



Fabrication of highly efficient coatable polarizer from tolane-based smectic reactive mesogen



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HIGHLIGHTS

- Reactive mesogen with smectic A phase was synthesized for coatable polarizer.
- Coatable polarizer was fabricated on a single substrate by “host-guest” method.
- Coatable polarizer exhibits considerable optical property and excellent stability.
- LCD with in-cell structure was demonstrated by using the prepared coatable polarizer.

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ABSTRACT

This work is aimed to fabricate ultra-thin coatable polarizers on a single substrate based on “host-guest” effect between highly ordered smectic reactive mesogen (RM) and dichroic dye. We designed and synthesized a new tolane-based RM with a highly ordered smectic A phase at room temperature. Polymerizable “host-guest” mixture was formulated from the host RM, dichroic dye and additives, then spin-coated on a single substrate having an alignment layer. Subsequent in-situ photopolymerization by UV irradiation successfully resulted in a coatable polarizer with good polarizing properties. The fabricated coatable polarizer showed a dichroic ratio (DR) of 16.4 and a degree of polarization (DOP) of 99.3% with the thickness of 4 μm. The resulting coatable polarizer possessed a considerable solvent resistance, good thermal stability and robust mechanical properties. Moreover, we prepared a TN-mode LC cell by using the prepared coatable polarizers inside the cell (in-cell), in which the coatable polarizers acted as a polarizer and an alignment layer, simultaneously. The resulting TN cell with in-cell polarizers exhibited a decent electro-optical behavior. We believe that the coatable polarizer proposed in this study possesses practical application potential in ultra-thin LCDs or flexible OLEDs.

1. Introduction

Linear polarizer is one of the most essential optical parts in the current display devices such as LCDs and OLEDs [1]. It generates a linearly polarized light from unpolarized natural light, and acts as a light control valve in LCDs. Linear polarizers are also an indispensable component of the anti-reflection film in OLED display. The anti-reflection film is a circular polarizer fabricated by combining a $\lambda/4$

retarder film and a linear polarizer. It can shield the reflected light generated by the in-coming light mirrored at the metal electrode surface of an OLED [2]. The conventional linear polarizer in the current display devices is a film polarizer of H-sheet form, which is fabricated by uniaxially stretching of poly(vinyl alcohol) (PVA) film doped with iodides [3]. These H-sheet polarizers have excellent optical properties such as high polarization efficiency and high single transmittance. Nonetheless, these conventional polarizers still have several drawbacks

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such as a large overall thickness, inferior heat and moisture stability, and bending or distortion issues originated from the stretching-induced residual stress [4,5]. Due to these reasons, they are not suitable for applications in ultra-thin LCDs. Moreover, the fast evolution of flexible OLEDs also raised a strong demand for a thinner and more flexible polarizer. Therefore, a so-called coatable polarizer with a thickness less than 5 μm have attracted a great attention. Many advantages can be anticipated for the ultra-thin coatable polarizer against the conventional H-sheet polarizer. In addition to a significant decreasing of thickness and weight, the bending or distortion issues resulting from the residual shrinkage force of conventional polarizer film can be avoided [6]. Furthermore, the parallax-related issues and birefringence problems can also be improved when the coatable polarizers are assembled inside the LCD cell (in-cell), so that the inexpensive, robust and flexible plastic substrate can be used as a substrate for flexible display devices [7,8]. However, despite the various advantages and possible applications of coatable polarizers, some drawbacks such as low optical properties and complicated film fabrication processes should be overcome prior to the commercialization.

To challenge the fabrication of ultra-thin coatable polarizers, self-assembled columnar structures of lyotropic chromonic liquid crystal (LCLC) have been proposed since 1990s [9–11]. Previously, we also reported a promising approach to fabricate the ultra-thin coatable polarizers by using an in-situ photopolymerization of self-assembled lyotropic chromonic liquid crystals (LCLC) [8,12–15]. The LCLC molecules oriented along the shearing direction exhibited a significant anisotropic absorption of visible light. A subsequent drying of solvent or in-situ photopolymerization stabilized the oriented LCLC molecules. Nevertheless, the practical applications of LCLC-based coatable polarizers are impeded due to poor film qualities and color limitations as well as an insufficient polarization performance. Another promising approach has been proposed based on the dichroic “host-guest” system [7,16,17]. It was reported that the anisotropic absorption of visible light can be achieved by co-aligning “guest” dichroic dye molecules along the highly ordered polymerizable “host” liquid crystal molecules. While the low viscosity of polymerizable “host” liquid crystals enabled an easy alignment of dichroic molecules, a subsequent in-situ polymerization provided a freedom to immobilize the optimum phase and molecular ordering [7,18]. In these works, a mixture of polymerizable liquid crystalline (LC) compounds and a dichroic dye (2.0 wt %) was injected in a sandwich cell having anti-parallel alignment layers, and in-situ photopolymerized in the highly ordered smectic B phase. After detaching the top substrate, the resulting polarizer on a single substrate exhibited a superior performance to the previously reported thin-film polarizers with an average dichroic ratio of 50. However, there still have a limitation in this method, because the polarizer was fabricated in a sandwich cell which restricts a large-scale fabrication process. In addition, there are only a few host LC compounds showing a highly ordered smectic B phase, and it is relatively difficult to achieve a defect-free alignment in large area due to the high viscosity of smectic B phase. Kim et al. have reported the fabrication of coatable “host-guest” polarizer by a spin coating process utilizing a liquid crystalline polymer as the “host” materials, which provided a simple and practical fabrication

process for the coatable polarizer [19–21]. On the other hand, the resulting coatable polarizer from the liquid crystalline polymer exhibited inferior dichroic ratio mainly due to the low molecular ordering of nematic host materials. More importantly, there are still lack of reports on the coatable polarizer utilizing “host-guest” systems based on highly ordered host materials, especially, fabricated on a single substrate.

Presented herein is the first study on the fabrication of ultra-thin coatable polarizer on a single substrate based on a smectic A phase “host-guest” system. In this work, firstly, we designed and synthesized a new reactive mesogen (RM) with highly ordered smectic A phase at room temperature, which was further investigated by DSC, polarized optical microscopy (POM), and wide-angle X-ray diffraction (WAXD). Secondly, the “host-guest” effect between the RM (host) and dichroic dye (guest) molecules was investigated. The “host-guest” mixture exhibited a uniform homogeneous alignment with high molecular ordering at room temperature, which was in-situ photopolymerized to form a crosslinked network structure stabilizing the highly oriented guest molecules. Thirdly, the vertical alignment of LC molecules on a single substrate due to the air/LC interface was suppressed by using a surfactant to decrease the surface energy. Consequently, a coatable polarizer was fabricated by a coating process on a single substrate such as a glass substrate or plastic film. Finally, we prepared a TN-mode LC cell with coatable polarizers inside the cell (in-cell), which is advantageous to decrease the device thickness as well as the parallax issues. In this case, the coatable polarizer layer also acted as an alignment layer. The coatable polarizer proposed in this work can be a promising alternative to the H-sheet polarizer in ultra-thin and flexible display devices.

2. Experimental

2.1. Materials

Ethyl 4-hydroxybenzoate, 6-chlorohexanol, acryloyl chloride, N,N-dimethylaniline, 4-dimethylaminopyridine (DMAP), N,N'-dicyclohexylcarbodiimide (DCC), *p*-iodophenol, *p*-iodobenzoic acid, *n*-1-hexanol, copper (I) iodide, tetrakis(triphenylphosphine) palladium (0), 75% (w/w) tetrabutylammonium fluoride solution in water, 1,6-hexandiol, methanesulfonic acid, 2-butanone, dichloromethane, triethylamine, ethanol, 1,4-dioxane were purchased from Aldrich Chem. Co., and used without further purification. NaI, NaOH, KOH and HCl were purchased from TCI and used without further purification. Azo-based dichroic red dye (DAD, $\lambda_{\text{max}} = 485 \text{ nm}$), as shown in Fig. 1, was synthesized according to the procedure described in the Supporting Information. Dichroic black dyes (Orasol® Black CN, Irgaphor® Black X12 and Irgaphor® Black X13) were obtained from Ciba Specialty Chem. Co. and BASF Co., and used without further purification.

2.2. Synthesis of RM

The “host” RM containing a tolane mesogenic core structure with two acrylate groups at both ends is abbreviated as DAT (tolane diacrylate), and the structure is illustrated in Fig. 1. The synthetic route for

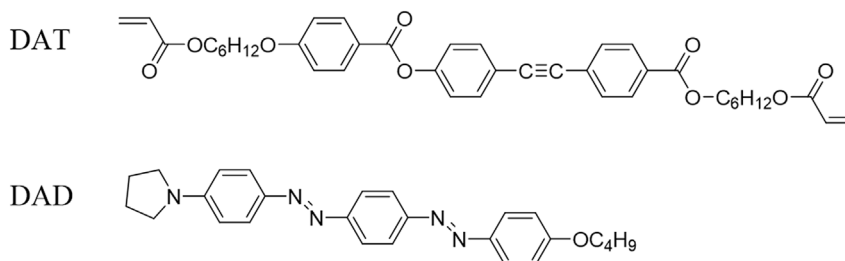


Fig. 1. Structure of tolane-based reactive mesogen (DAT) and azo-based dichroic dye (DAD).

DAT, 6-(acryloyloxy)hexyl 4-((4-((6-(acryloyloxy)hexyl)oxy)benzoyl)oxy)phenyl)ethynyl)benzoate, is displayed in [Scheme S1](#). The synthetic procedures for DAT are described in detail in the Supporting Information.

2.3. Characterizations

To confirm the structure of DAT, ^1H NMR spectra were recorded with JNM-AL400 FT/NMR spectrometer (400 MHz, JEOL Ltd., Japan) in chloroform- d or DMSO- d_6 . The detailed results can be reported in the Supporting Information. The mesomorphic behaviors of DAT and the “host-guest” mixtures were studied by polarized optical microscopy (POM), differential scanning calorimetry (DSC) and X-ray diffraction (XRD) at various temperatures. The polarized optical microscopy was carried out with Nikon ECLIPSE LV100 (Nikon Co., Japan) equipped with a Nikon DS-Ri1 digital camera and a hot-stage. Differential scanning calorimetry (DSC) was conducted on DSC 2010 differential scanning calorimeter (TA Instruments Inc., USA) at heating and cooling rates of $5\text{ }^\circ\text{C min}^{-1}$ under nitrogen atmosphere. Phase transition temperatures were obtained from the onset temperature during heating and cooling processes. To analyze the phase structure evolution, 1D WAXD experiments were conducted in the reflection mode of Rigaku 12 kW rotating-anode X-ray (Cu $K\alpha$ radiation) generator coupled with a diffractometer. To observe molecular packing structures at different temperatures, a hot stage calibrated to be within $\pm 1\text{ }^\circ\text{C}$ error was coupled to the diffractometer. Samples were scanned across a 2θ -angle range of $1.5\text{--}30^\circ$ at a scanning rate of 2° min^{-1} . Oriented 2D WAXD patterns were also obtained using a Rigaku X-ray imaging system with an 18 kW rotating-anode X-ray generator. The diffraction peak positions and widths were also calibrated with silicon crystals. At least 30 min exposure time was required for a high-quality pattern. Macroscopically aligned samples were prepared by mechanical extruding at $30\text{ }^\circ\text{C}$ on the cooling process and then quenched below $0\text{ }^\circ\text{C}$. In 2D WAXD experiments, the background scattering was subtracted from the sample scans.

2.4. Fabrication of thin-film polarizers in a sandwich cell

The fabrication process of thin-film polarizer in a sandwich cell is illustrated as below. The “host-guest” mixture was prepared by mixing DAT with 1.5 wt% dichroic red dye (DAD), and 1.0 wt% of photo initiator (Irgacure[®] 369). *p*-Methoxyphenol (0.1 wt%) was added as a radical inhibitor to prevent an unwanted thermal polymerization during the heating processes. The mixture was injected into a sandwich cell of $5\text{ }\mu\text{m}$ gap containing rubbed anti-parallel alignment layers by capillary force at above the isotropic temperature ($135\text{ }^\circ\text{C}$). The alignment layer was prepared by coating a conventional alignment layer (AL-16470, JSR Co.) on a glass substrate followed by a standard process of two-step baking and rubbing. The sandwich cell filled with the “host-guest” mixture was firstly heated above the isotropic temperature ($135\text{ }^\circ\text{C}$), followed by an annealing step at $100\text{ }^\circ\text{C}$ to obtain a uniform homogeneous alignment, and then, cooled to room temperature to obtain a uniformly aligned smectic phase. The in-situ photopolymerization was carried out at room temperature by irradiating UV light with an intensity of 10 mW cm^{-2} (@ 365 nm) for a certain period of time.

2.5. Fabrication of coatable polarizers on a single substrate

The fabrication process of coatable polarizer on a single substrate is illustrated in [Figure S2](#). DAT was mixed with 4.5 wt% of dichroic black dye, 1.0 wt% of photo initiator, 0.1 wt% of radical inhibitor, and 0.5 wt% of additive. The mixture was diluted in a mixed solvent (toluene/cyclohexanone = 1:1) with a solid content of 30.0 wt% to prepare a “host-guest” mixture solution. The solution was coated on a single substrate having a rubbed alignment layer by spin coating or bar-

coating. After evaporating the solvent at $60\text{ }^\circ\text{C}$, the sample was firstly heated to the clearing point ($135\text{ }^\circ\text{C}$), and then, followed by an annealing process at $100\text{ }^\circ\text{C}$. After slowly cooling to the room temperature, the sample was cured by UV irradiation with an intensity of 10 mW cm^{-2} (@ 365 nm) for a certain period of time. Finally, we obtained the coatable polarizer sample with a thickness of approximately $4\text{ }\mu\text{m}$.

2.6. Evaluation of polarizing properties

To evaluate polarizing properties of coatable polarizers in a sandwich cell or on a single substrate, angle-dependent polarized UV-Vis spectra were obtained with a UV-Vis spectrophotometer (S-3100, Scinco Co., Korea) equipped with a Glan-Taylor rotating polarizer. To investigate the temperature dependence of polarizing properties, polarized UV-Vis spectra of the sandwich cell were obtained on a hot-stage with a temperature controller. In this case, the sample was heated firstly above the clearing point, and then, cooled down gradually at a rate of $2\text{ }^\circ\text{C min}^{-1}$ while the polarized UV-Vis spectra were recorded at every $10\text{ }^\circ\text{C}$. The dichroic ratio (DR), order parameter (S) and the degree of polarization (DOP) were calculated from the equations as follows:

$$\text{DR} = \frac{A_{\parallel}}{A_{\perp}} \quad (1)$$

$$S = \frac{\text{DR}-1}{\text{DR}+2} \quad (2)$$

$$\text{DOP} = \frac{T_{\parallel} - T_{\perp}}{T_{\parallel} + T_{\perp}} \times 100\% \quad (3)$$

where A_{\parallel} and A_{\perp} are defined as the absorbance of the sample when the polarizer is parallel and perpendicular to the average orientation of long axis of dye chromophores, respectively. T_{\parallel} and T_{\perp} are defined as the transmittance of the sample when the polarizer is parallel and perpendicular to the average orientation of long axis of dye chromophores, respectively. For all the samples, DR, S, and DOP values were obtained by an average of 3 measurements to minimize the experimental errors.

2.7. Fabrication and electro-optical measurement of TN-mode LC cell with in-cell coatable polarizers

To prepare a TN-mode LC cell with coatable polarizers inside the cell, the coatable polarizer was fabricated on an ITO substrate coated with a rubbed alignment layer by the same process described above. Two coatable polarizers on ITO substrates were assembled with the polarization direction perpendicular to each other (cell gap = $5\text{ }\mu\text{m}$). Neither an alignment layer or a rubbing process was applied on the polarizer layer. The LC material (5CB, Merck) was injected into the cell by a capillary force. The electro-optical property and response time of the resulting TN-mode LC cells were measured with the LCMS-200 (Sesim Photonics Technology Inc., Korea) electro-optical evaluation system.

3. Results and discussions

3.1. Syntheses and characterizations of DAT

The RM containing a tolane core structure with two acrylate groups at both ends (DAT) was newly designed and synthesized according to [Scheme S1](#), and the detailed synthetic procedures are described in the Supporting Information. Structure of DAT was characterized by ^1H NMR spectrum, as shown in [Figure S1](#).

3.2. Liquid crystalline phase behavior of DAT

Firstly, the phase transition behavior of liquid crystalline DAT was

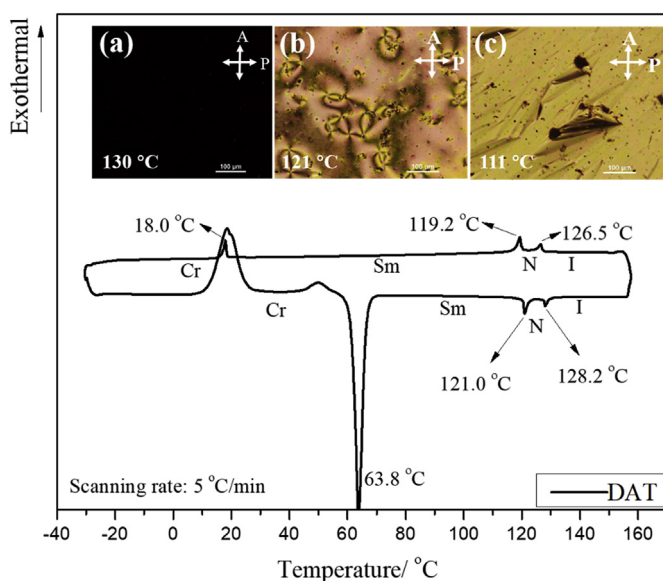


Fig. 2. DSC thermogram and phase transition behavior of DAT. Insets are POM images representing (a) dark image of isotropic phase at 130 °C, (b) Schlieren texture of nematic phase at 121 °C and (c) fan-shaped smectic phase at 111 °C.

investigated by DSC and polarized optical microscope (POM). DSC results of DAT are shown in Fig. 2. In the cooling process from isotropic temperature, DAT showed three exothermic peaks at 126.5, 119.2 and 18.0 °C indicating two mesogenic phase transitions are present. From the heating and cooling processes, it was found that the peak at the lowest temperature is an enantiotropic phase transition. The mesogenic phases of DAT were further investigated by POM during the cooling process. As can be seen in Fig. 2(b), the fluidic Schlieren textures were observed at 121 °C, which was assigned to a typical nematic phase. At 111 °C, a fan-shaped texture was observed (Fig. 2(c)), which was ascribed to a typical smectic phase. The results confirmed that DAT exhibits a smectic phase in the temperature range of 18.0–119.2 °C.

To further confirm the smectic phase of DAT molecule, 1D and 2D wide-angle X-ray diffraction (WAXD) experiments were conducted during the heating process. As shown in Fig. 3(a), when the temperature was increased above 64 °C, one low angle reflection at $2\theta = 2.28^\circ$ ($d = 3.87$ nm) and an amorphous halo $2\theta = 20.13^\circ$ ($d = 0.44$ nm) were detected with the dissolution of many sharp peaks as observed at 100 °C. This indicates the formation of the layered structure of a smectic

liquid crystal phase from crystalline phase. After subsequent heating, the typical 1D WAXD patterns of nematic and isotropic phase were observed at 125 °C and 140 °C, respectively. To precisely determine the molecular packing structures in the highly ordered smectic phase, 2D WAXD pattern of uniaxially oriented DAT was obtained at 100 °C. As shown in Fig. 3(b), a pair of diffraction peak indicating the expanded layer d-spacing was observed at $2\theta = 2.22^\circ$ ($d = 3.98$ nm) on the meridian at 100 °C. Meanwhile, the weak and diffused halo at $2\theta = 20.06^\circ$ ($d = 0.44$ nm) originated from the lateral molecular close packing was detected on the equator. It's noteworthy that the average long axis of the DAT remained normal to the layer direction and DAT molecules were stacked in the layer with the formation of short-range positional order. Based on the results, this liquid crystal structure at this temperature range is identified as a smectic A (Sm A) phase, as illustrated in Fig. 3(c). The results of XRD analyses are described in detail in the Supporting Information.

3.3. Evaluation of polarizing properties in a sandwich cell

In order to optimize the fabrication condition with respect to the temperature, the “host-guest” mixture was filled into a sandwich cell with anti-parallel rubbed alignment layers (5 μm cell gap). The polarized UV–Vis spectra in parallel and perpendicular direction to the rubbing direction were obtained at various temperatures. Fig. 4(a) displays the polarized UV–Vis spectra of DAT + DAD mixture at 135 °C, which showed almost identical absorbance in parallel and perpendicular direction indicating a random orientation of the “host-guest” molecules, as expected for the isotropic phase. At 120 °C, the polarized UV–Vis spectra (Fig. 4(b)) showed an anisotropic absorption, where the absorbance parallel to the rubbing direction was significantly higher than that of the perpendicular direction. This indicates that the “guest” DAD dye molecules are co-aligned with the “host” molecules along the alignment (rubbing) direction. The average DR in the wavelength range of 450–550 nm and S were calculated to be 5.7 and 0.61, respectively, which are well agreed with those of previously reported “host-guest” system based on nematic LCs [22]. Fig. 4(c) shows the polarized UV–Vis spectra taken at 20 °C, at which the DAT + DAD mixture is believed to have a highly ordered smectic phase. It is apparent that parallel and perpendicular absorption spectra show a more significant difference. The DR and S were determined to be 32.8 and 0.914, respectively, which are much higher than that of the nematic phase. This is due to the higher ordering of the DAD dye molecules achieved by “host-guest” interactions in the smectic phase of “host” molecules. Fig. 4(d) represents the temperature dependent DR and S values obtained from the

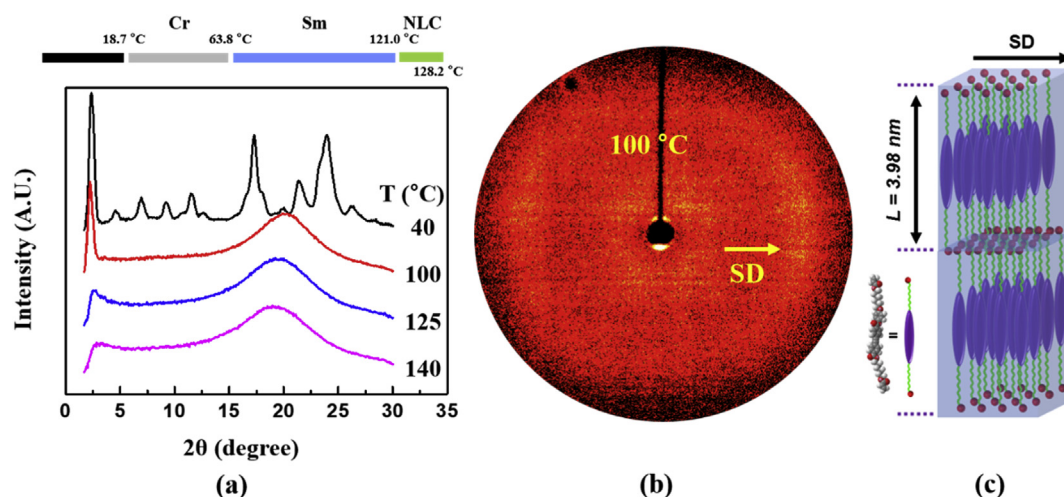


Fig. 3. XRD analysis of DAT monomer, (a) 1D-WAXD spectra at different temperature, (b) 2D-WAXD pattern at 100 °C and (c) Molecular model of DAT liquid crystal phase at 100 °C.

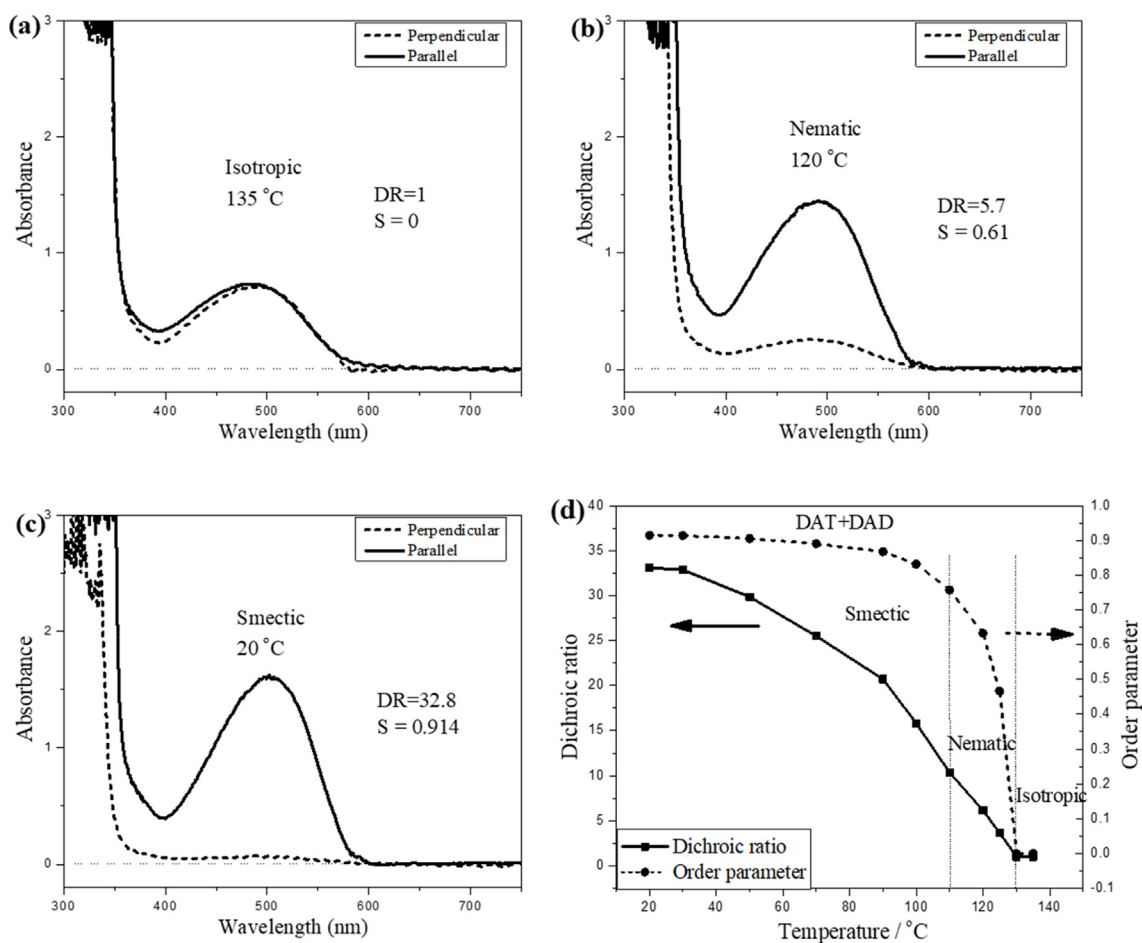


Fig. 4. Polarized UV-Vis spectra of DAT + DAD at (a) isotropic phase (135 °C), (b) nematic phase (120 °C), (c) smectic phase (20 °C) and (d) DR and S of the DAT + DAD sample with respect to temperature.

polarized UV-Vis spectra of DAT + DAD mixture at various temperatures. At above the isotropic temperature (> 130 °C), DR and S values were 1 and 0, respectively, indicating a random orientation of DAD molecules at isotropic temperature. When the temperature was decreased to 110 °C, in which temperature range the mixture shows a nematic phase, both DR and S increased up to 10 and 0.75, respectively. It is interesting to note that S increased more dramatically than DR. This implies that, though the molecular ordering occurs significantly fast with the temperature decrease, DR is relatively less affected in the low molecular ordering region. Upon further cooling below 110 °C, at which the mixture exhibits a smectic phase, DR and S increased continuously. DR and S were measured to be 33 and 0.91 at room temperature. It is noteworthy that, in this temperature range, DR increased significantly and reached at a plateau at near room temperature, whilst S increased only slightly. This indicates that the ordering of dye molecules become more perfect at the lower temperature, at which, in addition to the maximum order parameter of the total system, the thermal motion of molecules is more restricted. Above result suggests that the process temperature of UV irradiation should be fixed as low as possible. It should be noted that DAT + DAD mixture exhibits a smectic phase even at room temperature during the cooling process due to its enantiotropic property, which is advantageous to obtain the highest ordering of dye molecules.

For comparison, we also prepared the thin-film polarizer by using a commercial reactive mesogen, RM257, which possesses only a nematic LC phase. The polarized UV-Vis spectra were measured and displayed in Figure S3. The resulting “host-guest” thin-film polarizer showed maximum DR = 8.8, which is much lower than that of the “host-guest”

thin-film polarizer prepared in this work. This confirmed that the smectic host material can provide a higher ordering of the guest materials in the “host-guest” system.

To stabilize the uniaxially ordered dichroic dye molecules in the “host-guest” mixture, in-situ photopolymerization was carried out, which resulted in a stable crosslinked polymer film. The photopolymerization was performed at room temperature to obtain the highest DR and S values. The influence of polymerization on the ordering of dichroic dye molecules was investigated by measuring the polarized UV-Vis spectra during the photopolymerization process. From the result, DR and S values were estimated as a function of photopolymerization time as displayed in Fig. 5. It is noticeable that DR and S values decreased dramatically during the initial several minutes. With continuous UV irradiation, both values declined slowly and finally reached a steady stage after 10 min. The decrease of DR is probably attributed to the configurational change of acrylate terminal from sp^2 to sp^3 and the volume shrinkage during the polymerization of acrylate groups resulting in the disordering of mesogenic cores in the polymer network [23–25]. Based on the above results, the photopolymerization was performed for 10 min to ensure a sufficient photopolymerization, which gives DR = 19.2 and S = 0.86, respectively.

3.4. Evaluation of polarizing properties on a single substrate

In this study, we aimed to fabricate a coatable polarizer on a single substrate. However, it is noteworthy that, in general, thin layer of smectic phase liquid crystals prefers a homeotropic orientation on a single substrate even with a planar alignment layer at the bottom, as

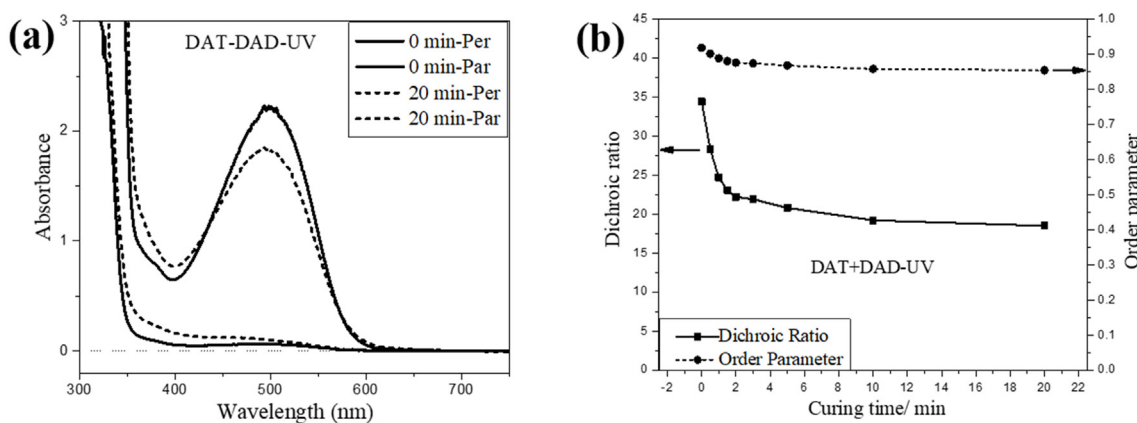


Figure 5. (a) polarized UV–Vis spectra of DAT + DAD mixture before (solid line) and after photopolymerization (dash line) at 20 °C and (b) dichroic ratio (solid line) and order parameter (dash line) as a function of photopolymerization time for DAT + DAD mixture.

shown in Figure S4. The orthoscopic POM image of DAT (Figure S4(a)) on a glass substrate with a rubbed planar alignment layer also showed a black state in a smectic phase (50 °C, cooling from T_{NI}), and the corresponding conoscopic POM image (Figure S4(b)) displayed a distinct Maltese cross extinction image clearly indicating a homeotropic alignment. The non-polar environment at the air/LC interface induces the homeotropic orientation of LC molecules on the surface [26]. To fabricate the coatable polarizer on a single substrate, therefore, the homeotropic orientation of smectic liquid crystalline phase should be suppressed. Hence, we attempted to utilize surfactants as an additive to reduce the surface energy of the air/LC interface. In this work, several different types of surfactants were introduced into DAT + DAD mixture. Among them, a surfactant based on silicone-modified polyacrylates was found to show a uniformly aligned homogeneous smectic texture.

For real display applications, in addition, dichroic dyes absorbing in the whole visible color range (black dye) should be used instead of dichroic red dye (DAD). To choose a suitable black dye for our system, we tested three different commercial black dyes as listed in Table S2. The “host-guest” coatable polarizers were successfully prepared on a glass substrate according to the fabrication method previously described in the experimental section, and their DR and S values were estimated from the polarized UV–Vis spectra as shown in Table S2. Among them, Irgaphor® Black X12 exhibited the highest values of DR and S (DR = 16.4, S = 0.84) with the thickness of approximately 4 μm . Therefore, Irgaphor® Black X12 was selected as a black dye for further research. Both absorbance and transmittance of the polarized UV–Vis spectra for Irgaphor® Black X12 were displayed in Fig. 6(a) and (b). The DAT + X12 coatable polarizer sample showed DOP as high as 99.3% with the single transmittance of 34.5%, as shown in Fig. 6(b).

By using this fabrication method, the coatable polarizer can also be fabricated on a flexible plastic substrate such as poly(ethylene naphthalate) (PEN) or poly(ethylene terephthalate) (PET) films. Firstly, the plastic substrate (PEN) was attached on a supporting glass substrate by a double-sided adhesive tape. Then, the alignment layer was prepared by coating a conventional alignment layer solution followed by a two-step baking and rubbing process. Further fabrication process was the same as previously described. Then, the plastic substrate was detached from the supporting glass substrate to obtain a “host-guest” coatable polarizer on a single plastic substrate. Fig. 6(c) and (d) displays the photographic images of the coatable polarizer fabricated on the PEN film, in which the coatable polarizer film showed excellent flexibility and robustness. The resulting coatable polarizer on PEN substrate was observed from POM as displayed in Fig. 6(e) and (f). The POM image showed a dark state (Fig. 6(e)) when the rubbing direction is parallel to the electric vector of analyzer direction. On the other hand, the POM image showed a bright state (Fig. 6(f)) when the rubbing direction of

the sample is 45° to the electric vector of analyzer, which confirmed the anisotropic orientation of the host RMs on plastic PEN substrate. The DR and DOP of the coatable polarizer fabricated on PEN film were determined from the polarized UV–Vis spectra as displayed in Figure S5(a) and (b). The coatable polarizer on PEN film showed maximum DR and DOP values of 15.2 and 98.8%, respectively, with the single transmittance of 34.5%, which is almost the same level of optical property compare to the as-prepared coatable polarizer on a single glass substrate.

Solvent resistivity of the coatable polarizer was also tested by dipping the sample in various organic solvents, and the results are listed in Table S3. The coatable polarizer sample showed a swollen state when treated with aprotic solvents of moderate polarity such as THF, dichloromethane, and chloroform. This is probably due to the similar polarity of the solvent and the polymer layer. On the other hand, the coatable polarizer exhibited excellent chemical stability either in less polar aprotic solvents such as hexanes, toluene, and diethyl ether, or in polar protic solvents such as H₂O, methanol, and ethanol. The sample was also stable in polar aprotic solvents such as DMF and DMSO. This suggests that the coatable polarizer possesses a considerable resistance to most of organic solvents except for those with medium polarity. The sample surface and DR values were stable and almost constant after the treatment in most of the common solvents. In addition, thermal stability of the coatable polarizer was also evaluated by monitoring DR and S values during the heating and subsequent cooling processes with a heating and cooling rate of 5 °C min⁻¹ as shown in Fig. 7(a) and (b). The DR and S values decreased gradually with increasing the temperature and returned to the initial values in the cooling process. Moreover, the surface morphology observed by POM (Fig. 7(c)–(e)) did not change significantly after the heat treatment at 80 °C and 110 °C for 30 min, respectively. These results indicate that the coatable polarizer possesses a decent chemical and thermal stability. Therefore, the coatable polarizer prepared in this work can be a promising alternative to the H-sheet polarizer in a harsh environment. Patterned coatable polarizer can also be prepared by roll-to-roll printing techniques on a flexible substrate to meet various applications.

3.5. Fabrication of in-cell type TN-LCD with coatable polarizer

In the conventional LCDs, the H-sheet polarizers with a thickness around 100 μm are assembled on both the front and rear side of cell as depicted in Fig. 8(a). If a coatable polarizers with the thickness of 4 μm are applied in the conventional LCD as an alternative for H-sheet polarizers, we could achieve much thinner LCDs. Moreover, if the polarizers are prepared inside the cell between two substrates (in-cell), the parallax issues from the substrates can also be eliminated. Especially, when the plastic substrates are used in the LCDs, it will not only reduce

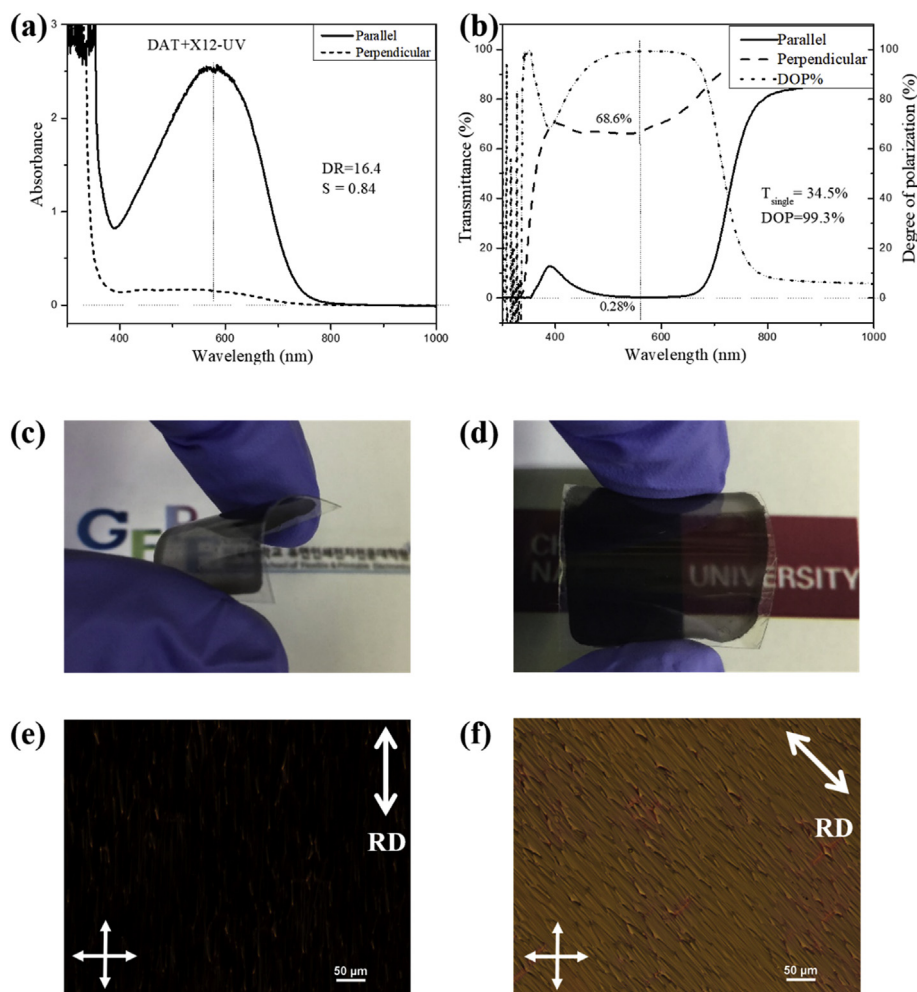


Fig. 6. (a) Polarized UV–Vis absorbance spectra and (b) polarized UV–Vis transmittance and DOP of DAT + X12 coatable polarizer sample. (c) Photographic images of the DAT + X12 coatable polarizer on PEN film and (d) flexible coatable polarizers crossed on a H-sheet polarizer. (e) POM images of the sample at rubbing direction parallel to analyzer, (f) POM images of the sample at rubbing direction 45° to analyzer.

the cost and thickness but also achieve a flexible LCD. In this study, we attempted to prepare a TN-mode LC cell with an in-cell configuration as shown in Fig. 8(b). Firstly, two coatable polarizers were fabricated on ITO glass substrates and assembled in anti-parallel direction with each other. Nematic LC was directly injected into the cell without an alignment layer, since the coatable polarizer acted as a polarizer and an alignment layer, simultaneously. The resulting TN-LCD cell with in-cell polarizers showed a reasonable electro-optical switching behavior at voltage-off and voltage-on states as shown in Fig. 8(c) and insets (d) and (e). The results suggest that the coatable polarizer fabricated by the smectic phase “host-guest” mixture is a promising alternative to the conventional H-sheet polarizer for ultra-thin and flexible display applications.

4. Conclusions

In conclusion, herein, we synthesized a reactive mesogen (DAT) based on tolane mesogenic core structure with two polymerizable acrylate groups attached at both ends. The liquid crystalline behavior was investigated by DSC, POM, and XRD, and it was revealed that DAT has a highly ordered smectic A phase in the temperature range from near room temperature to 121.0 °C, and a nematic phase at higher temperature. We demonstrated the fabrication of “host-guest” thin-film polarizers either in a sandwich cell or on a single substrate by in-situ polymerization of “host-guest” mixture. Dichroism of “host-guest” effect for DAT + diazo dye (DAD) mixture was investigated with respect

to its liquid crystalline phases. The dichroic ratio (DR) and order parameter (S) of the polarizer samples estimated from polarized UV–Vis spectroscopic results showed highest values of 32.8 and 0.914, respectively, in the smectic phase at room temperature, which are much higher than those of the nematic phase. DR and S values decreased during the photopolymerization, which is unavoidable in the “host-guest” system because the perturbation of molecular ordering is induced by the side chain polymerization. For DAT + DAD mixture, the resulting thin film polarizer showed DR = 19.2 and S = 0.86, respectively, after photopolymerization. The coatable polarizer was successfully fabricated on a single substrate of either glass or plastic film by spin coating method from DAT and a commercial black dye. The resulting coatable polarizer sample with a thickness of 4 μm showed DR = 16.4, S = 0.84 and the degree of polarization (DOP) = 99.3% with a single transmittance of 34.5%. The as-prepared coatable polarizer possesses a considerable solvent resistance, good thermal stability, and mechanical robustness. Finally, we also demonstrated a TN-mode LC cell with the coatable polarizer fabricated inside the cell (in-cell), where the coatable polarizer acted as a polarizer and an alignment layer, simultaneously. This could decrease the device thickness as well as the parallax issues. The resulting TN-LCD cell with an in-cell configuration exhibited a reasonable electro-optical switching behavior. We believe that the reactive mesogen and the fabrication method of coatable polarizer proposed in this study possess a high potential to be an alternative to the conventional H-sheet polarizers for ultra-thin and flexible display applications such as flexible LCDs and anti-reflection

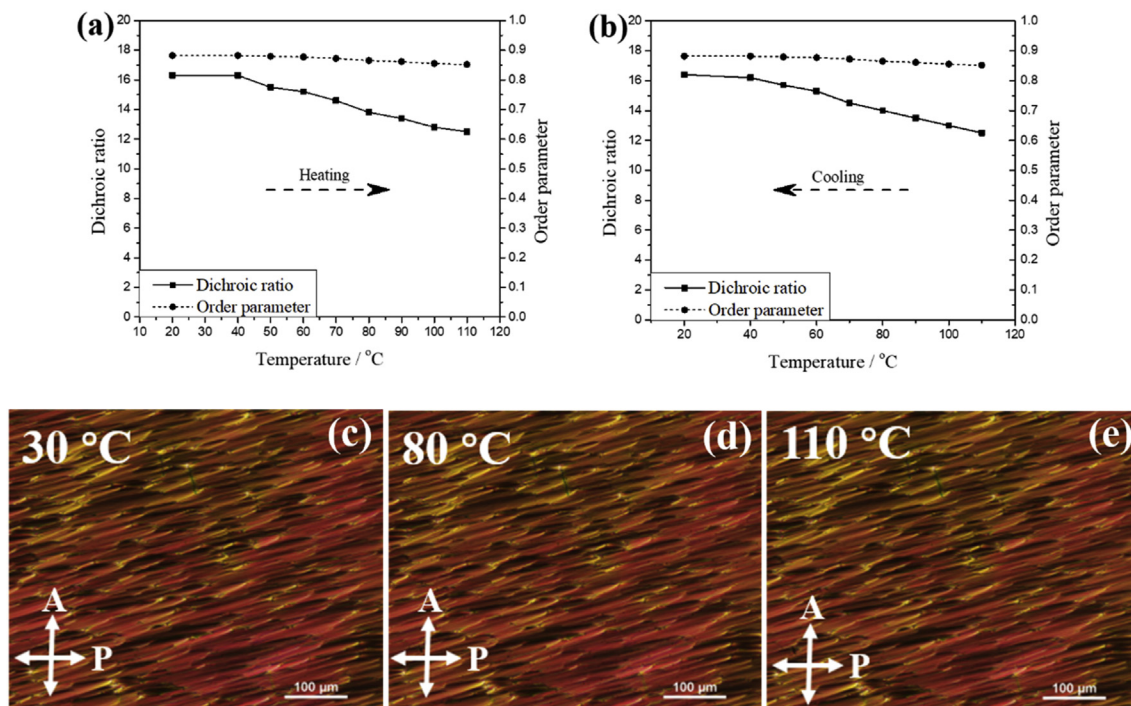


Fig. 7. Thermal stability of DAT + X12 coatable polarizer sample. DR and S values during (a) heating and (b) cooling process, respectively. POM images of the DAT + X12 coatable polarizer sample at (c) 30 °C, (d) 80 °C and (e) 110 °C.

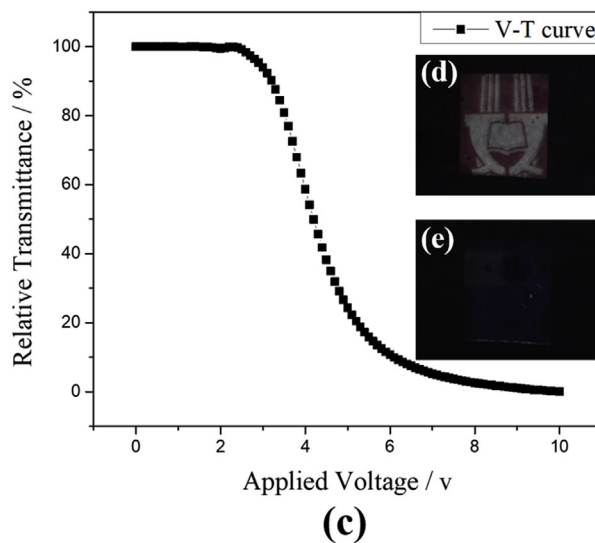
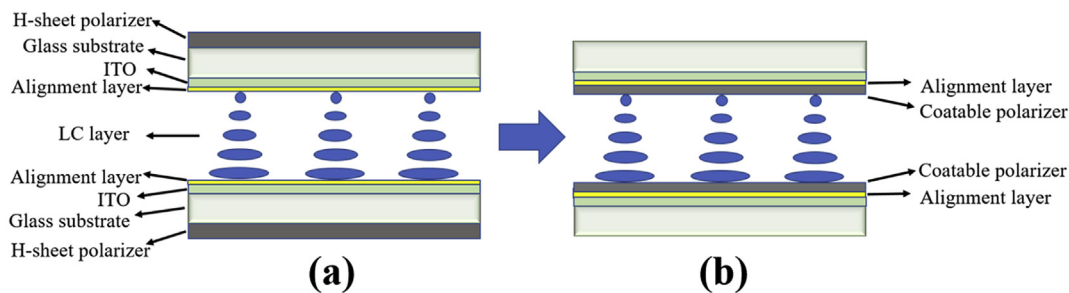


Fig. 8. Configuration of (a) conventional TN-LCD cell and (b) TN-mode LC cell with in-cell coatable polarizers. (c) V-T curve of the in-cell type TN-LCD cell with coatable polarizer. Inset images are POM images observed at (d) voltage-off and (e) voltage-on states, respectively.

films of flexible OLEDs.

Notes

The authors declare no competing financial interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.polymer.2019.05.032>.

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