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Optimized molecular structures of guest-host system for highly efficient

coatable polarizer

Jae Bok Chang^a, Jin Woong Namgoong^a, Chun Sakong^a, Jun Choi^b, Su Hyun Park^c, Byoung

Har Hwang^c, Jae Pil Kim^{a,*}

^aDepartment of Materials Science and Engineering, Seoul National University, Seoul 151-744, Korea ^bHuman and Culture Convergence Technology R&BD group, Korea Institute of Industrial Technology(KITECH), Ansan-si, Kyungki-do, 426-910, Korea ^cLG display Co., Ltd., Paju-si, Kyungki-do 413-811, Korea

* Corresponding author. Tel.: +82 2 880 7187; fax: +82 2 880 7238.

E-mail address: jaepil@snu.ac.kr (J. P. Kim).

Abstract

Various dichroic dyes were synthesized and applied to two different host materials for the study of optimized molecular structures of guest-host system for the coatable polarizer using liquid crystalline polymers. The host material containing planar and linear mesogens had an advantage in exhibiting high orientation orders, but easily formed disclinations due to causing the strong intermolecular attraction between the guest and host molecules. The balance of intermolecular attraction and repulsion between the guest and host molecules is important to simultaneously achieve high orientations and uniform alignments without disclinations. The highest dichroic ratio of coatable polarizers was obtained when the π -conjugation lengths of guest and host molecules have an appropriate ratio. Also, the guest molecules with a long π -conjugation length improved the orientation of host molecules.

Keywords: Guest-host system; Coatable polarizer; Liquid crystalline polymer; Dichroic dye; π -conjugation length; Disclination.

1. Introduction

In the guest-host system using dichroic dyes, the guests (dichroic dyes) are responsible for anisotropic absorption, and the hosts (liquid crystals) are responsible for the alignment of molecules along a particular direction [1–3]. Anthraquinone dyes to have easily liquid crystallinity have been usually used as the guests of the guest-host liquid crystal displays (GH-LCD), while azo dyes with high dichroisms are widely used in guest-host systems such as coatable polarizers [4–6]. Studies on the host have focused on the monomer types of liquid crystals rather than the polymer types [7–10]. The monomer types, which usually form films by a photo curing method, have limitations in complete film formation and maintaining the alignment of molecules in the guest-host coatable polarizer [11–13]. In comparison, the polymer types are more advantageous to use in film formation because they involve a thermal curing method, which is a simpler method than photo curing.

Liquid crystals can be classified as thermotropic and lyotropic liquid crystals [14, 15]. Thermotropic liquid crystals exhibit phase transitions according to temperature changes, whereas lyotropic liquid crystals exhibit phase transitions according to concentration changes in solvents. Liquid crystalline polymers generally consist of many side chains that contain rod-like mesogens and are usually used with a solvent. Additionally, liquid crystalline polymers exhibit the characteristics of both thermotropic and lyotopic liquid crystals.

The alignment of calamitic or rod-like liquid crystals varies according to temperature, and different alignments indicate phase changes. The phases are classified as smectic, nematic, and isotropic, depending on the degree of alignment. The smectic phases are further categorized as smectic A, smectic B, smectic C, etc. [16]. Liquid crystals have different numbers and kinds of phases, as well as diverse ranges of transition temperature depending on their molecular structures [17].

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In this study, the guest-host coatable polarizers were fabricated using two liquid crystalline polymers containing different mesogens as the host. The mesogen of each liquid crystalline polymer has a similar molecular structure to the nematic liquid crystals, which have transition temperatures that range from 30 to 75 °C [17-19]. To investigate the gust-host effects in relation to the molecular structures of the guest and host, various dyes were synthesized and applied to each liquid crystalline polymer. The resulting alignments and the dichroic ratios of the fabricated samples were compared and analyzed to determine the most appropriate molecular structures of the guest and the host for highly efficient coatable polarizers.

2. Experimental

2.1. Materials and instrumentation

Disperse Orange 3, acetic anhydride, 4-nitroaniline, 40% nitrosyl sulfuric acid, *o*-tolidine and sodium sulfide were purchased from Sigma-Aldrich. Disperse Red 1, 4,4'diaminostilbene dihydrochloride, 2-diethylamino-phenol, 2,5-dimethoxyaniline, *N*-(2cyanoethyl)-*N*-methylaniline, 2-(*N*-ehtylanilino)-ethanol, *N*,*N*-dibutylaniline and *o*dianisidine were obtained from TCI. All other chemicals used in this study were of synthesis grade. Host OPR-003(Host-003) and Host OPR-006(Host-006) was supplied by Osaka chemical Co. Ltd.

¹H NMR spectra were recorded on a Bruker Avance 500 spectrometer using DMSO- d_6 and TMS as the solvent and the internal standard, respectively. 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 a HP

8452A spectrophotometer. The absorption maxima and minima of the polarizer samples were measured by an Axoscan Mueller Matrix spectropolarimeter.

2.2. Synthesis of dyes

2.2.1. Synthesis of BP series

o-Tolidine (0.85g, 0.004 mol) was dissolved in 40ml of 1M aqueous hydrochloric acid solution at room temperature. The solution was cooled to 0-5 °C and 0.008mol of sodium nitrite 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-diethylamino-phenol (1.32g, 0.008 mol) dissolved in 50ml of water, 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. The crude product (BP1) was washed with brine and ethanol and dried in a vacuum oven. The other BP series dyes were prepared in a similar manner.

BP1 : Yield 88.3%; ¹H NMR (DMSO-*d*₆, ppm): 1.16 (t, 12H, CH₃), 2.54 (s, 6H, CH₃), 3.51 (m, 8H, CH₂), 6.46 (d, 2H, ArH), 6.53 (d, 2H, ArH), 7.52 (d, 2H, ArH), 7.67 (d, 2H, ArH), 7.94 (d, 2H, ArH), 8.01 (d, 2H, ArH), 14.94 (s, 2H, OH); Mass: *m*/*z* 564.32,(100%, [M+H]⁺); Found: C, 73.02; H, 7.05; N, 14.34. Calc. for C₃₄H₄₀N₆O₂: C, 72.31; H, 7.14; N, 14.88.

BP2 : Yield 90.6%; ¹H NMR (DMSO-d₆, ppm): 1.16 (t, 12H, CH₃), 3.52 (m, 8H, CH₂),
3.99 (s, 6H, CH₂), 6.48 (d, 2H, ArH), 6.53 (d, 2H, ArH), 7.00 (d, 2H, ArH), 7.43 (d, 2H, ArH), 7.63 (d, 2H, ArH), 7.86 (d, 2H, ArH), 14.96 (s, 2H, OH); Mass: *m/z* 596.31,(100%,

[M+H]⁺); Found: C, 68.38; H, 6.75; N, 14.23. Calc. for C₃₄H₄₀N₆O₄: C, 68.43; H, 6.76; N, 14.08.

BP3 : Yield 87.1%; ¹H NMR (DMSO-*d*₆, ppm): 1.16 (t, 6H, CH₃), 2.54 (s, 6H, CH₃), 3.52 (m, 8H, CH₂), 3.62 (m, 4H, CH₂), 4.83 (t, 2H, OH), 6.96 (d, 4H, ArH), 7.52 (d, 2H, ArH), 7.94 (d, 2H, ArH), 8.01 (d, 2H, ArH), 8.14 (d, 4H, ArH); Mass: *m*/*z* 564.32,(100%, [M+H]⁺); Found: C, 72.18; H, 7.21; N, 14.92. Calc. for C₃₄H₄₀N₆O₂: C, 72.31; H, 7.14; N, 14.88.

BP4 : Yield 85.2%; ¹H NMR (DMSO-*d*₆, ppm): 2.54 (s, 6H, CH₃), 2.76 (s, 6H, CH₃), 3.57 (m, 4H, CH₂), 3.72 (m, 4H, CH₂), 6.98 (d, 4H, ArH), 7.52 (d, 2H, ArH), 7.94 (d, 2H, ArH), 8.01 (d, 2H, ArH), 8.13 (d, 4H, ArH); Mass: *m/z* 554.29,(100%, [M+H]⁺); Found: C, 73.47; H, 6.15; N, 20.38. Calc. for C₃₄H₃₄N₈: C, 73.62; H, 6.18; N, 20.20.

2.2.2. Synthesis of ST series

4,4'-diaminostilbene-dihydrochloride (0.56g, 0.002 mol) was dissolved in 30ml of 0.6M aqueous hydrochloric acid solution at room temperature. The solution was cooled to 0-5 °C and 0.004mol of sodium nitrite 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*-Ethylanilino)-ethanol (0.66g, 0.004 mol) dissolved in 20ml of ethanol and 30ml of water, while maintaining the temperature and pH of the mixture at 0-5 °C and 4-5, respectively, during the course of addition. The reaction mixture was stirred for 2 h and the precipitate was filtered. The crude product (ST3) was washed with brine and ethanol and dried in a vacuum oven. The other ST series dyes were prepared in a similar manner.

ST1 : Yield 86.4%; ¹H NMR (DMSO-*d*₆, ppm): 1.16 (t, 12H, CH₃), 3.52 (m, 8H, CH₂), 6.45 (d, 2H, ArH), 6.52 (d, 2H, ArH), 7.24 (d, 2H, CH), 7.68 (d, 2H, ArH), 7.70 (d, 4H, ArH), 7.97 (d, 4H, ArH), 15.02 (s, 2H, OH); Mass: *m*/*z* 562.31,(100%, [M+H]⁺); Found: C, 73.17; H, 6.72; N, 14.96. Calc. for C₃₄H₃₈N₆O₂: C, 72.57; H, 6.81; N, 14.94.

ST2 : Yield 61.5%; ¹H NMR (DMSO-*d*₆, ppm): 0.91 (t, 12H, CH₃), 1.22(m, 8H, CH₂), 1.67(m, 8H, CH₂), 3.53 (m, 8H, CH₂), 6.94 (d, 4H, ArH), 7.25 (d, 2H, CH), 7.69 (d, 4H, ArH), 7.96 (d, 4H, ArH), 8.16 (d, 4H, ArH); Mass: *m*/*z* 642.44,(100%, [M+H]⁺); Found: C, 78.25; H, 8.55; N, 13.20. Calc. for C₄₂H₅₄N₆: C, 78.46; H, 8.47; N, 13.07.

ST3 : Yield 90.3%; ¹H NMR (DMSO-*d*₆, ppm): 1.16 (t, 6H, CH₃), 3.53 (m, 8H, CH₂), 3.62 (m, 4H, CH₂), 4.83 (t, 2H, OH), 6.96 (d, 4H, ArH), 7.24 (d, 2H, CH), 7.69 (d, 4H, ArH), 7.95 (d, 4H, ArH), 8.14 (d, 4H, ArH); Mass: *m*/*z* 562.31,(100%, [M+H]⁺); Found: C, 72.36; H, 6.96; N, 15.01. Calc. for for C₃₄H₃₈N₆O₂: C, 72.57; H, 6.81; N, 14.94.

ST4 : Yield 82.6%; ¹H NMR (DMSO- d_{6} , ppm): 2.76 (s, 6H, CH₃), 3.57 (m, 4H, CH₂), 3.73 (m, 4H, CH₂), 6.98 (d, 4H, ArH), 7.25 (d, 2H, CH), 7.68 (d, 4H, ArH), 7.96 (d, 4H, ArH), 8.14 (d, 4H, ArH); Mass: m/z 552.27,(100%, [M+H]⁺); Found: C, 73.31; H, 5.83; N, 20.86. Calc. for C₃₄H₃₂N₈: C, 73.89; H, 5.84; N, 20.27.

2.2.3. Synthesis of US series

A mixture of 0.276 g (0.002 mol) 4-nitroaniline, 18 ml of 2 M hydrochloric acid, and 0.14 g (0.002 mol) sodium nitrite 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, 0.002 mol) dissolved in 50 ml of water, 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 intermediate was heated in ethanol for 2 h under reflux, hot-filtered, washed with hot ethanol, and then dried in a vacuum oven.

The intermediate (1.43 g, 0.006 mol) was slowly introduced into concentrated sulfuric acid (10 mL), and the temperature of the mixture was kept below 40 °C. After stirring for 30 min at room temperature, the solution was cooled to 0–5 °C and 40% nitrosyl sulfuric acid (2.6mL) was dropped slowly. The mixture was stirred for 4 h at 0–5 °C. The resulting mixture was added dropwise to a solution of 2-diethylaminophenol 0.003 mol (0.495 g) dissolved in glacial acetic acid (100 ml) and ice-water (100 ml) to initiate the coupling reaction. The pH of the reaction mixture was adjusted to approximately 4 by adding 20 wt% aqueous sodium acetate solution. The reaction mixture was stirred for 3 h at 0–5 °C and then for 4 h at room temperature. The crude product (US1) was filtered, washed with brine, and dried in a vacuum oven.

US1 : Yield 63.2%; ¹H NMR (DMSO-*d*₆, ppm): 1.16 (t, 6H, CH₃), 3.58 (m, 4H, CH₂), 3.86 (s, 6H, CH₃), 6.53 (s, 1H, ArH), 6.84 (d, 1H, ArH), 7.06 (d, 1H, ArH), 7.44 (s, 2H, ArH), 7.82 (d, 2H, ArH), 8.46 (d, 2H, ArH), 15.4 (s, 1H, OH); Mass: *m*/*z* 478.20,(100%, [M+H]⁺); Found: C, 60.36; H, 6.06; N, 17.12. Calc. for C₂₄H₂₆N₆O₅: C, 60.24; H, 5.48; N, 17.56.

Disperse Orange 3 (0.97g, 0.004 mol) was dissolved in 60 ml of 0.3 M aqueous hydrochloric acid solution at room temperature. The solution was cooled to 0-5 °C, and 0.004 mol of sodium nitrite 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*-ethylanilino)ethanol (0.66 g, 0.004 mol) dissolved in 20 ml of ethanol and 30 ml of water, 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 (US2) was purified by recrystallization in methylene chloride.

US2 : Yield 77.0%; ¹H NMR (DMSO-*d*₆, ppm): 1.16 (t, 3H, CH₃), 3.53 (m, 4H, CH₂), 3.62 (m, 2H, CH₂), 4.84 (t, 1H, OH), 6.86 (d, 2H, ArH), 7.82 (d, 2H, ArH), 7.97 (d, 2H, ArH), 8.11 (d, 4H, ArH), 8.44 (d, 2H, ArH); Mass: *m/z* 418.18 (100%, [M+H]⁺); Found: C, 63.05; H, 5.36; N, 20.42. Calc. for C₂₂H₂₂N₆O₃: C, 63.15; H, 5.30; N, 20.08.

A solution of US2 (0.84 g, 0.002 mol) in 25 ml of ethanol was stirred for 1 h at 70 °C. Then, 50 ml of water was added, and 10 ml of aqueous sodium sulfide (1.5 g 0.005 mol) solution 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, 100 ml of water 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.

US3 : Yield 94.3%; ¹H NMR (DMSO-*d*₆, ppm): 1.16 (t, 3H, CH₃), 3.52 (m, 4H, CH₂), 3.62 (m, 2H, CH₂), 4.84 (t, 1H, OH), 6.53 (s, 2H, NH₂), 6.86 (d, 2H, ArH), 6.96 (d, 2H, ArH), 7.82 (d, 2H, ArH), 7.98 (d, 2H, ArH), 8.12 (d, 4H, ArH);Mass: *m*/*z* 388.20 (100%, [M+H]⁺); Found: C, 67.61; H, 6.95; N, 21.46. Calc. for C₂₂H₂₄N₆O: C, 68.02; H, 6.23; N, 21.63.

2.3. Fabrication of coatable polarizers

Host materials (Host-003 or Host-006) and the synthesized dyes were mixed in a vortex mixer for 60sec and stirred using a magnetic bar for 1h at 60 °C. The resulting mixtures

were spread by spin-coating on a rubbed polyimide alignment layer. The alignment layers were prepared by coating AL16301(JSR Co.) on glass. AL16301 is suitable for achieving a parallel homogeneous alignment [20–21]. The spin-coating was performed at 1100 rpm for 10 sec. The spin-coated samples were stabilized through the curing procedure.

2.4. Investigation of optical properties of coatable polarizers

The optical properties of the polarizing films were measured using a UV-vis spectrophotometer equipped with a Glan-Thompson polarizer. The dichroic ratio(\mathbf{R}) and order parameter (\mathbf{S}) were evaluated at the absorption maximum of the coatable polarizers according to Eqs. (1) and (2) [22]. The average angle of the deviated dye molecules ($\boldsymbol{\theta}$) can be derived from the order parameter \mathbf{S} defined as the average of the Legendre polynomia, as given in Eqs. (3)[23].

$$\mathbf{R} = \mathbf{A}_{\parallel} / \mathbf{A}_{\perp} \tag{1}$$

$$S = (R-1)/(R+2)$$
 (2)

$$\theta = \arccos \sqrt{\frac{2S+1}{3}} \tag{3}$$

where A_{\parallel} and A_{\perp} denote the parallel and perpendicular absorbance to the rubbing direction, respectively.

2.5. Theoretical calculation

Gaussian 09 software package was employed to optimize the geometry of the dye structures by using molecular mechanics MM3, conducting iterative energy-minimizing routines with the conjugate gradient minimizer algorithm [24]. The CONFLEX conformational search procedure was used for finding low-energy conformations of the dye molecules [25]. Optimization to transition state of the dichroic dyes were examined by DFT, with the B3LYP/6-31⁺G(d,p) basis set using the dye structures optimized by the above-mentioned calculation.

Aspect ratios (l/d) of the dye molecules were calculated from the geometry of the most stable conformer optimized by CONFLEX/MM3 calculation in consideration of the van der Waals radius, where l and d represent the length of the long axes and diameter of the circumscribed cylinders of the dye molecules, respectively.

3. Results and discussion

3.1. Difference between Host-003 and Host-006

Host-003 and Host-006 are both thermally curable liquid crystalline polymers that use cyclopentanone as a solvent. They contain side chains with ester links to the main alkyl chain; each side chain consists of a flexible part connected to a rigid part by an ether linkage. Host-003 contains a biphenyl rigid core with a cyano group, while Host-006 contains a monoazo benzene derivative as a rigid moiety (Fig. 1).

At 25 °C, Host-003 exhibits a solid content of 20.7 wt% and a viscosity of 6.1 mPa·s, whereas Host-006 exhibits a solid content of 20.0 wt% and a viscosity of 8.0 mPa·s.

Considering that the molecular weight of a side chain in Host-003 was 393.52 and that of Host-006 was 454.60, the mole fraction of Host-006 was 83.64% lower than that of Host-003. This means that the difference between the intermolecular interactions of Host-006 is stronger than that of Host-006.

The difference between the intermolecular interactions of both host molecules is attributed to the different molecular structures of the rigid parts. Because the host molecules lack hydrogen bonding donors, van der Waals forces and π - π interactions are likely the main intermolecular interactions between the host molecules. These interactions are influenced by the geometries of the host molecules. For example, the rigid parts of the host molecules exhibit different degrees of linearity and planarity, as shown in Fig. 2. Due to a short π -conjugation length and a twisted 35.5° dihedral angle, the rigid part of Host–003 exhibits a weaker intermolecular interaction than that of Host-006. This feature presumably results in the differing thicknesses of the samples spin-coated (1100 rpm/10 sec) by Host-003 and Host-006. The average thickness of Host-003 samples was 1.6 µm, while that of Host-006 samples was 1.9 µm.

Unlike Host-003, Host-006 absorbed visible light due to the presence of azo chromophores. Absorption spectrum of dilute solution (0.01 wt%) of Host-006 is depicted in Fig. 3(a). The absorption maximum wavelength of the azo chromophore in Host-006 was 360 nm in cyclopentanone. Meanwhile, the coatable polarizer composed of only Host-006 exhibited an absorption maximum wavelength of 420 nm, as shown in Fig. 3(b). Since the azo chromophore in Host-006 exhibited a dichroic property, the parallel and perpendicular absorbance spectra of the sample were measured and the dichroic ratio was calculated. Host-006 had a dichroic ratio of 7.66 and its order parameter was 0.69, which is within the order parameter range (0.4–0.7) of typical nematic phases [17].

3.2 Structure and characterization of dichroic dyes

Disperse Orange 3 (DO3) and Disperse Red 1 (DR1) were prepared as monoazo dyes, while three unsymmetric dyes (US series) and eight symmetric dyes (BP and ST series) were designed and synthesized as disazo dyes. As shown in Fig. 4, the monoazo dyes have D- π -A structures involving a primary amine group or a tertiary amine group. DO3 exhibited an aspect ratio of 2.74 while DR1 exhibited a slightly longer aspect ratio of 2.94 due to the alkyl chains of the tertiary amine group. Every disazo dye, except US1, exhibited greater linearity than the monoazo dyes. The lower aspect ratio of US1 was attributed to the lateral substituents, which increased solubility. US2 and US3 had aspect ratios on the order of four. The symmetric dyes had long conjugation lengths due to the introduction of either biphenyl or stilbene moieties. These long conjugation lengths decreased the influence of the terminal substituents on the linearity of the symmetric dyes. The aspect ratios of the BP series were on the order of five and those of the ST series were on the order of six.

DO3, which contains an electron donating group opposite to an electron withdrawing group, exhibited an absorption maximum wavelength of 436 nm (Table 1). DR1 exhibited an absorption maximum wavelength of 484nm, which is more bathochromic than DO3 by the stronger donating power of the tertiary amine group compared to the primary amine group. DR1 also exhibited higher solubility compared to DO3 due to the bulky alkyl chains of the tertiary amine group. The US series absorbed longer wavelengths than the monoazo dyes because the addition of azo linkages extended the π -conjugation lengths in the former. US1 exhibited the longest absorption maximum wavelength (554 nm) due to increased donation from additional substituents. Meanwhile, the absorption maximum wavelength of US2, a D- π -A structure, was 526 nm and that of US3, a D- π -D structure, was 500 nm. The

hypsochromic shifts in the US series correlated with the symmetries of the charge distributions.

BP1 and BP2 absorbed longer wavelengths than BP3 and BP4 because the former contain hydrazone forms of the azo linkages; these are due to intramolecular hydrogen bonding interactions between hydroxyl groups ortho to the azo linkages. BP2 exhibited a longer absorption maximum wavelength (526 nm) than BP1 as a result of stronger donation from the methoxy groups compared to the methyl groups. The BP series exhibited bathochromic shifts that increased with the degree of donation from their substituents. The relatively high solubilities of the BP series were caused by the twisted dihedral angles of both the biphenyl and the lateral moieties, such as the methoxy and methyl groups.

The ST series, on average, exhibited higher molar extinction coefficients than the dyes of the other series due to the linear and planar molecular structures of the stilbene moieties. Furthermore, the dyes in the ST series absorbed longer wavelengths than the dyes with identical terminal substituents in the BP series. However, this structural feature of the stilbene moiety resulted in stronger van der Waals forces and π - π interactions. Consequently, the solubilities of the ST series, excluding ST2, were less than half those of the BP series. ST2 exhibited the highest solubility due to its sterically bulky alkyl chains.

3.3. Orientation of dichroic dyes within Host-003

All samples containing Host-003 were aligned uniformly without any disclinations, as shown in Fig. 5. This means that Host-003 and 13 dyes were compatible, indicating that dye molecules did not disturb the uniform alignment of Host-003. The host properties, such as transition temperature, order parameter, and elastic constant, are known to change due to

the following molecular interactions between the guests: hydrogen bonding, van der Waals forces, and electrostatic forces [26–27]. Host-003 presumably exhibits different orientations based on the molecular structure of the guest. However, the partial loss of liquid crystallinity from interaction with the guest did not occur in guest-host systems containing Host-003.

The dichroic ratios (R), orientation order parameters (S), and average angles of deviated dye molecules (θ) of the samples containing Host-003 are presented in Table 2. The monoazo structures DO3 and DR1 exhibited dichroic ratios of 4.94 and 4.91, respectively. US1 exhibited the lowest dichroic ratio (3.46) because sterically bulky lateral substituents disrupted the orientation of the dye molecules. The disazo structure US2, which has the same terminal substituents as DR1, exhibited a dichroic ratio of 7.25. US3, which has a similar linearity but different polarity compared to US2, exhibited the highest dichroic ratio (12.37) in samples containing Host-003.

The dichroic ratios of the BP series were affected by intermolecular interactions between the hosts and guests. BP1 exhibits van der Waals forces and hydrogen bonding interactions because the hydroxyl groups are in the conjugated system of the dye molecules. The hydroxyl groups of BP1 are also involved in hydrophilic repulsive forces between the host and guest molecules. Due to these intermolecular interactions, BP1 exhibited a dichroic ratio of 6.51. The van der Waals forces and hydrogen bonding interactions in BP3 presumably interact separately within the host molecules; unlike the hydroxyl groups of BP1, those of BP3 are located at both ends of the dye molecule. This molecular structure causes BP3 to have a dichroic ratio of 7.39. BP4, which contains nitrile groups instead of hydroxyl groups, exhibited a dichroic ratio of 4.79. The nitrile groups were introduced in BP4 to change the partial charges of the terminal alkyl chains and are believed to adversely affect the orientation of BP4 in Host-003. Remarkably, BP2 exhibited the highest dichroic

ratio (7.96) in the BP series despite its low aspect ratio, which is attributed to its lateral methoxy groups. In contrast to the case of US1, the lateral methoxy groups of BP2 barely affect the orientation of the dye molecules because of the long molecular length of BP2. Instead, the lateral methoxy groups presumably prevent a decrease in the liquid crystallinity of BP2: the steric hindrance of the lateral methoxy groups helps maintain a certain distance between BP2 and the mesogens of Host-003. This effect is thought to improve the orientation of the dyes; thus, BP2 exhibited the highest order parameter (0.70) and the smallest angle (26.53°) of deviated dye molecules.

ST1, which has the same terminal substituents as BP1, exhibited a higher dichroic ratio (7.10) and order parameter (0.67) than BP1. However, the levels of these properties are relatively low within the ST series. These results suggest that the hydroxyl group located in the conjugated system negatively influences the guest-host effect in Host-003. ST2, which contains bulky alkyl chains, exhibited the lowest dichroic ratio (6.57) in the ST series. ST3 had the highest dichroic ratio (7.99) out of the dyes with symmetric structures because of its high linearity and its incorporation of substituents that encourage parallel alignment. ST4, which contains the same terminal substituents as BP4, exhibited a dichroic ratio of 7.80, and did not exhibit the adverse effects of nitrile substituents that were present in BP4. This means that nitrile substituents in a more linear and planar conjugated system have little adverse effects on the orientation of the dyes.

In the case of DR1 and US2, the linearities and dichroic ratios increased by 38.01% and 47.66%, respectively. However, the linearities of BP3 and ST3 increased by 32.76% and 53.20%, respectively, while their dichroic ratios only increased by 1.93% and 10.20%, respectively, compared to US2. Considering the importance of linearity in the dichroic ratio, these results indicate that other factors affect the relatively low dichroic ratios of BP3 and ST3. The two dyes presumably have no intrinsic factors, such as steric hindrance, polarity,

the direction of transition dipole moment, etc., that adversely affect their dichroic ratios. Therefore, extrinsic factors of dye structure are believed to affect the dichroic ratios of BP3 and ST3 in Host-003. The π -conjugation length ratio (Host-003 : monoazo : US series : BP series : ST series) is 1 : 1.38 : 2.31 : 3.02 : 3.33, as shown in Fig. 6. Depending on the conjugation length of the molecules, intermolecular interactions, such as π - π interaction and van der Waals forces, dominate the guest-host effect. The conjugation lengths of the BP and ST series are too long to interact effectively with the rigid segment of Host-003. Therefore, the BP and ST series are aligned by insufficient guest-host effects and have orientations with reduced order parameters in Host-003. In particular, ST3 exhibited a much higher dichroic ratio than US2 in Host-006, which has a longer rigid segment than Host-003. Further details of the dichroic properties of dyes in Host-006 are explained in section 3.5.

3.4. Alignment of Host-006 doped with dyes

The coatable polarizer composed of only Host-006 was fabricated without disclinations by curing at a temperature of 90 °C. The samples containing Host-006 doped with DO3 and DR1 exhibited uniform alignments without disclinations by curing at a temperature of 90 °C as well. However, the Host-006 samples cured at 90 °C and doped with disazo dyes showed disclinations in the samples cured at 90 °C. Thus, higher curing temperatures were applied to the samples containing disazo dyes to produce uniform alignments. The orientations of the Host-006 samples doped with disazo dyes changed according to curing temperature, as shown in Fig. 7.

The types of disclination varied with the molecular structures of the dyes and the curing temperatures, yet all samples exhibited sand-like disclination textures at the curing temperature of 120 °C. The fast evaporation rate of the solvent promotes the formation of a crystalline phase [28]. Since the boiling point of cyclopentanone is 130 °C, a curing temperature of 120 °C leads to a fast solvent evaporation rate and therefore results in the crystalline phases which are scattered in the samples. The disclinations are presumably affected by the intermolecular interactions between the dyes, the host molecules, and the solvent. Out of 11 disazo dyes, only US2, BP2, and ST3 aligned with Host-006 without disclinations at the curing temperature of 110 °C.

Alignments without disclinations in the samples containing Host-006 doped with disazo dyes were achieved by an additional heat treatment step. The disclinations in the sample with BP2, which was fabricated at the curing temperature of 90 °C, changed upon additional heat treatment and disappeared at 110 °C, as shown in Fig. 8. Further, the sand-like disclination texture was not formed at 120 °C upon additional heat treatment. This phenomenon is similar to the phase transition of thermotropic liquid crystals, in which the alignments vary with temperature. Host-006 presumably has a low orientational degree of freedom compared to liquid crystal monomers because of its polymer structure; yet, a certain orientational degree of freedom could remain in Host-006 even after the curing process. The driving forces that change the liquid crystal phase with increases in temperature supposedly realign the guest and host molecules. Even upon additional heat treatment, only US2, BP2, and ST3 exhibited alignments without disclinations.

The disclinations were formed in the samples with disazo dyes, but not in the samples with monoazo dyes. These results suggest that the π -conjugation lengths of dye molecules affect the alignment of Host-006. Also, the π -conjugation lengths of the rigid segments of the host molecules presumably play an important role in achieving alignments without

disclinations. As mentioned in section 3.1, Host-003 exhibits a weaker van der Waals force than Host-006 because its rigid segment is short and has a twisted dihedral angle. Overall, Host-006 exhibits stronger intermolecular interaction with guest dyes compared to Host-003. This difference is due to the ability of Host-003 to accommodate all dyes without the partial loss of liquid crystallinity that results in disclinations. However, Host-006 can easily agglomerate with guest dyes that have long π -conjugation lengths.

Disclination, which is a line singularity in the overall molecular orientation, is caused by discontinuities within the uniform alignment and provides various structures based on the liquid crystal phase [29–30]. In nematic liquid crystals, disclinations are observed as droplets-textures, thread-textures, or schlieren-textures in the boundary between an isotropic phase and a nematic phase [31–32]. The disclination shapes of the samples containing Host-006 are presented in Fig. 9. US1 and ST2, which have sterically hindered structures, displayed mixtures of thread-textures and schlieren-textures. BP1 and ST1, which have strong intermolecular interactions composed of hydrogen bonding and van der Waals forces, displayed mainly droplets-textures. BP4 and ST4, which contain nitrile substituents, clearly displayed grain boundaries. These different disclination shapes indicate changes in the liquid crystallinity of host molecules, which arise from the different intermolecular interactions that vary according to the molecular structures of the guest dyes.

US3, which has a short conjugation length among the disazo dyes, showed relatively few droplet-like disclinations. On the other hand, US2, which has a similar linearity but higher polarity compared with US3, showed uniform alignment without disclinations. The large difference in polarities between US2 (13.56 D) and the mesogen of Host-006 (0.56 D) decreases the affinity between US2 and Host-006. Therefore, compared to US2, US3 had a higher affinity for Host-006 as compared to US2. High affinity between the guest and host

molecules can lead to decreased liquid crystallinity of the host molecules due to agglomeration from strong intermolecular attractions.

The lateral methoxy substituents of BP2 provided structural repulsion between BP2 and host molecules. However, BP2 exhibited less steric hindrance compared to US1 and ST2 because of its long conjugation length. The degree of steric hindrance in BP2 is believed to achieve an alignment without disclinations by balancing intermolecular attraction and repulsion. In BP2, a certain distance between the guest and host molecules is maintained and is required to prevent disclination in Host-006. In the case of ST3, hydrophilic repulsion from the terminal hydroxyl groups presumably helps maintain a certain distance between the guest and host molecules. In other words, the hydrophilic/hydrophobic ratio of ST3 is believed to beappropriate to achieve uniform alignment with Host-006.

3.5. Dichroic properties of Host-006 doped with dyes

In samples containing Host-006, the absorption spectra of the dyes overlapped with the absorption spectrum of the azo chromophore of Host-006, as shown in Fig. 10. The overlapping absorption band depended on the absorption maximum wavelengths of the dyes. The absorption maximum of DO3 was measured at 460 nm, which is the peak of its absorption spectrum. The absorption maxima of the other dyes were measured at the shoulder peak above 500 nm.

DR1, US2, and ST3 exhibited higher dichroic ratios in Host-006 than they did in Host-003 (Table 3). DR1 and US2 exhibited dichroic ratio increases of 25.66% (6.17) and 58.07% (11.46), respectively. ST3 exhibited the highest dichroic ratio (17.04) increase by 113.27%.

These results indicate that Host-006 has a superior alignment ability compared to Host-003. Moreover, the remarkable increase in the dichroic ratio of ST3 is attributed to an extended π -conjugation length in the host molecules. Supposedly, the guest-host effect depends on the π -conjugation length of the guest and host molecules. ST3 exhibits a relatively low dichroic ratio in Host-003 that is attributed to the short π -conjugation length of Host-003. The π -conjugation length ratio of Host-003 and ST3 was calculated to be 1:3.33, whereas that of Host-006 and ST3 was calculated to be 1:2.41. The appropriate π -conjugation length ratio of the host and guest molecules causes the guest-host effect that enables guest molecules to have high orientation orders.

Both DO3 and BP2 exhibited lower dichroic ratios in Host-006 than in Host-003. However, while the sample with DO3 exhibited a dichroic ratio at 420 nm below 7.66, which is the dichroic ratio of Host-006 itself, the sample with BP2 exhibited a dichroic ratio at 420 nm above 7.66, as shown in Fig. 10(f). These results indicate that DO3 disrupts the orientation of the entire guest-host system, while BP2 improves the alignment of the host molecules regardless of its own low dichroic ratio. The low dichroic ratio of BP2 is supposedly caused by steric hindrance. The lateral substituents of BP2 had little effect on the orientation in Host-003 but not in Host-006 because of the increased lengths of the rigid segments of the host molecules.

The improved alignment ability of Host-006 depends on the properties of the dyes. For instance, BP2 and US2 raised the dichroic ratios of Host-006 to 9.72 and 10.60, respectively. US2 has a short π -conjugation length and decreased steric hindrance compared to BP2. ST3, which has the longest π -conjugation length and the highest dichroic ratio, increased the dichroic ratio of Host-006 to 13.46.

4. Conclusions

The intermolecular interactions between guest and host molecules greatly influence the orientations and alignments of coatable polarizers. The intermolecular interactions are determined by combinations of the following factors: van der Waals forces, hydrogen bonding interactions, electrostatic effects, hydrophilic/hydrophobic ratios, polarities, and steric hindrance. These factors depend on the molecular structures of the dyes and the mesogens of liquid crystalline polymers. The twist-shaped mesogens of Host-003 ensured uniform alignment without disclinations, but exhibited relatively low dichroic ratios compared to those of Host-006. The planar and linear mesogens of Host-006 favor high orientation orders, but easily form disclinations in association with disazo dyes. The molecular structures of the dyes affect the alignment of the host molecules and the orientation of the guest molecules. Dyes with strong intermolecular interactions caused disclinations to form in Host-006. Meanwhile, disazo dyes with appropriate intermolecular interactions led to improved dichroic ratios in Host-006. To simultaneously achieve high orientations and uniform alignments in guest-host coatable polarizers, intermolecular attraction and repulsion between the guest and host molecules should be balanced against each other.

The π -conjugation lengths of the host and guest molecules are important to achieve high dichroic ratios. When the π -conjugation length of the guest is much longer than that of the host, the guest cannot sufficiently align to achieve a high orientation order. Therefore, π -conjugation lengths of the dyes should be designed while considering those of the host molecules. The long π -conjugation lengths of the guest and host molecules presumably favor high orientation orders unless disclinations occur.

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Dye	λ_{max} (nm)	$\epsilon_{\rm max}$ (Lmol ⁻¹ cm ⁻¹)	Aspect ratio	Solubility(wt%)
DO3	436	26,000	2.74	1.2
DR1	484	27,000	2.94	2.0
US1	554	52,000	2.65	2.0
US2	526	35,000	4.06	0.8
US3	500	41,000	4.05	2.0
BP1	504	48,000	5.30	2.0
BP2	526	51,000	5.08	2.0
BP3	468	43,000	5.39	2.0
BP4	462	38,000	5.42	2.0
ST1	512	64,000	6.14	1.2
ST2	490	53,000	6.05	10.0
ST3	496	57,000	6.22	0.8
ST4	468	45,000	6.26	1.0

Table 1. Spectral properties, aspect ratio and solubility in cyclopentanone of the dichroic dyes.

Dye	R	S	θ(*)
DO3	4.94	0.57	32.36
DR1	4.91	0.57	32.44
US1	3.46	0.45	37.16
US2	7.25	0.68	27.61
US3	12.37	0.79	21.83
BP1	6.51	0.65	28.90
BP2	7.96	0.70	26.53
BP3	7.39	0.68	27.39
BP4	4.79	0.56	32.76
ST1	7.10	0.67	27.86
ST2	6.57	0.65	28.79
ST3	7.99	0.70	26.49
ST4	7.80	0.69	26.76

Table 2. Dichroic and orientaional properties of coatable polarizers using Host-003 doped with the respective dyes.

				6
Dye	λ_{max} (nm) ^a	R	S	θ(*)
DO3	460	4.14	0.51	34.68
DR1	510	6.17	0.63	29.55
US2	540	11.46	0.78	22.60
BP2	540	5.06	0.58	32.05

17.04

ST3

520

Table 3. Absoprtion maxima, dichroic and orientaional of coatable polarizers using Host-006 doped with the respective dyes.

^a Measured to coatable polarizer

18.85

0.84

Figure captions

- Fig. 1. Molecular structures of the a) Host-003 and b) Host-006.
- Fig. 2. Geometry-optimized structures of the a) Host-003 and b) Host-006.
- Fig. 3. a) Absorption spectrum of Host-006 (0.01wt% in cyclopentanone) and b) parallel and perpendicular absorbance spectra of coatable polarizer composed of only Host-006.
- Fig. 4. Molecular structures of the dichroic dyes (DO3, DR1, US series, BP series and ST series).
- Fig. 5. Microscopic image of coatable polarizers using Host-003 doped with the dyes under the polarizing microscope at 50X magnification.
- Fig. 6. The π -conjugation length ratio of Host-003, monoazo, US series, BP series and ST series dyes.
- Fig. 7. Optical microscopy texture of Host-006 doped with the dyes on the coatable polarizers having different curing temperature under the polarizing microscope at 50X magnification.
- Fig. 8. Change in the microscopy texture of Host-006 doped with BP2 depending on the heattreatment temperature a) 90 °C, b) 100 °C, c) 110 °C, d) 115 °C and e) 120 °C.
- Fig. 9. Microscopic image of coatable polarizers using Host-006 doped with the dyes under the polarizing microscope at 50X magnification.
- Fig. 10. Parallel and perpendicular absorbance of coatable polarizer using Host-006 doped with the dyes a) DO3, b) DR1, c) US2, d) BP2 and e) ST3 and f)dichroic ratio spectra of the coatable polarizers.



Fig. 1. Molecular structures of the a) Host-003 and b) Host-006.



Fig. 2. Geometry-optimized structures of the a) Host-003 and b) Host-006.





Fig. 3. a) Absorption spectrum of Host-006 (0.01wt% in cyclopentanone) and b) parallel and perpendicular absorbance spectra of coatable polarizer composed of only Host-006.



Fig. 4. Molecular structures of the dichroic dyes (DO3, DR1, US series, BP series and ST series).



Fig. 5. Microscopic image of coatable polarizers using Host-003 doped with the dyes under the polarizing microscope at 50X magnification.



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Fig. 9. Microscopic image of coatable polarizers using Host-006 doped with the dyes under the polarizing microscope at 50X magnification.



Fig. 10. Parallel and perpendicular absorbance of coatable polarizer using Host-006 doped with the dyes a) DO3, b) DR1, c) US2, d) BP2 and e) ST3 and f)dichroic ratio spectra of the coatable polarizers.

Research highlights

Host–003 has a shorter and twisted (35.5°) mesogen compared to Host-006.

Host-003 accommodated all synthesized dyes without disclinations.

Host-006 easily formed disclinations with synthesized dyes.

ST3 exhibited higher dichroic ratio in Host-006 than it did in Host-003.