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Controlling Thermo-chromism in a Photonic Block Copolymer

Joseph J. Walish, Yin Fan, Andrea Centrone and Edwin L. Thomas*

Dr. J. J. Walish

Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

Y. Fan

Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

Dr. A. Centrone

Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA and Center for Nanoscale Science and Technology, National Institute of Standards and Technology, Gaithersburg, MD 20899-6203, USA

Prof. E. L. Thomas

Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA and Brown School of Engineering, Rice University, Houston, TX 77030, USA

E-mail: (elt@rice.edu)

The tunable properties of stimulus-responsive materials attract great interest in a variety of technological applications. Photonic gels are a new class of these materials which can be tuned to reflect different wavelengths of light. Controlling this reflected color via temperature-induced changes of self-assembled photonic materials is important for their application in sensors and displays. In this work, the thermo-chromic behavior of a PS-P2VP photonic gel was found to originate from a temperature-induced change in the pKa of the P2VP blocks. Control was obtained through the manipulation of the solution pH. The findings of this work provide the basis for understanding and controlling the properties of thermo-chromic block copolymers fostering their use in technologically relevant applications.

Introduction

Thermochromic materials alter their color in response to temperature changes and find applications as sensors, as security labels, as coatings for thermal printing and have great appeal in fields like fashion and toys.^[1] Because of their inherent ease of processing and low cost, a number of thermally-tunable (mostly colloidal crystal- and liquid crystal-based) photonic crystals have been investigated for such applications.^[2] However, the strong sensitivity to temperature changes of some opal-based systems and their nature to swell in all three dimensions are disadvantageous, for example, in a display application where temperature-independent performance is desired. Because of their unidirectional swelling behavior imposed by a glassy domain, constrained lamellar block copolymer films^[3] undergo extensive 1D swelling in selective solvents and, if their thermal properties could be finely controlled, are well suited as display elements and sensory devices. The thermochromic behavior of block copolymer photonic crystals has been described previously,^[4] but the detailed molecular mechanism(s) underlying their highly-tunable properties is still not well understood.

In this work we report on the fundamental origins and control of the thermochromic properties of a symmetric poly(styrene)-*b*-(2-vinylpyridine) (PS-*b*-P2VP) block copolymer (BCP) in acetic acid-water solutions. At fixed composition, combined UV-Visible spectroscopy (UV-VIS) and Fourier Transform Infrared spectroscopy (FTIR) data indicate that changes in the acid dissociation constant (Ka) of the pyridine units in the P2VP block drive the material swelling behavior and regulate the reflectivity changes with temperature. The FTIR spectra show that the fraction of P2VP protonated pyridine groups decreases with temperature resulting in more hydrophobic (less swollen) P2VP domains. As the pyridine pKa ($pKa = -\log_{10}(Ka)$) decreases with temperature, the attractive polymer-polymer interactions start prevailing over the polymer-water interactions leading to an increase of the P2VP block density and to a reduction of the swelling. It is hypothesized that the change of the

reflectivity peak with temperature ($d\lambda_{\text{peak}}/dT$) would be maximized using an acid whose strength decreases with increasing temperature. It was also observed that the reflectivity peak position of the PS-*b*-P2VP in concentrated acetic acid solutions (0.5 mol L⁻¹ and 1 mol L⁻¹) was invariant with temperature which could be a desirable characteristic for developing sensors and displays with minimal thermal color shift.

Experimental Section

Materials

A symmetric PS-*b*-P2VP block copolymer with a number-average molecular weight of 57 kg mol⁻¹ (PS) – 57 kg mol⁻¹ (P2VP) and 1.08 polydispersity was purchased from Polymer Source Inc., Dorval Canada. The P2VP homopolymer used for the FTIR measurements with a viscosity average molecular weight of 200,000 was purchased from Scientific Polymer Products, Inc. Propylene glycol monomethyl ether acetate (Alfa Aesar) and chloroform (Mallinckrodt Chemicals) were used for the copolymer film sample preparation. All chemicals were used as received without further purification unless otherwise noted.

Film Preparation

The BCP photonic films were cast inside a quartz spectrometer cuvette. The cuvette surface was treated with a 3-aminopropyltriethoxysilane (99%, Aldrich) vapor before use. A PS-P2VP (5% mass fraction) solution (propylene glycol monomethyl ether acetate) was spread onto one wall of a cuvette and slowly dried in air. The film was then annealed at 50 °C in chloroform vapor overnight. The annealed film swelled into a photonic gel when the cuvette was filled with the acid solutions.

Materials Characterization

UV-VIS transmission spectra were collected on a UV-VIS spectrophotometer using a temperature controlled sample holder and 1 cm path-length quartz cuvettes. A cuvette with an

annealed film was filled with water and used as background. An equilibration time of 10 min was used after each temperature change. The spectra were recorded with a spectral resolution of 2 nm between $0\text{ }^{\circ}\text{C} \pm 0.5\text{ }^{\circ}\text{C}$ and $95\text{ }^{\circ}\text{C} \pm 0.5\text{ }^{\circ}\text{C}$.

FTIR spectra were recorded on a FTIR spectrometer and a temperature-controlled attenuated total reflection (ATR) accessory. 128 spectra (1 cm^{-1} resolution) were acquired and averaged for every sample in the 690 cm^{-1} to 1800 cm^{-1} spectral range. FTIR spectra of P2VP homopolymer (31% mass fraction) dissolved in acetic acid solutions (0.05 mol L^{-1}) were acquired between $22\text{ }^{\circ}\text{C} \pm 0.2\text{ }^{\circ}\text{C}$ and $60\text{ }^{\circ}\text{C} \pm 0.2\text{ }^{\circ}\text{C}$ using a liquid sample holder to avoid solvent evaporation. A 10 min equilibration time was allowed at each temperature before the spectral acquisition.

Results and Discussion

The symmetric PS-*b*-P2VP block copolymer was spun-cast on the cuvette, annealed (resulting in well oriented, essentially parallel lamellae) and immersed in acetic acid-water solutions before being cooled just above the solution's freezing point. The annealed PS-*b*-P2VP BCP displays a lamellar morphology with blocks of alternating composition and is transparent in its unswollen state due to the small lamellar period (50 nm) and almost equal refractive indices of PS and P2VP. When such a film is immersed in a solvent, one or both domains can swell depending on the affinity between the solvent and the component blocks. Tuning the solvent's affinity allows changing the respective block's size and index and consequently the reflected light wavelength. We used an extremely preferential solvent system for the P2VP block: acetic acid-water solutions from 0.01 mol L^{-1} to 1 mol L^{-1} . The acid-water solution changes the P2VP block's spacing and effective index of refraction giving rise to a sufficiently-large periodic lamellar structure that can reflect visible light (a "1D photonic crystal" (see **Figure 1a**)). Such solutions do not swell the PS domains which remain rigid and glassy. In addition, acetic acid does not display large hysteretic swelling behavior like

some stronger acids such as hydrochloric acid.^[5] The temperature-related properties of PS-P2VP samples were measured from 0 °C to 95 °C. Through our experiments we observed lower critical solution temperature (LCST) type behavior from P2VP in low concentration acetic acid-water solutions (from 0.01 mol L⁻¹ to 0.1 mol L⁻¹) as well as non-LCST behavior from samples immersed in 0.5 mol L⁻¹ and 1 mol L⁻¹ of acetic acid.

In order to identify the causes of the temperature-related reflectivity peak shift, several potential factors were considered including: changes in the index of refraction ($n_{effective}$) of the P2VP/solvent layer, changes of the solvent fraction (Φ) in the P2VP blocks, thermal expansion ($\alpha\Delta T$) of each layer, changes of the acetic acid pK_a or changes of the pK_a of the P2VP pyridine groups, changes in solubility ($\Delta\delta$), and changes in the effective Flory-Huggins interaction parameters between all the components. The variation of the pK_a of the pyridine groups in the P2VP block was identified as the main cause of the thermochromic behavior (see below) while the other factors were identified to have essentially negligible effects in this system (see supporting information). FTIR spectra were used to study in detail the interactions between the active P2VP block with the acetic acid-water solutions confirming our hypothesis - that the thermochromic behavior was attributable to the temperature-induced pyridine pK_a change.

Acetic acid-water solutions swell P2VP to different degrees depending on the pH of the solution. As the pH decreases, the fraction of protonated pyridine groups increases resulting in an increased swelling of the P2VP layers and in a red-shift of the reflectivity peak (**Figure 1b**). Several different acetic acid concentrations (0.01 mol L⁻¹, 0.02 mol L⁻¹, 0.05 mol L⁻¹, 0.1 mol L⁻¹, 0.5 mol L⁻¹, and 1.0 mol L⁻¹) were used to test the changes in BCP reflectivity with respect to the extent of protonation due to changes in temperature. In the range of temperatures tested (from 0 °C to 95 °C) samples swollen with the 0.5 mol L⁻¹ and 1 mol L⁻¹ acetic acid solutions showed little to no change in reflectivity (**Figure 1c and 2a**).

It is apparent that the rate of color change ($d\lambda_{\text{peak}}/dT$) mimics the rate of color change induced by changing the pH ($d\lambda_{\text{peak}}/d(-\log[H^+])$) (see Figure 1b and 2a). For instance, the 0.01 mol L^{-1} sample has a high degree of color tunability while the 1 mol L^{-1} sample does not change color at all. This suggests that the change in temperature is causing a change in protonation of the P2VP. There are two possible causes that can induce changes in P2VP protonation: a change in the acetic acid pKa or a change in the pKa of the pyridine groups of P2VP. A change in the pKa of the acid will result in a change in pH while a change in the pKa of the P2VP will result in a change of the number of protonated P2VP monomer units at a given pH . The equilibrium dissociation constant of acetic acid ($K_{eq}=10^{-pKa}$) is known to change with temperature.^[6] Converting the K_{eq} data of Calder and Barton^[6] into pKa , a shift from a pKa of 4.78 at $5 \text{ }^\circ\text{C}$ to 4.75 at $20 \text{ }^\circ\text{C}$ is seen, indicating that the solution is more acidic when heated. This decrease in pH upon heating (from $5 \text{ }^\circ\text{C}$ to $25 \text{ }^\circ\text{C}$) accounts for a theoretical 0.2 nm K^{-1} shift of the reflectivity peak (calculated by using a quadratic fit to the acetic acid pH -reflectivity curve - see **Figure 2b**).

Data on a temperature-related shift in K_{eq} for the conversion of un-protonated to protonated P2VP could not be found in the literature but reports suggest a decrease in the pKa of organic bases upon heating.^[7-9] The pKa of pyridine in a 50% methanol-water solution decreases from 4.14 at $20 \text{ }^\circ\text{C}$ to 3.81 at $50 \text{ }^\circ\text{C}$,^[8] while the change of the pyridine pKa with temperature in aqueous solutions was found to be approximately $-0.011 \text{ }^\circ\text{C}^{-1}$.^[9] The shift in the pKa of P2VP from $25 \text{ }^\circ\text{C}$ to $5 \text{ }^\circ\text{C}$ was estimated using a relationship given by Castells et al.^[8] for pyridine:

± 0.1 at 25 °C. Using this value and equation 1 gives a $d(pKa)/dT$ value of $-1.0 \cdot 10^{-2} \text{ } ^\circ\text{C}^{-1} \pm 2.5 \cdot 10^{-4} \text{ } ^\circ\text{C}^{-1}$ and a theoretical pKa of 3.87 ± 0.1 at 5 °C. This relatively large change in pKa of the pyridine groups leads to a marked change in solubility which directly affects the position of the reflectivity peak.

To further prove our interpretation, the interaction of P2VP with acetic acid solutions (0.05 mol L⁻¹ and 1 mol L⁻¹) was studied with FTIR spectroscopy as a function of temperature using an ATR accessory. A P2VP homopolymer was used for the FTIR experiments in place of PS-*b*-P2VP BCP because it was already determined that P2VP is responsible for the BCP photonic gels' thermochromic behavior (see supporting information). Additionally, the pyridine IR absorption bands are strongly overlapped with the phenyl absorption bands of the polystyrene.^[12, 13] Since the ATR configuration can probe only a few microns of the sample and because the IR absorption bands are proportional to the material's concentration (small for the swollen PS-*b*-P2VP) employing the PV2P homopolymer provides spectra with a better signal to noise ratio compared to the copolymer.

As the temperature increases, a larger fraction of molecules occupy excited vibrational states resulting in a decrease of the vibrational frequencies because of the chemical bonds' anharmonicity. Changes in the intermolecular interactions can also account for peak frequency shifts in vibrational spectra.^[14,15] In particular, attractive intermolecular interactions weaken the intramolecular bonds and can lead to a downshift in frequency, while repulsive interactions cause an up-shift in frequency.^[14] The frequency shift of one of the pyridine ring vibrations (quadrant stretching)^[13] as a function of temperature is reported in **Figure 3a**. From approximately 22 °C to 33 °C the expected moderate frequency softening due to the temperature increase is observed ($\Delta\nu_{22-33} = -0.06 \text{ cm}^{-1} \text{ K}^{-1}$); the frequency shift between 33 °C and 39 °C is much more pronounced ($\Delta\nu_{33-39} = -0.22 \text{ cm}^{-1} \text{ K}^{-1}$), while from 39 °C to 60 °C the frequency shift is again moderate ($\Delta\nu_{39-60} = -0.09 \text{ cm}^{-1} \text{ K}^{-1}$). The large peak shift between 33 °C and 39 °C indicates that the density of the polymer chains is increasing and that the chains

are experiencing attractive intermolecular interactions. In other words in this interval, P2VP becomes more hydrophobic (less protonated) and the swelling is reduced. Above 39 °C the swelling continues decreasing slowly. All the P2VP IR-active modes show very similar peak shifts with temperature (see for example **Figure S1** of the supporting information).

The FTIR intensities of bands characteristic of each component in the solution (P2VP, water and acetic acid) allow a detailed description of how the various interactions vary with temperature (**Figure 3b, 3c, 3d**). For this purpose we analyzed the intensity of the P2VP ring semicircle stretching^[13] at $\approx 1479 \text{ cm}^{-1}$ (I^P), the intensity of the water O-H bending peak at $\approx 1638 \text{ cm}^{-1}$ (I^W) and the intensity of the acetic acid peak at $\approx 1411 \text{ cm}^{-1}$ (I^A) which involves C-O stretching and C-O-H in plane bending^[16] (see **Figure S2**). As the temperature increases, the relative intensity of the polymer band increases with respect to the intensity of the water band (Figure 3b) indicating an increase in the polymer chain density and reduction of swelling. The transition is progressive and it is accentuated between 33 °C and 39 °C. Acetic acid molecules are bound as counter ions to protonated pyridine groups; since the intensity ratio between the acetic acid band and the polymer decreases with temperature (Figure 3c), we conclude that the fraction of the protonated pyridine groups (and of the pyridine pK_a value) decreases with temperature, thus confirming our previous interpretation. Such changes are again accentuated between 33 °C and 39 °C as the polymer-polymer interactions continue to increase at the expense of the polymer-water interactions. The ratio between the intensity of acetic acid and water bands decreases approximately linearly with temperature (Figure 3d). This observation suggests that the change in the pyridine pK_a is progressive with temperature and that the water molecules form hydrogen bonds with the pyridine groups as these become deprotonated. Over the range from 33 °C to 39 °C the attractive polymer-polymer interactions outweigh the polymer-water interactions which decrease with temperature as the pyridinium concentration decreases.

Conclusion

In summary, the thermochromic behavior of P2VP in acetic acid-water solutions was found to be primarily driven by a temperature-induced change in the pK_a of P2VP. The change in the pK_a is reflected in the FTIR spectra indicating that the fraction of protonated pyridine groups decreases with temperature leading to more hydrophobic (less swollen) P2VP domains. The reflectivity peak position of PS-P2VP in 0.5 mol L⁻¹ and 1 mol L⁻¹ acetic acid was not affected by a change in temperature which suggests these compositions are useful if a temperature-independent sensor is desired (e.g. for the measurement of ion concentration over a range of temperatures.)

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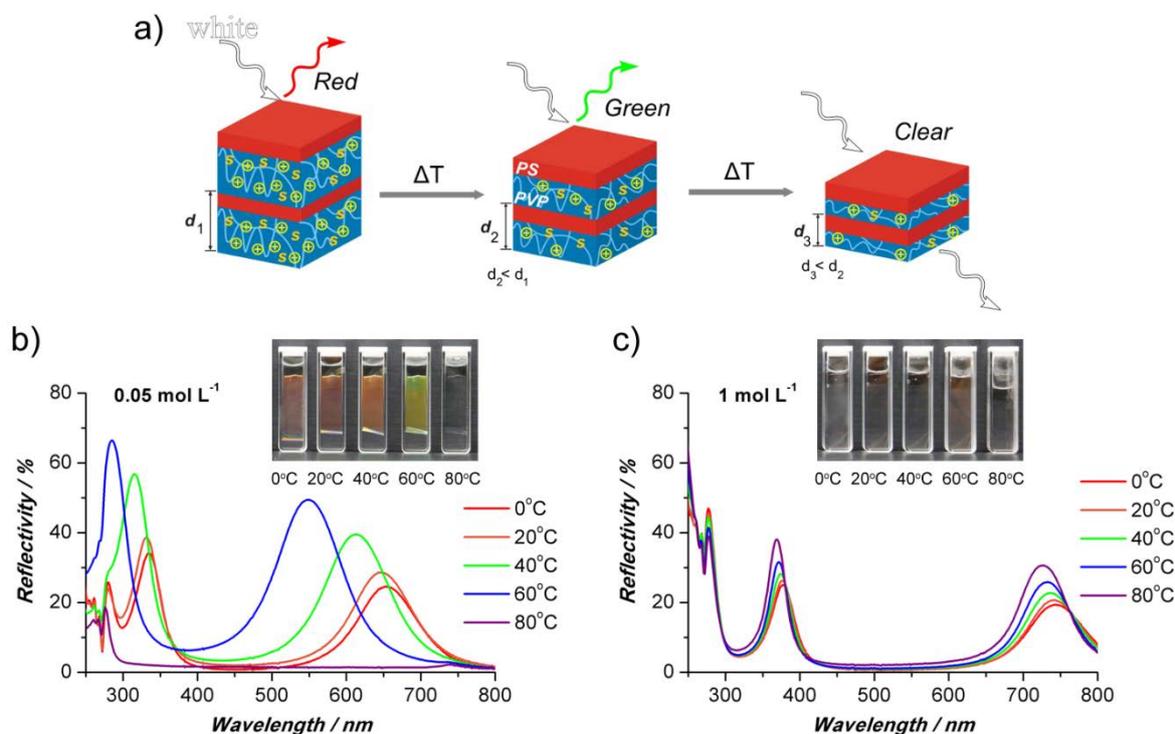


Figure 1. a) Schematic of the PS-b-P2VP BCP swelling behavior as a function of temperature and its effect on the BCP reflectivity- For low acid concentrations the copolymer domain spacing is reduced as the temperature increases until no visible light is reflected when the P2VP domains collapse. b) The change in reflectivity films with temperature for PS-b-P2VP immersed in a 0.05 mol L⁻¹ acetic acid-water solution. As the temperature is increased, the reflectivity of the film exposed to the 0.05 mol L⁻¹ solution blue-shifts and eventually disappears as the system approaches the transition temperature of the P2VP-acid solution. c) Reflective spectra of PS-P2VP film immersed in 0.5 and 1 mol L⁻¹ solutions show very limited peak-shift. The highest wavelength peak corresponds to the (001) reflection and the (002) reflection appears at half this value. In the 1 mol L⁻¹ case, the reflectivity peaks are in the near IR and UV regimes so the films exhibit no visible color.

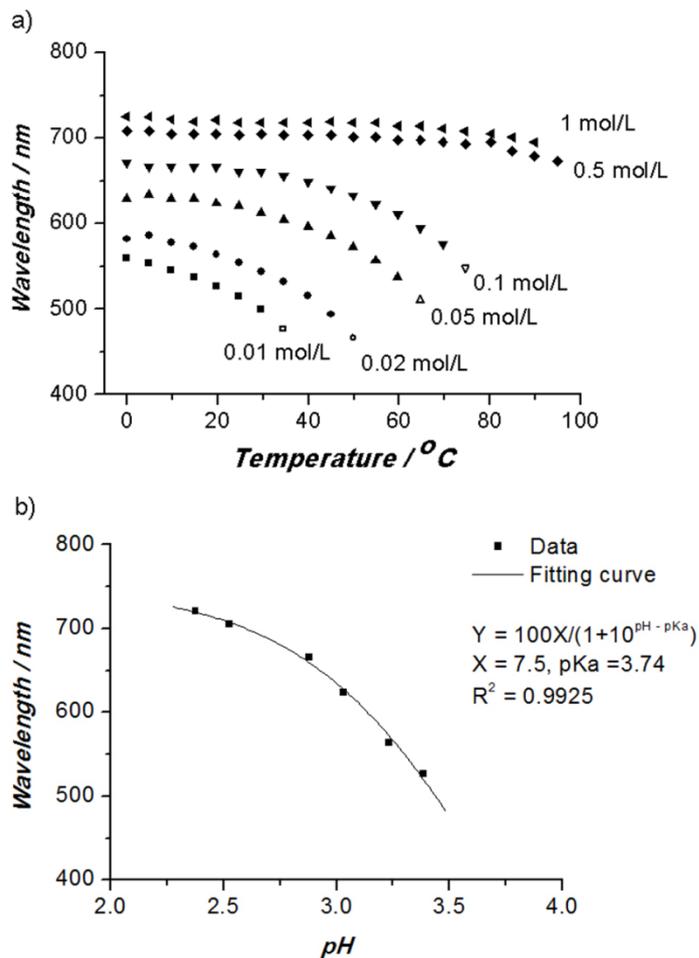


Figure 2. a) PS-b-P2VP reflectivity peak position as a function of temperature in different acetic acid-water solutions. As the fraction of protonated P2VP groups increases (with increasing acid concentration) the colored-to-clear transition-temperature shifts to higher and higher temperatures until no transition temperature is observed ($\approx 1 \text{ mol L}^{-1}$ acetic acid). (Data points with hollow markers indicate the film transitioned to a colorless state at higher temperatures.) b) As the solution becomes more acidic, more P2VP gets protonated (P2VP⁺). Since P2VP⁺ has a higher solubility, the P2VP layers expand and the photonic crystal reflects light of increasing wavelength. Maximum conversion occurs around pH 2.4 where no further P2VP can be converted to P2VP⁺. The pKa of P2VP was calculated by fitting an ionization curve to the reflectivity peak positions for PS-b-P2VP in acetic acid. The two-parameter (constant of proportionality between ionization percentage and peak position and pKa) best-fit curve gave a pKa value of 3.67 ± 0.1 . The error bars in Figure 2 are smaller than the marker size.

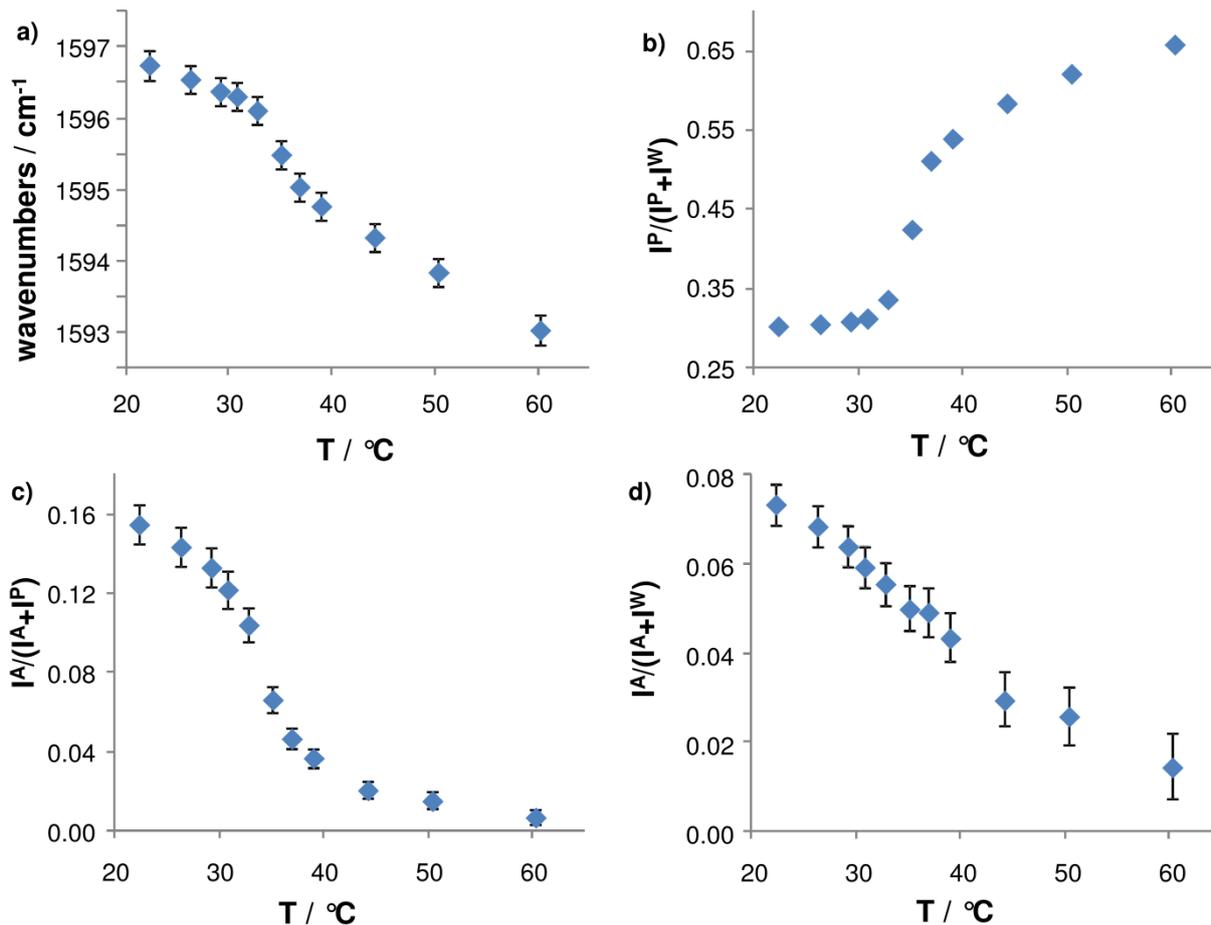


Figure 3. a) Frequency shift of P2VP pyridine quadrant stretching ring vibration ($\approx 1595 \text{ cm}^{-1}$) as a function of temperature. b) Intensity ratio between the P2VP ring breathing vibration at $\approx 1479 \text{ cm}^{-1}$ (I^P) and the sum of the intensity of the water O-H bending mode at $\approx 1638 \text{ cm}^{-1}$ (I^W) and I^P ; c) intensity ratio between the acetic acid peak at $\approx 1411 \text{ cm}^{-1}$ (I^A) and the sum of the intensity of I^A and I^P ; d) intensity ratio between I^A and $I^A + I^W$. The error bars represent a single standard deviation ($n=3$) due to baseline uncertainty. In the case of the intensity ratios the error bars were determined by calculating the propagation of the uncertainties associated with the different peak intensities. The error bars in Figure 3b are smaller than the marker size.

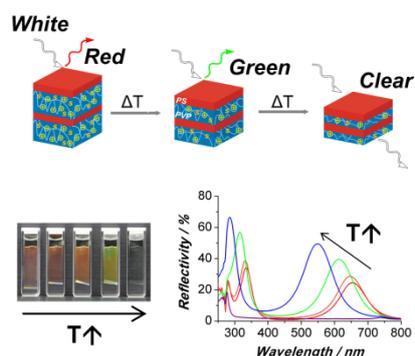
The table of contents entry

The ability to control the color of self-assembled, photonic materials via temperature-induced changes is important for their use in sensors and displays. The thermochromic behavior of a PS-P2VP photonic gel was studied (UV-VIS, FTIR) and found to originate from a temperature-induced change in the pK_a of the P2VP blocks in different acetic acid-water solutions. Control of the thermochromic response was obtained through the manipulation of the solution pH .

J. J. Walsh, Y. Fan, A. Centrone, E. L. Thomas*

Controlling Thermochromism in a Photonic Block Copolymer

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Supporting Information

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Controlling Thermo-chromism in a Photonic Block Copolymer

Joseph J. Walsh, Yin Fan, Andrea Centrone and Edwin L. Thomas*

The position of the reflectivity maximum for a one-dimensional photonic crystal is given by:

[1]

length changes. Since the PS layers do not affect the reflectivity changes the role of the P2VP-solvent layers must be understood to explain the thermochromic phenomena (discussed in the main text.)

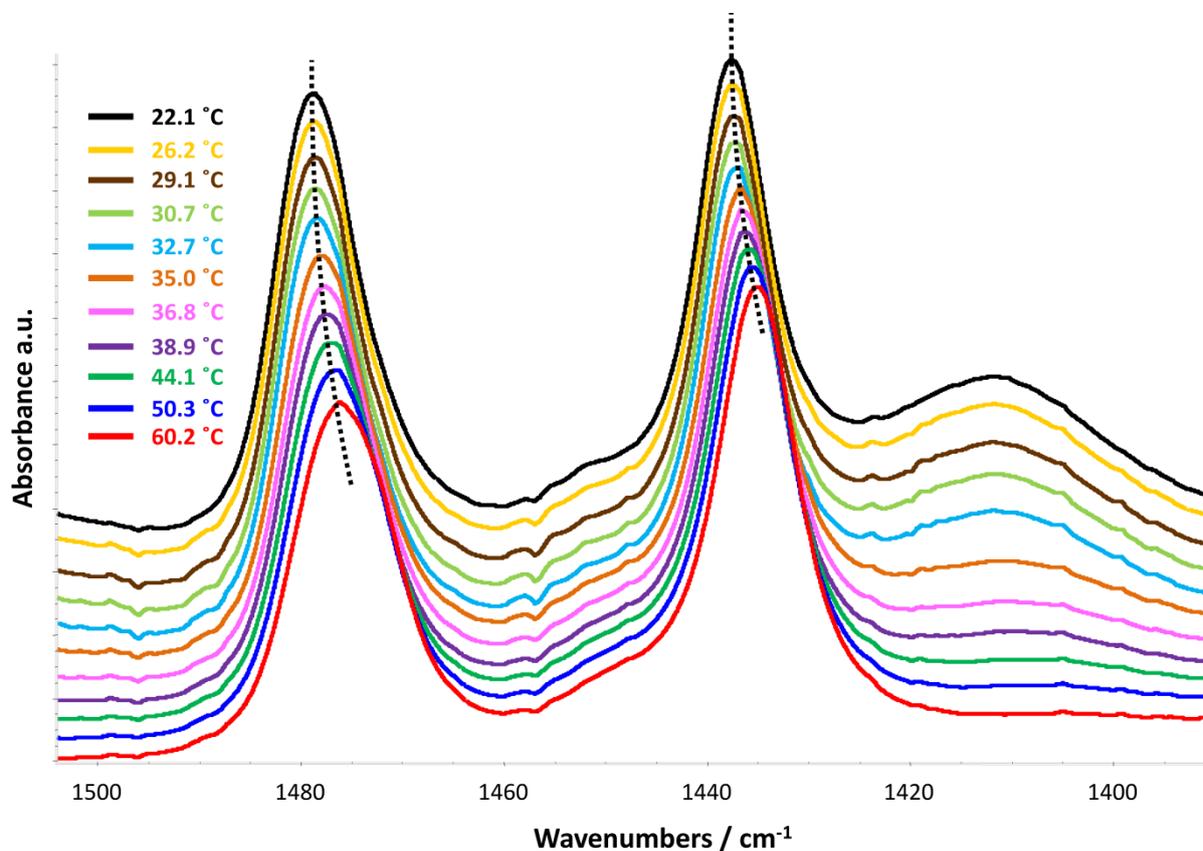


Figure S1: FTIR (ATR) spectra of P2VP polymer in 0.05 mol L⁻¹ acetic acid solution as a function of temperature. The PV2P peaks (at ≈ 1438 cm⁻¹ and ≈ 1479 cm⁻¹) shift to lower frequencies as the temperature is increased. The dotted lines are to guide the eye only.

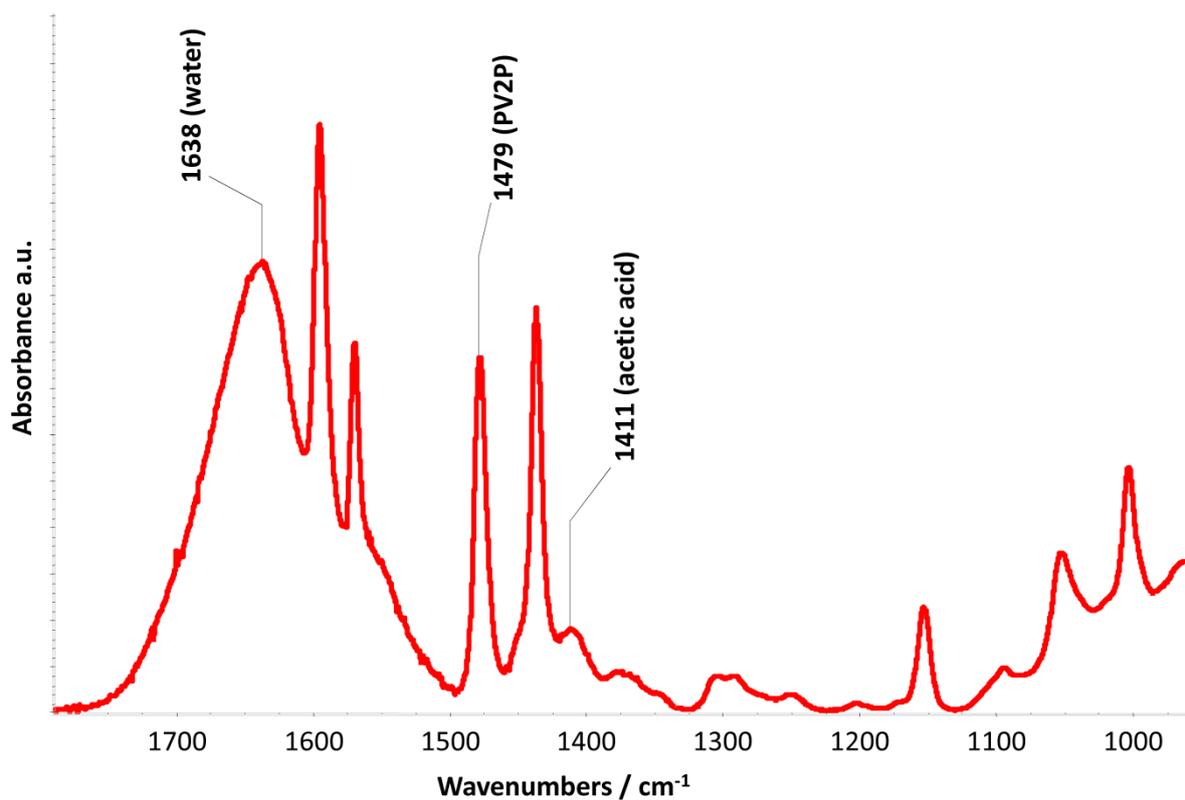


Figure S2: FTIR (ATR) spectra of P2VP homopolymer in 0.05 mol/L acetic acid solution at 35.0 °C. The peaks used for the intensity ratios are indicated in the figure: water (1638 cm⁻¹), P2VP (1479 cm⁻¹) and acetic acid (1411 cm⁻¹).

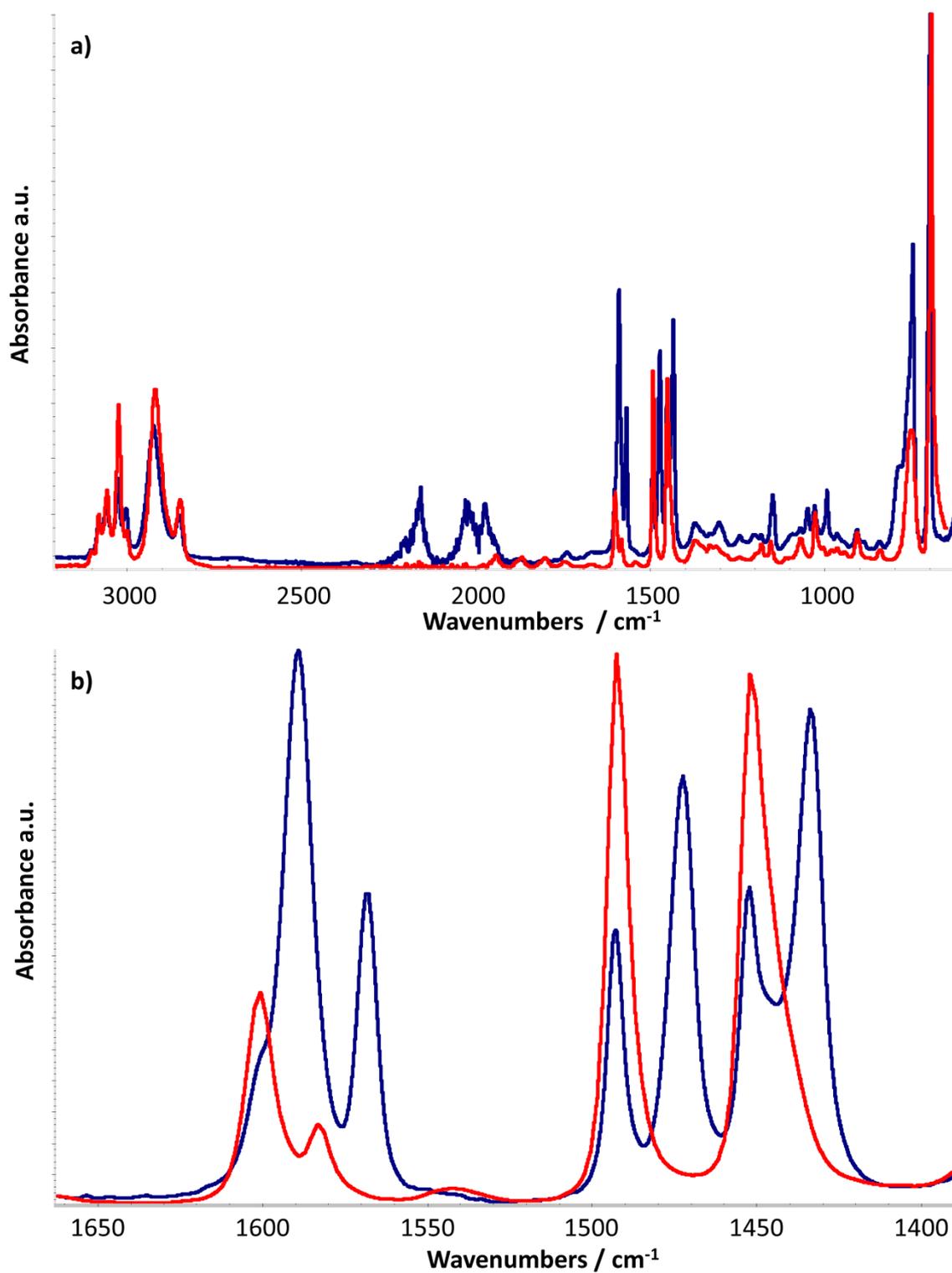


Figure S3: (a) A comparison of the IR solid state spectra for PS (in red) and PS-P2VP (blue) solid-state samples. (b) A magnified view of the 1400-1600 cm^{-1} region. Since ATR only probes a few micrometers of material and because the swelling with the solvent causes a decrease in intensity of the P2VP peaks (because of the reduced density), the BCP spectra in solution were of insufficient quality (See Figure S4).

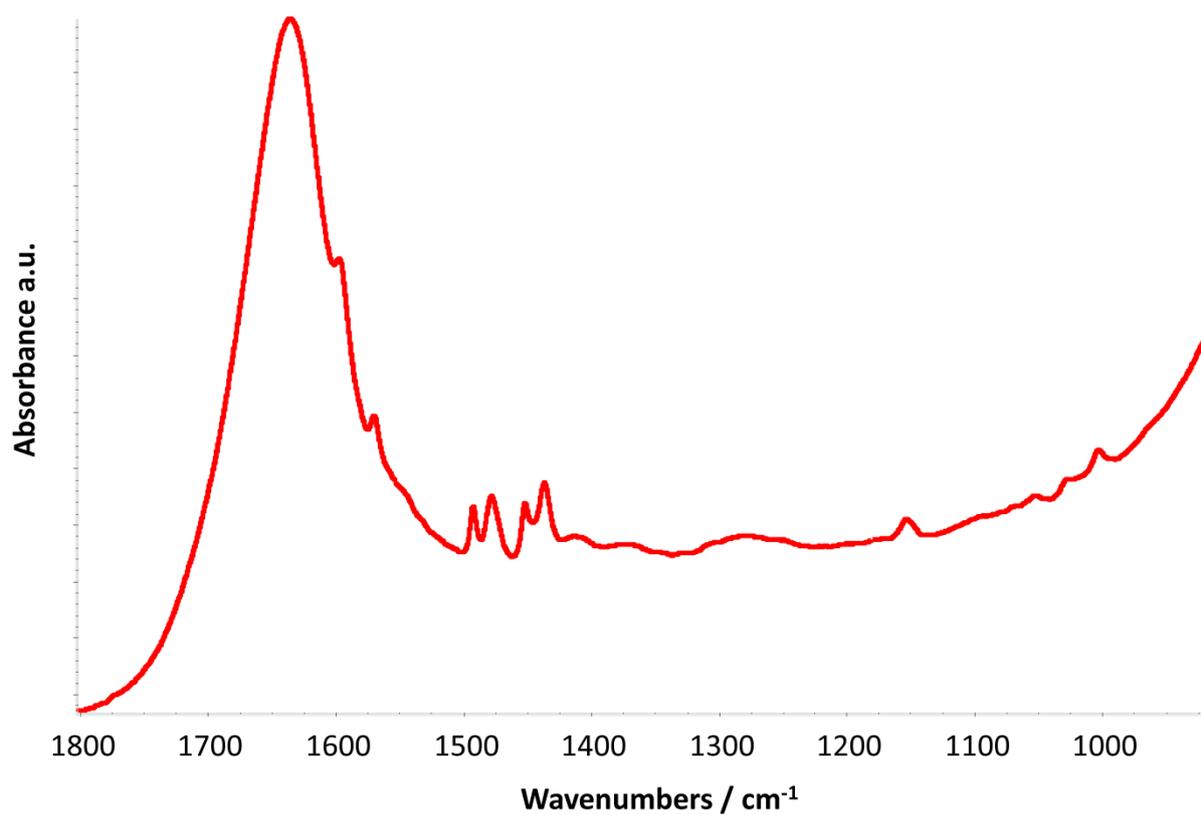


Figure S4: FTIR (ATR) spectrum of swollen PS-*b*-P2VP BCP (0.1 mol L⁻¹ acetic acid-water solution); the peaks are too weak to carry out the analysis described in the text.

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