

One-Dimensionally Periodic Dielectric Reflectors from Self-Assembled Block Copolymer–Homopolymer Blends

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Introduction. The well-ordered structures of block copolymer microdomains formed by self-assembly are potentially interesting optical materials, specifically as photonic crystals. Photonic crystals are structures with a periodic variation of refractive index.^{1–3} For light of the appropriate frequency, such crystals can be used to bend and steer the light, opening up many possible applications such as broad-band low loss waveguides for communication and efficient laser mirrors. The first photonic crystals were made by machining overlapping holes into a slab (millimeter length scales for microwave frequencies).⁴ Current work employs lithographic processing (at the micron and submicron length scale for IR and visible frequencies) to make dielectric structures.⁵ Very recent work has introduced self-assembly as a method to make photonic crystals with periodicities suitable for frequencies in the visible part of the spectrum. Materials used include colloidal crystal arrays,⁶ artificial opals and inverse opals,^{7,8} and hollow spherical micelles.⁹

Block copolymers can self-assemble into a wide variety of periodic structures including 1-, 2-, and 3-dimensional structures.¹⁰ There are several essential challenges to overcome in order to achieve desirable photonic crystal properties employing block copolymers. These include obtaining the correct size of domains for the optical frequencies of interest, attainment of long-range domain order and appropriate orientation, as well as providing sufficient dielectric contrast between the domains. Accessing large periodicities in block copolymers is of course possible using very high molecular weight blocks, but attaining well-ordered structures is difficult due to the very high viscosity of such systems. An alternative approach is to utilize a liquid crystalline block for which the domain thickness varies linearly with block molecular weight. In this way, spacings into the micron range can be produced.¹¹ Another approach is to blend block copolymers with homopolymers and thus swell the microdomains. Block copolymer/homopolymer blends have been investigated both experimentally^{12–14} and theoretically.^{15,16} Such blends offer tailorable domain spacings, as well as the processing advantage afforded by somewhat lower molecular weight components. The dependence of the lamellar repeat in bulk cast blends of homopolystyrene and polystyrene-*b*-polyisoprene block copolymers has been analyzed as a function of the percent homopolymer added and its molecular weight.¹⁴ The lamellar thickness depends on the many factors including homopolymer volume fractions and the block composition and molecular weight.

A regular lamellar morphology having a difference in the index of refraction between the respective domains is similar to a layered optical filter or quarter-wave

stack. In this article we demonstrate that a diblock copolymer/homopolymer blend, which can self-assemble into a lamellar microdomain structure, can exhibit a limited angular range stop band at visible frequencies.

Experimental Procedures. The poly(styrene-*b*-isoprene) (PS/PI) symmetric diblock copolymer employed was PS/PI 137K/137K with a polydispersity index (PDI) of 1.08. PS and PI polymers are highly transparent in the visible with the first strong absorption occurring in the near-IR at about 3 μm . Approximately 50 wt % of the copolymer was blended with 25 wt % of homopolyisoprene (hPI) (PDI = 1.05) and 25 wt % of homopolystyrene (hPS) (PDI = 1.06), each of molecular weight 13K. The ternary blends were cast from toluene, a nonpreferential solvent, and annealed at 180 °C for 1 week in an inert atmosphere to produce films of approximately 0.5 mm thickness and 10 mm diameter. After annealing, optical measurements of film transmission and reflectance properties in the UV, visible, and near-IR spectral ranges were performed on a Cary 5E UV–vis–NIR spectrophotometer equipped with a diffuse reflectance and transmission accessory. This accessory offers nearly 2π steradians solid collection angle for transmitted or reflected light to help compensate for any scattering losses.

After spectral measurements were obtained, we cut ultrathin sections from the films using a Reichert-Jung cryoultramicrotome and stained them with OsO₄ to provide mass thickness contrast of the microdomain structure. Transmission electron micrographs were obtained with JEOL 2000FX. Bright field images were used to determine the spatial characteristics of the morphology and the qualitative degree of domain order in the sample. Small-angle X-ray scattering (SAXS) was used to assess lamellar periodicity, orientation, and long-range order. SAXS was done at the Cornell High Energy Synchrotron Source (CHESS). We employed a sample-to-detector distance of 1.05 m, 1.5 Å radiation, and calibrated *d* spacings with a silver behenate sample.

Results and Discussion. During solvent evaporation the solution first becomes pale green, then bright green-blue, and finally, when dry, predominantly blue pearlescent to an observer viewing it in ambient. When the dry film is held between a white light source and the observer, it appears red/orange. After annealing, the films are somewhat translucent, likely originating from increased scattering due to grain growth. The reflection and transmission spectra of the film are shown in Figure 1a,b. One can clearly identify a band of high reflectivity from about 410–525 nm and a corresponding drop in the transmission characteristics of the film in this same spectral range. Due to the strong absorption of UV radiation by both PS and PI, the transmission is near zero for wavelengths below about 330 nm.

TEM micrographs (Figure 2) of the material revealed a regular symmetric lamellar morphology with a period of about 130 nm. The lamellae are reasonably well ordered and have a dominant in-plane orientation due to the influence of the substrate and air interfaces on the lamellar organization during evaporation.¹³ SAXS with the beam oriented parallel to the sample surfaces produces an arced pattern of two reflections. The spacings of these peaks are approximately 52 and 32

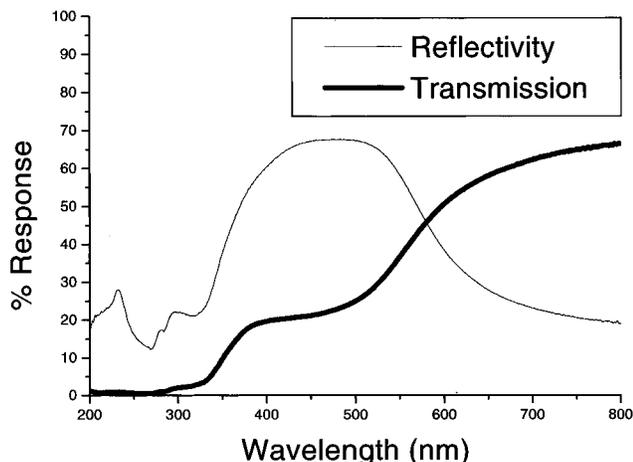


Figure 1. (a) Reflectivity spectrum of lamellar film showing a stop band over the 400–550 nm wavelength range. (b) Transmission spectrum of the same film showing the drop in transmission from the range of 350–550 nm due to the photonic band gap. The film exhibits approximately zero reflection and transmission below 330 nm due to the very strong UV absorption of the polymer.

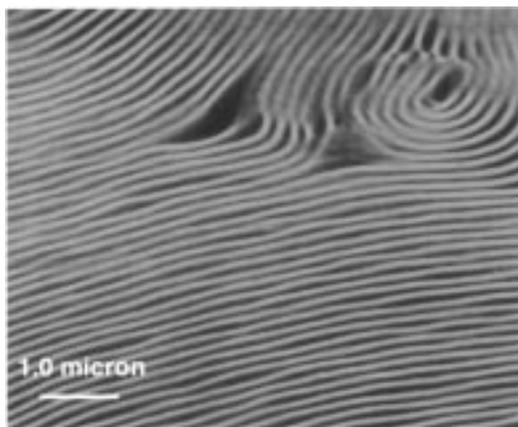


Figure 2. TEM micrograph of a microtomed cross section of the blend film. The isoprene is rendered white in this negative image due to OsO_4 staining. Shown are regions of well-ordered lamellae as well as defects typical of the film.

nm. Since the structure is approximately 46/54 PS:PI in volume, the odd Bragg orders are the strongest reflections. Assuming the 001 spacing is behind the beamstop, the two observed reflections correspond to the 003 and 005 peaks. Thus, the repeat spacing deduced by SAXS of approximately 160 nm is in reasonable agreement with that observed with TEM.

The spectral properties of the film can be understood by consideration of light incident over varying angles onto a system of 1-dimensional dielectric stacks of varying orientation. The lamellar structure and the difference in the layer index of refraction create a photonic crystal similar to multilayer “quarter-wave stack”. For such a structure, the gap for normally incident light would have a midgap wavelength of 4 times the average optical thickness (the domain thickness multiplied by the index of refraction) of a layer and a gap width that depends on the index of refraction contrast of the layers. Since the gap will vary with the angle of the incident light and its polarization, the effective spectral response of the film containing many grains of lamellae will be some superposition of the material's band structure.

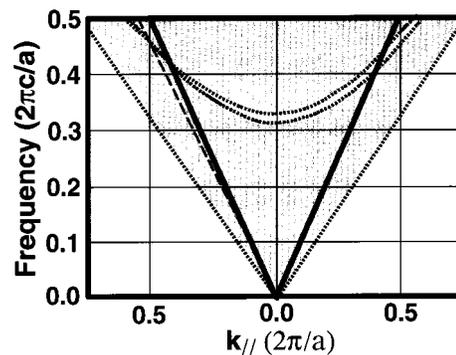


Figure 3. Photonic band structure of a multilayer film having the domain characteristics of the self-assembled polymer film. Shaded areas represent allowed propagation modes. Calculated using the transfer matrix method.¹⁷ The Brewster line is represented by the narrow dashed line originating at $k_{||} = 0$. The light cone is outlined by the thicker lines representing the light line. Band edges are represented by dotted curves. Note: the Brewster's angle is 46.5° .

Figure 3 shows the calculated band structure of a one-dimensional stack of layers using the refractive indices of polystyrene ($n = 1.59$) and polyisoprene ($n = 1.51$) and taking the optical thickness of layers as equal. (The optical thickness of the styrene is actually 1.1 times that of the isoprene in our system, but the effect is minor.) It is important to note that a one-dimensional stack does not possess a complete band gap but a partial gap, the wavelength of which varies with the incident angle of the light and with polarization. The incident light has a wave vector k and frequency $\omega = ck/n_0$ where c is the speed of light in a vacuum and n_0 is the index of refraction of the external medium. The incident wave vector and the normal to the layers allows specification of the two independent electromagnetic modes: transverse electric (TE or s-polarization) and transverse magnetic (TM or p-polarization). The band structure $\omega(k)$ is displayed versus the magnitude of the projected wave vector parallel to the layers $k_{||}$. The horizontal axis is normalized frequency ω in terms of $2\pi c/a$, where a is the lamellar periodicity. Propagating states inside the material (i.e., light of these frequencies is transmitted through the material) are indicated by gray regions while the white region corresponds to evanescent modes which decay exponentially within the material. (The photonic gap lies in the narrow white region in the center of the graph.) The dotted lines bonding the gray and white regions represent the band edges. The heavy straight lines represent the light line and delineate the extent of the light cone, the range of phase space accessible to light entering the material from an external homogeneous medium (i.e., air). Light incident at 90° to the film normal lies on the light line given by $\omega = ck_{||}/n_0$. The effect of this partial band gap would be the rejection by reflection of light with wavelengths and k vectors located in the gap region and transmission of light with wavelengths and k vectors outside of the gap. The wavelengths rejected shift to shorter values with increasing angle of incidence.

For the relatively small index difference in our self-assembled lamellar structure ($\Delta n = 0.08$), the gap is relatively narrow. At normal incidence ($k_{||} = 0$) the gap width to midgap frequency ratio is approximately 0.05. The midgap wavelength for light at normal incidence to the film calculated for a repeat period a of 160 nm is approximately 500 nm and the bandwidth only 25 nm.

Experimentally we observe a broad-band region of enhanced reflectivity between 410 and 525 nm. Our optical spectrum is primarily due to the polycrystalline nature of the lamellar morphology in our film. Light at normal incidence to the film encounters grains of lamellae at orientations departing significantly from normalcy and also of slightly varying lamellar thickness. Thus, the bulk film optical properties are those resulting from a superposition of photonic microcrystals with properties similar to those calculated above. The reflectivity region of our material should show a marked broadening, specifically toward shorter wavelengths. This superposition is also reflected in the bulk film optical spectrum as a lowered rejection efficiency of frequencies in the band gap and a softening of the band edges.

Summary. We have shown that by suitable blending of homopolymers with a diblock copolymer a self-assembled lamellar structure can be obtained in which the homopolymers swell the repeat spacing into the regime appropriate for visible photonic applications. Thus, block copolymer blends show potential as low-cost optical materials in the visible. Enhancement of the dielectric contrast between the domains can dramatically increase the potential applications. For example, 1D omnidirectional dielectric reflectors that reflect both s- and p-polarized light for all incident angles may be realized using high index of refraction additives that are selectively sequestered into one of the domains. Work along these lines is underway.¹⁸⁻²⁰

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