Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

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To cite this article: Takahiro Seki, Kei Fukuhara, Masami Sano, Mitsuo Hara & Shusaku Nagano (2015) Photoalignment of Liquid Crystalline Polymer Films Containing Mesostructures and a Free Surface Command Layer, Molecular Crystals and Liquid Crystals, 614:1, 118-123, DOI: 10.1080/15421406.2015.1050284

To link to this article: http://dx.doi.org/10.1080/15421406.2015.1050284

Published online: 18 Aug 2015.

Mol. Cryst. Liq. Cryst., Vol. 614: pp. 118–123, 2015

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2015.1050284

Photoalignment of Liquid Crystalline Polymer Films Containing Mesostructures and a Free Surface Command Layer

TAKAHIRO SEKI,[1,*] KEI FUKUHARA,[1] MASAMI SANO,[1] MITSUO HARA,[1] AND SHUSAKU NAGANO[2,*]

[1]Department of Molecular Design and Engineering, Graduate School of Engineering, Nagoya UniversityFuro-cho, Chikusa, Nagoya, Japan
[2]Nagoya University Venture Business Laboratory, Nagoya UniversityFuro-cho, Chikusa, Nagoya, Japan

Investigations on the photoaglinment processes of liquid crystalline materials started around 25 years ago, and currently great developments have been made in both academic and industrial areas. However, there remain many issues to be explored in this field. This short review introduces our recent advances regarding the photoalignment and realignment process using azobenzene-containing liquid crystalline polymer materials. Two topics are involved here: the photoalignment of microphase separation structures of block copolymer films, and photoalignment controls from the free surface of a liquid crystalline polymer film.

Keywords azobenzene; photoalignment; mesogen orientations; block copolymers; microphase separated structure; command surface; free surface; inkjet printing

1. Introduction

Ichimura et al. [1] first reported the phenomenon of surface photoalignment in 1988. The homeotropic/planar alignment of nematic liquid crystals (LCs) was switched photochemically by the isomerization of azobenzene on a substrate surface. This photoactive functional surface has been dubbed as a "command surface" or "command layer." Shortly after this finding, Gibbons et al. [2], Dyadyusha et al. [3], and Schadt et al. [4] demonstrated that angular selective in-plane excitation by linearly polarized light (LPL) on an azo dye-doped polyimide or a photocrosslinkable polymer film results in in-plane alignment control. At the same time, Kawanishi et al. [5] also found this effect using an Az self-assembled monolayer. Seki et al. [6, 7] made approaches by Langmuir-Blodgett (LB) technique to obtain precise understandings on the molecular design and packing density effect of the command layer. Since these early works, the photochemical command layer controls have been studied for a variety of systems including discotic LCs, lyotropic chromonic LCs,

*Address correspondence to Takahiro Seki and Shusaku Nagano, Department of Molecular Design and Engineering, Graduate School of Engineering, Nagoya UniversityFuro-cho, Chikusa, Nagoya 464-8603, Japan; Nagoya University Venture Business Laboratory, Nagoya UniversityFuro-cho, Chikusa, Nagoya 464-8603, Japan. E-mail: tseki@apchem.nagoya-u.ac.jp; snagano@apchem.nagoya-u.ac.jp

LC polymers, semiconducting molecules, and mesostructured organic-inorganic hybrids [8]. The overviews and details on photoalighment processes have been summarized in the previous review articles [8–14].

It is noteworthy that the surface photoalignment of nematic LCs on polymer films has recent been adopted in LC display panel production processes [15,16]. As has been revealed, photoalignment processes characterized by non-contact and high resolution processes have great advantages when compared with the conventional rubbing processes.

This short review will focus on our recent advances and extensions of the photoalignment processes. Two topics are involved: photoalignment and realignment of microphase separation (MPS) structure in thin films of Az-containing LC block copolymers, and photoalignment events from the free surface. We anticipate that both systems can indicate new directions in fabrication and device technologies of soft materials.

2. Photoalignment of Block Copolymer Films

Attempts to perform photoalignment of MPS structures in Az LC block copolymer films started in 2006. Yu et al. [17] and Morikawa et al. [18,19] independently manifested the in-plane photoalignment of MPS cylinder morphologies in Az-containing block copolymer films by irradiation with LPL. To minimize the elastic energy, the MPS structure (mostly cylinder domains) aligns parallel with the long axis of photoaligned LC mesogenic groups [8,12,13,20–22].

In a LC Az block copolymer possessing polystyrene (PS) block (PS-*b*-PAz), the cylindrical MPS domain of PS could be altered on-demand both between out-of-plane and in-plane directions [19]. Successful alignment control of PS cylinders could be performed when the film was first heated to 130 °C (above T_g of polystyrene and above the isotropization temperature of PAz), and successively LPL was irradiated with slow cooling via smectic A phase temperatures to room temperature. By heating up to 130 °C, the anisotropic domain formation disappears, and thus a 'reset (initialization)' of the film was attained.

To gain insight into such dynamic events, Nagano et al. [23] conducted synchrotron X-ray measurements to achieve in-situ simultaneous structural evaluations in the course of photoinduced alignment changes of both the Az layer and MPS cylinder morphology. For these experiments, the PBMA-*b*-PAz, (Figure 1) possessing the amorphous polymer block with lower T_g was employed. Unlike other LC block copolymers, this block copolymer persistently exhibited random planar or homogeneous (uniform planar) orientations of the mesogens and MPS cylinders without forming the homeotropic orientation. Owing to this in-plane preference, the alignment switching between the orthogonal directions were readily monitored at a constant temperature of smectic A phase of PAz (typically 95 °C). Here, the photoinduced realignment was performed without changing temperature for the initialization step. This feature is due to the coverage of PBMA layer on the topmost surface, which will be discussed in more details in the following section.

The time course profiles of the grazing incidence small angle X-ray scattering (GI-SAXS) measurements using the synchrotron X-ray indicated that the rates of the disappearance of the structure in the initial alignment and the structure formation in the other (orthogonal) direction were found to be the same for both the Az smectic layer structure and the MPS cylinder domains of PBMA. Therefore, the realignment process proceeds in a highly cooperative manner between the two different hierarchical structures. However, the detailed information on the pathway and mechanism of the realignment process of the hierarchical structures still remained as an open question.

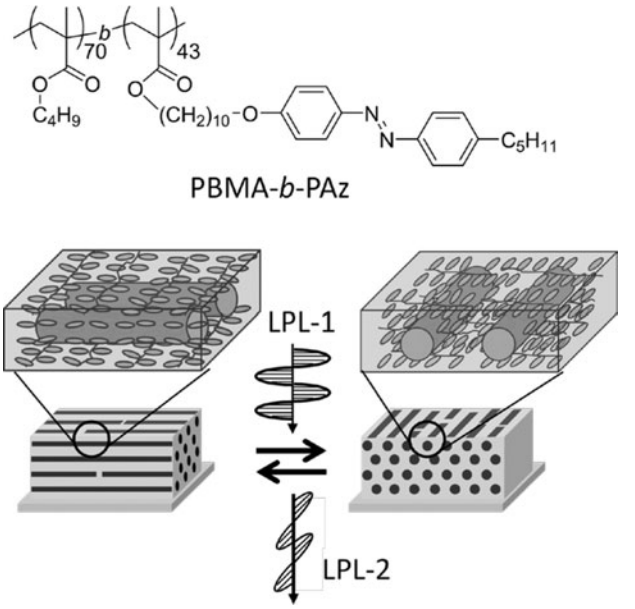

Figure 1. Chemical structure of PBMA-*b*-PAz and a schematic drawing of the alternative changes of LC orientation and MPS cylinders of PBMA-*b*-PAz by LPL irradiation.

Very recently, Sano et al. [24] succeeded in the observations of the intermediate state during the photo-realignment process. Evaluations by dichroic ratio of the Az mesogens, GI-SAXS, polarized optical microscopy, transmission electron microscopy (TEM) provided a more detailed view of the dynamic realignment process as follows (Figure 2). LPL irradiation in the orthogonal direction breaks up the large domains to sub-micrometer levels during an induction period (Stage I), and the collective rotation of the divided domains occur at Stage II. After the rotation is ceased, the sub-domains were fused to form larger domains aligned in the subsequent direction (Stage III).

3. Command Effect from the Free Surface

How LC molecules orient by the existence of an interface has been a matter of scientific interest. For calamitic LC crystals, the long axis of the rodlike molecule is mostly oriented vertically (homeotropically) to the plane of the free surface to reduce the excluded volume. This vision has been confirmed from both experimental data [25, 26] and theoretical considerations [27–30]. From the industrial side, the important role of the free surface was pointed out by a group of Fuji Photo Film Co. Ltd. (currently Fujifilm Corporation) [31]. They developed new photopolymerizable discotic LCs that can be used for expanding the viewing angle of LC display panels. The fabrication of hybrid orientation has been based on the orienting behavior of the LC molecules between the free surface and the solid substrate.

In the PBMA-*b*-PAz film mentioned in the previous section, the lower surface tension with high flexibility of the PBMA block resulted in the segregation to the free surface upon annealing. Fukuhara et al. [32] demonstrated that a PS-*b*-PAz film forming vertical alignment of PS cylinders could be converted to the planar one by mixing a small amount of PBMA-*b*-PAz and successive annealing. Without PBMA-*b*-PAz, annealing of PS-*b*-PAz film at 130 °C gave homeotropically aligned mesogens and PS cylinders. By mixing some

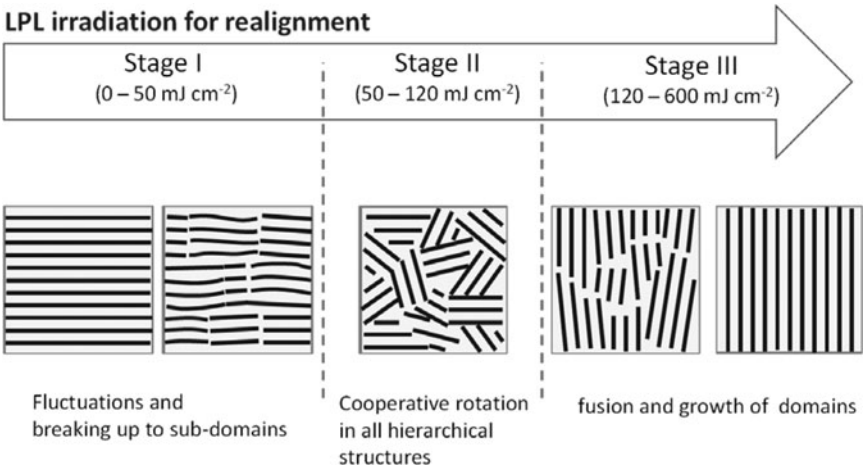

Figure 2. Schemes of the process of cylindrical MPS alignment change upon LPL irradiation set orthogonal to the initial one. The stripe pictures show schematic MPS structure and orientation viewed from the top. A sequence of the process consists of three stages: Induction period where the large domains are divided into a sub-micrometer level (Stage I), actual overall collective alignment change (Stage II), and self-assembly step to form large domains in the realigned direction (Stage III).

weight % of PBMA-*b*-PAz and subsequent annealing led to fully different results. The Az mesogens and PS cylinders were oriented parallel with the substrate. The cross section of the photoaligned film was observed by TEM. The TEM image clearly showed the existence of the segregated skin layer (ca. 20 nm thickness) of PBMA-*b*-PAz on the air side.

In the above case, the photoalignable Az-containing polymer films were used. More interesting results were obtained for *non-photoresponsive* LC polymer films when a small amount of PBMA-*b*-PAz was blended in this polymer (Figure 3). Fukuhara et al. [13, 33] showed that the photoresponsive skin layer of PBMA-*b*-PAz was segregated by annealing, and this layer actually worked as a free-surface command layer for side chain LC polymer films of PPBz (Figure 4). The mesogens of PPBz was fully commanded by the photo-orienting action of the PBMA-*b*-PAz skin layer. Various kinds of substrate including inorganic substrates such as silica plates and flexible polymer sheets could be used. This fact suggests the wide applicability of this method.

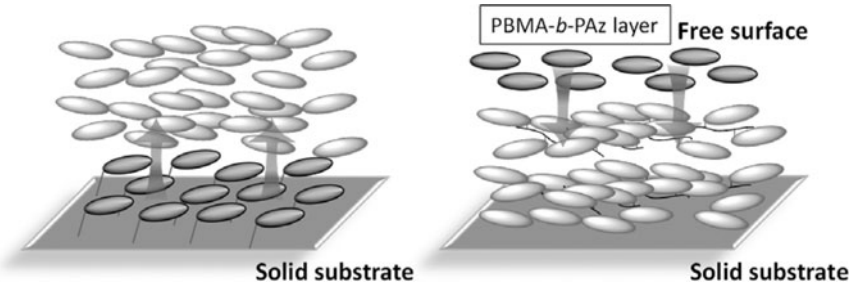

Figure 3. Schematic illustrations of an ordinary alignment system in which the photo-command layer is placed on a solid substrate (left), and a newly proposed system with command layer existing at the free surface (right).

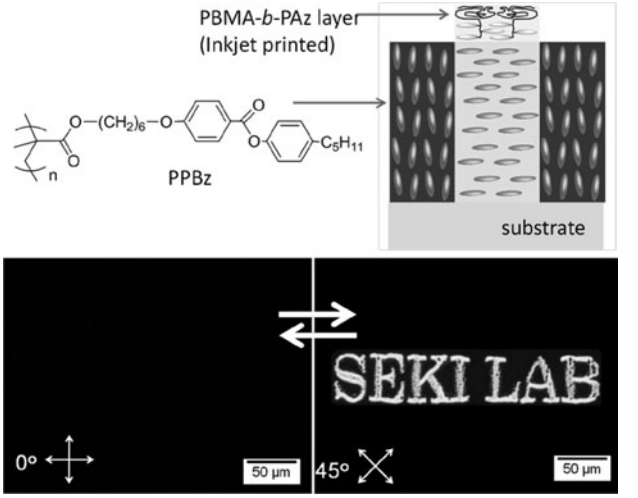

Figure 4. An example of the birefringence patterning of PPBz film obtained by the PBMA-*b*-PAz command layer prepared by inkjet printing. The letters appear and disappear alternatively according to the 45° rotation of the crossed polarizers.

To provide a surface layer, an alternative way is to adopt inkjet printing. After preparation of a PPBz film, inkjet printing was achieved. After successive annealing, LPL irradiation was made in the same manners. In this command system, a resolution with 1 μm could be readily obtained as confirmed by the birefringence contrast under the crossed polarizers. An example of inkjet drawing is shown in Figure 4. Unprinted regions were observed as a dark field irrespective of the rotation of the crossed polarizers [33]. The printed areas, on the other hand, became bright when the crossed polarizers were rotated by 45°, indicating that the phenyl benzoate mesogens were homogeneously photoaligned in these areas. In this way, the block copolymer of PBMA-*b*-PAz can be regarded as a "command surface ink."

4. Conclusion

This paper has briefly summarized our current efforts and advances on the photoalignment process of mesoscopic level structures formed by block copolymers, and a new strategy for photoalighment utilizing the free surface. The photoalignment technologies have already been becoming indispensable in LC display industries. However, we believe that there are still many issues to be explored, and directions to be extended in the basic LC research area.

Acknowledgment

We thank Dr. Y. Morikawa, Y. Koizuka, T. Murase, and Y. Nagashima in our group for their experimental efforts. We also thank Profs. Y. Amemiya and Y. Shinohara of the University of Tokyo for technical help in synchrotron X-ray measurements.

Funding

This work was supported by a Grant-in-Aid for Scientific Research (S23225003 to TS and B25286025 to SN) and for Young Scientists (B25810117 to MH) from The Ministry

of Education, Culture, Sports, Science and Technology (MEXT), Japan, and the PRESTO program of Japan Science and Technology Agency to SN. The synchrotron X-ray scattering experiments were performed at BL-6A of the KEK-Photon Factory, Tsukuba (proposal No. 2012G629).

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