Photoreactive polymer thin films for controlling nanostrucures

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1. Introduction

Light is of particular use in materials processing. Needless to say, photoresists and photocurable polymer materials are typical well-known examples that are now indispensable and of great demand for industrial products. A recent stream of research attempts to adopt reversible photoreactions (photochromic reactions) which further inscribe the directional information into materials. In the studies of photochromism, it has long been studied for fabrication of photon-mode optical memories and switching of various performances including physical, chemical and biological functions. The versatility of photochromism is rapidly expanding to tune various physical properties and to trigger morphologies of materials.[1]

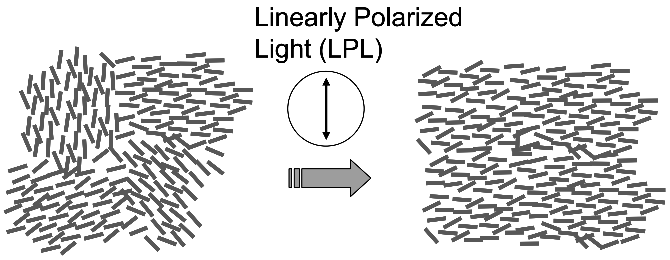


Figure 1. Scheme of photoinduced orientation of LC molecular assemblies by linearly polarized light.

To fabricate systems that effectively recognize directional information of light, design of molecular and polymer assemblies are of particular importance. Such systems include polymeric Langmuir-Blodgett films, self-assembled monolayers, layer-by-layer built up layers, liquid crystals (LCs), crystals microphase separated (MPS) patterns of block copolymers etc. In these frameworks, great efforts have been made to create dynamic photoresponsive functions. Molecular and polymer assembled systems, typically in LC states, exhibit strong cooperative behaviors, leading to fascinating effects including macroscopic photoalignment and various types of motions such as expansion/contraction, bending, mass transport etc. When linearly polarized light (LPL) is irradiated, the photoreacting units show a directionally-selective excitation, which allows the directional alignment of the system from the molecule to larger material scales.[2-4] This process is schematically illustrated in Figure 1. This paper introduces some recent investigations on light-directed dynamic structure formation and alignment of polymer materials confined in two dimensions, mostly in monolayer and thin film states.

2. Photomechanical response of monolayers and application to block copolymers

Poly(vinyl alcohol)s (PVA) possessing an azobnenzene (Az)-containing side chain show large photoinduced area changes on a water surface upon alternative illumination with UV (365 nm) and visible (436 nm) light.[5] In a particular case, the monolayer exhibits ca. 3-fold expansion and contraction by alternating illumination with UV and visible light in a fully reversible manner. This effect can be explained by the polarity change of Az unit as the result of the trans/cis photoisomerization. When the trans-Az is isomerized to the cis form, the increased dipole moment (polarity) allows a contact of the unit onto the water surface. The molecular packing model exactly explains the degree of area changes, indicating that the macrosize effect correctly reflects the molecular events. Atomic force microscopic (AFM) observations indicated actual expansion/contraction behavior at sub-micrometer scales.[6] In-situ X-ray reflectivity (XR) analysis on the water surface by Matsuoka et al.[7] also revealed the actual thickness change on water. Quite recently, Itoh et al. directly evaluated the orientations of the individual chemical bonds of thiis polymer in detail by sum frequency generation spectroscopy.[8]

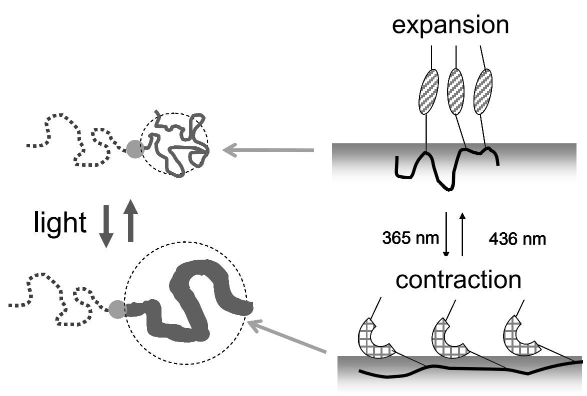
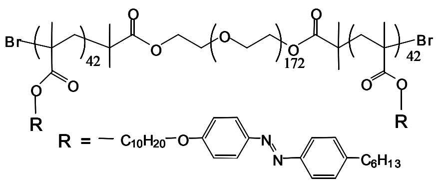


Figure 2. Schematic drawing for the concept to alter 2D MPS structure of a photoresponsive block copolymer monolayer.



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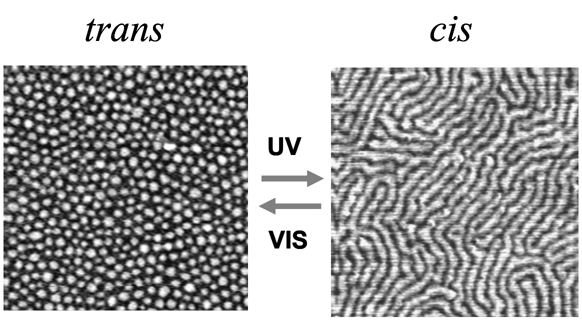


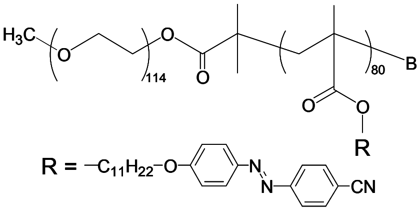
Figure 3. Photocontrolled MPS structure of block copolymer **1** on water. 3 x 3 μm topological AFM images are indicated.

This motion of area change has been applied to bock copolymer systems. It is anticipated that, when one of the blocks is composed of a photoresponsive segment (area variable component), the change in the area fraction of the blocks may alter the microphase separated (MPS) nanostructures formed in the monolayer (Figure 2). Such light induced modulations in the monolayer have been actually attained for a triblock copolymer (**1**) (Figure 3).[9] The trans and cis isomeric states of Az result in dot and strip structures, respectively, of the Az-containing domain in a reversible manner.

This fully tunable behavior of the morphology also provides an important aspect on the chain conformation on water. The middle block of poly(ethylene oxide) (PEO) chain should adopts predominantly loop conformations rather than bridge ones. This fact coincides with the tendency of segregation rather than interpenetration of polymer chains in the 2D state.[10] This morphological change is also observed on a solid substrate of mica surface when a high humidity condition is provided.[11]

3. Photo-controlled macroscopic alignment of microphase separated structures

Many efforts have been made to induce macroscopic alignment of the MRS patterns from viewpoints of new nanotechnologies.[12] When block copolymers with LC nature is employed, the regular MPS structure is formed over large areas by the cooperative effect. The importance of liquid crystallinity for large scale alignment of MPS structure is demonstrated by Iyoda et al.[13]



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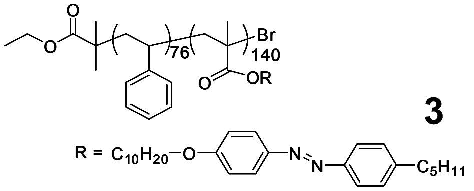

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The obvious effect of LPL irradiation to align MPS in block copolymer films in the in-plane direction is demonstrated for a soft PEO-based Az-containing LC block copolymer film[14] (**2**) and a polystyrene (PS)-based block copolymers[15] possessing higher T_g (**3**) (Figure 4). The MPS structure of nanocylinders of the light-inert blocks aligned orthogonal to the direction of the electric field vector of the irradiated LPL. The normally oriented nanocylinder in the initial state can be changed to an in-plane direction orthogonal to LPL direction. This direction can be further altered to another in-plane direction corresponding to the subsequent illumination of LPL. Irradiation with a non-polarized light in the normal incidence leads to a normal orientation of the cylinders again. These alignments are inter-convertible (Figure 5). For a rigid segment polymer of **3**, an adjustment of annealing temperature is an important factor for the successful alignment. The macroscopically aligned MPS structure evolves at an annealing temperature slightly above T_g of PS block and below the smectic to isotropic transition of the LC Az polymer block. It is to be noted that the MPS alignment can be successively altered on-demand both in the in-plane and out-of plane directions.[15] The requirement of illumination above the order-disorder transition temperature of the block copolymer implies that the erasure of the MPS structure is needed for subsequent evolution of the MPS structure directing another direction. The successful convertible alignment between the in-plane and out-of-plane directions strongly suggests this assumption.

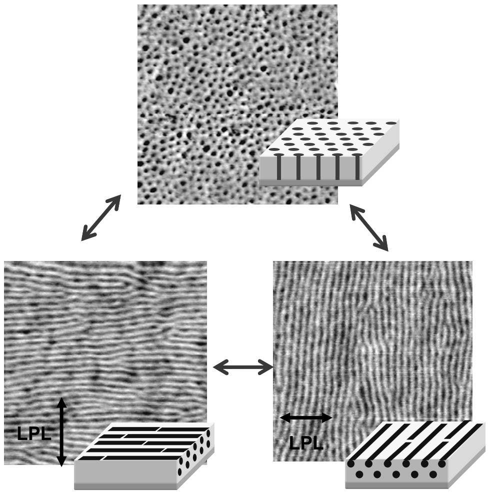

Figure 5. Light-directed orientation changes of MPS nanocylinders of polystyrene in a thin film of **3**. The figures indicate 3 x 3 μm phase mode AFM images. The out-of-plane and in-plane directions are inter-convertible.

4. Inscription of hierarchical structures via photo-triggered mass transfer

Surface relief gratings (SRG, regular topological surface modification) formed via irradiation with an interference pattern of coherent argon ion laser beam (488 or 512 nm) were found about a decade ago[16] and is perhaps the most interesting target in the current research in Az polymers. A great deal of data has been accumulated rapidly due to its basic phenomenological interest and its technological applications.[17] A distinguishing type of photo-activated mass migration systems has been proposed by our group using soft LC polymer systems such as binary component materials and random copolymers containing an oligo(ethylene oxide) (EO) segment.[18] The hybrid films were irradiated with non-polarized UV light in advance to attain a cis-rich photo-equilibrated state (UV light treatment). Starting from this state, an argon ion laser beam (488nm) or a 436 line from a mercury lamp, which induce the isomerization to the trans form, is irradiated to the film. The mass migration is completed at surprisingly small dose levels (<100 mJ cm^{-2}), which is three orders of magnitude smaller than those required for the conventional amorphous polymer systems. A very recent study revealed that the photochemical phase change of the smectic LC to isotropic phase is essential for the migration.[19] Therefore, this class of materials can be dubbed as phase transition (PT)-type.[4]

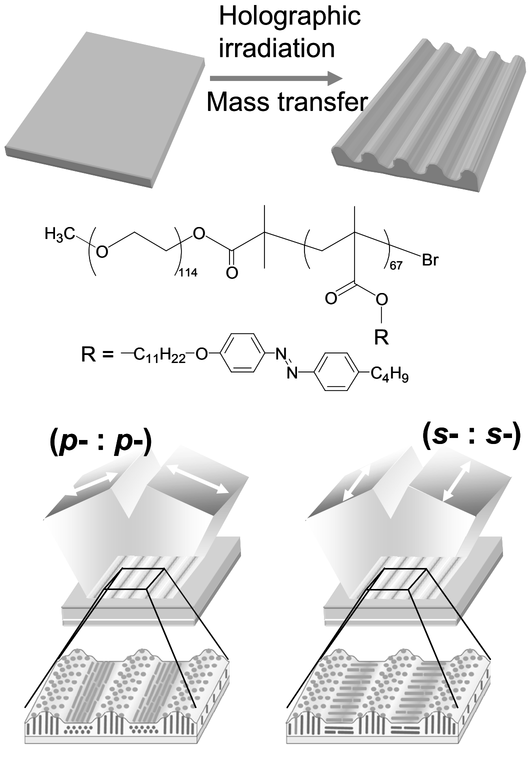

Figure 6. Inscription of hierarchical structures in a block copolymer film via photo-triggered mass transfer (For details see the text).

So far photo-triggered mass migrations have been achieved for homopolymers and random copolymers. Recently a block copolymer has also been subjected to the mass migration process.[20] After the inscription of the relief structure with an interfering laser beam followed by an appropriate annealing procedure, hierarchical structures of MPS and molecular orientations are involved in the resulting film (Figure 6). Two types of holographic irradiation ((*p*-:*p*-) and (*s*-:*s*-)) were performed. When the thickness after the migration is adjusted as to possess thicknesses above and below 70 nm in the thick and thin regions, respectively, the out-of-plane control is achieved, namely the cylinders align normal (thicker area) or parallel (thinner area) to the substrate plane depending on the relief thickness. The difference in the holographic irradiation mode of (*p*-:*p*-) and (*s*-:*s*-) leads to contrasting in-plane orientations of the laid cylinders in the thin areas. The (*p*-:*p*-) and (*s*-:*s*-)

mode interferences provide cylinders oriented parallel and orthogonal to the relief undulations, respectively (Figure 6).

The key for the out-of-plane alignment (whether the cylinders orients normal or parallel to the substrate surface) is the film thickness and that for the in-plane control is the direction of LPL as indicated in the former section. This polymer adopts hexagonally packed PEO cylinders orienting normal to the substrate plane over long distance ranges in thin film due to its liquid crystallinity.[13] However, the nanocylinders orient parallel to the substrate plane when the thickness becomes below 70 nm.[20] It is stressed here that a single irradiation leads to the formation of three different hierarchy levels, namely, the molecular orientation (nm level), MPS structure (several ten nanometers), and SRG (micrometers).

5. Summary

The importance of photo-assisted material processing is of no doubt in view of versatile applications. However, multiplied information possessed by light is not in a matured stage and there a number issues to be developed. This article introduced some examples may provide new directions for photo-directed processes in the future. The processes utilize both photoreaction and information of directions possessed by light, which is widely investigated for photoalignment of nematic liquid crystals. It is stressed here that the polarized light controls not only the molecular orientations but structures of larger scale structures is also feasible as indicated for block copolymers. We anticipate that the light-directed processes will provide more expanded possibilities and opportunities for future materials processing.

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