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Structural Color for Additive Manufacturing: 3D-Printed Photonic Crystals from Block Copolymers

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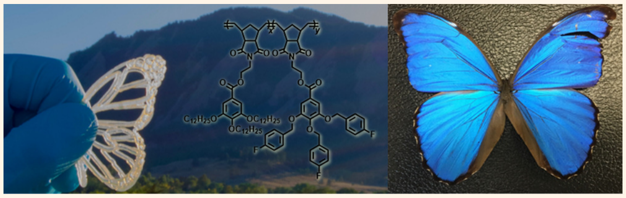
Supporting Information



ABSTRACT: **The incorporation of structural color into 3D printed parts is reported, presenting an alternative to the need for pigments or dyes for colored parts produced through additive manufacturing. Thermoplastic build materials composed of dendritic block copolymers were designed, synthesized, and used to additively manufacture plastic parts exhibiting structural color. The reflection properties of the photonic crystals arise from the periodic nanostructure formed through block copolymer self-assembly during polymer processing. The wavelength of reflected light could be tuned across the visible spectrum by synthetically controlling the block copolymer molecular weight and manufacture parts that reflected violet, green, or orange light with the capacity to serve as selective optical filters and light guides.**

KEYWORDS: *additive manufacturing, photonic crystals, block copolymers, self-assembly, structural color*

The importance of color broadly ranges from aesthetics to communications, and although a vast array of brilliant colors can be displayed using dyes or pigments, many such colorants are based on toxic molecules or heavy metals.[1] In contrast, nature presents an inspirational approach to sustainable color that is exemplified in butterflies, beetles, peacocks, and opals.[2−4] The color visualized in these objects arises from their nanostructure and is termed a photonic crystal (PC). PCs are periodic dielectric materials possessing a photonic band gap inhibiting the propagation of specific frequencies of light.[5] As the color of a PC arises from the nanostructure of the material, embedded structural color has been suggested as a more environmentally friendly alternative to pigments and dyes.[1] Thus, the ability to mimic the structural color observed in nature represents a sustainable approach to integrate color into objects.

Although several routes to visible-light PCs have been developed, access to an intermediate size regime of the periodic dielectric presents limitations. Synthetic PCs have been implemented as light guides, optical filters, and reflective coatings, with the potential to enable smaller and faster optical computing devices.[6−13] Lithography can yield precise PCs, but requires specialized apparatus.[14−16] Co-extrusion, fiber pulling, or layer-by-layer deposition of multiple materials are typically restricted by geometry,[17−23] while the self-assembly of colloidal crystals requires uniform particles and controlled self-assembly conditions.[24−26] In sum, the development of a versatile technology for the economical and scalable production of PCs is required for broad incorporation of sustainable structural color.

Additive manufacturing promises to revolutionize the future of manufacturing and has enabled the rapid production of parts and prototypes composed of designer materials with tailored chemical, mechanical, or thermal properties;[27−31] however, the incorporation of optical properties into such objects is less developed.[32,33] Recognizing the potential of AM, we were motivated to explore the feasibility of integrating structural color into 3D printed parts for the incorporation of objects possessing structural color. Furthermore, due to the light reflecting capability of PCs, such 3D printed objects could have the potential to serve as selective optical filters or guides. Herein, we report the 3D printing of block copolymers (BCPs) using fused deposition modeling (FDM). PC objects with 3D geometries of centimeter sizes (Figures S14−S20) were manufactured and reflect specific frequencies of light across the visible spectrum by controlling the domain size of the nanostructure through modulation of the BCP molecular weight (Figure 1).

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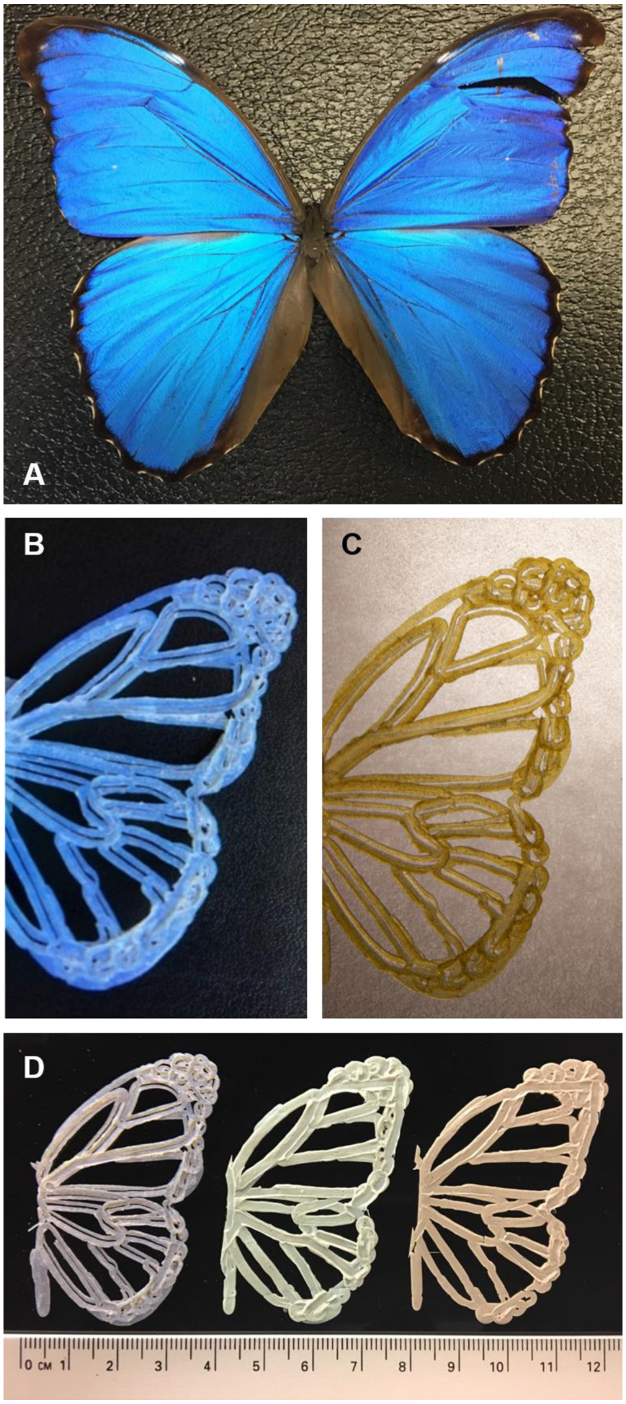

Figure 1. Photographs of PC butterflies. Photograph of a morpo butterfly (A). Photograph of a 3D-printed butterfly wing in reflection (B) and transmission (C). Photograph of 3D-printed PC butterfly wings from BCPs-1, -2, and -3 reflecting violet, green, and red light, respectively (D).

RESULTS AND DISCUSSION

The self-assembly of BCPs to nanostructured materials possessing a photonic bandgap provides the potential for an economical and scalable solution through the bottom-up self-assembly of commodity materials.[34−38] However, the self-assembly of BCPs to nanostructured materials with periodicity within the intermediate size regime needed to yield a photonic bandgap in the visible spectrum is challenging.[39,40] Domain size swelling coupled with extended self-assembly conditions can overcome this challenge, but are not broadly amendable to the time-scale and standard operating conditions of FDM 3D printers.[41−50] The inherent characteristic of macromolecular chain entanglement introduces an energetic barrier for the self-assembly to ordered nanostructures, preventing facile access to visible-light PCs.[51,52] To circumvent this fundamental property, the design and synthesis of macromolecules with rigid-rod characteristics and reduced capability for chain entanglement allow for rapid self-assembly to PCs, reflecting light across the visible and into the near-IR spectrum.[53−59] Molecular brush and dendritic copolymers composed of sterically bulky repeat units limit the potential for chain entanglement[60] and have been successfully synthesized *via* a grafting through approach using ruthenium-mediated ring-opening metathesis polymerization (ROMP).[61] ROMP is a robust and efficient methodology for the synthesis of such high molecular weight (MW) polymers with low dispersity ($Đ$).[62−66]As such, we hypothesized that dendritic BCPs possessed the potential to self-assemble to visible-light reflecting PCs under the conditions of FDM for the production of 3D-metamaterial objects.

To investigate if dendritic BCPs could self-assemble to PCs *via* filament extrusion and FDM en route to 3D printing of PC objects, a dendritic BCP composed of a benzyl and alkyl wedge-type monomer was synthesized. The BCP possessed a weight-average molecular weight (M_w) of 484 kDa and $Đ = 1.10$ (Figure 2). The rapid self-assembly of this dendronized BCP was highlighted during filament extrusion at 200 °C, yielding a PC filament in the time scale of minutes. The as-isolated, unassembled, BCP was colorless due to a lack of ordered nanostructured periodicity; however, during filament extrusion, the BCP self-assembled to a nanostructured material possessing photonic properties, reflecting violet light (yellow-transmitting) (Figure 2). Examination of the material located in the extruder nozzle revealed the most intense color was located at the heated barrel metal interface. As such, although shear forces during the extrusion process are imposed on the BCP, we propose the self-assembly mechanism is strongly thermally induced.[67]

Previous studies revealed modulating the BCP MW directly controlled the domain size of the resulting nanostructure, and the wavelength of reflected light of the PC could be tuned from the UV, through the visible, and into the near IR.[6−13,34] However, with this BCP composition, the wavelength of reflected light of the PC only gradually increased with increasing BCP MW. The highest MW BCP in this series (M_w = 909 kDa) only reflected green light (λ_{max} = 480 nm) (Figure S21, Table S7). As such, extremely high MW BCPs of this chemical composition would be required for the production of PC objects able to reflect longer wavelengths of light, which raised concern about the processability during extrusion and 3D printing with high MW BCPs.

Therefore, a BCP was designed and synthesized from a combination of a dodecyl and fluorobenzyl wedge-type monomers with the motivation to access longer wavelength-reflecting PCs from a lower MW BCP. This combination of monomers was designed to minimize chain entanglement with sterically bulky monomer repeat units and to encourage rapid self-assembly by chemically distinct blocks. Investigating the effects of BCP MW on the wavelength of reflected light revealed this composition could assemble to PCs reflecting across the visible spectrum, where the maximum peak

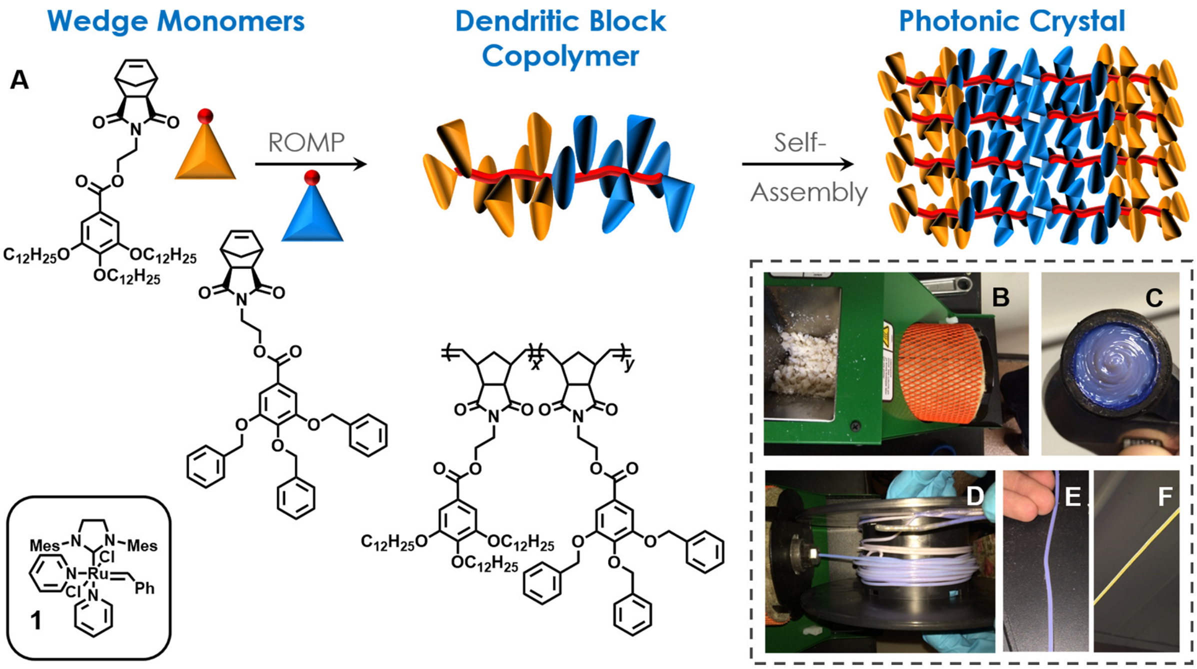

Figure 2. Synthetic approach to rigid-rod dendritic BCPs and schematic representation of the self-assembly of BCPs to PCs (A). Photographs of the unassembled, colorless BCP loaded in the extruder hopper (B), self-assembly to a PC during filament extrusion in the extruder nozzle (C), to yield a filament reflecting violet (D, E) and transmitting yellow light (F).

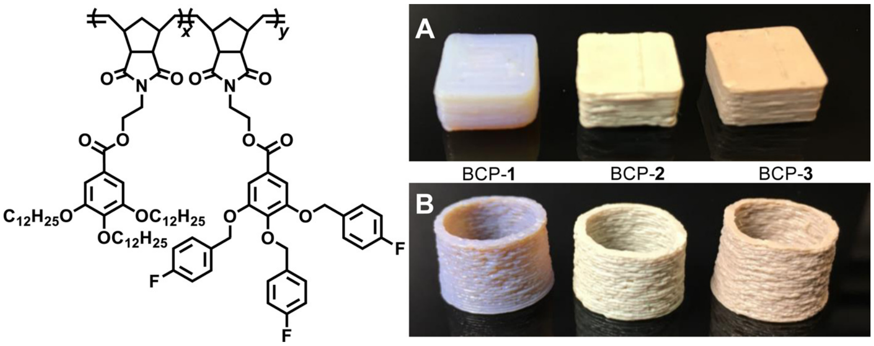

Figure 3. Structure of the BCP used for 3D printing (left). Cuboids (1.0 × 1.0 × 0.6 cm; A) and cylinders (diameter =1.6 cm; B) 3D printed using BCP-1, -2, or -3 reflecting violet, green, and orange light.

wavelength (λ_{max}) was linearly related to the BCP MW (Figure S22, Table S8). Three BCP samples were subsequently synthesized on multigram scale through the sequential ROMP of equal molar ratios of the two monomers to produce BCPs with M_ws of 581 (BCP-**1**), 876 (BCP-**2**), and 1130 (BCP-**3**) kDa. The bulk BCPs were then extruded into filaments for 3D printing using FDM.

For all three BCPs, the as-isolated materials are colorless. PC thin films of the three BCPs were fabricated through thermal annealing and reflected violet (λ_{max} = 412 nm), green (λ_{max} = 530 nm), and orange (λ_{max} = 610 nm) light for BCP-**1**, -**2**, and -**3**, respectively (Figure 4G–I). Scanning electron microscopy (SEM) was used to visualize the nanostructured morphology of the cross sections of these films after freeze fracturing and staining with RuO_4 (Figure 4A–C). For films made from BCP-**2** and -**3**, lamellar morphologies were observed with periodicities correlating to the observed reflection of the films. Interestingly, although the film from BCP-**1** efficiently reflected violet light, the observed morphology was not a lamellar morphology, but a spherical morphology reminiscent of kinetically trapped morphologies observed in similar dendronized BCPs.[54] Regardless, for all three BCPs possessing the same empirical formula, the observed color was a result of the nanostructured periodicity of the BCP. The observed structural color of both the BCP derived films and 3D printed objects has been stable for at least one year under ambient conditions.

Filaments from each BCP were drawn using a benchtop extruder. The filament produced from BCP-**1** reflected a slightly higher energy wavelength (λ_{max} = 387 nm) than when assembled to the thin film, although both processing methods yielded PC materials with relatively similar reflection profiles (Figure S23, Table S8). In contrast, the filaments produced from BCP-**2** and -**3** reflected longer wavelengths of light (λ_{max} = 552 and 737 nm, respectively), and the reflection profiles of the filaments became broader. As such, the filament from BCP-**1** transmitted light well, while the filaments from BCP-**2** and -**3** were not visually transparent. SEM was used to visualize the

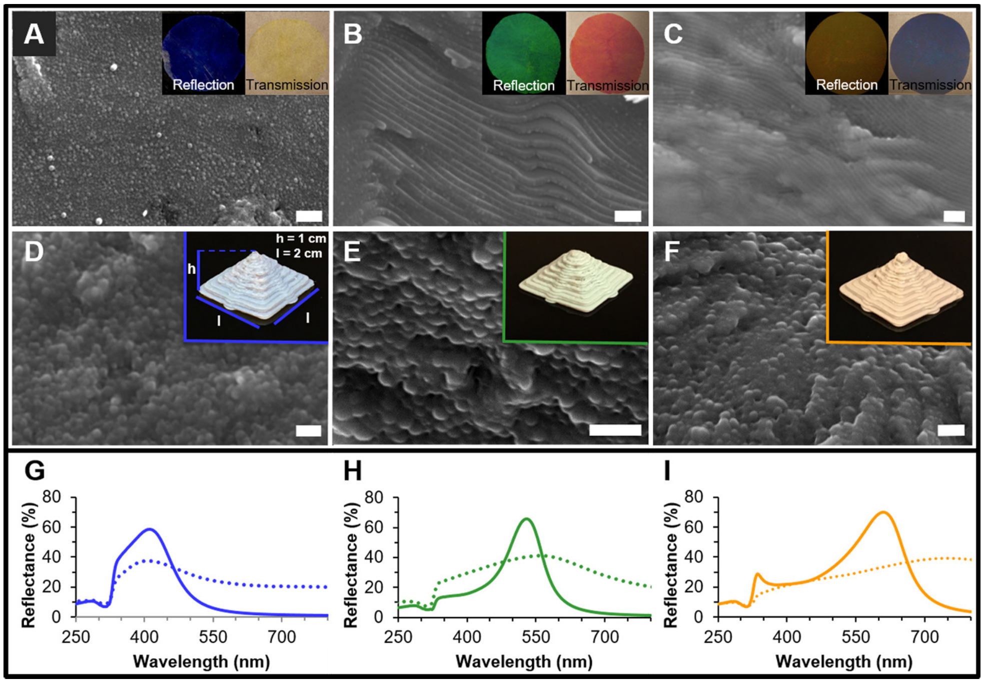

Figure 4. SEM images of freeze-fractured cross sections of thin films of poly(DDW-*b*-FBnW) BCP-1 (A), BCP-2 (B), and BCP-3 (C) and photographs of the films in reflection and transmission (insets). SEM images of the freeze-fractured cross sections and photographs of the 3D printed pyramids (2 × 2 × 1.0 cm) using BCP-1 (D), BCP-2 (E), and BCP-3 (F). Reflectance spectrum of thin films (solid line) and 3D-printed object (dashed line) for BCP-1 (G), BCP-2 (H), and BCP-3 (I). Scale bars in SEM images are 1 μm.

morphology of these materials (Figure S27). In the case of all three filaments, spherical morphologies were observed, similar to the PC thin film produced from BCP-**1**.

The filaments were printed using FDM to manufacture 3D cuboids (1.0 × 1.0 × 0.6 cm; Figure 3), cylinders (diameter = 1.6 cm; Figure 3), or pyramids (2.0 × 2.0 × 1.0 cm) possessing photonic properties and reflecting violet (λ_{max} = 412 nm), green (λ_{max} = 560 nm), or red (λ_{max} = 743 nm) light when using BCP-**1**, -**2**, or -**3**, respectively (Figure 4). FDM did not appear to alter the photonic properties or the self-assembly of the nanostructure as compared to the filaments. The λ_{max}, reflection profiles, and morphologies of the printed objects remained nearly the same as the filaments they were printed from. Thin objects printed using BCP-**1** could transmit light with the potential to serve as optical filters (Figure 1B), yet thicker objects were not visually transparent. Objects printed from BCP-**2** and -**3** reflected green or red light, respectively, but were not transparent (Figures 3 and 4).

To demonstrate further application potential of objects printed from these BCPs, a hollow U-shaped tube was printed from BCP-**2** (Figure 5). We envisioned this geometry would serve as a frequency selective light-guide around a curved geometry. In fact, when white light (emission spectrum, Figure S26) was introduced into one opening of the object, only green light exited the other opening. This experiment demonstrated the feasibility of using such 3D printed PC objects in more advanced optical devices or circuits and will be the focus of our future work.

Figure 5. Model of object and concept of a polymer-based PC acting as a light guide (A). Photograph of the 3D-printed object with an outer diameter of 0.5 cm (B) that, when irradiated with a white flashlight from one opening, can guide green light to exit the other opening (C).

CONCLUSIONS

Dendritic BCPs were designed and synthesized to act as PCs able to reflect across the visible spectrum. These polymeric PCs were then processed *via* 3D printing to create geometrically unrestricted objects possessing photonic properties. The rapid self-assembly of these polymers to nanostructured photonic materials was thermally induced during filament extrusion, yielding filaments reflecting across the visible spectrum and printed to 3D objects exhibiting structural color. This proof of concept represents an approach for the direct additive manufacturing of complex parts with tailored optical properties, without the use of pigments or dyes. In addition to introducing materials possessing photonic stop bands to 3D printing, the ability to control the flow of light with such materials was demonstrated, where printed photonic objects could filter light or even guide specified light frequencies around a curved geometry.

EXPERIMENTAL METHODS

(H_2IMes) (PPh_3) $(Cl)_2$RuCHPh was received as a research gift from Materia Inc. and was converted to (H_2IMes) $(py)_2(Cl)_2$RuCHPh (**1**) *via* a literature procedure.[68] *N*-(hydroxylethyl)-*cis*-5-norbornene-*exo*-2,3-dicarboximide (**2**) was prepared according to a literature procedure.[69] All other chemicals were purchased from Sigma-Aldrich and VWR. All polymerizations were performed in a nitrogen-filled glovebox. NMR spectra were recorded on a Varian INOVA 400 MHz spectrometer (^{1}H/^{13}C/^{19}F). Chemical shifts were referenced to internal solvent resonances using $CDCl_3$ (^{1}H: 7.26 ppm; ^{13}C: 77.16 ppm) and d_6-DMSO (^{1}H: 2.50 ppm ; ^{13}C: 39.52 ppm) and are reported as parts per million relative to tetramethylsilane. High-resolution mass spectra were provided by the University of Colorado, Boulder Central Analytical Mass Spectrometry Facility using a Waters Synapt G2 HDMS Qtof with acetonitrile as the solvent. Polymer molecular weights were determined by multiangle light-scattering (MALS) gel permeation chromatography (GPC), with THF as the eluent, using a miniDAWN TREOS light-scattering detector and a TrEX differential refractometer, all from Wyatt Technology. An Agilent 1200 UV−vis detector was also present in the detector stack. Absolute molecular weights were determined using d*n*/d*c* values calculated by assuming 100% mass recovery of the polymer sample injection into the GPC.

Batches of polymer of consistent molecular weight were thoroughly mixed by dissolving in methylene chloride to ensure homogeneity of the samples. After the removal of solvent, polymer batch mixtures were sufficiently dried in a VWR vacuum oven at 50 °C to a constant weight before extrusion. Differential scanning calorimetry (DSC) was conducted using a Mettler Toledo DSC823e. To reset thermal history, an initial sweep ramped from 25 to 250 °C (10 °C/min), where it was held constant for 2 min before cooled to 25 °C (−10 °C/min). Thermal data were collected from the second sweep after holding at 25 °C for 2 min, ramping to 250 °C (5 °C/min), holding for 2 min, and then returning to 25 °C (−5 °C/min).

Polymer thin films were prepared by compressing polymer sample between two glass slides (rinsed with methanol, hexanes, and methylene chloride then dried) and annealed in a VWR vacuum oven at 100 °C for 24 h. Polymer filaments were extruded using a Filabot EX2 extruder from 125 to 145 °C. Objects were printed using a FlashForge Creator Pro Dual Extrusion 3D printer (print temperature: 200 °C, nozzle diameter: 1.0 mm, layer height: 0.5 mm, object infill: 0%, 1 Shell, print-bed temperature: 40 °C, feed rate: 10 mm/s, travel feed rate: 10 mm/s). The 3D models were obtained from FlashForge preloaded calibration models, 3D modeling in SketchUp Make software, and from the open-source Web site www.thingiverse.com. All 3D models were visualized, sliced, and made into G-code using the Replicator G 0040r24-Sailfish software in tandem with the Skeinforge 50 slicing program.

SEM images were taken on a JEOL JSM-6480LV scanning electron microscope after staining films with RuO_4. Reflection measurements were performed on a Cary 5000 UV−vis/NIR spectrophotometer, equipped with an integrating sphere diffuse reflectance accessory (DRA) (Internal DRA-2500) using the standard wide-open aperture. The samples were scanned at a rate of 1.0 nm/s with a 1.0 nm data interval, from 1100 to 200 nm, and with a detector crossover (PbS to PMT) at 850 nm.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.7b00032.

> Materials and methods; procedures; characterization of polymer samples; characterization of block copolymer photonic crystal thin films, filaments, and 3D-printed objects (PDF)

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Notes

The authors declare no competing financial interest.

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