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Effect of transition moments and orientational behavior of dichroic dyes on the optical anisotropy of poly(vinyl alcohol) polarizing films

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ABSTRACT

In order to examine the orientational behavior of dichroic dyes in terms of their structural characteristics and its effect on the optical anisotropy in stretched poly(vinyl alcohol) films, six azo dichroic dyes were synthesized and employed in dye/polarizing films. The dichroic ratios, order parameters and transition moments of the dyes were calculated. Molecular orbital calculation revealed that the transition moments of the dyes scarcely deviated from their molecular axes, resulting in minimal effect upon the optical anisotropy of the polarizing films. However, the dichroic ratios of the films increased as the angle of deviation of the dye molecular axes from the drawn direction of the host films decreased. In terms of the orientational behavior of the dyes, the number and position of hydrogen bonding sites had a significant effect on the alignment of the dyes when the host films were drawn. The orientational behavior of the dyes was more important in terms of the length of the dye molecular axes rather than their aspect ratios.

1. Introduction

Polarizing film, which controls the transmittance of light associated with liquid crystal, is a very important optical component for liquid crystal display. In general, polarizing films use iodine or dichroic dyes as polarizing materials. Iodine is the most widely used dichroic material, but dichroic dyes are used when high resistance to heat and/or moisture is required [1–3].

Dye/polarizing film is obtained through stretching of PVA polymer film doped with dye molecules in boric acid solution. Drawing of PVA film makes the dye molecules oriented along the host polymeric chains and the major absorption axis of the dye lies towards the stretching direction of the PVA polymer film, resulting in the anisotropic absorption of light in the visible wavelength range [4–6].

Until recently, mostly optical properties of dye/polarizing films such as dichroic ratio and order parameter have been focused, but orientational behavior of dyes, which is a crucial factor determining the optical anisotropy of the polarizing films, has not been investigated [7–10]. Furthermore, a systematic research on the relation between the optical anisotropy of the dye/polarizing films and the structural characteristics of the dichroic dyes has not been carried out.

In this study, six dichroic dyes were synthesized and dye/polarizing films were manufactured using those dyes. Transition dipole moments of the dichroic dyes were obtained by molecular orbital (MO) calculation to investigate the orientational behavior of the dyes in stretched PVA films. In addition, the effect of the structural characteristics of the dyes, such as aspect ratios and hydrogen bonding sites, on the alignment of the dye molecules towards stretched PVA polymer films was scrutinized based on the calculated transition dipole moments of the dyes.

2. Experimental

2.1. Materials and instrumentation

6-Amino-4-hydroxy-2-naphthalenesulfonic acid (γ acid), 7-amino-4-hydroxy-2-naphthalenesulfonic acid (J acid), 4-amino-5-hydroxy-2,7-naphthalenedisulfonic acid (H acid), *p*-nitroaniline, acetic anhydride, sodium sulfide and boric acid from Sigma–Aldrich, and 4,4′-diaminostilbene dihydrochloride and 8-amino-4-hydroxy-2-naphthalenesulfonic acid (M acid) purchased from TCI were used. Among these, three kinds of acids (J, γ and M acids) were used after further purification. All other chemicals used in this study were of synthesis grade. Poly(vinyl alcohol) film was supplied by Kuraray Co. Ltd., with a degree of polymerization of 1700, a degree of saponification of 99.9% and a thickness of about 75 μm.

^{1}H NMR spectra were recorded by Bruker Avance 500 at 500 MHz using DMSO-d_6 as the solvent and TMS as the internal

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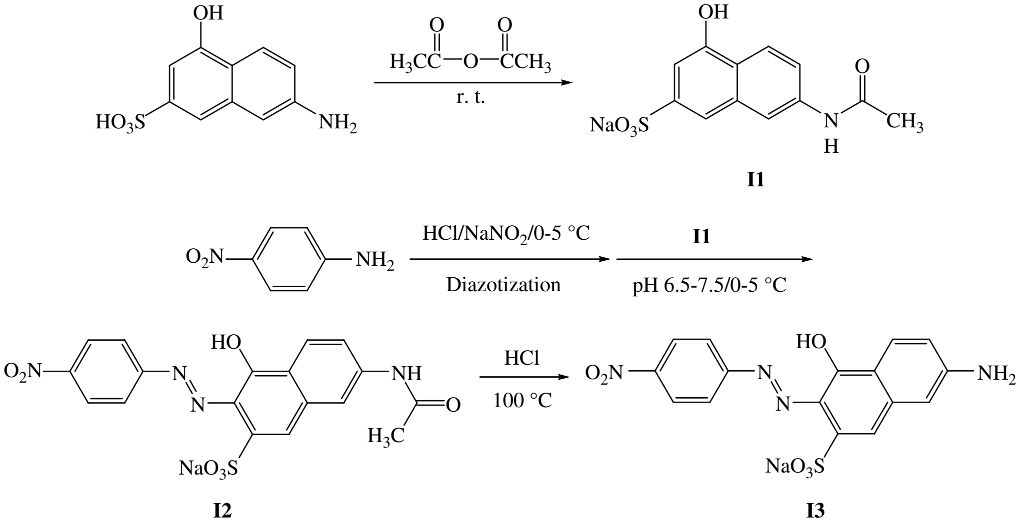


Scheme 1. Synthesis of dye intermediates (**I1**–**I3**).

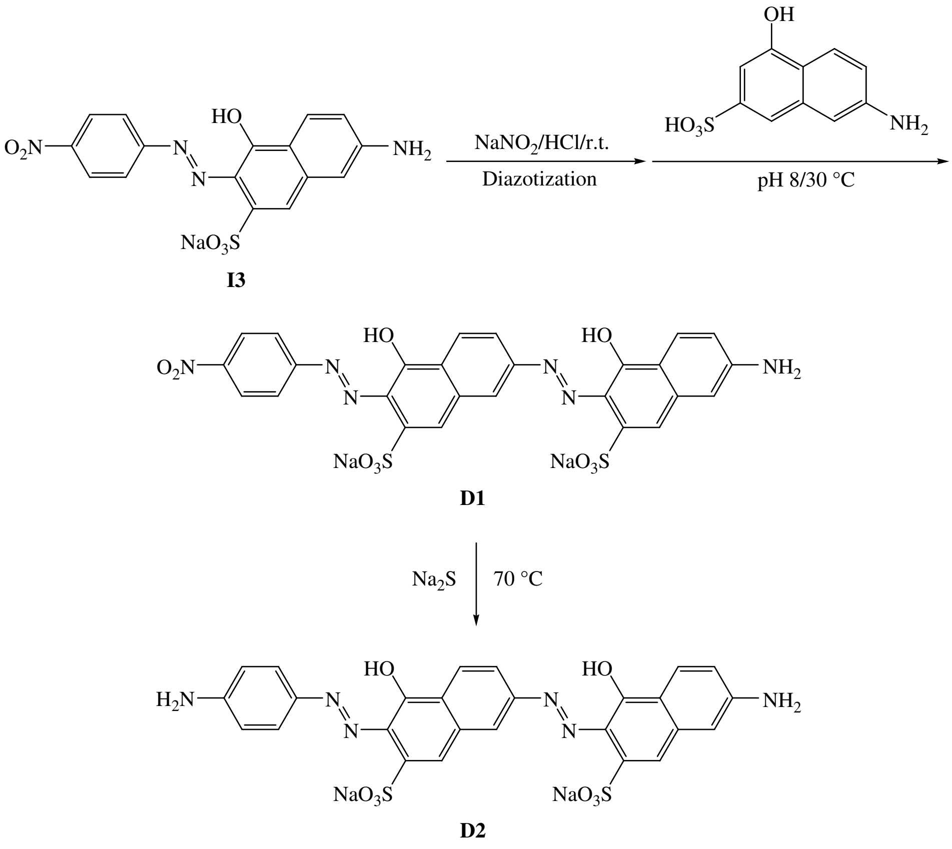
standard. FT-IR spectra were recorded with MIDAC PRS infrared spectrometer using KBr discs. Melting points were measured using BÜCHI Melting Point B-540 and are uncorrected. Absorption spectra were measured on a HP 8452A spectrophotometer which was equipped with a Glan-Thompson polarizer.

2.1.1. *Purification of acids (J, γ and M acids)*

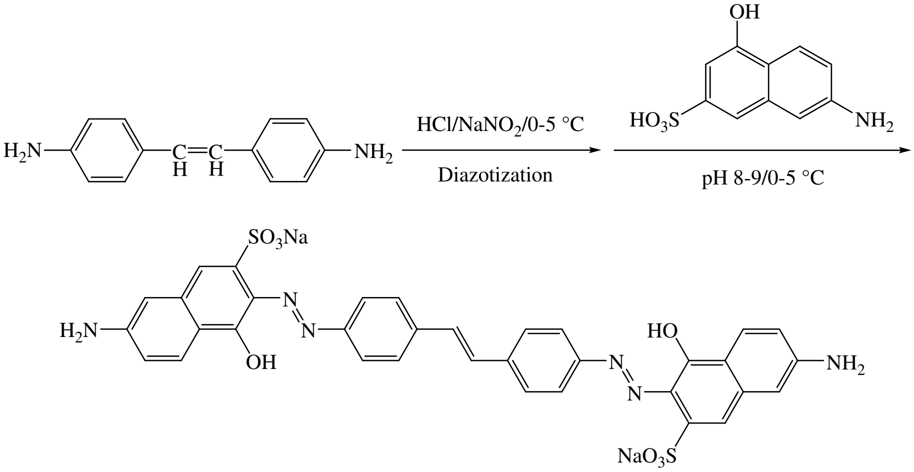
Sufficient sodium carbonate (*ca.* 4.5 g) to make the solution slightly alkaline was added to a solution of 20 g of the dry acid (J, γ and M acids) in 150 ml of hot water, followed by addition of 1 g of activated charcoal. The suspension was stirred for 1 h and vacuum-filtered using a filter aid, Celite®. The acid was precipitated by adding *ca.* 8 ml of concentrated HCl, then filtered and washed with water. The purification process was repeated three times. The acid was dried in a vacuum oven overnight.

2.2. *Synthesis of dye intermediates*

Dye intermediates (**I1**–**I3**) were synthesized as depicted in Scheme 1.



Scheme 2. Synthesis of dichroic dyes (**D1** and **D2**).



D3

Scheme 3. Synthesis of dichroic dye (**D3**).

2.2.1. Synthesis of dye intermediate (*I1*)

7-Amino-4-hydroxy-2-naphthalenesulfonic acid (J acid) (14.4 g, 0.06 mol) was dissolved in 250 ml of water as the pH was adjusted to 7.0 by addition of 10% sodium carbonate solution. Sodium acetate crystal (9.0 g) and 7.35 g (0.07 mol) of acetic anhydride were added into the solution and this mixture was stirred for 3 h at room temperature. After 105 g of sodium chloride was added to the solution, the precipitate formed was filtered, washed with chloroform and dried in a vacuum oven: yield = 97.8%; mp > 300 °C (decomp.); ^{1}H NMR (DMSO-d_6, ppm): 2.09 (s, 3H, CH_3), 7.03 (s, 1H, ArH), 7.43 (s, 1H, ArH), 7.60 (d, $J = 9.0$ Hz, 1H, ArH), 7.99 (d, $J = 9.0$ Hz, 1H, ArH), 8.08 (s, 1H, ArH), 10.1 (s, 1H, NH), 10.1 (s, 1H, OH); FT-IR (KBr, cm^{-1}): 1049, 1200 (SO_3), 1672 (C=O), 3475 (O–H).

2.2.2. Synthesis of dye intermediate (*I2*)

A mixture of 6.90 g (0.05 mol) of 4-nitroaniline, 25 ml of water and 25 ml of 37% hydrochloric acid was heated until solution was clear. Ice (70 g) was added to the solution and then 3.45 g (0.05 mol) of sodium nitrite in a small portion of water was added dropwise. The solution was stirred for 2 h. The diazonium salt solution was added to a solution containing 15.2 g (0.05 mol) of the coupling component (**I1**) in 300 ml of water at 0–5 °C and pH of the solution was maintained between 6.5 and 7.5. After 2 h, the precipitated solid was filtered, washed with water and dried in a vacuum oven. The crude product was refluxed in ethanol for 2 h, hot filtered, washed with hot ethanol and subsequently dried in a vacuum oven: yield = 80.7%; mp > 300 °C (decomp.); ^{1}H NMR (DMSO-d_6, ppm): 2.13 (s, 3H, CH_3), 7.45 (s, 1H, ArH), 7.74 (d, $J = 8.3$ Hz, 1H, ArH), 7.88 (s, 1H, ArH), 7.93 (d, $J = 8.5$ Hz, 2H, ArH), 8.16 (d, $J = 8.5$ Hz, 1H, ArH), 8.29 (d, $J = 8.5$ Hz, 2H, ArH), 10.5 (s, 1H, NH), 15.5 (s, 1H, OH); FT-IR (KBr, cm^{-1}): 1057, 1221 (SO_3), 1335, 1498 (NO_2), 1595 (ArC=O), 1676 (CH_3C=O).

2.2.3. Synthesis of dye intermediate (*I3*)

A mixture of 4.52 g (0.01 mol) of **I2** and 200 ml of water was stirred at 100 °C for 12 h; 84 ml of 37% HCl was added to the solution and this mixture was stirred for three days. After cooling down to 0–5 °C, the solution was neutralized with sodium hydroxide. The solid product was separated by filtration, washed with water and dried in a vacuum oven: yield = 93.9%; mp > 300 °C (decomp.); ^{1}H NMR (DMSO-d_6, ppm): 6.61 (s, 2H, NH_2), 6.65 (s, 1H, ArH), 6.68 (d, $J = 8.6$ Hz, 1H, ArH), 7.30 (s, 1H, ArH), 7.81 (d, $J = 9.1$ Hz, 2H, ArH), 7.91 (d, $J = 8.6$ Hz, 1H, ArH), 8.26 (d, $J = 9.2$ Hz, 2H, ArH), 15.6 (s, 1H, OH); FT-IR (KBr, cm^{-1}): 1057, 1223 (SO_3), 1333, 1493 (NO_2), 1597 (C=O).

2.3. Synthesis of dichroic dyes

2.3.1. Synthesis of dichroic dye (*D1*)

A mixture of 12.3 g (0.03 mol) of the diazo component (**I3**), 300 ml of water and 2.1 g (0.03 mol) of sodium nitrite in a small portion of water was stirred overnight; 18 ml of 37% hydrochloric acid was added dropwise to the diazo component solution at room temperature and stirred for 3 h. A small portion of sulfamic acid was employed as a nitrous acid scavenger. The diazonium salt solution was added to a solution having 7.18 g (0.03 mol) of coupling component (J acid) in 800 ml of water at 30 °C and pH of the solution was maintained at 8. The solution was stirred for 2 h and the precipitated solid was filtered, washed with water and dried in a vacuum oven. The crude product was refluxed in ethanol for 2 h, hot filtered, washed with hot ethanol and subsequently dried in a vacuum oven (Scheme 2): yield 75.6%; mp > 300 °C (decomp.); ^{1}H NMR (DMSO-d_6, ppm): 6.53 (s, 2H, NH_2), 6.66 (s, 1H, ArH), 6.68 (d, $J = 8.6$ Hz, 1H, ArH), 7.29 (s, 1H, ArH), 7.53 (s, 1H, ArH), 7.84 (s, 1H, ArH), 7.87 (d, $J = 8.7$ Hz, 1H, ArH), 7.94 (d, $J = 8.6$ Hz, 1H, ArH), 7.95 (d, $J = 9.1$ Hz, 2H, ArH), 8.22 (d, $J = 8.6$ Hz, 1H, ArH), 8.30 (d, $J = 9.2$ Hz, 2H, ArH), 15.5 (s, 1H, OH), 15.7 (s, 1H, OH); FT-IR (KBr, cm^{-1}): 1052, 1219 (SO_3), 1330, 1489 (NO_2), 1606 (C=O).

2.3.2. Synthesis of dichroic dye (*D2*)

Dichroic dye **D1** (1.7 g, 2.49 mmol) in 150 ml of water was stirred overnight and then the temperature of the solution was raised to 70 °C. Sodium sulfide (1.8 g, 7.50 mmol) in a small portion of water was added to the prepared solution and reacted for 3 h. The precipitate formed by salting-out was separated by filtration, washed with water and dried in a vacuum oven (Scheme 2): yield 90.3%; mp > 300 °C (decomp.); ^{1}H NMR (DMSO-d_6, ppm): 5.88 (s, 2H, NH_2), 6.46 (s, 2H, NH_2), 6.66 (s, 1H, ArH), 6.69 (d, $J = 8.4$ Hz, 2H, ArH), 6.70 (d, $J = 8.3$ Hz, 1H, ArH), 7.28 (s, 1H, ArH), 7.65 (d, $J = 8.5$ Hz, 2H, ArH), 7.70 (s, 1H, ArH), 7.91 (s, 1H, ArH), 7.94 (d, $J = 9.6$ Hz, 1H, ArH), 7.95 (d, $J = 8.6$ Hz, 1H, ArH), 8.27 (d, $J = 8.8$ Hz, 1H, ArH), 16.0 (s, 1H, OH), 16.7 (s, 1H, OH); FT-IR (KBr, cm^{-1}): 1052, 1187 (–SO_3), 1607 (C=O).

2.3.3. Synthesis of dichroic dyes (*D3–D6*)

A mixture of 1 g (3.53 mmol) of 4,4′-diaminostilbene dihydrochloride, 20 ml of water and 1.47 ml of 37% hydrochloric acid was heated until solution was clear. After cooling down to 0–5 °C, 0.5 g (7.06 mmol) of sodium nitrite in a small portion of water was added dropwise to the solution and the diazotization was continued for 2 h. 7-Amino-4-hydroxy-2-naphthalenesulfonic acid (J acid) (2 g,

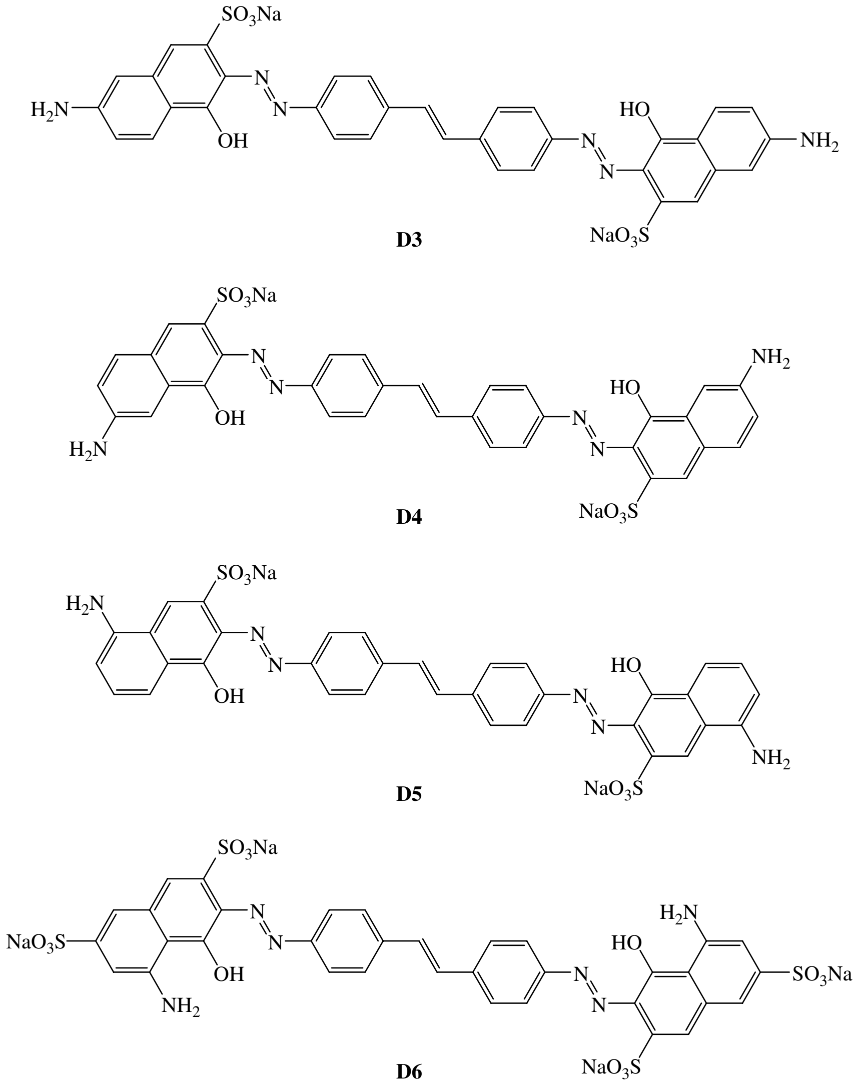


Fig. 1. Structures of dichroic dyes (**D3–D6**).

7.77 mmol) was dissolved in 200 ml of water at pH 7. The prepared diazonium salt liquor was added into the coupling solution at 0–5 °C and pH of the solution was maintained between 8 and 9. The solution was stirred for 2 h and sodium chloride solution (3 wt%) was added to the solution. The precipitate formed was filtered, washed with water and dried in a vacuum oven. The crude product was refluxed in ethanol for 2 h, hot filtered, washed with hot ethanol and subsequently dried in a vacuum oven (**D3**) (Scheme 3). Dichroic dyes **D4**–**D6** were prepared in a manner similar to **D3**. The structures of dichroic dyes **D3**–**D6** are given in Fig. 1. The yields, melting points, ^{1}H NMR and FT-IR data of the dyes are given below.

Dye (**D3**): yield 83.7%; mp > 300 °C (decomp.); ^{1}H NMR (DMSO-d_6, ppm): 6.36 (s, 4H, NH_2), 6.66 (s, 2H, ArH), 6.71 (d, $J = 8.7$ Hz, 2H, ArH), 7.24 (s, 2H, –CH=CH–), 7.28 (s, 2H, ArH), 7.66 (s, 8H, ArH), 7.95 (d, $J = 8.8$ Hz, 2H, ArH), 16.2 (s, 2H, OH); FT-IR (KBr, cm^{-1}): 1051, 1182 (SO_3), 1609 (C=O), 3417 (N–H).

Dye (**D4**): yield 87.3%; mp > 300 °C (decomp.); ^{1}H NMR (DMSO-d_6, ppm): 5.69 (s, 4H, NH_2), 6.98 (d, $J = 8.3$ Hz, 2H, ArH), 7.33 (s, 2H, –CH=CH–), 7.40 (s, 4H, ArH), 7.42 (d, $J = 8.4$ Hz, 2H, ArH), 7.71 (d, $J = 8.7$ Hz, 4H, ArH), 7.77 (d, $J = 8.6$ Hz, 4H, ArH), 16.1 (s, 2H, OH); FT-IR (KBr, cm^{-1}): 1050, 1212 (SO_3), 1623 (C=O), 3422 (N–H).

Dye (**D5**): yield 85.1%; mp > 300 °C (decomp.); ^{1}H NMR (DMSO-d_6, ppm): 5.73 (s, 4H, NH_2), 6.96 (d, $J = 7.8$ Hz, 2H, ArH), 7.21 (t, $J = 15.5$ Hz, 2H, ArH), 7.36 (s, 2H, –CH=CH–), 7.54 (d, $J = 7.6$ Hz, 2H, ArH), 7.74 (d, $J = 8.5$ Hz, 4H, ArH), 7.76 (s, 2H, ArH), 7.81 (d, $J = 8.4$ Hz, 4H, ArH), 16.3 (s, 2H, OH); FT-IR (KBr, cm^{-1}): 1050, 1194 (SO_3), 1616 (C=O), 3440 (N–H).

Dye (**D6**): yield 78.5%; mp > 300 °C (decomp.); ^{1}H NMR (DMSO-d_6, ppm): 6.90 (s, 2H, ArH), 7.05 (s, 2H, ArH), 7.27 (s, 2H, –CH=CH–), 7.31 (s, 2H, ArH), 7.66 (d, $J = 8.9$ Hz, 4H, ArH), 7.69 (d, $J = 8.8$ Hz, 4H, ArH), 15.6 (s, 2H, –OH); FT-IR (KBr, cm^{-1}): 1043, 1214 (SO_3), 1616 (C=O), 3420 (N–H).

2.4. Preparation of polarizing films

Dyebaths were prepared with **D1**–**D6** (4% on the weight of film) and 0.1 wt% Na_2SO_4. PVA films were immersed in the dyeing solutions at 50 °C for 10 min. The dyed PVA films were drawn in 3 wt% boric acid solution at 50 °C. The draw ratio was 6:1. The

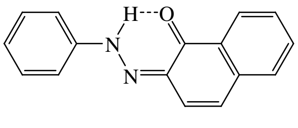


Fig. 2. Intramolecular hydrogen bond of 2-azo-1-naphthol derivative.

Table 1
Spectral data of dichroic dyes

Dye	λ_{max} (nm)	ε_{max} (L mol^{-1} cm^{-1})
D1	548^a	83,000
D2	560^a	55,000
D3	542^a	88,000
D4	576^a	40,000
D5	592^a	54,000
D6	594^b	74,000

[a] Measured in DMF.
[b] Measured in H_2O.

stretched films were washed with water and dried at room temperature under a uniform tension for one day.

2.5. Optical anisotropy of polarizing films

Optical anisotropy of polarizing films was examined by UV–vis spectrophotometer equipped with a Glan-Thompson polarizer. Dichroic ratio (R), order parameter (S), single-piece transmittance (T_{sp}) and degree of polarization (DP) were investigated at the absorption maximum of the polarizing films according to Eqs. (1)–(4). Dichroic ratio and order parameters are dependent solely on the optical characteristics and orientation of the dyes. Single-piece transmittance and degree of polarization are important parameters to evaluate commercial values [11].

$$R = A_{\parallel}/A_{\perp} \tag{1}$$

$$S = (R-1)/(R+2) \tag{2}$$

$$T_{sp} = 1/2\left(T_{\parallel} + T_{\perp}\right) \times 100 \tag{3}$$

$$\mathrm{DP} = \left(T_{\perp} - T_{\parallel}\right)\Big/\left(T_{\perp} + T_{\parallel}\right) \times 100 \tag{4}$$

where $A_{\parallel}$ and $A_{\perp}$ are the absorbance of the dyed polymer for polarized light vibrating parallel and perpendicular to the direction of drawing, respectively. Transmission parallel ($T_{\parallel}$) and perpendicular ($T_{\perp}$) to the stretching direction are calculated from the absorbance ($T = 10^{-A}$).

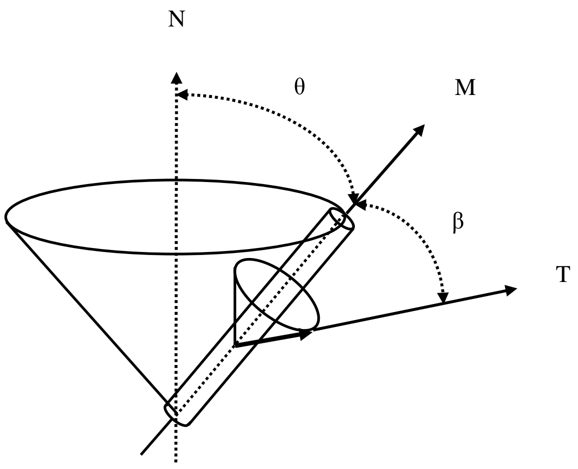


Fig. 3. Geometrical relationship of the drawing direction of a PVA film (**N**), dye molecular axis (**M**) and transition moment (**T**).

2.6. Molecular orbital (MO) calculation

CAChe 6.1.8 software package [12] was used in order to optimize the geometry of dye structures by using molecular mechanics MM3, conducting the iterative energy-minimizing routines with the conjugate gradient minimizer algorithm [13]. CONFLEX [14] conformational search procedure was used for finding low-energy conformations of the dye molecules. The semi-empirical method, PM5, was also examined with respect to geometry optimization, but was found to be no more satisfactory than the molecular mechanical method. On optimization of conformers, the dye molecules were assumed to have azo linkages and central cyanine bridge being the *trans* forms.

Aspect ratios (l/d) of dye molecules were calculated from the geometry of the most stable conformer optimized by CONFLEX/MM3 calculation in consideration of 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. Directions of the transition dipole moments of the dichroic dyes were examined by INDO/1 in the ZINDO package [15] using the dye structures optimized by the above-mentioned calculation. Configuration interaction (CI) calculation up to 676 configuration functions was performed by adapting the occupied orbitals of (HOMO − 25 to HOMO) and the vacant orbitals of (LUMO to LUMO + 25). Each configuration function was generated through the single excitation (S-CI) from the ground-state function [16,17].

3. Results and discussion

3.1. Synthesis and characterization of dichroic dyes

To make dichroic dyes linear and coplanar, the diazo components of the dyes were coupled to the *ortho* position of hydroxyl group in the coupling components. 2-Azo-1-naphthol derivatives exist predominantly in the hydrazone form via intramolecular hydrogen bonds, which result in the linearity and coplanar conformation of the dyes (Fig. 2) [18]. The proton peaks involved in intramolecular hydrogen bonding appeared at much lower field than the normal proton peak of hydroxyl group [19] and these (15.5–16.7 ppm for **D1**–**D6**) were confirmed by ^{1}H NMR. In case of **D2**, the additional proton peak of the amino group generated by the reduction of the nitro group in **D1** was identified in ^{1}H NMR spectrum. Two bands of the nitro group stretching vibrations (asymmetric and symmetric) of **D1** disappeared in the spectrum of **D2**. In case of **D3**–**D6**, the peaks due to the central bridge, cyanine, appeared at 7.24–7.49 ppm. Peaks observed at 1606–1623 cm^{-1} resulted from C═O stretching vibration of the dyes existing mainly in the hydrazone form.

3.2. Spectral properties of dichroic dyes

Table 1 shows the spectral properties of synthesized dyes. Absorption maxima of the dyes were observed in the range of 542–594 nm, which was purple to blue shade. All the dyes had a tendency of high tinctorial strength due to their hydrazone structures. Intramolecular hydrogen bond in the hydrazone form makes a dye molecule more rigid and planar, resulting in higher extinction coefficient than a non-bonded analogue [20]. On the one hand, degree of polarization, a parameter related to commercial applications, is increased with an increase of dye concentration in a polarizing film. However, the amount of dye molecules which can be adsorbed onto the host film was limited as shown in our previous study [21]. From this point of view, dyes with higher extinction coefficients have advantage over dyes with lower extinction coefficients, and consequently, prepared dichroic dyes having high extinction coefficients are expected to have a favorable influence on the degree of polarization of the polarizing films.

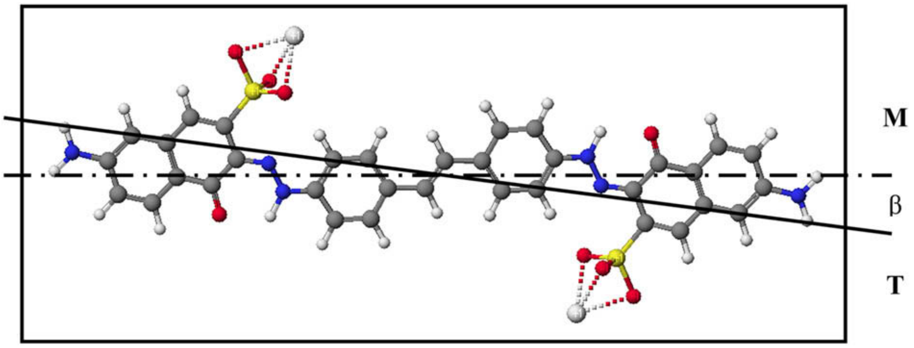


Fig. 4. Angle (β) between the molecular axis (**M**) and transition moment (**T**) of a dye molecule.

3.3. Transition moments and orientational behavior of dichroic dyes

Dichroic dye molecules in a stretched PVA film align towards the drawing direction of the film. However, the direction of each dye molecule deviates from the drawing direction of the film **N** as shown in Fig. 3, where **M** is the direction of dye molecular axis and **T** is that of the transition moment of a dye molecule [22]. If θ denotes the angle between **N** and **M**, the order parameter S_M of **M** can be defined as the average of Legendre polynomial and is given by Eq. (5) [23].

$$S_M = 1/2\left(3\left\langle\cos^2\theta\right\rangle - 1\right) \tag{5}$$

where $\langle\cos^2\theta\rangle$ is the average of $\cos^2\theta$ for all the dye molecules. As the deviation of the dye molecules from the drawing direction decreases ($\theta \to 0^\circ$), the order parameter S_M approaches unity ($S_M \to 1$).

In the same manner, the transition dipole moment of the dye (**T**) is not parallel to the dye molecular orientation axis (**M**), but deviates from it by the angle β. The transition moment order parameter S_T and molecular order parameter S_M are related by Eq. (6) [24].

$$S_T = 1/2\left[S_M\left(2 - 3\sin^2\beta\right)\right] \tag{6}$$

On the other hand, aforementioned order parameter S of a dye can be misunderstood as that of a molecular axis S_M, but S will substantially be that of transition dipole moment S_T. Namely, dichroic ratio is more related to the transition moment order parameter S_T than the molecular order parameter S_M. Therefore, the angle between **M** and **T**, β is required in order to obtain the molecular order parameter S_M, which will elucidate the orientational behavior of the dye molecules.

A molecular axis **M** of a dye is defined as the longest axis through the molecule that encompassed the dye π chromophore as shown in Fig. 4 [25,26]. The β values in the most stable conformation of the dichroic dyes were calculated using CAChe with the CONFLEX/MM3 method followed by ZINDO method [27].

Transition dipole moments of the dichroic dyes (**D1**–**D6**) deviated little from their molecular axes as shown in Table 2. This is understandable in terms of vector-addition diagrams of the component transition dipole moments at HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) levels. As shown in Fig. 5, the transition moment of **D4** at HOMO level was in accordance with the dye molecular orientation axis. And the vector sum of those at LUMO level was nearly parallel to the direction of dye molecular axis. Consequently, the transition moment of the dye, which is the vector sum of the component transition moments at HOMO and LUMO levels, was in good agreement with the dye molecular axis.

Table 2
Parameters relevant to the optical anisotropy of polarizing films

Dye	R	S (S_T)	S_M	T_{sp} (%)	DP (%)	β (°)	θ (°)	l (Å)	d (Å)	l/d
D1	12.2	0.79	0.79	30.8	99.2	1.79	21.9	26.3	12.1	2.17
D2	19.2	0.86	0.86	33.1	99.9	1.87	17.7	25.8	12.0	2.15
D3	25.2	0.89	0.89	37.1	99.8	2.30	15.6	32.6	14.6	2.23
D4	22.5	0.88	0.88	39.1	99.1	0.22	16.6	32.0	14.9	2.15
D5	19.7	0.86	0.86	35.3	99.7	3.21	17.5	30.5	14.7	2.04
D6	25.4	0.89	0.89	39.6	99.4	1.55	15.6	38.4	14.8	2.59

Table 2 shows a variety of parameters relevant to the optical anisotropy of the polarizing films. Molecular order parameters S_M were almost equal to the transition moment order parameters S_T of the dyes due to their small deviation angles β. In the meantime, the dichroic ratios of the films increased as θ values of the dyes decreased, which means closer alignment of the dyes towards the drawing direction of the host films results in the improvement of their optical anisotropy. This result is caused by the fact that the β values of the dichroic dyes were relatively small in comparison with their θ values.

Comparing **D1** with **D2**, **D2** had a smaller θ value than **D1** in spite of the structural similarities (analogous aspect ratio). This result suggests that additional hydrogen bonding site, the amino group, which was generated by the reduction of the nitro group in **D1**, exerted a favorable influence on the alignment of the dye. In case of **D3**–**D5**, the location of the amino groups in the naphthalene ring affected the orientation of the dichroic dyes. Dichroic dye **D3** containing the amino groups as hydrogen bonding sites parallel to the molecular axis, showed better alignment than **D4** with a similar aspect ratio. Dichroic dye **D5** with the lowest aspect ratio and hydrogen bonding sites tilted from the molecular long axis had the highest θ value. This result means that the position of hydrogen bonding sites can have a significant effect on the orientation of dichroic dyes when poly(vinyl alcohol) films are stretched. Although the amino groups of **D6** are not located on the molecular axis, **D6** had similar θ value to **D3**, which is believed that its higher aspect ratio than **D3** and the extra intramolecular hydrogen bond between the carbonyl group and amino group in the naphthalene ring, which makes the dye more planar, and consequently, the interaction between the dye molecules and the host polymer chains stronger, resulted in better orientation. In comparison of **D3** with **D2**, **D3** showed better alignment than **D2** despite the fact that they had almost the same aspect ratios and hydrogen bonding sites parallel to the molecular axes. This would be due to the longer dye molecular axis of **D3** than that of **D2**, which implies that the dye with a longer dye molecular axis can adhere to the polymer chains much more closely than that with a shorter molecular axis during the stretching of the host film.

Based on the orientational behavior of the dyes, the dye molecular orientation axes deviated from the drawing direction of

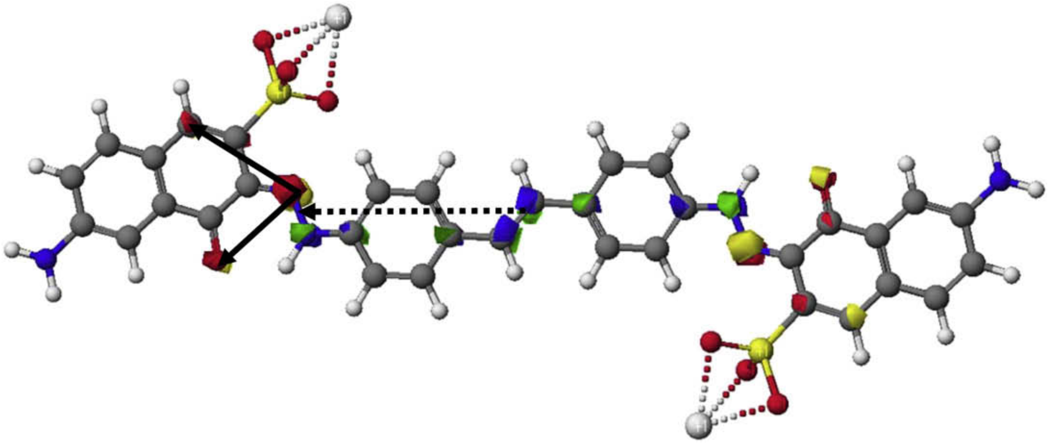


Fig. 5. Vector sum of the component transition moments at HOMO and LUMO levels of **D4** (dotted arrow: transition moment at HOMO level; solid arrow: component transition moments at LUMO level).

the films by above 15°. These deviation angles of the dye molecules deteriorated the optical anisotropy of the polarizing films even if the transition dipole moments of the dyes deviated little from their molecular axes. Therefore, the aforementioned deviation angle between the dye molecular orientation axis and drawing direction of the film will have to be reduced in order to obtain the dye/polarizing films with better optical anisotropy. At this time, it cannot be concluded that which is a more crucial factor affecting the deviation of the dye molecular axes, the orientation of the host polymer chains towards the drawing direction of the polarizing films or the alignment of the dye molecules towards the host polymer chains. In order to clarify this question, the orientational behavior of the host polymer chains will be studied next.

4. Conclusions

Six dichroic dyes with a variety of structural characteristics were synthesized and PVA polarizing films were prepared with them for the interpretation of the relation between the structural characteristics of the dyes and their orientational behavior. Relation between the orientational behavior of the dyes and the optical anisotropy of the polarizing films was investigated as well. Based on the MO calculation, the transition moments of the dyes were almost coincident with the long axes of the dye molecules. Due to this minor change of β values to θ values, the dichroic ratios of the films increased as the dyes aligned better towards their drawing direction. In terms of the orientational behavior of the dyes, the number and position of hydrogen bonding sites exerted a meaningful influence on the orientation of the dichroic dyes when PVA films were stretched. Orientational behavior of the dyes was in more connection with the length of the dye molecular axes than their aspect ratios.

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