

Novel Coatable Polarizer Based on Polymer-Stabilized Lyotropic Chromonic Liquid Crystals

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Abstract

We fabricated thin film polarizer by coating lyotropic chromonic liquid crystals (LCLCs) dissolved in anionic monomer solution. Compared to water-based technique, the new method provided many advantages such as excellent coatability, good adhesion to various substrates, and superb surface hardness.

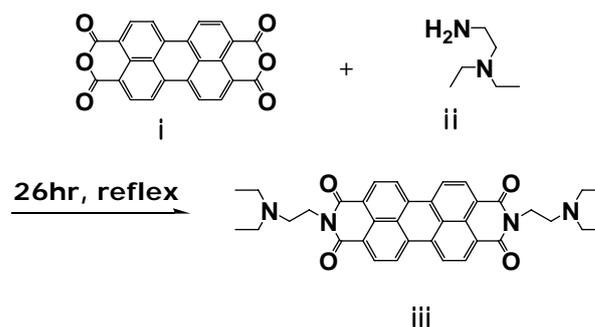
1. Introduction

Lyotropic chromonic liquid crystals (LCLCs) are known to form a columnar discotic liquid crystalline (LC) phase in aqueous solution by molecular self-assembly due to the strong π - π interaction between the aromatic cores of chromonic dye molecules, and ionic interaction of charged peripheries.^[1,2] Chromonic dyes, for example 3,4,9,10-perylene diimides (PDIs) used in this work, have been used in various application area such as organic semiconductors, optical films, organic photoconductor, and sensor. The aqueous solution of these LCLCs can be coated on a substrate such as glass or plastic with maintaining the LC phase. After the removal of solvent, the self-assembled columnar structure can form a crystalline thin film. Thus, if such columnar structures can be anisotropically oriented by a special coating technique such as a shear coating, the resulting thin crystal film can absorb a polarized light parallel to the molecular axis transmitting a polarized light parallel to the columnar axis to form E-polarizer.^[4] However, the concept of the coatable polarizer known as a thin crystal film (TCF) polarizer has not been commercially successful due to numerous problems related with coating process as well as the mechanical stability of the resulting TCF.

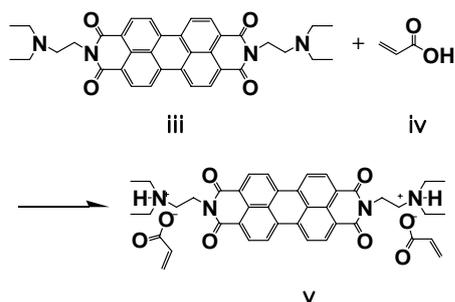
These problems are mainly originated from the use of aqueous LCLC solution. In this work, we demonstrate a novel preparation method in which PDI-based LCLCs are dissolved in an ionic monomer solution containing photo-polymerizable compositions such as photoinitiator and crosslinking agents. The organic solution-based LCLCs instead of water-based solution provided many advantages such as excellent coatability, good adhesion to various substrates, and superb surface hardness. Optical and physical properties of the resulting thin film polarizers were evaluated by measuring polarization efficiency, polarized UV-vis spectroscopy, pencil hardness and adhesion test.

2. Experimental

2.1 Synthesis of lyotropic chromonic liquid crystal: 5 g (12.7 mmol) of 3,4,9,10-perylenetetracarboxylic dianhydride and 30 ml of *N,N*-diethylethylenediamine were mixed and refluxed for 26 h. After cooling, the



Scheme 1. Synthesis of PDI



Scheme 2. Preparation of PDI/AA salt

reaction mixture was filtered, washed with methanol and ethyl acetate, and dried in a vacuum oven for 24 h. Bis-(N,N-diethylaminoethyl)perylene-3,4,9,10-tetracarboxylic diimide (PDI) was obtained in 98% yield.^[5]

2.2 Film preparation and Measurements: Generally PDIs are prepared as a HCl salt to dissolve in an aqueous solution due to their low solubility in organic solvents. In this work, neutral PDI was dissolved in an anionic monomer, acrylic acid (AA). Nematic LC phase was confirmed by the polarized microscope when the concentration was at 25-35 wt%. 10 wt% of photoinitiator (TPO) and crosslinking monomer (pentaerythritol tetraacrylate) to AA amount were added to the mixture, respectively. The LCLC solution was shear-coated on a glass substrate or a plastic substrate followed by UV irradiation for 15 min. The resulting thin polarizer film was evaluated by observing polarized optical microscope (POM) and polarized UV spectrometer for polarization efficiency measurement as well as testing pencil hardness and tape adhesion test (ASTM D3359B) for physical properties of film.

3. Results and discussion

UV-vis spectroscopy of the thin composite film revealed that the λ_{\max} of PDI/AA composite was ca.



Fig. 1 Polarized optical microscope images of the thin film prepared from photocurable organic-based lyotropic LCLC solution by shear-coating (cured): Polarization axis of incident light is (a) parallel, and (b) perpendicular to the shearing direction, respectively.

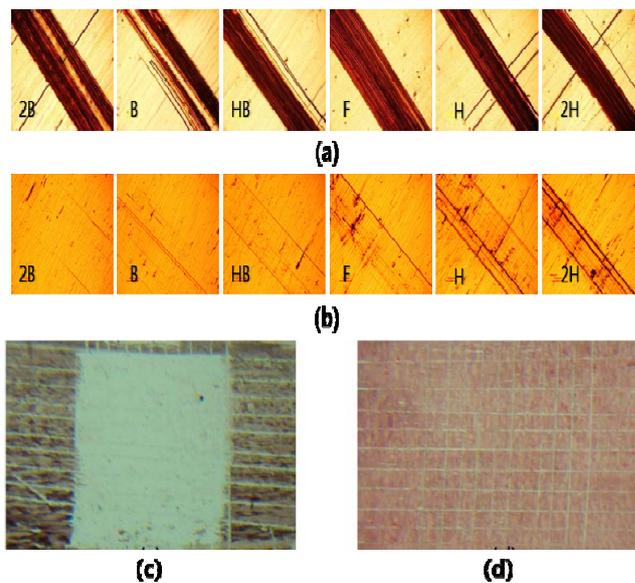


Fig. 2 Pencil hardness and adhesion test of thin films obtained from aqueous lyotropic solution (a and c), and organic-based lyotropic solution (after cure) (b and d), respectively.

482 nm. From the POM observation, it was confirmed that the PDI molecules in the film oriented in one direction after the photocuring as shown in Fig. 1.^[6] Considering the shear-coating was performed manually, the coating was almost defectless without any cracks or tiger skin patterns.

Pencil hardness and adhesion of the cured thin film polarizers were tested and compared to that obtained from water-based LCLC solution as shown in Fig. 2. In Fig. 2a and 2b, POM images of samples after the pencil hardness test were compared, where the incident polarized light is parallel to the shearing direction. While the thin film polarizer obtained from an aqueous solution exhibited soft surface with pencil hardness of less than 2B, the photocured thin film polarizer showed hardness of >2H. In addition, tape adhesion test results on a glass substrate shown in Fig. 2c and 2d for the samples obtained from aqueous solution and photocurable organic-based solution, respectively, revealed that the new polarizer possesses remarkably better adhesion with grade 5B. On the other hand, the polarizer from aqueous solution displayed poor adhesion with grade 0B. Further tests on the plastic substrates showed much distinct results, which reveals the new method can provide many advantages against the aqueous solution method.

In Fig. 3, the calculated optical transmissions of the thin film polarizer prepared from 35 wt% PDI solution were displayed. Firstly, polarized UV-vis spectra were obtained with parallel and perpendicular direction of

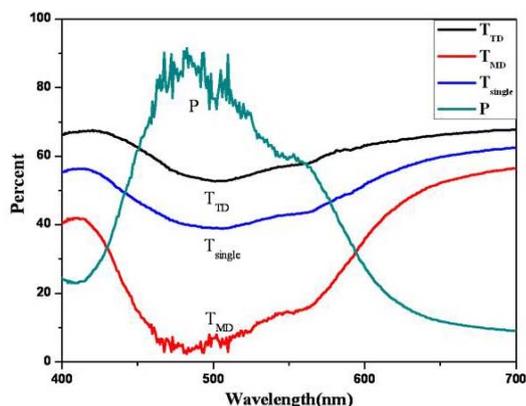


Fig. 3 Optical properties of thin film polarizer prepared from a 35wt% of PDI-AA.

shearing and calculated to obtain T_{TD} and T_{MD} for $T_{single} = 40\%$ at 482 nm. T_{single} and polarization efficiency (P) were also calculated from the equations, $T_{single} = [T_{TD} + T_{MD}]/2$ and $P = 100\% \times [T_{MD} - T_{TD}]/[T_{MD} + T_{TD}]$, respectively. The maximum polarization efficiency (P) was obtained to be 91% at 482 nm. The maximum P for aqueous samples was 98.4%. The organic-solution based LCLC can also be coated on the plastic substrate (polyethylene terephthalate, PET). The new LCLC solution exhibited remarkably better coating performance with good adhesion and defect-free surface on the plastic substrate after UV curing compared to water-based solution.

In addition, we also demonstrate a patterned polarizer prepared from the organic based LCLC solution. Selective irradiation through a patterned photomask (line and dot) on the shear-coated thin film was performed, which was followed by a subsequent developing in organic solvent to randomize the orientation of chromonic dye columns. As shown in the POM images (Fig. 5), only the irradiated parts exhibited a transmission of polarized light parallel to the shear direction (Fig. 5, 0°), and blocking of polarized light perpendicular to the shear direction (Fig. 5, 90°). Unirradiated part does not respond to the direction of polarization.

4. Summary

We demonstrated a new preparation method of coatable polarizer from an organic-based LCLC solution in which PDI is dissolved in ionic monomer solution containing acrylic acid, photoinitiator, and crosslinking agent. The lyotropic LC phase was confirmed by POM observation for 25 – 35 wt% PDI

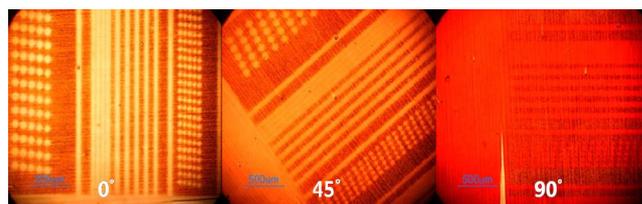


Fig. 3 POM image of patterned photo polarizer

solution. The organic-based solution was shear-coated to induce anisotropic orientation of columnar structure in the LC phase, which was followed by a subsequent UV irradiation to obtain stable thin film polarizer. The maximum polarization efficiency was $> 91\%$. The resulting thin film polarizer showed excellent coating characteristics such as good adhesion to various substrates and superior surface hardness. In addition, a patterned polarizer was demonstrated from the selective UV irradiation through a photomask followed by subsequent developing.

Acknowledgement

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5. References

1. J. Lydon, in *Handbook of Liquid Crystals*, edited by D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess, and V. Vill (Wiley-VCH, Weinheim, 1998), Vol. 2B, pp. 981–1007, and references therein.
2. J. Lydon, *Curr. Opin. Colloid Interface Sci.* **3**, 458 (1998); **8**, 480 (2004).
3. (a) Law, K. Y. *Chem. Rev.* **1993**, *93*, 449. (b) O'Neil, M. P.; Niemczyk, M. P.; Svec, W. A.; Gosztola, D.; Gaines, G. L.; Wasielewski, M. R. *Science (Washington, D.C.)* **1992**, *257*, 63-65. (c) Langhals, H. *Heterocycles* **1995**, *40*, 447-500. (d) Holtrup, F. O.; Müller, G. R. J.; Quante, H.; De Feyter, S.; De Schryver, F. C.; Müllen, K. *Chem. Eur. J.* **1997**, *3*, 219-225. (e) Cormier, R. A.; Gregg, B. A. *Chem. Mater.* **1998**, *10*, 1309-1319.
4. Yu. A. Nastishin, H. Liu, T. Schneider, V. Nazarenko, Rk. Vasyuta, S.V. Shiyanovskii, and O.D. Laverentovich, *Physical Review E* **72**, 041711(2005).
5. Isaac K. Iverson and Suk-Wah Tam-Chang. *J. Am. Chem. Soc.* **1999**, *121*, 5801-5802
6. Hasegawa, M. ; Matano, T.; Shindo. Y.; Sugimura, T. *Macromolecules* (1996), **29**, 7897-7909.