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VIP **Block Copolymers**

Precisely Tunable Photonic Crystals From Rapidly Self-Assembling Brush Block Copolymer Blends**

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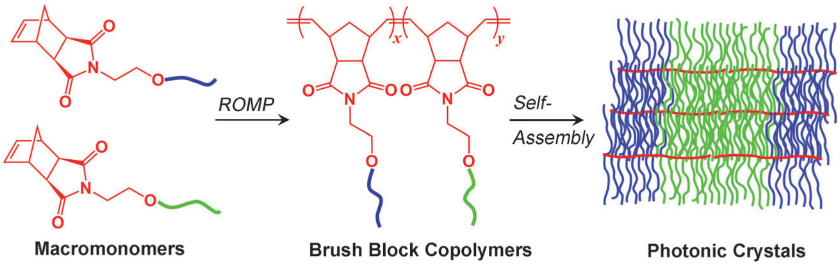
Block copolymers (BCPs) are ideal large-area, nanostructured materials because both the raw materials and "bottom-up" fabrication through self-assembly are inexpensive and scalable.[1] The microphase segregation of chemically distinct polymer blocks[2] to materials that possess a periodic dielectric function can yield a photonic band gap that forbids the propagation of certain wavelengths of light through the bulk. Such materials are termed photonic crystals (PCs) and have many applications, such as optical filters, mirrors, and cavities.[3] In the simplest scenario, 1D PCs are constructed from alternating layers of materials, where the reflection properties are determined by the thickness and refractive index of each layer. However, chain entanglement—a definitive polymer characteristic—most often restricts the ability of ultra-high molecular weight (MW) BCPs to self-assemble to ordered domains that are large enough to reflect long wavelengths of light. Thus, BCP-based PCs usually only reflect wavelengths of light as long as green;[4] longer wavelengths are only accessible with domain swelling with added components (i.e., solvent[5] or homopolymers[6]), typically requiring complex annealing procedures, which greatly reduces their potential applications.

We recently reported that high MW *brush* BCPs are able to rapidly self-assemble, due to their reduced chain entanglement, to PCs that can reflect all wavelengths of light from the UV to the near-infrared (NIR) without relying on any additional swelling components.[7] Utilizing ruthenium-mediated ring-opening metathesis polymerization (ROMP),[8] we have developed a "grafting-through" polymerization of macromonomers (MMs) to ultra-high MW brush copolymers.[9] The "grafting-through" polymerization of MMs affords highly uniform brush copolymers, in which the sterically demanding array of low MW side chains greatly reduces chain entanglement, enforcing the unifying main chain to assume a highly elongated conformation.[10] As such, symmetric brush BCPs readily self-assemble without complicated annealing methods to stacked lamellae that are composed of alternating layers of the different blocks, thus providing a facile means to 1D PC architectures (Scheme 1).[7] The domain sizes directly scale with the MW of the BCP, thus enabling the wavelength of reflected light to be predictably modulated by synthetically controlling the MW of the polymer.[7] Although this approach successfully produces PCs that reflect target wavelengths of light, it requires that a specific MW brush BCP be synthesized to reflect each wavelength of light; a more flexible and desirable technology would be post-synthetically tunable, bypassing such application-specific synthetic requirements.



Scheme 1. ROMP of macromonomers to brush block copolymers and their self-assembly to photonic crystals.

In the case of linear, random-coil symmetric BCPs, it has been demonstrated that polymer blends of BCPs of two different MWs can self-assemble to stacked lamellar morphologies if the ratio of the polymer MWs is less than five.[11] The resulting size is an average of the relative ratio of the two components and is permitted by the conforming and flexible characteristics of linear random-coil BCPs as they access low-energy morphologies that minimize interaction parameters through a proposed mechanism involving stretching of the low-MW BCP and a compression of the high-MW BCP. Similar blends of linear BCPs, in the presence of a swelling solvent and shear alignment, can exhibit temporary PC characteristics (reflecting light across the visible spectrum), which are lost upon solvent evaporation.[5a] Thus, we were motivated to investigate if blends of brush BCPs of different MW could adopt similar conforming morphologies, despite their inherently rigid architectures, as a means to readily modulate the domain sizes and thus the bandgaps of the PCs. Using this technique, it was found that the wavelength of reflected light is precisely tunable across the visible spectrum of light and into the NIR region simply through controlling the relative incorporation of the two polymers, greatly enhancing the practicality of brush BCP PCs.

The two brush BCPs of different MW employed in this study were constructed through sequential ROMP of equal

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amounts of *exo*-norbornene-functionalized hexyl isocyanate (MM-1) and 4-phenyl butyl isocyanate (MM-2) MMs (Figure 1).[7b] A film of the lower-MW brush BCP (BCP-1: weight average MW $[M_w] = 1512 \times 10^3\,\text{g mol}^{-1}$, molecular weight distribution [MWD] = 1.08), prepared by the controlled evaporation from dichloromethane, exhibited a maximum peak reflectivity (λ_{max}) of 360 nm, while the film of the higher-MW brush BCP (BCP-2: $M_w = 4167 \times 10^3\,\text{g mol}^{-1}$, MWD = 1.20), prepared in identical fashion, exhibited a λ_{max} of 785 nm. A film prepared from the controlled evaporation of a solution of BCP-1 and BCP-2 in a weight-percent ratio of 50:50 in dichloromethane exhibited a single reflection peak with $\lambda_{max} = 541$ nm. By varying the weight-percent ratio of the two brush BCPs from 100% BCP-1 to 100% BCP-2, at 10% intervals, a total of 11 different films were prepared. Each PC film showed a primary reflection peak, with λ_{max} observed at increasing wavelengths of light with increasing incorporation of BCP-2. Most impressively, a highly linear trend ($R^2 = 0.989$) in increasing λ_{max} as a function of increasing percentage of BCP-2 was established, thus allowing the production of PCs that reflect all wavelengths of light across the visible spectrum and into the NIR (Figure 2).

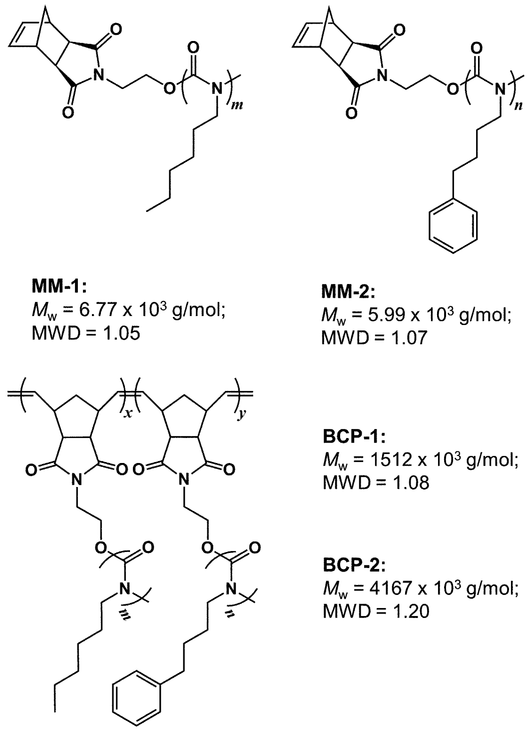

Figure 1. Structures and molecular-weight properties of macromonomers and brush block copolymers utilized in this study.

These results strongly suggest that despite the rigid architecture of the brush BCPs, the blends of the two polymers of different MW are able to assemble to uniform domains, in which the size is dictated by the relative ratio of the two components. We have previously established that the brush BCPs rapidly self-assemble to stacked lamellae. However, the mechanism by which the blends form such uniform domains remained unclear. The two most obvious routes would include the conforming assembly of the blends to stacked lamellae, in which the domains scale as an average of the two BCPs, similar to the mechanism followed by linear BCPs, or through a gradual change to an entirely different polymer morphology to compensate for the varying ratios of the two BCPs. To gain insight into the blending mechanism, scanning electron microscopy (SEM) was utilized to visually image the morphologies of the films.

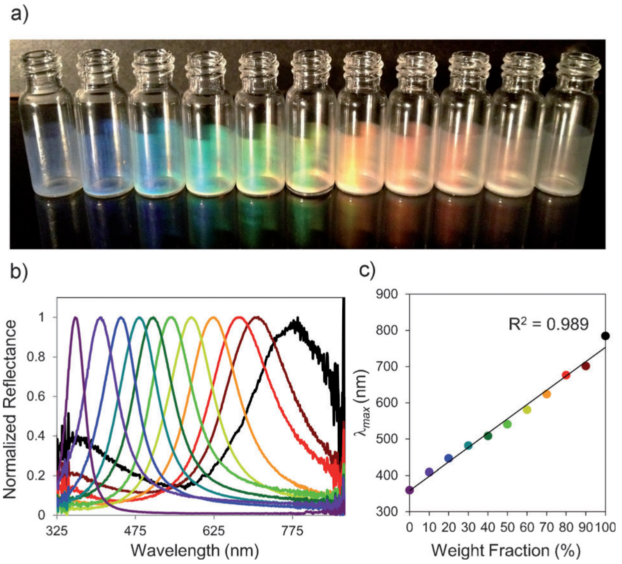

Figure 2. a) Photograph of brush block copolymer blends reflecting light across the visible spectrum (*top*). Plots of b) reflectance against wavelength, and c) maximum peak wavelength of reflectance against weight fraction of blend (% BCP-2) of the different brush block copolymer blends.

For all BCP blends, highly ordered stacked lamellae were observed in the SEM analysis (Figure 3). These data strongly support the proposal that the BCPs of different MW are able to adopt structures similar to their linear analogues,[11] thus necessitating an elongation of BCP-1 and a structural distortion of BCP-2. Although it is highly unlikely that the brush

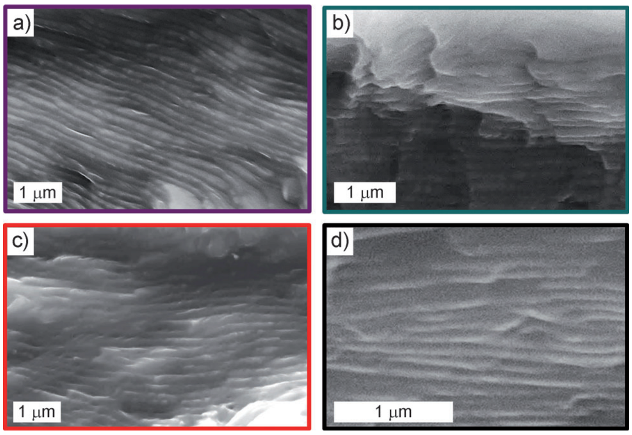

Figure 3. SEM images of cross-sections of brush block copolymer blends with a) 0%, b) 30%, c) 80%, and d) 100% of BCP-2. The perspective places the glass substrate parallel with the text.

BCPs are able to participate in extreme chain folding because of their inherently rigid structures, bending of BCP-2 to access the lowest-energy state must be occurring to some extent to explain the resulting highly uniform domains of the blends.

We have shown that blends between brush BCPs of different MW form highly uniform, stacked lamellar morphologies. The resulting domains of the 1D PC architectures scale linearly with the weight-percent incorporation of the two polymers. Thus, a wide range of photonic-band-gap materials can be easily fabricated, simply through blending of two polymers. Because the rigid architecture of brush BCPs greatly minimizes chain entanglement, these blends rapidly self-assemble through controlled evaporation from a volatile solvent. Despite their rigidity, there appears to be sufficient flexibility to conform to uniform, layered structures. We foresee that this simple, "bottom-up", approach provides an attractive means to precisely tunable photonic band gap materials through the rapid self-assembly of brush BCP blends.

Experimental Section

The synthesis and characterization of the macromonomers and brush block copolymers has been described previously.[7b] Blends were prepared by mixing stock solutions ($c = 1.5\ \mathrm{g\,L^{-1}}$; CH_2Cl_2) of BCP-1 and BCP-2 (10 mL total volume) in a 20 mL vial. A glass slide that had been previously washed with methanol and hexanes was placed vertically into the vial and the solvent was allowed to evaporate. Reflection measurements were performed on a Cary 5000 UV/Vis/NIR spectrophotometer, equipped with an "integrating sphere" diffuse reflectance accessory (Internal DRA 1800). All measurements were referenced to a LabSphere Spectralon 99% certified reflectance standard. The samples were illuminated through a Spectralon-coated aperature with a diameter of 1 cm, with a beam area of approximately $0.5\ \mathrm{cm}^2$. The samples were scanned at a rate of $600\ \mathrm{nm\,min^{-1}}$ with a 1 nm data interval from 1800 to 200 nm, with a detector crossover (InGaAs to PMT) at 875 nm. SEM images of freeze-fractured samples that were stained with RuO_4 and carbon coated were taken on a ZEISS 1550 VP Field Emission SEM.

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