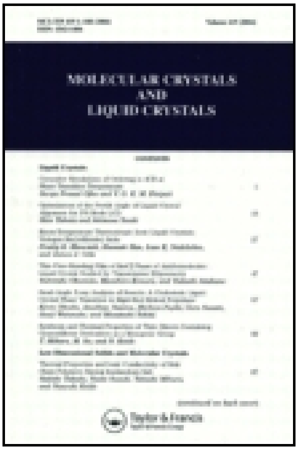


Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Photoresponsive Liquid Crystals for Tuning and Aligning Nanostructures

Takahiro Seki [a], Yuichi Morikawa [a], Takayuki Uekusa [a] & Shusaku Nagano [a]

[a] Department of Molecular Design and Engineering, Graduate School of Engineering, Nagoya University, Chikusa, Nagoya, Japan

Version of record first published: 05 Oct 2009

To cite this article: Takahiro Seki, Yuichi Morikawa, Takayuki Uekusa & Shusaku Nagano (2009): Photoresponsive Liquid Crystals for Tuning and Aligning Nanostructures, Molecular Crystals and Liquid Crystals, 510:1, 21/[1155]-33/[1167]

To link to this article: http://dx.doi.org/10.1080/15421400903057827

Mol. Cryst. Liq. Cryst., Vol. 510, pp. 21/[1155]–33/[1167], 2009
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400903057827

Photoresponsive Liquid Crystals for Tuning and Aligning Nanostructures

Takahiro Seki, Yuichi Morikawa, Takayuki Uekusa, and Shusaku Nagano
Department of Molecular Design and Engineering, Graduate
School of Engineering, Nagoya University, Chikusa, Nagoya, Japan

The photoalignment of liquid crystalline azobenzene-containing polymers has been an active area of research, which intends to apply for optical elements such as rewritable optical memory, photorefractive and photomechanical devices. However, the photoalignment behavior is hardly studied in nano-confined environments. We introduce herein our current activities on the new types of photoalignment controls of azobenzene-containing liquid crystalline polymer materials; (i) polymer chains tethered (grafted) onto a substrate and (ii) nanostructures formed by a block copolymer. New platforms for the photoalignment technologies are anticipated in these photoactive thin film systems.

Keywords: azobenzene; block copolymers; micrcophase separation; molecular orientation; surface-grafted polymer

I. INTRODUCTION

Research on photoresponsive molecules and materials based on introduction of a photochromic unit has been a very active area in materials chemistry. It has long been studied for fabrication of photon-mode optical memories and switching of various performances including physical, chemical and biological functions. To alter various physical properties, photochromic units, most typically azobenzene (Az), have been widely employed [1,2]. The structure and property of

---

This work was supported by the Grant-In-Aid for the priority areas “New Frontiers in Photochromism (No. 471)” and for Scientific Research B (No. 19050005) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Address correspondence to Takahiro Seki, Department of Molecular Design and Engineering, Graduate School of Engineering, Nagoya University, Chikusa, Nagoya 464-8603, Japan. E-mail: tseki@apchem.nagoya-u.ac.jp

systems are effectively altered in molecular assemblies such as 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. Molecular and polymer assembled systems, typically in LC states, exhibit strong cooperative behaviors, leading to fascinating effects including macroscopic photoorientation. When linearly polarized light (LPL) is irradiated, the photochromic units show a directionally-selective excitation, which allows the directional alignment of the system from molecule to larger scale structures [3–7].

We wish to describe herein our current investigations regarding the photocontrols of structure and orientation of thin polymer films. Photoinduced molecular orientation in LC polymer thin films is well recognized. This paper focuses onto the photoorientation behavior of Az-containing LC polymer film in nano-constrained spaces such as end-grafted LC polymers and block copolymers exhibiting MPS structures.

II. SURFACE-GRAFTED AZ-CONTAINNG LC POLYMER

In recent years, polymer brushes have become fascinating subjects in polymer research. They are defined as dense layers of end-grafted polymer chains confined to a solid surface or interface [8]. Introduction of LC properties into the surface-graft chains seems of great interest in view of fabrication of ‘smart’ responsive surfaces [9,10]. High density and well-defined polymer brushes have been synthesized by utilizing surface-initiated ‘living’ polymerization techniques such as atom transfer radical polymerization (ATRP) [11,12]. Since various functionalized monomers are tolerable in the ATRP method, many types of polymer brushes have been explored introducing the ionic groups [13,14], thermoresponsive molecules [15,16], photofunctional units [17,18], electrochemical units [19], and liquid crystalline groups [20,21]. Such polymer brushes show deviated properties in various aspects such as the thermophysics [22], tribology [23–25], adhesion [26], wettability [27] and crystallization process [28].

Preparation and Structural Properties

We have synthesized LC polymer brushes bearing an Az mesogenic group in side chains by adopting surface-initiated ATRP method [29]. The chemical structure of the polymer is shown in Figure 1. The surface-grafted and free LC polymers of identical chemical structure are termed as **1** and **2**, respectively. The thermal phase transition

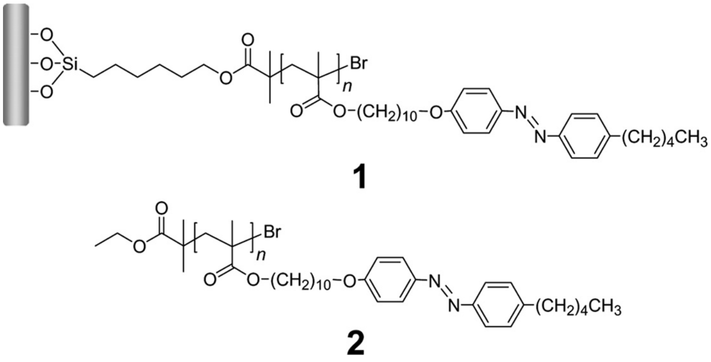


FIGURE 1 Chemical structures of side-chain liquid crystalline polymer brush bearing an azobenzene mesogenic group on a substrate (**1**) and a corresponding free polymer (**2**).

behavior of this polymer was glass-51°C-smectic A-108°C-isotorpic. As described in this section, the polymer brushes **1** have characteristic properties quite different and unpredictable from those of the spincast film of **2**.

Figures 2a and 2b show the UV-visible absorption spectra of the grafted polymer (a) and spincast film (b) on a quartz substrate before and after annealing. Absorption maximum (λ_{max}) of the π–π^* long-axis transition of Az in tetrahydrofuran solution was positioned at 352 nm, whereas that of the grafted polymer showed a peak around 338 nm, indicative of the formation of H-type aggregates of Az units. The molecular orientation of Az units in the side chain can be roughly estimated by the ratio of absorption intensities at the π–π^* to ϕ–ϕ^* band, since the π–π^* transition is directional dependent while the ϕ–ϕ^* transition at 244 nm is insensitive to the chromospheres orientation. For the grafted polymer film, the ratio of $A_{\phi-\phi^*}/A_{\pi-\pi^*}$ was ca. 0.61 and essentially unchanged by annealing. This indicates that the Az units exhibit a homogeneous (parallel) orientation to the substrate. Interestingly, the spectral features were essentially unchanged dipping into organic solvents such as THF and chloroform. Also, the film did not show any de-wetting in the isotropic state, which exhibits a marked contrast from the behavior of the spincast film. This robustness should stem from the covalent anchoring onto the substrate. In sharp contrast, large spectral changes were observed for the spincast film (b) by annealing at 100°C for 2 h. The absorbance of the π–π^* transition band significantly decreased from 0.11 to 0.051 accompanied by a hypsochromic shift from 334 nm to 320 nm. The $A_{\phi-\phi^*}/A_{\pi-\pi^*}$ ratio became

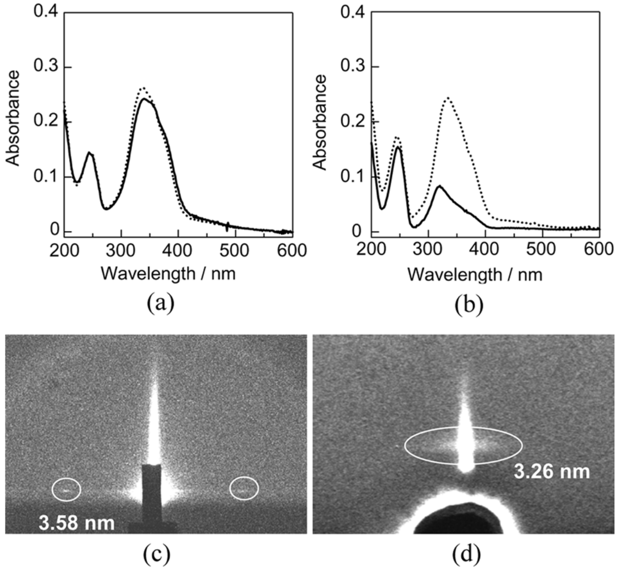


FIGURE 2 UV-vis absorption spectra before (dashed line) and after thermal annealing (solid line) of the grafted polymer film (**1**, a), and spincast film of **2** (b). The thicknesses were 20 nm for both films. The grafted polymer film was prepared on both sides of the substrate. 2D GI-XRD pattern of the grafted polymer film (c) and the spincast films (d) recorded on an imaging plate.

0.71 from 1.85 after this procedure. Thus, stronger H-type aggregation was formed with orientational change to a more perpendicular state to the substrate. Such normal orientation of the mesogenic groups are commonly observed for the spincast films of smectic LC Az polymer.

The LC state and orientation of the mesigonic Az groups in the grafted polymers on the substrate were investigated in more detail by grazing-angle incidence X-ray diffraction (GI-XRD) measurements. Figures 2c and 2d show 2-dimensional XRD profiles of the grafted polymer film and the spincast one recorded on an imaging plate, respectively. An intense comet-tail-like image running orthogonal to the substrate is an artifact of specular reflection. Diffraction patterns were only observed in the in-plane direction, i.e., the periodic structures derived from the smectic LC phase were formed perpendicular to the substrate plane with LC mesogens being aligned parallel to the substrate (c). This result is in agreement with the data indicated by the UV-vis absorption spectra. In-plane orientation of mesogens is often observed in a microphase separated state of LC block copolymers. However in this case, such orientation is observed for the first time in the homopolymer system by grafting from the surface. A clear peak was observed at $2\theta = 2.48^\circ$, which corresponds to a layer spacing of 3.56 nm. This spacing corresponds to a long-range ordering of approximately the length of the fully extended Az side chain suggesting a formation of interdigitated structures of Az side chains. In contrast, a diffraction pattern on the spincast films of **2** was observed only in the out-of-plane direction at $2\theta = 2.73^\circ$ ($d = 3.26$ nm), which is derived from the smectic LC phase (d). Thus, virtually identical smectic structure is formed both in the grafted polymer film and spincast film, only with contrasting orientations.

Photoinduced In-Plane Dichroism

Figure 3 shows polarized UV-vis absorption spectra of **1** and a cast film of **2** (20 nm thickness) before (dotted line) and after irradiation (two

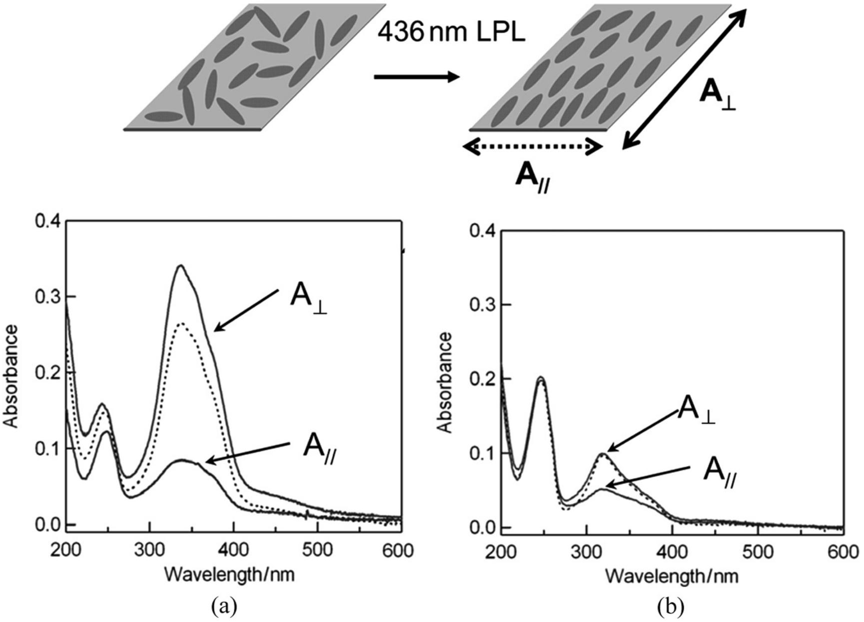


FIGURE 3 Polarized UV–vis absorption spectra of the grafted film of **1** (a) and the spincast film of **2** (b) before and after exposure to LPL at 436 nm at 60°C. Dotted and solid lines are spectra taken with non-polarized beam and polarized ones set perpendicular ($A_\perp$) and parallel ($A_\parallel$) to the actinic LPL at 436 nm, respectively. The film thickness was ca. 20 nm for both cases.

solid lines) with LPL at 436 nm. In both cases, the irradiation was performed at 60°C, namely, a temperature slightly above the glass transition temperature (T_g) of the polymer (51°C). Before irradiation, no in-plane anisotropy was recognized at the macroscopic level of spectroscopic measurements. Probably, the mesogens are aggregated to form a polydomain structure. The absorbance of the π–π^* transition band for the polarized probing light set orthogonal to the electric vector (E) of the actinic LPL ($A_\perp$) became significantly larger than that in parallel direction ($A_\parallel$). The level of photoinduced in-plane optical anisotropy of films was evaluated as the order parameters (S) of the Az in the as following equation, $S = (A_\perp - A_\parallel)/(A_\perp + 2A_\parallel)$, where $A_\perp$ and $A_\parallel$ denote absorbances at $\lambda_{\max}$ (=338 nm) obtained by measurements using polarized light with the electric vectors perpendicular and parallel to that of actinic polarized light. S reached ca. 0.5 (a).

For the spincast film, annealing at the LC temperature also brought about the perpendicular orientation of Az mesogens with respect to the substrate plane, but the dichroic ratio was significantly reduced (b). Since the mesogens were oriented preferentially the out-of-plane direction, LPL irradiation at 465 nm induced only a small degree of in-plane dichroism at the same temperature, 60°C even at an excess exposure dose of 2 J cm^{-2} ($S = 0.24$). In this way, the in-plane (parallel) mesogen orientation for the grafted-p(5Az10MA) enhances the probability of LPL absorption by the Az groups, which will then cause the large in-plane anisotropy.

Photoalignment of the Smectic Layer Structure

As described above, highly ordered photoinduced in-plane orientation of Az mesogenic groups was confirmed. The orientation of smectic LC layers in the film of **1** (20 nm thickness) after exposure to 436 nm LPL was evaluated by GI-XRD measurements. The configuration of the incident X-ray beam and polarized UV-vis spectra were shown in the scheme of Figure 4. The direction of the incident beam are expressed as A and B, which are parallel and orthogonal to the electric vector of the actinic LPL, respectively. Figures 4a and 4b show 2D GI-XRD scattering image of the photoaligned grafted polymer film recorded on an imaging plate in the incident direction of A and B, respectively.

When the incident beam was set in the A direction, diffraction patterns were observed in the in-plane direction as shown with two white arrows (a). Thus, the periodic layer structure of the smectic LC phase was formed perpendicular to the substrate plane with LC Az

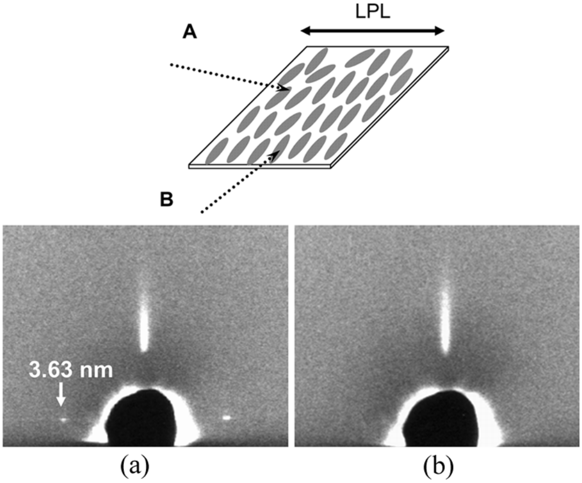


FIGURE 4 Schematic illustration of the incident beam directions, A and B, for the GI-XRD measurements of the grafted film of **1**. 2D GI-XRD patterns of the grafted polymer film recorded on an imaging plate taken with the incident direction A and B are shown in a and b, respectively.

mesogenic groups aligned parallel to the substrate. The mesogen orientation is in agreement with the data of the polarized UV-vis absorption spectroscopy (Fig. 3). The XRD profile monitored in the in-plane direction showed that a peak was observed at $2\theta = 2.43^\circ$, which corresponds to a layer spacing of 3.63 nm. On the other hand, when the X-ray beam was set in the incident direction of B, no diffraction peak was observed in any direction (b). Thus, obvious regular structures derived from the smectic LC layer are not observed in this direction. The above data clearly indicates that not only the Az mesogenic groups are aligned by LPL but the smectic LC layer of the larger assembly hierarchy was also aligned to form a monodomain films over the irradiated area.

In summary of this section, schematic drawings of the molecular and layer orientations of **1** and **2** are displayed in Figure 5. In the above manners, there are essential differences in the degree of in-plane orientational control between the surface-grafted Az polymer film and the spincast one [29]. This fact indicates the significant role of the design of polymer architecture in the film, i.e., free or anchored to the substrate. Since the light irradiation is achieved with normal incidence to the substrate, the surface-grafted Az polymer film becomes much more sensitive to LPL [30].

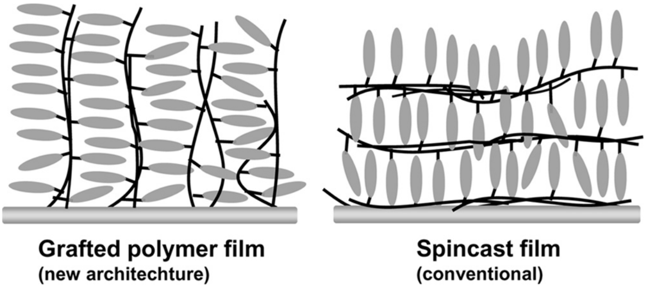


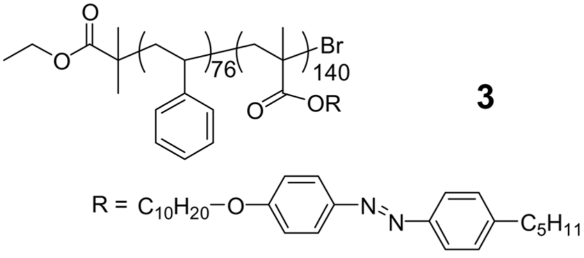
FIGURE 5 Schematic illustration of the orientations of mesogenic Az groups and layer structure in the grafted film of **1** (left) and spincast film of **2** (right).

III. PHOTORESPONSIVE LC BLOCK COPOLYMER SYSTEMS

Microphase separation (MPS) leading to regular patterns at nanometer levels formed by block copolymers in thin films has recently been a subject of intensive study. Such nanostructures allows for fabrication of ever smaller feature sizes than those obtained by the photolithography process, and have potentials for future nanofabrications [31]. Attempts to create active and photocontrollable MPS systems are of fascinating challenge. For practical applications toward nanotechnologies, the MPS structures should be uniformly aligned over large macroscopic areas in the film. However, infant development for large scale alignment of MPS structure and patterning at the present stage has been impeding effective promotions of research. This section introduces our new approaches on the photo-tuning and photoalignment of MPS nanostructures of block copolymers containing a LC Az-containing block.

Many efforts have been made to induce macroscopic alignment of the MRS patterns [32]. 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.* [33].

The obvious effect of LPL irradiation to align MPS in block copolymer films is demonstrated for a soft poly(ethylene oxide)-based Az-containing LC block copolymer film by Yu *et al.* [34] and a polystyrene (PS)-based block copolymers possessing higher T_g (**3**) by us [35]. The structure and the thermal properties of **3** are indicated in Figure 6. The structure of the Az block is the same as that used for the investigation of grafted polymer films described in section II, thus the thermal properties are essentially the same. The polymer **3** forms



3

T_g (PS) = ca. 100 °C

Sm→Iso (Az LC) = ca. 108 °C

FIGURE 6 Chemical structure and thermal transition properties of block copolymer **3**.

a nanocylinder structure in the film. After annealing above 108°C, the nanocylinders adopted an upright orientation with respect to the substrate plane following the orientation of the mesogenic groups of Az. The diameter of the cylinders was 14 ± 1 nm with an average cylinder to cylinder distance of 32 nm. As indicated below, the MPS nanocylinders of the light-inert blocks aligned orthogonal to the direction of the electric field vector of the irradiated LPL. As a rigid segment polymer, an adjustment of annealing temperature is an important factor for the successful alignment.

Figure 7 indicates the AFM images of the surface (phase mode) and spectral data of the film of **3** before and after LPL irradiation performed at room temperature. The spectral data obviously reveal that LPL illumination induces large in-plane anisotropy in the Az mesogen orientation, however, no change in the morphology of MPS was admitted. The cylinder structure was always in the upright orientation. This situation is schematically drawn in the bottom of Figure 7. The Az photoresponsive groups are readily reoriented by LPL, but this orientational change is not reflected to the MPS cylinder structure of the larger size.

Figure 8 indicates the surface morphologies observed by AFM images (phase mode) after LPL irradiation in combination with appropriate heating and annealing treatments. As shown, obvious effects of LPL irradiation on the morphology of MPS were observed, in these cases. Non-irradiated film provided PS cylinders in the upright orientation (a) after annealing. After LPL irradiation, a stripe morphology whose direction was highly controlled orthogonal to the direction of LPL was observed (b). Here, the irradiation was performed during

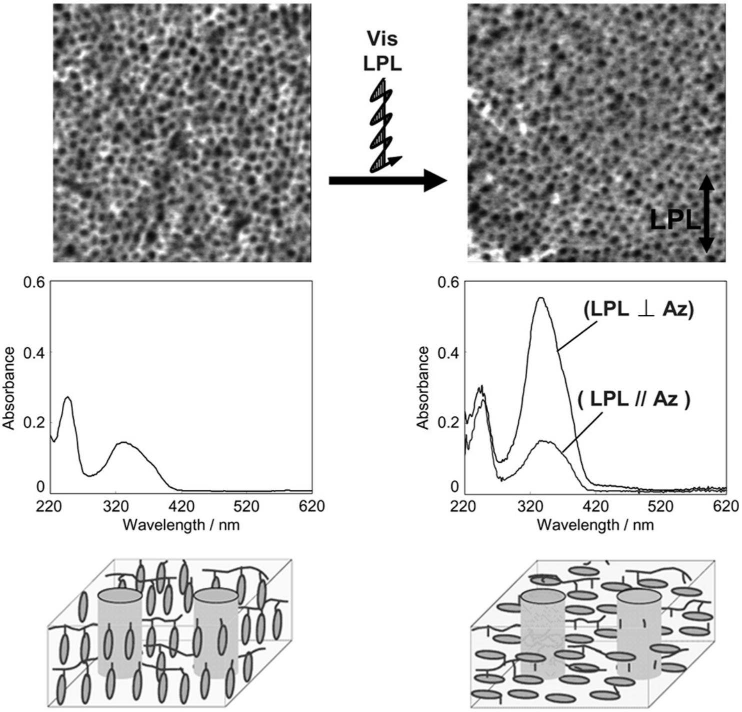


FIGURE 7 Irradiation with LPL to the film of **3** at room temperature. Surface structures observed by AFM (phase mode) (upper) and the polarized UV-vis absorption spectra (middle). Note that only Az mesogenic groups are reoriented and the MPS structure stayed unchanged by LPL irradiation at this temperature. The orientations of the Az mesogens and polystyrene cylinders are schematically illustrated at the bottom.

gradual cooling from 130°C to room temperature followed by annealing at 105°C, a temperature slightly above T_g of polystyrene and below the isotropidization temperature of the Az LC block, for several hours. The line to line distance was 32 nm, which exactly agrees with that evaluated in the upright orientation. Also, the Az group showed a strong in-plane anisotropy with the orientational order parameter of 0.68 (the spectral data not shown). The same procedure was successively performed using LPL set at another angle, orthogonal to the previous irradiation (c). Essentially the same results on the MPS morphology and spectral data were obtained except for the direction of molecular orientation with $S = 0.68$ and MPS morphology. The stripe morphology was turned to the other direction following the direction

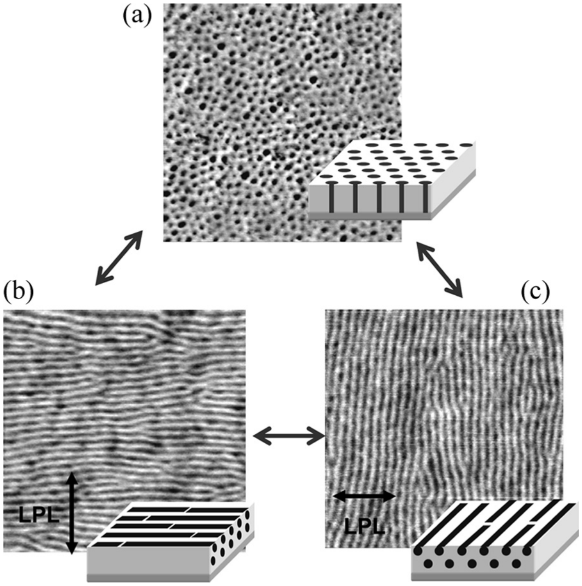


FIGURE 8 Optical orientational controls the mesogenic Az groups and MPS nanocylinder domains of PS in the film of **3** (thickness = ca. 50 nm) evaluated by phase mode AFM. (a) The initial state. (b) After irradiation with LPL (436 nm) accompanied by heating and annealing (for conditions, see the text). (c) Successive irradiation with LPL (436 nm) at the orthogonal polarization angle followed by annealing. These structures and states are convertible with each other.

of the subsequently irradiated LPL (c). The cylinders aligned in the in-plane direction were again reverted to the out-of-plane (normal) mode by irradiation of non-polarized light irradiation in the normal direction (a). The state obtained in the final state virtually exactly coincides with that of the initial state (a). These facts unequivocally indicate that 3D alingnment, namely both in-plane and out-of plane orientational control, of nano cylinder of PS domain is achieved by light.

IV. CONCLUSIONS

In this paper, two topics that are currently undergoing in our group on the photoresponsive thin polymer films are introduced. In the LC molecular and polymer assembly systems, the light trigger is effectively converted to the molecular motions to induce orientation and migration in cooperative manners. Motions are basically driven by thermal self-assembly processes of the soft materials. As demonstrated in the grafted polymer film, the default orientation of Az mesogenic groups provides significant influence in the film structure and the photoresponsive behavior. The surface-grafting strategy largely enhances the in-plane anisotropy and mechanical strength, which will favor the applications for photoresponsive optical elements. With respect to the alignment control of the block copolymer system, it is stressed that the photoalignment is not limited at the molecular level but amplified to regulate the MPS structure of the larger feature size. Understanding the interplay between different size hierarchies with retention of dynamic features should be a significant strategy to create future soft materials. The ultimate goal would be to create sophisticated dynamic 3D systems similar to the biological ones. It is anticipated that studies on the photo-regulated motions of photoresponsive films in new architectures can give proper clues to future directions of research.

REFERENCES

[1] Irie, M. (Ed.). (2000). *Chem. Rev.* (Special issue of Photochromism: Memories and Switches), *100*(5), 1685–1890.

[2] Natansohn, A. & Rochon, P. (2002). *Chem. Rev.*, *102*, 4139.

[3] Ichimura, K. (2000). *Chem. Rev.*, *100*, 1847.

[4] Seki, T. (2004). *Polym. J.*, *36*, 435.

[5] Seki, T. (2007). *Bull. Chem. Soc. Jpn.*, *80*, 2084.

[6] Ikeda, T. (2003). *J. Mater. Chem.*, *13*, 2037.

[7] Ikeda, T., Mamiya, J., & Yu, Y. (2007). *Angew. Chem. Int. Ed.*, *46*, 506.

[8] Advincula, R. C., Brittain, W. J., Caster, K. C., & Rühe, J. (Eds.). (2004). *Polymer Brushes*, Wiley-VCH, Weinheim.

[9] Peng, B., Johannsmann, D., & Rühe, J. (1999). *Macromolecules*, *32*, 6759.

[10] Hamelinck, P. J. & Huck, W. T. S. (2005). *J. Mater. Chem.*, *15*, 381.

[11] Tsujii, Y., Ohno, K., Yamamoto, S., Goto, A., & Fukuda, T. (2006). *Adv. Polym. Sci.*, *197*, 1.

[12] Matyjaszewski, K., Miller, P. J., Shukla, N., Immarapom, B., Gelman, A., Luokala, B. B., Siclovan, T. M., Kickelbick, G., Vallant, T., Hoffmann, H., & Pakula, T. (1999). *Macromolecules*, *32*, 8716.

[13] Iwata, R., Suk-In, P., Hoven, V. P., Takahara, A., Akiyoshi, K., & Iwasaki, Y. (2004). *Biomacromolecules*, *5*, 2308.

[14] Feng, W., Brash, J., & Zhu, S. (2004). *J. Polym. Sci. A, Phys. Chem.*, *42*, 2931.

[15] Balamurugan, S., Mendez, S., Balamurugan, S. S., O'Brien, M. J., & López, G. P. (2003). *Langmuir*, *19*, 2545.

[16] Jones, D. M., Smith, J. R., Huck, W. T. S., & Alexander, C. (2002). *Adv. Mater.*, *14*, 1130.

[17] Ito, S., Kuno, J., Yamashita, K., Ohoka, M., Ohkita, H., Tsujii, Y., & Fukuda, T. (2005). *Trans. Mater. Res. Soc. Jpn.*, *30*, 687.

[18] Piech, M. & Bell, N. S. (2006). *Macromolecules*, *39*, 915.

[19] Sakakiyama, T., Ohkita, H., Ohoka, M., Ito, S., Tsujii, Y., & Fukuda, T. (2005). *Chem. Lett.*, *34*, 1366.

[20] Hamelinck, P. J. & Huck, W. T. S. (2005). *J. Mater., Chem.*, *15*, 381.

[21] Westlund, R., Carlmark, A., Hult, A., Malmström, W., & Saez, I. M. (2007). *Soft Matter.*, *3*, 866.

[22] Yamamoto, S., Tsujii, Y., & Fukuda, T. (2002). *Macromolecules*, *35*, 6077.

[23] Yamamoto, S., Ejaz, M., Tsujii, Y., Matsumoto, M., & Fukuda, T. (2000). *Macromolecules*, *33*, 5602.

[24] Yamamoto, S., Ejaz, M., Tsujii, Y., & Fukuda, T. (2000). *Macromolecules*, *33*, 5608.

[25] Sakata, H., Kobayashi, M., Otsuka, H., & Takahara, A. (2005). *Polym. J.*, *37*, 767.

[26] Lin, J. J., Silas, A., Bermudez, H., Milam, V. T., Bates, F. S., & Hammer, D. A. (2004). *Langmuir*, *20*, 5493.

[27] Granville, A. M. & Brittain, W. J. (2004). *Macromol. Rapid Commun.*, *25*, 1298.

[28] Zheng, Y., Bruening, M. L., & Baker, G. L. (2007). *Macromolecules*, *40*, 8212.

[29] Uekusa, T., Nagano, S., & Seki, T. (2007). *Langmuir*, *23*, 4642.

[30] Uekusa, T., Nagano, S., & Seki, T. (2009). *Macromolecules*, *42*, 312.

[31] Lazzari, M., Liu, G. J., & Lecommandoux, S. (Eds.) (2006). *Block Copolymers in Nanoscience*, Wiley-VCH, Weinheim.

[32] Lazzari, M. & De Rosa, C. (2006). Method for the alignment and the large-scale ordering of block copolymer morphologies. In: *Block Copolymers in Nanoscience*, Lazzari, M., Liu, G., & Lecommandoux, S. (eds), Wiley-VCH, Weinheim, 191–231.

[33] Tian, Y., Watanabe, K., Kong, X., Abe, J., & Iyoda, T. (2002). *Macromolecules*, *35*, 3739.

[34] Yu, H. F., Iyoda, T., & Ikeda, T. (2006). *J. Am. Chem. Soc.*, *128*, 11010.

[35] Morikawa, Y., Kondo, T., Nagano, S., & Seki, T. (2007). *Chem. Mater.*, *19*, 1540.