

Photoalignment of an Azobenzene-Based Chromonic Liquid Crystal Dispersed in Triacetyl Cellulose: Single-Layer Alignment Films with an Exceptionally High Order Parameter

Masaki Matsumori,^{*,†,‡} Ayami Takahashi,[†] Yasushi Tomioka,[†] Takaaki Hikima,[#] Masaki Takata,[#] Takashi Kajitani,^{‡,##} and Takanori Fukushima^{*,‡}

[†]Hitachi Research Laboratory, Hitachi, Ltd., 7-1-1 Omika, Hitachi, Ibaraki 319-1292, Japan

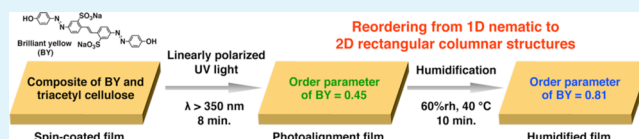
[‡]Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

[#]RIKEN SPring-8 Center, 1-1-1 Kouto, Sayo, Hyogo 679-5148, Japan

Supporting Information

ABSTRACT: Single-layer thin alignment films of dye molecules are of growing importance, particularly for state-of-the-art LCD technology. Here we show that a sequential process involving the photoalignment and humidification of a chromonic liquid crystalline azobenzene (brilliant yellow; BY) dispersed in a triacetyl cellulose (TAC) matrix gives a thin alignment film with an exceptionally high order parameter (0.81). Spectroscopic and X-ray diffraction analyses of a BY/TAC composite film in each alignment process revealed that brief humidification triggers restructuring of the BY assembly from 1D nematic-like order to anisotropic 2D columnar order, resulting in the dramatic increase in the order parameter.

KEYWORDS: azobenzene dye, chromonic liquid crystal, photoalignment, alignment film, order parameter



Alignment films play important roles in many applications such as polarizers in liquid crystal displays (LCDs), optical modulation device, optical data storage, and polarization holography.^{1–4} Conventionally, polarizers for LCDs have been fabricated by the mechanical stretching of iodine-doped poly(vinyl alcohol) (PVA).⁵ In the present state-of-the-art LCD technology, there is a strong demand for thin in-cell-type polarizers,^{6,7} which, however, is difficult to fabricate by mechanical stretching. In this context, alignment films with dichroic dye molecules have become a focus of attention, since they potentially exhibit large absorption over a wide range of visible regions.^{8,9} Two methods are available for the fabrication of such alignment films. One uses mechanically oriented polymer films as a substrate to align dichroic dyes,^{10,11} giving bilayer-type polarizers.^{12,13} Although this method can achieve a high order parameter of dye molecules (up to 0.8), it needs a multistep process and is limited in its ability to reduce the film thickness. The other method makes use of the direct alignment of dichroic dyes dispersed in a polymer matrix, where photoalignable dichroic azobenzene dyes have widely been used.^{2,14–17} Upon exposure to linearly polarized ultraviolet light (LPUV), azobenzene molecules tend to align in such a way that the longer molecular axis is oriented perpendicular to the polarizing direction of the incident light.^{3,18–22} The photoalignment mechanism involves the iterative trans–cis photoisomerization of the azobenzene chromophore. This method allows the fabrication of single layer-type thin polarizers by a single step, which is a great advantage over the former method. However, the order parameters that have been achieved by this method are at most 0.5.⁶

In this report, we show that an alignment film with an exceptionally high order parameter (0.81) can be realized by a sequential process involving the photoalignment and humidification of an azobenzene dye, referred to as brilliant yellow (BY, Figure 1a), dispersed in triacetyl cellulose (TAC, Figure 1a) as a polymer matrix. BY is known to be a photoalignable dichroic dye^{4,23,24} and behaves as a chromonic liquid crystal, a class of lyotropic liquid crystal composed of dye molecules.^{25–28} The photoalignment of BY dispersed in polymer matrices has been investigated previously.⁴ For instance, upon exposure to LPUV, BY molecules in polyvinylpyrrolidone (PVP) can align, whereas those in PVA hardly undergo photoalignment, where the hydrogen bonding interaction between BY and PVA molecules has been suggested to have a negative effect. Nevertheless, the best order parameter ever reported for BY in alignment films is lower than 0.3.⁴ The key to the present achievement, in which we realized a very high order parameter (0.81), is the combination of humidification to trigger the structural reordering of BY and the use of TAC as a polymer matrix (Figure 2). TAC is optically transparent and thermally stable, and has a high glass-transition temperature (171 °C).²⁹ TAC is hydrophobic but possesses moisture permeability to a certain extent. Because of these properties, TAC serves as an excellent polymer matrix for the dispersion, photoalignment, and humidification-driven reordering of BY.

Received: March 24, 2015

Accepted: May 18, 2015

Published: May 18, 2015

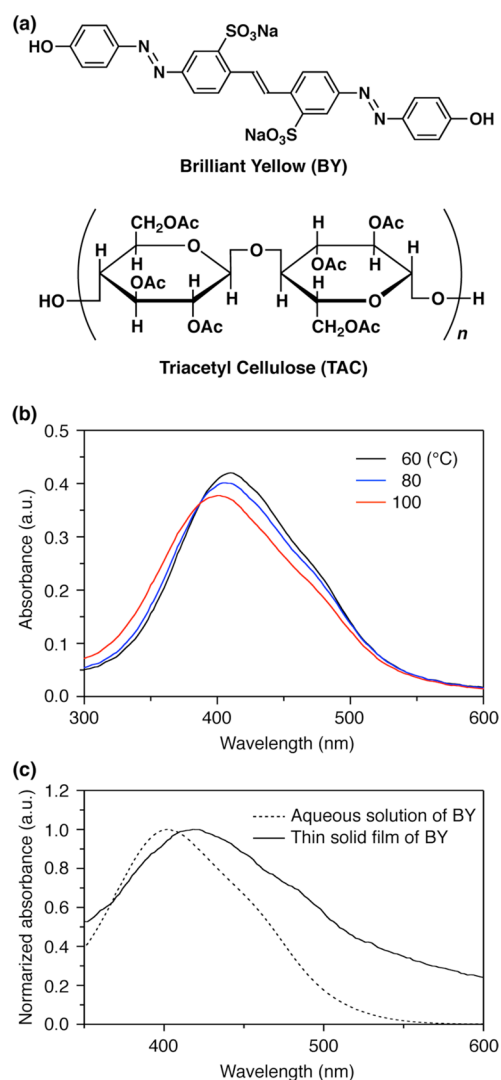


Figure 1. (a) Molecular structures of brilliant yellow (BY) and triacetyl cellulose (TAC). (b) Electronic absorption spectra of spin-coated BY/TAC films after they were heated at 60 (black), 80 (blue), and 100 °C (red) for 30 s. (c) Normalized electronic absorption spectra of an aqueous solution (broken curve) of BY (2.0×10^{-5} mol/L) and a thin solid film (solid curve) of BY.

Typically, spin-coating a *N*-methylpyrrolidone (NMP) solution (0.3 mL) of a mixture of BY (1.0 wt %) and TAC (1.0 wt %) onto a quartz substrate (3.0×2.0 cm²), followed by annealing at 100 °C for 30 s, affords a BY and TAC composite (BY/TAC) film with a thickness around 60 nm. As observed by optical microscopy (Figure S1 in the Supporting Information), the resulting thin film does not contain large grain aggregates. Thus, BY are miscible in the TAC matrix without macroscopic phase separation. To align the BY molecules in the TAC matrix, the spin-coated film was exposed to LPUV (5.0 J/cm²) for 8 min through a cut filter ($\lambda > 350$ nm, Figure 2). We confirmed

that such a short-term exposure is enough for achieving the maximal order parameter of BY (Figure 3b). Polarized electronic absorption spectroscopy of the irradiated film showed that, when the polarizing direction of the incident light for spectroscopy was parallel to that of incident LPUV for photoalignment, the absorption maximum ($A_{//}$) at 402 nm due to the azobenzene chromophore was decreased (Figure 3a, orange), compared with that observed for the as-annealed film (Figure 3a, blue). On the other hand, when the polarizing direction of the incident light was perpendicular to that of incident LPUV, the absorption maximum (A_{\perp}) was increased (Figure 3a, red). Figure 3c shows polar plots of the relative absorbance at 410 nm (A_{rel}) observed for the irradiated film versus the azimuthal angles (θ) between the polarizing directions of the incident lights for spectroscopy and photoalignment. The obvious dichroic feature with maxima at $\theta = 90^\circ$ and 270° (Figure 3c, red) indicates that the BY molecules in the TAC matrix align perpendicular to the polarizing direction of LPUV. Based on the polar plot (Figure 3c), the order parameter of BY (S), given by $S = (A_{\perp} - A_{//}) / (A_{\perp} + 2A_{//})$, is determined to be 0.45. This value is much higher than that reported for BY in PVP ($S = 0.3$).⁴

The annealing temperature of the spin-coated BY/TAC film affects the order parameter of BY. When a spin-coated film was heated at 80 °C for 30 s and then exposed to LPUV (5.0 J/cm², $\lambda > 350$ nm, 8 min), the S value of the resultant film was 0.40. The order parameter further decreased to 0.22, when a spin-coated film was thermally processed at a lower temperature (60 °C) under otherwise identical conditions. Gas chromatographic (GC) analysis showed that the spin-coated BY/TAC films, after being annealed at 60, 80, and 100 °C, contain 4.9, 5.0, and 4.2 wt % of NMP, respectively. Considering the negligible difference in the amount of NMP, it is unlikely that the residual solvent affects the ordering of the BY molecules. The effect of the annealing temperature on the order parameter is presumably due to the enhancement of the dispersibility of the BY molecules in the TAC matrix at a high temperature. As shown in Figure 1b, the absorption maxima of the azobenzene chromophore in the films, after being heated at 60 and 100 °C, appear at 410 and 402 nm, respectively. The former absorption maximum agrees with that observed for a solid film composed of BY alone (Figure 1c, solid curve), and the latter is identical to that observed for a diluted aqueous solution of BY (Figure 1c, broken curve). These results suggest that heating at 100 °C, which leads to the improvement of the dispersibility of the BY molecules in the TAC matrix, produces a larger free volume around BY to facilitate the trans–cis isomerization.³⁰

We found that the order parameter (S) of BY in the photoalignment film is increased upon humidification (Figure 2). For example, when the photoalignment BY/TAC film ($S = 0.45$) was allowed to stand under humid conditions (60%rh at 25 °C) for 100 min, the S value was increased to 0.58. Noteworthy, when the photoalignment BY/TAC film was processed in a similar manner, except that humidification was performed at a higher temperature (40 °C) for just 10 min, the

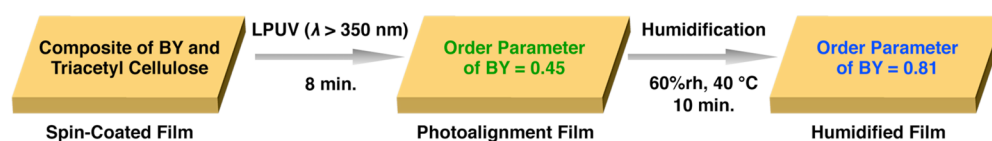


Figure 2. Schematic illustration for the alignment process of the BY molecules dispersed in a TAC matrix.

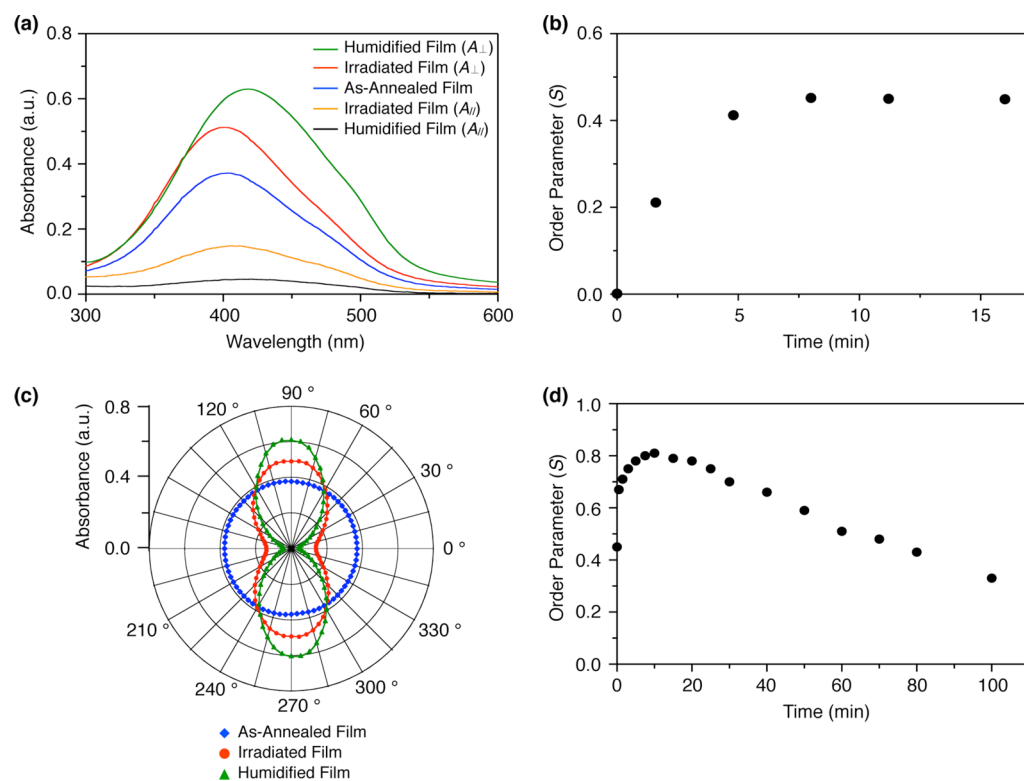


Figure 3. (a) Polarized electronic absorption spectra of a BY/TAC film after it was heated at 100 °C for 30 s (blue), exposed to LPUV (5.0 J/cm^2 , $\lambda > 350 \text{ nm}$, 8 min; red and orange), and then humidified (60%rh, 40 °C, 10 min; green and black). The red and green spectra were obtained by setting the film in such a way that the polarizing direction of the incident light for spectroscopy is perpendicular to that of incident LPUV. The orange and black spectra were obtained by setting the film in such a way that the polarizing direction of the incident light for spectroscopy is parallel to that of incident LPUV. (b) Exposure-time dependence of the order parameters (S) of BY in the BY/TAC film. (c) Polar plots of the relative absorbance at 410 nm (A_{rel}), recorded upon rotation of a polarizer at 5° increments, for the BY/TAC film after being heated (blue), exposed to LPUV (red), and humidified (green). The azimuthal angle (θ) is defined as zero when the polarizing direction of the incident light for spectroscopy is parallel to that of incident LPUV. (d) Time-dependence of the order parameters (S) of BY in the BY/TAC film, upon continuous humidification (60%rh) at 40 °C.

S value was dramatically increased from 0.45 to 0.81 (Figure 3d), as determined by the polar plot (Figure 3c, green). The order parameter decreased under continuous humidification at 40 °C, and fell to a value that was even lower (e.g., $S = 0.33$, after 100 min) than the original ($S = 0.45$). This seems reasonable, because prolonged humidification decreases the concentration of BY in the film by hydration of its ionic pendants and eventually causes the disordering of the BY molecules below the critical concentration for generating the liquid crystal phase. Meanwhile, once the 10 min-humidified film ($S = 0.81$) was dried, no change of the S value was observed even after the film was allowed to stand under atmospheric humidity and temperature conditions for at least 3 months. As a control experiment, when the photoalignment film ($S = 0.45$) was simply left standing at 40 °C for 10 min without humidification, the order parameter was unchanged. Even upon heating at a higher temperature (e.g., 100 °C), the photoalignment film showed a negligibly small increase in the order parameter ($S = 0.47$). We also confirmed that the thickness of the BY/TAC film has little influence on the order parameter of BY in each alignment process (Table S1 in the Supporting Information).

Electronic absorption spectroscopy demonstrates the re-ordering of BY associated with brief humidification at 40 °C. As described above, the photoalignment film before humidification displays an absorption maximum at 402 nm (Figure 3a, red and orange). Upon 10 min-humidification (60%rh) at 40 °C, the

absorption maximum shifts to 418 nm (Figure 3a, green and black). The analogy of the spectroscopic features between the humidified film (Figure 3a, green and black) and the solid BY film (Figure 1c, solid curve) suggests that brief humidification triggers the reordering of the BY molecules into a particular assembling structure due to the lyotropic liquid crystalline nature.

Using wide-angle X-ray diffraction (XRD), we investigated the assembling structure of BY caused by humidification. Thus, an alignment film, fabricated by 10 min-humidification (60%rh) at 40 °C, was exposed to an X-ray beam ($\lambda = 1.542 \text{ \AA}$) in the direction parallel to the incident LPUV for photoalignment. The resultant out-of-plane XRD profiles displayed a weak diffraction peak with a d -spacing of 3.5 Å (red curve in Figure S2 in the Supporting Information), which is assignable to the plane-to-plane separation of π -stacked BY.²⁶ On the other hand, when the direction of the incident X-ray beam was perpendicular to that of incident LPUV, no diffraction was observed from the film (black curve in Figure S2 in the Supporting Information). These observations indicate that the BY molecules assemble to form a one-dimensional (1D) column, the axis of which is parallel to the polarizing direction of incident LPUV.

By means of grazing incidence X-ray diffraction (GI-XRD) using a synchrotron X-ray beam ($\lambda = 1.0 \text{ \AA}$), we further investigated how the BY molecules assemble in the alignment film with such an exceptionally high order parameter ($S =$

0.81). For this purpose, we fabricated a thin cast film of BY/TAC (60 nm in thickness) on quartz substrates and processed them sequentially by LPUV irradiation (5.0 J/cm^2 , $\lambda > 350 \text{ nm}$, 8 min) and humidification (60%rh, 40°C , 10 min). Upon exposure to the X-ray beam in a direction parallel to the polarizing direction of the incident LPUV, the resultant film showed three diffraction arcs with d -spacings of 15.5, 11.7, and 10.1 \AA , which can be assigned, respectively, to the diffractions from the (101), (200), and (002) planes of a two-dimensional (2D) rectangular lattice (Figure 4a and Figure S3a in the Supporting Information). The lengths of the longer (a) and shorter (c) axes are determined to be 23.4 and 20.3 \AA , respectively. Importantly, the length of the $[101]$ axis (30.9 \AA)

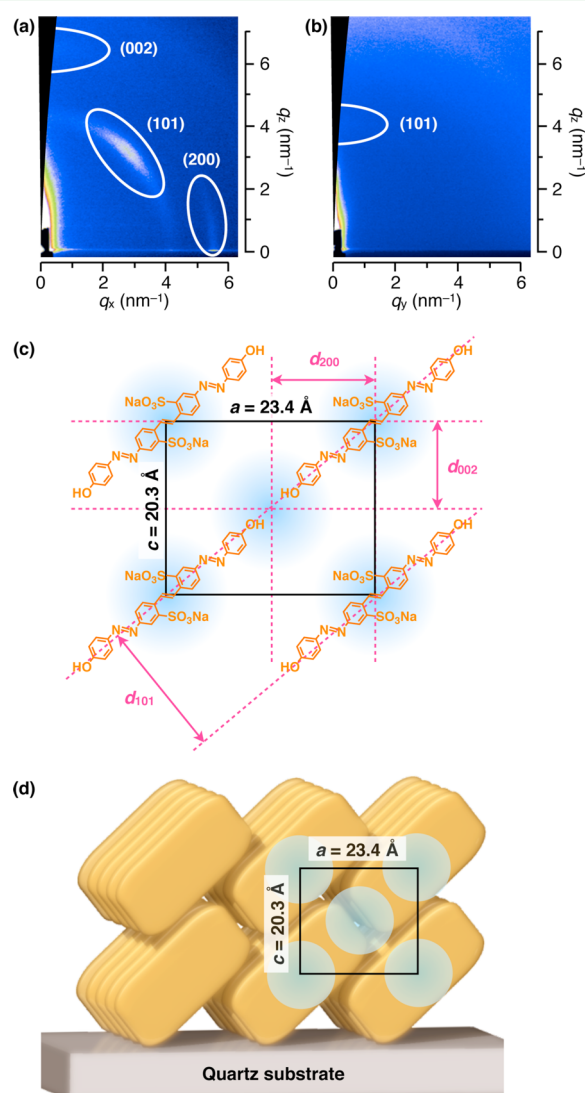


Figure 4. 2D GI-XRD images of a photoalignment film of BY/TAC (60 nm in thickness) with humidification, where the film was set in such a way that the direction of incident X-ray beam is (a) parallel and (b) perpendicular to the polarizing directions of the incident LPUV. Values in parentheses indicate Miller indices. The black sections in the out-of-plane direction are inaccessible areas in the q -space (see also Figure S3 in the Supporting Information). Schematic illustrations of (c) the 2D rectangular lattice and (d) the assembled structure of the BY molecules (orange) formed in the humidified film. Most likely, water molecules are localized in the light blue regions to increase the relative electron density.

of the rectangular lattice is in excellent agreement with the sum of the length of the longer molecular axis of BY (27.0 \AA) and the size of a water molecule (3.8 \AA). We speculate that the longer molecular axis of BY aligns along the $[101]$ axis across a water molecule (Figure 4c), most likely due to hydrogen bonding between the terminal hydroxyl groups of BY and a water molecule. Meanwhile, when the 2D GI-XRD image of the processed film was measured by exposing it to an X-ray beam in a direction perpendicular to the polarizing direction of the incident LPUV, only weak diffraction from the (101) plane appeared in the out-of-plane direction (Figure 4b and Figure S3b in the Supporting Information). This observation indicates that the ac plane of the 2D lattice is oriented parallel to the direction of the incident X-ray beam, i.e., perpendicular to the polarizing direction of the incident LPUV. As a reference, we also performed GI-XRD experiments on the BY/TAC film before humidification, where a diffraction arc was observed in the in-plane direction, only when the polarizing direction of incident LPUV and the direction of the X-ray beam were identical to one another (Figure S4 in the Supporting Information). Because the d -spacing (15.9 \AA) for this diffraction is consistent with the distance between two sodium sulfonate groups in BY (i.e., the shorter molecular axis), the BY assembly before humidification has just 1D nematic-like order.

From all of the above observations, we can conclude that the formation of a 2D rectangular lattice composed of columnar assembled BY molecules plays a key role in achieving such a high order parameter ($S = 0.81$). BY bears sodium sulfonate groups at the inside phenylene rings. In the humidification process, hydration may occur site-selectively around the hydrophilic functionality (Figure 4d), bringing out the lyotropic liquid crystalline property of BY to facilitate the reordering of the molecules. Consequently, the BY assembly, which originally has 1D nematic-like order, becomes a higher order 2D assembly with a large structural anisotropy, thus leading to a dramatic increase in the order parameter.

In summary, we have demonstrated the photoalignment of an azobenzene-based dye (brilliant yellow; BY) in a polymer matrix (triacyetyl cellulose; TAC) to allow the fabrication of a single-layer alignment film with an exceptionally high order parameter (S). The resulting S value (0.81) is the highest among those reported for alignment films fabricated by photoalignment. We have also highlighted the importance of the humidification-driven 1D-to-2D structural reordering of the BY molecules in TAC, which is enabled by the lyotropic liquid crystalline nature of BY, together with the compatibility of BY with the polymer matrix. The present work might offer a new avenue for the development of thinner and higher-performance alignment films.

■ ASSOCIATED CONTENT

Supporting Information

Materials and methods, Table S1, optical micrographs, XRD patterns, and GI-XRD images. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b02577.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: masaki.matsumori.bp@hitachi.com.

*E-mail: fukushima@res.titech.ac.jp.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The GI-XRD experiments were performed at the BL45XU in the SPring-8 with the approval of the RIKEN SPring-8 Center (proposal 20130025 and 20140056).

REFERENCES

- (1) Yang, D. K.; Wu, S. T. In *Fundamentals of Liquid Crystal Devices*; Wiley: Chichester, U.K., 2006; Chapter 6, pp 157–178.
- (2) Ichimura, K. Photoalignment of Liquid-Crystal Systems. *Chem. Rev.* **2000**, *100*, 1847–1874.
- (3) Fukuhara, K.; Nagano, S.; Hara, M.; Seki, T. Free-Surface Molecular Command Systems for Photoalignment of Liquid Crystalline Materials. *Nat. Commun.* **2014**, *5*, 3320.
- (4) Chaplanova, Z. D.; Murauski, A. A.; Rogachev, A. A.; Agabekov, V. E.; Gracheva, E. A. Multi-Layered Anisotropic Films Based on the Azo Dye Brilliant Yellow and Organic Polymers. *J. Appl. Spectrosc.* **2013**, *80*, 658–662.
- (5) Shurcliff, W. A. In *Polarized Light Production and Use*; Harvard University Press: Cambridge, MA, 1962; pp 43–64.
- (6) Ohyama, T.; Ukai, Y.; Fennell, L.; Kato, Y.; Bae, H. G.; Sung, P.-W. TN Mode TFT-LCD with In-Cell Polarizer. *Dig. Technol. Pap.–Soc. Inf. Dispersion Int. Symp.* **2004**, *35*, 1106–1109.
- (7) Ukai, Y.; Ohyama, T.; Fennell, L.; Kato, Y.; Paukshto, M.; Smith, P.; Yamashita, O.; Nakanishi, S. Current Status and Future Prospect of In-Cell Polarizer Technology. *Dig. Technol. Pap.–Soc. Inf. Dispersion Int. Symp.* **2004**, *35*, 1170–1173.
- (8) Bastiaansen, C.; Schmidt, H. W.; Nishino, T.; Smith, P. Transparency and Dichroism of Ultra-Drawn UHMW-PE Films in the Visible Wavelength Range. *Polymer* **1993**, *34*, 3951–3954.
- (9) Filippovich, L. N.; Ariko, N. G.; Agabekov, V. E. Optical Anisotropy and Photostability of Polarizing Films Dyed with Brilliant Yellow. *J. Appl. Spectrosc.* **2009**, *76*, 440–446.
- (10) Dreyer, J. F. The Fixing of Molecular Orientation. *J. Phys. Chem.* **1948**, *52*, 808–810.
- (11) Dreyer, J. F. Light Polarization from Films of Lyotropic Nematic Liquid Crystals. *J. Phys. (Paris)* **1969**, *C4*, 114–116.
- (12) Matsunaga, D.; Tamaki, T.; Akiyama, H.; Ichimura, K. Photofabrication of Micro-Patterned Polarizing Elements for Stereoscopic Displays. *Adv. Mater.* **2002**, *14*, 1477–1480.
- (13) Ruslim, C.; Hashimoto, M.; Matsunaga, D.; Tamaki, T.; Ichimura, K. Optical and Surface Morphological Properties of Polarizing Films Fabricated from a Chromonic Dye by the Photoalignment Technique. *Langmuir* **2004**, *20*, 95–100.
- (14) Todorov, T.; Nikolova, L.; Tomova, N. Polarization Holography. 1: A New High-Efficiency Organic Material with Reversible Photoinduced Birefringence. *Appl. Opt.* **1984**, *23*, 4309–4312.
- (15) Natansohn, A.; Rochon, P.; Barrett, C.; Hay, A. Stability of Photoinduced Orientation of an Azo Compound into a High- T_g Polymer. *Chem. Mater.* **1995**, *7*, 1612–1615.
- (16) Yu, H. Recent Advances in Photoresponsive Liquid-Crystalline Polymers Containing Azobenzene Chromophores. *J. Mater. Chem. C* **2014**, *2*, 3047–3054.
- (17) Priimagi, A.; Barrett, C. J.; Shishido, A. Recent Twists in Photoactuation and Photoalignment Control. *J. Mater. Chem. C* **2014**, *2*, 7155–7162.
- (18) Morikawa, Y.; Nagano, S.; Watanabe, K.; Kamata, K.; Iyoda, T.; Seki, T. Optical Alignment and Patterning of Nanoscale Microdomains in a Block Copolymer Thin Film. *Adv. Mater.* **2006**, *18*, 883–886.
- (19) Stumpe, J.; Kulikovska, O.; Goldenberg, L. M.; Zakrevskyy, Y. In *Smart Light-Responsive Materials*; Zhao, Y., Ikeda, T., Eds.; Wiley: Weinheim, 2009; Chapter 2, pp 47–94.
- (20) Kawatsuki, N. Photoalignment and Photoinduced Molecular Reorientation of Photosensitive Materials. *Chem. Lett.* **2011**, *40*, 548–554.
- (21) Nagano, S.; Koizuka, Y.; Murase, T.; Sano, M.; Shinohara, Y.; Amemiya, Y.; Seki, T. Synergy Effect on Morphology Switching: Real-Time Observation of Photo-Orientation of Microphase Separation in a Block Copolymer. *Angew. Chem., Int. Ed.* **2012**, *51*, 5884–5888.
- (22) Seki, T.; Nagano, S.; Hara, M. Versatility of Photoalignment Techniques: From Nematics to a Wide Range of Functional Materials. *Polymer* **2013**, *54*, 6053–6072.
- (23) West, J.; Linli, S.; Reznikov, Y. Photo-Alignment using Adsorbed Dichroic Molecules. *Mol. Cryst. Liq. Cryst.* **2001**, *364*, 199–210.
- (24) Yaroshchuk, O.; Gurumurthy, H.; Chigrinov, V. G.; Kwok, H. S.; Hasebe, H.; Takatsu, H. Photoalignment Properties of Brilliant Yellow Dy. In *Proceedings of the 14th International Display Workshops*; Sapporo, Japan, Dec 5–7, 2007; Society for Information Display: Campbell, CA, 2007; pp 253–256.
- (25) Lydon, J. In *Handbook of Liquid Crystals: Low Molecular Weight Liquid Crystals, Vol. 2b*; Demus, D., Goodby, J., Gray, G. W., Spiess, H. W., Vill, V., Eds.; Wiley: Weinheim, Germany, 1998; Chapter 18, pp 981–1007.
- (26) Ruslim, C.; Matsunaga, D.; Hashimoto, M.; Tamaki, T.; Ichimura, K. Structural Characteristics of the Chromonic Mesophases of C. I. Direct Blue 67. *Langmuir* **2003**, *19*, 3686–3691.
- (27) Lydon, J. Chromonic Review. *J. Mater. Chem.* **2010**, *20*, 10071–10099.
- (28) Bae, Y. J.; Yang, H. J.; Shin, S. H.; Jeong, K. U.; Lee, M. H. A Novel Thin Film Polarizer from Photocurable Non-Aqueous Lyotropic Chromonic Liquid Crystal Solutions. *J. Mater. Chem.* **2011**, *21*, 2074–2077.
- (29) Mori, H. High Performance TAC Film for LCDs. *Proc. SPIE* **2006**, *6135*, 613503–613510.
- (30) Ichimura, K.; Suzuki, Y.; Seki, T.; Hosoki, A.; Aoki, K. Reversible Change in Alignment Mode of Nematic Liquid Crystals Regulated Photochemically by Command Surfaces Modified with an Azobenzene Monolayer. *Langmuir* **1988**, *4*, 1214–1216.