UV Polarizers Based on Oriented Poly(vinyl alcohol)–Chrysophenine–Congo Red Blend Films

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ABSTRACT: The availability of efficient low-cost ultraviolet (UV) film polarizers is of vital importance to a number of applications, which rely on the use of polarized light in the near-UV regime. We describe here the preparation of such elements based on stretch-oriented films comprising poly(vinyl alcohol) and a combination of two commercially available azo dyes, Congo Red and Chrysophenine. Films of various dye contents were prepared and oriented by uniaxial tensile deformation. Moderately stretched films (draw ratio $l/l_0 = 4-8$) exhibit a pronounced optical dichroism, characterized by a polarizing efficiency up to 0.98 at a wavelength of 365 nm. Initial experiments suggest that, even under rather harsh irradiation conditions and without any packaging, these azo-dye-based polarizers are surprisingly inert under simulated operating conditions. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 1235–1239, 2002

Key words: dye; optic; orientation

INTRODUCTION

Polymeric sheet polarizers are important optical components for a variety of commercial applications, including antiglare sunglasses, photography filters, optical instruments, and liquid crystal displays (LCDs).[1] Interestingly, the most commonly employed polarizer is still the so-called H-polarizer, which was introduced by Land and Rogers over 50 years ago.[2] The latter consists of an oriented poly(vinyl alcohol) (PVA) film, which, upon treatment with an I_2/KI solution, exhibits a highly anisotropic optical absorption. As an alternative to these PVA/iodine polarizers, oriented blend films based on a semicrystalline polymer and one or multiple dichroic dyes are considered for use as polarizing elements.[3-6] However, broad commercial success of these elements has been stifled by the difficulty to produce so-called neutral gray polarizers within this framework,[3] that is, dichroic polarizers, which absorb optical energy evenly over the entire visible regime of the electromagnetic spectrum.

Triggered by the demands of the aforementioned applications, the development of conventional sheet polarizers has been focused on, among other aspects, optimizing their optical characteristics in the *visible* range. As a consequence, most of the dichroic sheet polarizers developed to date cannot be employed in the ultraviolet (UV) regime, that is, at wavelengths below about 400 nm.[2-6] Many of the experimental systems contain dyes, which, due to their absorption characteristics and/or their limited optical stability, are not suitable for this particular wavelength regime.[3-6] Further, most of the commercially available polarizers comprise UV cutoff filters that absorb light at wavelengths shorter than 400 nm to provide protection from undesired UV irradiation.[7] Some near-UV sheet polarizers are commercially available, but rather expensive and inefficient when compared to standard PVA/iodine polarizers.

The availability of efficient low-cost UV polarizers is, however, of vital importance to a number of applications that rely on the use of polarized light in the near-UV. Examples include photoluminescent LCDs,[8,9] detection systems for photoluminescent security features,[10] and transparent polarizing windows for self-verifying bank notes.[11] Thus, with the above-mentioned practical relevance of near-UV polarizers in mind and with the notion that low-pressure mercury lamps emitting at 365 nm are widely employed, we recently embarked on the preparation and investigation of PVA-based UV sheet polarizers. We elected to prepare blend films of PVA and a combination of commercially available azo dyes and here report our initial results on this conceptually most promising system.

EXPERIMENTAL

Materials

All dyes and solvents were purchased from the Aldrich Chemical Co. (Milwaukee, WI). Congo Red (dye content 97%) was used as received. Chrysophenine
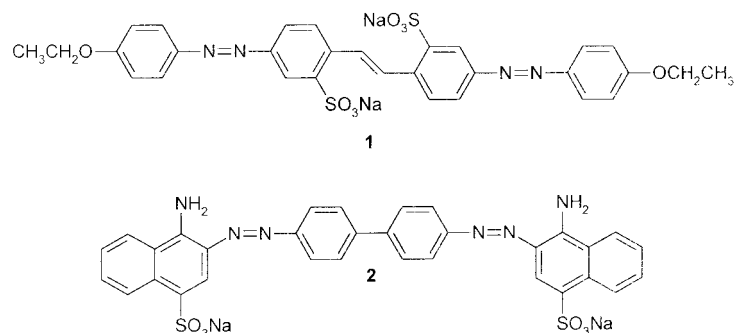
Figure 1 Chemical structures of Chrysophenine (**1**) and Congo Red (**2**), the dyes employed here.

(dye content ~65%) was purified prior to use by dissolving the dye in boiling methanol and removing insoluble impurities by filtration. The filtrate was dried under reduced pressure and the remaining solid was collected and dried at 50°C for 24 h *in vacuo*. PVA (Aldrich; M_w 85,000–146,000) was used as the matrix polymer and HPLC-grade water was used as the solvent.

Methods

Blend films were prepared by mixing a 2% w/w aqueous solution of PVA with the appropriate amount of an aqueous solution of the dye combination, casting the resulting mixture into a polystyrene Petri dish and allowing the solvent to evaporate at ambient over a period of several days. From the resulting films, tapes were cut (approximate size 30×10 mm $\times 50-80$ μm), which were subsequently stretched on a Wagner & Munz WME hot stage at a temperature up to 200°C and to a draw ratio, l/l_0 (final length/initial length of the sample), up to 8. The draw ratio was determined by measuring the displacement of ink marks applied to the films. For the optical characterization, the films were sandwiched between two Suprasil quartz slides and a small amount of poly(dimethylsiloxane-*co*-methylphenylsiloxane) 550 fluid (Aldrich) was applied to minimize scattering effects at the film surfaces.

UV-vis absorption spectra were measured on a Perkin–Elmer Lambda 800 spectrophotometer, which, for the polarized measurements, was equipped with a Glan–Thomson polarizer. An appropriate baseline correction for the Suprasil quartz slide/poly(dimethylsiloxane-*co*-methylphenylsiloxane) 550 sandwich was applied.

The absorption dichroic ratio, DR_A, of the present films at a given wavelength was determined by dividing the *p*-polarized absorption $A_\parallel$ (measured through a polarizer oriented with its optical axis parallel to the drawing direction of the film) by the *s*-polarized absorption $A_\parallel$ (measured through a polarizer oriented with its optical axis perpendicular to the drawing

direction) . Similarly, the polarizing efficiency, *PE*, and the single-piece transmittance, T_{sp}, were calculated from the *p*- and *s*-polarized transmittance of the films ($T_\parallel$ and $T_\perp$) according to the equations [eqs. (2) and (3)] derived elsewhere[12]:

$$DR_A = \frac{A_\parallel}{A_\perp} \tag{1}$$

$$PE = \frac{|T_\perp - T_\parallel|}{T_\perp + T_\parallel} \tag{2}$$

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

The aging behavior of the films under simulated operation conditions was investigated under ambient conditions on freestanding films, which were mounted on a supporting frame and exposed to the light of a low-pressure Hg UV lamp with an intensity maximum around 365 nm (Spectroline ENF-280C UV lamp, 350 μW/cm^2). The absorption spectra of the films were measured in intervals of about 100 h, and the absorption at 365 nm, which we used here as a relative measure for the extent of possible degradation, was plotted versus the exposure time.

RESULTS AND DISCUSSION

The dyes employed in the present study are Chrysophenine (**1**, also known as Direct Yellow 12) and Congo Red (**2**, also known as Direct Red 28) (Fig. 1), two well-known, rather inexpensive, commercially available azo dyes.[13] Both these dyes offer a high molecular aspect ratio, which usually allows for a high degree of uniaxial orientation upon incorporation in a suitable oriented matrix.[14] Earlier studies suggest that the electronic transition dipole moment of these dyes coincides with their molecular long axis.[15] As a result, oriented PVA films, which contain these chromophores *separately*[16] or in combination with other dyes,[17] have been investigated for use as linear polar-
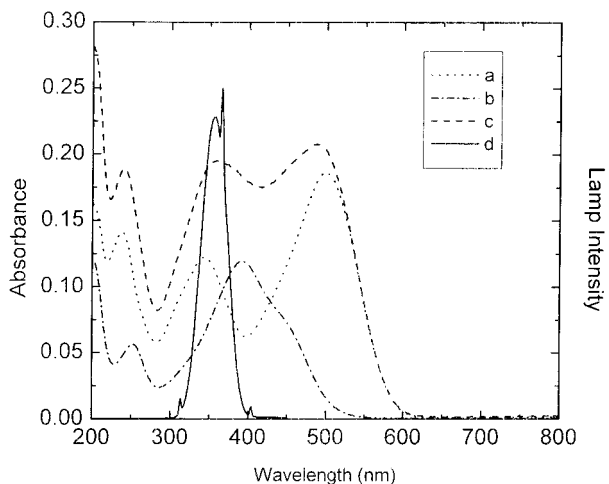
Figure 2 Absorption spectra of aqueous solutions of (a) Congo Red and (b) Chrysophenine. Curve (c) visualizes a linear combination of the above spectra, assuming a molar ratio of 1.4:1, while (d) shows the UV emission spectrum of a commercial low-pressure Hg lamp operating at 365 nm.

izers in the visible regime. As is evident from Figure 2, the absorption spectra of these dyes in an aqueous solution feature maxima around 393 nm (Chrysophenine) and 352 and 500 nm (Congo Red). Thus, neither dye would *individually* be suitable for a near-UV polarizer. Nevertheless, it appears that the absorption spectra of these chromophores ideally complement each other. Indeed, as shown in Figure 2, a linear combination of their absorption spectra offers an almost constant absorption in the range between 350 and 500 nm when adjusting the system to a Chrysophenine-to-Congo Red molar ratio of 1:1.4. At least in an aqueous solution, the absorption displayed by this combination almost optimally overlaps the emission of commercial low-pressure Hg lamps operating at 365 nm (Fig. 2). Consequently, we elected to exemplarily investigate the characteristics of uniaxially oriented PVA films, which comprise **1** and **2** in a molar ratio of 1:1.4.

Blend films comprising 0.1, 0.2, and 0.4 % w/w of the chromophore combination in PVA were prepared by solution-casting aqueous PVA/dye solutions (see Experimental section for details). The resulting films were drawn at temperatures up to 200°C and to draw ratios, l/l_0, up to 8, which appeared to be the maximum draw ratio of the materials investigated. The oriented films were found to exhibit a pronounced optical anisotropy, as shown in Figure 3 for a blend film characterized by a draw ratio of 8 and comprised 0.1 % w/w of the dye combination. Unfortunately, the absorption spectra of the blend films exhibit a substantial bathochromic shift when compared to the respective aqueous solutions. As a result, the optical anisotropy in the near-UV regime is less pronounced than in the visible range. For example, the aforementioned

sample (l/l_0 = 8, dye content = 0.1 % w/w) was characterized by a dichroic ratio, DR_A, of 11 at 365 nm, while dichroic ratios of 20 and 34 were measured at 437 and 512 nm, respectively. The polarizing efficiency (*PE*), which is a measure of the contrast achieved by two crossed polarizers, is limited to a value of 0.67 at 365 nm. This value is comparably low, considering that the *PE* of commercial PVA/iodine polarizers approaches a value of unity. Gratifyingly, the polarizing efficiency of the present polarizers at 365 nm was found to improve significantly upon increasing the dye content (Table I). For example, an oriented (l/l_0 = 8) blend film comprising 0.4% w/w of the Chrysophenine/Congo Red mixture exhibited a polarizing efficiency of 0.98, indicating that this polarizing element almost reaches full contrast. The data compiled in Table I show that the improvement in *PE* is achieved at the expense of the single-piece transmittance, T_{sp}. The latter is reduced from 0.51 to 0.30 when increasing the dye concentration from 0.1 to 0.4% w/w. Although the single-piece transmittance of 0.3 is substantially below the theoretical limit of about 0.5,[3] it compares rather well with the characteristics of available UV sheet polarizers and, importantly, seems to be useful for at least some potential practical applications (*vide supra*).

To investigate with more detail the orientational behavior of the absorbing guest molecules in the above-described films, the dichroic ratio (measured at 365 nm) of oriented 0.1% w/w Chrysophenine/Congo Red/PVA blend films was studied as a function of the draw ratio. As can be seen from Figure 4, the value of DR_A first increases linearly with an increasing draw
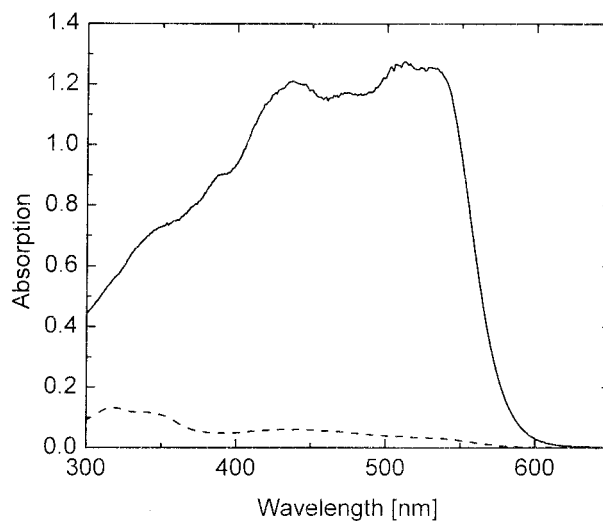

Figure 3 Polarized absorption spectra of an oriented blend film (draw ratio, l/l_0, = 8) comprising 0.1% w/w of a combination of Congo Red and Chrysophenine (molar ratio of 1.4:1) in PVA. The spectra were recorded through a polarizer aligned (solid line) parallel and (dashed line) perpendicular to the drawing direction of the blend film.

TABLE I
Optical Anisotropy of Oriented (l/l_0 = 8) Chrysophenine/Congo Red/PVA Blend Films

Dye content[a] (% w/w)	DR_A[b] at 365 nm (−)	PE[c] at 365 nm (−)	T_{sp}[d] at 365 nm (−)	DR_A[b] at 512 nm (−)
0.1	10.9	0.67	0.51	34
0.2	9.6	0.83	0.41	22
0.4	10.0	0.98	0.30	33

[a] Based on the amount of PVA and comprising Congo Red/Chrysophenine in molar ratio of 1.4:1.
[b] Absorption dichroic ratio.
[c] Polarizing efficiency.
[d] Single-piece transmittance.

ratio, before leveling off to a plateau of ~11 at an l/l_0 of ~4, thus following the generally observed pattern.[3,4,18,19] The magnitude of the plateau (i.e., the maximally achievable DR_A) was found to be independent of the blend composition in the investigated concentration regime of 0.1–0.4% w/w, suggesting that the blends investigated here are intimately mixed and of a homogeneous nature.[18]

Crucial to extended use is the observation that the oriented Chrysophenine/Congo Red/PVA blend films exhibit an outstanding stability under simulated operation conditions, that is, when kept under ambient conditions and continuous excitation at 365 nm (see Experimental section for details). The aging behavior of the present polarizers was investigated under ambient conditions on freestanding, *unpackaged* films, which were exposed to light of a low-pressure Hg UV lamp emitting around 365 nm. The absorption spectra of the films were measured in intervals of about 100 h. As a relative measure for the extent of possible degradation, the absorption at 365 nm was plotted versus the exposure time (Fig. 5). The data show that the absorption of a 0.1% w/w blend film remained unchanged over a period of more than 500 h, suggesting that the effect of photobleaching is, at least within this time frame, negligible. While substantially longer lifetimes are desired for practical applications, this initial experiment unequivocally demonstrates that, even under rather harsh irradiation and without any packaging, these azo-dye-based polarizers are extremely inert.

CONCLUSIONS

In summary, we have shown that the use of oriented blend films based on PVA and commercially available azo dyes may represent an attractive approach for the fabrication of low-cost UV sheet polarizers. We demonstrated that moderately stretched PVA films comprising a combination of Congo Red and Chrysophenine exhibit a pronounced optical dichroism. Initial
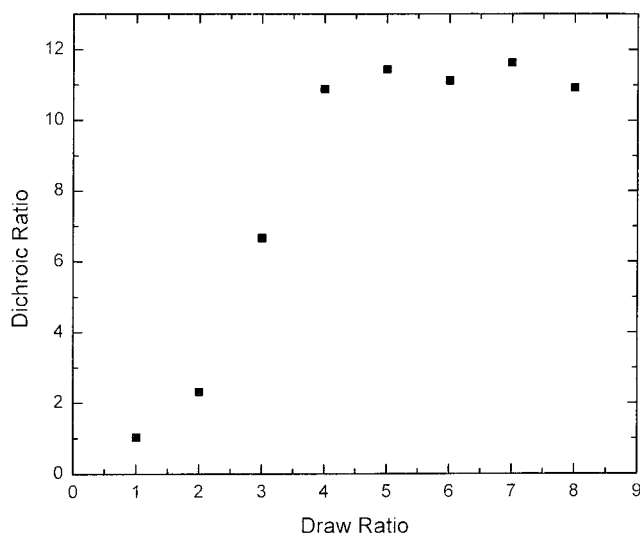
Figure 4 Dichroic ratio of oriented PVA films comprising 0.1% w/w of a combination of Congo Red and Chrysophenine (molar ratio of 1.4:1) as a function of draw ratio, measured at 365 nm.
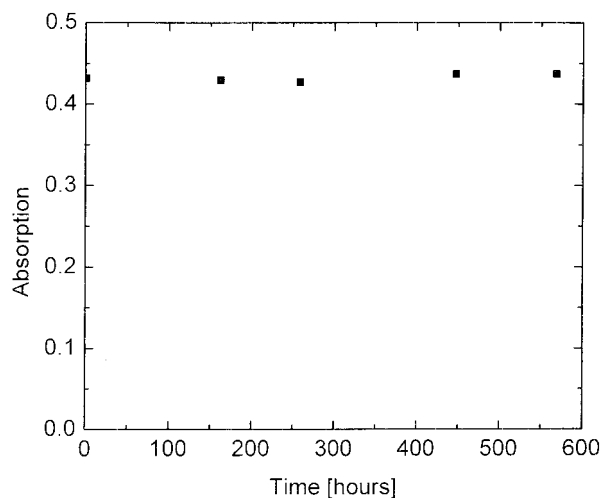
Figure 5 Development of the (isotropic) absorption of an oriented blend film (draw ratio, l/l_0, = 8), comprising 0.1% w/w of a combination of Congo Red and Chrysophenine (molar ratio of 1.4:1) in PVA, as a function of irradiation time. The unpackaged sample was exposed to light of a 365-nm UV lamp under ambient conditions.

experiments suggest that, even under rather harsh irradiation conditions and without any packaging, these azo-dye-based polarizers are surprisingly inert under simulated operating conditions.

A few critical remarks regarding the performance of the new materials seem to be appropriate. The optical anisotropy of the new elements at the absorption maxima of the dye combination, that is, in the visible regime, is appreciable, indicating that the chromophores indeed adopt a high degree of uniaxial orientation. However, as a result of the substantial bathochromic shift that the absorption of the investigated PVA/dye blend films shows when compared to that of the corresponding aqueous solution, the optical dichroism in the targeted near-UV-range is comparably low. As a result, a useful polarizing efficiency is achieved only at a high optical density and at the expense of reducing the single-piece transmittance. Clearly, it is desirable to improve this situation, and we plan to investigate alternative dye systems in the future.

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