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Two-dimensional block copolymer photonic crystals

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Abstract

A high molecular weight polystyrene-block-polyisoprene copolymer was synthesized by anionic polymerization of styrene and isoprene monomers. Polystyrene cylindrical domains in a hexagonal lattice with relatively large periodicity and controlled orientation have been produced through roll casting of the polystyrene-block-polyisoprene copolymer with a total molecular weight of 1.0×10^6 g/mol. The large periodicity and effective processing lead to reflectivity of about 70% in the visible regime, and generate a two-dimensional photonic crystal with a partial band gap.

Keywords: Block copolymer; Photonic crystal; Roll casting

This communication reports a two-dimensional photonic crystal structure based on cylindrical microdomain-forming high molecular weight block copolymers. Our group has previously demonstrated one- and three-dimensional photonic crystal structures based on self-assembly of block copolymers [1–3]. The successful demonstration of two-dimensional block copolymer-based photonic crystal structures expands this block copolymer approach. The system reported in this paper also shows the potential for further development in this area.

Light is an effective medium for communicating, computing, and information storage [4]. The generation and manipulation of light requires the construction and engineering of active and passive light-interactive structures. Photonic crystals have been emerging as vital structures in manipulating light [5], in an analogous way as the manipulation of electrons by semiconducting crystals. The concept of photonic crystals was proposed independently by Yablonovitch [6] and John [7]. There have been many approaches for fabricating photonic crystal structures since Yablonovitch built the first photonic crystal structure (operating in the microwave regime) using machining [8]. Generally fabrication approaches fall into two categories: one is based on top-down processes, such as lithography [9], holography [10], and microassembly [11]. The other one is the bottom-up self-assembly approach [1,12,13]. So far the self-assembly approach that was reported the most is that of colloid assembly [12,13], in which photonic crystal structures, predominantly face center cubic structures, form by spontaneous assembly of uniform diameter microspheres.

Another system capable of self-assembly into photonic crystal structures is that of block copolymers, wherein microphase separation creates one-, two-, and three-dimensional periodic microdomain structures [1,14]. Block copolymers consist of two or more chemically distinct blocks. The interaction between the blocks is characterized by the Flory–Higgins segment–segment interaction parameter, χ_{AB}. In simple linear diblock copolymers, microphase separation depends on the product of χ_{AB} and the total number of segments $N_A + N_B$. Typically χ varies inversely with temperature, so cooling a block copolymer from the homogeneous high temperature melt results in microphase separation. For the very high molecular weight block copolymers of interest for photonic applications, however, access to the homogeneous melt is not possible due to thermal degradation well before reaching the order–disorder temperature. Another strategy is to lower χ_{AB} via solvent screening. Thus as the solvent evaporates, the respective blocks can form microdomains above the order–disorder concentration. Depending on the

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composition of block copolymers, microphase-separated block copolymers can form numerous morphologies. For example, the simplest linear AB diblock copolymers have sphere, cylinder, double gyroid, and lamella morphologies. More complex block copolymers, e.g. miktoarm star terpolymers, show many other morphologies [15]. By employing high molecular weight copolymers as well as by blending nonvolatile solvents or homopolymers, the periodicity of the structures can be tuned over length scales that enable them to interact with visible light [2,14]. Block copolymers are also able to incorporate both passive (e.g. TiO_2) and active (e.g. dyes, quantum dots) additives, which greatly broaden their potential applications as passive and active photonic devices in the visible and near IR regimes.

The successful formation of one- and three-dimensional photonic crystals based on self assembled lamellar and double gyroid morphologies has been demonstrated [1–3]. In two-dimension, a periodic array of parallel, infinitely long, dielectric cylinders could work as a two-dimensional photonic crystal structure. This structure will prohibit the propagation of incident light in a direction perpendicular to the cylinder axis for a limited range of frequencies. Linear AB diblock copolymers can self-assemble into the cylindrical structure for minority component volume fractions between approximately 13–30%. The cylinder radius to cylinder spacing (r/a) ratio is therefore tunable from 0.19 to 0.29 in a pure diblock copolymer and may be further varied by adding homopolymer. A cylindrical block copolymer system, which possesses large periodicity, strong dielectric contrast, and long-range order, will be an excellent candidate for two-dimensional photonic crystals, with the advantages of simple processing and possible large scale manufacturing from inexpensive resources.

In the present work, we construct a two-dimensional photonic crystal structure based on cylindrical microdomain morphology. A dielectric structure with large periodicity and controlled orientation was produced through roll casting of a high molecular weight polystyrene-block-polyisoprene (PS-b-PI, 320/680 kg/mol) diblock copolymer. In this case, the self-assembly process takes place in an evaporating solution undergoing orientation along the flow field. The roll-cast film consists of cylindrical polystyrene microdomains and was characterized optically.

The high molecular weight PS-b-PI copolymer was synthesized by anionic polymerization [16] of styrene and isoprene monomers at room temperature for 48 h in cyclohexane and benzene. The initiator was *sec*-butyllithium in hexane solution. The molecular weight was calculated using gel permeation chromatography of the styrene precursor polymer in combination with ^1H nuclear magnetic resonance spectroscopy. The molecular weight of PS-b-PI is $M_n = 1.0 \times 10^6$ g/mol and the polydispersity is $M_w/M_n = 1.08$. The polyisoprene block is predominately (95%) 1, 2 units. The reaction proceeded at room temperature and at large scale (10–40 g).

Fig. 1 shows the apparatus for roll casting block

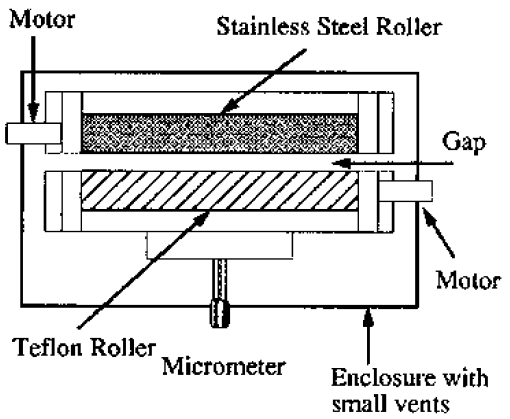
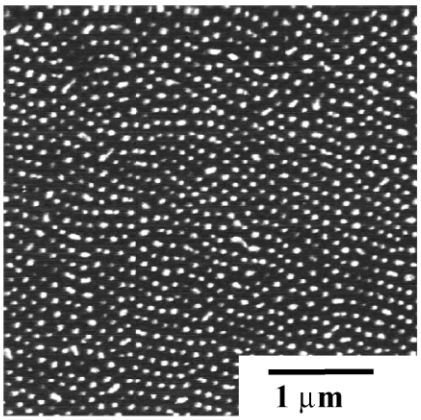


Fig. 1. Set up of the rollers for roll casting of block copolymers.

copolymers [17]. There are two rollers in the setup: one is steel and the other is Teflon. Two motors attached to the rollers counter rotate the two rollers at desired speed. A micrometer controls the precise gap between the two rollers

(a)



(b)

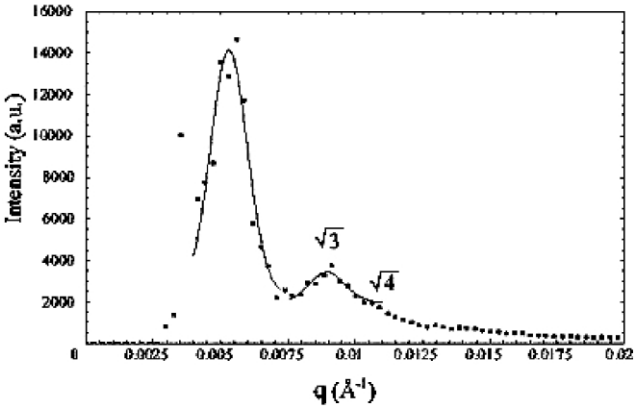


Fig. 2. (a) Cross section AFM phase image of the polystyrene microdomains viewed parallel to the cylinder axis. The cylinders of polystyrene have higher modulus than polyisoprene matrix and are shown as white spots in the image. (b) Small angle X-ray scattering of the PS-b-PI block copolymer.

(a)

(b)

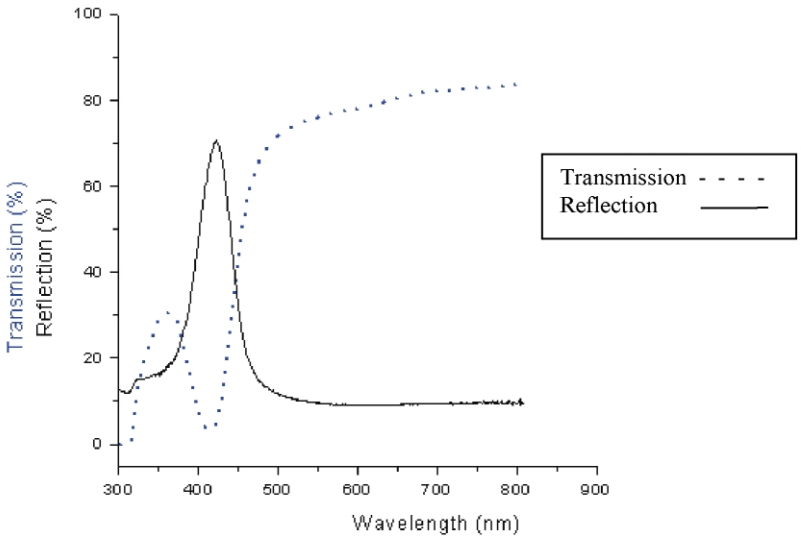


Fig. 3. (a) Optical micrograph of a roll-cast 320/680 PS-b-PI diblock copolymer film on the steel roller (with residual cumene ~10% w/w). Ambient light that was reflected off the film generated the blue color. The white roller in the foreground is the Teflon roller. (b) Transmission (dot curve) and reflectance (solid curve) spectra of the roll cast film measured with normal incident unpolarized light. Reflectance spectrum shows a strong reflectance over the wavelength range of 390–440 nm. The film showed almost zero transmission at the wavelength of maximum reflectance.

and thus the thickness of the film. A solution of the block copolymer is placed between the gap before roll casting. During roll casting, solvent slowly evaporates and the block copolymer undergoes microphase separation. The initial solution is ~5% (w/v) PS-b-PI diblock copolymer dissolved in cumene.

The sample morphology was imaged with an atomic force microscope (AFM, Digital Instruments Nanoscope III) in tapping mode. Silicon cantilevers oscillating at a frequency in the range of 40–90 KHz were used in the characterization. The AFM image (Fig. 2(a)) shows a cross section of the film exhibiting the two-dimensional ordering of the polystyrene cylinders. This image allows estimation of the lattice dimension and the diameter of the polystyrene domains. The polystyrene domains have an average diameter of ~40 nm and the intercylinder spacing is ~120 nm.

Small-angle X-ray scattering (SAXS) was performed on beamline X-12B at the National Synchrotron Light Source in the Brookhaven National Laboratory. Fig. 2(b) shows SAXS data of a roll-cast sample viewed in a direction at a slight angle from the cylinder axis. The 1D intensity profile was obtained by a partial azimuthal integration of the 2D pattern. The ratio of the second peak position compared to the first is ~1.69, which agrees favorably with the expected 1.73 (sqrt(3)) for hexagonal packing of cylinders. The first peak at a spacing of ~116 nm can be assigned as the lowest order d_{1010} peak. The intercylinder spacing is thus calculated to be 134 nm.

Fig. 3(a) and (b) show an optical micrograph of the film

after roll casting and the transmission and reflection spectra of the film with residual cumene (~10% w/w). The aligned cylinders on the hexagon lattice give the reflected bright blue color. The blue region of the film occurs where the light is reflected at near normal incidence, whereas the film appears transparent for tilted illumination, consistent with the blue shift in reflectivity predicted from the band diagram in Fig. 4. Transmission and reflectance properties of the film were characterized on a Cary 5E spectrophotometer equipped with a diffuse reflectance and transmission accessory. This accessory offers nearly 2π steradians solid collection angle for transmitted or reflected light to compensate for any scattering losses. The reflection and transmission spectra of the roll cast film were shown in Fig. 3(b). Absorption of light by both polystyrene and polyisoprene occurs below 400 nm, and accounts for the low values of both reflectivity and transmission in this region of the spectrum. A band of high reflectivity (max. ~70%) in the range of 390–440 nm and a corresponding drop in the transmission of the film in this same spectral range indicate that the two dimensional periodic structure is acting as a photonic crystal.

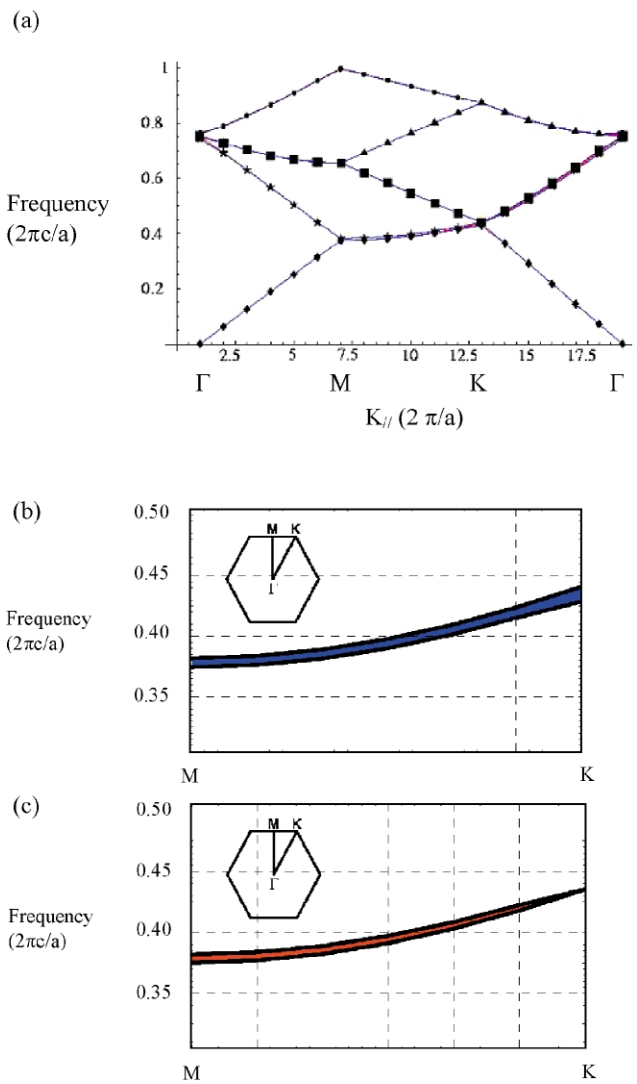


Fig. 4. (a) The calculated photonic band structure of two-dimensional hexagonally packed structure, using the high molecular weight PS-PI diblock copolymer as a model. The incident light has a wave vector k and frequency ω. The frequency is $2\pi c/a$, in which c is the speed of light and a is the intercylinder spacing. (b) The shaded area represents the band gap in TM mode. (c) The shaded area represents the band gap in TE mode.

Fig. 4 shows the calculated band structure of a two-dimensional photonic crystal using the high molecular weight PS-PI system as a model. The refractive index of rods is taken as that of polystyrene ($n = 1.59$) and that of the matrix as polyisoprene ($n = 1.51$). The r/a ratio, which indicates the ratio of the rod radius and the lattice constant, is calculated to be 0.29 for the 320/680 kg/mol PS-PI diblock copolymer. In two-dimensional structures, modes are classified into two distinct polarizations; either the TM mode (Fig. 4(b)) with electric field along the axis of rods or the TE mode (Fig. 4(c)) with magnetic field along the axis of rods. The incident light has wave vector k and frequency ω. It is important to note that this low index contrast two-dimensional system does not possess a complete band gap but a partial band gap, the middle-gap wavelength of which varies with the incident angle of the light and with polarization. For the relatively small index difference in our self-assembled cylindrical structure ($\Delta n < 0.08$), the partial gap is relatively narrow. Taking the average frequency of the reflected light as 0.4 (Fig. 4), and the wavelength at maximum reflection (λ_{max}) as 415 nm (Fig. 3), the intercylinder spacing can be calculated as 166 nm, larger than the value obtained from SAXS measurement (134 nm). Swelling by residual cumene, the red shift of λ_{max} due to the absorption of polystyrene and polyisoprene below 400 nm, and also the less than perfect ordering of the polystyrene cylinders in the real samples likely account for the difference between these two values.

The small intrinsic dielectric contrast between typical block copolymer microdomains precludes the formation of large photonic band gaps in such materials [1–3,14]. Increasing the dielectric contrast between domains in block copolymers offers the ability to further tailor the optical properties. There are several methods for enhancing dielectric contrast in block copolymers: (1) sequestration of semiconductor nanocrystals. For example, we have sequestered 4 nm diameter CdSe particles of high refractive index into a poly(styrene/isoprene/2-vinyl pyridine) triblock terpolymer using amine terminated polystyrene oligomers attached to the CdSe surface [1]; (2) in situ growth of nanocrystals in heteropolymer domains; (3) removal of one set of domains [18]; (4) filling the empty regions with high dielectric. The etching out of the cylinder phase enhances the dielectric contrast, which in turn leads to larger photonic band gaps. The complete band gap for both TE and TM polarization requires a minimum dielectric contrast of 7.2 [19–21]. Construction of a self-assembled complete band

gap in our two-dimensional block copolymer system is being pursued.

Conclusions

A high molecular weight diblock copolymer was self assembled into an oriented hexagonally packed cylindrical morphology. The large periodicity and the difference in the index of refraction in the two microphases create a 2D dielectric photonic crystal structure with a partial band gap. The sample reflectivity was measured perpendicular to the cylinder axis and showed a reflection peak centered around 415 nm. This proof-of-concept system demonstrates that block copolymers with rather large molecular weight (in the present case, 1×10^6 g/mol) can form two-dimension self-assembled optical structures for the construction of light-weight and flexible photonic devices and systems.

Acknowledgements

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