Transparency and dichroism of ultra-drawn UHMW-PE films in the visible wavelength range

C. Bastiaansen*†‡, H.-W. Schmidt§, T. Nishino†¶ and P. Smith§
** DSM Research, PO Box 18, 6160 MD Geleen, The Netherlands*
† Department of Polymer Chemistry, Eindhoven University of Technology, PO Box 513, 6500 MB Eindhoven, The Netherlands
§ Materials Department, College of Engineering, University of California at Santa Barbara, Santa Barbara, CA 93106, USA
¶ Department of Applied Chemistry, Kobe University, Rokko, Nada 657, Kobe, Japan
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The optical properties in the visible wavelength range (400–800 nm) of solution-cast, ultra-drawn, ultra-high-molecular-weight polyethylene (UHMW-PE, $\bar{M}_w > 10^6\,\mathrm{g\,mol^{-1}}$) films were investigated. UHMW-PE films, drawn 30 times at 125°C, possess a rather low transmittance (40–60%) in the visible wavelength range. However, highly transparent films with a transmittance exceeding 90% are obtained by applying a surface coating to the films. Dichroism in the visible wavelength range can be generated in drawn UHMW-PE films by incorporating dichroic dyes. Certain dichroic dyes were found to orient during solid-state drawing. Dichroic UHMW-PE films with a dichroic ratio of 30 and an order parameter of 0.91 were produced.

(Keywords: polyethylene; ultra-drawing; transmittance)

Introduction

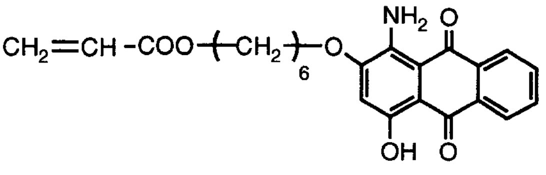
The drawing behaviour of semicrystalline, flexible polymers in the solid state has been investigated extensively in the past[1–7]. The main objective of these studies was to generate a high degree of chain orientation and extension in order to approach the theoretical modulus and strength of polymers[1–7]. A variety of techniques was developed to produce high modulus and high strength structures. For instance, with the so-called gel-spinning process[6,7], ultra-high-molecular-weight polyethylene (UHMW-PE, $\bar{M}_w > 10^6\,\mathrm{g\,mol^{-1}}$) fibres can be produced, possessing a Young's modulus and tensile strength of, respectively, >150 GPa and >4 GPa. Solid-state drawing was also used to modify other properties of semicrystalline, flexible polymers. It was shown that solid-state drawing enhances, for example, the barrier properties[8,9], thermal conductivity[8,10,11], electrical conductivity[12,13] and chemical resistance[8] of semicrystalline polymers. More recently, the orientation of macromolecules incorporated as guests in solution-processed, drawn UHMW-PE has received considerable attention[14–16]. In this approach a second polymer is added to solution-cast/spun fibres or films in order to introduce an additional property such as electrical conductivity. Solid-state drawing was subsequently used to orient the host and guest polymer and both the mechanical and the electrical properties were enhanced.

The orientation of low-molecular-weight guest molecules in drawn semicrystalline polymers has been used to modify the optical properties of polymers in the visible wavelength range. For example, commercial polarizers are produced from drawn poly(vinyl alcohol) (PVAl) films[17,18]. H-sheet polarizers are produced by absorbing iodine in a pre-stretched PVAl sheet. Relaxation of orientation of the host polymer, during dipping of the PVAl sheet into the iodine solution, is prevented by fixing the PVAl film to a substrate such as cellulose acetate. During the absorption and drying procedure, the iodine molecules align parallel to the host macromolecules and anisotropic optical properties in the visible wavelength range are obtained.

The maximum attainable draw ratio of PVAl is relatively low compared to solution-cast UHMW-PE, and consequently the attainable degree of orientation of the host polymer is limited[19,20]. 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 PEs is discussed[20]. An attempt is made to exploit the excellent solid-state drawing characteristics of linear PEs for the orientation of dichroic dyes. Preliminary results on the optical transparency and the attainable dichroic ratios will be presented.

Experimental

The UHMW-PE grade used in this study was Hostalen Gur 412 (Hoechst, Germany) which has a weight-average molecular weight of approximately $2 \times 10^6\,\mathrm{g\,mol^{-1}}$. The dichroic dye (BASF, Germany) was a red anthraquinone dye with a melting temperature of 119°C and the following chemical structure:



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‡ To whom correspondence should be addressed

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The anthraquinone dye was dissolved in xylene (0.03% w/v) at room temperature. Subsequently, 1.5% w/v UHMW-PE powder was added to the solution and the mixture was degassed at room temperature. A homogeneous solution was prepared by dissolving the polymer at 130°C. The solutions were cast and quenched to room temperature. Subsequently, the solvent was evaporated at ambient conditions. Dry UHMW-PE films containing approximately 2% w/w of the dichroic dye were obtained.

Ultra-drawing of the dried, solution-cast UHMW-PE films was performed on thermostatically controlled hot shoes at 125°C. The draw ratio was determined by measuring the displacement of ink-marks.

To avoid surface scattering during the optical measurements, a few drops of ethylene glycol were placed on the surface of the drawn films. The films were sandwiched between two glass slides. Transmission spectra of drawn films were measured with a Perkin–Elmer Lamda 9 instrument. The transmittance was measured in the wavelength range of 400–800 nm. Polarized absorption spectra were obtained with a Perkin–Elmer Lamda 9 instrument. Two linear polarizers were placed in the measuring and reference beams and a background correction was executed. The sample was inserted in the measuring beam and, by rotating the sample, the absorption of the dichroic dye was maximized. After recording an absorption spectrum, the sample was rotated over a preset angle and additional absorption spectra were taken.

Polarized optical micrographs were recorded at a magnification of 50×. Micrographs of drawn UHMW-PE films containing the dichroic dye were taken with the polarization direction of the incident light parallel and perpendicular to the drawing direction.

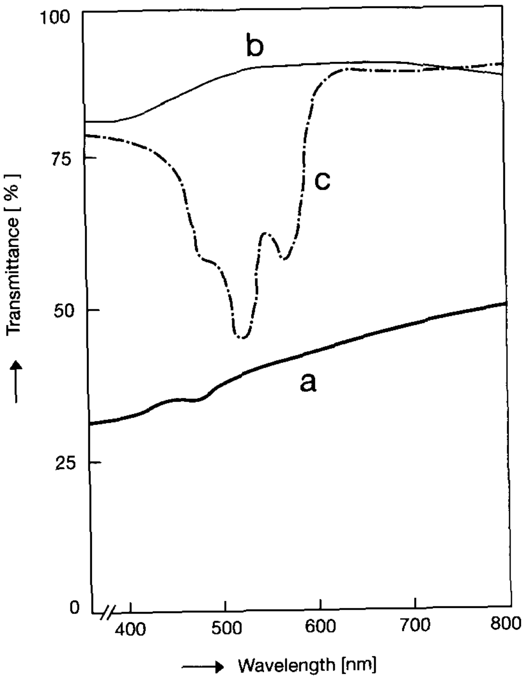

Figure 1 Transmission spectra of UHMW-PE films in the visible wavelength range (draw ratio 30, draw temperature 125°C): a, as-drawn film without dichroic dye; b, coated film without dichroic dye; c, coated film with 2% w/w anthraquinone dye

Results and discussion

In *Figure 1*, transmission spectra in the visible wavelength range (400–800 nm) of solution-cast, drawn UHMW-PE films are shown. The films were drawn at 125°C to a draw ratio of 30 and had a thickness of approximately 90 μm. The transmittance of the as-drawn UHMW-PE films is relatively low (spectrum a). The transmittance is drastically enhanced by coating with a low viscous fluid such as ethylene glycol (see Experimental section) and films with a high transmittance are obtained (spectrum b). Solution-cast, drawn UHMW-PE films and fibres possess a highly fibrillar structure[21]. The drastic improvement in transmittance upon coating indicates that light scattering takes place mainly at the film surface. The internal fibrillar structure hardly influences the optical properties and, as a consequence, highly transparent films are obtained if surface scattering is suppressed by applying an appropriate coating. A transmission spectrum of a drawn, ethylene glycol coated UHMW-PE film containing 2% w/w of a red anthraquinone dye is also shown in *Figure 1* (spectrum c). The absorption of the dye is around 420–600 nm and, consequently, the transmittance of the drawn films is reduced by the absorption in this wavelength region. The transmittance of the drawn films above 600 nm remains high, which indicates that the high transparency of the drawn films is preserved after incorporation of dichroic dye.

The anthraquinone chromophore of the dichroic dye is aligned in the drawn films and generates optical anisotropy in the visible wavelength range. In *Figure 2*, polarized optical micrographs of dye-containing drawn UHMW-PE films are shown. The micrographs are taken with the polarization direction of the incident light perpendicular (a) and parallel (b) to the drawing direction. A substantial difference in colour intensity is observed, which indicates that the dichroic dye is oriented after drawing of the UHMW-PE films.

Polarized absorption spectra were recorded in order to quantify the visible light dichroism of the drawn UHMW-PE films (*Figure 3*). 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 which indicates, once more, that the films are highly anisotropic with respect to visible light absorption.

The dichroic ratio (R) of the films can be calculated from the polarized absorption measurements using equation (1)[22–26]:

$$R = A_{\mathrm{par}}/A_{\mathrm{perp}} \qquad (1)$$

where A_{par} and A_{perp} are the absorptions at a given wavelength (520 nm) measured, respectively, parallel and perpendicular to the drawing direction. The order parameter (S) of the dye can be calculated with equation (2)[23–26]:

$$S = [R-1]/[R+2][R_0+2]/[R_0-1] \qquad (2)$$

where R_0 is the dichroic ratio of a perfectly oriented dichroic dye. The term $[R_0+2]/[R_0-1]$ is a correction factor which is determined by the transition moment of the dichroic dye. The R_0 value of the anthraquinone dye used in this study is not known and therefore the correction factor was omitted in the calculations of the order parameter (equation (3)). This results in a systematic

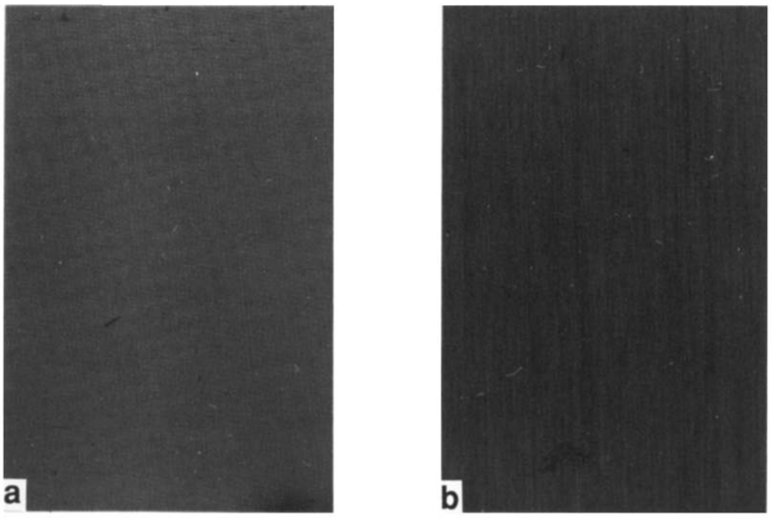

Figure 2 Optical micrographs of drawn UHMW-PE films (magnification 50×) (2% w/w dichroic dye, draw ratio 30, draw temperature 125°C): polarization direction of incident light perpendicular (a) and parallel (b) to the drawing direction

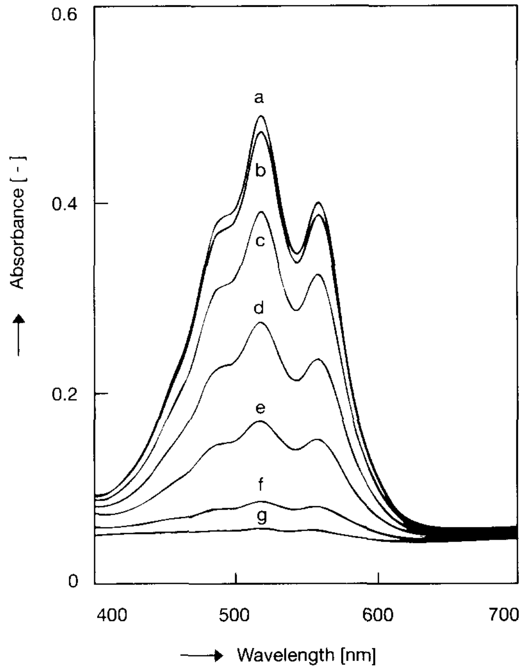

Figure 3 Polarized absorption spectra in the visible wavelength range of drawn UHMW-PE films (2% w/w dichroic dye, draw ratio 30, draw temperature 125°C) as a function of θ: a, 0°; b, 15°; c, 30°; d, 45°; e, 60°; f, 75°; g, 90°

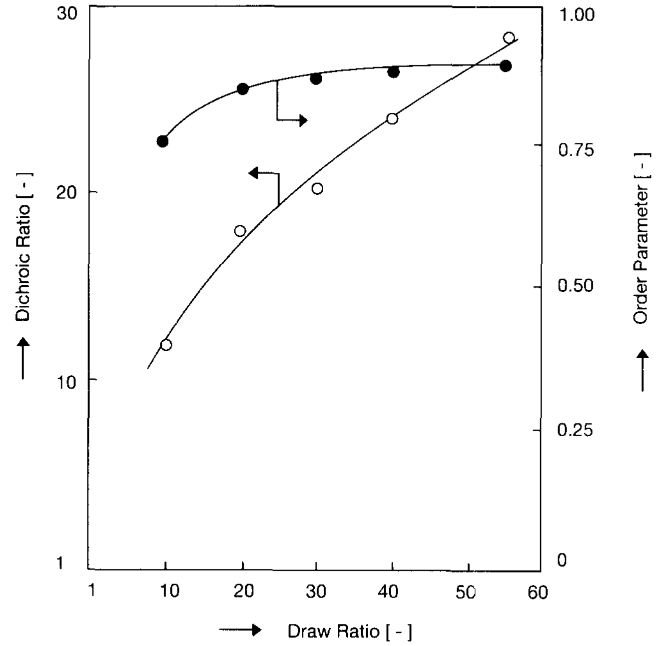

Figure 4 Dichroic ratio (○) and order parameter (●) of drawn UHMW-PE films (2% w/w dichroic dye, draw temperature 125°C) as a function of draw ratio

underestimation of the order parameters.

$$S=[R-1]/[R+2] \tag{3}$$

In *Figure 4*, the dichroic ratio and order parameter of dye-containing, solution-cast, drawn films are plotted as a function of the draw ratio. It is shown that the dichroic ratio increases systematically with increasing draw ratio and that high dichroic ratios up to 30 are obtained, which corresponds to an order parameter of 0.91. The dichroism of the same anthraquinone dye in macroscopically oriented nematic and smectic glasses of side-chain liquid crystal polymers was studied previously[27,28]. Maximum dye order parameters of 0.56 and 0.79 were found in nematic and smectic glasses, respectively. A comparison with the results of this study reveals that the enhanced orientation of solution-cast, drawn UHMW-PE films results in far superior dye order parameters.

In summary, the results of these investigations demonstrate that films with a high transmittance and a high level of optical anisotropy in the visible wavelength range can be produced from solution-cast, drawn UHMW-PE films. Apart from high transparency and dichroism, the UHMW-PE polarizers may have some additional advantages in comparison with PVAl polarizers. For instance, the durability of PVAl polarizers in a humid environment is rather poor, which is a severe limitation in some applications. UHMW-PE polarizers are hydrophobic and, consequently, enhanced durability is expected, especially in a humid environment[29].

A variety of other issues concerning drawn, dichroic

UHMW-PE films, such as the orientation mechanism of the dichroic dye and the relation between orientation of host polymer and guest molecule were hardly discussed. These topics are the subjects of ongoing experiments and will be discussed in future papers.

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