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The effect of dye structure on the dyeing and optical properties of dichroic dyes for PVA polarizing film

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ABSTRACT

The dyeing behaviour and optical properties of four novel dyes in PVA polarizing films were determined in terms of the linearity, hydrogen bonding ability, intermolecular interaction and transition moment. The linearity and H-bonding ability of the dyes were the dominant factors in terms of both the substantivity and orientation in PVA films, which, in turn, determined the dichroic ratios of the polarizing films. Dye adsorption and optical anisotropy of the dyes were further affected by the substituents within the dyes. The difference in the electrostatic interactions of the substituent within the dyes also had an influence on dye-uptake. Moreover, charge transfer within the dye molecules was reflected in higher dichroic ratios of the dyed polarizing film.

1. Introduction

A polarizing film is an optical component used to polarize back light in LCDs (Liquid crystal displays). Currently, PVA/Iodine polarizing films are used most widely owing to their high optical properties. However, iodine-based polarizing films have low thermal and humid stability due to the sublimation of iodine [1–3]. For applications where high stability is required, dye based polarizing films, which are produced by dyeing dichroic dyes on PVA films, are used as an alternative to iodine-based polarizing films with limited durability.

Dichroic dyes for polarizing films should have linear and planar structures for high dichroism as well as hydrogen bonding groups with an affinity to Poly(vinyl alcohol). For this purpose, direct dyes used for cellulosic fiber dyeing are the usual choices. However, the dichroic properties of the polarizing films produced with these dyes are lower than those produced with iodine. Therefore, an improvement in the dichroic properties has been of utmost concern for studies of dye based polarizing films. Most studies of the dichroic properties of polarizing films focused on the effects of the dyeing conditions, draw ratio of the PVA film, and the orientation of polymer chains and dye molecules rather than the structure of the dichroic dyes [4–9]. Therefore, a better understanding of the effect of the dye structure on the dichroic properties is needed to produce a more efficient dye based polarizing film.

In this study, four disazo dichroic dyes were designed and synthesized. All dyes were designed to have planar and linear structures. Carboxylic acid groups and the pyridine moiety were introduced to increase the dichroic and dyeing properties. Subsequently, polarizing films were produced by dyeing PVA films under a range of dyeing conditions, and their polarizing properties were measured and analyzed. The effect of the dye molecular structure on the optical and dyeing properties of the polarizing film was observed.

2. Experimental

2.1. Materials and instrumentation

7-amino-4-hydroxy-2-naphthalenesulfonic acid (J-acid) and 5-aminopyridine-3-carboxylic acid were purchased from TCI and 3-aminobenzoic acid, 4-aminobenzoic acid, and 5-amino-2-pyridinecarbonitrile were obtained from Sigma–Aldrich. All the above chemicals were used as received. All other chemicals used in this study were of synthesis grade. Poly(vinyl alcohol) film was supplied by Kuraray Co. Ltd., with the degree of polymerization of 2400, the degree of saponification of 99.9% and its thickness was 75 μm.

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The ^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. The FT-IR spectra were recorded on a Thermo Scientific Nicolet 6700 using ATR method. Densities of the dyes were measured using a Micromeritics AccuPyc II 1340. The absorption spectra were measured on a HP 8452A spectrophotometer which was equipped with a Glan-Thompson polarizer.

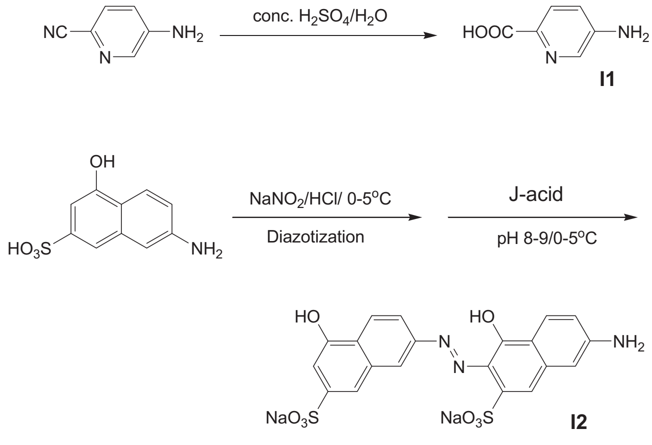
2.2. Synthesis of dye intermediates

2.2.1. Synthesis of dye intermediate (*I1*)

Dye intermediates were synthesized as shown in Scheme 1. 5-amino-2-cyanopyridine (2.0 g, 0.0167 mol) was slowly added to sulfuric acid (20 mL) with reaction stirring and the mixture was heated at 90 °C for 2 h in a sealed tube. The solution was diluted with water (40 mL) and heated at 100 °C for another 2 h. The reaction mixture was cooled to room temperature and poured into ice-water (200 mL). The solid separated was filtered, washed with cold water and dried in a vacuum oven: yield = 95.0%; ^1H NMR (DMSO-d_6, ppm): 5.85 (s, 2H, NH_2), 7.69 (d, $J = 8.5$ Hz, 1H, ArH), 7.69 (d, $J = 8.6$ Hz, 1H, ArH), 8,95 (s, 1H, ArH); FT-IR (ATR. cm^{-1}): 3039 (O–H, carboxylic acid), 3347 (N–H).

2.2.2. Synthesis of dye intermediate (*I2*, J-J acid)

7-amino-4-hydroxy-2-naphthalenesulfonic acid (5.30 g, 0.02 mol) was dissolved in 100 mL of water at room temperature and pH of the solution was adjusted to 7.0 by adding 10% sodium carbonate solution. The solution was cooled to 0–5 °C and 5 mL of 4 M aq sodium nitrite solution was added dropwise. The ensuing solution was dropped into 50 mL of 2 M hydrochloric acid and stirred for 1 h, after which time, 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 7-amino-4-hydroxy-2-naphthalenesulfonic acid (5.30 g, 0.02 mol) dissolved in 150 mL of water, while the temperature and pH of the mixture were maintained at 0–5 °C and 8–9, respectively, in the course of the addition. The reaction mixture was stirred for 2 h and the precipitate was filtered, washed with brine and dried in a vacuum oven. The crude product was heated in ethanol for 2 h under reflux, hot filtered, washed with hot ethanol and then dried in a vacuum oven: yield = 93.2%; ^1H NMR (DMSO-d_6, ppm): 6.37 (s, 2H, NH_2), 6.66 (s,1H, ArH), 6.70 (d, $J = 8.6$ Hz, 1H, ArH), 7.09 (s. 1H, ArH), 7.27 (s. 1H, ArH), 7.57 (s. 1H, ArH), 7.91 (s. 1H, ArH), 7.96 (d, $J = 8.5$ Hz, 2H, ArH), 8.10 (d, $J = 9.1$ Hz, 1H, ArH), 10.2 (s, 1H, OH), 16.3 (s, 1H, OH); FT-IR (ATR. cm^{-1}): 1041, 1180 ($-SO_3$), 1608 (C=O), 3363 (N–H).



Scheme 1. Synthesis of the dye intermediates (**I1** and **I2**).

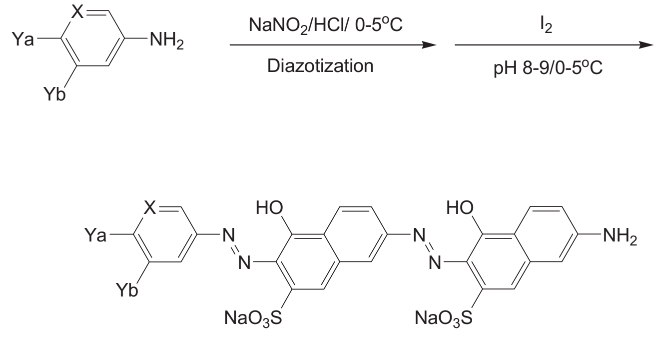
2.3. Synthesis of dichroic dyes (*Dye1*–*Dye4*)

Dyes 1–4 were synthesized as shown in Scheme 2. A mixture of 0.285 g (0.002 mol) of 5-amino-2-pyridine (**I1**), 18 mL of 2 M aq hydrochloric acid and 0.14 g (0.002 mol) of sodium nitrite in water (1 mL) was stirred for 1 h at 0–5 °C. To this solution, a small amount of sulfamic acid was added as a nitrous acid scavenger. The resulting diazonium salt solution was added to a coupling component solution of J-J acid (**I2**) (1.07 g, 0.002 mol) dissolved in 150 mL of water while the temperature and pH of the mixture were maintained at 0–5 °C and 8–9, respectively, in the course of the 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 crude product (**Dye2**) was refluxed in ethanol for 2 h, hot filtered, washed with hot ethanol and then dried in a vacuum oven. The other dichroic dyes (**Dye1**, **3**, **4**) were prepared in a similar manner. The yields, ^1H NMR and FT-IR data of the dyes are given below.

Dye 1: yield = 90.1%; ^1H NMR (DMSO-d_6, ppm): 6.55 (s, 2H, NH_2), 6.66 (s, 1H, ArH), 6.69 (d, $J = 8.7$ Hz, 1H, ArH), 7.29 (s. 1H, ArH), 7.51 (s. 1H, ArH), 7.80 (s. 1H, ArH), 7.82 (d, $J = 8.5$ Hz, 2H, ArH), 7.87 (s. 1H, ArH), 7.93 (d, $J = 8.6$ Hz, 1H, ArH), 7.98 (d, $J = 8.5$ Hz, 2H, ArH), 8.24 (d, $J = 8.6$ Hz, 2H, ArH), 15.7 (s, 1H, OH), 15.9 (s, 1H, OH); FT-IR (ATR. cm^{-1}): 1049, 1219 ($-SO_3$), 1605 (C=O), 2973 (O–H, carboxylic acids), 3347 (N–H).

Dye 2: yield = 88.2%; ^1H NMR (DMSO-d_6, ppm): 6.52 (s, 2H, NH_2), 6.65 (s, 1H, ArH), 6.68 (d, $J = 8.6$ Hz, 1H, ArH), 7.28 (s. 1H, ArH), 7.52 (s. 1H, ArH), 7.84 (s. 1H, ArH), 7.87 (d, $J = 9.0$ Hz, 1H, ArH), 7.93 (d, $J = 8.6$ Hz, 1H, ArH), 8.03 (d, $J = 8.4$ Hz, 1H, ArH), 8.13 (d, $J = 8.5$ Hz, 1H, ArH), 8.24 (d, $J = 8.7$ Hz, 1H, ArH), 8.89 (s. 1H, ArH), 15.7 (s, 1H, OH), 15.9 (s, 1H, OH); FT-IR (ATR. cm^{-1}): 1049, 1218 ($-SO_3$), 1605 (C=O), 2974 (O–H, carboxylic acids), 3340 (N–H).

Dye 3: yield = 88.3%; ^1H NMR (DMSO-d_6, ppm): 6.55 (s, 2H, NH_2), 6.66 (s, 1H, ArH), 6.69 (d, $J = 8.6$ Hz, 1H, ArH), 7.29 (s. 1H, ArH), 7.52 (s. 1H, ArH), 7.53 (t, $J = 7.8$ Hz, 1H, ArH), 7.77 (d, $J = 7.6$ Hz, 2H, ArH), 7.86 (s. 1H, ArH), 7.86 (d, $J = 7.8$ Hz, 1H, ArH), 7.93 (d, $J = 8.5$ Hz, 1H, ArH), 7.99 (d, $J = 8.5$ Hz, 1H, ArH), 8.17 (s. 1H, ArH), 8.25 (d, $J = 9.0$ Hz, 1H, ArH), 15.8 (s, 1H, OH), 16.2 (s, 1H, OH)–; FT-IR (ATR. cm^{-1}): 1049, 1219 ($-SO_3$), 1608 (C=O), 3066 (O–H, carboxylic acids), 3347 (N–H).



Dye1: X=C, Y_a=COOH, Y_b=H

Dye2: X=N, Y_a=COOH, Y_b=H

Dye3: X=C, Y_a=H, Y_b=COOH

Dye4: X=N, Y_a=H, Y_b=COOH

Scheme 2. Synthesis of the dichroic dyes (Dye 1–Dye 4).

Dye 4: yield = 87.6%; ^{1}H NMR (DMSO-d_6, ppm): 6.54 (s, 2H, NH_2), 6.66 (s, 1H, ArH), 6.69 (d, $J = 8.6$ Hz, 1H, ArH), 7.28 (s. 1H, ArH), 7.52 (s. 1H, ArH), 7.85 (s. 1H, ArH), 7.85 (d, $J = 8.2$ Hz, 1H, ArH), 7.93 (d, $J = 8.7$ Hz, 1H, ArH), 8.26 (d, $J = 8.6$ Hz, 1H, ArH), 8.40 (s, 1H, ArH), 8.82 (s, 1H, ArH), 8.99 (s. 1H, ArH), 15.8 (s, 1H, OH), 15.9 (s, 1H, OH); FT-IR (ATR. cm^{-1}): 1049, 1219 ($-SO_3$), 1608 (C=O), 2973 (O–H, carboxylic acids), 3340 (N–H).

2.4. Preparation of polarizing films

Dye baths were prepared with a dye (0.2 g), Na_2SO_4 (1.5 g) and distilled water (1L). PVA films (50 × 70 mm) were treated in the dyeing solution for a range of time (2–30 min) at 40 °C. The dyed PVA films were drawn 6 times in 2 wt% of boric acid solution at 50 °C. The stretched films were washed with water and dried in an oven for 10 min.

2.5. Investigation of optical properties of polarizing films

Optical properties of the polarizing films were measured with a UV–vis spectrophotometer equipped with a Glan-Thompson polarizer. Dichroic ratio(R), order parameter (S), single-piece transmittance (T_{sp}) and polarizing efficiency (PE) were evaluated at the absorption maximum of the polarizing films according to Eqs. (1)–(4) [10].

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

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

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

$$PE = \left\{\left(T_{\perp} - T_{\parallel}\right)\Big/\left(T_{\perp} + T_{\parallel}\right)\right\}^{1/2} \tag{4}$$

where $A_{\parallel}$ and $A_{\perp}$ are parallel and perpendicular absorbance to the drawing direction, respectively. $T_{\parallel}$ and $T_{\perp}$ were calculated from the absorbance ($T = 10^{-A}$).

3. Results and discussion

3.1. Synthesis and characterization of dichroic dyes

The dyes were designed and synthesized so that the diazo component bonds at the ortho-position of the hydroxyl group of the coupling component imparted linearity and planarity to the dyes (Fig. 1). For this purpose, the hydroxyl group of the coupling component was activated at pH 8–9. The hydroxyl group of the coupling component and azo linkage form a strong intramolecular hydrogen bond that imparts linearity and planarity to the dyes [11]. This was confirmed by the down fielded proton peaks of the hydroxyl group (15.7–16.3 ppm) in ^{1}H NMR [12].

Table 1 lists the optical and physical characteristics of the synthesized dyes. The dyes had maximum absorption wavelengths of 526–548 nm, and dyes with the pyridine moiety had lower molar extinction coefficients than those with the benzene moiety.

To examine the linearity of the dyes, which is a crucial factor for the dichroic properties, the aspect ratio (l/d) was calculated from the geometry of the optimized conformation of the dye by molecular modeling using CONFLEX/MM3 calculations (Fig. 2) [13]. The aspect ratio is subject to change according to the substituted position of the terminal carboxyl group. Dyes with a carboxyl group in the para position had higher aspect ratios than those with the carboxyl group in the meta position. When the carboxyl group was at the para position (Dyes 1 and 2), it was parallel to the longitudinal direction of the dye. A change in the dye structure caused by the introduction of a pyridine moiety had little effect on the aspect ratio.

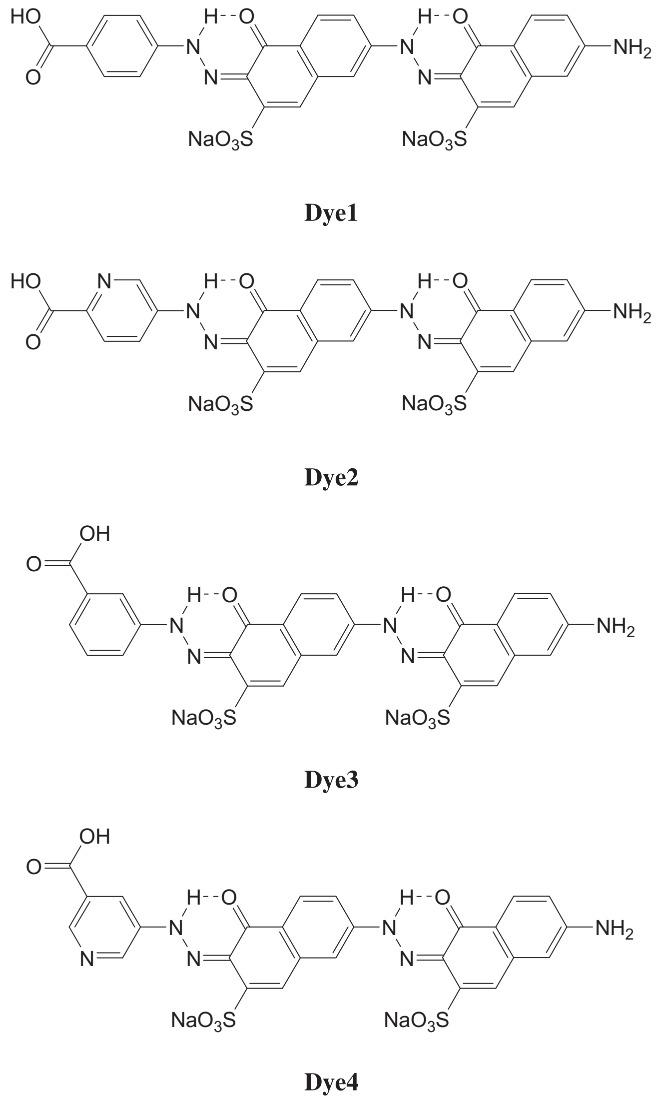


Fig. 1. Structures of the dichroic dyes (Dye1–Dye4).

To investigate the intermolecular interactions of dichroic dyes, their densities were measured. The strength of the intermolecular interaction of a molecule is generally recognized by its melting point. However, DSC analysis of the synthesized dyes showed only decomposition temperatures, and the melting peaks could not be confirmed. Between dyes with similar molecular weights and structures, a dye that is more closely packed by stronger intermolecular interactions will have a higher density. Therefore, the magnitude of the density is considered to be proportional to the strength of the intermolecular interaction. According to the density

Table 1
Material properties of the dichroic dyes.

Dye	λ_{max}^{a} (nm)	ε_{max}^{a} (L mol^{-1} cm^{-1})	Aspect ratio	Density (g cm^{-3})
1	526	35,000	2.70	1.868
2	534	30,000	2.70	1.952
3	548	47,000	2.45	1.686
4	528	22,000	2.45	1.855

[a] Measured in H_2O.

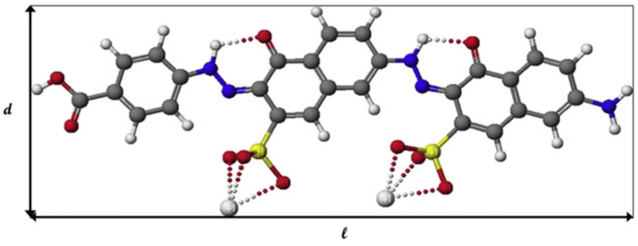


Fig. 2. Aspect ratio of the dichroic dye (Dye 1).

data, dyes with a carboxyl group in the para position had stronger intermolecular interactions than those with a carboxyl group in the meta position due to the increased linearity. Dyes with the pyridine moiety appear to show stronger intermolecular interactions than those with the benzene moiety because the electrostatic interactions and hydrogen bonding are increased by the nitrogen atom of the pyridine moiety [14,15].

3.2. Dyeing of PVA film with dichroic dyes

The rates of dyeing were investigated to compare dyeability of each dye. Fig. 3 shows the absorbance of the PVA films dyed at various dyeing times ranging from 2 to 30 min. The absorbance increased with increasing dyeing time and the increments slowly decreased. The absorbance is proportional to both the molar extinction coefficient and amount of dye adsorbed. Therefore, the adsorption of dyes was compared by dividing the absorbance of the dyed PVA films by the molar extinction coefficient of each dye. These values were again divided by the largest value (Dye 2 at a dyeing time of 30 min) to obtain the relative adsorption.

Fig. 4 shows the relative adsorption of the dyes at various dyeing times. Dyes 1 and 2, in which the carboxyl group was at the para position of the benzene or pyridine ring, showed greater adsorption than Dyes 3 and 4, in which the carboxyl group was at the meta position. This difference in the amounts of adsorbed dyes appears to be due to the linearity of the dyes. In addition, the adsorption of Dye 2 was higher than that of Dye 1. This may be due to the introduction of a pyridine moiety, which increased the substantivity of dyes to polymer chains. The nitrogen atom in the pyridine ring appears to act as a hydrogen bonding group to the PVA polymer.

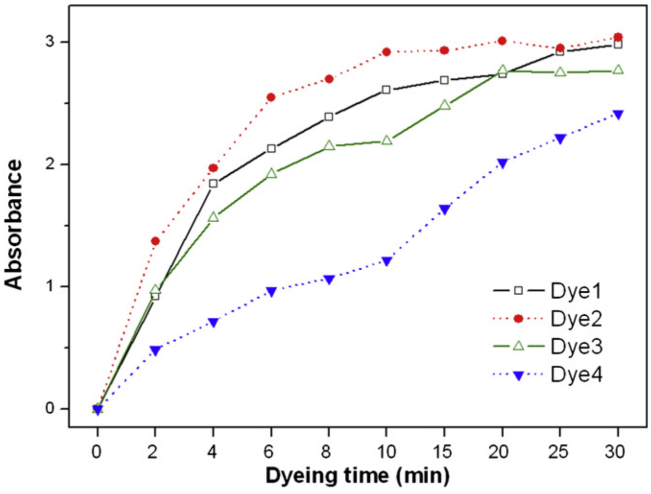


Fig. 3. Rate of dyeing of dichroic dyes on PVA films.

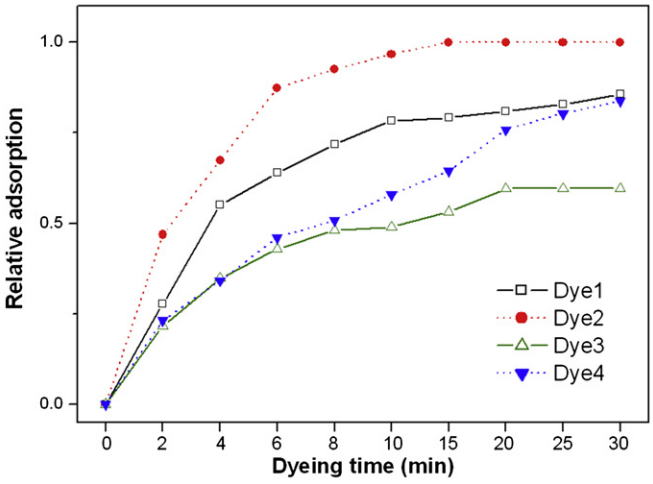


Fig. 4. Relative adsorption of dichroic dyes on PVA films.

Dyes 3 and 4 have a different number of hydrogen bonding groups similar to Dyes 1 and 2. However, their adsorption in the early stage of dyeing (before 10 min) had a smaller difference than that between Dye1 and Dye2. This is believed to be caused by the difference in the position of the hydrogen bonding group in the pyridine ring. In Dye 2, the nitrogen atom and carboxyl group are both on the same side of the dye molecule so that they can make hydrogen bonding with PVA together. However, the nitrogen atom and carboxyl group of Dye 4 were located on the opposite side of the pyridine ring, and they would not be able to participate in hydrogen bonding with polymer chains together. Therefore, while Dye 2 has enhanced affinity for the PVA chains compared to Dye1, Dye 4 would have a similar affinity to the PVA chains to Dye3.

The dye-uptake of Dye 4 was similar to that of Dye 3 in the early stages of dyeing, but the gap between them widened with increasing dyeing time despite the fact that Dyes 3 and 4 have the same linearity and similar hydrogen bonding ability. This means that the adsorption is affected by other factors rather than the affinity of the dyes for the PVA chains when the dyeing time is increased. In the early stages of dyeing, the dyes diffuse as single molecules into the polymer substrate and attach preferentially to the inner surface of the polymer substrate. However, as dyeing continues, the inner surfaces are occupied and the diffused dyes would aggregate inside the substrate [16]. This change in adsorption behavior is believed to be cause of the different dye-uptake of Dye 4 compared to Dye 3 after an 8 min dyeing time. As mentioned before, Dye 4 showed stronger intermolecular interactions between the dyes themselves than Dye 3 due to the stronger electrostatic interaction ability of the pyridine ring compared to the benzene ring. This means that, when dyes have similar structures, the dye with a stronger intermolecular interaction could have a larger dye-uptake. Indeed, the dye-uptake of each dye at a dyeing time of 30 min depended on the magnitude of the intermolecular interaction, which was estimated from the density of each dye (Fig. 4 and Table 1). These results suggest that the dominant factor of dye-uptake in the early stages of dyeing is the affinity between the dye molecules and PVA. However, as the level of adsorption is increased, the influence of the intermolecular interaction between dyes appears to play larger role in their adsorption to PVA.

3.3. Optical properties of the polarizing films

While the dye-uptake of PVA film increased steadily with increasing dyeing time and converged to a maximum, the dichroic ratios of the films increased to a maximum and then decreased

(Fig. 5). This change in dichroic ratio is caused by the difference in the parallel and perpendicular absorbance of the dyed film, as shown in Fig. 6. The rate of parallel absorbance decreased with increasing dyeing time, whereas that of the perpendicular absorbance increased steadily. This difference can be explained by the average orientation of the dyes in the film. The orientation of the dye is related to the drawing direction of the PVA film (**N**) and dye molecular axis (**M**), as shown in Fig. 7. The direction of each dye molecule deviates from the drawing direction of the film [17]. If θ denotes the angle between **N** and **M**, the order parameter $\mathbf{S_M}$ of **M** can be defined as the average of the Legendre polynomial, as given in equation (5) [18].

$$\boldsymbol{S}_{\mathbf{M}} = \left(3 < \cos^2\theta > -1\right)\Big/2 \tag{5}$$

where $<\cos^2\theta>$ is the average $\cos^2\theta$ for all dye molecules. The order parameter $\boldsymbol{S}_{\mathbf{M}}$ approaches unity ($\boldsymbol{S}_{\mathbf{M}} \rightarrow 1$) as the deviation of the dye molecules from the drawing direction decreases ($\theta \rightarrow 0°$).

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 ($\boldsymbol{S}_{\mathbf{T}}$) and molecular order parameter ($\boldsymbol{S}_{\mathbf{M}}$) are related by equation 6 [19].

$$\boldsymbol{S}_{\mathbf{T}} = \left[\boldsymbol{S}_{\mathbf{M}}\left(2 - 3\sin^2\beta\right)\right]\Big/2 \tag{6}$$

The order parameter (***S***) of Table 2 represents the transition moment order parameter ($\boldsymbol{S}_{\mathbf{T}}$) but β is a constant, which is characteristic of a dye molecule. Therefore, a change in dichroic ratio is related to θ, namely the orientational behavior of the dye molecules.

The orientational behavior of dye molecules in the film is affected by both the affinity between the dye molecules and PVA, and the intermolecular interaction between dye molecules. As mentioned previously, the affinity between the dye molecules and PVA is the dominant factor in the early stages of dyeing. Consequently, dyes adsorbed in the early stage of dyeing would be attached to the PVA polymer chains to have as small θ as possible. Therefore, a well oriented PVA film should have a maximum dichroic ratio and it should be maintained during the early stages of dyeing. However, the result showed that the films had low and increasing dichroic ratios in the beginning, which means that dyes are adsorbed with large θ in the film at first. The dyes with large θ are believed to be adsorbed in the defects of the PVA film. Since the orientation of the polymer chains in a drawn PVA film is not ideal, some part of the polymer chains that are less oriented would exist as defects. Dyes are

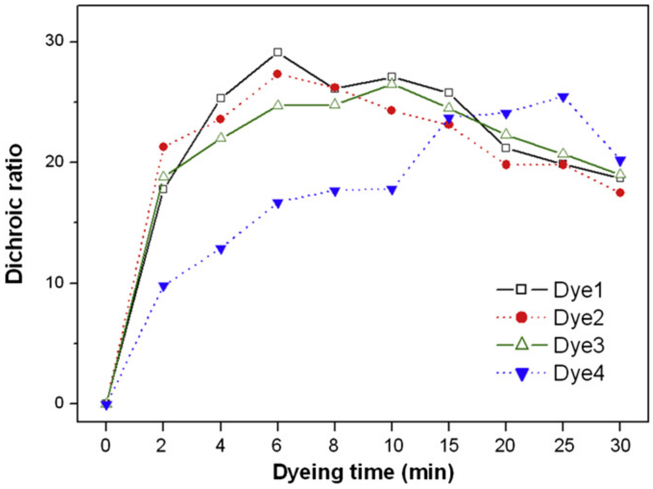


Fig. 5. Change in the dichroic ratio of polarizing films.

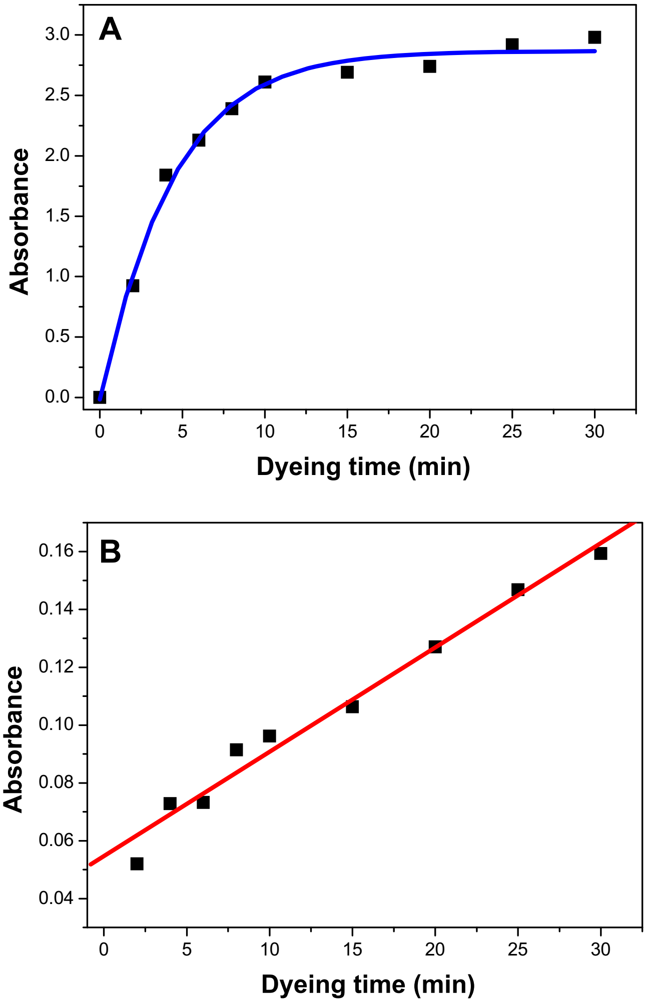


Fig. 6. (A) Parallel ($A_\parallel$) and (B) perpendicular ($A_\perp$) absorbance of polarizing films dyed with Dye 1.

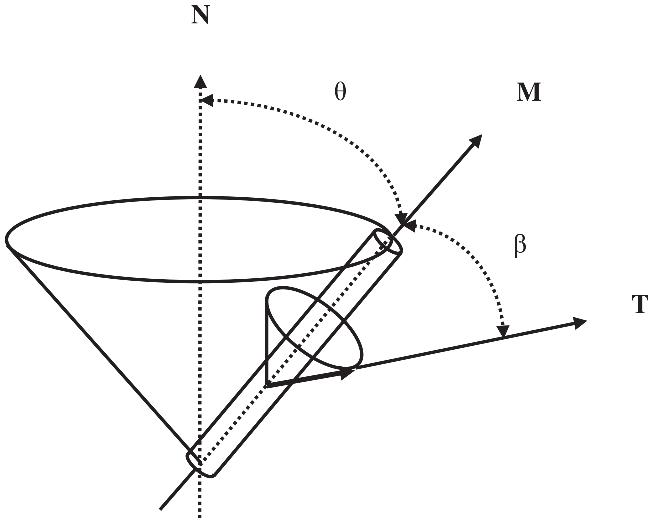


Fig. 7. Geometrical relationship of the drawing direction of a PVA film (**N**), dye molecular axis (**M**) and transition moment (**T**).

Table 2
Optical properties of the polarizing films with the maximum dichroic ratio for each dye.

Dye	***R***	***S***	T_{SP} (%)	PE (%)
1	29.1	0.903	42.61	99.13
2	27.3	0.898	40.46	99.65
3	26.5	0.895	42.13	99.02
4	25.5	0.891	40.39	99.52

believed to be adsorbed preferentially on these defects first because the diffusion of dyes in the defects is easier [20]. Therefore, as dyeing time increased, the portion of dyes with a larger θ decreased and the dichroic ratios increased to their maxima.

On the other hand, the decreases in the dichroic ratio after reaching the maximum means that the newly adsorbed dyes have larger θ values. This increase in θ is believed to be due to dye aggregation. Once the surface of the PVA polymer chain is occupied with dyes, the subsequently adsorbed dyes would aggregate and their orientation would have less relationship with the drawing direction of the PVA polymer chains. The increase in the amount of randomly oriented dyes is supported by a continuous increase in the perpendicular absorbance despite the decrease in the amount of the newly adsorbed dyes, as shown in Fig. 6.

Table 2 lists the parameters relevant to the optical anisotropy of the polarizing films when they have the maximum dichroic ratio of each dye. Single-piece transmittances and polarizing efficiencies are commercially important evaluation criteria for polarizing films. However, the dichroic ratio is a more useful term to easily compare the optical anisotropy of dyed polarizing films. Polarizing films with Dyes 1 and 2 had higher dichroic ratios than those with Dyes 3 and 4. Dyes 1 and 2 are more linear, and would have a better orientation with the PVA polymer chains, resulting in a higher dichroic ratio of the polarizing films. A linear conformation of dye molecule leads to good orientation of the dyes along the polymer chains in drawn PVA film.

When polarizing films dyed with dyes containing a pyridine ring were compared with those dyed with dyes containing a benzene ring, those containing the pyridine ring (Dyes 2 and 4) had lower dichroic ratios than those with a benzene ring. This appears to be due to the charge distribution of the pyridine ring. The nitrogen atom in the pyridine ring acts as a donating center when an electron withdrawing group is substituted on the pyridine ring, but acts as a withdrawing center when an electron donating group is substituted on it [21]. Therefore, the nitrogen atom in the pyridine ring will act as an electronic obstacle for smooth charge transfer within a dye molecule and decrease the transition moment of the dye by reducing the electron withdrawing effect of the carboxyl group.

4. Conclusions

This study examined the effect of the dichroic dye structure on the dyeing and optical properties of the PVA polarizing film. The affinity of the dyes to PVA acts as a dominant factor in dye-uptake. The linearity and hydrogen bonding ability of the dyes were decisive factors in determining the affinity of the dyes to PVA film. The dye-uptake was also influenced by the intermolecular interaction between the dyes themselves. The results of the optical properties suggest that dyes with higher linearity have superior optical properties owing to their improved orientation with a drawn PVA film. For further enhancement of the optical properties, the charge distribution of the terminal substituent was also found to be important. The introduction of a pyridine ring increased the number of intermolecular interactions without altering the linearity but worked to the disadvantage of the transition moment due to the adulteration of electron donating and withdrawing substituents on the aromatic ring of the dye. This suggests that a D-π-A(donor-πconjugated bridge-acceptor) structure would be favorable for dichroic dyes with higher dichroic ratios. These findings will be useful for the molecular design of novel dichroic dyes for highly efficient polarizing films.

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