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Orientation of Dichroic Dyes in Ultra-Drawn Polyethylenes

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Introduction

Solid state drawing has been used extensively to modify and/or to enhance properties of semi-crystalline, flexible polymers [1,2]. For instance, commercial H-sheet polarizers are produced from drawn poly(vinylalcohol) (PVAI) [2] by absorbing iodine in a pre-stretched PVAL sheet. During the absorption and drying procedure the iodine molecules align parallel to the host macromolecules and anisotropic optical properties in the visible wavelength range (400-800 nm) are obtained.

The maximum attainable draw ratio of PVAI is relatively low and consequently the degree of orientation of the host-polymer is limited [3]. Remarkably, the relation between orientation of the host-polymer and guest-molecule has received little attention in the past, despite its commercial relevance. Intuitively, one would expect that the orientation of the host-polymer determines, at least to some extent, the visible light dichroism of polarizers. In this study, the orientation of dichroic dyes in ultra-drawn polyethylenes is discussed. It is attempted to utilize the excellent solid state drawing characteristics of linear polyethylenes for the orientation of dichroic dyes.

Experimental

The polyethylene grades used in this study were Hostalen Gur 412 and Hostalen G.R. 7255 P (Hoechst/Germany) with a weight average molecular weight of respectively 2×10^6 and 4×10^5 g/mol. A anthraquinone dye and a trisazo dye were added to both polymers in a concentration of 2 % w/w. Melt-crystallized and solution-cast films were produced from the mixtures as described previously [1,3]. Solid state drawing of the films was performed on thermostatically controlled hot-shoes at a drawing temperature of 120 °C. The draw ratio was determined from the displacement of ink-marks.

To eliminate surface scattering during the optical measurements, a few droplets of ethylene glycol were placed on the drawn films. The films were covered with glass slides to yield a sandwich configuration.

Transmission and absorption measurements in the visible wavelength range were performed on a Perkin Elmer Lambda 9 instrument. In the polarized absorption measurements, two linear polarizers were placed parallel in the measuring and reference beam and a background correction was executed. A sample was inserted in the measuring beam and absorption spectra were measured as a function of the angle between the polarization direction of the incident light and the drawing direction. From these measurements the dichroic ratio (R) was calculated using equation 1 [3]:

$$R = A_{\text{par}}/A_{\text{perp}} \quad (1)$$

In equation 1, A_{par} and A_{perp} are the absorption, at a given wavelength, measured respectively parallel and perpendicular to the drawing direction.

The Young's modulus and birefringence of drawn films were measured according to standard procedures [1].

Results and Discussion

In figure 1, transmission spectra in the visible wavelength range (400-800 nm) of solution-cast, drawn UHMW-PE films are compared. It is shown that drawn polyethylene films are highly transparent (figure 1) if surface scattering is reduced by application of a coating. A transmission spectrum of a drawn UHMW-PE film containing 2 % w/w of an anthraquinone dye is also shown in figure 1. The absorption of the anthraquinone dye is between 420-600 nm and, consequently, the transmittance of the dye is reduced in this wavelength region. The transmittance of the drawn films above 600 nm remains high which indicating that the transparency of the dye-containing, drawn films is preserved.

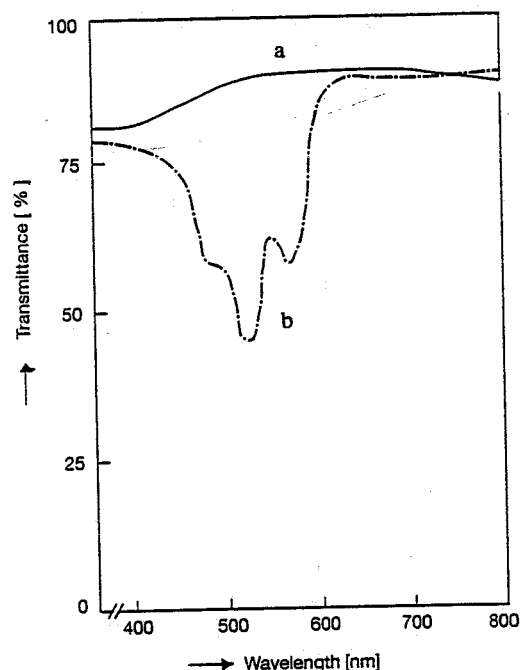


Figure 1: Transmission spectra of UHMW-PE films in the visible wavelength range (Drawing temperature=120 °C, Draw ratio=30).
a) Coated film without dichroic dye
b) Coated film with 2 % w/w anthraquinone dye.

In figure 2, polarized absorption spectra are shown of the drawn UHMW-PE films. The absorption spectra were recorded as a function of the angle (θ) between the drawing direction and the polarization direction of the incident light. The measurements show that the light absorption is strongly dependent on the polarization direction of the incident light which indicates that the films are highly anisotropic with respect to visible light absorption.

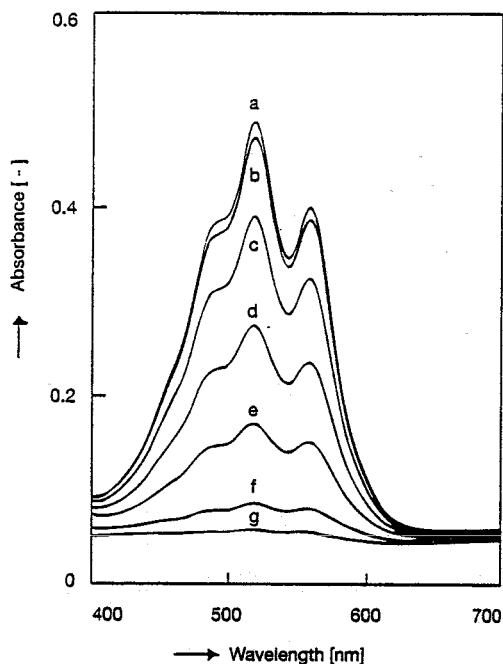


Figure 2 : Polarized absorption spectra in the visible wavelength range of drawn UHMW-PE films (2 % w/w dichroic dye, Draw ratio=30, Drawing temperature=125 °C). a) $\theta=0^\circ$, b) $\theta=15^\circ$, c) $\theta=30^\circ$, d) $\theta=45^\circ$, e) $\theta=60^\circ$, f) $\theta=75^\circ$, g) $\theta=90^\circ$

The dichroic ratio of dye-containing, solution-cast drawn films is plotted in figure 3 as a function of the draw ratio. The dichroic ratio of the films systematically increases with increasing draw ratio and high dichroic ratios, up to 30, are obtained.

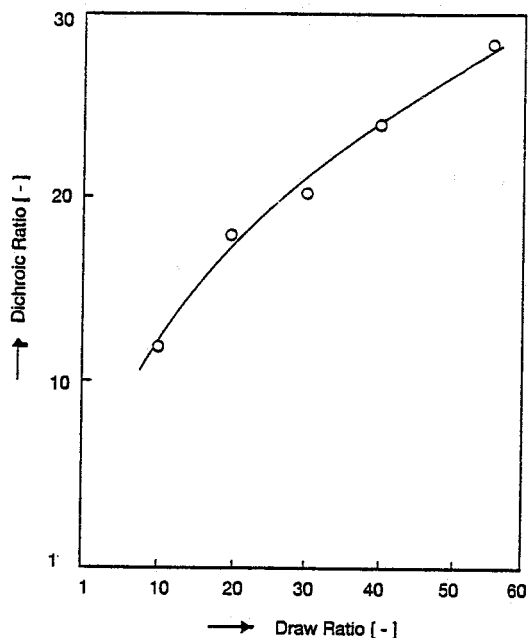


Figure 3 : Dichroic ratio of drawn UHMW-PE films (2 % w/w anthraquinone dye) as a function of the draw ratio (Drawing temperature=120 °C)

In figure 4, the dichroic ratio of drawn films is plotted as a function of the Young's modulus and birefringence. A linear relationship is observed between the dichroic ratio, Young's modulus and birefringence.

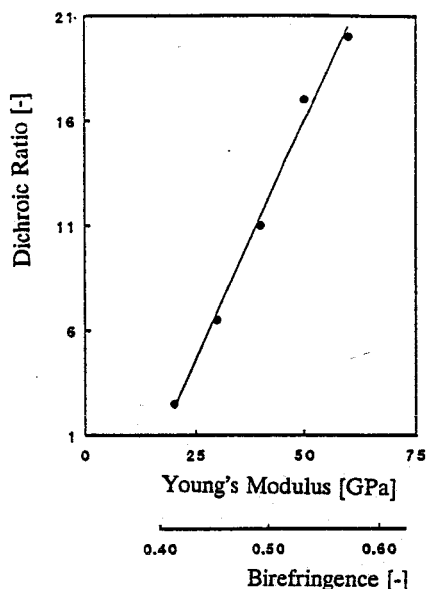


Figure 4 : Dichroic ratio of melt-crystallized polyethylene films (2 % w/w trisazo dye, Drawing Temperature=120 °C) as a function of Young's modulus and birefringence.

The Young's modulus and birefringence of drawn, semi-crystalline polymers are a unique function of the draw ratio independent of crystallization history and molecular weight of the polymer [1]. The experimentally observed correlation between the dichroic ratio, Young's modulus and birefringence illustrates that the orientation of the guest-molecule is directly linked to the orientation and draw ratio of the host-polymer. Moreover, this indicates that the enhanced drawability of linear polyethylenes, in comparison with PVAI films, can indeed be used effectively for the orientation of guest-molecules.

It was shown that polarizers with high transparency and high level of optical anisotropy can be produced from drawn polyethylene films. Apart from a high transparency and dichroism, the polyethylene polarizers may have additional advantages in comparison with PVAI polarizers. For instance, the durability of PVAI polarizers in a humid environment is rather poor and limiting in some applications. Polyethylene polarizers are hydrophobic and, consequently, an enhanced durability in a humid environment is expectable.

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