



## Effect of dye structure on orientational behavior and transition dipole moments in coatable guest–host polarizers



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### ABSTRACT

Guest–host coatable polarizers were manufactured by liquid crystalline polymers and dichroic azo dyes. The highest dichroic ratio of the polarizers was observed within the permissible limit of guest concentration, because any increase in the guest concentrations beyond the permissible limit decreased the alignment ability of the host. The orientational behavior of dye molecules in guest–host systems tend to be more sensitive to intermolecular steric hindrance as compared to that in PVA-based polarizing films. Also, the polarity difference between guest and host molecules had a great effect on the alignment of the guest–host system. Long conjugation, abundant  $\pi$ -electrons for transfer and the charge distribution without deviation from the long axis are required for a highly anisotropic transition dipole moment.

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### 1. Introduction

A polarizer is a widely used optical device to control the polarization states of light in various applications, including displays. Nowadays, the maximum demand for polarizers is in the area of liquid crystal displays (LCDs). PVA-iodine polarizing films, which exhibit the highest polarization efficiency among commercial polarizers, are mainly used in this area [1–3]. However, PVA-based polarizing films should be protected by tri-acetyl cellulose (TAC) because of their low stability. For this reason, PVA-based polarizing films must be a laminated structure which leads to increased film thicknesses and restricts their application to flexible displays [4,5]. As a solution to this problem, a coatable polarizer has been identified and has attracted industrial attention. The coatable polarizer is fabricated by coating the liquid crystal composite. Using this method, a film with a thickness of less than 10  $\mu\text{m}$  can be formed on any substrate. However, some drawbacks of the coatable polarizer, such as inferior optical properties and incomplete film formation, must be overcome before it can be commercialized by replace PVA-based polarizing films [6–10].

Coatable polarizers can be classified into two types: lyotropic chroemic liquid crystal (LCLC) types and guest–host types [11–15]. LCLC types employ the behavior of discotic liquid crystals and mechanical shear as the driving force for orientation. Guest–host types utilize the alignment ability of rod-like liquid crystals as the driving force for orientation.

In this study, guest–host coatable polarizers were fabricated using a liquid-crystalline polymer as the host. The liquid crystalline polymer contains side chains, which consist of a flexible alkyl chain and a rigid mesogen. The side chains having liquid crystallinity align along the rubbed direction, and the dichroic dyes are arranged along the side chains by the guest–host effect (Fig. 1) [8,10,16]. The arranged dyes conduct an anisotropic absorption. Polymer-type hosts can be simply fabricated by thermal curing, as opposed to monomer-type hosts, which require photostabilization [16]. The properties of the dyes related to the molecular structure, such as linearity, solubility, and polarity, were investigated to determine the requirements for high optical anisotropy in the guest–host coatable polarizer. The effect of guest concentration and coating thickness on the alignment was also investigated. The effect of charge distribution on the transition dipole moments and transition energies was compared and analyzed.

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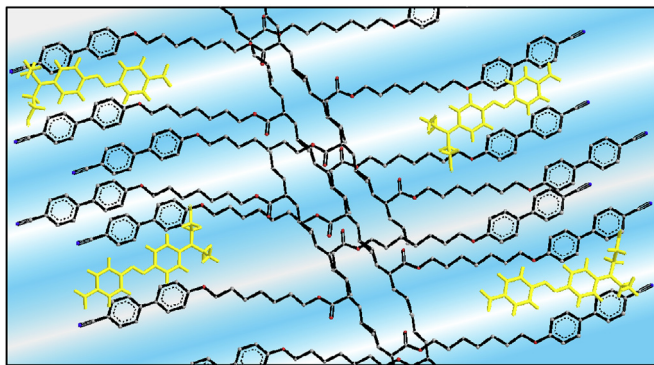


Fig. 1. Schematic diagram of the orientation of liquid crystalline polymer doped with dichroic dye molecules on rubbed polyimide alignment layer.

## 2. Experimental

### 2.1. Materials and instrumentation

Disperse Orange 3, acetic anhydride, 4-nitroaniline, 40% nitrosyl sulfuric acid, and sodium sulfide were purchased from Sigma–Aldrich. Disperse Red 1, 2-diethylaminophenol, 2,5-dimethoxyaniline, and 2-(*N*-ethylanylino)ethanol were obtained from TCI. All other chemicals used in this study were of synthesis grade. Host OPR-003(Host-003) was supplied by Osaka chemical Co. Ltd.

$^1\text{H}$  NMR spectra were recorded on a Bruker Avance 500 spectrometer using DMSO- $d_6$  and TMS as the solvent and internal standard, respectively. Melting points were determined with a BUCHI Melting point B-540. FT-IR spectra were recorded on a Thermo Scientific Nicolet 6700 using ATR method. Elemental analysis was carried out with a Flash EA 1112 CNH analyzer. Mass spectra were recorded in fast atom bombardment (FAB) ionization mode using a JEOL JMS-AX505WA/HP 6890 Series II gas chromatography-mass spectrometer. Absorption spectra of the dyes were measured on an HP 8452A spectrophotometer. The absorption maxima and minima of the polarizer samples were measured by using an Axoscan Mueller Matrix spectropolarimeter.

### 2.2. Synthesis of dyes

#### 2.2.1. Synthesis of Dye 2

Dye 2 and 3 were synthesized as shown in Scheme 1. Disperse Orange 3 (0.97 g, 0.004 mol) was dissolved in HCl (60 mL 0.3 M, aqueous) at room temperature. The solution was cooled to 0–5 °C,

and sodium nitrite (4 mmol) was added and stirred for 1 h. Then, a small portion of sulfamic acid was added as a nitrous acid scavenger. The resulting diazonium salt solution was added to a coupling component solution of 2-(*N*-ethylanylino)ethanol (0.66 g, 4 mmol) dissolved in ethanol (20 mL) and water (30 mL), while maintaining the temperature and pH of the mixture at 0–5 °C and 5–6, respectively, during the course of addition. The reaction mixture was stirred for 2 h, and the precipitate was filtered, washed with brine and ethanol, and dried in a vacuum oven. The crude product was purified by recrystallization in methylene chloride.

Yield 77.0%; MP: 280 °C;  $^1\text{H}$  NMR (DMSO- $d_6$ , ppm): 1.16 (t,  $J = 7.0$  Hz, 3H, CH<sub>3</sub>), 3.53 (m, 4H, CH<sub>2</sub>), 3.62 (m, 2H, CH<sub>2</sub>), 4.84 (t,  $J = 5.0$  Hz, 1H, OH), 6.86 (d,  $J = 9.0$  Hz, 2H, ArH), 7.82 (d,  $J = 9.0$  Hz, 2H, ArH), 7.97 (d,  $J = 8.5$  Hz, 2H, ArH), 8.11 (d,  $J = 8.5$  Hz, 4H, ArH), 8.44 (d,  $J = 8.5$  Hz, 2H, ArH); FT-IR (ATR.  $\text{cm}^{-1}$ ): 1335, 1493 (NO<sub>2</sub>), 3350 (O–H); Mass:  $m/z$  418.18 (100%, [M+H]<sup>+</sup>); Found: C, 63.05; H, 5.36; N, 20.42. Calc. for C<sub>22</sub>H<sub>22</sub>N<sub>6</sub>O<sub>3</sub>: C, 63.15; H, 5.30; N, 20.08.

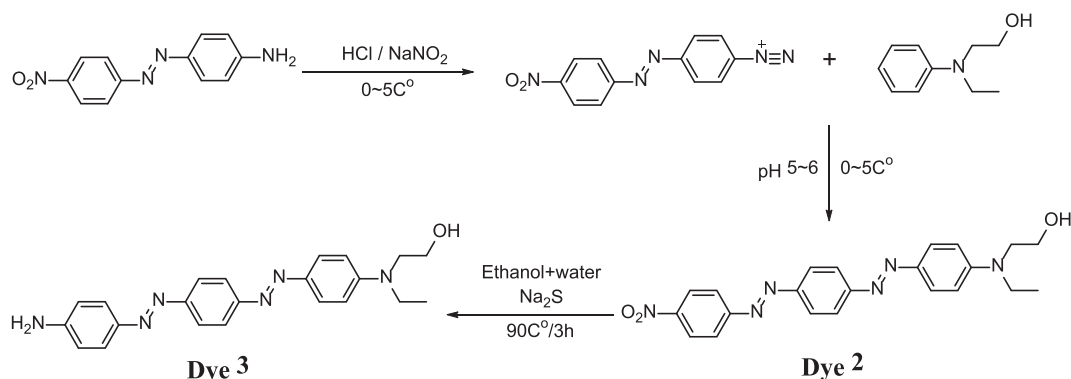
#### 2.2.2. Synthesis of Dye 3

A solution of Dye 2 (0.84 g, 2 mmol) in ethanol (25 mL) was stirred for 1 h at 70 °C. Then, water (50 mL) was added, and aqueous sodium sulfide solution (1.5 g/10 mL) was dropped into the prepared solution. The reaction mixture was heated to 90 °C and stirred for 3 h under reflux. After cooling the reaction mixture to room temperature, water (100 mL) was added and stirred for 1 h. The mixture was neutralized by adding dilute hydrochloric acid; the precipitate was filtered, washed with water, and dried in a vacuum oven.

Yield 94.3%; MP: 205 °C;  $^1\text{H}$  NMR (DMSO- $d_6$ , ppm): 1.16 (t,  $J = 7.0$  Hz, 3H, CH<sub>3</sub>), 3.52 (m, 4H, CH<sub>2</sub>), 3.62 (m, 2H, CH<sub>2</sub>), 4.84 (t,  $J = 5.0$  Hz, 1H, OH), 6.53 (s,  $J = 8.0$  Hz, 2H, NH<sub>2</sub>), 6.86 (d,  $J = 9.0$  Hz, 2H, ArH), 6.96 (d,  $J = 9.0$  Hz, 2H, ArH), 7.82 (d,  $J = 8.5$  Hz, 4H, ArH), 7.98 (d,  $J = 8.5$  Hz, 2H, ArH), 8.12 (d,  $J = 8.5$  Hz, 4H, ArH); FT-IR (ATR.  $\text{cm}^{-1}$ ): 3352 (O–H), 3420 (N–H); Mass:  $m/z$  388.20 (100%, [M+H]<sup>+</sup>); Found: C, 67.61; H, 6.95; N, 21.46. Calc. for C<sub>22</sub>H<sub>24</sub>N<sub>6</sub>O: C, 68.02; H, 6.23; N, 21.63.

#### 2.2.3. Synthesis of Dye 4

A mixture of 4-nitroaniline (0.276 g, 2 mmol), hydrochloric acid (18 mL 2 M), and sodium nitrite (0.14 g, 2 mmol) in water (1 mL) was stirred for 1 h at 0–5 °C. To this solution, a small portion of sulfamic acid was added as a nitrous acid scavenger. The resulting diazonium salt solution was added to a coupling component solution of 2,5-dimethoxyaniline (0.306 g, 2 mmol) dissolved in water (50 mL), while maintaining the temperature and pH of the mixture at 0–5 °C and 5–6, respectively, during the course of addition. After coupling, the solution was stirred for 2 h and the precipitate was filtered, washed with brine, and dried in a vacuum oven. The



Scheme 1. Synthesis of Dye 2 and Dye 3.

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