Block Copolymers as Photonic Bandgap Materials

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Abstract — Block copolymers self-assemble into one-, two-, and three-dimensional periodic equilibrium structures, which can exhibit photonic bandgaps. This paper outlines a methodology for producing photonic crystals at optical length scales from block copolymers. Techniques for enhancing the intrinsic dielectric contrast between the block copolymer domains, as well as increasing the characteristic microdomain distances, and controlling defects are presented. To demonstrate the applicability of this methodology, a self-assembled one-dimensional periodic structure has been fabricated that reflects visible light. The wealth of structures into which block copolymers can assemble and the multiple degrees of freedom that can be built into these materials on the molecular level offer a large parameter space for tailoring new types of photonic crystals at optical length scales.

Index Terms — Block copolymers, confinement of light, defects, enhanced refractive index, localization of light, mesoscopic, nanocrystals, optical components, one-, two-, and three-dimensional photonic bandgaps, photonic crystals, polymer blends, polymers, reflectors, self-assembling.

I. INTRODUCTION

The simplest A/B diblock copolymers self-assemble into equilibrium phases consisting of alternating layers, complex topologically connected cubics, cylinders on hexagonal lattices, and spheres on a body centered lattice. By controlling the composition and architecture of block copolymer macromolecules, a rich repertoire of one-, two-, and three-dimensional periodic dielectric structures can be accessed, many of which exhibit topologically connected features. These materials self-assemble into periodic dielectric structures typically on mesoscopic length scales (10–100 nm) depending on the overall molecular weight.

The small intrinsic dielectric contrast between typical block copolymer microdomains precludes the formation of large photonic bandgaps in such materials. The periodic structure gives rise to small photonic gaps around the edges of the Brillouin zone. To induce overlapping of the photonic bandgaps, one needs to significantly enhance the dielectric contrast between the microdomains. In this paper, we present the concept of using block copolymers as photonic bandgap materials as well as discuss the methods that are needed to achieve desirable optical properties.

II. SELF-ASSEMBLED BLOCK COPOLYMER STRUCTURES

Block copolymers (BCP’s) consist of chemically different macromolecules, or blocks, joined at their endpoints to form a chain. Due to the positive free energy of mixing of the A and B species, the respective blocks tend to segregate. Being restricted by their connectivity, block copolymers microphase separate into microdomains that are on the length-scales of the respective blocks. Fig. 1(a) depicts an A/B diblock copolymer, which has microphase separated into a layered structure. Each layer is composed of a different block. The interface between the layers is called the intermaterial dividing surface (IMDS) and is the location of the junctions that connect the different blocks.

The morphology diagram for a linear A/B diblock copolymer is presented in Fig. 1(b). The regimes of the different phases are mapped as a function of the volume fraction of the two blocks — and the product of the segment–segment interaction parameter and the total number of segments . At a given value of , as the volume fraction is changed, various periodic structures are encountered: spheres on a body centered cubic lattice, hexagonally packed cylinders, double gyroid cubic, and lamellae. A graphic rendering of the different equilibrium phases at increasing volume fraction of the minority component is presented in Fig. 1(c). Many block copolymer systems with additional structural degrees of freedom have been produced by adding more blocks, by choosing different chemical monomers, and by varying the architecture of the chain; e.g., connecting a number of blocks at a single junction to form a star molecule. For example, an ABC terpolymer can have three chemically distinct blocks connected in a linear fashion with two junctions per molecule or have the three blocks connected at a single junction resulting in a mixed arm star polymer. A wealth of two- and three-dimensional periodic structures are thus produced. One particularly striking example is the “knitting pattern” , which forms from a linear ABC tercopolymer composed of polystyrene-poly(ethylene-co-butylene) and polymethylmethacrylate with 0.35 : 0.27 : 0.38 volume fractions. A micrograph as well as a graphic rendering of the structure are presented in Fig. 2. The “knitting pattern” structure is two-dimensional (2-D) periodic and corresponds to the c2mm plane group.
Fig. 1. (a) Schematic of a diblock copolymer microphase separated into a lamellar structure. Block A has $N_A$ connected repeat units of type A, while block B has $N_B$ repeat units of type B. The two blocks are covalently connected at point c. The locus of the junction points is called the intermaterial dividing surface. On the bottom is the chemical structure of the junction region for a styrene isoprene diblock. (b) Experimental morphology diagram depicting the periodic microphases observed in the polystyrene-polydiene (PS-PD) diblock copolymer systems disordered homogeneous (x), BCC spheres (o), hexagonally packed cylinders (\(\triangle\)), double gyroid (\(\square\)), and lamellae (\(\square\)). The PS phase appears light, and the PD phase appears dark due to staining with OsO$_4$. \(\chi_{AB}N_{AB}\) is the Flory–Huggins parameter—\(N_{AB} = (N_A + N_B)\)—number of statistical segments in the copolymer [20]. (c) Graphic rendering of the equilibrium phases in linear diblock copolymer at increasing volume fraction of minority phase.

III. BANDGAPS IN ONE-, TWO-, AND THREE-DIMENSIONAL BLOCK COPOLYMER MESOCRYSTALS

An analysis of the band structures corresponding to the self-assembled BCP morphologies shows that plurally directional photonic bandgaps exist in these structures. Because of the low inherent dielectric contrast that exists in BCP systems, the gaps are nonoverlapping. An example of the nonoverlapping nature of the bandgaps is presented in Fig. 3. This figure represents the band structure for the two independent polarizations, TM and TE, for a layered system with equal optical thicknesses of each domain projected onto the invariant component of the wave vector—\(k_\parallel\). The values of the refractive indexes are 1.59 and 1.51 corresponding to the polystyrene (PS) and polyisoprene (PI). The gray regions correspond to propagating states, while the white regions are evanescent. This structure has small nonoverlapping gaps that vary considerably as a function of \(k_\parallel\). For waves propagating in the normal direction (i.e., \(k_\parallel = 0\)), one can identify a gap that shifts to higher frequencies as \(k_\parallel\) increases. To increase the overlap between the gaps for this simple system, one needs to increase the dielectric contrast between the layers. In fact, as was recently demonstrated [2], an overlapping band can exist that reaches the light line—thus forming an omnidirectional reflector.

The large number of block compositions and block arrangements leads to a wealth of periodic morphologies. These in turn can provide a materials template for novel and yet unobserved photonic bandgap structures. Providing that the index contrast is enhanced above the characteristic values that exist in block copolymers, one can in fact obtain complete photonic bandgaps in two and three dimensions. For example, the hexagonally packed cylinder structure will exhibit a complete gap in the plane providing that the contrast between the matrix and cylinders is relatively high.
IV. THE CHALLENGES FOR BLOCK COPOLYMER-BASED PHOTONIC BANDGAP MATERIALS AND HOW TO ADDRESS THEM

BCP mesocrystals need to be modified to achieve a substantial overlap in the photonic bandgap. To this end, the following issues need to be addressed. First, the intrinsic dielectric contrast between the phases in virtually all BCP systems is small, typically on the order of 1.1 (e.g., styrene/isoprene 2.5281/2.2801). This contrast is sufficient only for narrow-band openings near the edges of the Brillouin zone. In order to achieve larger gaps, one needs to enhance the dielectric contrast, which can be done in a variety of ways. For example, it is possible to preferentially sequester optically transparent nanocrystals [3] of one or more high dielectric constant materials into one or more of the block copolymer microdomains [4]. The nanocrystals are tailored to have a strong affinity to one of the phases. This can be achieved, for example, by grafting a surfactant molecule, which has a chemical structure similar to that of the target phase, onto the surface of the nanocrystal. The BCP PBG material is then produced by adding the surfactant nanocrystals to a solution of the block copolymer whereupon removal of the solvent they sequester into the targeted microdomains. The result is a substantial increase in the dielectric constant of that microphase.

Fig. 4 is a bright field transmission electron microscope (TEM) image of a layered self-assembled dielectric lattice
made by selective addition of high-index CdSe nanocrystals to the 2-vinyl pyridine (2VP) microdomains of a poly(styrene/isoprene/2VP) triblock copolymer. The contrast in this figure is due to the sequestration of the nanocrystals into the 2VP phase. A solution of CdSe nanocrystals in THF was prepared, then the triblock copolymer was added and the solution was roll cast [5] to form a highly oriented dielectric lattice. Another possible approach to enhance the dielectric contrast involves the selective etching by ozonolysis of one of the microphases.

Fig. 5 shows a bright field TEM image of poly(pentamethyldisilylet:yrene)-b-polysoprene, which forms the double gyroid morphology in the bulk. The sample was cast from toluene, annealed at 120 °C for two weeks, cryomicrotomed, and the polyisoprene preferentially stained with osmium tetroxide. As shown in Fig. 5(a), the PI channels appear dark in a matrix of P(PMDSS). An unstained microtomed section was also exposed to an atmosphere of 2 wt% ozone in oxygen for 45 min and then soaked in deionized water for 12 h. As seen in Fig. 5(b), the PI has been preferentially removed, leaving behind air channels, which results in the inversion of the image contrast as compared to Fig. 5(a). In addition, upon exposure to oxidation, PMDSS converts to silicon oxycarbide. The contrast in the micrograph is due entirely to the difference in electron density between the air and ceramic phases. The dielectric contrast in this material is approximately four [6]. The air channels could also be backfilled with a high-index material (such as tetrapproxy titane, a TiO₂ precursor) and calcinated to achieve a high-index dielectric network [7].

Another aspect of BCP-based PBG materials that needs to be considered is the competition between reflection and absorption of the materials for frequencies that are in the gap. Since the achievable dielectric contrast for block copolymer photonic structures in some cases will not be very large, we would expect a deep penetration depth of the evanescent wave into the structures. For the material to be useful as a bandgap material, one would want it to be as lossless as possible. The practical short wavelength limit for the use of polymers is probably around a wavelength of 300 nm due to their strong absorption in the ultraviolet regime.

The usefulness of BCP PBG materials would be greater if they exhibited bandgaps in the visible region of the spectrum [8]. Structures will begin to exhibit bandgaps in the visible portion of the spectrum if the characteristic domain size is on the order of or greater than 400/4π nm, where π is the index of refraction of the material in that domain. The domain sizes of typical block copolymers are usually 10–50 nm, although distances much larger than these are possible by employing rigid, extended chain blocks [9] and very high molecular weight flexible chain blocks as well as by swelling the domains by the addition of selective non-volatile solvents.

A self-assembled block copolymer layered structure that reflects visible light has been recently fabricated [11]. Fig. 6 is a reflectivity spectra taken from a styrene isoprene diblock copolymer (MW 194k : 197k) where the domains have been swollen by the addition of an isoprene homopolymer (20% by weight, MW 13k) and a thiol terminated polystyrene (20% by weight, MW 1.3k). The refractive index contrast between the domains was enhanced by the addition of CdSe nanoparticles. The sample was prepared by dissolving all of the components in toluene and subsequent casting on a glass microscope cover slide; the total film thickness is approximately 50 μm. The particles sequester into the polystyrene domains because of their affinity to the thiol group. The reflectivity was measured on a Cary spectrophotometer fitted with an integrating sphere. The maximal reflectivity peak is observed at 540 nm. The sample begins to reflect visible light after the solvent evaporates (which could take a few minutes if air is blown over the sample). The equilibrium structure for a symmetric diblock swollen with the respective homopolymers consists of alternating lamellae of polystyrene and polyisoprene with an approximate layer thickness of 85 nm.

The rejection potential of a finite dielectric lattice depends on the index contrast and on the number of lattice periods; lower contrast requires an increased number of periods for a given rejection value. In addition, since the wave penetrates deeply into the structure, imperfections become more important. It is therefore essential to achieve a high degree of control over defect formation in block copolymer systems. Quiescent casting leads to a small grain size with many grain boundary defects. Nearly single-crystal BCP’s can be formed.
by having the disorder-to-order transition occur in the present of a biasing force field. Fig. 7. is an example of cylinders on an hexagonal array, where the excellent long-range order in this sample was achieved by the roll casting technique. In this method, the polymer solution evaporates under the influence of an extensional flow field created by a pair of counter-rotating cylinders [12]. The disorder-to-order transition takes place in the presence of the flow field, leading to a global orientation of the microdomains. BCP’s can also be made to form single crystals by application of other force fields such as electric fields and substrate fields. For example, to achieve a particular orientation and location of the mesocrystal with respect to a substrate, one can introduce a chemically patterned surface that has an affinity to one of the microphases, which can lead to epitaxial relations between the surface and the polymer crystal [13].

V. THE 2-D TRIANGULAR ARRAY OF CYLINDERS—A CASE STUDY

The case of a photonic crystal made of a 2-D array of cylinders on a triangular lattice has been analyzed extensively, theoretically [14] as well as experimentally [15]. This structure has been shown to produce a complete 2-D gap for the TE, TM, or both polarizations. Hexagonal packed cylinders is one of the most commonly found morphologies in BCP systems. The simplest linear A/B block copolymer will self-assemble into this type of structure for minority component volume fractions between 13–30%. The range of volume fractions that assemble into the hexagonal morphology allows one to vary the filling factor (the ratio of the area of the cylinder to the area of the unit cell) between 13–30% and thus tune the cylinder radius to cylinder spacing ratios from 0.19 to 0.29. Note that by adding degrees of freedom to the BCP system, for example, employing an ABC triblock, one can access other regimes of the parameter space since ABC blocks form concentric cylinders with an r/a ratio outside this range that is smaller than 0.3.

The effect of varying the r/a ratio of dielectric cylinders on the band structure is presented in Fig. 8, where the gap for the TM modes is plotted as a function of the radius to cylinder spacing ratio. One can tune the midgap, gap width, and relative sizes of the different gaps by varying the r/a ratio and adjusting the dielectric contrast. One can tailor the dielectric contrast between the different phases by varying the type of dopant and the relative dopant volume fraction in the targeted domains. In Fig. 9, the TM gap is shown as a function of dielectric contrast for an r/a value of 0.3. It is interesting to note that the primary gap opens at a dielectric constant contrast that is close to 2(!), which is realistically achievable in BCP-based PBG materials using the enhancement methods described above.

As another example PBG material, we have fabricated a 2-D lattice of high-index cylinders in a low-index matrix by sequestering CdSe nanocrystals into the cylinders of a SIS triblock copolymer. The CdSe nanocrystallites were sequestered into the PS phase by using an amine terminated PS group as a surface modifier. Fig. 10(a) is a bright field TEM image of the CdSe doped cylindrical structure. The dielectric contrast is approximately 1.5, and the r/a is 0.3. Fig. 10(b) is an SAXS pattern that demonstrates the existence of long-range order by the roll-casting technique.
VI. THE ROLE OF DEFECTS

Defects play a crucial role in photonic crystals. Certain types of imperfections in a photonic band structure could lead to localized electromagnetic states, such that a point defect could act as a microcavity and a line defect like a waveguide [16]. Depending on the microdomain geometry, various point, line, and surface defects can occur during the transformation from the homogeneous disordered state to the microphase separated state. For example, in spherical microdomain block copolymers, planar stacking faults on \{110\} planes are commonplace, as well as high angle grain boundaries. In cylindrical microdomain block copolymers, two types of edge dislocations are common. It is quite likely that some of these imperfections will have interesting photon transport and localization properties. By tuning the shape, size, and topology of the defects, control over the symmetry properties of the electromagnetic modes is possible [17]. An example of a grain boundary surface imperfection in a cylindrical microdomain sample is shown in Fig. 7. An imperfection in a lamellar morphology is presented in Fig. 11. This imperfection resembles a microdisk cavity.

The challenge that remains is tailoring the dimensionality and position of the defects. One possible way to control the positions and structure of the defects is by creating heterogeneous nucleation sites such as by patterning a substrate to include ridges or elevated posts [13]. The self-assembly process then leads to the formation of defects at such predetermined sites during the disorder to order transition.

VII. APPLICATIONS

Polymeric photonic bandgap materials can utilize many of the properties that make plastics so attractive as materials. The method of incorporating high-index particles can be utilized to create large-area, low-cost, flexible, omnidirectional, self-assembled reflectors [2]. In addition, the self-assembling properties of block copolymers allow for the formation of these structures on arbitrarily shaped surfaces. One can envision the formation of self-assembled optical components by having the ordering event occur on a patterned surface. One could choose particular block constituents that will impart novel mechanical, electrical, or optical properties unattainable from rigid, monolithic photonic materials. For example, a rubbery ABA triblock (12.5%/75%/12.5% volume) when roll cast will form aligned cylinders of A in a matrix of B. This structure is anisotropic and can be stretched in the plane of periodicity to produce strains in excess of 100%. Upon removal of the force, the structure fully recovers its original dimensions—a mechanically tunable PBG with a wide range of stop bands. Another example would be to incorporate a liquid crystalline block in order to permit electrical control of transparency or reflectivity. Last, the nanocrystallites that are used to enhance the dielectric contrast are photoluminescent [19], so that a 2-D structure containing the nanocrystallites with a bandgap corresponding to the luminescence frequency will result in an inhibition of the emission in the plane of periodicity resulting in directional emission.

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