Communication

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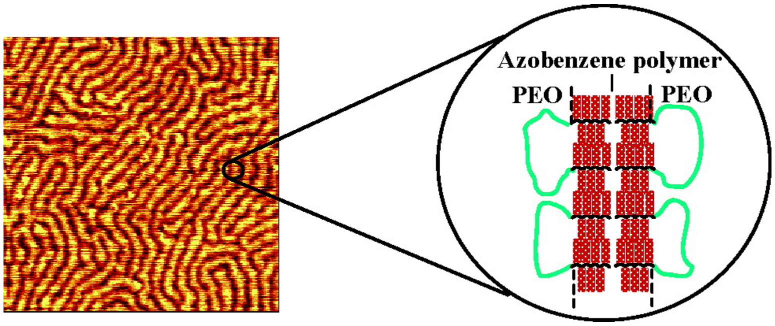

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Photocontrolled Microphase Separation of Block Copolymers in Two Dimensions

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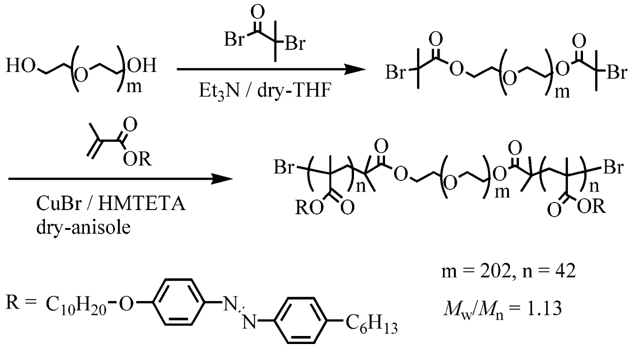
Microphase separation (nanostructure formation) by block copolymers in thin films has been a subject of intensive study from interest in phenomenological aspects of self-assembly in a confined state.[1,2] From practical viewpoints, such nanostructures also have been receiving considerable attention for fabrication of even smaller feature sizes than those obtained by the photolithography process. They have potential applications for high-density data storage media,[3−5] for ultrafine filters or membranes,[6] as templates for metal nanowires,[7] and so forth.

Monolayers prepared by the Langmuir−Blodgett (LB) method are attracting research attention because of the feasibility of precise structure control at molecular levels. Recent developments in visualization of polymer chains or nanopatterns of LB monolayers by atomic force microscopy (AFM) allow many new perspectives in polymer chemistry.[8−14] On an aqueous surface, molecular interactions of polymer chains with water and the intrinsic microphase separation property of block copolymers both play important roles in the evolution of characteristic nanostructures. Block copolymers used in LB studies can be divided into two categories. Polymers connecting a hydrophilic (or polar) block with a hydrophobic one belong to the first category. They form quasi 2D surface micelles or brushes with a 3D-coiled hydrophobic core.[8,13,14] In the second category, the polymers are comprised of polymer blocks having polar units in all components. In such cases, "true" 2D microphase separations are formed, maintaining the monolayer state of the polymer chain.[9] The chain extension and the phase-separated domain size can be discussed on the basis of the scaling theory in the 2D state.[9,10,15]

In the monolayers on water, the fractional composition of the blocks and surface pressure applied on water are the dominating parameters to control the pattern features.[8,14] To our knowledge, no attempt has been made so far to tune or modify the nanopatterns by light. We have formerly reported the large light-responsive expansion/contraction deformation behavior of a monolayer formed by an azobenzene (Az)-containing amphiphilic polymer, both on water[16] and on a hydrophilic substrate.[17] Inspired by such facts, we attempted to provide photoresponsive properties in an amphiphilic block copolymer. This communication reports the active photocontrol of 2D nanopattern features in the monolayer system of block copolymers.

In this work, a novel ABA-type triblock copolymer, where A and B correspond to azobenzene (Az) containing polymethacrylate and poly(ethylene oxide) (PEO), respectively, was synthesized by atom transfer radical polymerization (ATRP) according to a modified method of Tien et al.[18] An Az-containing methacrylate was polymerized from both ends of a PEO macroinitiator with a number-average weight of 9.0×10^3 (Scheme 1). The polymerization degree (n) estimated from the ^{1}H NMR spectrum was 42, and the polydispersity (M_w/M_n) evaluated from the size exclusion chromatography was 1.13. Ultraviolet (UV) light illumination at 365 nm was performed with a mercury halogen lamp passing through an appropriate optical glass filter.

Scheme 1



Surface pressure versus area ($\pi-A$) isotherms of the polymer, spread from a chloroform solution onto pure water, revealed that the trans-Az gave a pressure lift-off area and limiting area (obtained by extrapolation of the high-pressure limb of the curve to zero pressure) per Az unit at 1.4 and 0.32 nm^2, respectively. The features of the curves can be regarded as the superposition of those for an Az-containing random copolymer[16] and PEO.[19] The additive rule indicates that this ABA block copolymer forms "pure" 2D phase separation without 3D coils.[9] This is reasonably understood from the fact that both blocks possess a polar moiety in the chain. In the cis form (ca. 90% content), the lift-off area per Az unit was expanded to 2.2 nm^2, and no sharp pressure increase upon further compression was observed. Such behavior agrees well with that obtained for a photoresponsive monolayer of an amphiphilic Az random copolymer of poly(vinyl alcohol).[16,17] For this random copolymer, the trans-to-cis photoisomerization of Az induces ca. 3-fold expansion because the Az moiety gets in contact with the water surface due to the increased polarity.

The monolayer was transferred onto a freshly cleaved mica surface by vertical dipping method at 1 mN m^{-1}, and the topographic morphologies were observed by AFM (Seiko SPA400/SPI3800) in the dynamic force mode (Figure 1). As shown, the isomerization state of Az on water led to significant changes in the microphase separation patterns. The morphology in the trans-Az is characterized by a mixture of dot and rod shapes. Apparently, the rod aggregates consist of lined aggregates of dots.

The higher domains should be composed of the Az block, judging from the following facts. (i) The height difference (1.70 ± 0.25 nm) is in good agreement with the height of a monolayer of the identical Az side chain;[17] (ii) the ratio of the area of the higher and lower phases in the AFM image coincides well with that obtained from the $\pi-A$ data on water; and (iii) addition of the PEO homopolymer in the spreading process caused corresponding extensions of the lower flat areas. The Fourier transform of the image provides the width of rods or the diameter of dots to be ca. 30 nm. The length of the width essentially agrees with the double

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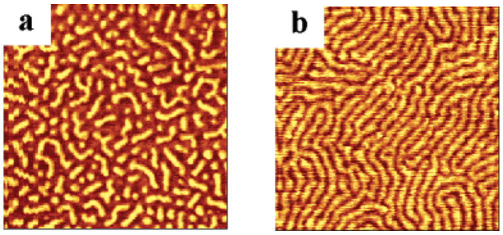

Figure 1. Topological AFM images (1 μm^2 scan) of the monolayer film of the triblock copolymer on mica substrate: trans (a) and cis (b) forms of Az.

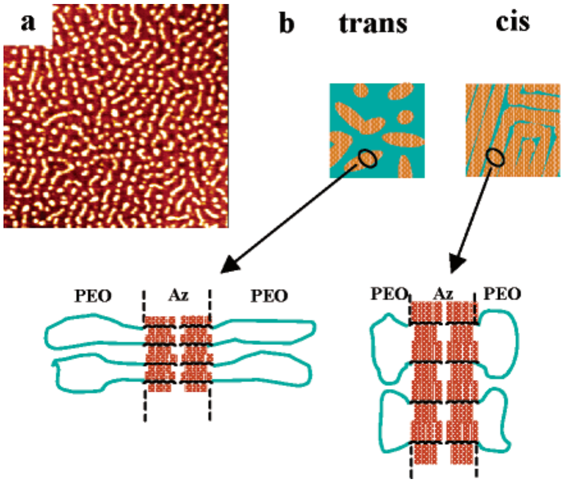

Figure 2. Topological AFM images (1 μm^2 scan) of the monolayer of the triblock copolymer on mica after the cis-to-trans thermal reversion for 6 days, starting from the initial state of Figure 1b (a), and schematic illustration of the packing model of the chain in the 2D state (b). Note that the cis-Az unit is in contact with water and thus occupies a larger area.

length of one-half of the Az block ($n = 42$) in a fully stretched, all-trans zigzag state (22 nm).[20] Thus, the bilayer (rod) or round micelle (dot) should be formed in the monolayer. For the poly(methyl methacrylate)-*block*-poly(octadecyl methacrylate) diblock copolymer, Kumaki indicated that the domain feature size is elongated in the 2D state but is still smaller than that for a fully stretched chain. In the present case, in contrast, the bulky mesogenic unit of Az in the side chain will impede conformational flexibility, leading to the almost fully stretched chain extension.[21] The monolayer in the cis-Az gave characteristic elongated branched flat stripe patterns maintaining the ca. 30 nm widths (Figure 1b). The invariable feature of the width is worth pointing out, which will be discussed below with a packing model. The height difference was significantly reduced to 1.05 ± 0.20 nm, supporting the molecular motion model in the film expansion.[16,17]

The monolayer of the block copolymer in the cis form on a mica surface was allowed to stand at room temperature for 6 days, during which the thermal reversion to the trans form fully proceeds. During this process, the stripe-shaped domains turned into dot structures (Figure 2a). Division of the round domain area by that of the Az unit obtained by the $\pi-A$ data indicates that the smallest dots contain the Az blocks of ca. 30 polymer chains. Formation of dot domains is dominated in this case probably because the Az association is attained from the diluted state of the cis-Az monolayer. Irradiation with 436 nm light from a Hg lamp was performed to allow the cis-to-trans photoisomerization. In such a rapid photoprocess, however, appreciable morphology change was not admitted. The morphology change required that the thermal process spend a time range of days at the ambient atmosphere (ca. 20 °C, relative humidity of 30−40%). An important aspect deduced from the large alternation of the patterns is that the PEO block chain should preferentially adopt flower-micelle-like 2D loop conformations since bridging between Az microdomains by the PEO chain will not cause the drastic morphology change from stripe to dot. The dominant population of loop conformations coincides with the tendency of segregations, rather than interpenetration of polymer chains in the 2D state.[9,15,17,22]

On the basis of all the features indicated above, schematic 2D packing models of the triblock copolymers in the trans and cis form of Az are proposed in Figure 2b. The almost fully stretched polymer chains of the Az block are oriented perpendicular to the domain interface. Thus, upon UV light illumination, the cis-isomerized Az side chains become in contact with the water surface orienting parallel to the interface, resulting in the characteristic anisotropic microdomain expansion parallel to the rod-shaped domain. This behavior is in contrast to the case of the homopolymer, in which only simple 2D-uncontrolled expansions are observed.[16,17]

In conclusion, this work first indicates the active and quasi reversible photocontrol of 2D microphase separation in a monolayer formed by an ABA-type triblock copolymer with an azobenzene in the side chain. We expect that the knowledge obtained here should provide new perspectives for the fundamental understanding of polymer chain behavior in the 2D state and practical nanotechnologies for a phototunable 2D template for material processing.

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Supporting Information Available: Surface pressure−area isotherms. This material is available free of charge via the Internet at http://pubs.acs.org.

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