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Synthesis of stilbene-based azo dyes and application for dichroic materials in poly(vinyl alcohol) polarizing films

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Abstract

Stilbene-based azo dyes were synthesized and poly(vinyl alcohol) polarizing films were prepared using these dyes. Spectral properties of synthesized dyes were affected by amino group and intramolecular hydrogen bond in the coupling component ring. Adsorption of dye molecules onto the film was mainly influenced by hydrogen bonding interaction. Sodium sulfate added in the dyeing solution reduced the repulsion between dye anions and the film resulting in high degree of polarization. The increase in draw ratio improved the optical properties of the polarizing films.

Keywords: Stilbene-based azo dyes; Poly(vinyl alcohol) polarizing films; Hydrogen bonding; Sodium sulfate; Draw ratio; Optical properties

1. Introduction

Polarizing films are widely used in a variety of applications, including high-precision optical devices, photography filters, antiglare sunglasses and liquid crystal displays (LCDs) [1]. The most commercially employed polarizing film is the poly(vinyl alcohol)–iodine complex, which was invented by E. H. Land in 1938. It consists of an uniaxially stretched poly(vinyl alcohol) film, stained with an aqueous solution of I_2/KI [2]. Anisotropic absorption of light results from the orientation of iodine molecules in agreement with the stretching direction of the host polymer film.

However, the polarizing film made of iodine and poly(vinyl alcohol) is vulnerable to heat and moisture attack so that iodine molecules are easily sublimed and released from the polymer film in high temperature and/or high humidity conditions [3]. A considerable amount of effort has been made to improve the heat and moisture resistance of the iodine polarizing film, but a polarizing film based on poly(vinyl alcohol)–dye complex is better from the viewpoint of durability at the moment [4].

Direct dyes are available for the polarizing films on the basis of structural similarity between cellulose and poly(vinyl alcohol). Like direct dyes for cellulosic fibers, direct dyes for the polarizing films are supposed to have the structural characteristics such as linearity, coplanar conformation, hydrogen bonding sites and water solubilizing groups [5]. Among these characteristics, linearity and coplanar conformation presumably exert a favorable influence on the alignment of direct dyes, and consequently, increase the optical anisotropy of the polarizing film.

In this study, three stilbene-based azo dyes were synthesized and the dye polarizing films were prepared using these dyes. The optical properties of the polarizing films were investigated from the viewpoint of the dye structure and preparation conditions of the polarizing films.

2. Experimental

2.1. Materials and instrumentation

4,4′-Diaminostilbene dihydrochloride and 1-hydroxy-4-naphthalenesulfonic acid sodium salt purchased from TCI

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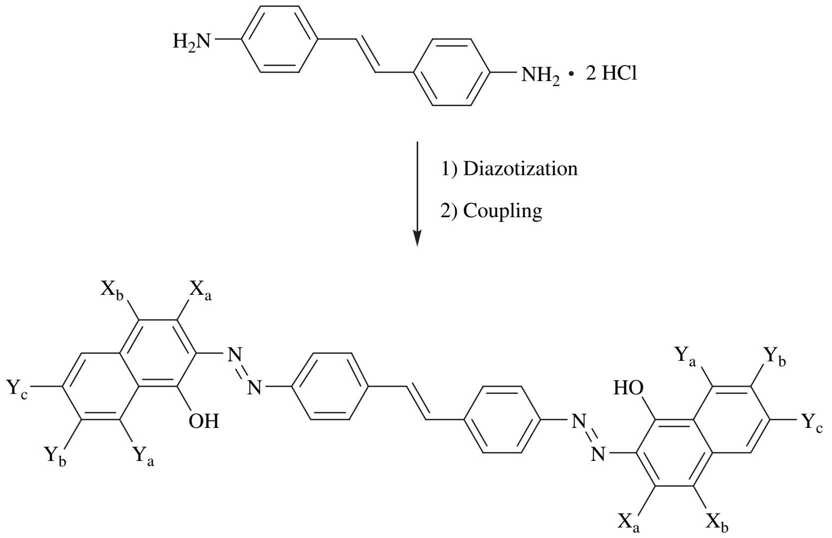


1: X_a=H, X_b=SO_3Na; Y_a, Y_b, Y_c=H

2: X_a=SO_3Na, X_b=H; Y_a, Y_c=H, Y_b=NH_2

3: X_a=SO_3Na, X_b=H; Y_a=NH_2, Y_b=H, Y_c=SO_3Na

Scheme 1. Synthesis of stilbene-based azo dyes.

and 6-amino-4-hydroxy-2-naphthalenesulfonic acid and 4-amino-5-hydroxy-2,7-naphthalenedisulfonic acid from Sigma–Aldrich were used without 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 and a degree of saponification of 99.9%. Melting points were measured using BÜCHI Melting Point B-540 and are uncorrected. ^{1}H NMR spectra were recorded by Bruker Avance 500 using DMSO-d_6 as the solvent and TMS as the internal standard. FT-IR spectra were recorded with MIDAC PRS infrared spectrometer using KBr discs. Absorption spectra were measured on a HP 8452A spectrophotometer which was equipped with a Glan–Thompson polarizer.

2.2. Synthesis of stilbene-based azo dyes

2.2.1. Diazotization

A mixture of 4,4′-diaminostilbene dihydrochloride (1 g 3.53 mmol), 20 ml of water and 1.47 ml of 37% hydrochloric acid was heated until solution was complete (Scheme 1). 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.

2.2.2. Coupling

1-Naphthol-4-sulfonic acid sodium salt (1.91 g, 7.77 mmol) was dissolved in 50 ml of water at pH 7. The prepared diazonium salt liquor was added to the coupling solution at 0–5 °C

Table 1
Yields, melting points, ^{1}H NMR and FT-IR data of synthesized dyes

Dye	Yield (%)	M.p. (°C)	^{1}H NMR (ppm, DMSO-d_6)	FT-IR (cm^{-1}, KBr)
1	83.7	>300 (Decomp.)	7.45 (s, 2H, –CH=CH–), 7.54 (t, 2H, ArH), 7.70 (t, 2H, ArH), 7.80 (d, 4H, ArH), 7.90 (d, 4H, ArH), 7.91 (s, 2H, ArH), 8.36 (d, 2H, ArH), 8.65 (d, 2H, ArH), 14.7 (s, 2H, –OH)	1619 (–C=O), 1176, 1051 (–SO_3)
2	87.3	>300 (Decomp.)	6.98 (d, 2H, ArH), 7.33 (s, 2H, –CH=CH–), 7.40 (s, 4H, ArH), 7.42 (d, 2H, ArH), 7.71 (d, 4H, ArH), 7.77 (d, 4H, ArH), 16.1 (s, 2H, –OH)	3422 (–NH_2), 1623 (–C=O), 1212, 1050 (–SO_3)
3	38.5	>300 (Decomp.)	6.90 (s, 2H, ArH), 7.05 (s, 2H, ArH), 7.27 (s, 2H, –CH=CH–), 7.31 (s, 2H, ArH), 7.66 (d, 4H, ArH), 7.69 (d, 4H, ArH), 15.6 (s, 2H, –OH)	3420 (–NH_2), 1616 (–C=O), 1214, 1043 (–SO_3)

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 at 30 °C. The crude product was refluxed in ethanol for 2 h, hot filtered, washed with hot ethanol and subsequently dried in a vacuum oven at 30 °C (dye **1**). Dyes **2** and **3** were prepared in a manner similar to dye **1** (Scheme 1). The purity of dyes was confirmed by thin layer chromatography using isopropanol/acetone/ammonia water (2:2:1) as the mobile phase. The yields, melting points, ^{1}H NMR and FT-IR data of synthesized dyes are summarized in Table 1.

2.3. Preparation of polarizing films

Dye baths were prepared with dyes **1–3** (4% o.w.f.) and with or without Na_2SO_4. The PVA film was immersed in the dyeing solution at 40 °C for 2–10 min. The dyed PVA films were drawn in 3 wt% boric acid solutions at 40 °C. The draw ratio was 4:1–6:1. The stretched films were washed with water and dried in a vacuum under a uniform tension for one day.

2.4. Investigation of optical properties

Optical properties of the polarizing films were examined by UV–vis spectrophotometer equipped with a Glan–Thompson polarizer which can change the angle of incident light. Single-piece transmittance (T_{sp}) and degree of polarization (DP) were investigated at the absorption maximum of the polarizing films according to Eqs. (1) and (2) [6].

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

$$\mathrm{DP} = \left(T_{\perp} - T_{\parallel}\right)/\left(T_{\perp} + T_{\parallel}\right) \tag{2}$$

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

3. Results and discussion

3.1. Synthesis of stilbene-based azo dyes

To render stilbene-based azo dyes linear and coplanar, diazotized 4,4′-diaminostilbene was coupled to the *ortho* position of hydroxyl group in the coupling components. 2-Azo-1-naphthol derivatives (dyes **1–3**) exist predominantly in the hydrazone form via intramolecular hydrogen bonds, which result in the linearity and coplanar conformation of dyes (Scheme 2) [7]. The proton peaks involved in hydrogen bonds appear at much lower field than normal proton peak of hydroxyl group [8] and these (14.7, 16.1 and 15.6 ppm for dyes **1**, **2** and **3**, respectively) were confirmed by ^{1}H NMR. Overall characterization of dye structures were carried out by ^{1}H NMR and FT-IR (Table 1).

Table 2
Spectral properties of synthesized dyes

Dye	λ_{max}^{a} (nm)	ϵ_{max}^{a} (l mol^{-1} cm^{-1})
1	548	36,000
2	580	31,000
3	594	74,000

[a] Measured in water.

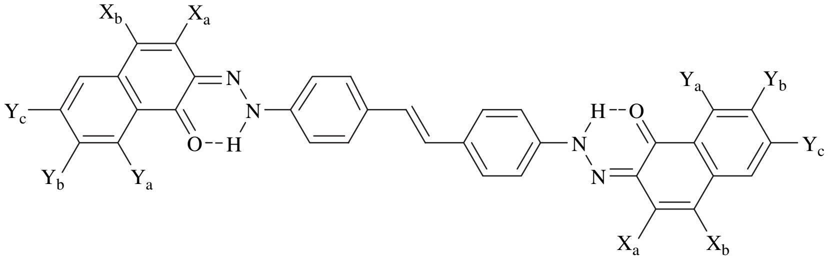
3.2. Spectral properties of dyes

Table 2 shows the spectral properties of synthesized dyes **1–3**. The absorption maxima of dyes were in the range of 548–594 nm, which was of purple to blue shade. The introduction of amino group in the naphthalene rings of dyes **2** and **3** caused bathochromic effect as compared with dye **1**. Molar extinction coefficients of dyes varied from 31,000 to 74,000. The highest tinctorial strength of dye **3** is due to the additional intramolecular hydrogen bond between carbonyl group and amino group in the naphthalene ring which makes the dye more planar.

3.3. Optical properties of polarizing films

3.3.1. Effect of dye structure on optical properties (adsorption behavior of dyes)

Fig. 1 shows the dye uptake on poly(vinyl alcohol) film which was prepared without stretching process. As dipping time increased, the absorbance of poly(vinyl alcohol) films dyed with dyes **2** and **3** increased rapidly but that of poly(vinyl alcohol) film stained with dye **1** increased rarely. In spite of the structural similarities of dyes, the adsorption of dye **1** was very low. The low dye uptake of poly(vinyl alcohol)



Scheme 2. Intramolecular hydrogen bonds of dyes.

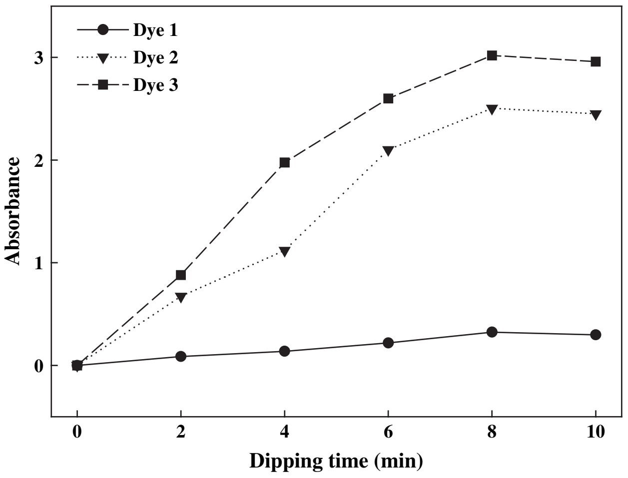


Fig. 1. Absorbance of the polarizing films dyed with dyes **1–3** (0.1 wt% Na_2SO_4).

film dyed with dye **1** can be attributed to the lack of hydrogen bonding sites unlike dyes **2** and **3** having additional hydrogen bonding sites such as amino groups. This result means that the effect of hydrogen bonding interaction on the adsorption of dye molecules onto poly(vinyl alcohol) film is much higher than that of vander Waals force. The equilibrium of adsorption was attained at 8 min for all dyes.

3.3.2. *Effect of salt on optical properties*

Degree of polarization and single-piece transmittance of the polarizing films dyed with dyes **2** and **3** are shown in Figs. 2 and 3, respectively. Without salt, repulsion between dye anions and poly(vinyl alcohol) films resulted in higher transmittance and lower degree of polarization. Especially, in case of poly(vinyl alcohol) film dyed with dye **3**, dye molecules were hardly adsorbed onto the film due to the four sulfonic acid groups, which can bring about high repulsion between dye and the film. When salt was added to the dyeing solution, degree of polarization more than 99% and single-piece transmittance near 40% were obtained (100% of degree of polarization and 50% of single-piece transmittance for an ideal polarizer).

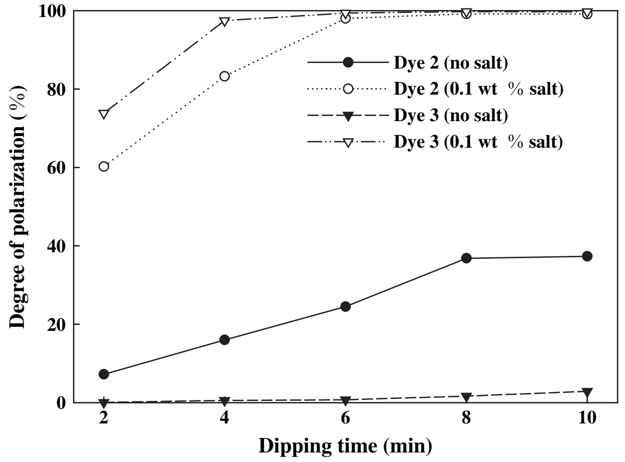


Fig. 2. Degree of polarization of the polarizing films dyed with dyes **2** and **3** (draw ratio 6:1).

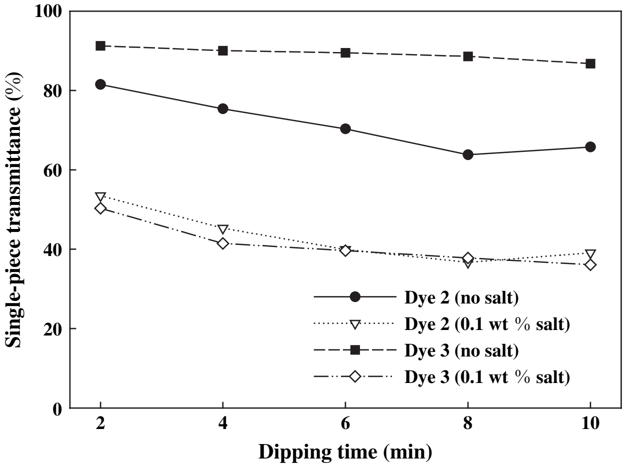


Fig. 3. Single-piece transmittance of the polarizing films dyed with dyes **2** and **3** (draw ratio 6:1).

3.3.3. *Effect of draw ratio on optical properties*

Table 3 shows degree of polarization (DP) and single-piece transmittance (T_{sp}) of the polarizing films dyed with dyes **2** and **3** according to draw ratio. As draw ratio increased, single-piece transmittance of the film increased gradually with degree of polarization almost the same. This result suggests that the effective orientation of polymer segment–dye complex in accord with the stretching direction of the host film was achieved with increased draw ratio.

4. Conclusions

Three stilbene-based azo dyes were synthesized and the dye polarizing films were prepared using these dyes. Introduction of amino group in the coupling component ring resulted in bathochromic effect. Intramolecular hydrogen bond of coupling component ring increased the tinctorial strength of dye. Hydrogen bonding interaction was a crucial factor in the adsorption of dye molecules onto the poly(vinyl alcohol) film. Salt used in the preparation of the polarizing film relieved the repulsion between dye anions and the film, and consequently, conferred high degree of polarization on the polarizing film. The increase in draw ratio made it possible for polymer segment–dye complex to be aligned more effectively with the stretching direction of the film. As a result,

Table 3
Optical properties of the polarizing films dyed with dye **2** and **3**

Draw ratio		4:1	5:1	6:1
Dye **2** polarizing film	T_{sp}	32.8	35.6	39.1
	DP	99.8	99.7	99.2
Dye **3** polarizing film	T_{sp}	31.9	34.5	37.8
	DP	99.5	99.8	99.7

single-piece transmittance of the film increased gradually with degree of polarization almost unchanged.

Acknowledgements

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