

Orientation Factor of Polypropylene Film by Infrared Dichroism

YASUJI KOBAYASHI, SABURO OKAJIMA, and AKIYOSHI NARITA,
Faculty of Technology, Tokyo Metropolitan University, Tokyo, Japan

Synopsis

The orientation factor by infrared dichroism of polypropylene film was compared with the other orientation factors. After the correction of imperfect polarization and the suitable choice of the base line, it was found that infrared dichroism is a reliable indicator of the orientation factor. Orientation factors obtained from the 998 and 842 cm.^{-1} bands agreed with the x-ray orientation factor, and that from the 975 cm.^{-1} band agreed with the optical orientation factor.

INTRODUCTION

It is common knowledge that an orientation factor of polymer can be measured by means of infrared dichroism, but few papers¹⁻⁵ have been published which treat the problem quantitatively besides the papers by Stein et al.⁶⁻¹⁰). To examine reliability of the obtained values, the orientation factor of polypropylene film as obtained by infrared dichroism was compared with orientation factors determined by x-ray, birefringence and visible dichroism methods.

EXPERIMENTAL

Calculation of Dichroic Ratio in the Infrared Region

Two sources of error have been frequently ignored in the quantitative measurements of dichroic ratios of polymer films in the infrared region. One of these errors is caused by imperfect polarization of the transmitted beam from a pile of silver chloride plates inclined at Brewster's angle, and the other error is due to partial polarization of the incident beam resulting from the difference in Fresnel reflection of the components of the radiation incident parallel and perpendicular to the prism face.

When a polarizer is imperfect, the beam transmitted through the polarizer has parallel (α) and perpendicular (β) components; the fractions of each component are α and β , and then $\alpha + \beta = 1$. For an ideal polarizer, of course, $\alpha = 1$, $\beta = 0$. The transmitted beam through the spectrometer also consists of vertical (A) and horizontal (B) components, and $A + B = 1$. The true transmission coefficients for an ideal polarizer of a

TABLE I

Spectrom- eter	Stretched film	Polarizer	Equation
$\begin{array}{c} A \\ + \\ B \end{array}$	$\begin{array}{c} I_{\parallel} \\ + \\ I_{\perp} \end{array}$	None	$\frac{A}{A+B} I_{\parallel} + \frac{B}{A+B} I_{\perp} = \frac{I_1}{I_0}$ (1)
$\begin{array}{c} A \\ + \\ B \end{array}$	$\begin{array}{c} I_{\perp} \\ + \\ I_{\parallel} \end{array}$	None	$\frac{A}{A+B} I_{\perp} + \frac{B}{A+B} I_{\parallel} = \frac{I_2}{I_0}$ (2)
$\begin{array}{c} A \\ + \\ B \end{array}$	$\begin{array}{c} I_{\parallel} \\ + \\ I_{\perp} \end{array}$	$\begin{array}{c} \alpha \\ + \\ \beta \end{array}$	$\frac{A\alpha}{A\alpha+B\beta} I_{\parallel} + \frac{B\beta}{A\alpha+B\beta} I_{\perp} = \frac{I_3}{I_0}$ (3)
$\begin{array}{c} A \\ + \\ B \end{array}$	$\begin{array}{c} I_{\perp} \\ + \\ I_{\parallel} \end{array}$	$\begin{array}{c} \alpha \\ + \\ \beta \end{array}$	$\frac{A\alpha}{A\alpha+B\beta} I_{\perp} + \frac{B\beta}{A\alpha+B\beta} I_{\parallel} = \frac{I_4}{I_0}$ (4)
$\begin{array}{c} A \\ + \\ B \end{array}$	$\begin{array}{c} I_{\parallel} \\ + \\ I_{\perp} \end{array}$	$\begin{array}{c} \beta \\ + \\ \alpha \end{array}$	$\frac{A\beta}{A\beta+B\alpha} I_{\parallel} + \frac{B\alpha}{A\beta+B\alpha} I_{\perp} = \frac{I_5}{I_0}$ (5)
$\begin{array}{c} A \\ + \\ B \end{array}$	$\begin{array}{c} I_{\perp} \\ + \\ I_{\parallel} \end{array}$	$\begin{array}{c} \beta \\ + \\ \alpha \end{array}$	$\frac{A\beta}{A\beta+B\alpha} I_{\perp} + \frac{B\alpha}{A\beta+B\alpha} I_{\parallel} = \frac{I_6}{I_0}$ (6)
$\begin{array}{c} A \\ + \\ B \end{array}$	None	$\begin{array}{c} \alpha \\ + \\ \beta \end{array}$	$A\alpha + B\beta = I_7$ (7)
$\begin{array}{c} A \\ + \\ B \end{array}$	None	$\begin{array}{c} \beta \\ + \\ \alpha \end{array}$	$A\beta + B\alpha = I_8$ (8)
			$I_7 + I_8 = (A\alpha + B\beta) + (A\beta + B\alpha) =$ $(A+B)(\alpha + \beta) = 1$ (9)
			$I_1 + I_2 = I_3 + I_4$ $= I_5 + I_6$ (10)
			$I_8 = \frac{(I_3 - I_4) + (I_2 - I_1)}{(I_3 - I_4) + (I_6 - I_5)}$ (11)

stretched film are I_{\parallel} and I_{\perp} for the parallel and perpendicular stretching directions, respectively.

Combination of the direction of the stretched film and a polarizer yields the equations given in Table I.

Relations (10) and (11) are useful for checking the accuracy of observed values. A , B , α , and β are evaluated from the observed values by eqs. (12) or (13) and (14).

$$\frac{I_8(2I_8 - 1)}{I_8 - 2\beta(1 - \beta)} = \frac{I_2 - I_1}{I_6 - I_5} \quad (12)$$

$$\frac{I_8}{I_7} \left(1 - \frac{2I_8 - 1}{I_8 - 2\beta(1 - \beta)} \right) = \frac{I_3 - I_4}{I_6 - I_5} \quad (13)$$

$$A = (\alpha - I_8)/(\alpha - \beta) \quad (14)$$

$$A + B = 1$$

$$\alpha + \beta = 1$$

The true transmission coefficients I_{\parallel} and I_{\perp} of samples for the completely polarized beam are calculated by eqs. (15) when the polarizer is fixed horizontally and a stretched sample is mounted in the vertical or horizontal direction:

$$\begin{aligned} I_{\parallel} &= I_6 + (I_6 - I_5)F_0 \\ I_{\perp} &= I_5 - (I_6 - I_5)F_0 \end{aligned} \quad (15)$$

where

$$F_0 = \beta[\alpha/(\alpha - A) - 1]$$

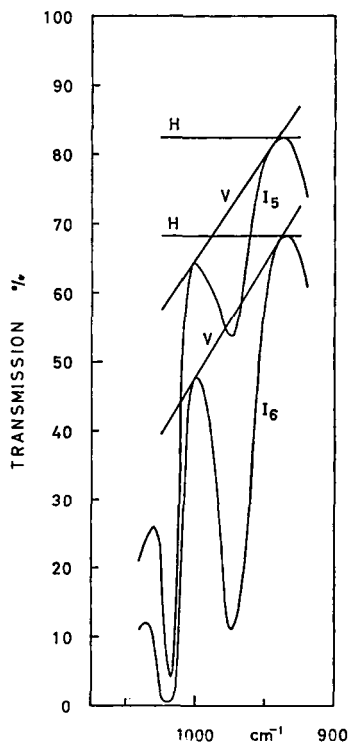


Fig. 1. There are at least two positions for the base-line of a band, i.e., the H and V lines. This example is the dichroic spectrum at 973 cm^{-1} of a stretched poly(ethylene terephthalate) film.

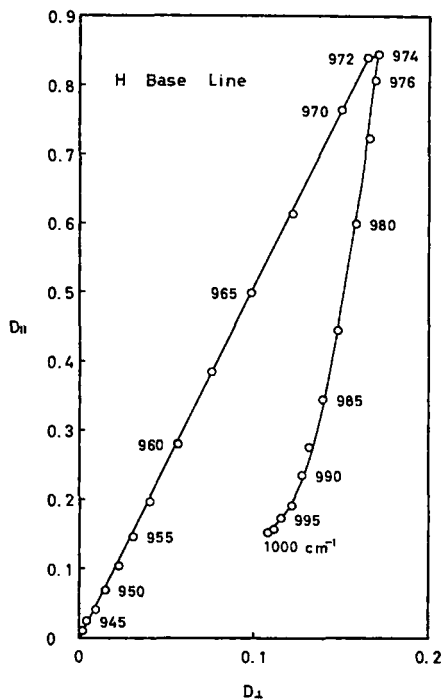


Fig. 2. Relation between the parallel D_{\parallel} and perpendicular D_{\perp} absorbances with use of the H base line.

When the sample is fixed vertically and the polarizer is settled in the vertical or horizontal direction, I_{\parallel} and I_{\perp} are obtained by eqs. (16):

$$I_{\parallel} = I_3 + (I_3 - I_5)F_1 \quad (16)$$

$$I_{\perp} = I_5 - (I_3 - I_5)F_2$$

where

$$F_1 = \beta \{ [\alpha/A(\alpha - \beta)] - 1 \}$$

$$F_2 = \beta \{ [\alpha/B(\alpha - \beta)] - 1 \}$$

On our instrument, Hitachi EPI-2, for example, the following values were found for the 1440 cm^{-1} band of polyethylene: $A = 0.294$, $B = 0.706$, $\alpha = 0.905$, $\beta = 0.095$, $F_0 = 0.046$, $F_1 = 0.266$, $F_2 = 0.055$, A , B , α , and β vary according to the wavelength, but the correction coefficients F_0 , F_1 , F_2 are practically constant in the region of $3000\text{--}800 \text{ cm}^{-1}$, as the value B is smaller at the lower wavelength, while α is larger.

Determination of the Baseline

Another source of error is caused by the difficulty of *a priori* drawing of the baseline. At least two baselines may be considered for each band, for

example, H and V in Figure 1, which shows the dichroic spectrum at 973 cm.^{-1} band of a stretched ($4.8\times$ at 65°C.) poly(ethylene terephthalate) film. On correcting as mentioned above, the relations between the parallel D_{\parallel} and perpendicular D_{\perp} absorbances are given in Figures 2 and 3.

When the H line is adopted as the baseline, the absorbances on the right side of the band ($940\text{--}970\text{ cm.}^{-1}$) fall on a straight line passing through the origin. The absorbances on the left side do not fall on a straight line on either baseline as a result of the neighbor bands (988 and 1018 cm.^{-1}). Hence on the right side the H baseline is better than the V line

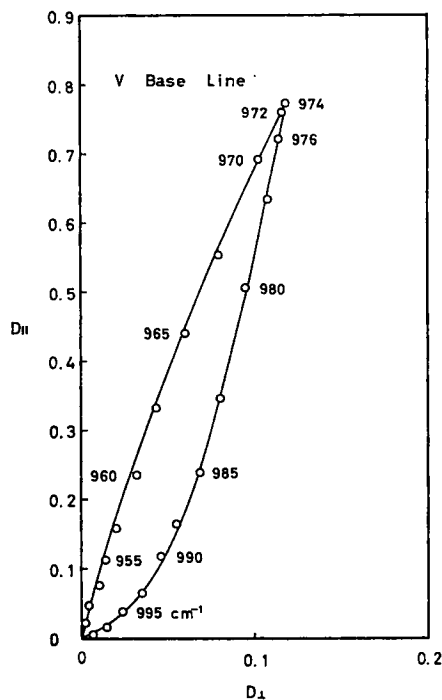


Fig. 3. Relation between D_{\parallel} and D_{\perp} absorbances with use of the V baseline.

and this region is not affected by neighbor bands. Then the slope of the straight line refers to the dichroic ratio D , and dichroic orientation factor f_{ir} is given by eq. (17):

$$f_{\text{ir}} = (D - 1)/(D + 2) \quad (17)$$

The dichroic ratio at the very peak of the band is lower than that of the slope as described above. This is related to the slit width of spectrometer. At the very peak, true absorbance is given only by extrapolation to zero width, but at the side of a band, the true dichroic ratio can be obtained even when the slit is a wide, as the shape of band at the side is practically straight.

RESULTS AND DISCUSSION

Polypropylene film was stretched several times in a poly(ethylene glycol) bath at 130°C.

The bands at 998 and 842 cm^{-1} are crystalline-sensitive bands which are caused by the parallel vibration in crystalline region.^{11,12} As the orientation factors by infrared dichroism (998 and 842 cm^{-1}) showed practically the same value, the mean value of the two was taken and compared with the orientation factor f_x obtained by the x-ray method (Fig. 4). The two orientation factors are very similar. The x-ray orientation factor was calculated according to Wilchinsky's principle¹³ by using the (040) and (110) reflections.

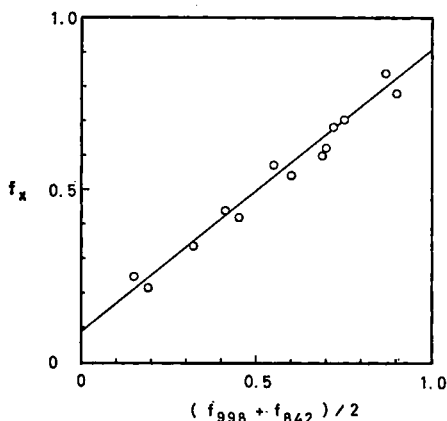


Fig. 4. Orientation factors by infrared dichroism (998 and 842 cm^{-1}) vs. the x-ray orientation factors f_x .

As the intensity of the 975 cm^{-1} band at room temperature is nearly equal to that in the melt,¹⁴ it is expected that the orientation factor by the infrared dichroism (975 cm^{-1}) gives an overall orientation. The infrared dichroism (975 cm^{-1}) was therefore compared with the optical orientation factor f_0 in Figure 5. The observed values fall on a straight line, the slope of which is similar to that in Figure 4. Here the observed birefringence value Δn was corrected by density and then the optical orientation factor f_0 was calculated

$$f_0 = \Delta n d_c / \Delta n_c d$$

where the crystalline birefringence is¹⁵ $\Delta n_c = 41.5 \times 10^{-3}$ and the crystalline density¹⁶⁻¹⁸ is $d_c = 0.936$.

The orientation factor of the amorphous region, f_a or f_{ia} can be estimated by following eqs. (18)–(20):

$$\begin{aligned} f_0 &= f_x X + f_a(1 - X) \\ f_{975} &= f_{ic} X + f_{ia}(1 - X) \\ f_{ic} &= (f_{998} + f_{842})/2 \end{aligned}$$

where X is density crystallinity calculated by using the values crystalline density $d_c = 0.936$ and amorphous density $d_a = 0.87$.¹⁹⁻²¹ It is noteworthy that both orientation factors f_a and f_{ia} coincide almost completely as shown in Figure 6, although they are obtained by quite different principles.

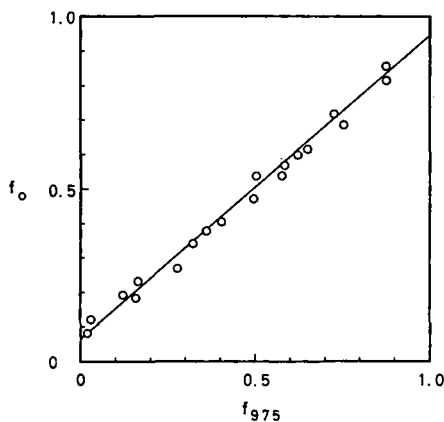


Fig. 5. Orientation factors by infrared dichroism (975 cm.^{-1}) vs. the optical orientation factors f_0 by birefringence.

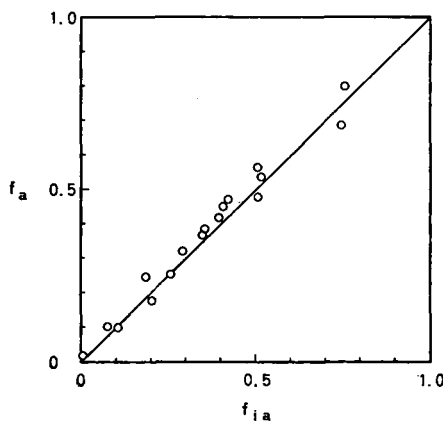


Fig. 6. Two orientation factors of amorphous region f_a and f_{ia} coincide almost completely, although they are obtained by the quite different principles.

f_{ia} was again compared with another independent orientation factor, i.e., that obtained by the visible dichroism. For this purpose a strip of polypropylene film was dyed with a disperse dye (Cayalon Fast Yellow 4R) before stretching, the dye molecules being absorbed in the amorphous region. The visible dichroism f_D developed by stretching is related to amorphous orientation according to studies on other polymers,²²⁻²⁸ and this f_D agreed expectedly with f_{ia} as indicated in Figure 7.

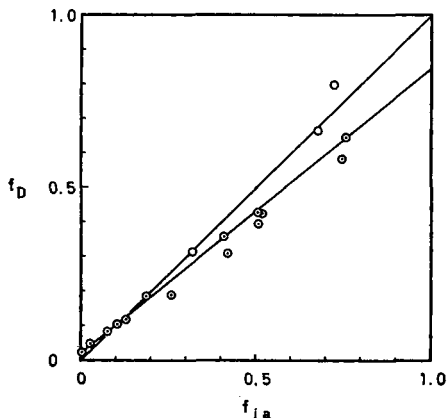
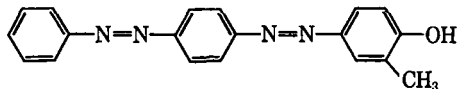


Fig. 7. Amorphous orientation factors f_{ia} by infrared dichroism vs. the orientation factors f_D by visible dichroism for strips of polypropylene film: (O) dyed before stretching; (\odot) dyed after stretching.



Cayalon Fast Yellow 4R

It seems therefore that (1) the long dye molecule is absorbed parallel to the polymer chain, and (2) this dye molecule has no perpendicular absorbance in the visible wavelength region, as is the case for Congo Red.²⁹

On the other hand, when a stretched strip is dyed, the dye molecules are absorbed prominently in the less oriented parts, because it is rather difficult for the dye to penetrate into the higher ordered region of polymer chain. So the visible dichroism of such a stretched, dyed strip shows the lower orientation rather than the mean orientation of the whole amorphous region as is given by infrared dichroism f_{ia} (Fig. 7).

In summation, the study shows that infrared dichroism is a reliable quantitative indicator of orientation factor after the correction for imperfect polarization and the suitable choice of the baseline.

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Résumé

Le facteur d'orientation déterminé par dichroïsme infrarouge des films de polypropylène a été comparé avec les autres facteurs d'orientation. Après correction de la polarisation imparfaite et après avoir choisi une ligne de base, on a trouvé que le dichroïsme infrarouge fournit un facteur d'orientation reproductible: les facteurs d'orientation obtenus au départ des bandes à 998 cm^{-1} et 842 cm^{-1} sont en accord avec le facteur d'orientation obtenu aux rayons-X et celui déterminé au départ de la bande à 975 cm^{-1} est en accord avec le facteur d'orientation optique.

Zusammenfassung

Der aus dem Infrarotdichroismus erhaltene Orientierungsfaktor eines Polypropylen-filmes wurde mit anderen Orientierungsfaktoren verglichen. Nach Korrektur für unvollständige Polarisation und geeigneter Wahl der Bezugslinie lieferte der Infrarotdichroismus den richtigen Orientierungsfaktor: die aus den Banden bei 998 cm^{-1} und 842 cm^{-1} erhaltenen Orientierungsfaktoren stimmten mit dem Röntgen-Orientierungsfaktor und derjenige aus der Bande bei 975 cm^{-1} mit dem optischen Orientierungsfaktor überein.

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