 The optical measurements of PS-*block*-P4VP(MSA)_{1.0}(PDP)_{1.5} as a function of temperature. **a**, and **b**, are UV-vis specular transmission and **c**, diffuse reflectance graphs at different temperatures. **a**, On heating, the position of the bandgap remains the same up to 117 °C. A further increase in temperature caused a large change of the position of the bandgap to the smaller wavelengths (more than 100 nm) in a narrow temperature range. **b**, Reversible behaviour with small hysteresis was observed on cooling. The small difference between the position of the bandgap (~15 nm) at room temperature before and after the heating ramp is due to the different cooling rates in annealing and transmission measurement. **c**, A similar response was observed in the reflectance measurements, where peaks were located at 530 nm, 530 nm, 420 nm and 370 nm for the corresponding temperatures 26 °C, 80 °C, 120 °C and 134 °C, respectively.

change in colour of the sample from green to uncoloured. Note that the transmission and reflection measurements agree, taking into account the optical absorption of the materials below ~330 nm.

The mechanism underlying the reversible bandgap switching will be discussed next. Separate optical microscopy using homopolymeric PS and P4VP(MSA)_{1.0} shows that near room temperature PDP is not soluble in PS, whereas PDP is soluble in P4VP(MSA)_{1.0}, as expected due to the proposed hydrogen bonding. As described above, the P4VP(MSA)_{1.0}(PDP)_{1.5} domains contain an internal structure at room temperature due to formation of comb-shaped architecture by hydrogen bonding PDP to the sulphonates. This architecture leads to considerable stretching of the polyelectrolytic P4VP(MSA)_{1.0} chains, which also leads to concurrent stretching of the PS chains. This would explain the large periodicity comparable to the optical wavelengths, in agreement with previous studies on PS-*block*-P4VP(DBSA)_{1.5} (ref. 20). On heating, hydrogen bonds between PDP and P4VP(MSA)_{1.0} are gradually broken and PDP starts to migrate into the PS-domains at ~120–130 °C and becomes a non-specific solvent for both PS and P4VP(MSA)_{1.0} (ref. 27). These facts induce a very strong decrease in the long period of the lamellar structure within a narrow temperature range, as the comb-shaped supramolecular architecture of the P4VP(MSA)_{1.0} chains is 'purged', thus allowing more compact coiling of the polymer. The previous studies, where the bandgap properties were slightly modified due to the temperature-dependent refractive indices²², encouraged us to measure the refractive indices of PS, P4VP(MSA)_{1.0} and P4VP(MSA)_{1.0}(PDP)_{1.5} separately as a function of temperature. They changed only a few percent when heated up to ~140 °C and their temperature behaviour was smooth, suggesting that they do not explain the thermal switching of the bandgap. We finally point out that disappearance of the self-assembled internal structure within the P4VP(MSA)_{1.0}(PDP)_{1.5} domains at ~125 °C probably does not cause the photonic bandgap switching, because, for example, in PS-*block*-P4VP(MSA)_{1.0}(PDP)_{2.0} the internal structure disappears at ~60 °C but the photonic bandgap switching continues to take place at ~125 °C.

We have demonstrated a concept for a self-assembled polymeric system, which shows a reversible and large bandgap switching in the solid state in a narrow temperature range. Such a large switching (~30%) is uncommon, and the concepts shown suggest that on combining additional effects to self-assembly, such as selective/non-selective dissolution of small molecular additives, one can obtain responsive optically active materials in the solid state with large and reversible bandgap switching.

METHODS

PS-*block*-P4VP diblock copolymer was supplied by Polymer Source, and was used without further purification ($M_{n,PS} = 238,100 \text{ g mol}^{-1}$, $M_{n,P4VP} = 49,500 \text{ g mol}^{-1}$, $M_w/M_n = 1.23$). MSA was 99% pure and was purchased from Fluka. PDP was acquired from Pfaltz & Bauer (purity 97%) and chloroform was of analysis grade (Riedel-de Hën, 99%).

PS-*block*-P4VP, MSA and PDP were dissolved in chloroform separately. The solutions were combined leading to mixture that is denoted as PS-*block*-P4VP(MSA)_{1.0}(PDP)_{1.5}. Here 1.0 and 1.5 denote the nominal number of MSA and PDP groups versus one repeat unit of 4-vinylpyridine, respectively. The solution was stirred for 24 hours and the solvent was slowly evaporated at 4 °C (for about one week). Thereafter the sample was dried in vacuum at 30 °C for 48 hours and annealed for 3 days at 130 °C and finally slowly cooled to room temperature (cooling rate was ~0.5 °C min⁻¹). For optical measurements, annealing was performed between two quartz glass plates to decrease surface roughness of the sample. The TEM samples were prepared as follows: To study the structure at room temperature, the sample was first annealed for 3 days at 130 °C, thereafter cooled to 110 °C and kept there for 24 hours and finally cooled to room temperature at ~0.5 °C min⁻¹. To study the structure at high temperature, the sample was quenched from 170 °C into liquid propane.

The X-ray measurements were mainly performed at the Dutch–Belgian beamline (BM26) of the European Synchrotron Radiation Facility in Grenoble, using a beam of 8 keV with an area of 0.35 × 0.5 mm² at the sample position. The SAXS data were collected with a two-dimensional wire chamber camera at a distance of 8.0 m from the sample (for a more detailed description of the beamline see ref. 29). The SAXS measurements for Fig. 2b was performed using a setup described elsewhere³⁰.

Ultrathin sections (approximately 70 nm) of PS-*block*-P4VP(MSA)_{1.0}(PDP)_{1.5} for TEM characterization were cryomicrotomed using a Leica Ultracut UCT-ultramicrotome and a Diatome-diamond knife at ~120 °C. Dry sections were picked up onto 600-mesh copper grids and, to enhance contrast, the microtomed sections were stained for 2–3 hours in vapours of I₂ crystals. Bright-field TEM was performed on a JEOL-1200EX TEM operating at an accelerating voltage of 60 kV.

The specular transmission spectra were measured by Hitachi U-2000 double-beam spectrophotometer in the wavelength range 200–1,000 nm as a function of temperature. Temperature was increased/decreased in ~10 °C steps and before the measurement temperature was allowed to stabilize for 3 minutes. Spectral diffuse reflectance was measured by using the facilities at the Metrology Research Institute of Helsinki University of Technology in the wavelength range 300–950 nm. The angle of incidence was 8° and light was collected with an integrating sphere detection system, where the specular component was included. The spectral bandwidth of the spectrometer was set to 2.9 nm and the diameter of the measurement beam was adjusted to 6 mm.

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Competing financial interests:

The authors declare that they have no competing financial interests.