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NOTE

Disorder-to-Order Transition of Diblock Copolymers Induced by Alkyne/Azide Click Chemistry

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Linear diblock copolymers (BCPs) consist of two chemically different chains, covalently end-linked together. The phase behavior of BCPs is determined by the volume fraction of one block (f) and the product of χN, where χ is the Flory−Huggins segmental parameter and N is the degree of polymerization of the BCP. At low χN, BCPs are phase mixed and, with increasing in χN, the BCP will microphase separate into ordered arrays of lamellar, hexagonally packed cylindrical, or body-centered cubic spherical microdomains or into a bicontinuous gyroid morphology, depending on the volume fraction of the components.[1−3] Thin films of microphase-separated BCPs are being increasingly used as scaffolds and templates for the fabrication of nanostructured materials.[4]

The phase behavior of BCPs can be more complex when mixed with an additive that preferentially interacts with one of the block. Not only will this affect the volume fraction of the components, which can alter the nature of the morphology, but the additive can have a significant effect on χN. This provides a simple route to tune the microphase separation of BCPs. For example, metal ions that selectively coordinate with one block can result in a significant increase in χ and lead to a stronger tendency toward microphase separation.[5−7] Some small molecules can be also selectively incorporated into one block by hydrogen bonding, which not only can induce a transition from disordered state to microphase separation[8,9] but also can give rise to hierarchically ordered morphologies[10−12] due to the ordering of the small molecules within the BCP microdomains.

Here, we report on the incorporation of an additive to one block of a BCP via alkyne/azide click chemistry that can be used to induce a disorder-to-order transition. "Click chemistry" has recently been introduced[13] to develop novel polymeric materials.[14] The most well-known and widely used click chemistry reaction is the "alkyne/azide click chemistry", that is, Huisgen 1,3-dipolar cycloaddition between terminal alkynes and azides to form a 1,2,3-triazole linkage. The reaction can occur at elevated temperature without addition of catalyst and can also be catalyzed by Cu(I) salt at room temperature.[15,16]

We first synthesized a poly(ethylene oxide)-*block*-poly(*n*-butyl methacrylate-*random*-propargyl methacrylate) (PEO-*b*-P(nBMA-*r*-PgMA)) diblock copolymer using atom transfer radical polymerization (ATRP) starting from a PEO macroinitiator (Scheme 1). The use of trimethylsilyl (TMS) groups has been reported by several other groups as an efficient protecting group for the terminal alkyne groups to avoid side reactions during radical polymerization.[17−20] TMS groups were then quantitatively removed by tetrabutylammonium fluoride (TBAF). Gel permeation chromatography (GPC) characterization (Figure S1) showed a shift in the peak of the PEO macroinitiator to a higher molecular weight after polymerization and a polydispersity index of 1.10. The ^{1}H NMR spectrum (Figure S2) further confirmed the chemical structure of the diblock copolymer. The diblock copolymer had a molecular weight of 19 kg/mol for the PEO block and 10 kg/mol for the P(nBMA-*r*-PgMA) block. On average, each polymer chain contained 33 PgMA repeating units. The mole ratio between nBMA and PgMA repeating units was close to their feed ratio, indicating the two monomers have similar reactivity, in agreement with the results of Ladmiral et al.[17]

The bulk morphology of the neat BCP was determined by small-angle X-ray scattering (SAXS) (Figure 1 and Figure S3). SAXS profiles did not show any sharp reflections, suggesting that the BCP was disordered or very weakly ordered over the temperature range investigated. On the contrary, before deprotection of the TMS groups, the diblock copolymer phase separated into a lamellar morphology with a period of 27.0 nm, as seen by SAXS (Figure S4). Such a change in the morphology suggests that miscibility of PEO block and P(nBMA-*r*-PgMA) block may arise from a favorable interaction between PEO block and terminal alkyne groups.

To test the click chemistry reactivity toward azide molecules, rhodamine B azide was synthesized from rhodamine B (Scheme 2) and mixed with the BCP with a mole ratio of 1:1 between PgMA repeating units and rhodamine B azide molecules, i.e., equivalent ratio between the terminal alkyne group and azide group. The BCP and rhodamine B azide were dissolved in dichloromethane at a weight fraction of 5%, drop-cast onto a Kapton film, and annealed at 110 °C under vacuum for 12 h. The SAXS profile of the annealed sample (Figure 1) clearly showed sharp scattering peaks occurring at q values of 0.191 nm^{-1} for the first-order reflection, 0.383 nm^{-1} for the second-order reflection, and 0.750 nm^{-1} for the fourth-order reflection, indicating a lamellar morphology with a domain spacing of 32.9 nm. Infrared spectra (IR) showed that the peak at 2095 cm^{-1}, which corresponds to stretching vibration of azide group, disappeared after annealing (Figure S5). On the other hand, when rhodamine B (no azide functionality) was used, no microphase separation was observed after annealing (Figure 1). Actually, the SAXS profile indicated a macrophase separation between unfunctionalized dye and the BCP. Therefore, we can conclude that the cycloaddition between the terminal alkyne groups and the azide groups occurred during annealing and induced a transition from a disordered state to a microphase-separated state. After the reaction, the rhodamine B group is attached to the side chain of P(nBMA-*r*-PgMA) block via 1,2,3-triazole linkage. Such changes in chemical structure may lead to nonfavorable interactions between the two blocks of modified PEO-*b*-P(nBMA-*r*-PgMA) BCP, resulting in a microphase separation. The volume fraction and chain conformation may also change.

To determine whether the phase transition induced by the alkyne/azide click chemistry can be also observed in thin films, a 0.9 wt % solution of the BCP and rhodamine B azide in a mixture

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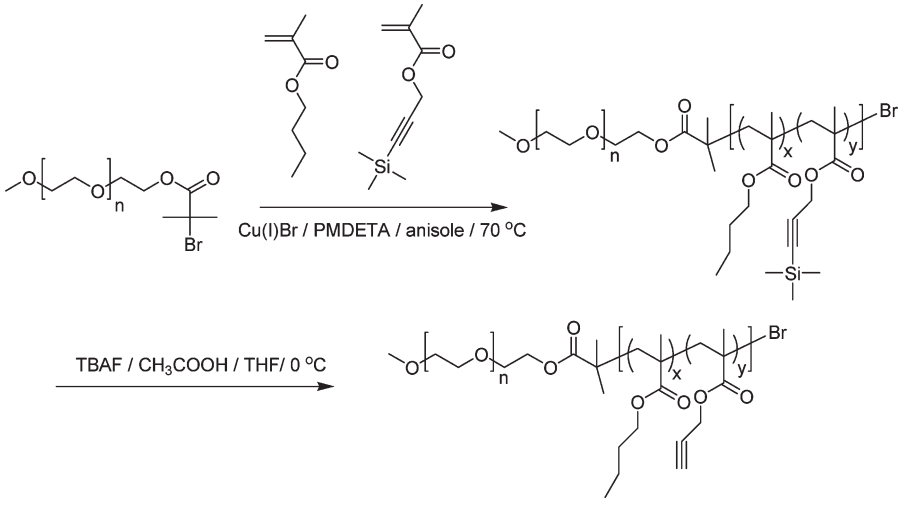
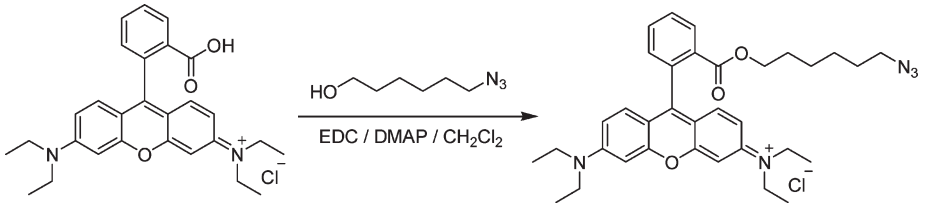
Scheme 1. Synthesis of PEO-*b*-P(nBMA-*r*-PgMA) Diblock Copolymer[a]



[a] Note: PMDETA = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine.

Scheme 2. Synthesis of Rhodamine B Azide[a]



[a] Note: EDC = *N*-(3-(dimethylamino)propyl)-*N′*-ethylcarbodiimide hydrochloride; DMAP = 4-(dimethylamino)pyridine.

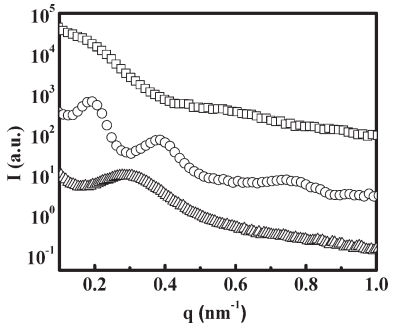


Figure 1. SAXS profiles of neat PEO-*b*-P(nBMA-*r*-PgMA) BCP annealed at 130 °C for 1 day (△); BCP mixed with rhodamine B azide with a 1:1 mole ratio between PgMA repeating units and rhodamine B azide molecules and annealed at 110 °C for 12 h (○); BCP mixed with rhodamine B with a 1:1 mole ratio between PgMA repeating units and rhodamine B molecules and annealed at 110 °C for 12 h (□).

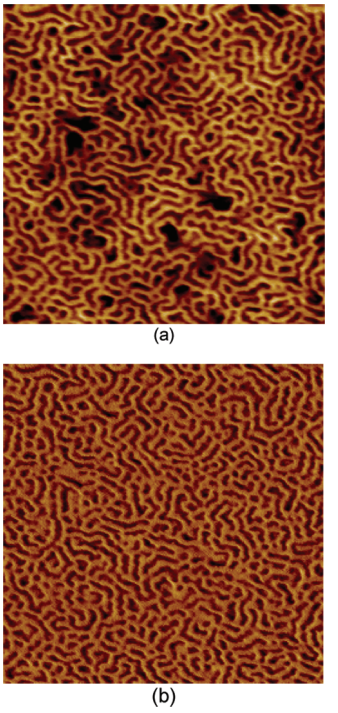


Figure 2. SFM height (a) and phase (b) image of a thin film of PEO-*b*-P(nBMA-*r*-PgMA) mixed with rhodamine B azide with a mole ratio of 1:1 between PgMA repeating units and rhodamine B azide molecules and annealed at 110 °C for 12 h. Scan size is 1 μm × 1 μm.

of benzene and dichloromethane (benzene:dichloroethane = 5:1 by weight) was spin-coated on silicon wafers yielding a 40 nm thick film and annealed at 110 °C under vacuum for 12 h. The mole ratio between PgMA repeating units and rhodamine B azide molecules was 1:1. The surface morphology, shown in Figure 2, was measured by scanning force microscopy (SFM) where a wormlike texture was observed, indicative of a microphase-separated morphology at the surface of the film. Grazing-incidence small-angle X-ray scattering (GISAXS) experiments were performed at an incidence angle of 0.20°, which is above the critical angle of polymer but below the critical angle of Si, allowing the X-ray to penetrate through the film. As can be seen in Figure 3, sharp in-plane reflections were observed at $q_y = \pm 0.17$ nm^{-1}, corresponding to a domain spacing of 37 nm, that were extended along q_z direction. Such "Bragg rod" scattering indicates that the microphase-separated morphology is oriented

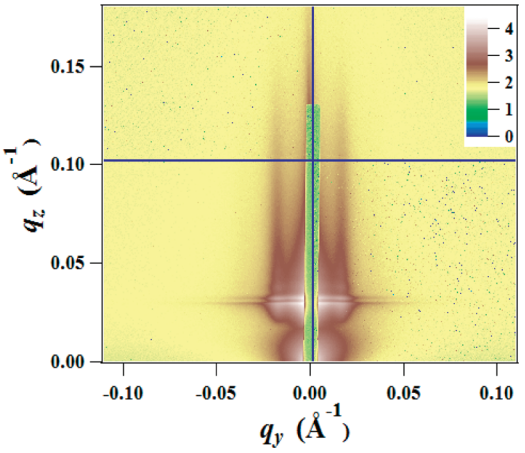


Figure 3. GISAXS pattern of a thin film of PEO-*b*-P(nBMA-*r*-PgMA) mixed with rhodamine B azide with a mole ratio of 1:1 between PgMA repeating units and rhodamine B azide molecules and annealed at 110 °C for 12 h. Incidence angle was 0.20°.

normal to the surface and penetrates through the film. The absence of higher order reflection arises from the lack of long-range ordering, which is consistent with the SFM results in Figure 2. The GISAXS data along with the SFM results are consistent with a lamellar morphology with microdomains perpendicular to the surface and suggest that PEO-*b*-P(nBMA-*r*-PgMA) diblock copolymer can also under go Huisgen 1,3-dipolar cycloaddition with rhodamine B azide in thin films upon heating and form a microphase-separated morphology.

In summary, we have reported a disorder-to-order transition induced by alkyne/azide click chemistry in a binary blend of a BCP with pendant alkyne functionality in one block and azide molecules. Microphase separation in both the bulk and thin films has been confirmed. This phase transition is currently being investigated for use in generating long-range lateral ordering in thin films of BCPs. The mechanism and morphology evolution of such blend system is currently under investigation.

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Supporting Information Available: Synthesis procedure and characterization of the diblock copolymer and rhodamine B azide; *in-situ* SAXS profiles of neat diblock copolymer; SAXS profile of neat diblock copolymer before deprotection of TMS group; IR speactra of binary blend of the diblock copolymer and rhodamine B azide before and after annealing. This material is available free of charge via the Internet at http://pubs.acs.org.

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