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Blends of PS-PMMA Diblock Copolymers with a Directionally Hydrogen Bonding Polymer Additive

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Block copolymers self-assemble into a range of morphologies that enable their utility in a number of potential applications such as lithography, plastics, and other nanostructured materials.[1] The ordered phases obtained are largely dictated by polymer composition, degree of polymerization, and the effective segment−segment compatibility parameter (χ). Blends comprised of homopolymers and diblock copolymers present a convenient method to tune and yield a variety of morphologies.[2,3] The homopolymer additive is often identical in composition to one of the segments of the diblock copolymer. Alternatively, homopolymers which do not share the same composition as either segment of the diblock copolymer can utilize hydrogen bonding to improve miscibility.[3] Matsushita and co-workers[3b,c] have investigated the morphologies afforded from blends of poly(hydroxystyrene) with poly(styrene-*b*-2-vinylpyridine) and demonstrated well-ordered nanostructures.

Using our understanding of natural systems such as DNA and proteins as inspiration, many researchers have utilized[4−7] well-defined molecular interactions to control the assembly of synthetic macromolecules, including block copolymers. Several research groups have employed ionic functionalities[5,6] at specific locations within a block copolymer to alter the bulk morphological structures. Wiesner and co-workers,[5] for example, demonstrated that poly(styrene-*b*-isoprene) diblock copolymers with oppositely charged ionic groups at each chain end have tunable control over lamellar spacing with the addition of salt. Tang et al. demonstrated[7] the formation of highly ordered square arrays using hydrogen bonding A-B/B′-C diblock copolymers, wherein the B and B′ blocks were comprised of either pyridyl or phenolic functionalities. In this example, a small number of hydrogen bonding interactions had a profound effect on the self-assembly of the block copolymers. Thus, the incorporation of supramolecular motifs into block copolymer systems can result in a greater degree of control over aspects including size, order, and morphology, which are critical to the application of block copolymers in nanofabrication.

Herein we describe the thin film morphologies observed for blends of poly(styrene-*b*-methylmethacrylate) (PS-PMMA) with poly(styrene) possessing a hydrogen bonding tetra-urea segment at its center. Other research groups[8−10] have utilized hydrogen bonding arrays of ureas to afford materials with unique properties. Bisurea-based supramolecular polymers are known to form anisotropic rods in a highly cooperative manner.[9,10] Meijer and Sijbesma[10] have further investigated the morphology and properties of segmented copolymers comprised of urea hard blocks and poly(tetramethylene oxide) hard blocks. The thermoplastic elastomers were comprised of well-defined bis-urea segments which showed no evidence of phase mixing with the soft block.

In our own interest to develop block copolymer thin films for lithographic applications,[11] we sought to investigate the impact of urea-mediated hydrogen bonding assemblies upon the morphology of PS-PMMA thin films. A PS chain with a tetra-urea segment at its center was chosen as a blending partner that would be compatible with the PS block of PS-*b*-PMMA. In order to develop hydrogen bonding polymers with PS-*b*-PMMA that are suitable for a semiconductor manufacturing environment, the materials must withstand the elevated temperatures[12] (> 200 °C) required for fast thin film annealing. Therefore, a tetra-urea segment was chosen given the stability of its hydrogen bonds at elevated temperatures.

Bromine-terminated polystyrene polymers were synthesized using atom transfer radical polymerization[13] and reacted with sodium azide to obtain azide end-functional polystyrene **2** (Scheme 1).[14] For these investigations, PS with M_n of 12.0 and 5.5 kg/mol were synthesized. The presence of azide end group on the polymer chain was confirmed by the presence of a peak at 2104 cm^{-1} in the FT-IR spectrum. Polymer **2** was reduced in the presence of ammonium formate and Pd/C to obtain the amine end-functional PS **3**. The reduction to the amine was confirmed by the disappearance of the azide peak in FTIR spectrum. The resulting amine functional polymer was then reacted with 30 molar excess of 1,6 hexanediisocyanate to obtain isocyanate end-functional PS **4**. A slight excess of the isocyanate polymer (2.1 equivalents) was reacted with one equivalent of ethylenediamine to obtain quadruple urea-centered polystyrene **1** as shown in scheme 1. The resulting values for M_n of the quadruple urea-centered polystyrenes **1a** and **1b** were 13.0 and 24.0 kg/mol, respectively.

To process PS-*b*-PMMA on a time-scale suitable for semiconductor manufacturing, the block copolymer must be annealed within 1−2 min at elevated temperatures. Infrared spectroscopy was employed to observe the stability of the tetra-urea segment at 240 °C over time. It has been previously reported by Versteegen et al. that segmented copolymers with three to four urea groups in their hard segments do not flow below 200 °C.[10b] Urea groups have a reported onset of decomposition of 200 °C.[15] FT-IR experiments were utilized to observe changes to the N−H vibration band for tetra-urea polymer **1a** was heated at 240 °C for 2, 10, and 15 min. A broad peak at 3320 cm^{-1} was observed in the FT-IR spectrum (Supporting Information) for polymer **1a**, which is indicative of hydrogen bonding urea N−H groups. This peak also shifts to larger wavenumbers that suggests the loss of hydrogen bonding with longer heating times. The FT-IR spectrum for the sample heated for two minutes at 240 °C showed little change in the peak intensity at 3320 cm^{-1} when compared to the FT-IR spectrum of sample with no heating. On the other hand, samples heated for 10 and 15 min showed a significant change in the spectra for N−H vibration frequency region. The peak intensity was significantly reduced after heating for 10 min whereas it was completely absent for the sample heated for 15 min, which indicates complete decomposition of the urea groups. Discoloration of the films was observed for the samples heated for extended periods of time, while no such change was observed for samples heated for two minutes at 240 °C. Hence for the processing conditions employed in this study (2 min at 240 °C), the urea groups were indeed present in the blend films in their hydrogen bonded state.

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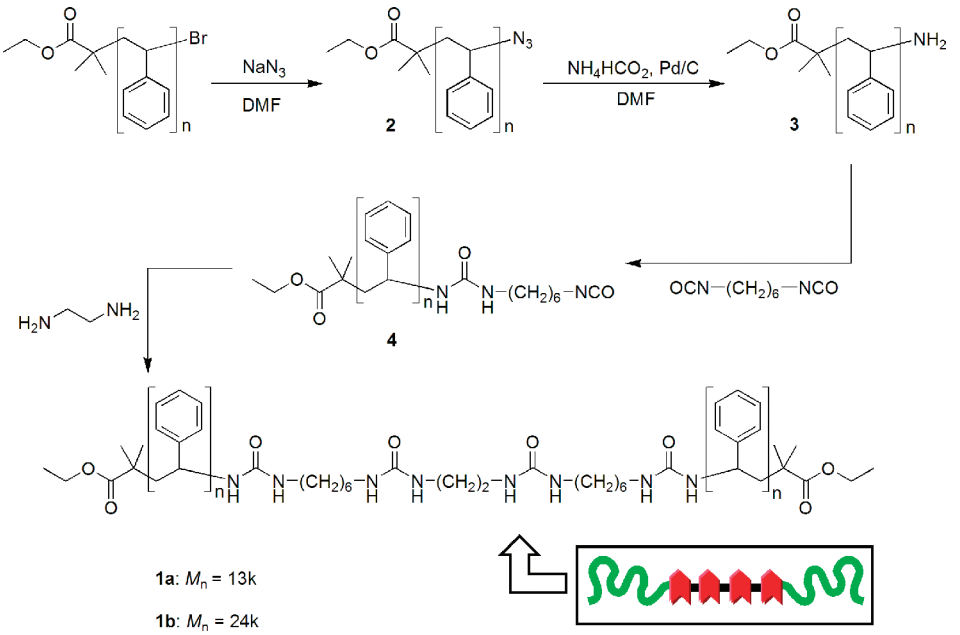
Scheme 1. Synthesis of Tetra-Urea Polystyrenes 1a and 1b



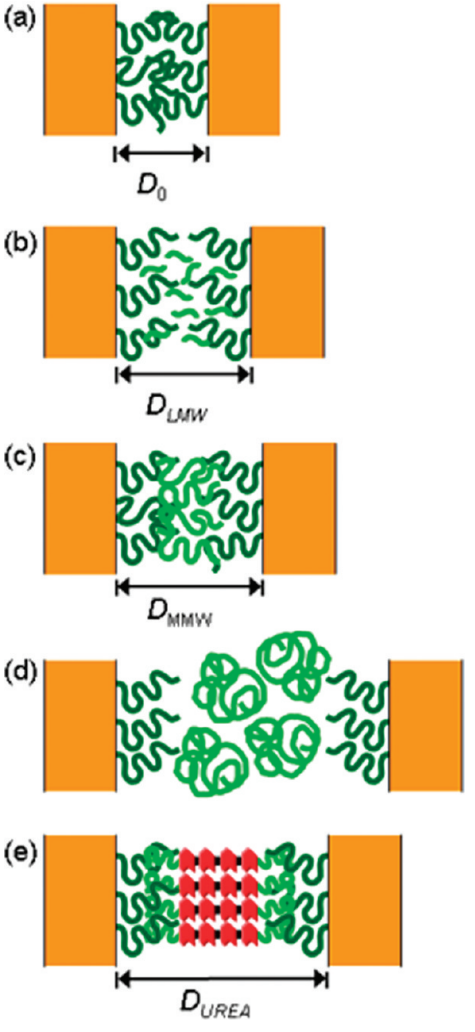


Figure 1. Schematic representations of (a) PS-*b*-PMMA, (b) low molecular weight hPS, (c) intermediate molecular weight hPS, and (d) high molecular weight hPS blended with PS-*b*-PMMA; (e) proposed distribution of tetra-urea polystyrene (**1**) within the PS domains of PS-*b*-PMMA.

In general, blending of homopolymers with block copolymers provides a simple way to access a variety of morphologies. Blend morphologies of homopolymer/diblock copolymer mixtures have been reported for polymer compositions in the bulk and thin film.[2] Domain spacing and morphology were used to investigate the distribution of the homopolymer with respect to its complementary component of the diblock copolymer with a periodicity D_0 (Figure 1a). The homopolymer miscibility with the corresponding polymer block was correlated to the observed morphologies, and can be estimated from the ratio (r) of the molecular weights of the homopolymer and the corresponding block of the block copolymer. When $r < 1$, the homopolymer was solubilized homogeneously within the corresponding block (Figure 1b). As a result, the homopolymers uniformly swell the corresponding block which ultimately increases the domain dimension ($D_{LMW} > D_0$), as well as interfacial curvature. When $r \geq 1$, the homopolymer is localized at the center of the corresponding domain of the block copolymer (Figure 1c). The amount of homopolymer near the block interface decreases, as it becomes more localized toward the center of the microdomains. This further increases the domain size ($D_{MMW} > D_{LMW}$) but has less effect on the interfacial curvature. When $r \gg 1$, the unfavorable entropy of mixing between high molecular weight polymer and the corresponding polymer block results in the macrophase segregation of the homopolymers. The macrophase segregation impairs the correlation between domains and there is no specific periodicity in such blends. (Figure 1d).

Blends of tetra-urea polystyrenes **1a** and **1b** and PS-*b*-PMMA afford significantly different morphologies compared to those from the blends of linear homopolystyrene (hPS) and PS-*b*-PMMA. Anisole solutions of PS-*b*-PMMA (with 23.7 kg/mol PS and 25.6 kg/mol PMMA) blended with tetra-urea PS or hPS of various molecular weights were cast onto neutral substrates and baked at 240 °C for 2 min to form a 25 nm thick film with vertically oriented self-assembled domains. As shown in Figure 2A, the PS-*b*-PMMA diblock copolymer formed vertically oriented lamellae with a pitch of 33.5 nm.

We performed a series of control experiments to understand the effect of introducing hPS with PS-*b*-PMMA. hPS with molecular weights 10, 21, 32, 50, and 200 kg/mol were combined with PS-*b*-PMMA to form polymer blends with two different hPS

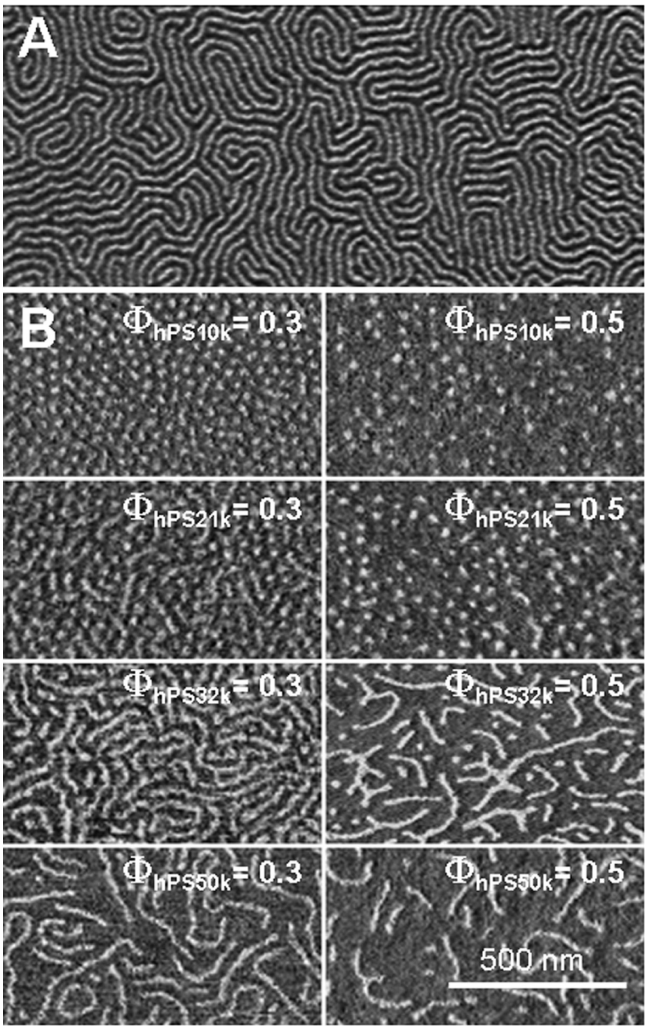


Figure 2. AFM phase images of PS-*b*-PMMA (A) and hPS/PS-*b*-PMMA blends with varying hPS molecular weights and weight fractions (B).

weight fractions (Φ_{hPS} = 0.3 and Φ_{hPS} = 0.5) (Figure 2). Similar molecular weight dependence was observed in our control experiments as the phenomena observed in the bulk[2] and therefore, similar arguments can be used to explain the thin film morphologies in our control and tetra-urea PS blends. When 10 kg/mol hPS was combined with PS-*b*-PMMA (r < 1), the homopolymers were observed to be relatively homogeneously distributed within the polystyrene domain of the block copolymer. Perpendicular cylinders (Φ_{hPS} = 0.3) or cylinder/sphere mixtures (Φ_{hPS} = 0.5) occur as a result of the increased interfacial curvature caused by the homopolymer. A blend of 20 kg/mol hPS and PS-b-PMMA ($r \sim 1$) was found to generate perpendicular cylinder/lamellae mixtures at Φ_{hPS} = 0.3 and cylinder/sphere mixtures at Φ_{hPS} = 0.5. The presence of some lamellar domains at Φ_{hPS} = 0.3 indicates that 20 kg/mol hPS is slightly more localized away from the PS-*b*-PMMA interface compared to the 10 kg/mol hPS in its blend.

When the molecular weight of the hPS was increased to a slightly higher 32 kg/mol (r > 1), the hPS was even more localized and resulted in perpendicular lamellar structures of periodicity of 42.8 nm with broad dimensional variation with a standard deviation of 7.2 nm (measured from the peak in 2D FFT of the corresponding AFM image.) The large increase in the lamellar periodicity from the parent diblock and significant dimensional variation suggest that 32 kg/mol hPS is highly localized at the center of the PS domains and perturbs the regularity of

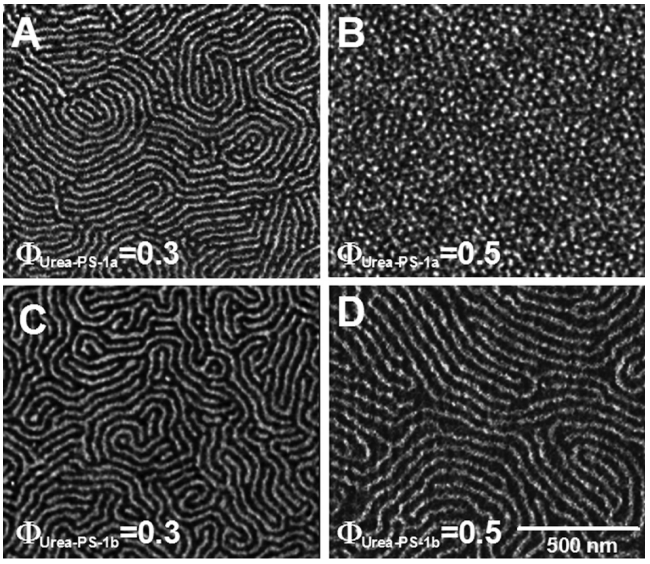


Figure 3. AFM phase images of tetra-urea **1a** (A and B) or **1b** (C and D) blended with PS-*b*-PMMA with varying weight fractions of the hydrogen bonding polymer.

coassembling structure. With higher fraction (Φ_{hPS} = 0.5) or higher molecular weight of hompolymer (such as 50 and 200 kg/mol hPSs ($r \gg 1$)), drastic segregation of hPS from the block copolymer was observed, as shown by the loss of the spatial correlation between microdomains. Therefore, it is difficult to use linear hPS to generate well-controlled asymmetric lamellae morphology with a wide range of tunability.

The intermolecular hydrogen bonding interactions among tetra-urea PS polymers manifested itself during the coassembly of tetra-urea **1a** or **1b** with PS-*b*-PMMA. Blends comprised of 30 wt % tetra-urea PS (either **1a** or **1b**) and 70 wt % PS-*b*-PMMA (Figure 3A,C) ($\Phi_{tetra\text{-}urea\ PS}$ = 0.3) formed well-organized lamellar structures in the thin film. In comparison, the hPS/PS-*b*-PMMA blend compositions wherein the hPS is 10 kg/mol or 21 kg/mol produce cylindrical structures, indicating that the tetra-urea PS in the blend compositions with PS-*b*-PMMA is more localized and causes less interfacial curvature. The architecture of the tetra-urea aggregate likely reduces the miscibility between the tetra-ureaPS and the PS domains of the block copolymers without leading to macrophase segregation.[16] As a result, modest increases were observed for the lamellar periodicity from 33.5 nm (for PS-*b*-PMMA) to 36.2 nm (for **1a**) or 40.8 nm (for **1b**). The localization of the hydrogen bonding polymers within the blend does not appear to lead to complete segregation of the tetra-urea polymers from the PS component of the diblock copolymer. At the same blending ratio, the 2D power spectrum densities of Figure 3A,C give much sharper peaks with a third of the standard deviation obtained from the blend of 32 kg/mol hPS/PS-*b*-PMMA, indicating that the lamellae from the tetra-urea PS are more regular than the lamellae from 32 kg/mol hPS/PS-*b*-PMMA blend. In addition, hPS polymers with 50 kg/mol molecular weight was macrophase segregated at the same blending ratio. Thus, although the tetra-urea **1a** and **1b** can self-assemble into supramolecular arrays via intermolecular hydrogen bonds, the aggregates that are formed do not behave equivalently to high molecular weight PS.

Blend compositions of tetra-urea **1a** with PS-*b*-PMMA with $\Phi_{tetra\text{-}urea\ PS}$ = 0.5 resulted in perpendicular cylinders (Figure 3B) while tetra-urea **1b**/PS-*b*-PMMA blends yielded well-organized perpendicular lamellae structures with a periodicity of 50.8 nm (Figure 3D). In contrast, there was no well-organized structure from any of the hPS/PS-*b*-PMMA blends at Φ_{hPS} = 0.5. Although it is difficult to identify the exact architecture of the tetra-urea aggregate, it is possible that a short comblike

configuration with a semirigid urea-bonding backbone is formed as a consequence of the directional and cooperative hydrogen bonding interactions. Such connectivity among the tetra-urea polystyrene would reduce the penetration of its PS chains into the block copolymer and therefore reduce its miscibility with the corresponding PS domain of the block copolymer. On the other hand, no macrophase segregation of tetra-urea PS from the PS-PMMA block copolymers was observed, even though the aggregate may have a relatively high molecular weight and higher immiscibility. A possible explanation may be that both the PS block of the copolymer and the PS chains of the tetra-urea-PS could have partial brushlike character; the copolymer chains are "grafted" to the PS-PMMA interface while the tetra-urea PS chains are grafted to a core formed from the hydrogen bonded urea groups. In the case of two opposed identical brushes separated by mobile homopolymer, Matsen and Gardiner have predicted a preference for the brushes to be separated by a fixed distance rather than undergo macrophase separation.[17] A simple interpretation is that the entropy gain from macrophase segregation of the tetra-urea aggregate is much smaller than the entropy gain for the linear homopolymer. Having a unique combination of low-miscibility and low-phase segregation propensity, these hydrogen bonding mediated polymer additives offer an interesting and distinct blend behavior.

In conclusion, the regular structures observed in tetra-urea PS/PS-*b*-PMMA blend compositions (relative to the non-hydrogen bonding blends) suggest that the supramolecular assembly formed from the hydrogen-bonding polymers provides unique tunability of domain dimensions of the thin film which is difficult to achieve by typical linear PS homopolymers. The hydrogen bonding polymer was localized within the PS domain of the diblock copolymer (whereas low molecular weight PS is more delocalized throughout the PS domain), yet did not entirely segregate (as has been observed for high molecular weight PS). Thus, the architecture of the supramolecular assembly appears to have an impact upon the miscibility of the assembly with the PS domain. The tunability of this system, in addition to the short thin film annealing times, lends itself for use in block copolymer lithography applications for semiconductors.

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Supporting Information Available: Details of the synthesis and characterization of the polymers is provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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