Molecular Crystals and Liquid Crystals

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

UV-Induced Stable Planar Alignment of Nematic Liquid Crystals Using a Polypropyleneimine Dendrimer Having a Mesogen Consisting of Cinnamate and Azobenzene Moieties

Osamu Haba, Hiroki Itabashi, Syun Sato, Keisuke Machida, Tomonori Koda, Koichiro Yonetake, Musun Kwak, Yuichi Momoi, Nakwon Kim, Sangpyo Hong, Dongwoo Kang & Youngseok Choi

To cite this article: Osamu Haba, Hiroki Itabashi, Syun Sato, Keisuke Machida, Tomonori Koda, Koichiro Yonetake, Musun Kwak, Yuichi Momoi, Nakwon Kim, Sangpyo Hong, Dongwoo Kang & Youngseok Choi (2015) UV-Induced Stable Planar Alignment of Nematic Liquid Crystals Using a Polypropyleneimine Dendrimer Having a Mesogen Consisting of Cinnamate and Azobenzene Moieties, Molecular Crystals and Liquid Crystals, 610:1, 201-209, DOI: 10.1080/15421406.2015.1026737

To link to this article: http://dx.doi.org/10.1080/15421406.2015.1026737

Published online: 06 Jul 2015.

Submit your article to this journal

Article views: 22

View related articles

View Crossmark data

Full Terms & Conditions of access and use can be found at
http://www.tandfonline.com/action/journalInformation?journalCode=gmcl20

Download by: [University Town Library of Shenzhen] **Date:** 02 January 2016, At: 04:21

Mol. Cryst. Liq. Cryst., Vol. 610: pp. 201–209, 2015
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2015.1026737

Downloaded by [University Town Library of Shenzhen] at 04:21 02 January 2016

UV-Induced Stable Planar Alignment of Nematic Liquid Crystals Using a Polypropyleneimine Dendrimer Having a Mesogen Consisting of Cinnamate and Azobenzene Moieties

OSAMU HABA,[1,*] HIROKI ITABASHI,[1] SYUN SATO,[1] KEISUKE MACHIDA,[1] TOMONORI KODA,[1] KOICHIRO YONETAKE,[1] MUSUN KWAK,[2] YUICHI MOMOI,[3] NAKWON KIM,[2] SANGPYO HONG,[2] DONGWOO KANG,[2] AND YOUNGSEOK CHOI[2]

[1]Graduate School of Science and Engineering, Yamagata University, Jonan, Yonezawa, Yamagata, Japan
[2]Process Development Division, LG Display Co., Ltd., Deogeun-ri, Wollong-myeon, Paju-si, Gyeonggi-do, South Korea
[3]Japan Laboratory, LG Display Co., Ltd., Glass Cube Shinagawa, Higashi Shinagawa, Shinagawa-ku, Tokyo, Japan

*A liquid crystalline dendrimer having a cinnamate mesogen containing an azobenzene moiety (**D-6AC2**) was prepared as an alignment agent of nematic liquid crystals for a planar homogeneous alignment. **D-6AC2** is a thermotropic liquid crystal showing smectic phases. A mixture of ZLI-4792 with 1wt% of **D-6AC2** exhibited a homeotropic alignment. After UV irradiation of the same sample, the schlieren texture due to a planar orientation was observed, and the texture was maintained even after 133 days. Thus **D-6AC2** can induce the stable planar alignment of NLC upon UV irradiation. Furthermore, **D-6AC2** could induce a planar homogeneous alignment by polarized UV light irradiation.*

Keywords planar alignment; azobenzene; cinnamate; dendrimer; UV irradiation

Introduction

Liquid crystal (LC) molecules with a dipole respond to an electric field to align along the field, but the director without the electric field generally cannot be determined. During LC display production, the orientation without the electric field is especially important because this determines the switching properties of the LC molecules. Alignment

*Address correspondence to Osamu Haba, Graduate School of Science and Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992-8510, Japan. E-mail: haba@yz.yamagata-u.ac.jp

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

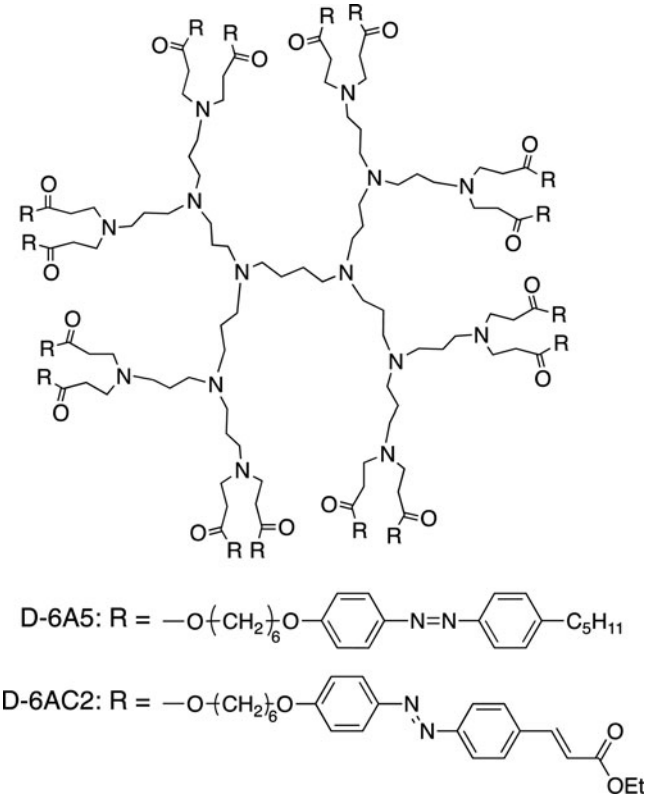


Figure 1. Chemical structure of the LC dendrimers.

layers are widely used today to determine the orientation of the alignment without the electric field. They are mainly polyimide wrinkled by a rubbing process which has a negative influence on the integrated circuits of the LCDs and cleanliness of the clean rooms.

We have reported that polypropyleneimine dendrimers (PPID) having peripheral mesogenic units tend to homeotropically align on native glass surfaces [1–3]. Mixing a few% of the dendrimer into nematic liquid crystals (NLCs) induced the vertical alignment of the entire NLCs [4, 5]. Using this property, we could prepare a liquid crystalline display without *any* polyimide alignment layers [4]. Some LC displays, especially in the in-plane switching (IPS) and twist nematic (TN) modes, require a planar homogeneous alignment, but our dendrimer is not suitable for such displays.

In this study, we prepared a liquid crystalline dendrimer having a cinnamate mesogen containing an azobenzene moiety (D-6AC2) as shown in Fig. 1 in order to achieve a stable planar alignment upon UV irradiation. It is well known that the azobenzene unit, which is stable in the *trans*-form, converts into the *cis*-form upon UV irradiation. Our previous attempt[6] using azobenzene mesogens on the dendrimer (D-6A5) induced the planar alignment of matrix NLCs under UV light, but the alignment was not stable and immediately went back to a vertical alignment under visible light. In order to fix the planar alignment, we tried to introduce the cinnamate group, which is expected to dimerize and prevent the transformation of the *cis*-azobenzene to the *trans*-form.

Downloaded by [University Town Library of Shenzhen] at 04:21 02 January 2016

Downloaded by [University Town Library of Shenzhen] at 04:21 02 January 2016

Experimental Section

Measurements

The NMR spectra were measured as a 0.5% $CDCl_3$ solution by a JEOL JNM-ECX 400 (400 MHz for ^1H and 100 MHz for ^{13}C) spectrometer. Tetramethylsilane (0.0 ppm) and the solvent peak (77.0 ppm) were used for the internal reference peak for the ^1H and ^{13}C NMR measurements, respectively. Differential scanning calorimetry (DSC) was recorded by a Q200 instrument (TA instruments) at the heating/cooling rate of 10°C/min in nitrogen. Optical textures of the samples were examined using a polarizing optical microscope (POM) equipped with a hot stage (Linkam Co., TH-600RMS). X-ray diffraction experiments were carried out using a RAD-rA diffractometer (Rigaku Denki Co., Ltd.) equipped with a heating device. Wide-angle X-ray diffraction (WAXD) experiments were carried out by a MiroMax007 diffractometer (Rigaku Denki Co., Ltd.) operated at 40 kV and 20 mA. CuK_α X-ray beams monochromatized with a confocal mirror were irradiated the specimen through a pinhole collimator of 0.2 mm diameter. The imaging plate R-AXIS IV^{++} system was utilized as an X-ray detector at a camera length of 150 mm. All measurements were conducted at room temperature (26°C).

Materials

Ethyl 4-nitrocinnamate (1) (TCI), 6–bromohexanol (TCI) and acryloyl chloride (Aldrich) were purchased and used as received. A fluoride-type nematic liquid crystal mixture, ZLI-4792 (nematic to isotropic transition temperature: 93°C), was purchased from Merck. Tetrahydrofuran (THF) was distilled from sodium – benzophenone ketyl just before use. The synthetic procedure of the dendrimer having peripheral azobenzene mesogens (**D-6A5**) was previously described [7]. Unless otherwise noted, all other chemicals were commercially available and used without further purification.

Ethyl 4-aminocinnamate (2)

Ethyl 4-nitrocinnamate (1) (3.0 g, 14 mmol) was dissolved in 70 mL of ethanol and then 28 mL of water was added. Iron powder (2.3 g, 41 mmol) and NH_4Cl (2.2 g, 41 mmol) were added and the resulting suspension was heated to reflux for 2 h. The insoluble materials were filtered off through a Celite pad and the filtrate was concentrated under reduced pressure. The aqueous residue was extracted with ethyl acetate. The organic layer was washed with brine, dried over Na_2SO_4, then concentrated under reduced pressure. The yellow solid residue was used without further purification. Yield 2.7 g. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.60 (d, J = 15.8 Hz, 1H, = CHAr), 7.34 (d, J = 8.2 Hz, 2H, Ar-$H_{2,6}$), 6.64 (d, J = 8.2 Hz, 2H, Ar-$H_{3,5}$), 6.23 (d, J = 15.8 Hz, 1H, = CHCO), 4.24 (q, J = 7.2 Hz, 2H, OCH_2), 3.97 (br, 2H, NH_2), 1.32 (t, J = 7.2 Hz, 3H, CH_3).

Ethyl 4-(4-hydroxyphenylazo)cinnamate (3)

A suspension of 2 (2.0 g, 11 mmol) in 63 mL of water containing 2.5 mL of concentrated hydrochloric acid was stirred in an ice bath. A solution of $NaNO_2$ (3.8 g, 55 mmol) in water (12 mL) was added and the mixture was stirred at 0°C for 1 h. A solution of phenol (1.3 g, 14 mmol) and NaOH (0.84 g, 21 mmol) in 6.3 mL of water was then added and the mixture was stirred at room temperature for 1 h. The resulting suspension was extracted with ethyl

acetate. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was recrystallized from methanol to give a dark red powder. Yield 1.2 g (39%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.90−7.87 (2×d, J = 9.1 Hz and 8.7 Hz, 4H, Ar-$H_{3,5}$ and Ar-$H_{2',6'}$), 7.64 (d, J = 15.8 Hz, 1H, = CHAr), 7.65 (d, J = 8.6 Hz, 2H, Ar-$H_{2,6}$), 6.51 (d, J = 8.7 Hz, 2H, Ar-$H_{3',5'}$), 6.04 (s, 1H, –OH), 4.30 (q, J = 7.2 Hz, OCH_2), 1.36 (t, J = 7.2 Hz, CH_3).

Ethyl 4-(4-(6-hydroxyhexyloxy)phenylazo)cinnamate (4)

To a solution of 3 (1.0 g, 3.4 mmol) in butanone (23 mL), potassium carbonate (0.58 g, 4.2 mmol) was added. The resulting suspension was heated to reflux for 1 h. After cooling to room temperature, a solution of 6-bromohexanol (0.74 g, 4.1 mmol) in butanone (2.0 mL) was dropwise added. The resulting suspension was again heated to reflux for 14 h. The resulting suspension was poured into 100 ml of water, and extracted with ethyl acetate. The organic layer was washed with water, dried over $MgSO_4$, and evaporated to dryness. The residue was recrystallized from ethyl acetate to give tiny dark red prisms. Yield 0.69 g (49%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.92 (d, J = 9.1 Hz, 2H, Ar-$H_{2',6'}$), 7.89 (d, J = 8.2 Hz, 2H, Ar-$H_{3,5}$), 7.73 (d, J = 15.8 Hz, 1H, = CHAr), 7.66 (d, J = 8.2 Hz, 2H, Ar-$H_{2,6}$), 7.01 (d, J = 9.1 Hz, 2H, Ar-$H_{3',5'}$), 6.51 (d, J = 15.8 Hz, 1H, = CHCO), 4.29 (q, J = 7.2 Hz, 2H, $COOCH_2$), 4.06 (t, J = 6.8 Hz, 2H, ArO-CH_2-), 3.68 (t, J = 6.8 Hz, 2H, HO-CH_2-), 1.89-1.82 (m, 2H, CH_2), 1.67-1.44 (m, 6H, CH_2), 1.36 (t, J = 7.2 Hz, 3H, -CH_3).

Ethyl 4-(4-(6-acryloyloxyhexyloxy)phenylazo)cinnamate (5)

To a solution of 4 (0.50 g, 1.3 mmol) and triethylamine (0.37 mL, 1.9 mmol) in 130 mL of CH_2Cl_2, acryloyl chloride (0.13 mL, 1.5 mmol) was added at 0°C and the mixture was stirred at room temperature for 24 h. The mixture was then washed with 0.1 M hydrochloric acid, a saturated $NaHCO_3$ aqueous solution, and then brine. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was recrystallized from ethyl acetate to give dark red needles. Yield 0.15 g (26%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.92 (d, J = 9.1 Hz, 2H, Ar-$H_{2',6'}$), 7.89 (d, J = 8.2 Hz, 2H, Ar-$H_{3,5}$), 7.73 (d, J = 15.8 Hz, 1H, = CHAr), 7.66 (d, J = 8.2 Hz, 2H, Ar-$H_{2,6}$), 7.01 (d, J = 9.1 Hz, 2H, Ar-$H_{3',5'}$), 6.51 (d, J = 15.8 Hz, 1H, = CHCO), 6.41 (dd, $^3J_{trans}$ = 17.7 Hz, ^2J = 1.3 Hz, 1H, CH_2 =), 6.13 (dd, $^3J_{trans}$ = 17.7 Hz, $^3J_{cis}$ = 10.4 Hz, 1H, CH_2 = CHCOOCH_2), 5.83 (dd, $^3J_{cis}$ = 10.4 Hz, ^2J = 1.3 Hz, 1H, CH_2 =), 4.29 (q, J = 7.2 Hz, 2H, $COOCH_2$), 4.19 (t, J = 6.8 Hz, 2H, CH_2 = CHCOO-CH_2), 4.06 (t, J = 6.8 Hz, 2H, ArO-CH_2-), 1.89-1.81 (m, 2H, CH_2), 1.77-1.70 (m, 2H, CH_2), 1.57-1.45 (m, 4H, CH_2), 1.36 (t, J = 7.2 Hz, 3H, -CH_3).

Synthesis of D-6AC2

A solution of the second-generation polypropyleneimine dendrimer (20 mg, 0.026 mmol) and **5** (0.80 g, 2.1 mmol) in THF (3.6 mL) was stirred at 50°C for 4 weeks. The solvent was removed under reduced pressure. The residue was dissolved in a minimum amount of $CHCl_3$, and poured into ethyl acetate twice to produce a dark red powder. Yield 0.18 g (44%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.93-7.87 (br, 64H, Ar-H), 7.74-7.64 (m, 48H, = CHCOO and Ar-H), 7.01-6.99 (br, 32H, Ar-H), 6.52–6.48 (br, 16H, = CHAr), 4.30–4.25 (br, 32H, COO−C$H_2$$CH_3$), 4.19−4.03 (m, 64H, COO−C$H_2$$CH_2$ and CH_2OAr),

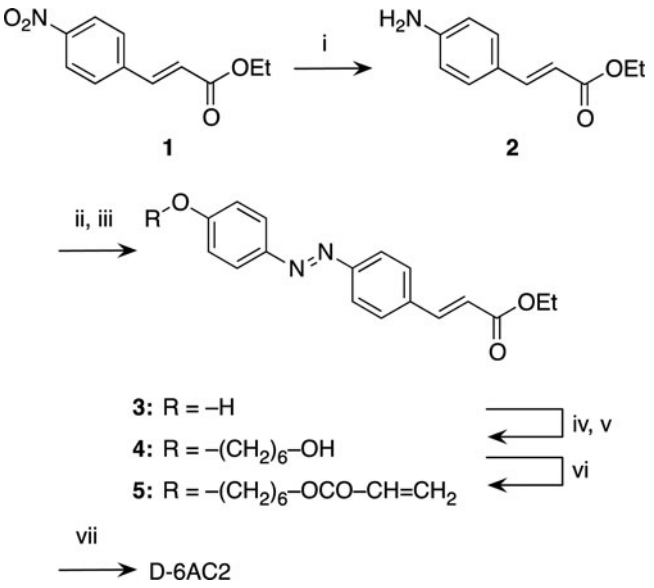
Downloaded by [University Town Library of Shenzhen] at 04:21 02 January 2016

2.83-2.70 (m, 32H, N-C*H*$_2$CH$_2$CO), 2.51-2.30 (m, 84H, N-CH$_2$ and CH$_2$CO), 1.91-1.33 (m, 204H, CH$_2$ and CH$_3$).

Results and Discussion

Synthesis of D-6AC2

The target dendrimer D-6AC2 was prepared according to Scheme 1. The azo-cinnamate phenol (3) was originally synthesized by Vorländer *et al*. [8]. We prepared 3 based on their procedure with slight modifications. First, commercial ethyl 4-nitrocinnamate (1) was hydrogenated by iron in the presence of ammonium chloride to give ethyl 4-aminocinnamate (2), which was converted to the diazonium salt by treatment with nitrous acid and then coupled with phenol to give 3. A C-6 spacer was introduced by the reaction of 3 with 6-bromohexanol, then the resulting 4 was reacted with acrylic chloride to give the acrylate 5. Finally, 5 was reacted with the commercial 2nd generation PPID at 50°C for 4 weeks to give D-6AC2.



Scheme 1. Synthesis of **D-6AC2**. i) Fe, NH_4Cl, ii) $NaNO_2$, HCl iii) PhOH, iv) K_2CO_3, v) HO–$(CH_2)_6$–Br, vi) $CH_2 = CHCOCl$, Et_3N, vii) Propyleneimine dendrimer (G = 2).

Phase Transition of D-6AC2

Figure 2 shows a DSC trace of D-6AC2 for the 2nd cooling and heating scan. Upon heating, D-6AC2 shows four endothermic peaks at 58, 105, 149 and 174°C. Because the POM observation at 180°C showed a dark field due to an isotropic melt, the phase transition at 174°C is caused by the mesophase - isotropic transition. Figure 3 shows WAXD profiles of D-6AC2 between each phase transition. All profiles shows a sharp diffraction in a small-angle area, and thus D-6AC2 exhibits a smectic phase with a 35-36 Å distance between the layers. At room temperature, three relatively sharp peaks were identified in the wide-angle area, and assigned to the (110), (200), and (210) reflections of an orthorhombic packing

Downloaded by [University Town Library of Shenzhen] at 04:21 02 January 2016

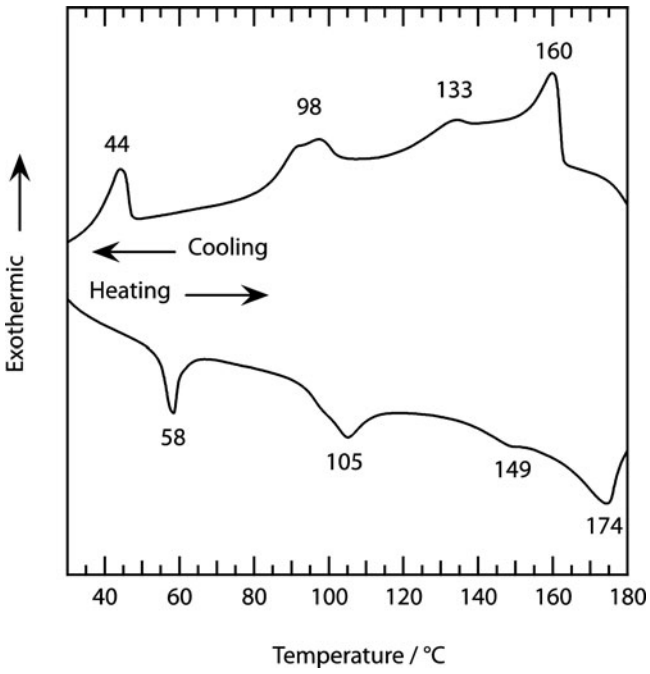


Figure 2. DSC trace of D-6AC2 on the 2nd scan. $\Delta T = 10^{\circ}\mathrm{C\ min^{-1}}$.

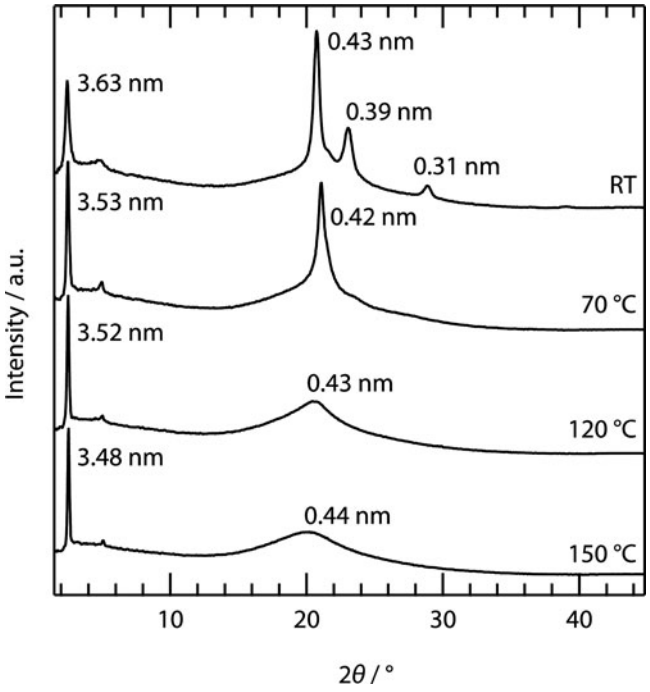


Figure 3. WAXD traces of **D-6AC2** at various temperatures.

Downloaded by [University Town Library of Shenzhen] at 04:21 02 January 2016

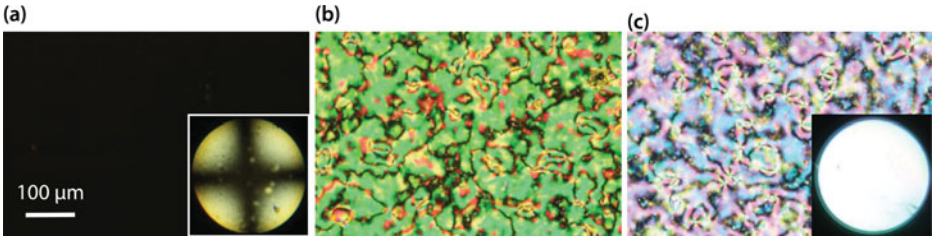


Figure 4. POM images under crossed polarizers of ZLI-4792/**D-6AC2** mixture (99/1, wt/wt) (a) before, (b) just after, and (c) 133 days after the UV irradiation

Downloaded by [University Town Library of Shenzhen] at 04:21 02 January 2016

mode. Thus, the liquid crystalline phase at room temperature is smectic E (SmE). The single sharp peak was observed in the wide-angle region at 70°C, and thus D-6AC2 exhibited a hexatic smectic B (SmB) phase with a 0.42 nm lateral distance between the mesogens at this temperature. At a temperature higher than 70°C, a wide-angle diffuse reflection was observed. Although the difference in the phase structure at 120 and 150°C is not clear, **D-6AC2** exhibits a smectic A (SmA) or smectic C (SmC) phase at these temperatures. Because the SmC phase usually appears at a temperature lower than the SmA phase, the **D-6AC2** might exhibit the SmC phase between 105 and 149°C. Based on these results, **D-6AC2** is a thermotropic liquid crystal showing the following phase transition behavior upon heating: SmE 58°C SmB 105°C SmC(?) 149°C SmA 174°C Iso.

Orientation of D-6AC2/NLC Mixtures

In order to investigate the orientation behavior of the NLC/D-6AC2 mixture, 1.0wt% of D-6AC2 was mixed with the commercial F-type NLC, ZLI-4792. Although the solubility of **D-6AC2** in ZLI-4792 was poor and most of the samples showed typical schlieren textures, a few samples exhibited a totally dark field in the POM observation under crossed polarizers as shown in Fig. 4a. The conoscopic observation exhibited a crossed isogyre indicating the homeotropic orientation of the whole NLC as previously reported for the dendrimer/NLC systems [5]. Upon UV irradiation (85 J cm^{-2}) of this sample, the schlieren texture due to the nematic phase was observed as shown in Fig. 4b, and the texture was maintained even after 133 days (Fig. 4c). Thus D-6AC2 can induce the planar alignment of NLC upon UV irradiation and the orientation was stable for at least a few months. On the other hand, D-6A5 having no cinnamate groups, which could similarly induce the homeotropic alignment to ZLI-4792 as shown in Fig. 5a, can change the direction to planar upon UV

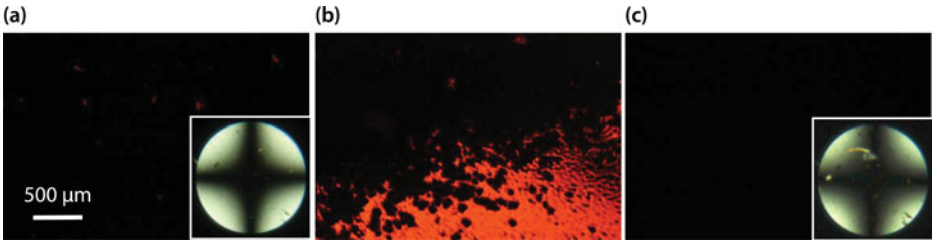


Figure 5. POM images under crossed polarizers of ZLI-4792/**D-6A5** mixture (99/1, wt/wt) (a) before, (b) just after, and (c) 2 minutes after the UV irradiation

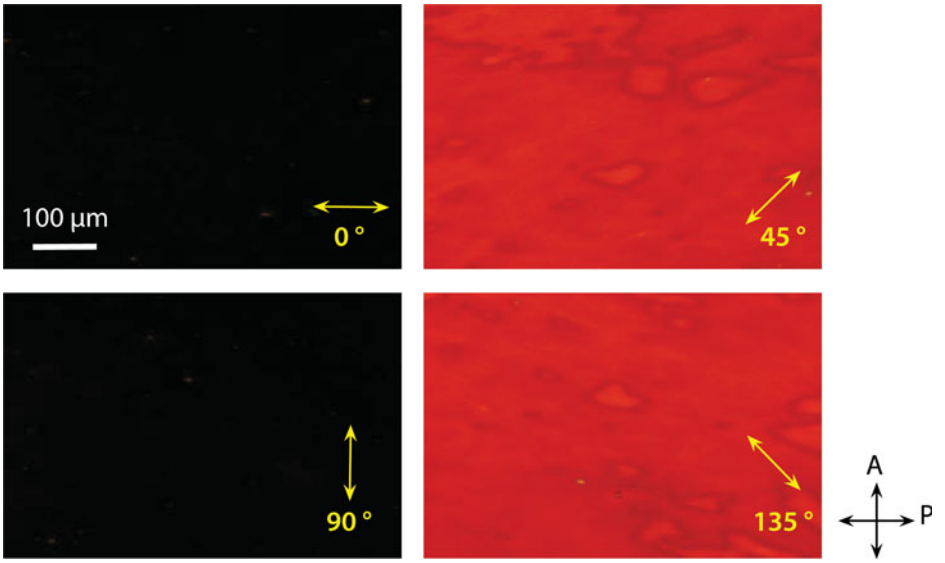


Figure 6. POM images under crossed polarizers of ZLI-4792/**D-6A5** mixture (99/1, wt/wt) after polarized UV irradiation. The bidirectional arrows within the images indicate the direction of vibration of the polarization.

irradiation as shown in Fig. 5b. However, the orientation disappeared immediately after the irradiation, and the homeotropic orientation was regenerated after 2 minutes (Fig. 5c). Thus the cinnnamate group in D-6AC2 can effectively stabilize the planar alignment.

Polarized UV light then irradiated the ZLI-4792/D-6AC2 sample that exhibited a homeotropic alignment. Figure 6 shows the POM images after 360 J cm^{-2} of irradiation under crossed polarizers with rotating the sample. The direction of the vibration of the polarized light is shown by the bidirectional arrows within the images. Dark fields were observed when the polarizer and the polarization are parallel (0° and 90°), whereas bright red fields were observed at 45° and 135°. Thus the NLC should exhibit a homogeneous alignment, and **D-6AC2** has the potential to induce such an alignment by polarized UV light irradiation.

Summary

As already described, the 2nd generation polypropyleneimine dendrimer having peripheral mesogens consisting of azo and cinnnamate moieties (D-6AC2) was synthesized. Upon polarized UV irradiation, a mixture of ZLI-4792 and D-6AC2 exhibited a homogeneous alignment. This might lead the way to develop polyimide-free displays that require such an alignment. However, some problems still exists, such as the poor solubility of D-6AC2 in NLC and requirement of a significant exposure dose of UV light. Further studies investigating these concerns are currently underway.

References

[1] Yonetake, K., Masuko, T., Morishita, T., Suzuki, K., Ueda, M., & Nagahata, R. (1999). *Macromolecules*. *32*, 6578.

Downloaded by [University Town Library of Shenzhen] at 04:21 02 January 2016

[2] Haba, O., Okuyama, K., Osawa, H., & Yonetake, K. (2005). *Liq. Cryst.*, *32*, 633.
[3] Haba, O., Hiratsuka, D., Shiraiwa, T., Koda, T., Yonetake, K., Momoi, Y., & Furuta, K. (2013). *Mol. Cryst. Liq. Cryst.*, *574*, 84.
[4] Momoi, Y., Kwak, M., Choi, D., Choi, Y., Jeong, K., Koda, T., Haba, O., & Yonetake, K. (2012). *J. Soc. Inf. Display.*, *20*, 486.
[5] Haba, O., Hiratsuka, D., Shiraiwa, T., Funakoshi, N., Awano, H., Koda, T., Takahashi, T., Yonetake, K., Kwak, M., Momoi, Y., Kim, N., Hong, S., Kang, D., & Choi, Y. (2014). *Opt. Mater. Express.*, *4*, 934.
[6] Lee, G., Araoka, F., Ishikawa, K., Momoi, Y., Haba, O., Yonetake, K., & Takezoe, H. (2013). *Part. Part. Syst. Charact.*, *30*, 847.
[7] Li, W., Dohi, T., Hara, M., Nagano, S., Haba, O., Yonetake, K., & Seki, T. (2012). *Macromolecules*, *45*, 6618.
[8] Vorländer, D., Wilke, R., Haberland, U., & Ost. K. (1937). *Ber. Dtsch. Chem. Ges. A/B*, *70*, 2096.

Downloaded by [University Town Library of Shenzhen] at 04:21 02 January 2016