Thermochromic Block Copolymer Photonic Gel

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Because of their potential as technologically useful materials such as sensor platforms, variable-wavelength lasers, and reflective color displays, tunable band-gap photonic crystals have been intensively investigated.[1–8] Optical characteristics of photonic crystals can be manipulated over a desired wavelength range by tailoring either one or a combination of their characteristic parameters: dielectric constant, volume fraction, characteristic size, and geometry. To date, a host of materials and various external stimuli have been exploited to attain tunable photonic band-gap systems. For example, a variety of one- (1D), two- (2D), or three-dimensional (3D) photonic crystals were doped with nematic liquid crystals (LCs) and utilized as electro-optic or thermo-optic tunable optical elements. The refractive index of the LC-containing domains can be modulated via reorientation of the optic axis of the LC with applied electric fields or through phase transformation of the LC with temperature.[1,5] The lattice dimension and the effective refractive index of a crystalline colloidal array in an elastomeric (rubber or gel) matrix can be altered by applied mechanical, chemical (e.g., pH or ionic strength), or thermal stimuli, resulting in a reversible shift in their spectral responses.[2–4,8–11]

Recently, block copolymers have attracted attention as a versatile self-organizing material platform for creating photonic crystals due in large part to a range of accessible periodic structures and a possibility to incorporate various optically active/passive guest molecules or nanoparticles to engineer desired optical functionalities.[12] Block copolymer based photonic structures also offer novel routes to tune the photonic band gap by manipulating materials properties and microstructure. One previous method of altering the peak reflectivity of 1D lamellar stack involved swelling block copolymers with homopolymers, where the microdomain size and thus the stop band of the blends depended on the amount of added homopolymers.[13] The idea of using a nanocomposite composed of block copolymers and surface-functionalized inorganic[14] or metallic[15] nanoparticles offered another way to tune and enhance photonic properties of block copolymer based photonic materials. Block copolymers having an LC-containing block have also been demonstrated as thermally tunable photonic band gap structures by changing the domain spacing and/or by changing the refractive index of the LC-containing domains with temperature.[6,16] More recently, an amphiphilic block copolymer of poly(styrene-*b*-quaternized 2-vinylpyridine) (PS-*b*-P2VP) was used as a chemically tunable photonic gel, in which a selective swelling of polyelectrolyte block by aqueous solvents induced a change in both the P2VP domain size and refractive index, resulting in a reversible shift of the stop band over a very broad wavelength range.[17]

In this communication, we present thermally responsive self-assembled reflectors based on 1D photonic gels comprised of poly(styrene-*b*-isoprene) (PS-*b*-PI) block copolymer and cumene (the neutral solvent). A near-symmetric composition block copolymer can form a 1D periodic lamellar dielectric stack and give rise to a reflectivity peak in the visible portion of the spectrum. The effect of temperature on the spectral properties, or *thermochromism*, was investigated, holding the composition of the block copolymer–solvent system approximately constant. The high molecular weight PS-*b*-PI block copolymer used in this study was anionically synthesized with sequential addition of styrene and isoprene monomers in cyclohexane/benzene mixed solvent. The molecular weight and composition of the resultant block copolymer are 8.40×10^5 g/mol (PDI 1.08) and 57/43 (PS/PI, w/w) as determined by gel permeation chromatography (GPC) and nuclear magnetic resonance (NMR) analysis, respectively.

The PS-*b*-PI block copolymer was dissolved in cumene and cast from a solution of about 50 wt % solvent content between two glass substrates, and then the sample was enclosed with a fast-curing epoxy to maintain a constant solvent concentration, as schematically shown in Figure 1. The sample temperature was then varied by using a temperature-controllable hot stage (Linkam, THMS 600), and reflectivity spectra at near normal incidence were taken at various temperatures using a fiber-optic spectrometer (Stellarnet Inc. EPP2000) attached to an optical microscope (Zeiss Axioskop).[18] The film appears green at normal incidence while appearing blue when viewed at a low angle, confirming that the lamellae oriented parallel to the substrate. Figure 2 shows measured reflectivity spectra between 30 and 140 °C in 10 °C increments, in which the sample temperature was increased at a rate of 5 °C/min and the reflectivity data were taken at each temperature after thermal equilibrium of the system was reached (after ∼10 min). As the sample temperature increases, the peak reflectivity wavelength shifts to a shorter wavelength range from 510 nm (30 °C) to 450 nm (140 °C) while the width of reflectivity band remains almost unchanged (the full width at half-maximum (fwhm): ∼12 nm).

The optical thickness of each domain, which is defined as the domain thickness (d_i) multiplied by the domain refractive

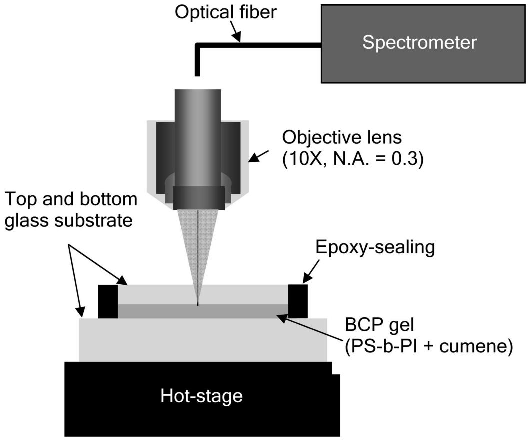

Figure 1. Schematic of the experimental setup for recording reflectivity vs wavelength as a function of sample temperature for the 1D PS-*b*-PI lamellar photonic gel.

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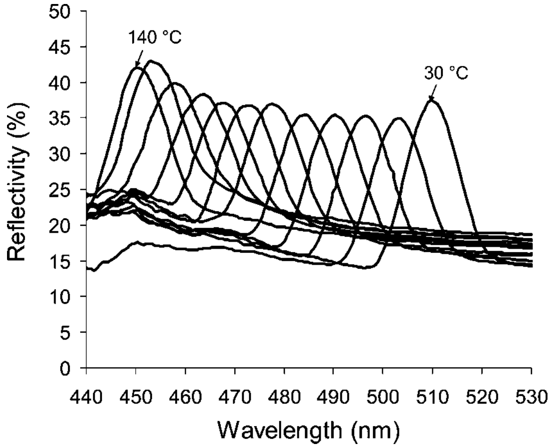

Figure 2. Measured normal incidence reflectivity spectra of the PS-*b*-PI block copolymer lamellar photonic gel at 12 different temperatures between 30 and 140 °C in 10 °C increments.

index (n_i), controls the position of the band gap. There are three factors that contribute to the change in optical thickness of the respective layers with temperature: refractive index, thermal expansion, and the segregation strength between the blocks. The temperature-dependent refractive indices, $n(T)$, of the solvent (cumene) and the polymers (PS and PI) depend upon the respective densities (ρ), which all decrease with temperature ($d\rho/dT < 0$). Such a decrease in the refractive index results in the decrease of the optical thickness of each layer and therefore shifts the reflectivity band to a shorter wavelength range. Thermal expansion of the layers will increase optical thickness by an amount of $\alpha_i \Delta T d_i$ (α_i: thermal expansion coefficient of the domain) and induces a red shift of the reflectivity band with temperature.

The most important factor contributing to the thermochromic effect in the block copolymer gel is the variation of lamellar domain spacing due to the temperature variation of the degree of segregation between the PS and PI blocks. As the temperature increases, the segregation strength between blocks, as represented by Flory–Huggins interaction parameter ($\chi \sim 1/T$), becomes smaller, resulting in the relaxation of the stretched chains and therefore a decrease of the domain thickness. Hashimoto and co-workers experimentally showed that the thermodynamically controlled domain periodicity (L) of PS-*b*-PI lamellar block copolymer in solution varies with absolute temperature (T) given by $L \sim (1/T)^{1/3}$ for a nonselective solvent.[19,20]

In order to quantitatively examine the respective contributions of the three above-mentioned factors on the position of the peak reflectivity, we modeled the reflectivity band shift with temperature using a 1D photonic structure. Starting from the set of physical parameters determined by fitting the experimentally measured reflectivity spectrum at 30 °C (Table 1), where the peak reflectivity occurs at 510 nm with a fwhm of 12 nm, the temperature-dependent reflectivity data can be systematically modeled to determine the evolution of the domain thicknesses and refractive indices by means of the transfer matrix method (TMM). For this calculation, we assume refractive indices of the PS and PI homopolymers at 30 °C as 1.590 and 1.510, a uniform lamellar orientation parallel to the glass substrates, normal incidence of light, a constant ratio of PS and PI domain thicknesses (i.e., $d_{PS}/d_{PI} = 1.1/0.9$ as observed in TEM for a dried sample (d_{PS}: 110 nm; d_{PI}: 90 nm), cumene as a nearly neutral solvent with refractive index of 1.491, and a sample with 400 layers. The neutrality of cumene in PS–PI is suggested since we do not observe any noticeable difference in phase behavior compared with using toluene on a large number of PS–PI samples studied over a number of years. Toluene has been extensively used as a nearly neutral solvent for PS-*b*-PI, for example, as indicated by Hashimoto et al. via SAXS.[19] We estimated the effective refractive index of each type of solvent-swollen layer by a simple rule of mixtures.

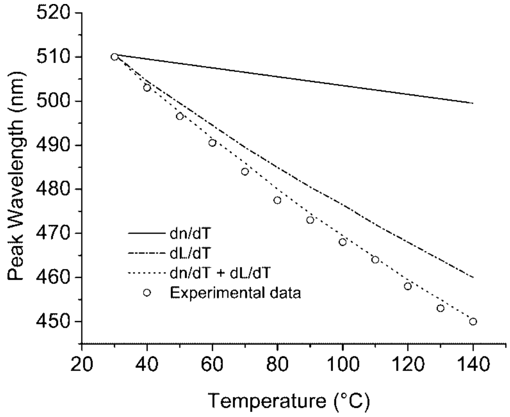

Figure 3. Center wavelength of the peak reflectivity obtained from TMM calculations with temperature-dependent refractive indices, with temperature-dependent domain thicknesses, and with both temperature-dependent refractive indices and domain thicknesses at various temperatures. The experimentally observed peak reflectivity wavelengths are well matched by assuming a blue shift in the reflectivity peaks arises from the decrease in refractive indices and from the decrease in polymer layer thicknesses resulting from the lower degree of block incompatibility at higher temperatures. The experimental data are thermoreversible.

The shift of the reflectivity band can now be calculated as a function of temperature due to the temperature variation of the refractive indices of the solvent and the respective block polymers as well as changes in the lamellar domain spacing. The dn/dT of cumene was estimated as that of toluene ($\sim -5.68 \times 10^{-4}\ \mathrm{K}^{-1}$)[21] and the dn/dT for both blocks were assumed the same as that of PS ($\sim -1.42 \times 10^{-4}\ \mathrm{K}^{-1}$),[22] since with cumene plasticization both blocks are well above their glass transition temperatures.

Using the estimated dn/dT for the solvent and each block, the effective refractive indices of respective domains at various temperatures were calculated. Taking the domain thicknesses as their values at 30 °C (i.e., $d_{\mathrm{eff,\,PS}}$: 91.8 nm; $d_{\mathrm{eff,\,PI}}$: 75.1 nm), the effect of only the dn/dT on the reflectivity peak position as a function of temperature obtained by the TMM calculation is shown as the top set of data in Figure 3. Next, the effect of the temperature variation of the lamellar domain spacing upon the reflectivity peak can be taken into account using the scaling law found by Hashimoto and co-workers, $L \sim (1/T)^{1/3}$, where L is the lamellar domain periodicity and T is absolute temperature.[19] Taking the domain thicknesses at 30 °C as their initial values and assuming the 30 °C values of refractive indices as fixed, the respective domain spacings at various temperatures can then be calculated. Employing TMM, we then compute the variation of the peak reflectivity position with temperature, shown as the middle curve in Figure 3. (This takes into account both the change in the Flory–Huggins parameter and the thermal expansion of the domain thicknesses.) This is seen as a much stronger effect than the contribution from the change of the refractive indices with temperature. Combining the effects of both the temperature dependence of the respective refractive indices and the temperature dependence of the domain spacings matches the experimental data in Figure 3 very well. Therefore,

Table 1. Determination of the Initial Layer Thickness and Solvent Content by Matching the 30 °C Reflectivity Peak Characteristics through TMM Calculations[a]

w_s (wt %)	$n_{\mathrm{eff,PS}}$	$n_{\mathrm{eff,PI}}$	$d_{\mathrm{eff,PS}}$ (nm)	$d_{\mathrm{eff,PI}}$ (nm)	fwhm (nm)
10	1.580	1.508	90.6	74.1	16.3
20	1.570	1.506	91.0	74.5	15.2
30	1.560	1.504	91.4	74.8	14.9
40	1.550	1.502	91.8	75.1	11.8
50	1.541	1.501	92.2	75.4	11.1

[a] The TMM calculation is quite sensitive to layer orientation with the peak reflectivity shifting to a shorter wavelength range as the lamellar normal tilts away from the film normal (e.g., a 3 nm blue shift for 10° and a 13 nm blue shift for 20°). All of the effective refractive indices ($n_{\mathrm{eff,PS}}$, $n_{\mathrm{eff,PI}}$) and effective domain thicknesses ($d_{\mathrm{eff,PS}}$, $d_{\mathrm{eff,PI}}$) of PS and PI domains at various solvent concentrations (w_s) give a peak wavelength of the corresponding reflectivity spectrum at 510 nm. The 40 wt % sample provides the best match to the peak position and peak width (fwhm).

the observed thermochromism from the self-assembled block copolymer reflector is nicely accounted for as a consequence of both the change of refractive indices and the change of lamellar domain spacing induced by the variation of segregation strength between blocks and thermal expansion of the layers. These thermally responsive tunable self-assembled reflectors can be potentially used for novel sensor and display applications.

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