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Self assembly using block copolymers enables the formation of nanoscale patterns necessary for future technologies. Herein, we describe the blending of hydrogen bonding polystyrene polymers with polystyrene-*b*-polymethylmethacrylate and the resulting thin film morphologies. The hydrogen bonding polymer is comprised of a tetra-urea segment at its midpoint, which is capable of forming linear hydrogen bonding arrays. When this polymer was blended with PS-*b*-PMMA, the tetra-urea polymer was observed to be compatibilized with the PS component of the diblock copolymer. Moreover, highly regular cylindrical or lamellar structures were observed in their thin films. The polymer blends showed unique tunability of domain dimensions which could be useful for block copolymer lithography applications.

Block copolymers self assemble into a range of morphological structures 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 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 coworkers^X 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 utilized⁴⁻⁷ a few well-defined molecular interactions to control the assembly of synthetic macromolecules, including block copolymers. For example, several research groups have employed ionic functionalities^{5,6} at specific locations within a block copolymer to alter its bulk morphological structures. Wiesner and coworkers,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. demonstrated⁷ 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 groups⁸⁻¹⁰ have utilized hydrogen bonding arrays of ureas to afford materials with unique properties. Bis urea-based supramolecular polymers are known to form anisotropic rods in a highly cooperative manner.^{9,10} Meijer and Sijbesma¹⁰ 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 temperatures¹² (>200 °C) required for fast thin film annealing times. 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^{RR} and reacted with sodium azide to obtain azide end-functional polystyrene **2** (Scheme 1).^{QQ} 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 FTIR spectrum. Polymer **2** was reduced in the presence of ammonium formate and Pd/C to obtain the amine end-functional PS **3**. This 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**. **One equivalent of ethylenediamine was reacted with** polymer 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 24.0 and 13.0 kg/mol, respectively.

In order to process PS-*b*-PMMA on a time-scale suitable for semiconductor manufacturing, the block copolymer must be annealed within minutes at elevated temperatures. Infrared spectroscopy was employed in order to observe the stability of the tetra-urea segment at 240 °C over time. It has been previously reported by Versteegen et al. that polymers with three to four urea groups do not flow below 200 °C.^{10b} Urea groups have a reported onset of decomposition of 200 °C.¹³ FT-IR experiments were utilized to observe changes to the N-H vibration band for tetra-urea polymer **1a** exposed at 240 °C for two, 10, and 15 minutes. The FT-IR spectrum (Supporting Information) 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 minutes showed a significant change in the spectra for N-H vibration frequency region. The peak intensity was significantly reduced after heating for 10 minutes where as it was completely absent for the sample heated for 15 minutes, 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 it can be concluded that 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.

In general, blending of homopolymers with block copolymers provides a simple way to access a variety of morphologies. 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 (1.5 wt%) 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 was cast onto neutral substrates and baked at 240 °C for 2 minutes to generate vertically oriented self-assembled domains. As shown in Figure 3a, the PS-*b*-PMMA diblock copolymer formed vertically oriented lamellae with a pitch of 33.5nm.

Blend morphologies of homopolymer/diblock copolymer mixtures have been reported for polymer compositions in the bulk[Hashimoto 1990, Winey 1991], thin film[Mayes 1992, Jeong 2003, Liu 2009], and confined geometry[Tanaka 2009]. Domain spacing and morphology have been used to characterize the distribution of the homopolymer with respect to its complementary component of the diblock copolymer. The homopolymer miscibility with the corresponding polymer block, which is derived from the homopolymer molecular weight, has been correlated to the observed morphologies. Low molecular weight homopolymers are solubilized homogeneously within the corresponding phase of the block copolymer (Figure 1b). As a result, the homopolymers cause lateral expansion of the domain which ultimately causes changes in the observed morphology. When the homopolymer molecular weight

increases, the concentration of the homopolymer near the block interface decreases, as the polymer becomes more localized toward the center of the microdomains. The unfavorable entropy of mixing between high molecular weight polymer and the corresponding polymer block results in the segregation of the homopolymer, and a greater axial expansion (Figure 1c).

We performed a series of control experiments to understand the effect of introducing hPS with PS-*b*-PMMA. hPS with molecular weights 10 kg/mol, 21 kg/mol, 32 kg/mol, 50 kg/mol and 200 kg/mol were combined with PS-*b*-PMMA to form polymer blends with two different hPS weight fractions ($\Phi_{\text{hPS}} = 0.3$ and $\Phi_{\text{hPS}} = 0.5$) (Figure 2). When 10 kg/mol and 21 kg/mol hPSs were combined with PS-*b*-PMMA, the homopolymers were observed to be homogeneously distributed within the polystyrene domain of the block copolymer. Moreover, these hPS blends resulted in either perpendicular cylinders ($\Phi_{\text{hPS}} = 0.3$) or cylinder/sphere mixtures ($\Phi_{\text{hPS}} = 0.5$). When the molecular weight of the hPS was increased to a slightly higher molecular weight (32 kg/mol), the hPS was distributed less homogeneously and resulted in perpendicular lamellar structures with broad dimensional variation and an average periodicity of 44.5 nm. The 50 kg/mol and 200 kg/mol hPSs were observed to drastically segregate from the block copolymer microdomains and therefore yielded micellar block copolymer structures. These results are consistent with the molecular weight dependence that has previously been observed.

The intermolecular hydrogen bonding interactions among tetra-urea PS polymers manifested itself during the co-assembly 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 and 3C) ($\Phi_{\text{tetra-urea PS}} = 0.3$) formed well organized lamellae structures in the thin film. Thus, in comparison to the hPS/PS-*b*-PMMA blend compositions wherein the hPS is 10 kg/mol or 21 kg/mol (which afforded cylindrical structures), the distribution of the tetra-urea PS in the blend compositions with PS-*b*-PMMA was more localized. The hydrogen bonding interactions between tetra-urea segments likely reduces the penetration tetra-urea PS into the PS domains of the block copolymers. As a result, modest increases in 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. In contrast, hPS polymers with molecular weights >32 kg/mol exhibited larger periodicity and greater irregularity when blended with PS-*b*-PMMA. 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 as high molecular weight PS.

Blend compositions of tetra-urea **1a** with PS-*b*-PMMA with $\Phi_{\text{tetra-urea PS}} = 0.5$ resulted in perpendicular cylinders (Figure 3B and 3D) while tetra-urea **1b**/PS-*b*-PMMA blends yielded well-organized perpendicular lamellae structures with a periodicity of 50.8 nm (Fig 3F). In contrast, there was no well-organized structure from hPS/PS-*b*-PMMA blend compositions at $\Phi_{\text{tetra-urea PS}} = 0.5$. In general, the tetra-urea PSs within its blends with PS-*b*-PMMA remain localized and evenly distributed about the PS domains of PS-*b*-PMMA, while high molecular weight hPS (>21 kg/mol) appear localized, yet segregated from the PS domains of the diblock copolymer.

The highly regular structures observed in tetra-urea PS/PS-*b*-PMMA blend compositions 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 blends of the tetra-urea polymer appear to show behavior that is in between what is observed for blends which include either high or low molecular weight PS homopolymer. 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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FIGURE CAPTIONS

Figure 1. Schematic representations of a) PS-*b*-PMMA, and proposed distribution of b) high molecular weight hPS, c) low molecular weight hPS, and d) tetra-urea PS, within PS-*b*-PMMA.

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

Figure 3. AFM height 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.

SCHEMES

Scheme 1. Synthesis of tetra-urea polystyrenes **1a** and **1b**.

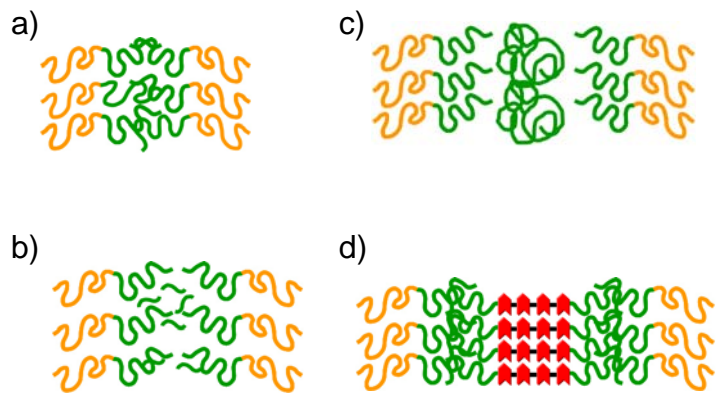


Figure 1

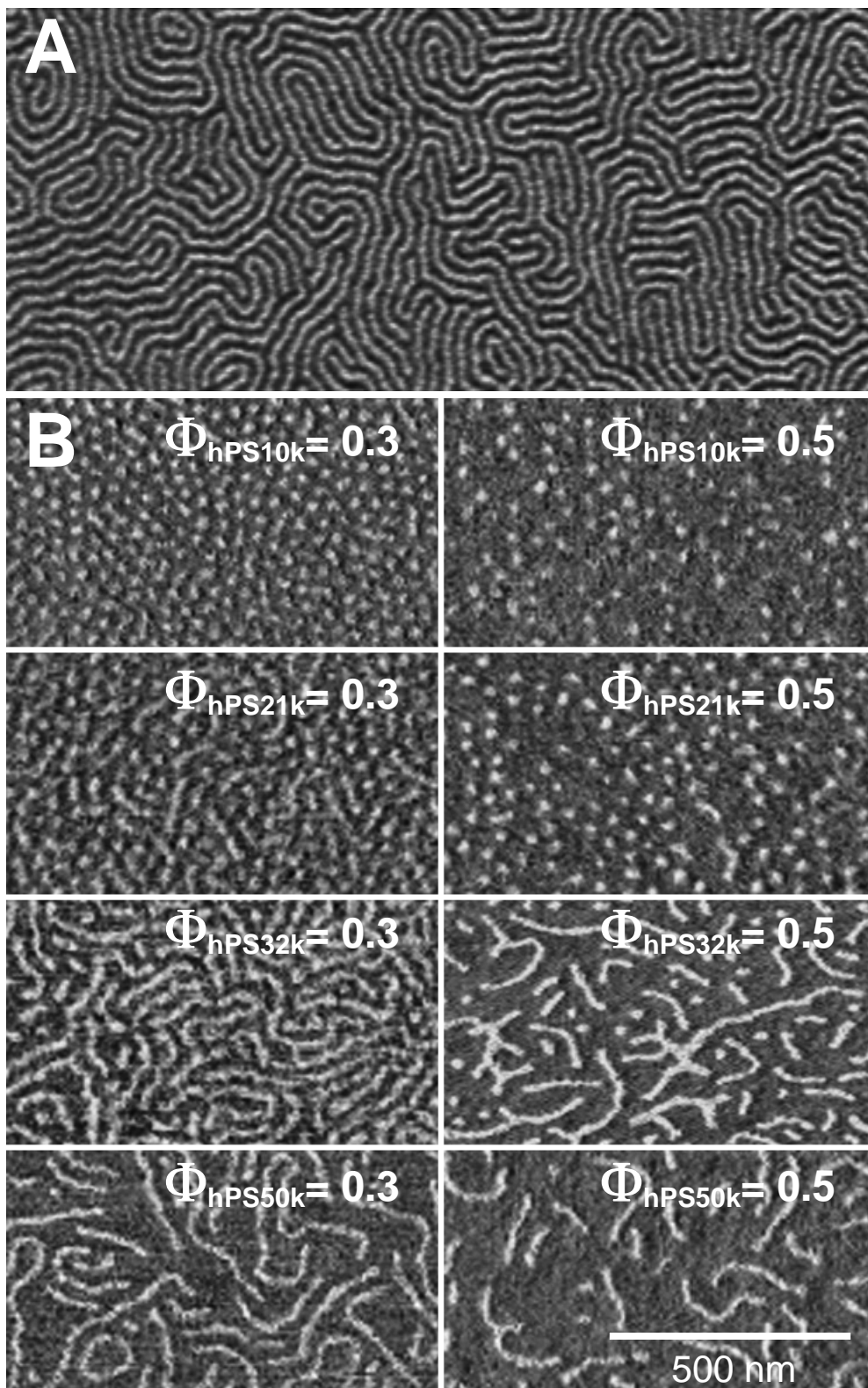


Figure 2

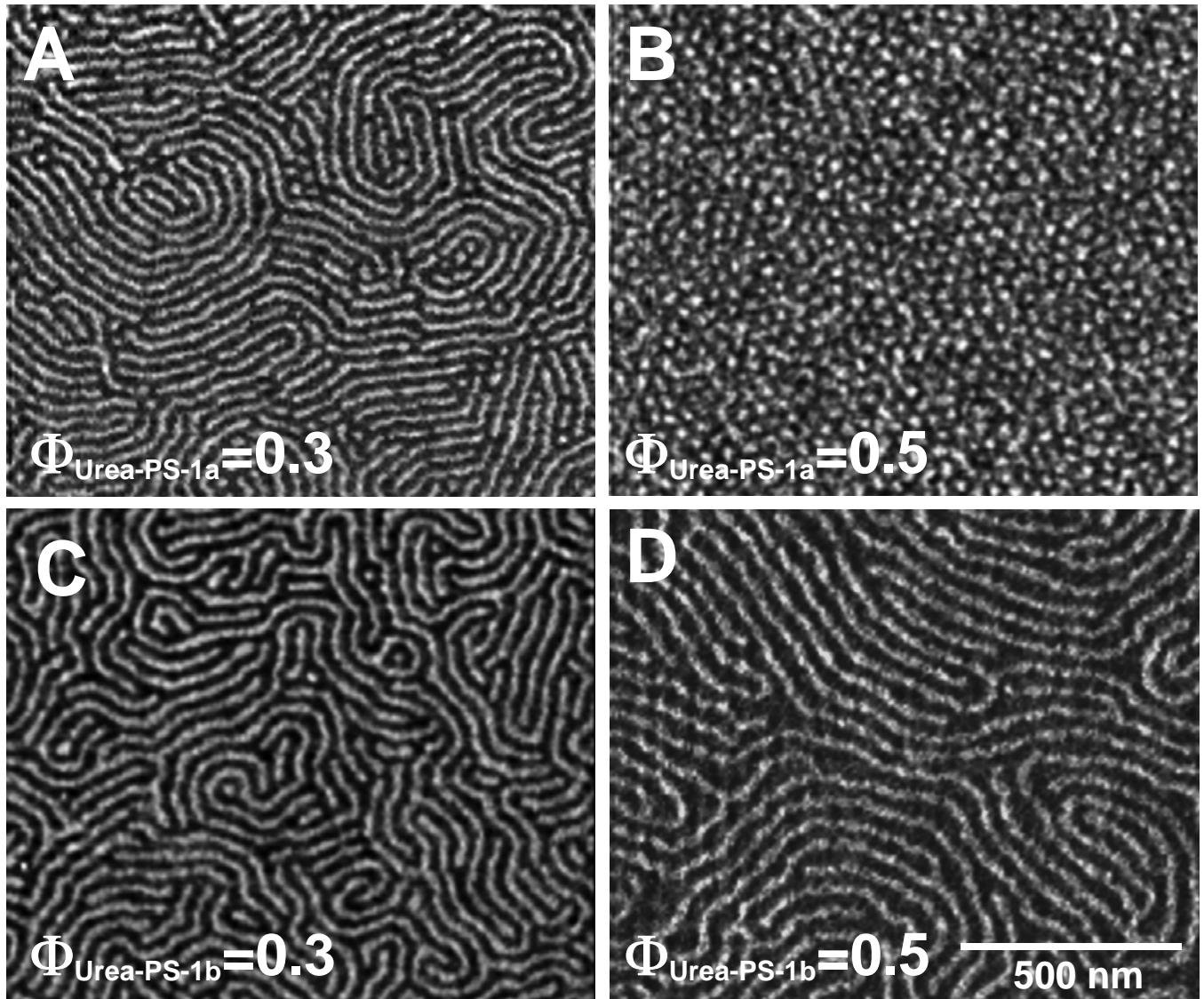
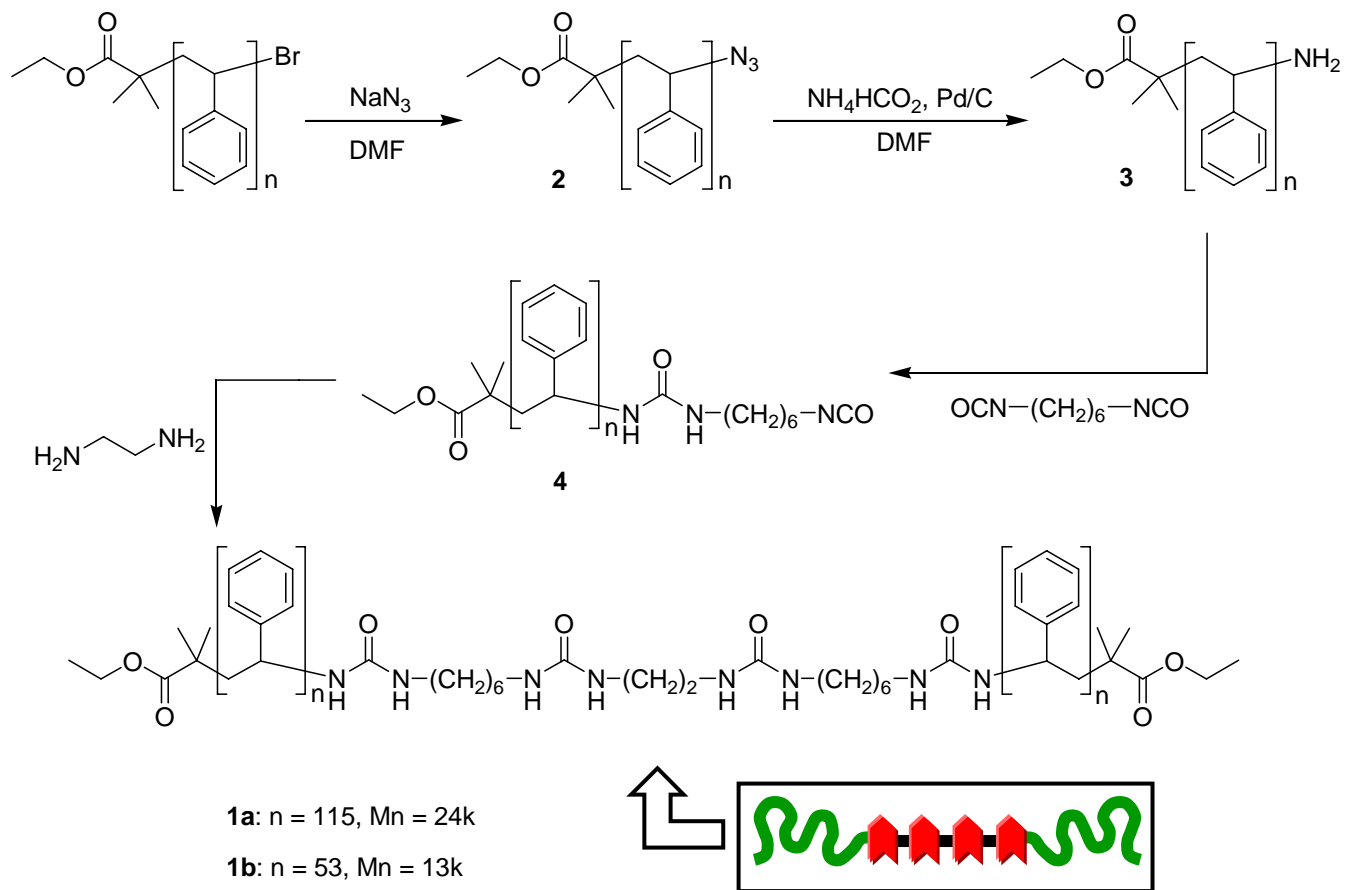


Figure 3



Scheme 1