Tunable Block Copolymer/Homopolymer Photonic Crystals[**]

By *Augustine Urbas*, *Rachel Sharp*, *Yoel Fink*,
Edwin L. Thomas,* *Maria Xenidou*, and *Lewis J. Fetters*

Interest in the photonic properties of dielectrically structured materials is growing rapidly. This is fueled by the potential application of such materials in a broad range of fields. Much recent work has focused on lithographically fabricated photonic materials,[1,2] and on self-assembled colloidal crystals[3,4] and inverse opal structures.[5–7] The former need to be fabricated on small-area flat surfaces, the latter tend to have long timescales inherent in the fabrication and both have limited tunability with respect to the precursor materials. Our recent work[8,9] has shown that self-assembled block copolymer systems can exhibit a one-dimensionally periodic lamellar structure with component domains having widths large enough ($\lambda/4n$) to act as visible light photonic materials. Their use in photonics would bring many advantages in terms of materials properties, processability, as well as cost, and would enable the fabrication of large-area conformable photonic materials. In this communication we show that multilayer photonic crystals active within a broad range of wavelengths in the visible spectrum can easily be produced from a simple system comprised of a block copolymer and two homopolymers.

Ternary blends of a poly(styrene-*b*-isoprene) (S/I) diblock copolymer, polystyrene, and polyisoprene were solution cast from cumene. As the samples begin to dry they selectively reflect light, giving the appearance of green or red color. After drying, each sample showed a single well-defined peak in reflectivity in the visible wavelength range (350–600 nm) and a corresponding drop in the transmission profile. This implies that the reflection was fairly efficient and that the color observed in the samples was not due to significant absorption. In Figure 1a, we show typical reflectivity curves for several blend samples. The relative width of the reflectivity peaks (or transmission dips), $\Delta\lambda/\lambda$, varies approximately from 0.15 to 0.25, widening as the fraction of homopolymer in the blend increases. The wavelength of the reflectivity peak versus the homopolymer composition is plotted in Figure 1b. There is a monotonic increase in the peak reflective wavelength with the fraction of homopolymer.

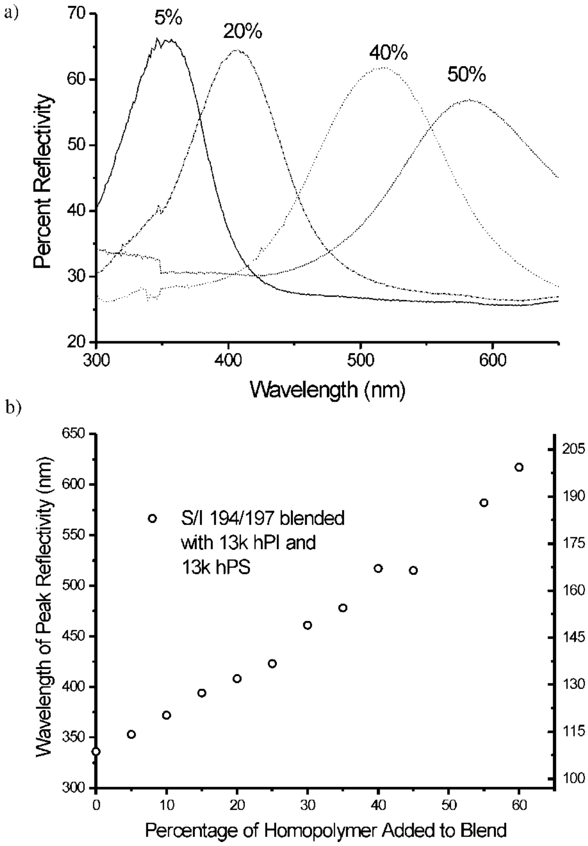

Fig. 1. a) Reflectivity of samples containing 5 %, 20 %, 40 %, and 50 % total added homopolymer. The progression to longer wavelengths and broader peaks with increasing homopolymer content is evident. b) Wavelength of peak reflectivity vs. homopolymer weight fraction. The right axis is the lamellar spacing inferred from the peak reflectivity wavelength.

Scanning electron microscopy (SEM) of the samples confirmed that a lamellar morphology was present in the samples, with typical grain sizes of the order of several micrometers. The backscattered electron imaging (BEI) image of a sample containing 40 % homopolymer is shown in Figure 2a. The bright regions correspond to the OsO_4 stained polyisoprene domains and the dark regions are the unstained polystyrene. The lamellar repeat from the micrograph is about 140 nm, although the dimensions of structures in the micrograph will depend on the angle of the fracture plane relative to the lamellar normal, and expansion/shrinkage due to electron beam damage and OsO_4 staining. The layers appear approximately symmetric in thickness. The lamellae have a tendency to orient in-plane. The homopolymers can be seen concentrating at defects in the lamellar structure (in arrowed regions of Fig. 2a).

The ultra-small angle X-ray scattering (USAXS) data for samples containing 20 % and 40 % homopolymer are presented in Figure 2b. The higher order scattering peaks fall at integer multiples of the first-order peak, implying that

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[*] Prof. E. L. Thomas, A. Urbas, R. Sharp, Prof. Y. Fink
Department of Materials Science and Engineering, MIT
Cambridge, MA 02139 (USA)
Dr. M. Xenidou, Dr. L. J. Fetters
ExxonMobil Research Corp.
Annandale, NJ 08801 (USA)

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the morphology is indeed lamellar. The relative weakness of the even order peaks indicates that the thickness of the styrene and isoprene lamella are approximately equal. Detailed comparison of the intensity with model calculations of peak intensities of a lamellar structure suggests that the layers are 0.52L and 0.48L thick, where L is the lamellar thickness.[10]

The blend films are self-organized photonic crystals. The alternating regions of styrene and isoprene create a periodic dielectric structure. The structure possesses a stop band for certain electromagnetic modes. These modes are rejected when incident on the surface of the material. We observe this as a reflection of these selected modes that imparts the appearance of color to the samples.

The properties of a photonic crystal can be derived from Maxwell's equations. A compact and analytical formalism for the 1D periodic multilayer dielectric film was derived by Yeh et al.[11] This method allows us to create a band diagram for our system. A band diagram is a map of all optical modes in the material, and displays information on whether a mode is allowed to propagate or if it is evanescent, i.e., the mode decays exponentially within the material. We note that the lamellar stack is translationally symmetric in the x–y plane and periodic in the z direction. Thus an incident wave with frequency, ω, and wave vector, $\boldsymbol{k}$, can be described relative to the periodic film simply by decomposing the wave vector into its components parallel and perpendicular to the surface, $\boldsymbol{k} = k_{\parallel} + k_z$. Since $\omega = ck/n$, we need only specify the frequency, $k_{\parallel}$, and polarization in order to specify a mode. There are two unique polarizations, transverse electric (TE) and transverse magnetic (TM). An incident wave is TM polarized if the magnetic field is parallel to the surface and TE polarized if the electric field is. The band diagram is plotted such that one half represents TE and one half represents TM modes. The band diagram is normalized in terms of the lamellar thickness, L. In Figure 3, we show the band diagram for the styrene/isoprene system where the optical path lengths are equal (i.e., $n_{\mathrm{ps}} \times l_{\mathrm{ps}} = n_{\mathrm{pi}} \times l_{\mathrm{pi}}$) using refractive indices for polystyrene and polyisoprene of $n_{\mathrm{ps}} = 1.59$ and $n_{\mathrm{pi}} = 1.51$, respectively. Note that since the styrene layer thickness is approximately 0.48 of the lamellar repeat, the equal optical path condition is closely met. Features in the plot to note are the gray shaded areas where modes are allowed to propagate and the white areas

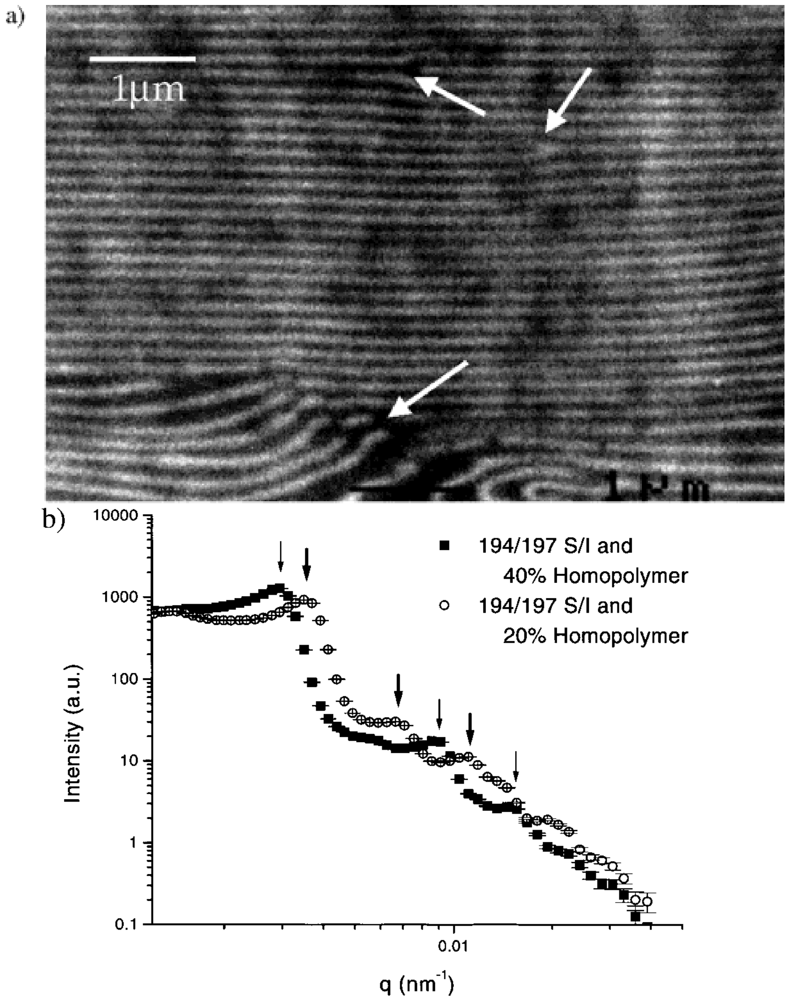

Fig. 2. a) BEI image of a fracture surface of a block copolymer/40 % homopolymer blend film. White areas are polyisoprene stained with OsO$_4$ and dark areas are polystyrene. Arrows indicate defects where the homopolymer tends to concentrate. b) USAXS data from samples containing 20 % and 40 % homo-

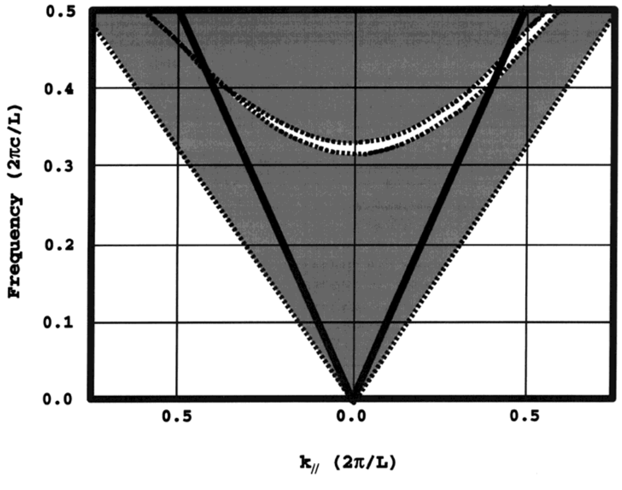

Fig. 3. Band diagram for equal optical thickness polystyrene and polyisoprene layers. Shaded areas represent allowed propagation modes. The light cone is outlined by the thicker lines representing the light line. Band edges are represented by dotted curves.

where they are evanescent, especially the narrow white band centered in the graph. This is what gives rise to reflection in our samples, since modes in this region cannot propagate within the material and are reflected.

SEM images show that the lamellae in our system preferentially orient parallel to the surfaces of the film. If we then consider that these grains of lamellae with their layer normal parallel to the incident light will present more area from which to reflect, we reason that the wavelength of peak reflectivity is approximately the same as the midgap wavelength at normal incidence. Thus we can use this single plot to interpret the normal incidence reflective behavior of all of our samples and infer the lamellar spacing from our reflectivity data (shown on the right axis of Fig. 1b). This allows us to simply express the lamellar spacing in terms of the wavelength of peak reflectance, λ_p. The lamellar spacing of a sample is thus given by $L = \lambda_p/(n_{ps} + n_{pi})$.

We have shown that photonic crystals spanning the visible spectrum can be easily fabricated from a ternary blend of a diblock copolymer and two homopolymers. We were able to fabricate films with reflective bands of $\Delta\lambda/\lambda = 0.15$–$0.25$ with a peak reflective wavelength tunable over a range of $\lambda = 350$–600 nm. These films had peak reflectivities in the range of 60–70 %. This simple method demonstrates the ease with which large-area, tunable, highly reflective, flexible films can be fabricated from block copolymer–based materials.

Experimental

A near symmetric S/I diblock copolymer with a total molecular weight of 391 kg/mol and a polydispersity index (PDI) of 1.02 as determined by size exclusion chromatography (SEC) was synthesized by anionic polymerization in benzene at 25 °C. The styrene block had a molecular weight of approximately 194 kg/mol and the isoprene block had a molecular weight of approximately 197 kg/mol. The homopolymers used were a polystyrene (hPS) with a molecular weight of 13 kg/mol and PDI = 1.04 obtained from Polysciences and a polyisoprene (hPI) with a molecular weight of 13 kg/mol and PDI = 1.06 obtained from the Pressure Chemical Company.

The blends were made by mixing together calculated amounts of stock solutions of 100 mg/mL polymer in cumene. The stock solutions were prepared from the diblock copolymer and each homopolymer. We mixed blends containing 100 % to 40 % diblock copolymer at 5 % increments, with the remainder composed of equal fractions of the two homopolymers (i.e., samples contained 0–60 % total homopolymer). About 0.25 mL of the resulting blended solution was dispensed onto one side of a glass cover slip 25 mm in diameter. The solution-coated disks were placed in a cumene-rich atmosphere for one week. Samples can also be made by rapidly drying them in about 10 min, yielding approximately the same optical characteristics. The resulting films of polymer blend on glass were then further dried in ambient conditions for three days, yielding a film of approximately 20–50 µm thickness.

Spectral measurements were then performed on each disk. These consist of transmission measurements at normal incidence and diffuse reflectance measurements taken with a Cary 5E spectrophotometer equipped with a diffuse reflectance accessory (DRA). We collected reflectance data from the air side of the polymer film in order to eliminate reflection from the air–glass interface. Typical reflectivities were 60–70 % measured relative to a diffuse reflective Halon standard (aggregated microparticulate PTFE), which has greater than 97 % reflectance over the range of wavelengths of interest to us in this paper. Scattering from the textured uppermost surface of the polymer film surface should not interfere with the measurements since the collection angle of the DRA is nearly 2π steradians.

SEM was used in order to verify the lamellar morphology and to qualitatively examine the orientation of the lamellae. These samples were cooled in liquid nitrogen and then fractured. The fracture surface was exposed to OsO_4 for 15 min and then coated with carbon by thermal evaporation. Samples were imaged in a JEOL 6320 FESEM using the backscattered (BEI) electron detector. Domain contrast was obtained by the selective staining of the isoprene layers by OsO_4, which, due to its high atomic number, gives increased backscattered electron yields.

Several bulk films, (1 mm thickness) prepared in the same way as the samples above, were analyzed using USAXS. This technique gives a more accurate measurement of the lamellar spacing than SEM, and allows a comparison with the lamellar repeat determined from the reflectivity data. The USAXS measurements were performed at the advanced photon source (APS) on the UNICAT beamline 33-ID at the Argonne National Laboratory.

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Structural Stabilization of New Compounds: MoS_2 and WS_2 Micro- and Nanotubes Alloyed with Gold and Silver[**]

By *Maja Remškar*,[*] *Zora Škraba*, *Pierre Stadelmann*, and *Francis Lévy*

Inorganic micro- and nanotubes have been synthesized. Their unusual crystal forms and typical physical and chemical properties are the subjects of much study. Two techniques were successfully used for growing MoS_2 and WS_2 tubular crystals. These fullerene-like structures and nanotubes, a few micrometers in length, have been grown by annealing oxidized transition metal films in a stream of H_2S gas.[1–5] Microtubes, nanotubes, and nanoropes a few millimeters in length, have been synthesized by chemical transport reactions.[6–10]

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[*] Dr. M. Remškar, Z. Škraba
J. Stefan Institute, Solid-State Physics Department
Jamova 39, SI-1000 Ljubljana (Slovenia)

Prof. P. Stadelmann
Centre de microscopie électronique-CIME
Ecole Polytechnique Fédérale de Lausanne
CH-1015 Lausanne (Switzerland)

Prof. F. Lévy
Institute of Applied Physics
Ecole Polytechnique Fédérale de Lausanne
CH-1015 Lausanne (Switzerland)

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