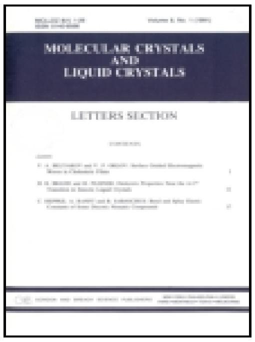

Taylor & Francis
Taylor & Francis Group

Molecular Crystals and Liquid Crystals

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

Photoinduced Orientation of Hydrogen Bonding Liquid Crystalline Polymers / Pyridine Derivatives Composite Films

Satoshi Minami, Ryoichi Ashizawa, Mizuho Kondo & Nobuhiro Kawatsuki

To cite this article: Satoshi Minami, Ryoichi Ashizawa, Mizuho Kondo & Nobuhiro Kawatsuki (2015) Photoinduced Orientation of Hydrogen Bonding Liquid Crystalline Polymers / Pyridine Derivatives Composite Films, Molecular Crystals and Liquid Crystals, 617:1, 40-49, DOI: 10.1080/15421406.2015.1075817

To link to this article: http://dx.doi.org/10.1080/15421406.2015.1075817

Mol. Cryst. Liq. Cryst., Vol. 617: pp. 40–49, 2015
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2015.1075817

Photoinduced Orientation of Hydrogen Bonding Liquid Crystalline Polymers / Pyridine Derivatives Composite Films

SATOSHI MINAMI,[1,2,*] RYOICHI ASHIZAWA,[2]
MIZUHO KONDO,[1] AND NOBUHIRO KAWATSUKI[1]

[1]Department of Materials Science and Chemistry, Graduate School of Engineering, University of Hyogo, Hyogo, Japan
[2]Electronic Materials Research Laboratories, Display Materials Research Department, Nissan Chemical Industries, LTD., Funabashi, Chiba, Japan

This paper describes the photoalignment behavior of composite thin films comprised of polymethacrylate with cinnamic acid side groups (pM6CA) and pyridine derivatives. Linearly polarized (LP) UV irradiation to composite films undergoes the photoreaction of cinnamic acid side groups, and the axis-selection is observed regardless of the content of pyridine derivatives. The negative dichroism is generated in all conditions and the photoinduced anisotropy is amplified when the exposed films are annealed. The photoinduced anisotropy and the exposure dose margin for the effective amplification of the molecular orientation improves when specific pyridine derivatives are doped with pM6CA. Using the reoriented pM6CA/pyridine derivatives composite films for the LC alignment layer, anti-parallel LC cell is prepared, where the LC alignment uniformity is related to the in-plane orientation order of the composite films.

Keywords Photoalignment; photoreactive polymer; pyridine-caroboxylic acid interaction

I. Introduction

The photoresponsive polymer films have received much attention due to its potential capability as many kinds of optical and photonic applications. Especially, photoalignment method for a uniform liquid crystal (LC) alignment has been practically used to replace a conventional mechanical rubbing method. The photoalignment is based on an axis-selective photoreaction of photosensitive materials to generate optical and mechanical anisotropy of the alignment layer. To date, numerous photoreactive materials have reported, such as photoisomerization in azobenzene derivatives[1–6] and photo-crosslinking of cinnamate, coumarin and chalcone derivatives.[7–11] Polymeric films with these photoreacctive groups are axis-selectively photoreacted by irradiating with linear polarized (LP) UV light.[7] We have previously investigated photo-crosslinkable liquid crystalline polymers

---

[*] Address correspondence to Satoshi Minami, Department of Materials Science and Chemistry, Graduate School of Engineering, University of Hyogo, 2167 Shosha, Himeji, Hyogo 671-2280, Japan. E-mail: minamisa@nissanchem.co.jp

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gmcl.

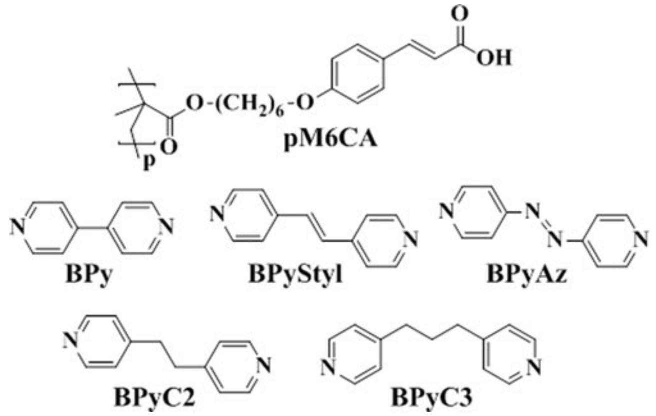

Figure 1. Chemical structure of pM6CA and abbreviation of pyridine derivatives.

(PLCPs) containing mesogenic side chain terminated with cinnamate derivatives.[12-16] Irradiating the PLCP films with LPUV light generates a photoinduced optical anisotropy, and a subsequent thermal treatment enhances the molecular reorientation due to LC characteristics of the material. We have also reported that a polymethacrylate comprised of a hexylene spacer group terminated with a cinnamic acid (CA) moiety in its side chain (pM6CA) exhibits a large photoinduced molecular reorientation with a high photoreactivity toward LPUV light.[16] An axis-selective photoreaction of CA groups of pM6CA film induces a small optical anisotropy, and the subsequent annealing process thermally generates the self-organization of the mesogenic groups.[16] Furthermore, adjusting the exposure doses achieves uniform alignment control of low molecular LCs on the resultant film.

To date, there are many types of supramolecular LCs based on the H-bonding between pyridine and carboxylic acid derivatives.[17-19] For example, Kato et al. have conducted pioneering studies that stabilized the mesophase through H-bonding in mixtures of BA groups and a monomer with stilbazole derivatives or bifunctional pyridine derivatives such as 4,4′-bipyridyl (BPy) or 1,2-bis(4-pyridyl)ethylene (BPystyl). However photoreaction of complex consisting of pyridine derivatives and a polymer having a CA moiety such as pM6CA has not yet been explored.

In this paper, we report on photoalignment behavior of thin film of pM6CA combined with various kinds of pyridine derivatives. H-bonding formation between CA moiety and pyridine derivatives alters LC property of the materials and photoalignment behavior. In addition, uniform alignment controls of low molecular liquid crystals on the resultant film are achieved.

2. Experimental

2.1. Materials

Chemical structures of pM6CA and pyridine derivatives used in this study are shown in Fig. 1 pM6CA was synthesized by a free radical polymerization of monomer M6CA in THF solution using AIBN as the initiator at 60°C for 6 h.[16] The concentration of monomer M6CA was 15 wt% and AIBN was 1 mol%. After the polymerization, the polymer was

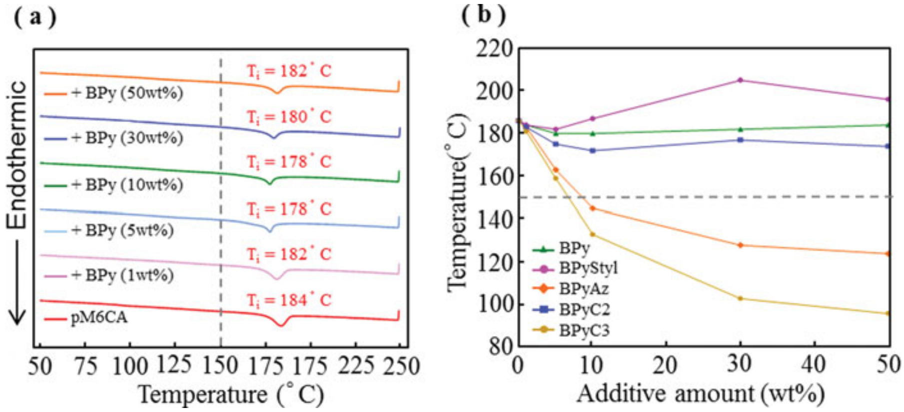

Figure 2. (a) Thermal properties of pM6CA/BPy (0–50 wt%) in bulk by DSC, (b) Isotropic temperature (T_i) of pM6CA/pyridine derivatives (0–50 wt%) composite as a function of additive amount. All data are results of 2nd heating (heating rate:10°C/min.).

purified by precipitating several times from THF solution to methanol/H_2O (6:1 v/v) and methanol/NMP (10:1 v/v). The synthetic yield was 75 wt%. ^{1}H NMR (THF-d_8): δ (ppm) 0.96-1.96 (m, 13H), 3.8-3.9 (m, 4H), 6.28 (d, J = 16.0 Hz, 1H), 6.88 (d, J = 8.1Hz, 2H), 7.45 (d, J = 8.1Hz, 2H), 7.57 (d, J = 16.0Hz, 1H). Mn = 40000, Mw = 87000.

2.2. *Preparation of Composite Powder and Thin Films*

pM6CA/pyridine derivatives (99/1-50/50wt/wt) composite powder were prepared by dissolving the pM6CA and pyridine derivatives in THF, followed by evaporating the THF gradually. Thin pM6CA/pyridine derivative films (thickness: 100 nm) were prepared by spin-coating polymer/pyridine derivatives (99/1–50/50 wt/wt) in 4 wt% *N*-methyl-2-pyrrolidone (NMP)/ butyl-cellosolve (BCS) mixed solution onto quartz substrate or glass substrate, and subsequently annealed at 70°C for 90 s.

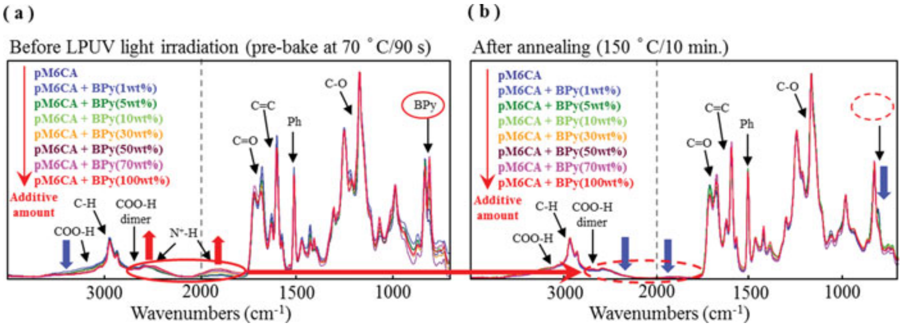

Figure 3. FT-IR spectra of the pM6CA/BPy (0–100 wt%) thin films (a) before LPUV light irradiation (after pre-baked at 70°C/90s), (b) after annealing at 150°C/10min.

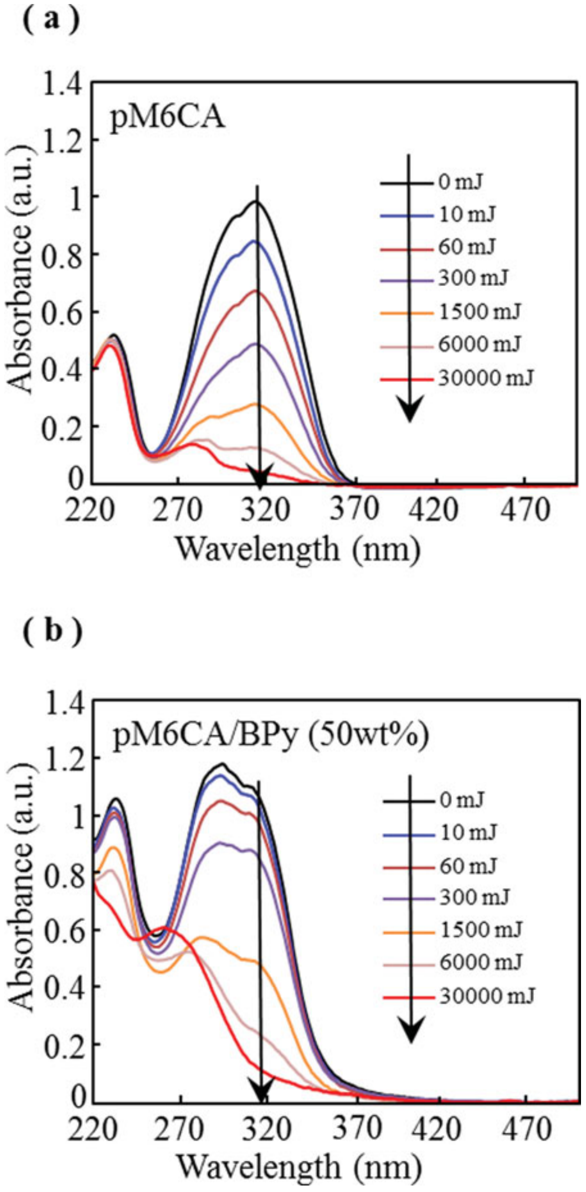

Figure 4. UV absorption spectral changes of (a) pM6CA and (b) pM6CA/BPy (50 wt%) film irradiated with LPUV light as a function of exposure dose.

2.3. Photoreaction and Molecular Reorientation of Composite Thin Films

Photoreaction of thin films was carried out using LPUV light source (Cerma Precision MUL-S60POL equipped with ultrahigh pressure mercury lamp (HG-1000MPK) with a band path filter (300–330nm)). After irradiation, thin films were annealed at 150°C for 10 min. The photoinduced optical anisotropy of thin films was measured by polarization UV-vis spectroscopy. Dichroism (ΔA: Eq. 1) after LPUV light irradiated and in-plane order parameters (S: Eq. 2) after the annealing are calculated from the measured absorbance

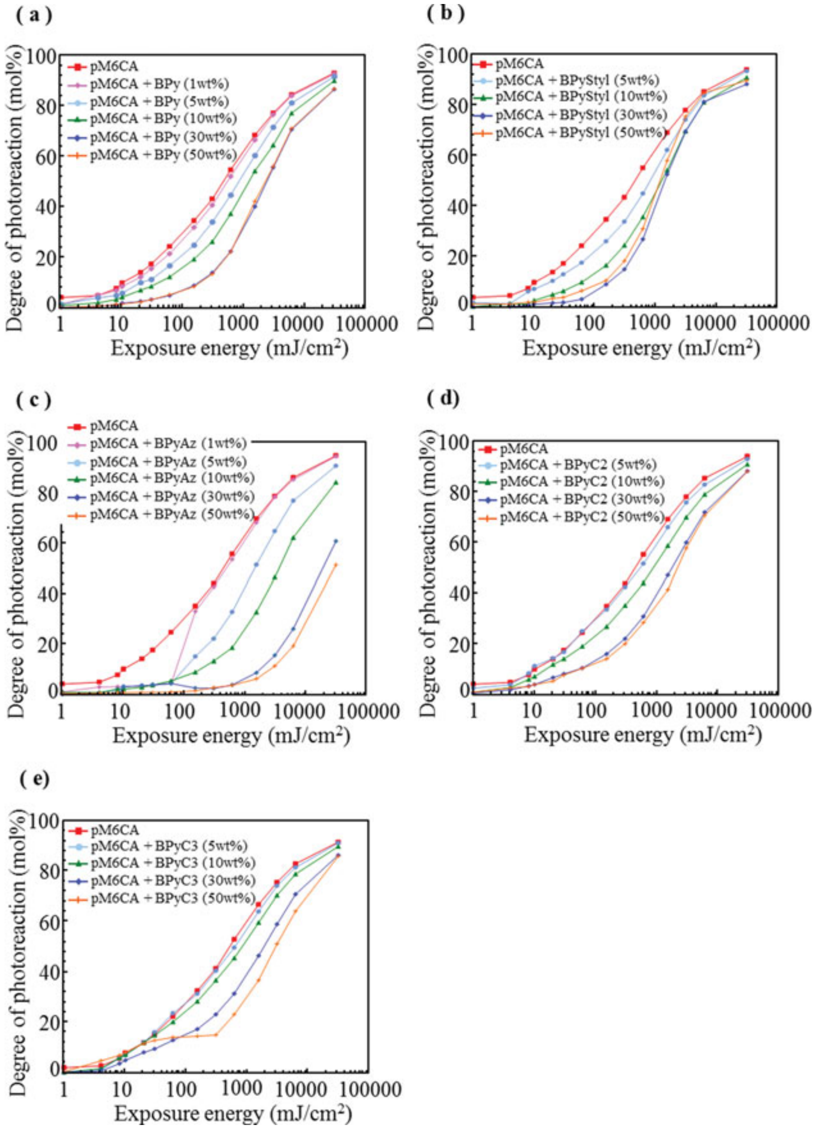

Figure 5. The degree of photoreaction of (a) pM6CA/BPy (0–50 wt%), (b) pM6CA/BPyStyl (0–50 wt%), (c) pM6CA/BPyAz (0–50 wt%), (d) pM6CA/BPyC2 (0–50 wt%) and (e) pM6CA/BPyC3 (0–50 wt%) films after LPUV light irradiation as a function of exposure dose.

parallel ($A_{||}$) and perpendicular ($A_{\perp}$) to the polarization electric field (**E**) of the LPUV light. Degree of photoreaction was estimated in Eq. 3 by monitoring the decrease in the absorbance at 314 nm.

$$\text{Dichroism}\Delta A = A_{||} - A_{\perp} \qquad (1)$$

$$\text{In} - \text{plane order parameter } S = (A_{\perp} - A_{||})/(A_{\perp} + 2A_{||}) \qquad (2)$$

$$\text{Degree of photoreaction (mol\%)} = (1 -_{\text{Airradiated}} / A_{\text{initial}}) \times 100 \qquad (3)$$

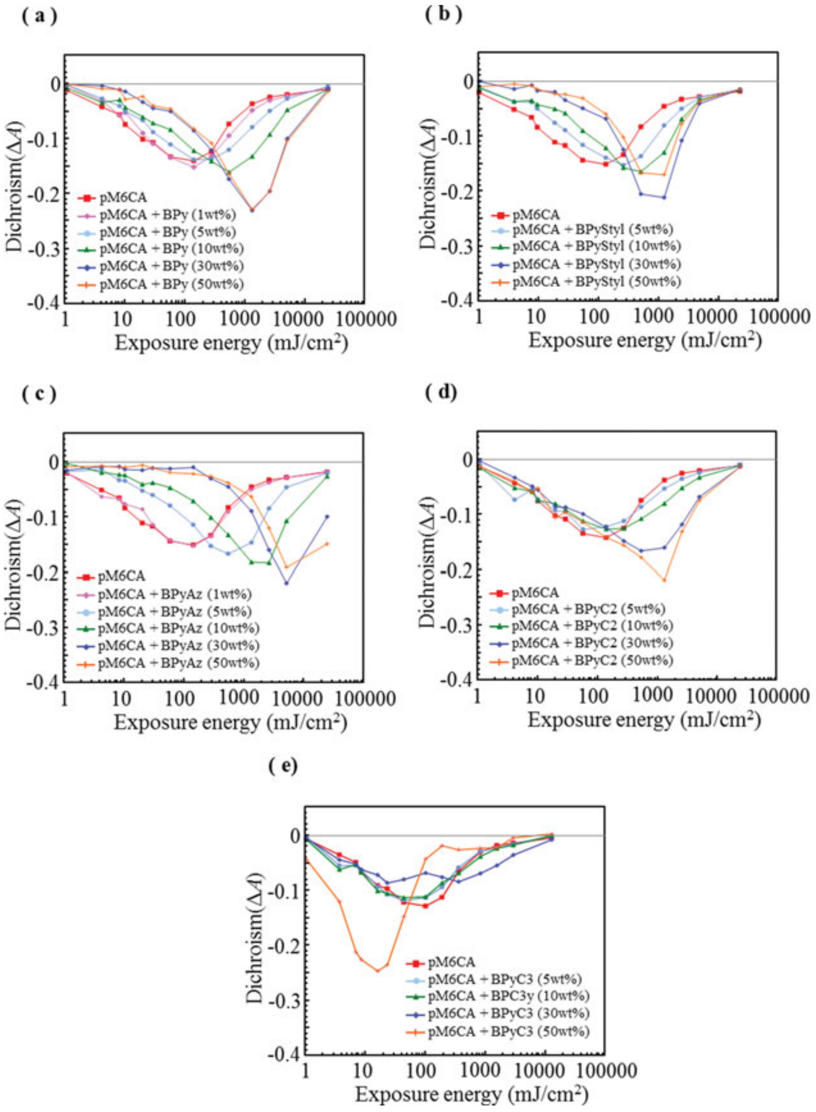

Figure 6. Dichroism (Δ*A*) of (a) pM6CA/BPy (0–50 wt%), (b) pM6CA/BPyStyl (0–50 wt%), (c) pM6CA/BPyAz (0–50 wt%), (d) pM6CA/BPyC2 (0–50 wt%) and (e) pM6CA/BPyC3 (0–50 wt%) films after LPUV light irradiation as a function of exposure dose.

2.4. Measurement

The thermal properties of the pM6CA/pyridine derivatives powder samples were evaluated by differential scanning calorimetry (DSC: METTLER TOLEDO DSC 1) analysis at a heating and cooling rate of 10°C/min. Polarization UV-vis spectra were measured using a UV/vis spectrometer (SHIMADZU UV-3600) equipped with Glan-Taylor polarizing prisms.

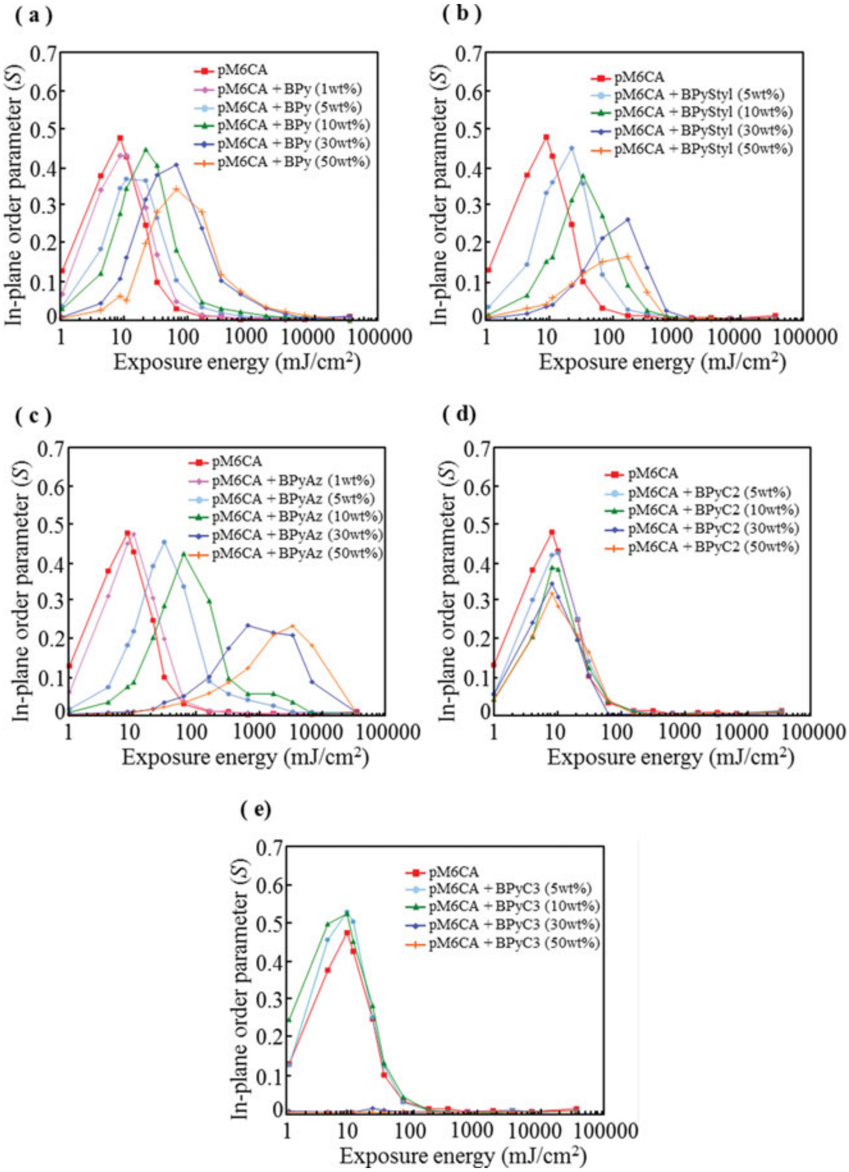

Figure 7. In-plane order parameter S of (a) pM6CA/BPy (0–50 wt%), (b) pM6CA/BPyStyl (0–50 wt%), (c) pM6CA/BPyAz (0–50 wt%), (d) pM6CA/BPyC2 (0–50 wt%) and (e) pM6CA/BPyC3 (0–50 wt%) films after LPUV light irradiation, following annealing at 150°C for 10min. as a function of exposure dose.

2.5. Preparation of Low-Molecular LC Cells Using for Photoalignment Layer of Reorientation Films

Anti-parallel LC cells were fabricated using two LPUV photoreacted pM6CA/pyridine derivative thin films to evaluate the LC alignment behavior. The cell (6μm thick) was filled with a nematic LC mixture (MLC-2041: Merck Japan, $T_i = 80°C$) by vacuum pressure impregnation method. Orientation of cells prepared was observed by visual test.

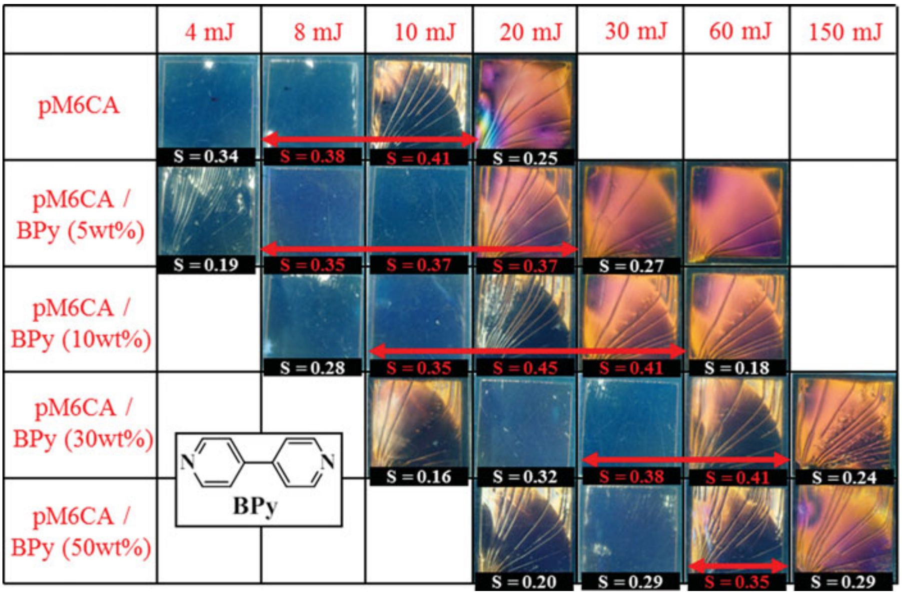

Figure 8. Photographs of the anti-parallel LC cell prepared by using the reoriented pM6CA/BPy (0–50 wt%) films. The numerical values are described below each cell represent the in-plane order parameter *S* shown

Results and Discussion

3.1. Thermal Properties of Composite Materials

Figure 2a shows DSC curves of pM6CA/BPy (0–50 wt%) composites. In this case, T_i values are around 180°C regardless of the BPy composition. Similar T_i behaviors are observed for BPyStyl and BPyC2 (Fig. 2b). However, when increasing the content of BPyAz and BPyC3, pyridine content increases, T_i decreases.

The formation of H-bonding interaction among the pyridine-carboxylic acid is detected by FT-IR spectrum. For example, Fig. 3a shows the FT-IR spectra of the pM6CA/BPy (0–100 wt%) thin films before LPUV light irradiation. In the each sample before a LPUV light irradiation, a broad absorption around 2700 cm^{-1} is observed, which is ascribed to H-bonded COOH dimer. In addition, two peaks observed in lower wavenumber side (around 2500 and 1900 cm^{-1}) are the absorption bands derived from the pyridine-carboxylic acid interaction. These two peaks increase where content of BPy increases, and another broad peak around 3200 cm^{-1} based on free carboxylic acid decreases. In contrast, in the each sample after annealed at 150°C for 10min., two broad peaks derived from the pyridine-carboxylic acid interaction and absorption at 600 cm^{-1} based on BPy disappear (Fig. 3b). These results indicate the sublimation of pyridine derivatives upon heating. Similar behavior is confirmed for other films regardless of the content of pyridine derivatives.

3.2. Photoreaction

Figure 4 shows changes in the UV absorption spectra of a (a) pM6CA and (b) pM6CA/BPy (50/50) films upon irradiating with LPUV light. The more the intensity of irradiated LPUV light increases, the more the absorption peak of the cinnamoyl groups at 314nm decreases. Similar photoreaction behavior is observed when other pyridine derivatives are used although the photoreaction rate is somewhat different.

Figures 5a-e plot the degree of the photoreaction of pM6CA/BPy (0–50 wt%), pM6CA/BPyStyl (0–50 wt%), pM6CA/BPyAz (0–50 wt%), pM6CA/BPyC2 (0–50 wt%) and pM6CA/BPyC3 (0–50 wt%) films after LPUV light irradiation as a function of exposure dose, respectively. In all cases, additive amount of each pyridine derivatives increases, photoreactivity gradually decreases. This is due to the photoabsorption of pyridine derivatives.

It is well known that irradiation of polymric films containing cinnamoyl groups with LPUV light leads to negative optical anisotropy ($\Delta A<0$) as a result of axis-selective [2+2] photodimerization. Figures 6a-e plot ΔA of pM6CA/BPy (0–50 wt%), pM6CA/BPyStyl (0–50 wt%), pM6CA/BPyAz (0–50 wt%), pM6CA/BPyC2 (0–50 wt%) and pM6CA/BPyC3 (0–50 wt%) films as a function of exposure dose, respectively. In all cases, the axis-selective photoreaction occurs regardless of content of pyridine derivatives. In pyridine derivatives except for BPyC3, it requires higher exposure doses as increasing the pyridine derivatives content.

Figures 7a-e plot the thermally enhanced in-plane order parameter S of pM6CA/BPy (0–50 wt%), pM6CA/BPyStyl (0–50 wt%), pM6CA/BPyAz (0–50 wt%), pM6CA/BPyC2 (0–50 wt%) and pM6CA/BPyC3 (0–50 wt%) films after LPUV light irradiation, followed by annealing at 150°C for 10min as a function of exposure dose, respectively. In case of BPy, BPyStyl and BPyAz, additive amount of pyridine derivatives increases, region with a relatively high degree of orientation shifts to a higher irradiation region side. Thus, adjusting the pyridine derivative content controls the appropriate exposure energy for sufficient orientation. On the other hand, in case of BPyC2, S gradually decreases as increasing additive amount of pyridine derivatives. Slightly larger S values are obtained where the BPyC3 content is less than 10wt%. However, anisotropy completely disappears, when the BPyC3 content is higher than 30wt%, where the T_i of the composite film is lower 100°C. Lower exposure range of the composite film will not generate the thermal amplification.

3.3. LC Alignment

Figure 8 show LC cell photographs between crossed polarizers of anti-parallel LC cells prepared using the reoriented pM6CA/BPy (0–50 wt%) films. They indicate that optimal orientation areas slightly shifted to the low irradiation side overall than it expected from in-plane order parameter S. However, correlation is found between the actual orientation behavior of the large S reagion. It should be noted that the pM6CA/pyridine derivatives composite films using BPyStyl and BPyAz, show the same LC alignment behavior.

4. Conclusion

In conclusion, we have investigated for photoreactivity and photoinduced orientation of H-bonding composite thin films comprised of liquid crystalline methacryate with cinnamic acid side groups (pM6CA) and pyridine derivatives. All composite films show H-bondings between pyridine derivatives and pM6CA, and LPUV light exposure generates as negative anisotropy of the films similar to the pM6CA films. Additionally, when increasing the additive amount of pyridine derivatives, photoreactivity decreases. The annealing process to the exposed films amplifies the photoinduced anisotropy, but the efficiency depends on the type of pyridine derivatives and the content. The photoinduced anisotropy and exposure dose margin for the effective amplification of the molecular orientation increases when BPy, BPyStyl and BPyAz are doped with pM6CA. On the other hand, in case of BPyC2 and BPyC3, in-plane order parameter *S* decreases with increasing irradiation dose. Using the reoriented films, LC cells were fabricated. Uniform LC alignment was obtained when the alignment films exhibit sufficient molecular orientation. These composite film are useful for LC alignment layer, where adjusting the structure and amount of the pyridine derivatives can control the effect of pyridine-carboxylic acid interactions and the photoalignment ability.

References

[1] (a) Ichimura, K. (2000). *Chem. Rev. 100*, 1847. (b) Natansohn, A., & Rochon, P. (2002). *Chem. Rev. 102*, 4139. (c) Ikeda, T. (2003). *J. Mater. Chem. 13*, 2037.

[2] O'Nell, M., & Kelly, S. M. (2002). *J. Phys. D: Appl. Phys. 33*, R67.

[3] Kawatsuki, N., & Ono, H., (2007). *Organic Electronics and Photonics* Nalwa, H. S., Ed., American Sci. Publishers: Stevenson Ranch, CA, **2**, 301.

[4] Wu, Y., Natansohn, A., & Rochon, P. (2004). *Macromolecules. 37*, 6801.

[5] Häckel, M., Kador, L., Kropp, D., & Schmidt, H.-W. (2007). *Adv. Mater. 19*, 227.

[6] (a) Saishoji, A., Sato, D., Shishido, A., & Ikeda, T., (2007). *Langmur. 23*, 320. (b) Ishiguro, M., Sato, D., Shishido, A., & Ikeda, T., (2007). *Langmur. 23*, 332.

[7] Kawatsuki, N. (2011). *Chem. Lett. 40*, 548.

[8] Schadt, M.; Schmitt, K.; Kozinkov, V.; & Chigrinov, V. (1992). *Jpn. J. Appl. Phys.*, *31*, 2155–2164.

[9] (a) Akita, Y., Akiyama, H., Kudo, K., Hayashi, Y., & Ichimura, K. (1995). *J. Photopolym. Sci. Technol. 8*, 75. (b) Ichimura, K., Akita, Y., Akiyama, H., Kudo, K., & Hayashi, Y., (1997). *Macromolecules. 30*, 903.

[10] Iimura, Y., Saitoh, T., Kobayashi, S., & Hashimoto, T., (1995). *J. Photopolym. Sci. Technol. 8*, 257.

[11] (a) Kawatsuki, N., Ono, H., Takatsuka, H., Yamamoto, T., & Sangen, O. (1997). *Macromolecules. 30*, 6680. (b) Kawatsuki, N., Matsuyoshi, K., Hayashi, M., Takatsuka, H., & Yamamoto, T., (2000). *Chem. Mater. 12*, 1549.

[12] (a) Kawatsuki, N., Takatsuka, H., Yamamoto, T., & Sangen, O. (1998). *J. Polym. Sci., Part A: Polym. Chem. 36*, 1521–1526. (b) Kawatsuki, N., Suehiro, C., & Yamamoto, T. (1998). *Macromolecules. 31*, 5984.

[13] Kawatsuki, N., Goto, K., Kawakami, T., & Yamamoto, T. (2002). *Macromolecules. 35*, 706.

[14] Kawatsuki, N., Tsutsumi, R., Takatsuka, H., & Sakai, T. (2007). *Macromolecules. 40*, 6355.

[15] (a) Kawatsuki, N., An, M. X.; Matsuura, Y., Sakai, T., & Takatsuka, T. (2004). *Liq. Cryst. 31*, 55. (b) Kawatsuki, N., Tachibana, T., An, M. X., & Kato, K. (2005). *Macromolecules. 38*, 3903. (c) Kawatsuki, N., Kato, K., Shiraku, T., & Ono, H., (2006). *Macromolecules. 39*, 3245.

[16] Uchida, E., & Kawatsuki, N. (2006). *Macromolecules. 39*, 9357.

[17] Kato, T., & Fréchet, J., M. J. (1989) *Macromolecules. 22*, 3818.

[18] (a) Kato, T., & Fréchet, J., M. J. (1989). *J. Am. Chem. Soc. 111*, 8533. (b) Kumar, U., Kato, T., & Fréchet, J. M., J. (1992). *J. Am. Chem. Soc. 114*, 6630. (c) Kato, T., Kihara, H., Uryu, T., Fujishima, A., & Fréchet, J., M. J. (1992). *Macromolecules. 25*, 6836. (d) Kato, T., Fukumasa, M., & Fréchet, J., M. J. (1995). *Chem. Mater. 7*, 368. (e) Kato, T., Mizoshita, N., & Kanie, K. (2001). *Macromol. Rapid Commun. 22*, 797.

[19] (a) Kato, T., Wilson, P. G., Fujishima, A, M. J., & Fréchet, J. (1990). *Chem. Lett. 11*, 2003. (b) Kato, T., Mizoshita, N., & Kishimoto, K. (2006). *Angew. Chem. Int. Ed. 45*, 38. (c) Kato, T., J. M., & Fréchet, J. (1990). *Macromolecules. 23*, 360. (d) Kato, T. (1994). *Angew. Chem. Int. Ed. 33*, 1644.