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Optical Properties of Oriented Polymer/Dye Polarizers

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ABSTRACT: A theoretical framework is presented to describe the optical properties of polarizers produced by tensile deformation of semicrystalline polymers containing dichroic dyes. In the model it is assumed that orientation of both the host polymer and guest molecule occurs in the affine mode. The development of optical anisotropy with orientation is described using an aggregate model. The theory is employed to evaluate the optical characteristics of the polarizers, i.e., dichroic ratio, order parameter, polarizing efficiency, and single-piece transmittance. Good agreement is observed between theoretical predictions and experimental data produced in this work on oriented linear polyethylene/Sudan Red polarizing films. It is shown that the model is useful to estimate the limiting polarizing efficiency and single-piece transmittance of the polarizing films at hand.

Introduction

Several processes exist for the production of polymeric sheet polarizers, chiefly for use in the visible wavelength range.[1−9] These polarizers are widely employed in, for instance, liquid-crystalline display applications. In most of the aforementioned processes, semicrystalline polymers, such as poly(vinyl alcohol) and polyolefins, are oriented by tensile drawing at temperatures close to, but below, the melting temperature of the polymer;[1−9] dichroic chromophores are introduced in the oriented films either by chemical modification of the polymer or by incorporation of dichroic dyes in the films prior to or after drawing. In this manufacturing process, the dichroic chromophores appear to adopt the orientation of the polymer, and the films thus obtained exhibit the desirable characteristics of polarizers: i.e., the absorption of light is dependent on the polarization direction of the incident radiation.[1−9]

The performance of polymeric sheet polarizers is commonly expressed in terms of a variety of optical characteristics such as the dichroic ratio (R), order parameter (S), polarizing efficiency (PE), and single-piece transmittance (T_{sp}).[10−15] The dichroic ratio and order parameter are dependent solely on the optical characteristics and orientation of the chromophores. The polarizing efficiency and single-piece transmittance are relevant parameters for specific applications and are related to respectively the contrast ratio in transmittance between two parallel and two perpendicular polarizers and to the transmittance through a single polarizer.

The dichroic ratio and polarizing efficiency of a model system based on dye-containing oriented linear polyethylene, described in more detail hereafter, are plotted in Figure 1 as a function of the draw ratio of the films. The experimental data indicate that the dichroic ratio increases with increasing draw ratio, but, by contrast and seemingly contradictory, the polarizing efficiency decreases at high draw ratios.

In this study, a theoretical treatment is presented to describe the optical properties of polarizers based on oriented host polymer/dichroic dye systems. The principal objective of this work is to provide a simple theoretical framework for the development of a variety of optical characteristics of these polarizers and to analyze the above apparent discrepancy.

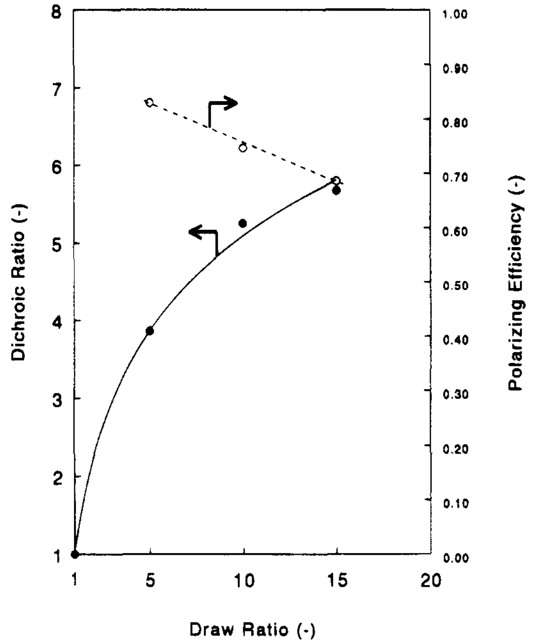

Figure 1. Dichroic ratio (●) and polarizing efficiency (○) as a function of draw ratio.

Theoretical Section

According to the pseudoaffine deformation scheme, the average orientation of statistical chain segments ($\langle\cos^2\theta\rangle$) with respect to the direction of [uniaxial] deformation is given by eq 1.[16] In eq 1, λ is the draw

$$\langle\cos^2\theta\rangle = \frac{\lambda^3}{\lambda^3 - 1} - \frac{\lambda^3}{(\lambda^3 - 1)^{3/2}}\arctan((\lambda^3 - 1)^{1/2}) \quad (1)$$

ratio and θ the angle between a statistical chain segment and the draw direction. It was shown previously that the pseudoaffine deformation scheme reasonably describes the development of orientation upon drawing of semicrystalline polymers.[17−19] Generally, it is assumed that a guest molecule, such as a dichroic

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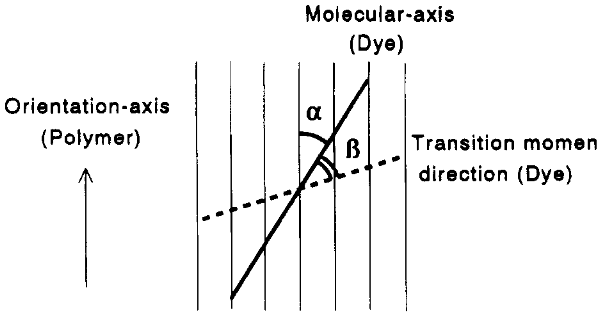

Figure 2. Orientation of the dye molecule with respect to the orientation of the polymer.

dye, adopts the orientation of the host polymer.[20-22] In other words, the development of the orientation of the dichroic dye during tensile deformation is taken to be identical to that of the host polymer, as is represented by eq 2, where the subscripts "dye" and "pol" refer to

$$\langle\cos^2\theta\rangle_{\text{dye}} = \langle\cos^2\theta\rangle_{\text{pol}} \qquad (2)$$

the dichroic species and the polymer, respectively. The probability for a certain transition to an exited state of a chromophore molecule is described by an electric dipole transition moment $\vec{\mu}$, which can be treated as a vector attached to the chromophore. The absorption intensity due to an electric dipole absorption process, of a set of chromophore molecules having all the transition moments oriented in the same direction, is proportional to the square of the scalar product between the electric field vector of light and the transition moment vector $\vec{\mu}$.[23] The absorption will be maximum when the light vector is polarized parallel to the transition moment and zero when perpendicular to it, and therefore this set of chromophores will have an infinite dichroic ratio, R. As a complicating factor, it should be noted, however, that the transition dipole of a chromophore is not necessarily parallel to its molecular axis[23,24] (Figure 2, angle β). In addition, in the present case of an oriented semicrystalline host polymer and a dispersed dichroic dye, the latter not necessarily adopts a molecular [crystallographic] orientation parallel to the polymer chains (Figure 2, angle α). For these reasons, even a system of perfectly aligned chromophores will have a finite dichroic ratio, R_0.[25] Unfortunately, the angles α and β are usually unknown which complicates the derivation of the optical properties from first principles.

In this study, it is therefore assumed that the present systems are comprised of optically transverse-isotropic elements, ignoring physical details like the angles α and β. The extinction coefficient tensor, ϵ_{ij}, of such an element is represented by eq 3, where the subscripts

$$\epsilon_{ij} = \begin{pmatrix} \epsilon_\perp & 0 & 0 \\ 0 & \epsilon_\perp & 0 \\ 0 & 0 & \epsilon_\parallel \end{pmatrix} \qquad (3)$$

"⊥" and "∥" denote the directions perpendicular and parallel to the axis of transverse isotropy of the elements.[23,24]

The macroscopic molar extinction coefficients ($E_\parallel$ and $E_\perp$) of an aggregate of optically anisotropic elements (where the subscripts "⊥" and "∥" now denote the directions perpendicular and parallel to the drawing direction) can be calculated from the extinction coefficient tensor ϵ_{ij} by a coordinate transformation from the microscopic frame to the laboratory frame, followed by an averaging procedure.[23,24] For fiber symmetry, this results in eqs 4 and 5,[26] where $\langle\cos^2\theta\rangle$ ($=1 - \langle\sin^2\theta\rangle$) is the average orientation of the elements with respect to the drawing direction.

$$E_\parallel = \langle\sin^2\theta\rangle\epsilon_\perp + \langle\cos^2\theta\rangle\epsilon_\parallel \qquad (4)$$

$$E_\perp = \frac{1}{2}(\langle\cos^2\theta\rangle + 1)\epsilon_\perp + \frac{1}{2}\langle\sin^2\theta\rangle\epsilon_\parallel \qquad (5)$$

Substitution of eq 1 in eqs 4 and 5 directly yields the relationships between the draw ratio, λ, applied to the guest–host system, and the macroscopic extinction coefficients ($E_\parallel$ and $E_\perp$).

The absorbance parallel and perpendicular to the direction of draw ($A_\parallel$ and $A_\perp$, respectively) can be calculated from eqs 4 and 5 using Lambert–Beer's law[27] (eqs 6 and 7). In eqs 6 and 7, d and c denote respectively

$$A_\parallel = E_\parallel c\, d \qquad (6)$$

$$A_\perp = E_\perp c\, d \qquad (7)$$

the specimen thickness (cm) and the concentration of dichroic dye (mol/L) in the host polymer.

The corresponding transmissions (T) are calculated using eqs 8 and 9.[27]

$$T_\parallel = 10^{-A_\parallel} \qquad (8)$$

$$T_\perp = 10^{-A_\perp} \qquad (9)$$

From the respective absorptions and transmissions, all relevant optical properties of the polarizer can be calculated. The equations for the dichroic ratio (R), order parameter (S), polarizing efficiency (PE), and single-piece transmittance (T_{sp}) are given in eqs 10–13.[15]

$$R = \frac{A_\parallel}{A_\perp} \qquad (10)$$

$$S = \frac{R-1}{R+2} \qquad (11)$$

$$\text{PE} = \frac{T_\perp - T_\parallel}{T_\perp + T_\parallel} \qquad (12)$$

$$T_{\text{sp}} = \frac{1}{2}(T_\parallel + T_\perp) \qquad (13)$$

Model Predictions

The material and experimental parameters in the equations above are (i) the extinction coefficient tensor of the optically anisotropic elements, (ii) the dye concentration, and (iii) the thickness of the polarizer. For illustrative purposes only, the following (arbitrarily chosen) values of these parameters are used to demonstrate some of the properties of the model:

$$\epsilon_\parallel = 100 \times 10^3\ [\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}]$$

$$\epsilon_\perp = 2.5 \times 10^3\ [\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}]$$

$$c = 2 \times 10^{-3}\ [\text{mol}\cdot\text{L}^{-1}]$$

$$d_0 = 0.5, 1, 2\ [\times 10^{-2}\ \text{cm}]$$

Here, d_0 is the initial thickness of the (unoriented) film prior to drawing. During tensile deformation, the

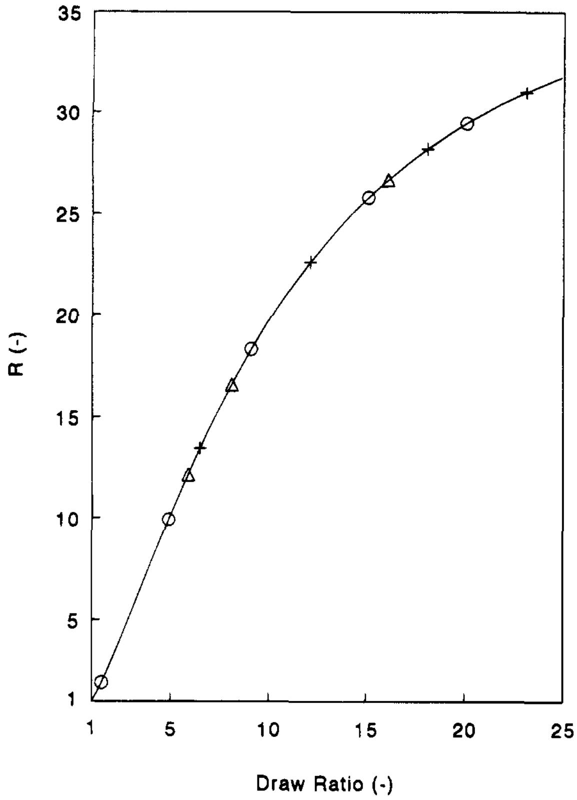

Figure 3. Dichroic ratio (R) as a function of the draw ratio and initial film thickness (d_0); (○) 0.005, (△) 0.01, (+) 0.02 cm.

values of $\epsilon_{\parallel}$, $\epsilon_{\perp}$, and c remain, of course, constant. By contrast, the thickness of the films decreases with increasing draw ratio. In the case of uniaxial drawing, assuming isotropic lateral contraction and deformation at constant volume (neglecting the volume change in the elastic region), the thickness of the film, d, is reduced with increasing draw ratio as:

$$d = \frac{d_0}{\lambda^{1/2}} \qquad (14)$$

The effect of decreasing thickness on the optical properties can now be calculated by substitution of eq 14 into eqs 8 and 9.

In Figure 3, the dichroic ratio is plotted as a function of the draw ratio. In accordance with expectations, it is found that the dichroic ratio increases with increasing draw ratio and is independent of the initial thickness of the films. The polarizing efficiency, however, passes through a maximum and decreases at high draw ratios (Figure 4). Moreover, the polarizing efficiency is strongly dependent on the original thickness of the films (Figure 4). Clearly, in contrast to the dichroic ratio, the polarizing efficiency is not normalized with respect to trivial parameters such as film thickness (and dye concentration).

The single-piece transmittance (T_{sp}) of drawn films is plotted in Figure 5 as a function of the draw ratio and initial film thickness. The data in this figure show that T_{sp} increases with increasing draw ratio and decreasing film thickness. The polarizing efficiency and single-piece transmittance appear to be mutually dependent and oppositely affected by variation of the film thickness. For instance, increasing the thickness, at a given draw ratio, enhances the polarizing efficiency (Figure 4) but simultaneously reduces the single-piece transmittance (Figure 5).

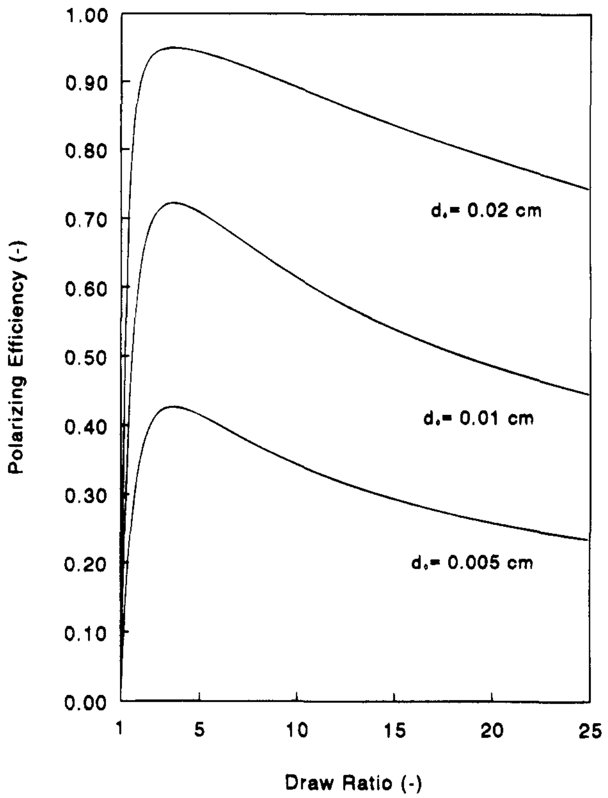

Figure 4. Polarizing efficiency (PE) as a function of the draw ratio and initial film thickness.

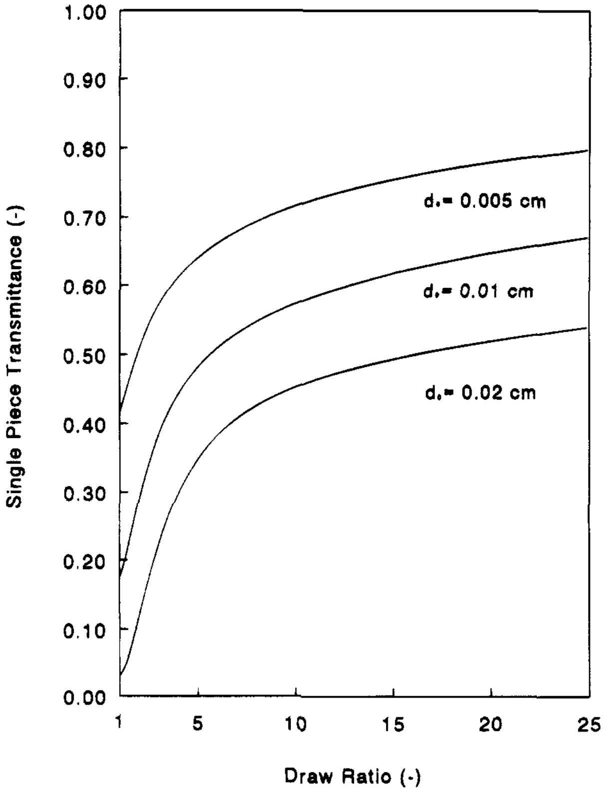

Figure 5. Single-piece transmittance (T_{sp}) as a function of the draw ratio and initial film thickness.

Most applications of polarizers demand the combination of a high polarizing efficiency and high single-piece transmittance. In Figure 6, the polarizing efficiency is plotted as a function of the single-piece transmittance at a constant draw ratio. This figure illustrates that the values of PE and T_{sp} can be varied within a wide

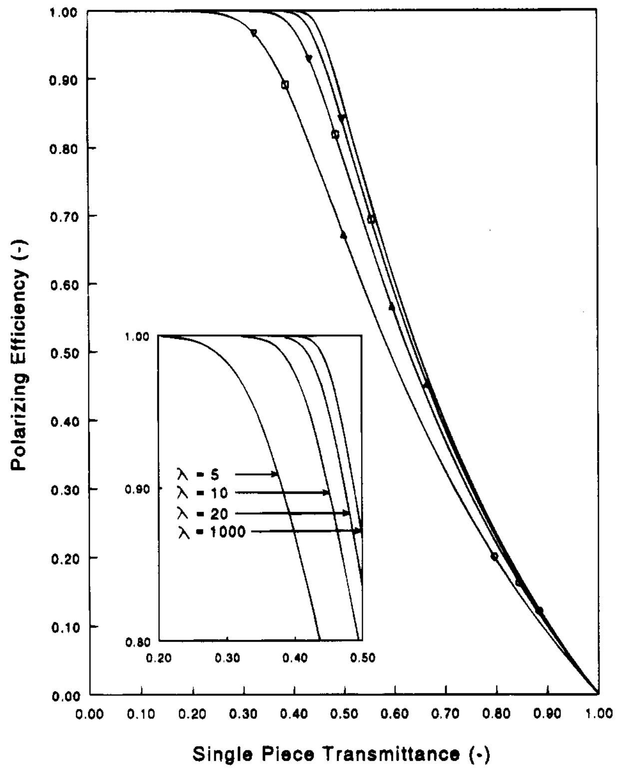

Figure 6. Polarizing efficiency (PE) as a function of single-piece transmittance (T_{sp}) at different draw ratios (λ): (○) $d_0 = 10^{-3}$ cm; (△) $d_0 = 4 \times 10^{-3}$ cm; (□) $d_0 = 7 \times 10^{-3}$ cm; (▽) $d_0 = 10^{-2}$ cm.

range simply by adjusting the film thickness (and/or dye concentration). Moreover, it is shown that, at a constant film thickness, the polarizing efficiency and single-piece transmittance are enhanced by increasing the draw ratio of the films.

Model Verification

a. Experimental Section. Linear polyethylene used in this work was Hostalen G.R. 7255P (Hoechst/Ruhrchemie, Germany; M_w = 350 000). A diazo dye (Sudan Red) was used (Aldrich, Germany).

Sudan Red was added to the polymer at a concentration of 0.2% w/w. The dichroic dye and the polymer were mixed in the melt at 180 °C in a Brabenber batch-scale mixing device for a period of 20 min. After mixing, films with a thickness of 0.1 and 0.07 mm were produced by compression molding at 180 °C for 15 min and subsequent quenching to room temperature.

Tensile drawing of the films was carried out at a temperature of 120 °C. The draw ratio was determined by measuring the displacement of ink marks printed onto the specimen prior to drawing.

To reduce surface scattering, the films were coated with a thin layer of paraffin oil and placed in between two glass slides. Absorption spectra in the visible wavelength range (400–800 nm) were measured with a double beam UV–vis spectrometer (Perkin-Elmer Lambda 3B). Two linear polarizers were placed in both the measuring and the reference beam. The coated sample was inserted in the measuring beam. Absorption spectra were recorded with the two polarizers positioned parallel and perpendicular, respectively, to the draw direction of the sample. A standard base-line correction was performed to correct the spectra for surface reflection, etc.[15,28,29]

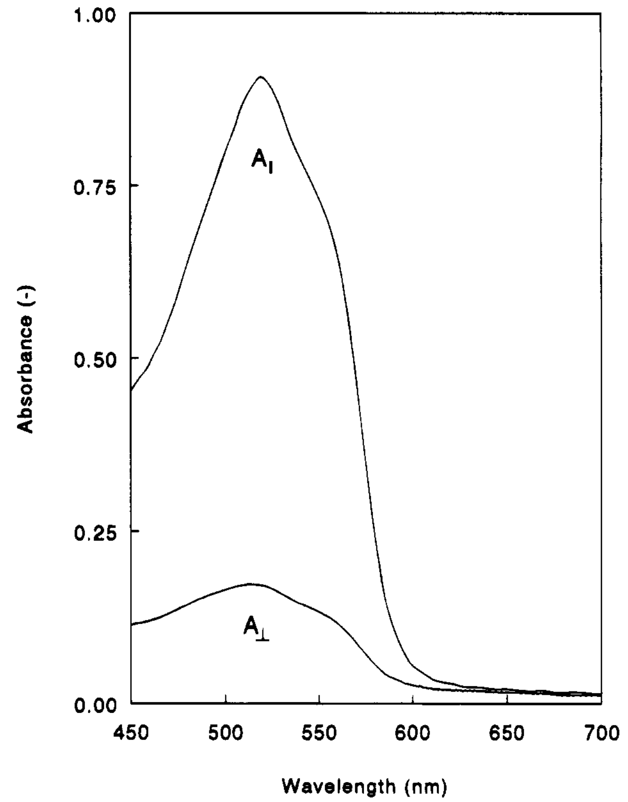

Figure 7. Absorption spectra of a drawn (λ = 10) HDPE–Sudan Red tape with incident light polarized parallel ($A_\parallel$) and perpendicular ($A_\perp$) to the direction of draw.

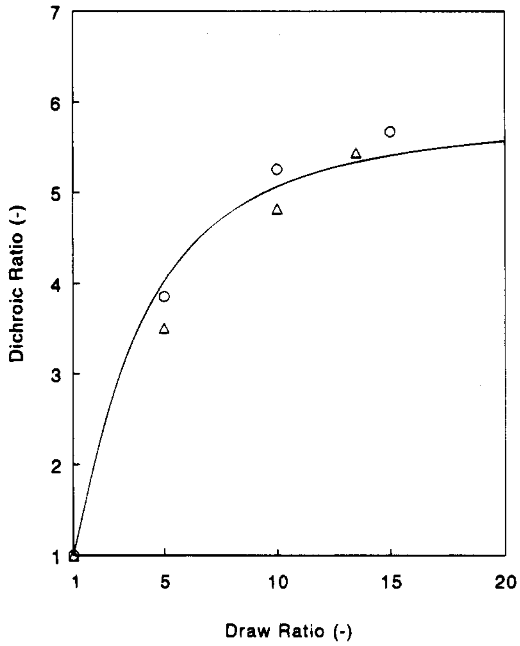

Figure 8. Dichroic ratio (R) as a function of the draw ratio and initial film thickness: (○) d_0 = 0.01 cm; (△) d_0 = 0.007 cm; (—) theoretical.

b. Results. In Figure 7, absorption spectra are presented of a drawn (λ = 10) HDPE–Sudan Red tape. The experimental values of the dichroic ratio, polarizing efficiency, and single-piece transmission, calculated from the absorption maximum of the dye (520 nm), are plotted in Figures 8–10 (open symbols). Comparison of the experimental data with the theoretical predictions in Figures 3–5 indicates that the general trends are correctly predicted. The absolute values, of course, deviate due to the arbitrary selection of the values for $\epsilon_\parallel$, $\epsilon_\perp$, d_0, and c in the previous section.

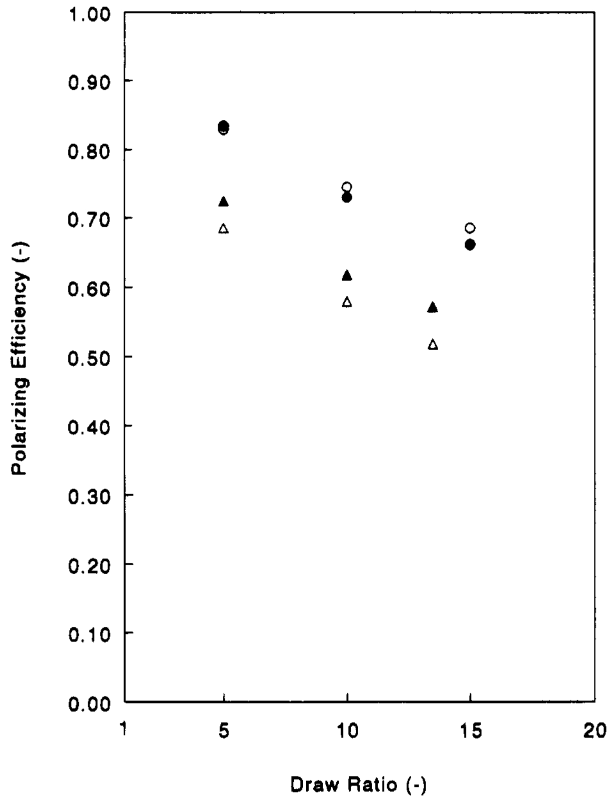

Figure 9. Polarizing efficiency (PE) as a function of the draw ratio and initial film thickness: experimental [(○) $d_0 = 0.01$ cm; (△) $d_0 = 0.007$ cm]; theoretical (●), $d_0 = 0.01$ cm; (▲) $d_0 = 0.007$ cm].

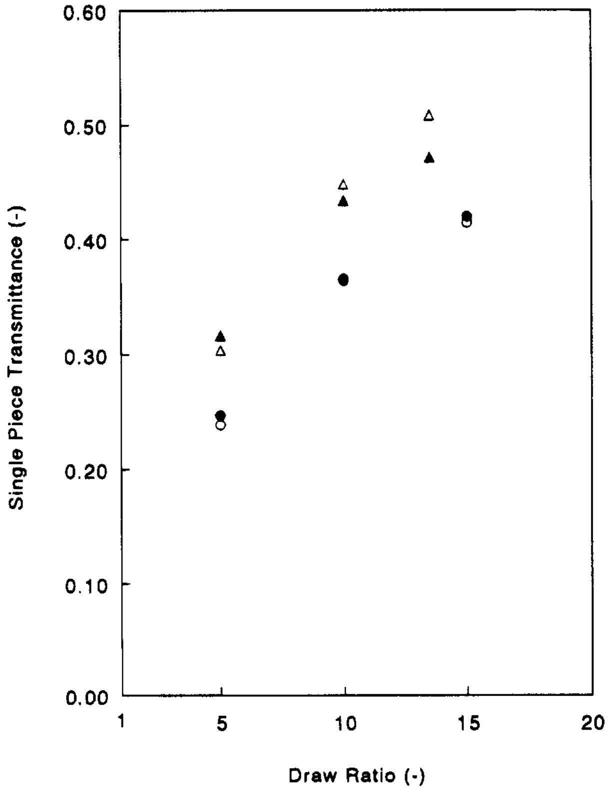

Figure 10. Single-piece transmittance (T_{sp}) as a function of the draw ratio and initial film thickness: experimental [(○) $d_0 = 0.01$ cm; (△) $d_0 = 0.007$ cm]; theoretical [(●) $d_0 = 0.01$ cm; (▲) $d_0 = 0.007$ cm].

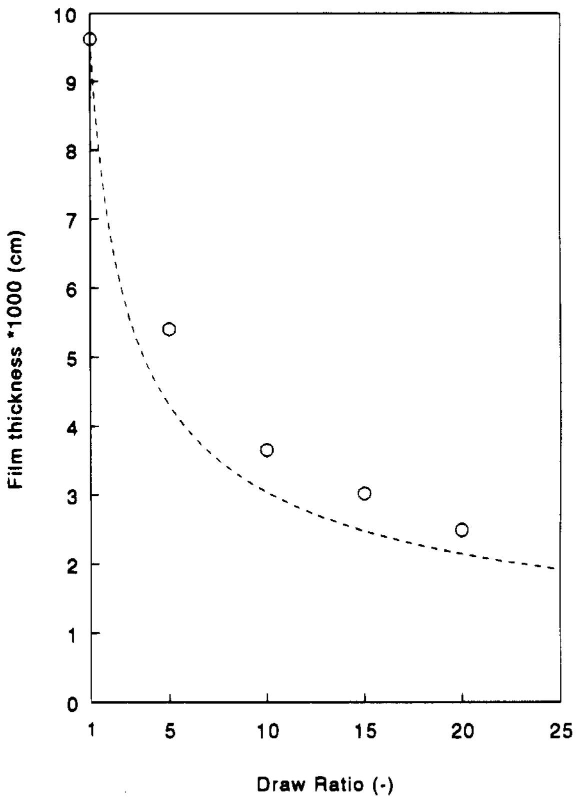

Figure 11. Film thickness after drawing: (○) experimental; (- - -) theoretical.

To obtain a more accurate description of the various characteristics of the polarizing films, the correct values of the above-mentioned parameters need to be substituted in the relevant equations. In the Theoretical Section it was discussed that the absolute values of $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ cannot simply be derived from first principles. Therefore, a rather simple experimental procedure is used to estimate the values of $\epsilon_{\parallel}$ and $\epsilon_{\perp}$. This method was first used by Ward et al. in modeling of the mechanical properties of drawn semicrystalline polymers.[24,30] It employs experimental data of an oriented aggregate for the estimation of the characteristics of the constituting elements. In this particular case, the absorptions ($A_{\parallel}$ and $A_{\perp}$) of a particular specimen are measured (here, with $d_0 = 0.1$ mm, $c = 0.2\%$ w/w, $\lambda = 10$), and the macroscopic extinction coefficients ($E_{\parallel}$ and $E_{\perp}$) are calculated using eqs 6 and 7. In this calculation one should, in principle, use eq 14 to calculate the thickness at $\lambda = 10$. However, it was observed that the thickness of the films after drawing deviates significantly from the values according to eq 14 (Figure 11). Invariably, the thickness of the drawn films was found to be above that expected. Therefore, the experimental values of the film thickness after drawing were used in the calculation of the macroscopic extinction coefficients ($E_{\parallel}$ and $E_{\perp}$) of the tape. From $E_{\parallel}$, $E_{\perp}$, and the average orientation ($\langle\cos^2\theta\rangle$; eq 1), the values of $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ are calculated using eqs 4 and 5. The values of $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ thus obtained are used to calculate the optical properties of drawn films with the above model. The results of the calculations are shown in Figures 8–10. A good agreement is observed between theoretical predictions and experimental data, which, in our view, strongly supports the validity of the present approach.

Discussion and Conclusions

In this work, a simple model was presented for the description of the optical properties of drawn semicrystalline polymers containing a dichroic dye. The model is based on the following assumptions: (i) the material is unoriented prior to drawing; (ii) deformation of the polymer and orientation of the dichroic dye occurs in an affine mode; (iii) the uniaxial drawn films possess fiber symmetry; (iv) the properties of the drawn systems can be described with an aggregate-type model. The validity of these assumptions has been verified previously in a large number of experimental and theoretical studies, chiefly related to mechanical properties of oriented polymers.[17,19] A good agreement between experimental data and theoretical predictions is observed. Although experimental verification of the theory was performed with only one oriented polymer/dichroic dye system, it is expected that it is equally applicable to other guest–host systems, provided that the principal assumptions above are met.

The main attribute of the present model is that the influence of a wide variety of experimental parameters, such as the draw ratio, dye characteristics, film thickness, and dye concentration, on the polarizer performance can be quantatively predicted. The apparent inconsistency in certain experimental observations, pointed out in the Introduction, is accurately predicted by the model. It is demonstrated that enhanced performance with respect to PE and T_{sp} can be achieved through proper optimalization of rather trivial parameters like film thickness and dye concentration. Moreover, it is shown that the optimum balance between polarizing efficiency and single-piece transmittance can be predicted for specific systems, which should provide for a useful tool in the development of polymeric sheet polarizers.

A few critical remarks regarding the presented model are in order. First, it is common practice in the determination of the polarizing efficiency and single-piece transmittance to perform an averaging procedure over the entire wavelength range of interest.[15] The calculations and experimental data in this study are, by contrast, limited to a single wavelength (the absorption maximum of the dichroic dye). Second, in the present calculations, background scattering due to, for instance, light reflection at the polymer surfaces is not included. In the absorption measurements, the background scattering is eliminated by standard base-line corrections. Usually, these base-line corrections are not performed, and consequently discrepancies may arise upon comparison of the present theory with experimental data in the literature. As a final comment, the model was derived for polymeric sheet polarizers produced by uniaxial deformation. In industrial processes, polymer films often are constrained in the lateral direction during drawing,[31] which results, of course, in deviations from the simple uniaxial deformation scheme analyzed above. This variation can be incorporated in the model but is considered outside the scope of the present work.

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(26) Verification of eqs 4 and 5 can be performed by substitution of these equations in the Herman's orientation function (f_h):[25,32,33]

$$f_h = \frac{(E_\parallel/E_\perp) - 1}{(E_\parallel/E_\perp) + 2}\,\frac{(\epsilon_\parallel/\epsilon_\perp) + 2}{(\epsilon_\parallel/\epsilon_\perp) - 1}$$

This substitution correctly results in the well-known expression for the Herman's orientation function:[25,31,32]

$$f_h = \frac{3\langle\cos^2\theta\rangle - 1}{2}$$

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