Improving Brush Polymer Infrared One-Dimensional Photonic Crystals via Linear Polymer Additives

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S *Supporting Information*

ABSTRACT: Brush block copolymers (BBCPs) enable the rapid fabrication of self-assembled one-dimensional photonic crystals with photonic band gaps that are tunable in the UV-vis-IR, where the peak wavelength of reflection scales with the molecular weight of the BBCPs. Due to the difficulty in synthesizing very large BBCPs, the fidelity of the assembled lamellar nanostructures drastically erodes as the domains become large enough to reflect IR light, severely limiting their performance as optical filters. To overcome this challenge, short linear homopolymers are used to swell the arrays to ~180% of the initial domain spacing, allowing for photonic band gaps up to ~1410 nm without significant opacity in the visible, demonstrating improved ordering of the arrays. Additionally, blending BBCPs with random copolymers enables functional groups to be incorporated into the BBCP array without attaching them directly to the BBCPs. The addition of short linear polymers to the BBCP arrays thus offers a facile means of improving the self-assembly and optical properties of these materials, as well as adding a route to achieving films with greater functionality and tailorability, without the need to develop or optimize the processing conditions for each new brush polymer synthesized.

Figure 1. Brush block copolymers generated from norbornene-terminated polystyrene (PS) and polylactic acid (PLA) macro-monomers adopt rigid rod-like conformations that allow them to form lamellar arrays with large periodicities. Adding small PS and PLA homopolymers swells these arrays, increasing their domain spacing.

Self-assembly is a powerful means of generating nanometer-scale ordering in materials that often possess emergent photonic, plasmonic, magnetic, or other physical phenomena as a result of nanoscale structure control.[1] However, self-assembled materials with resonant optical properties such as photonic band gaps are often difficult to achieve, as they require structures with large periodicities, comparable to the wavelengths (λ) of light being manipulated.[1b,e,2] Brush block copolymers (BBCPs) show promise as building blocks for assembling photonic band gaps in the ultraviolet, visible, and infrared, as these BBCPs can be readily synthesized using multiple polymerization strategies to generate ultrahigh molecular weight (MW) materials with contour lengths in the range necessary to generate photonic band gap architectures.[3] Recently, a "grafting-through" method for synthesizing these BBCPs was developed that uses a highly active ruthenium metathesis catalyst to polymerize norbornene-
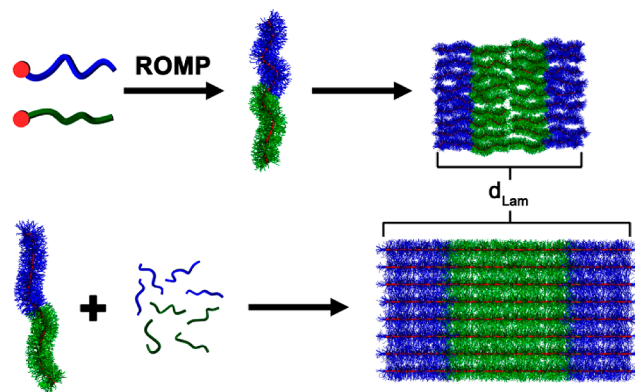
terminated polymer macromonomers via ring-opening meta-thesis polymerization (ROMP).[3e,f] This results in high-MW (up to ~6.5 MDa) polymers with relatively low dispersity and 100% grafting density of polymer brushes along the polynorbornene backbone (Figure 1). Because of the steric hindrance that the densely grafted macromolecule brushes impose upon the polynorbornene chain, these BBCPs act as rigid rod-like structures that do not exhibit significant chain entanglement despite their high MWs.[3f] As a result, they can rapidly self-assemble into one-dimensional (1D) stacks with domain spacings up to several hundred nanometers, generating highly reflective Bragg stacks, where the wavelength of reflected light can be tuned throughout the UV-vis-IR by altering the degree of polymerization (DP) of the BBCPs.[3e]

Despite significant progress in their synthesis, major challenges remain in the development of BBCP-based photonic band gap materials, including synthesizing films that are reflective in the telecommunications regime ($\lambda \approx 1200-1650$ nm) without being opaque in the visible, enhancing the processability of BBCPs

during and after their synthesis, and incorporating different functional groups that would enable applications such as alignment, cross-linking, or manipulation of refractive indices. Although different macromonomers have been used to attempt to address some of these challenges,[4] the difficulty inherent to generating such high-MW polymers with low dispersity requires re-optimization of the synthesis protocols for each new type of BBCP or macromolecule brush architecture.

In this work, we show that blending low-MW homopolymers (HPs) with BBCPs is a powerful means of manipulating their assembly (Figure 1). Blending short, readily synthesized HPs with BBCPs prior to casting a polymer film allows one to control the lamellar array periodicity between ~100 and 500 nm, tune the photonic band gaps that can be achieved in these films from the UV all the way to the IR telecomm regime (up to $\lambda \approx 1410$ nm), and incorporate different chemical species into the arrays without the need to develop new macromonomers or re-optimize the BBCP synthesis.

It is well known that adding HPs to linear block copolymers causes them to swell in a predictable manner.[2,5] However, it is not necessarily obvious that such a methodology would be readily applicable to BBCPs, which are generally regarded as rigid rods—indeed, the increased steric hindrance that causes the BBCP rod-like morphology is the very reason they are able to achieve lamellar arrays with large periodicities in the first place.[3e,f]

The first necessary task was thus to examine the extent to which these HPs could change the domain spacing of the BBCP arrays. All target BBCPs in this work are symmetric, containing roughly equivalent numbers of polystyrene (PS) and polylactic acid (PLA) macromolecular brushes (MW ~3.5 and ~3.1 kDa, respectively), and in all blends, the BBCPs were combined with equal amounts of PS and PLA HPs by weight. The initial blends used to test if HPs could controllably swell BBCP arrays utilized a BBCP of ~987 kDa and HPs that were of comparable weight (~3 kDa) to the BBCP brushes. All relevant polymer MWs and PDIs can be found in the Supporting Information (SI, Tables S1–S4). These blends were annealed and the resulting films characterized with UV-vis reflectance measurements, scanning electron microscopy (SEM), and small-angle X-ray scattering (SAXS) to determine the quality and domain spacing of the self-assembled arrays (Figures 2 and S1).

Despite the relatively rigid nature of the BBCP, incorporating low-MW HPs caused the arrays to swell to ~140% of the periodicity of the non-blended BBCP (Figure 2). Moreover, the relationship between periodicity and HP:BBCP weight ratio followed a linear trend up to 67.5 wt% HP (weight ratio of ~2:1), beyond which the arrays exhibited much poorer band gaps with a large degree of disorder, most likely indicating that the materials had begun to phase-separate at these high wt% blends (Figures 2B and S1). Self-consistent field theory (SCFT, details in SI) showed that the HPs are dispersed evenly throughout both BBCP blocks, with HPs located in the lamellar blocks containing brushes of the same composition (i.e., PS HP in the PS block), with only slightly larger amounts of HP at the center of the lamellae and the interface between two different blocks (Figure 2C). As a result, the BBCPs can tolerate the presence of a large degree of HP before phase segregation occurs; thus, the BBCPs can be swollen to a significant degree despite their relatively rigid nature.

Interestingly, the BBCP arrays did not lose any of the ideal self-assembly properties (fast kinetics of assembly, relatively narrow reflectance peak widths), even in blends consisting of >2:1 HP:BBCP by weight. Higher MW HPs were also examined as
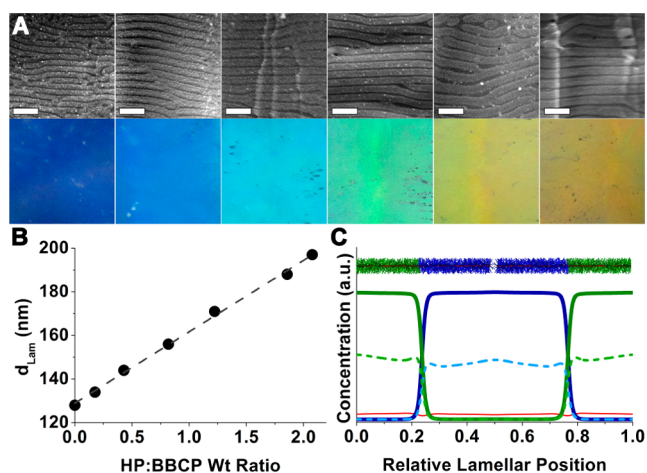

Figure 2. (A) SEM cross-sectional images of BBCP arrays with 0, 30, 45, 55, 65, and 67.5 wt% HP (wt ratio of 0 to ~2); below each SEM image is a plain view image of the film showing increasing photonic band gap positions with added HP. Scale bars are 500 nm. (B) Lamellar domain spacing as a function of added HP (same films as in (A); data obtained via SAXS). (C) Relative concentrations of BBCP brushes and HPs at various positions along a lamella as determined by SCFT simulations: blue traces, PS; green traces, PLA; red trace, the polynorbornene backbone; solid lines, BBCP; dashed lines, HPs. Sample is 45 wt% HP.

additives and showed similar effects, but these heavier HPs induced a greater amount of disorder in the arrays; this is discussed in more detail in the SI (Figures S20–S23). Blending low-MW polymers with the BBCPs is thus the best method to post-synthetically tune the lamellar domain spacing without the need to synthesize high-MW BBCPs. This significantly simplifies the process of generating these materials via ROMP, as lower MW BBCPs are often easier to synthesize with lower dispersity and better control over polymer quality.[3e,f,4a]

To fully investigate the ability of these blends to control the domain spacing of the self-assembled arrays and thus the wavelength of reflected light, a series of BBCPs with overall DP ranging from ~300 to ~900 (MW 987–3035 kDa) was synthesized and blended with different amounts of ~3 kDa HPs. These BBCPs possessed backbone lengths commensurate with those of the BBCPs previously shown to give highly ordered arrays that reflect light ranging from the UV to the near-IR (up to ~900 nm).[3e] Upon annealing the blends, three interesting observations were made from examining their reflectance spectra (Figures 3, S2–S12, and S44–S50, Table S6).

First, although the lowest MW BBCP examined above could only be swollen to ~140% before the quality of the films decreased, higher MW BBCPs could be swollen to accommodate higher levels of HP; they also exhibited a greater degree of swelling with equivalent amounts of HP. The BBCPs could even be swollen to a periodicity that was 180% the value of the corresponding unblended BBCP (Figure 3A). This increase in the extent to which heavier BBCPs could be swollen is most likely due to the fact that, while higher MW BBCPs possess longer contour lengths, the overall persistence length of this PLA-PS BBCP system is fixed. Thus, the larger BBCPs would be expected to be more contorted in the unblended arrays, allowing for greater swelling upon addition of HPs.

Second, the optical properties of the arrays noticeably improved when small to modest amounts of HP were added, especially for the longest BBCPs (Figure 3B). Specifically, the values of $\Delta\lambda/\lambda$ (a measurement of the full-width at half-maximum
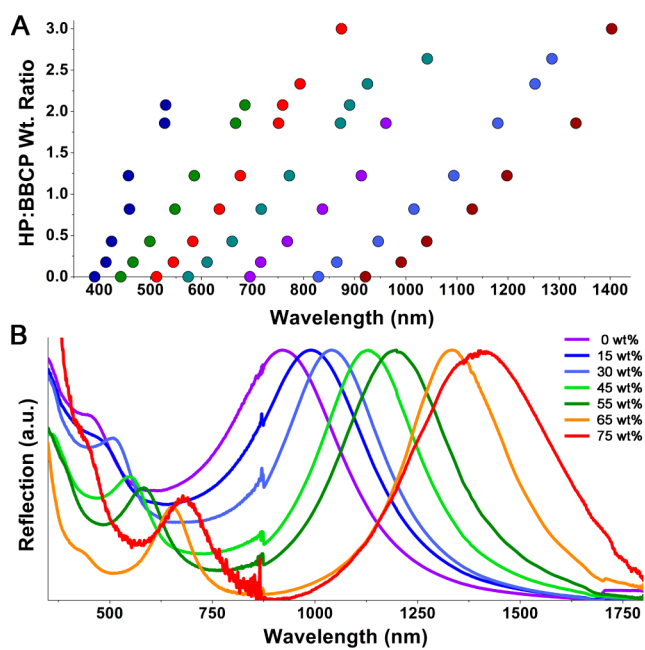
Figure 3. (A) BBCP/HP blends allow the photonic band gap of the self-assembled arrays to be easily tuned from 390 to 1410 nm. Each color corresponds to a specific BBCP; some BBCPs could be swollen to ~180% of their initial domain spacing. (B) UV−vis spectra of the highest MW BBCP (brown circles in A) with increasing HP wt%. Samples were well-ordered enough to observe higher order resonances at λ/m (e.g., at ~625 nm (m = 2) and ~450 (m = 3) in the orange trace).

of the peak relative to the peak maximum) narrowed, indicating greater homogeneity in lamellar periodicity. Additionally, the amount of scattered light at wavelengths outside of the photonic stop bands (e.g., ~500−750 nm in the 0 wt% system or ~750−1000 nm in the 65 wt% system) decreased, indicating less uncontrolled scattering of light from disordered regions of the sample. These phenomena can be explained by the fact that, although the ROMP process produces polymers with low dispersity, there is still some inherent polydispersity to the BBCP backbone lengths. The steric hindrance that the macromonomers impart to the BBCP makes it difficult for the materials to accommodate these deviations and properly pack into perfectly ordered lamellae, generating strain in the BBCP backbone; the added HPs are able to fill in gaps between the BBCPs caused by inhomogeneities in BBCP backbone length, alleviating this strain.

Most importantly, adding HPs to the BBCP arrays allowed for photonic band gaps at wavelengths significantly longer than have been demonstrated previously (Figure 3). Unblended PS-PLA BBCPs have been shown to generate highly reflective films with λ_{max} up to ~900 nm, generally with modest opacity in the visible range.[3e] Materials with $\lambda_{max} \approx 1300$ nm were also obtained with these unblended materials, but the ordering was poor, and thus the materials were broadly scattering in the visible portion of the spectrum. In this study, lamellar arrays that reflect light at ~1410 nm were readily synthesized, with almost no opacity in the visible. These blended materials were even well-ordered enough to observe second- and third-order harmonic reflectance peaks in some samples, indicating a degree of ordering within the materials not previously achieved at these large periodicities.

While the HP/BBCP blends clearly show an advantage in generating materials with enhanced optical properties, they also present another distinct advantage over non-blended BBCPs, specifically the incorporation of different functional groups into
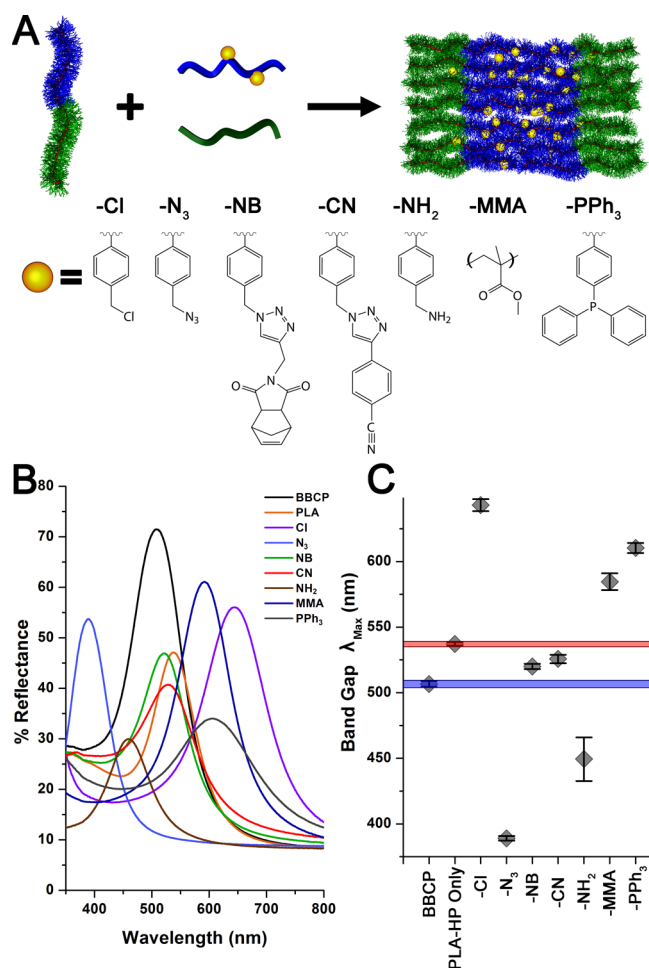

Figure 4. (A) Modifying a PS homopolymer with additional functional groups (yellow spheres) allows this random copolymer to act as a "Trojan horse" to bring these functional groups into the BBCP array. (B) All BBCP/RCP blends generated well-ordered arrays with clear photonic band gaps; the amount of reflection varied as a function of sample thickness and degree of disorder within the sample, but the quality of the lamellar arrays remained mostly unchanged. (C) The photonic band gap λ_{max} values (measured in triplicate) of the RCP blends do not overlap with either the BBCP λ_{max} (blue region) or PLA-HP-only λ_{max} (red region) controls, indicating that the RCPs were indeed incorporated into the arrays. All blended samples contained ~25 wt% each PLA-HP and RCP, with the exception of the BBCP-only control, the PLA-only control (which contained the same amount of BBCP and PLA-HP as the others but no RCP), and PPh$_3$, which was 12.5 wt% each PLA-HP and RCP.

the BBCP arrays (Figure 4). In principle, a random copolymer (RCP) composed predominantly of monomers identical to those in the BBCP macromonomers could provide a useful "Trojan horse" to bring pendant functional groups into the arrays without the need to directly attach them to the BBCPs. Such functional groups could be used to increase the utility of these films by altering the refractive index of a given block (thereby increasing reflectivity),[6] providing a means to cross-link the films and increase their stability,[7] or allowing the films to be dynamically manipulated with the application of external stimuli.[2c,8]

To test this hypothesis, an array of RCPs was synthesized, consisting of styrene monomers and monomers containing additional functional groups (MW ~6−8 kDa, with ~10−25% incorporation of the various functional groups; full details are listed in the SI, Figures S13−S19, Table S5), including moieties

that are known to challenge or deactivate the metathesis polymerization catalyst (Figure 4A).[9] Importantly, these materials were able to generate reflective lamellar arrays at 25 and 50 combined wt% of RCP and PLA HP (Figure 4B), even in the presence of multiple different functional groups. It should be noted that many of these functional groups (specifically norbornenes, nitriles, amines, and phosphines) would either cause side reactions during metathesis polymerization or deactivate the metathesis catalyst, thus preventing their direct incorporation into a BBCP. However, when these RCPs were blended with the BBCPs, all blends generated photonic band gap structures, and the photonic band gaps of all films were shifted when compared to an unblended BBCP, as well as a control sample to which only the PLA HP was added (Figure 4C). This indicates that the RCPs must be incorporated into the lamellae in some manner, and do not have significant negative impact on the ability of the BBCPs to form ordered arrays. SEM also showed no evidence of large regions of phase-segregated RCP (Figures S24–S30), and surface FTIR and NMR analyses confirmed that the functional groups were still present in the assembled films, even after the annealing and self-assembly processes (Figures S31–S38).

Interestingly, while all of the blends still generated ordered arrays, some of the materials resulted in swollen lamellae, while others actually resulted in a shrinking of the lamellar periodicity, as confirmed with SAXS, SEM, and UV-vis measurements (Figures S24–S30). One possible explanation for the observed differences in lamellar periodicity is that the addition of different functional groups into the RCP changed the effective χ (a measure of polymer/polymer miscibility) between the RCP and BBCP components. SCFT simulations (Figures S39–S43) for BBCP/RCP blends indicated that blends with the RCP-PLA χ equal to or greater than the PS-PLA χ always increased the periodicity of the lamellae, as stronger segregation between the PLA and RCP placed the RCP in the center of the PS domains, separating the opposing PS blocks of the BBCPs. However, decreasing the PLA-RCP χ below the PS-PLA χ caused the RCP to segregate toward the interface between the PS and PLA blocks, resulting in a decrease of the overall lamellar spacing in order to alleviate strain in the system at the cost of more interfacial area.

In conclusion, we have demonstrated that blending linear HPs with BBCPs is a powerful means of synthesizing highly reflective polymer films with controlled periodicities up to ∼500 nm, generating photonic band gaps up to $\lambda \approx 1410$ nm. Adding HPs to the BBCPs improves their overall ordering, thus improving the optical properties of the films, and also enables the incorporation of functional groups that might otherwise be difficult to attach to the BBCPs directly. Future efforts will investigate the use of these BBCP/RCP blends to induce the previously mentioned effects of alignment, refractive index tuning, and cross-linking, thereby increasing their applicability as thin-film coatings with programmable photonic properties.

■ ASSOCIATED CONTENT

ⓈSupporting Information

Synthetic procedures, polymer characterization data (NMR, GPC, IR), SAXS data, additional optical spectra, plain-view images of films, additional SEM data, and SCFT simulations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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