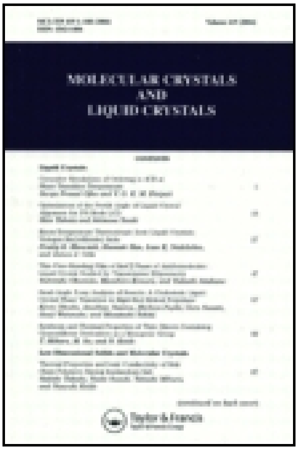

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Polarizing Films Based on Oriented Poly(vinyl alcohol)-Dichroic Dyes

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Polarizing films were prepared using three dichroic dyes and iodine. The direction of transition moment in dichroic dyes was in accord with the orientation of the host polymer. The polarizing efficiency of PVA/dye polarizing films reached almost full contrast but their single-piece transmittances were rather low. PVA/dye polarizing films were superior to PVA/iodine polarizing film in their stability to high temperature and high humidity.

Keywords: dichroic dyes; optical properties; polarizing films; stability; transition moment

INTRODUCTION

High dichroic polarizers are required in a variety of commercial applications such as antiglare sunglasses, photography filters, optical instruments, and liquid crystal displays (LCDs) [1]. These polarizers are manufactured from oriented sheets of semicrystalline PVA polymers containing polyiodine molecules or dichroic dyes as the dichroic materials. The orientation of the host polymer is introduced by tensile drawing of the film. During drawing, the dichroic materials are oriented in agreement with the host polymer film, and consequently, anisotropic absorption of light in the visible wavelength range is generated. This results in the typical characteristics of a polarizer,

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i.e., two crossed polarizers hardly transmit light whereas two parallel polarizers are highly transparent [2–4].

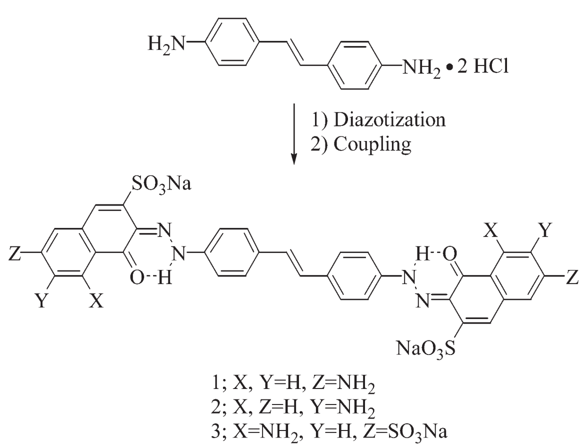
Currently, most of commercially available polarizing films employ iodine as a dichroic chromophore because polyiodine molecules exhibit high dichroism. However, in high temperature and/or humidity conditions, polyiodine molecules are easily sublimed and released from the host polymer. To overcome this drawback, dichroic dyes can be used as a dichroic material [5,6].

In this paper, three dichroic azo dyes were synthesized and PVA/dye polarizing films were prepared using these dyes. PVA/iodine polarizing film was also manufactured to compare the stability of two types of polarizing films. The optical properties of the polarizing films were investigated. Their stability to temperature and humidity was examined as well.

EXPERIMENTAL

Synthesis of Azo Dyes 1–3 (Scheme 1)

Azo dyes **1–3** were prepared by the direct diazotization of 4,4′-diaminostilbene dihydrochloride, followed by coupling of the diazonium salt with 7-amino-4-hydroxy-2-naphtalenesulfonic acid, 6-amino-4-hydroxy-2-naphtalenesulfonic acid, and 4-amino-5-hydroxy-2,7-naphtalenedisulfonic acid in alkaline medium. The purity of the dyes **1–3** was confirmed by thin layer chromatography using isopropanol/acetone/ammonia (2:3:1) as the mobile phase. The yields, melting



SCHEME 1 Synthesis of dichroic azo dyes **1–3**.

TABLE 1 The Yields, Melting Points, ^{1}H-NMR, and FT-IR Data of the Synthesized Dyes

Dye	Yield (%)	m.p. (°C)	^{1}H-NMR (ppm, DMSO-*d6*)	FT-IR (cm^{-1}, KBr)
1	43.0	>300 (decomp.)	6.66 (s, 2H, ArH), 6.71 (d, 2H, ArH), 7.24 (s, 2H, −CH=CH−), 7.28 (s, 2H, ArH), 7.64(d, 4H, ArH), 7.68 (d, 4H, ArH), 7.95 (d, 2H, ArH)	3417 ($-NH_2$), 1609 (−C=O), 1182, 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)	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)	3420 ($-NH_2$), 1616 (−C=O), 1214, 1043 ($-SO_3$)

points, ^{1}H-NMR, and FT-IR data of the synthesized dyes are summarized in Table 1.

Preparation of Polarizing Films

The PVA film used in this study was supplied by Kuraray Co. Ltd., with a degree of polymerization of 1700 and a thickness of about 75 μm. Dyeing solutions were prepared with dyes **1–3** (4 wt%) and 0.1 wt% Na_2SO_4. The PVA film was immersed in the dyeing solution at 40°C for 6 min. A PVA film was iodinated with aqueous solution of KI/I_2 at 25°C for 50 sec. The dyed or iodinated PVA films were drawn in 3 wt% boric acid solutions at 40°C. The draw ratio was 6:1. The stretched films were washed with water and dried in a vacuum for one day.

Measurement of Optical Properties

UV-vis absorption spectra of the polarizing films were measured on a HP 8452 A spectrophotometer which was equipped with a Glan-Thompson polarizer. Dichroic ratio (R), order parameter (S), single-piece transmittance (T_{sp}), and polarizing efficiency (PE), were measured at the absorption maximum of the dye according to Eqs. (1)–(4) [7]. $A_{\parallel}$ and $A_{\perp}$ denote the absorbances parallel and perpendicular to the drawing direction. $T_{\parallel}$ and $T_{\perp}$ are the transmissions parallel and perpendicular to the orientation direction, which were calculated from the absorbances ($T = 10^{-A}$).

$$R = \frac{A_{\parallel}}{A_{\perp}} \quad (1)$$

$$S = \frac{(R - 1)}{(R + 2)} \quad (2)$$

$$T_{sp} = \frac{1}{2}(T_{\parallel} + T_{\perp}) \quad (3)$$

$$PE = \frac{(T_{\perp} - T_{\parallel})}{(T_{\perp} + T_{\parallel})} \quad (4)$$

Investigation of Stability to Temperature and Humidity

The polarizing films were stored in temperature and humidity chamber at 80°C and 70% relative humidity for 150 hrs. The stability of the polarizing films was evaluated from the difference of PE (ΔPE).

RESULTS AND DISCUSSION

In Figure 1, the absorption of polarizing films doped with dyes **1–3** showed maximum when the light vector was polarized parallel and

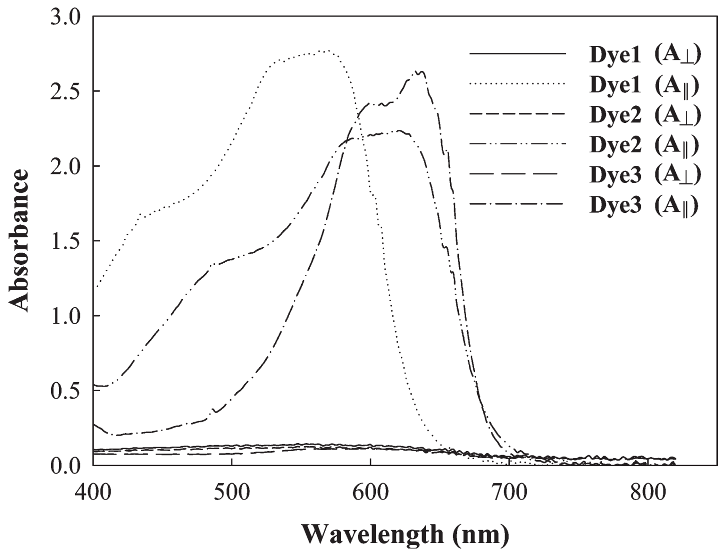


FIGURE 1 The absorption spectra of the polarizing films doped with dyes **1–3**.

TABLE 2 The Optical Properties of the Polarizing Films Doped with Dyes **1–3**

Dye	λ_{max} (nm)	R	S	T_{sp}	PE
1	570	25.2	0.89	0.39	0.99
2	622	21.0	0.87	0.40	0.98
3	636	26.0	0.89	0.40	0.99

minimum when the vector was perpendicular to the drawing direction. This result means that the direction of transition dipole moment in dichroic dyes is in good agreement with the orientation of the polarizing film.

The optical properties of the polarizing films are given in Table 2. The polarizing efficiency of the polarizing films approached almost full contrast; i.e., no light passes two crossed polarizing films. However, single-piece transmittances were rather low in comparison to a perfect polarizer ($T_{sp} = 0.5$). The order parameters calculated from the dichroic ratios were near the value of 0.9, which suggests that the orientation distribution of the dye molecules is narrow.

In Figure 2, ΔPE of the PVA/iodine polarizing film decreased over time, which may be attributed to the sublimation of iodine molecules

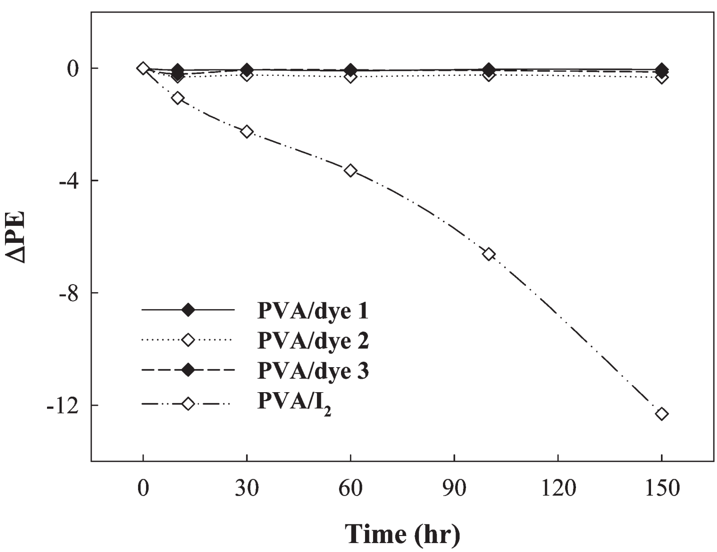


FIGURE 2 The change of polarizing efficiency difference (ΔPE) of the polarizing films over time (80°C, 70% relative humidity).

from the host polymer. However, ΔPE of the PVA/dye polarizing film remained unchanged. Clearly, the PVA/dye polarizing film has an advantage over the PVA/iodine polarizing film with respect to temperature and humidity resistance.

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