[Electronic Supplementary Informations]

Novel Thin Film Polarizer Based on Non-Aqueous Lyotropic Chromonic Liquid Crystal Solutions

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EXPERIMENTALS

Synthesis of bis-(N,N-diethylaminoethyl)perylene-3,4,9,10-tetracarboxylic diimide (PDI) : The synthetic procedure for PDI is displayed in Scheme S1. 5 g (12.7 mmol) of 3,4,9,10-perylenetetracarboxylic dianhydride (Aldrich) and 30 ml of N,N-diethyl-ethylenediamine were mixed and refluxed for 26 h. After cooling, the reaction mixture was first filtered and washed with methanol and ethyl acetate, and then dried in a vacuum oven for 24 h at room temperature. Bis-(N,N-diethylaminoethyl)perylene-3,4,9,10-tetra-carboxylic diimide (PDI) was obtained in 98% yield.¹

FT-IR (KBr pellet): 2970, 2811, 1693, 1653, 1590, 1296, 1515, 1444, 1353, 1291, 1245, 1166, 1098, 746, 803, and 851 cm⁻¹; ¹H-NMR (CF₃COOD, δ in ppm): 8.97(4H), 8.97(4H), 4.88(4H), 3.81(4H), 3.61(8H), and 1.57(12H).

Synthesis of PDI-HCl salt : In a 100 ml round bottom flask, 0.2 g of PDI was completely dissolved with excess amount (ca. 50 ml) of aqueous 0.1N HCl. The solvent was removed by using rotary evaporator followed by drying in a convection oven at 100 °C for 12 h.

¹⁾ I. K. Iverson and S.-W. Tam-Chang, J. Am. Chem. Soc., **121**, 5801 (1999)

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Scheme 1. Synthetic Procedure for PDI and PDI-HCl

Preparation of PDI-AA/AA solution: Acrylic acid (Junsei Chem.) was purchased and vacuum distilled in the presence of spiral copper wire prior to use. Photoinitiator, 2,4,6-trimethylbenzoyl- diphenyl phosphine (TPO) was used as purchased from Ciba-Geigy. Crosslinking agent (pentaerythritoltetraacrylate, PETA) was purchased from Aldrich and used as received. To prepare a 25 wt% PDI solution, 0.10 g of PDI was completely dissolved in 0.3 g of acrylic acid contained in an amber-colored vial wrapped with aluminum foil. Then, 0.03 g of TPO (10 wt% to AA amount) and 0.6 g of PETA (20 wt% to AA) were added to this solution and homogeneously mixed by using ultrasonic treatment below 30 °C. Solutions having different concentrations of PDI, TPO and PETA had been also prepared in a similar method for the optimization of conditions. For example, solution containing PETA higher than 30 wt% showed a phase separation.

Film preparation: 25 wt% PDI-AA/AA solution was manually coated on a substrate by using a glass rod, followed by a subsequent UV irradiation by using a conventional high pressure Hg arc light source (15 mW/cm²) for 3-10 min. For comparison, PDI-HCl/water solution (20 wt% PDI) was shear-coated in the same method, and dried at 60 °C for 1 h.

Measurement of degree of polarization (P_{40%}): Home-made polarized UV-vis spectroscopy was constructed as shown in Figure S1a. On a UV-vis spectrometer (Scinco S-3100), rotational polarizer and sample stage were installed between a light source and a photo-detector. By rotating polarizing axis, angular-dependent transmission spectra of the film were obtained as shown in Figure S1b.



Figure S1. (a) Schematic diagram and photogram of polarized UV-vis spectrometer, and (b) angular-dependent transmission spectra.

 $T_{//}$ and T_{\perp} are defined as a measured transmittance when the shearing direction is parallel and orthogonal to the incident polarized light, respectively. The mean transmittance (or transmittance of single polarizer), T_{single} , is defined by following equation:

$$T_{\text{single}} = (T_{//} + T_{\perp})/2 \tag{1}$$

Degree of polarization (P) is also defined by following equation:

$$P = (T_{//} - T_{\perp})/(T_{//} + T_{\perp})$$
(2)

Since, in general, maximum degrees of polarization are compared at the same transmittance level, the spectral data of $T_{//}$, T_{\perp} and T_{single} are normalized so that minimum mean transmittance (T_{single}) becomes 40 % at the maximum absorption. Therefore, $P_{40\%}$ is defined as the modified degree of polarization when minimum T_{single} is 40 % at the maximum absorption.



Figure S2. AFM images of shear-coated films on glass substrate: (a) 20 wt% PDI-HCl/water, dry 1h, 60 °C, and (b) 25 wt% PDI-AA/AA, UV cure, 5 min.



Figure S3. SEM images of (a, c) PDI-HCl/water film, (b, d) PDI-AA/AA film



Figure S4. POM images of pencil hardness tests.



Figure S5. TGA thermogram of PDI-AA/AA 25 wt% after UV curing.



Figure S6. POM images of PDI-AA/AA film at various temperatures.

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Figure S7. WAXD patterns of films prepared from (a) PDI-HCl/water (black), (b) PDI-AA/AA before UV curing (red), and (c) PDI-AA/AA after UV curing (blue) for 5 min.

Samples	2θ (<i>d</i> -spacing)	2θ (<i>d</i> -spacing)	
PDI-HCl/water (after drying)	5.78° (15.29 Å)	26.64° (3.35 Å)	
PDI-AA/AA (before UV curing)	5.38° (16.43 Å)	26.28° (3.39 Å)	
PDI-AA/AA (after UV curing)	5.38° (16.43 Å)	26.28° (3.39 Å)	

	Table S1.	2θ and <i>d</i> -spacings detected by WA	AXD.
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