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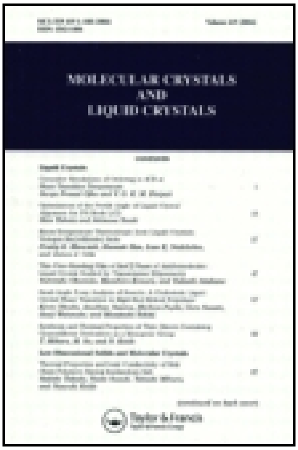

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Orientation Behavior of Dichroic Azo Dyes in Stretched Poly(vinyl alcohol) Films

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Polarizing films doped with three kinds of dichroic azo dyes were prepared to investigate the effect of dye structures on the orientation behavior of dyes in stretched poly(vinyl alcohol) films. One reactive group exerted an unfavorable influence on the alignment of dye molecules toward the polymer segments orientation. However, two reactive groups resulted in the effective alignment and showed the best optical properties among three kinds of dyes.

Keywords: dichroic azo dyes; optical properties; orientation behavior; polarizing films

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INTRODUCTION

Polarizing film is very important optical component for TFT-LCD. This polarizing film is obtained by the orientation of poly(vinyl alcohol) polymer film having iodine or dye molecules as dichroic materials. Optical anisotropy of PVA/dye polarizing films, which introduce dye molecules as the dichroic material, results from the molecular orientation of dyes in stretched PVA films [1,2]. The orientation of dyes makes the transition dipole moment vectors of dye molecules lie at a specific direction and maximum absorption of light in the visible wavelength range occur at that direction [3,4]. Therefore, the effective orientation of dye molecules in accord with the drawing direction of host PVA films is the most important element in preparing polarizing films.

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In this paper, three kinds of azo dyes (**D1** & **D2**, **R1** and **R2**) as the dichroic materials were synthesized and PVA polarizing films were prepared using those dichroic dyes. The effect of dye structures on the orientation behavior of dyes in stretched PVA films was examined on the basis of optical properties(single-piece transmittance, degree of polarization, dichroic ratio and order parameter) of the polarizing films.

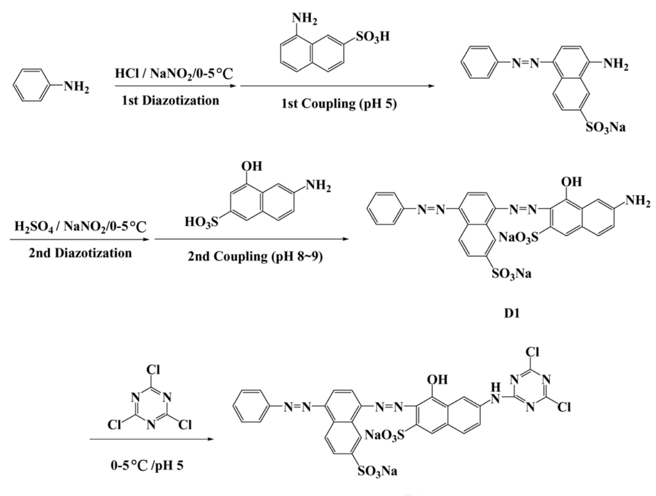
EXPERIMENTAL

Synthesis of Dichroic Azo Dyes (Schemes 1 & 2)

Azo dyes **D1** and **D2** were synthesized by the conventional diazotization and coupling reaction. **R1** and **R2** were prepared by the substitution reaction between amino groups of **D1** and **D2** and cyanuric chloride (2,4,6-trichloro-1,3,5-triazine) respectively.

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 synthesized dyes (4 wt%) and 0.1 wt% Na_2SO_4. The 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 solutions at 50°C. The draw ratio was 5:1. The



SCHEME 1 Synthesis of dichroic azo dyes **D1** and **R1**.

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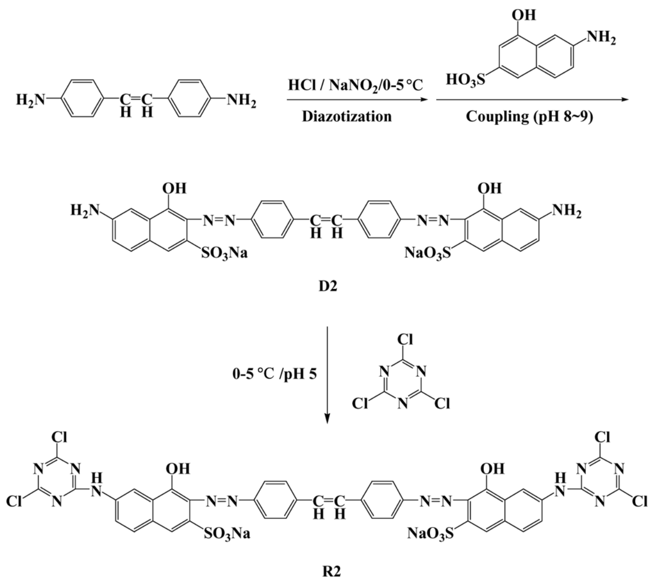

SCHEME 2 Synthesis of dichroic azo dyes **D2** and **R2**.

stretched films were washed with water and dried under uniform tension for one day.

Measurement of Optical Properties

UV-vis absorption spectra of the polarizing films were measured on a HP 8452 A spectrophotometer equipped with a Glan-Thompson polarizer which can change the angle of incident light. Dichroic ratio (R), order parameter (S), single-piece transmittance (T_{sp}) and degree of polarization (DP) were measured at the absorption maximum of the dye according to Eqs. 1–4 [5]. $A_{\parallel}$ and $A_{\perp}$ denote the absorbances parallel and perpendicular to the stretching direction. $T_{\parallel}$ and $T_{\perp}$ are the transmittances parallel and perpendicular to the orientation direction, which were calculated from the absorbances ($T = 10^{-A}$).

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

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

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

$$DP = (T_{\perp} - T_{\parallel})/(T_{\perp} + T_{\parallel}) \tag{4}$$

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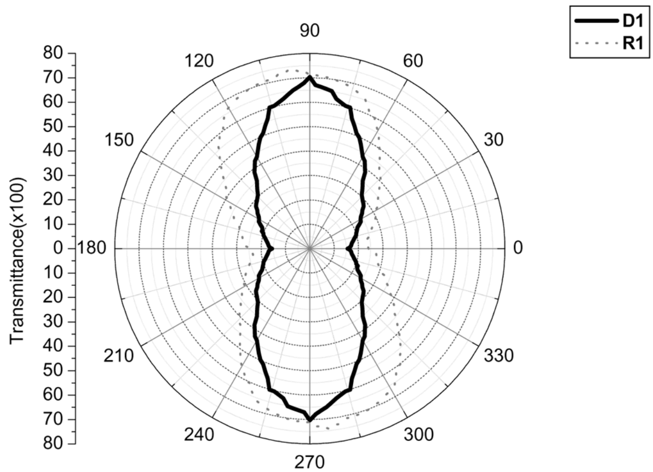

FIGURE 1 The transmittances of the polarizing films containing **D1** and **R1** according to the angle of incident light.

RESULTS AND DISCUSSION

As shown in Figure 1 and 2, the long axis of transmittance curve of the polarizing film containing **R1** tilted 10 degrees from vertical (incident light is perpendicular to the stretching direction of the polarizing film)

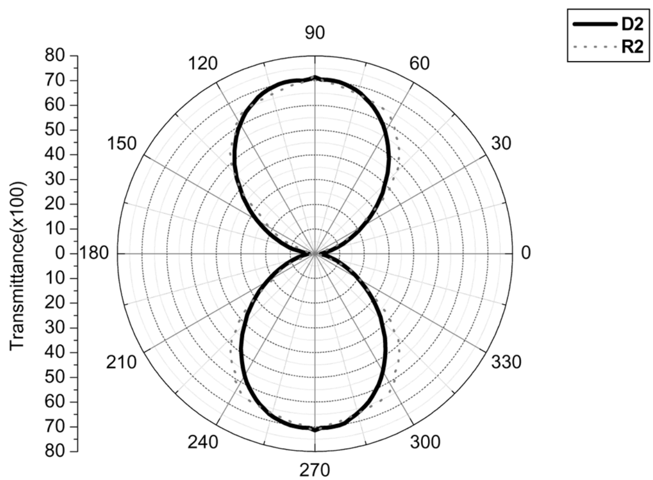

FIGURE 2 The transmittances of the polarizing films containing **D2** and **R2** according to the angle of incident light.

TABLE 1 The Optical Properties of the Polarizing Films Doped with Dichroic Azo Dyes

Dye	λ_{max} (nm)	R	S	T_{sp}	DP
D1	504	5.3	0.59	0.43	0.64
R1	504	4.3	0.52	0.48	0.50
D2	622	10.8	0.77	0.37	0.93
R2	614	15.8	0.83	0.36	0.98

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unlike the polarizing films doped with **D1**, **D2** and **R2**. This result means that one reactive group had an unfavorable effect on the alignment of dye molecules toward the polymer segment orientation because one reactive group, which is covalent-bonded with a hydroxyl group of the PVA polymer, disturbs the effective interaction between dye molecules and polymer chains. And the transmittances of the polarizing films containing **D1** and **R1**, which havelower aspect ratios than **D2** and **R2**, did not approach zero when the incident light was parallel to the drawing direction of the polarizing films. This result suggests that higher aspect ratio can render better alignment of dye molecules toward the PVA polymer chains and better optical properties of the polarizing films.

The optical properties of the polarizing films are given in Table 1. Due to the low aspect ratio of **D1** compared with **D2**, **D1** had lower dichroic ratio (R) and order parameter (S) than **D2**, and consequently, lower degree of polarization. **R2** showed better optical properties than **D2**. It can be seen that two reactive groups, which form covalent bonds between polymer segments and dye molecules, make the effective alignment possible and reduce the possibility of random redistribution of molecular orientation of dyes when the polarizing film is stretched.

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