Dyes and Pigments 121 (2015) 265–275

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Optimized molecular structures of guest–host system for highly efficient coatable polarizer

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ARTICLE INFO

Article history:
Received 25 February 2015
Received in revised form
6 May 2015
Accepted 8 May 2015
Available online 28 May 2015

Keywords:
Guest–host system
Coatable polarizer
Liquid crystalline polymer
Dichroic dye
π-Conjugation length
Disclination

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.

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 lyotropic 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].

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

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http://dx.doi.org/10.1016/j.dyepig.2015.05.010
0143-7208/

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*-(2-cyanoethyl)-*N*-methylaniline, 2-(*N*-ethylanilino)-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.

^{1}H 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 an 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 (0.85 g, 0.004 mol) was dissolved in 40 ml of 1 M aqueous hydrochloric acid solution at room temperature. The solution was cooled to 0–5 °C and 0.008 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-diethylamino-phenol (1.32 g, 0.008 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. 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%; ^{1}H NMR (DMSO-d_6, ppm): 1.16 (t, 12H, CH_3), 2.54 (s, 6H, CH_3), 3.51 (m, 8H, CH_2), 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 $C_{34}H_{40}N_6O_2$: C, 72.31; H, 7.14; N, 14.88.

BP2: Yield 90.6%; ^{1}H NMR (DMSO-d_6, ppm): 1.16 (t, 12H, CH_3), 3.52 (m, 8H, CH_2), 3.99 (s, 6H, CH_2), 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 $C_{34}H_{40}N_6O_4$: C, 68.43; H, 6.76; N, 14.08.

BP3: Yield 87.1%; ^{1}H NMR (DMSO-d_6, ppm): 1.16 (t, 6H, CH_3), 2.54 (s, 6H, CH_3), 3.52 (m, 8H, CH_2), 3.62 (m, 4H, CH_2), 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 $C_{34}H_{40}N_6O_2$: C, 72.31; H, 7.14; N, 14.88.

BP4: Yield 85.2%; ^{1}H NMR (DMSO-d_6, ppm): 2.54 (s, 6H, CH_3), 2.76 (s, 6H, CH_3), 3.57 (m, 4H, CH_2), 3.72 (m, 4H, CH_2), 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 $C_{34}H_{34}N_8$: C, 73.62; H, 6.18; N, 20.20.

2.2.2. Synthesis of ST series

4,4′-Diaminostilbene-dihydrochloride (0.56 g, 0.002 mol) was dissolved in 30 ml of 0.6 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 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%; ^{1}H NMR (DMSO-d_6, ppm): 1.16 (t, 12H, CH_3), 3.52 (m, 8H, CH_2), 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 $C_{34}H_{38}N_6O_2$: C, 72.57; H, 6.81; N, 14.94.

ST2: Yield 61.5%; ^{1}H NMR (DMSO-d_6, ppm): 0.91 (t, 12H, CH_3), 1.22 (m, 8H, CH_2), 1.67 (m, 8H, CH_2), 3.53 (m, 8H, CH_2), 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 $C_{42}H_{54}N_6$: C, 78.46; H, 8.47; N, 13.07.

ST3: Yield 90.3%; ^{1}H NMR (DMSO-d_6, ppm): 1.16 (t, 6H, CH_3), 3.53 (m, 8H, CH_2), 3.62 (m, 4H, CH_2), 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 $C_{34}H_{38}N_6O_2$: C, 72.57; H, 6.81; N, 14.94.

ST4: Yield 82.6%; ^{1}H NMR (DMSO-d_6, ppm): 2.76 (s, 6H, CH_3), 3.57 (m, 4H, CH_2), 3.73 (m, 4H, CH_2), 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 $C_{34}H_{32}N_8$: 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 (2.6 ml) 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