Highlight Review

Light-directed Dynamic Structure Formation and Alignment in Photoresponsive Thin Films

Takahiro Seki* and Shusaku Nagano

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Abstract

Light provides practical and versatile tools for structure formation and its tuning of soft materials. This article briefly overviews recent developments of photoalignment and phototuning of nanostructured materials focusing onto the 2D material systems. Two topics are involved; i) phototuning and alignment of microphase-separated nanostructures in block copolymers containing a photoisomerizable unit and ii) photoalignment of organic/silica nanohybrids prepared on a polymer film with photocrosslinkable unit.

♦ *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. Such processes, however, only utilize light excitation to allow a photoreaction without effectively clutching directional information, namely, polarization, propagation direction, coherency, etc., to the material. Furthermore, the processes are of once use. On the other hand, a recent stream of research attempts to adopt reversible photoreactions (photochromic reactions) which further recognize 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 alter various physical properties and to trigger morphologies of materials.[1] Photocrosslinkable compounds are also of significance in addition to photochromic units as will be described in the latter part.

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 behavior, 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 review article 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.

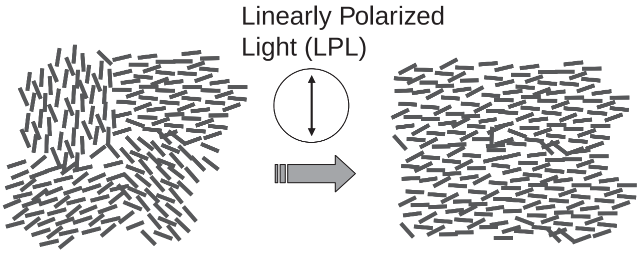


Figure 1. Scheme of photoinduced orientation of LC molecular assemblies by linearly polarized light.

♦ *Photomechanical Response of Monolayers and Application to Block Copolymers*

Poly(vinyl alcohol)s (PVA) possessing an azobenzene (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 this polymer in detail by sum frequency generation spectroscopy.[8]

Prof. Takahiro Seki and Assist. Prof. Shusaku Nagano*
Department of Molecular Design and Engineering, Graduate School of Engineering, Nagoya University,
Chikusa-ku, Nagoya 464-8603
E-mail: tseki@apchem.nagoya-u.ac.jp

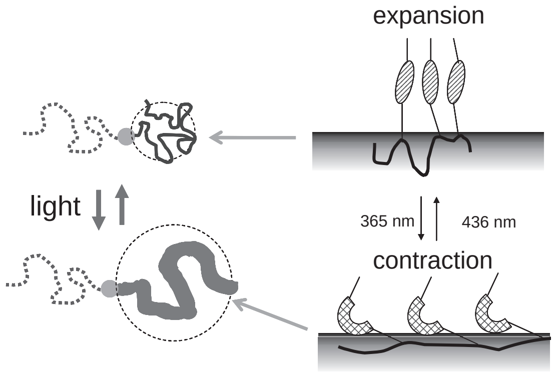
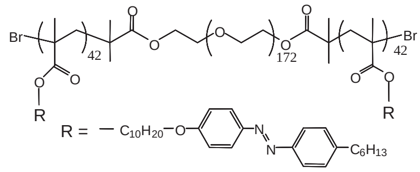


Figure 2. Schematic drawing for the concept to alter 2D MPS structure of a photoresponsive block copolymer monolayer.



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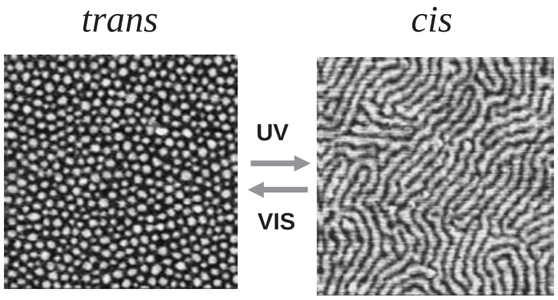

Figure 3. Photocontrolled MPS structure of block copolymer **1** on water. 3 × 3-μm topographical AFM images are indicated.

This motion of area change is applied to block 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]

Photocontrolled Macroscopic Alignment of MPS 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]

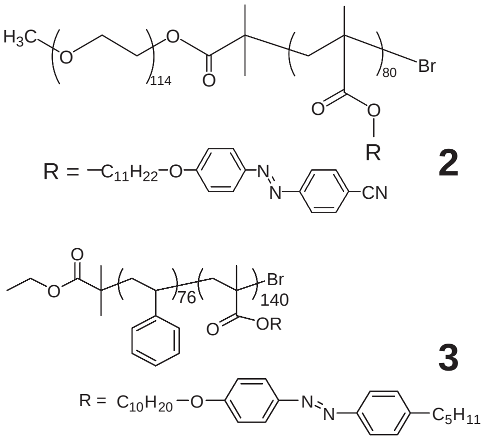

Figure 4. Az-containing block copolymers used for photoalignment of MPS structures.

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 interconvertible (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.

Formation of Hierarchical Structures via Phototriggered 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

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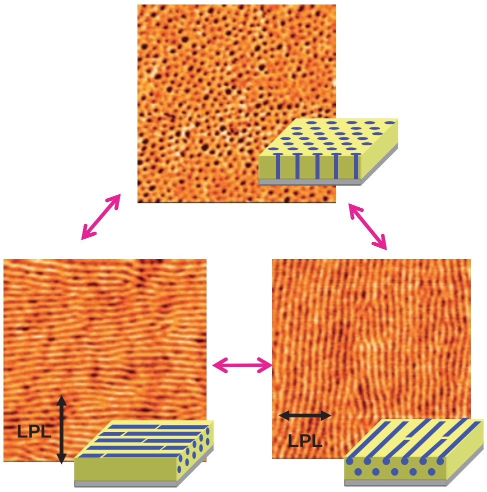

Figure 5. Light-directed orientation changes of MPS nanocylinders of polystyrene in a thin film of **3**. The figures indicate 3 × 3-μm phase mode AFM images. The out-of-plane and in-plane directions are interconvertible.

type of photoactivated 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 nonpolarized UV light in advance to attain a cis-rich photoequilibrated state (UV light treatment). Starting from this state, an argon ion laser beam (488 nm) 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]

So far phototriggered 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).

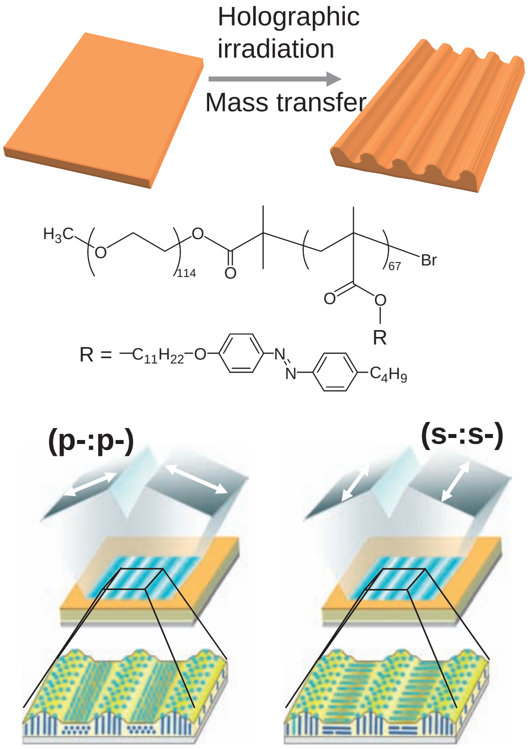

Figure 6. Inscription of hierarchical structures in a block copolymer film via phototriggered mass transfer (For details see the text).

◆ *Photoalignment of Organic/Inorganic Nanohybrids*

A photochoromic and photocrosslinkable polymer films control the alignment of LC materials contacting with the surface. A pioneering work was reported by Ichimura et al. in 1988.[3,21] They showed that the trans/cis photoisomerization reaction of an Az monolayer can reversibly switch the alignment of nematic LCs, and proposed a concept of command surface effect. Recent attempts by Seki et al. revealed that photoalignment of organized materials are not limited to typical thermotropic LCs, but a certain type of polysilane[22] and even an anisotropic structure of inorganic/organic hybrid materials[23–25] are controlled by LPL (Figure 7). The in-plane control utilizes the angular selective reaction of photoreactive units by irradiation with LPL followed by the ordering due to the cooperative self-assembling.[2–4] In this section, some attempts to align organic/silica nanohybrids by using a photoaligning polymer film are introduced.

Defined-sized mesoporous metal oxide materials are synthesized by templating organic molecular assemblies. To date, a

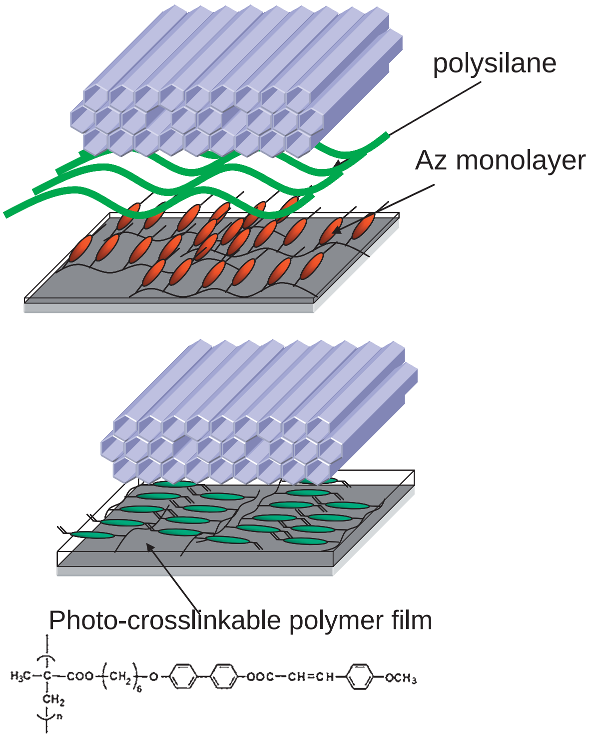

Figure 7. Schematic illustrations of photoaligning systems of surfactant/silica nanohybrids (2D hexagonally mesostructured silica) by using an azobenzene monolayer and a photocrosslinkable LC polymer.

vast number of studies have been undertaken to fabricate mesoporous silica materials[26,27] using various surfactant-templated nanostructures. To attain new functions in optics, molecular electronics, etc., macroscopic uniaxial alignment of the hexagonal columnar mesostructured silica is of importance. In this context, many efforts have been made to align macroscopically the nanohybrids and resulting mesoporous materials by applying external electric[28] and magnetic fields,[29] depositions on rubbed polyimide films,[30] Langmuir–Blodgett films,[31] and incorporation into a porous alumina membrane.[32] Thus, the immobilization of fluid ordered lyotropic liquid crystalline states by the sol–gel condensation processes constitute a central strategy in constructing desired nanostructures.

The photoalignment of surfactant/silica nanohybrid by an Az monolayer is first demonstrated by two-step transfer via photoalignment of polysilane thin film.[23] An alternative simpler way is to use a photocrosslinkable LC polymer film containing a cinnamate unit and a LC mesogen in the side chain.[33] The photocrosslinkable polymer as the alignment layer possesses higher stability against heating and solvent exposure and is more favorable for the fixation of the lyotropic LC state and the siloxane condensation.[24,25] Morphological observations, X-ray diffraction measurements, and transmission electron microscopic observations all indicate that the surface anisotropy imposed by LPL is transferred to the orientation of the rod-like micelle template, therefore, photoaligned mesochannels silica is obtained after removal of the organic component. Interestingly, even when the dip-coating is applied, the channel orientation is predominantly controlled by the direction of photoaligning polymer layer and not by the lifting direction.[25] Thus, the orienting power from the photoaligned polymer film is stronger than that of the flow orientation during the lifting. In a micropatterning experiment, the resolution of ca. 10 μm is obtained.[25]

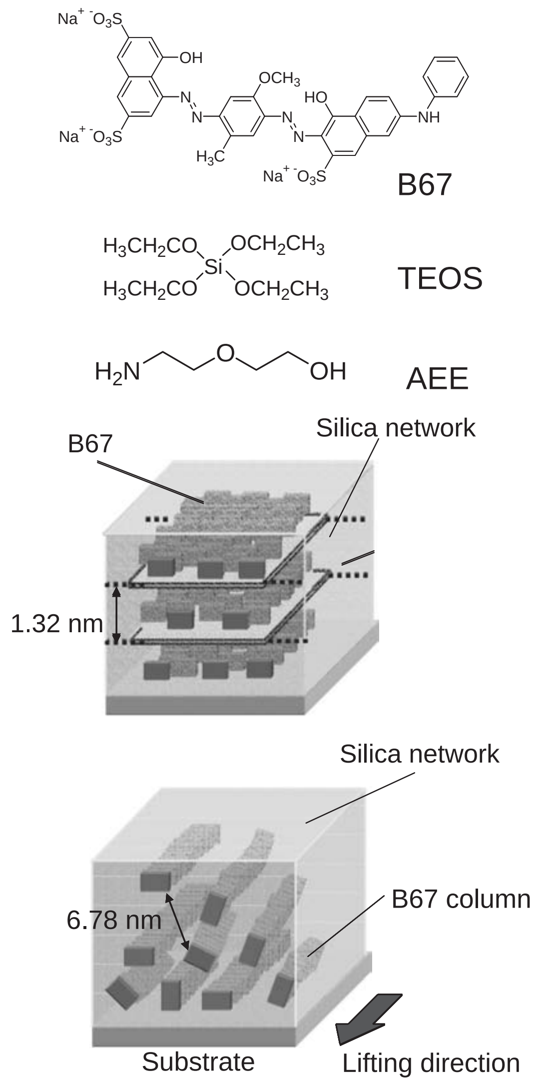

Figure 8. Chemical structure of a chromonic phase forming azo dye (B67) and reagents for silica network formation, and schematic drawings of the B67/dye nanohybrids formed without AEE (upper, lamella structure) and with AEE (lower, column structure).

To date, almost all of the templates employed for these strategies are limited to typical surfactant aggregates of low-molecular-weight surfactants or amphiphilic block copolymers that exhibit the lyotropic liquid crystal nature.[26] A new templating system of chromonic dye aggregates (chromonic lyotropic liquid crystals; chromonic LLCs) is quite recently proposed.[34] The chromonic LLCs are composed of disc-like or plank-like aromatic dye molecules with hydrophilic units at the peripheries, and they can spontaneously self-assemble via π–π stacking interaction and stack face to face to form columnar structures in aqueous solutions.[35] In this paragraph, the first demonstration of the immobilization of columnar structure of the chromonic LLC by formation of silica networks is presented (Figure 8). As a typical example for the chromonic LLC material, C.I.

direct blue 67 (B67) is employed.[36] The resulting hybrid films are found to possess macroscopic in-plane alignment of the chromonic structure when the dipping deposition is adopted.

When the silica network is formed simply from tetraethoxysilane (TEOS), the columnar structure B67 aggregates is transformed to a lamella phase. This can be ascribed to a destabilization of change repulsion between the anionic nature of both B67 and silica surface (silanol groups). The immobilization of the columnar structure is successfully attained when an appropriate mediating molecule, 2-(2-aminoethoxy)ethanol (AEE), is present. This molecule neutralizes the surface anionic charge of the B67 column and adapts the column into the silica network. The significant role of such mediator molecules in the structural stabilization of LLC materials[37] is realized.

A macroscopic uniform in-plane alignment of B67 is attained when the dipping method is applied to prepare the hybrid film. The column orientation is in parallel to the lifting (dipping) direction, namely the dye plane is orthogonal to it.[34] Preliminary experiments have quite recently revealed that the column orientation is also found to be aligned by light on the photocrosslinkable polymer film.[38]

♦ Summary

The importance of photo-assisted material processing is widely recognized in the light of practical applications. However, multiplied information possessed by light (energy, polarization, propagation direction, etc.) is, in general, not effectively utilized. There should remain a number of breakthroughs to be made. This article introduced some examples that may provide new directions for photodirected processes in the future. It is stressed here that the polarized light controls not only the molecular orientations but also the structures of larger scale hierarchies as typically indicated for block copolymers. We anticipate that accumulated efforts in this direction will provide more expanded possibilities and opportunities for future materials processing.

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