Evaluation of Orientation in Vinyl Alcohol–Ethylene Copolymer Films by Means of Infrared Dichroism and Birefringence

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ABSTRACT: Coupled measurements of birefringence and IR dichroism of drawn films of vinyl alcohol–ethylene copolymers have led to a value of around 46° for the angle α between the dipole moment vector of the IR band at 610 cm^{-1} and the chain axis. The increase of the second moment of the orientation function is well fitted to the pseudoaffine scheme of deformation. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 791–796, 1997

Key words: vinyl alcohol–ethylene copolymers; films orientation; infrared dichroism; birefringence

INTRODUCTION

The drawing of a semicrystalline polymer usually produces a fibrous material with an anisotropy of physical properties and this anisotropy is closely connected with the orientation of chains in both crystalline and amorphous regions. At small draw ratios, the chains in the crystal lattice are almost completely oriented in the draw direction, and the orientation only slightly increases with further drawing. In amorphous regions, the chain orientation is much less perfect but increases steadily over the whole range of the drawing process.

Several techniques for the evaluation of the orientation exist: X-ray diffraction, birefringence, sonic modulus, polarized fluorescence, broadline NMR, UV and infrared dichroism, and polarized Raman spectroscopy.[1,2] Among these techniques for measuring the orientation, birefringence and infrared dichroism provide information on the sec-

ond moment of the orientation function. Birefringence, Δn, is a measure of the overall molecular orientation of a uniaxially stretched polymer and has been extensively used for this purpose.[1,2] It is defined as the difference between the refractive indices in the stretch direction and that one perpendicular to the stretching. If additivity of the polarizabilities for the molecular aggregates composing the partially oriented polymer is assumed, and the Lorentz–Lorenz equation is used to obtain the refractive indices, the birefringence is given by the equation

$$\Delta n = \Delta n_{\max}(3\,\overline{\cos^2 \theta} - 1)/2 \qquad (1)$$

where $\Delta n_{\max}$ is the maximum birefringence at full orientation characteristic of the polymer, θ is the angle between the chain axis and the stretch direction, and $(3\cos^2\theta - 1)/2$ is the orientation function, sometimes called the Hermans orientation function. Moreover, infrared spectroscopy is an attractive method of deducing the chain orientations using specific vibrations, in which there are differences in the orientation of the transition moment vectors of the absorbing molecular groups relative to the direction of stretching. If

the angle α between the transition moment vector and the chain axis is known, then the dichroic ratio can be used to evaluate the average orientation of this axis.[3–5] But if this angle α is unknown, it is possible to calculate it from other experimental methods for determining the overall orientation, after evaluating the dichroic ratio, R. R values can be obtained by dividing the infrared absorbances measured at parallel ($A_\parallel$) and perpendicular ($A_\perp$) directions with respect to the stretching axis and each absorption band will display R values which will increase or decrease as the draw ratio increases. The relationship between the second moment of the orientation function, $\langle P_2(\cos\theta)\rangle$, and the dichroic ratio is[3–6]

$$\langle P_2(\cos\theta)\rangle = (3\,\overline{\cos^2\theta} - 1)/2$$

$$= \frac{R - 1}{R + 2}\frac{R_0 + 2}{R_0 - 1} \quad (2)$$

where R_0 is $2\cot^2\alpha$ and α is the angle between the dipole moment vector of the vibration and the chain axis.

By using coupled birefringence and infrared dichroism measurements, it is possible to study the influence of composition, crystallization conditions, draw ratio, and strain rate on the observed overall orientation in three vinyl alcohol–ethylene (VAE) copolymers. These VAE copolymers, with high molar fraction values of the former component, are being presently used as barrier layers and this application makes necessary a quick evaluation of the orientation in the stretched films, which determines their properties, including the mechanical ones. For instance, the storage modulus at room temperature (obtained from dynamic mechanical measurements) of drawn VAE copolymers (draw ratio equal to 4) in the stretching direction is three times higher than their storage modulus in the transverse direction and around four times higher than the same parameter in the diagonal (45°) direction.[7]

EXPERIMENTAL

Three commercially available samples of VAE copolymers, VAE-1, VAE-2, and VAE-3, were used. Table I shows the composition in vinyl alcohol determined using ^{1}H- and ^{13}C-NMR spectroscopies. Sheet specimens were obtained as films by compression molding in a Collin press between

Table I   Vinyl Alcohol (VAL) Composition of VAE Copolymers

| Copolymer | Composition (f_{VAL}) | | |
	Nominal	^{1}H-NMR	^{13}C-NMR
VAE-1	0.71	0.78	0.77
VAE-2	0.68	0.75	0.72
VAE-3	0.56	0.63	0.62

hot plates (210°C) at a pressure of 2.5 MPa for 15 min.

Each one of the VAE samples was crystallized under two different conditions (Q and S). The first treatment, Q, consisted of fast cooling between plates cooled with water at 10°C, after melting in the press. The S specimens were slowly cooled from the melt at a rate of ~ 2°C min^{-1}.

Samples for infrared and birefringence measurements of the three copolymers were cut and uniaxially stretched in an Instron tensile testing machine (at 80°C for infrared analysis and at 23, 40, and 80°C for birefringence) and at two different draw rates: 0.5 and 10 cm min^{-1}. The draw ratio was defined as $\lambda = l/l_0$ (l_0 is the initial length, and l, the final length after drawing) and measured from the displacement of ink marks printed on the sample before stretching.

Birefringence was measured at a wavelength of 546 nm using an Amplival Pol D microscope fitted with a rotary Ehringhaus compensator. The thickness of the sample was measured with a micrometer at the same portion of the microscope observation.

The polarized spectra were recorded using a Nicolet 520 Fourier transform infrared spectrometer. The polarization of the infrared beam was obtained by the use of a Specac gold wire-grid polarizer. To eliminate the effects of machine polarization, the sample axis was placed at −45° position with respect to the spectrometer slit and the polarizer axis was oriented with its axis at −45 and +45°. Infrared dichroism was calculated from the dichroic ratio previously defined, using the absorbances at the absorption maximum.

RESULTS AND DISCUSSION

To evaluate the orientation function given by the birefringence measurements, $\langle P_2(\cos\theta)\rangle$, it was necessary to calculate the maximum birefrin-
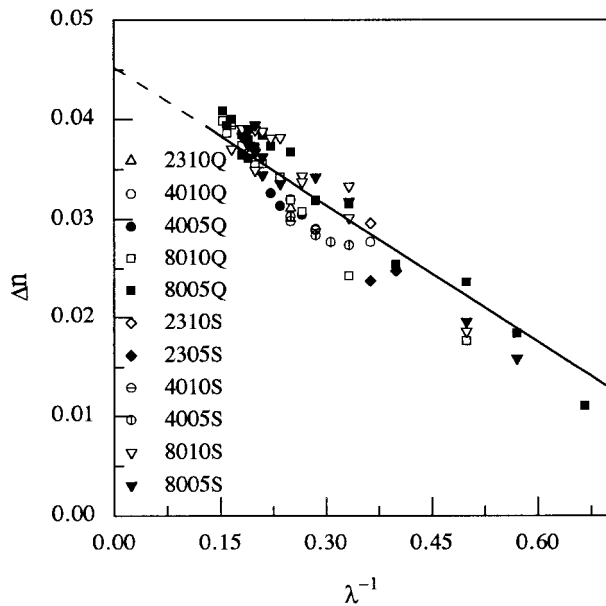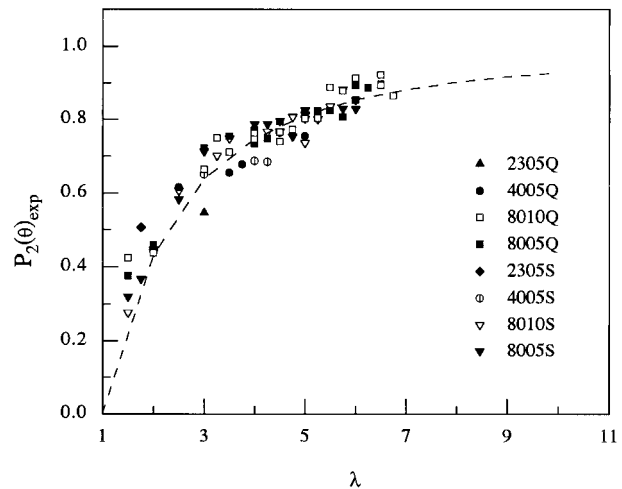
Figure 1 Maximum birefringence value of VAE-2, obtained by extrapolating different stretched specimens. The two first numbers of the code refer to the stretching temperature (°C), the other two, to the strain rate (cm min^{-1}); and Q or S, to crystallization conditions.

Figure 2 Experimental orientation function values for VAE-3 specimens. The dashed line corresponds to the pseudoaffine deformation scheme (for specimens codes, see Fig. 1).
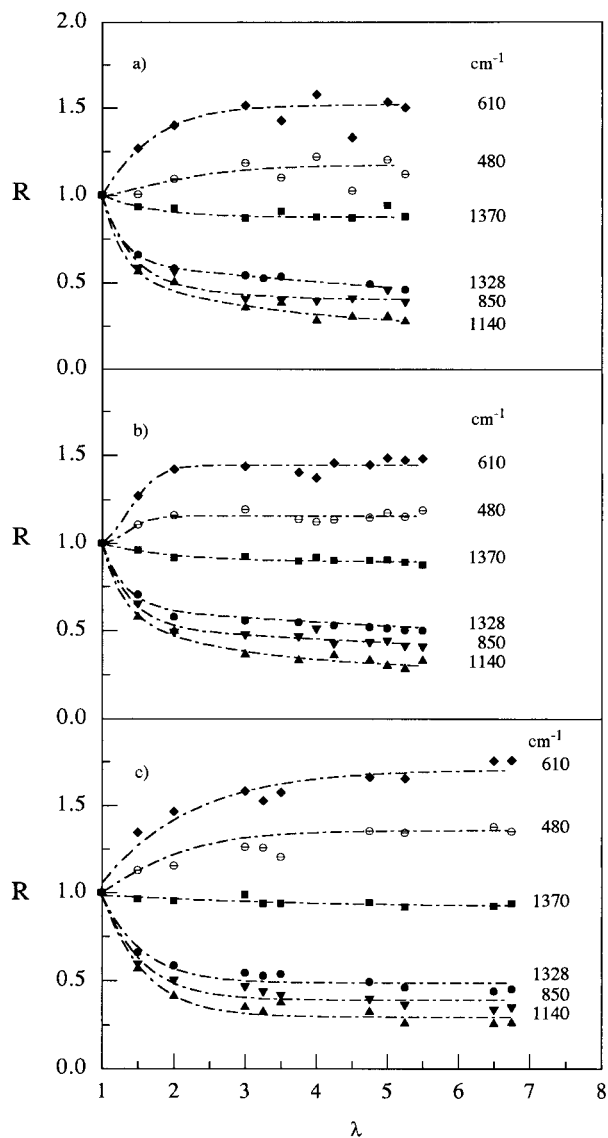
$$\langle P_2(\cos\theta) \rangle = \frac{1}{2} \left\{ \frac{2 + k^2}{1 - k^2} - \frac{3k \cos^{-1} k}{(1 - k^2)^{3/2}} \right\} \quad (3)$$

where

$$k = \lambda^{-3/2} \quad (4)$$

Equations (3) and (4) were proposed by Ward for the pseudoaffine scheme of orientation in semicrystalline polymers.[8] It can be seen from Figure 2 that the birefringence results lead to $\langle P_2(\cos\theta) \rangle$ values well fitted to those of the pseudoaffine scheme, because VAE copolymers are semicrystalline in the composition range studied.[7]

Taking into account that some of the absorption bands of the infrared spectrum are assigned to vibration modes in a phase of the polymer (amorphous or crystalline) and/or a particular chemical group, the overall information provided by the birefringence can be refined by the changes of the dichroic ratio. Thus, Figure 3 presents the change of the dichroic ratio with the draw ratio for the copolymer Q samples, stretched at 10 cm min^{-1}, referred to some of the most significative IR bands. These results show a perpendicular dichroism corresponding to the bands at 1370 cm^{-1} (bending CH), 1328 cm^{-1} (bending OH + wagging CH), 850 cm^{-1} (rocking CH_2), and 1140 cm^{-1} (H bonds in crystalline phase).[9] On the other hand, the bands situated at 610 cm^{-1} (wagging OH) and 480 cm^{-1} (bending OH) show a parallel dichroism. The dichroic ratio achieved after a draw ratio of

gence, assuming it as that observed in a copolymer sample infinitely stretched. Figure 1 shows the results corresponding to one of the copolymer samples and Table II lists the maximum birefringence values for all copolymer samples and parent homopolymers. The differences on $\Delta n_{\max}$ among the copolymers are slight and an increase in $\Delta n_{\max}$ is observed when increasing the ethylene molar fraction because this homopolymer presents the highest $\Delta n_{\max}$ value.

The orientation function was calculated using eq. (1) and its values for VAE-3 specimens are shown in Figure 2. The experimental values were compared with the theoretical line obtained from the equation

Table II Maximum Birefringence Values Obtained by Extrapolation on Δn vs. λ^{-1} Plots

Sample	$\Delta n_{\max}$
PVAL	0.0287
VAE-1	0.0445
VAE-2	0.0453
VAE-3	0.0461
PE	0.0527

Figure 3 Dichroic ratio as a function of draw ratio for quenched (Q) samples stretched at 10 cm min^{-1}: (a) VAE-1; (b) VAE-2; (c) VAE-3.

4 remains practically constant for all the bands analyzed and it allows one to conclude that the maximum orientation of the polymeric chains at 80°C corresponds to this elongation value.

The effect of the strain rate is very slight for bands showing perpendicular dichroism, as can be observed in Figure 4. However, the bands with parallel dichroism (610 and 480 cm^{-1}) display a higher value of the dichroic ratio for samples stretched at a higher crosshead speed (10 cm min^{-1}). The crystallization conditions do not essentially change the dichroic ratio in bands with perpendicular dichroism although they modify

those bands with parallel dichroism, corresponding the higher values to slowly crystallized samples, as Figure 5 shows.

In comparing a series of birefringence and dichroic ratio values for the 610 cm^{-1} band (typical of vinyl alcohol), the plot $\langle P_2(\cos\theta)\rangle$ vs. $(R-1)/(R+2)$ results in a straight line (correlation coefficient always higher than .991). This agreement between optical and dichroic results can be expected because it is based on the theoretical grounds of both measurements: Birefringence and infrared absorbances are related to the phase retardation and amplitude attenuation of the light, respectively, in the expression of the complex index of refraction. Figure 6 shows the plot corresponding to one of the samples. The slope of the
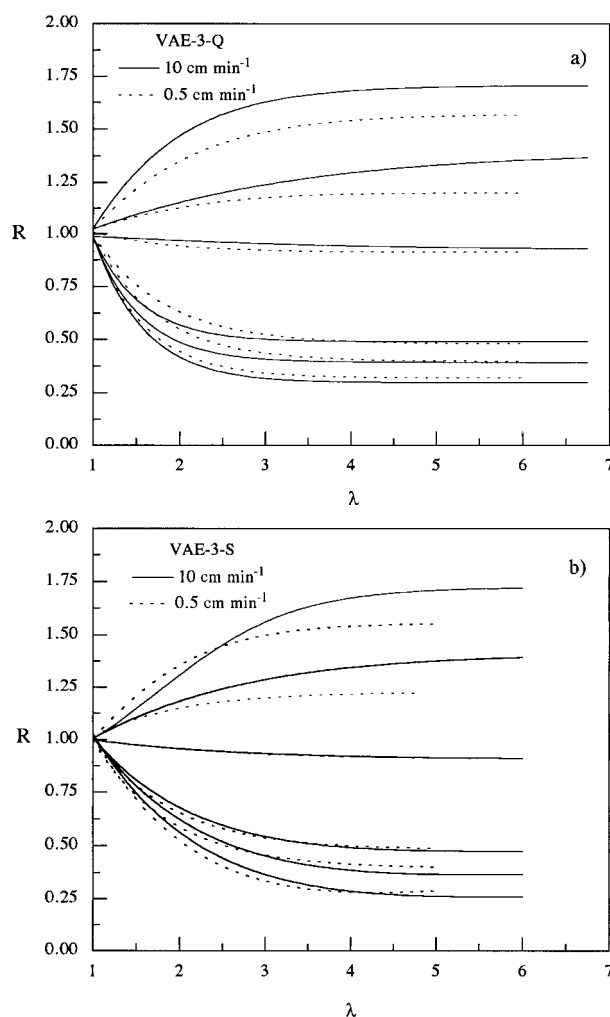
Figure 4 Changes in dichroic ratio with draw ratio for VAE-3 samples, at two crystallization conditions, when strain rate is changed: (a) Q samples; (b) S samples. Experimental points are omitted for clarity.
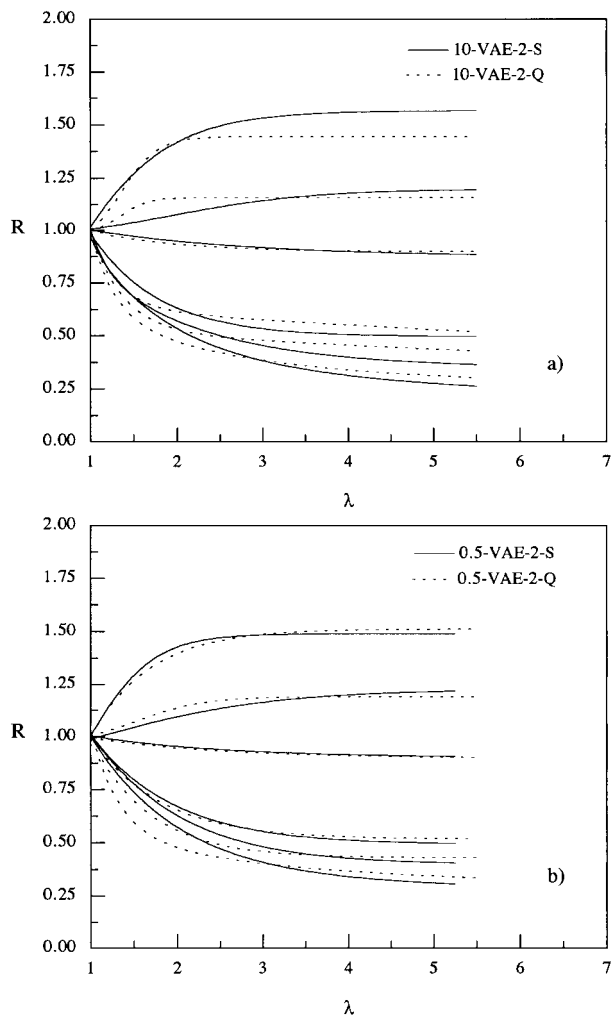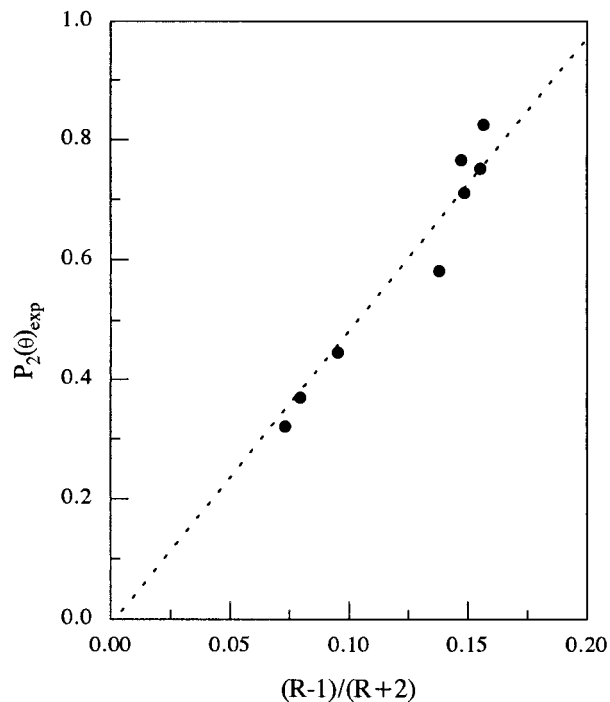
Figure 5 Changes in dichroic ratio with draw ratio for VAE-2 samples, at two strain rates, when crystallization conditions are changed: (a) 10 cm min^{-1}; (b) 0.5 cm min^{-1}. Experimental points are omitted for clarity.

Figure 6 Determination of the angle between the transition moment and the chain axis, using dichroic ratios, for the 610 cm^{-1} band of VAE-3-S stretched at 0.5 cm min^{-1}.

straight line is $(R_0 + 2)/(R_0 - 1)$, according to eq. (2), and this slope allows the estimation of the angle α. The results for all the stretched samples and the different thermal and mechanical histories are summarized in Table III.

The results listed in Table III display the effect of strain rate and crystallization conditions on the VAE copolymer samples. The VAE-3 copolymer shows the smaller α values and the higher values of parallel dichroism and draw ratios, because it is the copolymer with more ethylene content and so the intra- and intermolecular hydrogen bonds are weaker than those of VAE-1 and VAE-2 samples and hydroxyl groups are more easily oriented (Fig. 3).

Summing up, three main conclusions arise from the present results:

- The stretching process of VAE copolymers is well fitted to the pseudoaffine scheme of deformation, i.e., they show a rapid increment of birefringence from the first stages of the stretching.
- Samples stretched at a high strain rate and/ or slowly crystallized from the melt display a high value of the dichroic ratio, for the IR bands with parallel dichroism, which are mostly related to hydroxyl group motions.

Table III   Values of Angle α for the Band at 610 cm^{-1}

Sample	α_{610}
VAE-1-Q-0.5	47.5
VAE-1-Q-10	47.0
VAE-2-Q-0.5	47.5
VAE-2-Q-10	47.5
VAE-2-S-0.5	47.0
VAE-2-S-10	46.5
VAE-3-Q-0.5	46.5
VAE-3-Q-10	45.5
VAE-3-S-0.5	46.5
VAE-3-S-10	45.0

- Birefringence and dichroic ratio values are readily correlated. The angle α (between the dipole moment vector of the vibration and the chain axis) for the IR band at 610 cm^{-1} (wagging of the hydroxyl group) ranges from 45 to 47.5°, decreasing slightly as the ethylene content of the copolymer increases.

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