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# A new approach to the characterization of molecular orientation in uniaxially and biaxially oriented samples of poly(ethylene terephthalate)

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## Abstract

The usual approach that is used to characterize the molecular orientation in biaxially oriented samples by infrared spectroscopy is to measure spectra with polarization in all three directions: machine, transverse and normal (or thickness). However, the latter measurement is rather difficult to make experimentally. In the present work we propose a new approach to characterizing the molecular orientation in both uniaxially and biaxially oriented samples of PET, based on the use of front-surface reflection spectra. It makes use of the ratio of the absorption bands at 1330–1240 and 1729 cm$^{-1}$, the first of which shows parallel dichroism and the second perpendicular dichroism. An equation is developed that relates this ratio to the molecular orientation with respect to the direction of measurement. Thus, it is possible to determine individually the orientation functions with respect to the machine and transverse directions. The validity of functions determined in this way is confirmed by comparison with birefringence results. Crown copyright © 1999 Published by Elsevier Science Ltd. All rights reserved.

*Keywords:* Poly(ethylene terephthalate); PET; Orientation

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## 1. Introduction

Many processing methods for producing polymeric articles can introduce molecular orientation into the final products. Some of them, like fibre spinning, introduce uniaxial orientation, while others, like extrusion blow moulding, can introduce some degree of biaxial orientation. It was found that the final degree of orientation in the moulded products can affect both their optical and their mechanical properties. Therefore, its exact determination is of great importance since it can provide a better characterization of the end properties of the products. Various techniques are used to measure both uniaxial and biaxial molecular orientation in amorphous and semi-crystalline polymers. These include heat shrinkage, birefringence, infrared spectroscopy, X-ray diffraction, differential scanning calorimetry and nuclear magnetic resonance. Of these, the birefringence technique is widely employed because of its simplicity.

The characterization of molecular orientation by means of optical methods was described in detail by Ward and co-workers [1,2] and by Zbinden [3]. To completely describe the orientation, it is necessary to determine the detailed probability distribution function for the orientation of a coordinate axis system fixed in the molecular frame with respect to one fixed in the sample. Because many industrial samples possess at least orthorhombic symmetry, it is usually easy to define the sample axis system in terms of machine (*M*), transverse (*T*) and normal (*N*) or thickness directions. The molecular axis system (*a*, *b*, *c*) is usually chosen so that one axis (generally *c*) coincides with the chain axis of the polymer molecule. The choice of the other two axes is important when the polymer possesses a well-defined crystalline structure, in which case the orientation of the *a* and *b* axes may be quite different. However, in many cases, including amorphous polymers, the polymer structural units may be considered as having rotational symmetry around the chain axis and the distinction between the *a* and *b* axes can be neglected. Under these circumstances, it is sufficient to define the orientation of the chain axis *c*, which can be described in terms of three Hermans-type orientation functions:

$$f_{cM} = \frac{1}{2}\left(3\left\langle\cos^2\theta_{cM}\right\rangle - 1\right) \tag{1a}$$

$$f_{cT} = \frac{1}{2}\left(3\left\langle\cos^2\theta_{cT}\right\rangle - 1\right) \tag{1b}$$

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$$f_{cN}=\frac{1}{2}\left(3\left\langle\cos^2\theta_{cN}\right\rangle-1\right) \tag{1c}$$

where the three $\theta$ variables represent the angles made by the chain axis $c$ with respect to the $M$, $T$ and $N$ directions and the angle brackets indicate an average over all chain orientation. The three angles are not independent. The sum of the three squared cosines is equal to unity, and the sum of the three orientation functions is equal to zero:

$$f_{cM}+f_{cT}+f_{cN}=0 \tag{2}$$

Thus, any two $f$ values are sufficient to define the orientation and the third can be determined by difference. The value of $f$ ranges from $-0.5$, if the chain axes are perfectly perpendicular to the reference axis, to $+1$ if they are perfectly parallel. This representation of the orientation amounts to approximating the exact distribution function by an ellipsoid [3], but for moderate levels of orientation this is sufficient and in fact many techniques, including birefringence and infrared spectroscopy, cannot provide a more detailed representation.

White and Spruiell [4,5] have proposed somewhat different, but related, orientation factors that are useful for describing biaxial orientation. The following equations give their definition, as well as their relationship to the previously mentioned orientation functions and to the refractive indices measured by birefringence:

$$f^B_{cM}=\left\langle\cos^2\theta_{cM}\right\rangle-\left\langle\cos^2\theta_{cN}\right\rangle \text{ or } 2\left\langle\cos^2\theta_{cM}\right\rangle+\left\langle\cos^2\theta_{cT}\right\rangle-1 \tag{3a}$$

$$=\frac{2}{3}\left(f_{cM}-f_{cN}\right) \text{ or } \frac{2}{3}\left(2f_{cM}+f_{cT}\right)$$

$$=\frac{\Delta n_{MN}}{\Delta^0}$$

$$f^B_{cT}=\left\langle\cos^2\theta_{cT}\right\rangle-\left\langle\cos^2\theta_{cN}\right\rangle \text{ or } 2\left\langle\cos^2\theta_{cT}\right\rangle+\left\langle\cos^2\theta_{cM}\right\rangle-1 \tag{3b}$$

$$=\frac{2}{3}\left(f_{cT}-f_{cN}\right) \text{ or } \frac{2}{3}\left(2f_{cT}+f_{cM}\right)$$

$$=\frac{\Delta n_{TN}}{\Delta_0}$$

In these equations, $\Delta n_{MN}=n_M-n_N$ and $\Delta n_{TN}=n_T-n_N$, where $n$ is the index of refraction in the particular direction indicated and $\Delta^0$ is the maximum or intrinsic birefringence. A number of methods may be used to evaluate the orientation factors of Eq. (3a), Eq. (3b). White and Spruiell use the birefringence and wide angle X-ray methods and one advantage of the factors defined in Eq. (3a), Eq. (3b) is their simple relationship to the birefringence results.

In a sample that is uniaxially oriented in the machine direction $M$, the $T$ and $N$ directions are equivalent, in which case $n_{\mathrm{T}}=n_{\mathrm{N}}$, $f_{cT}=f_{cN}=-1/2f_{cM}$ and $f^B_{cT}=0$. Only one parameter ($f_{cM}=f^B_{cM}$) is required to define the orientation. For biaxially oriented samples, two parameters are required (for example, $f_{cM}$ and $f_{cT}$, or $f^B_{cM}$ and $f^B_{cT}$). This means that the refractive index must be determined in all three directions $M$, $T$ and $N$, rather than in just the $M$ and $T$ directions.

Infrared (IR) spectroscopy is another valuable technique for characterizing orientation [3] and has the advantage of being able to provide specific information on the different phases (amorphous and crystalline) and molecular conformations present in the polymer. Dichroic IR spectroscopy measures the absorption intensity of different molecular vibrational modes with an IR beam whose electric field vector is polarized in a specific direction with respect to the sample. Each vibrational mode possesses a transition moment that can usually be considered to make a fixed angle $\alpha$ with respect to the chain axis. For the case of rotational symmetry about the chain axis, when a sample is analyzed with radiation polarized in any particular direction $J$, it can be shown that the absorption intensity of a particular band is given by:

$$A_J=A_0\left\{1+\frac{1}{2}\left(3\left\langle\cos^2\theta_{cJ}\right\rangle-1\right)\left(3\cos^2\alpha-1\right)\right\}$$

$$=A_0\left\{1+f_{cJ}\left(3\cos^2\alpha-1\right)\right\} \tag{4}$$

where $A_0$ represents the absorption intensity that would be observed for an equivalent unoriented sample, $\theta_{cJ}$ is the angle between the chain axis and the direction of polarization $J$, and $f_{cJ}$ is the orientation function with respect to that direction. Thus, if measurements are made in the three directions $M$, $T$ and $N$, the following quantities are obtained:

$$A_M=A_0\left\{1+f_{cM}\left(3\cos^2\alpha-1\right)\right\} \tag{5a}$$

$$A_T=A_0\left\{1+f_{cT}\left(3\cos^2\alpha-1\right)\right\} \tag{5b}$$

$$A_N=A_0\left\{1+f_{cN}\left(3\cos^2\alpha-1\right)\right\} \tag{5c}$$

and $A_0$ can be calculated from:

$$A_0=\frac{1}{3}\left(A_M+A_T+A_N\right) \tag{6}$$

For the case of uniaxial orientation, where $f_{cT}=f_{cN}=-1/2f_{cM}$, one needs to make measurements in only the $M$ and $T$ directions, then calculate the dichroic ratio $D$ to eliminate the unknown quantity $A_0$:

$$D=\frac{A_M}{A_T}=\frac{1+f_{cM}\left(3\cos^2\alpha-1\right)}{1+f_{cT}\left(3\cos^2\alpha-1\right)} \tag{7}$$

Because $f_{cT}=-1/2f_{cM}$, Eq. (7) can be inverted to give the well known equation:

$$f_{cM}=\frac{D-1}{D+2}\cdot\frac{2}{3\cos^2\alpha-1} \tag{8}$$

The single quantity $f_{cM}$, equivalent to the well known Hermans orientation function, is sufficient to describe the uniaxial orientation.

For general biaxial orientation, the $M$, $T$ and $N$ directions are all different. In principle, it is possible to calculate $f_{cM}$ and $f_{cT}$ by means of Eq. (5a) and Eq. (5b), but this requires the knowledge of $A_0$. Usually this quantity is unknown, because it depends on the properties of the particular specimen being analyzed (for example, the thickness in the case of a transmission spectrum, or the surface quality in the case of a reflection spectrum). Thus, for biaxially oriented samples, the usual approach is to measure the absorption intensities $A_M$, $A_T$ and $A_N$ in all three directions, calculate $A_0$ from Eq. (6), then determine $f_{cM}$, $f_{cT}$ and $f_{cN}$ according to Eq. (5a)– Eq. (5c). However, the measurement of the spectrum in the normal direction is more difficult than that for the other two. For thin films in transmission it can be obtained by making measurements on tilted films, and for attenuated total reflection (ATR) it can be obtained by making measurements with different positions of the sample with respect to the plane of incidence. However, in both cases the analysis is considerably more tedious than that required for uniaxial samples. An alternative approach is to overcome the dependence of $A_0$ on specimen properties by using the ratio of two different bands in the same spectrum. This approach was applied by Mirabella [6–8] to ATR spectra of oriented polypropylene.

In recent papers, one of the authors and his co-workers [9–11] as well as other groups [12–15] have demonstrated the possibilities of using front-surface infrared reflection for characterizing the surface orientation of thick uniaxially drawn samples. Further, the present authors have shown that for polymers with glass transition temperatures above room temperature, careful milling and polishing of the specimen results in spectra of high quality without affecting the polymer structure [16]. One way to apply this technique to biaxially oriented samples (i.e. to determine $A_N$) is to section the sample and make measurements in the $N$ direction with an infrared microscope. Because of the special equipment and considerable work required for this, we have developed an alternative approach. In the present paper we expand upon the peak ratio approach used by Mirabella and show how it can be successfully applied to front-surface reflection spectra of poly(ethylene terephthalate) or PET.

## 2. Experimental

The proposed method for characterizing orientation was developed with the use of data from samples that were prepared by uniaxially drawing thick PET sheet (extrusion grade, DuPont Selar PT 7086) at 80°C to different values of the draw ratio λ. Details on sample preparation and the measurement of FT IR (Fourier transform infrared) spectra are given in earlier publications [9–11]. Although these samples were not polished, they gave spectra of good quality. With the aid of the software Spectra-Calc™ from Galactic Industries Corporation, the measured reflectance spectra were subjected to Kramers–Kronig transformation in order to obtain the refractive index ($n$) and absorption index ($k$) spectra. The software was slightly modified in-house to allow calculation from the $n$ and $k$ spectra of the imaginary molecular polarizability function spectrum $\phi$. The latter provides the closest correlation to the molecular properties, especially for the more intense absorption bands [17]. From the $\phi$ spectra, conventional dichroic ratios and orientation functions were calculated according to the usual procedures [9]. To account for variations in the overall intensity of the spectra, arising from effects like surface quality and sample positioning, the spectra were normalized with respect to the area of the peak at 1410 $\mathrm{cm}^{-1}$, which is known to be insensitive to both orientation and conformation [18].

The validity of the method was checked on two PET samples made from Eastman Chemicals PET 9921. A uniaxially oriented sample was prepared by stretching amorphous sheet (obtained by moulding in a laboratory press at 285°C followed by quenching in water) at 80°C and 2 cm $\mathrm{min}^{-1}$ to a draw ratio of 2.8 in an Instron tensile tester equipped with an environmental chamber. For this sample $M$, $T$ and $N$ denote the drawing, width and thickness directions respectively. A biaxially oriented sample was obtained from injection blow-moulded bottles. These had a length of 248 mm and a rounded rectangular cross-section of 84 mm × 40 mm. The sample used in this study was cut from the surface that was highly stretched in the hoop direction. For this sample, $M$ denotes the length direction of the bottle, $T$ the hoop direction and $N$ the thickness direction.

The molecular orientation of these samples was characterized using front-surface specular reflection IR spectroscopy. Spectra were measured on a Nicolet 170SX FT IR spectrometer equipped with a Model 134 specular reflectance accessory and zinc selenide wire grid polarizer from Spectra-Tech Inc. Each spectrum was the result of an accumulation of 128 scans at a resolution of 4 $\mathrm{cm}^{-1}$. The angle of incidence was 11° and a front-surface gold mirror was used as reference. For both samples used in the validation, spectra were first measured on the surface with polarization in both the $M$ and $T$ directions. The uniaxial sample was then cut parallel and perpendicular to the stretching direction and reflection spectra were measured on the cross-sectional $MN$ and $TN$ planes. This was done with the use of a Spectra-Tech IR Advantage microscope. The measurement area was equal to 50 $\mu$m × 50 $\mu$m. To ensure a high quality for these spectra, the cut specimens were mounted in epoxy resin and the $MN$ and $TN$ planes were carefully polished to a finish of 0.05 $\mu$m [16]. In the case of the biaxially oriented sample, spectra were measured in the $MT$ plane only, but at different depths across the thickness direction. This was done by removing layers of material by means of the polishing technique developed by the authors [16]. The average molecular orientation functions across the thickness were compared to those obtained by means of the birefringence technique. Details on the measurement of the degree of biaxial molecular orientation using the birefringence technique are given elsewhere [19]. It is to be noted that these birefringence measurements were performed before the mounting and polishing of the sample for infrared characterization.

## 3. Results and discussion

Some typical spectra of polished specimens of PET are shown for illustrative purposes. Fig. 1 shows spectra of an amorphous undrawn sample measured with polarization in two mutually perpendicular directions that are designated *M* and *T* (although in this case the choice of *M* is arbitrary). As expected for an unoriented sample, the two polarizations give effectively identical spectra. The peaks in the reflectance spectra [Fig. 1(a)] show a dispersion-like shape because of the contribution of the refractive index. The polarizability function ($\phi$) spectra obtained by Kramers–Kronig transformation [Fig. 1(b)] show peak shapes that more closely resemble those of conventional infrared absorption spectra. Fig. 2 shows spectra of the same material after uniaxial drawing to $\lambda = 3.8$; in this case *M* designates the draw direction. The very obvious difference between the *M* and *T* spectra is caused by the dichroism resulting from molecular orientation. Some peaks, like the carbonyl band at 1729 cm$^{-1}$ and the out-of-plane benzene ring C-H bands at 875 and 730 cm$^{-1}$ are more intense in the *T* direction because their transition moments make a large angle $\alpha$ with respect to the polymer chain axis (i.e. they tend towards perpendicular). Other peaks are stronger in the *M* spectrum, because their transition moments tend to be more parallel to the chain axis (small angle $\alpha$). These include the glycol CH$_2$ wagging peak at 1340 cm$^{-1}$, the in-plane benzene ring C-H peak at 1018 cm$^{-1}$ and the intense complex bands around 1330–1240 and 1160–1080 cm$^{-1}$ that arise mainly from ester group vibrations.

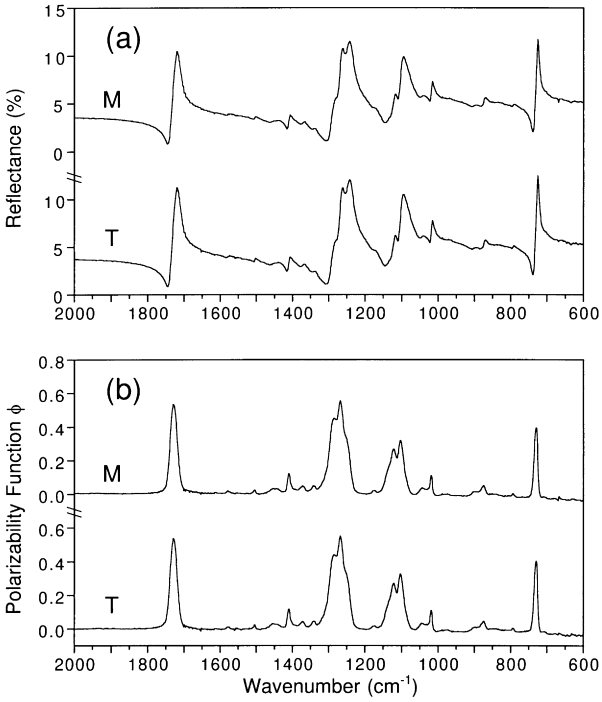

Fig. 1. Front-surface reflection IR spectra measured with polarization in two mutually perpendicular directions (arbitrarily designated *M* and *T*) at the surface of a polished unoriented amorphous PET sample: (a) reflectance spectra as measured (%*R*); (b) imaginary molecular polarizability spectra ($\phi$) obtained by Kramers–Kronig transformation of reflectance spectra.

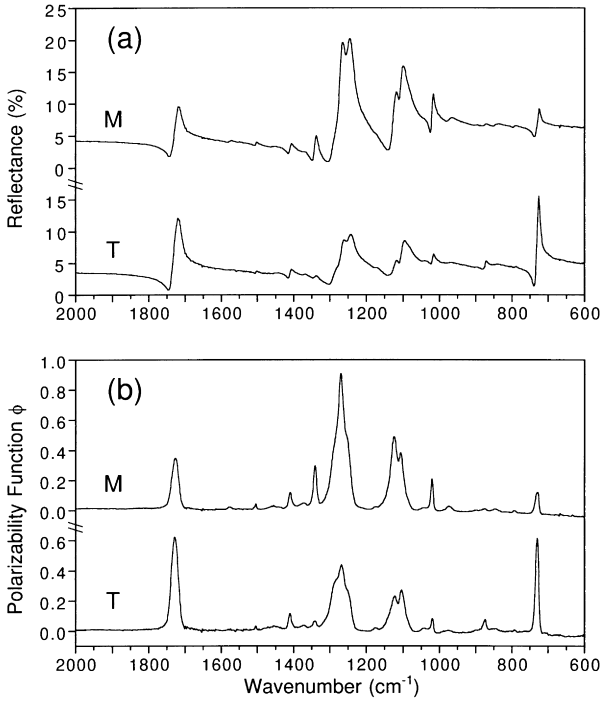

Fig. 2. Front-surface reflection IR spectra measured with polarization in machine (*M*) and transverse (*T*) directions at the surface of a polished PET sample uniaxially drawn to a draw ratio of 3.8: (a) reflectance spectra as measured (%*R*); and (b) imaginary molecular polarizability spectra ($\phi$) obtained by Kramers–Kronig transformation of reflectance spectra.

The isotropic or 'structural factor' spectrum, corresponding to $A_0$, can be calculated from the $A_\mathrm{M}$ and $A_\mathrm{T}$ spectra by means of Eq. (6), which reduces to $A_0 = 1/3A_M + 2/3A_T$ for a uniaxial sample because $A_N = A_T$. Structural factor spectra for the undrawn and drawn samples are shown in Fig. 3. In this case the difference between the two is not caused by dichroism but to changes in the molecular conformation

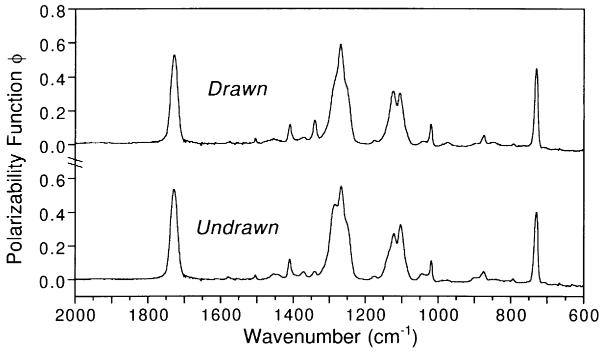

Fig. 3. Calculated structural factor spectra for the undrawn and drawn PET samples corresponding to Figs. 1 and 2.

produced by drawing, in particular the transformation of *gauche* glycol conformers into *trans* conformers.

For the set of samples drawn uniaxially to different values of λ, it was possible to calculate the overall orientation function $f$ from the $\phi$ spectra by means of Eq. (8), based on certain peaks for which the value of the angle $\alpha$ is known or can be reasonably assumed. These include the benzene ring C-H in-plane bending peak at 1018 cm$^{-1}$, for which $\alpha$ was reported [20] to be 20°, the C-H out-of-plane bending peak at 875 cm$^{-1}$, for which $\alpha$ was reported [21] to be 85° and the C-H out-of-plane bending peak at 730 cm$^{-1}$, for which $\alpha$ should be close to 90°. The evolution of $f$ with draw ratio is shown in Fig. 4. The three peaks show the same trend, with some scatter, so they were combined to give an average result, also shown in the figure.

Of the remaining peaks in the PET spectrum, the most intense are the carbonyl peak at 1729 cm$^{-1}$ and the complex ester peak at 1330–1240 cm$^{-1}$, which involves at least three components. The value of $\alpha$ is not known for these bands. Dichroic ratios were calculated from integrated band areas and the quantity $(D-1)/(D+2)$ was plotted against the averaged overall orientation function $f$, as shown in Fig. 5. Reasonably good proportionality is observed, as expected from Eq. (8), and from the slopes of the regression lines the values of $\alpha$ were estimated to be 65° for the carbonyl band and 45° for the complex ester band. Because these bands are so intense, they have seldom been studied in transmission spectra. However, Dulmage and Geddes [22] have reported data for a set of very thin (2–6 $\mu$m) films drawn up to 500% extension. They were able to calculate dichroic ratios for the peaks at 1724, 1018, 875 and 728 cm$^{-1}$. The ratios shown graphically in their paper were analyzed by us in the same manner used for our reflection spectra and the two sets of data were found to be quite consistent. Their data gives a value of 66° for $\alpha$ for the carbonyl peak. However, they did not report data for the ester peak.

Because the two peaks at 1330–1240 and 1729 cm$^{-1}$ are quite intense in the reflection spectrum (and therefore can be quantified with good precision) and because they show opposite dichroic behaviour, their ratio should be a good indicator of orientation. As mentioned previously, taking the ratio of two bands in the same spectrum can eliminate the problem of the dependence of the overall spectral intensity on the specific specimen and on the polarization direction. From Eq. (4), this ratio is given by (introducing subscripts 1 and 2 to designate the two different bands):

$$R_J = \frac{A_{1J}}{A_{2J}} = \frac{A_{10}}{A_{20}} \cdot \frac{1 + f_{cJ}\left(3\cos^2\alpha_1 - 1\right)}{1 + f_{cJ}\left(3\cos^2\alpha_2 - 1\right)} = R_0 \cdot \frac{1 + f_{cJ}\left(3\cos^2\alpha_1 - 1\right)}{1 + f_{cJ}\left(3\cos^2\alpha_2 - 1\right)} \qquad (9)$$

where $R_0 = A_{10}/A_{20}$ is the band ratio corresponding to an unoriented sample. This equation can be inverted to give the relationship between the orientation function $f_{cJ}$ and the ratio $R_J$:

$$f_{cJ} = \frac{R_J - R_0}{R_0\left(3\cos^2\alpha_1 - 1\right) - R_J\left(3\cos^2\alpha_2 - 1\right)} \qquad (10)$$

With Eq. (10), the orientation function with respect to any direction can be determined by making a measurement with the polarization in that direction. Thus, for biaxially oriented samples, measurements in the $M$ and $T$ directions allow determination of $f_{cM}$ and $f_{cT}$, from which $f_{cN}$ can be calculated (Eq. (2)). However, in order for this approach to succeed, certain conditions must be met. First of all, the two bands used must have significantly different values of $\alpha$. Secondly, they should both measure the same orientation function, generally the average orientation. For example, if one band is sensitive to the orientation of the amorphous phase and the other to that of the crystalline phase, the $f_{cJ}$

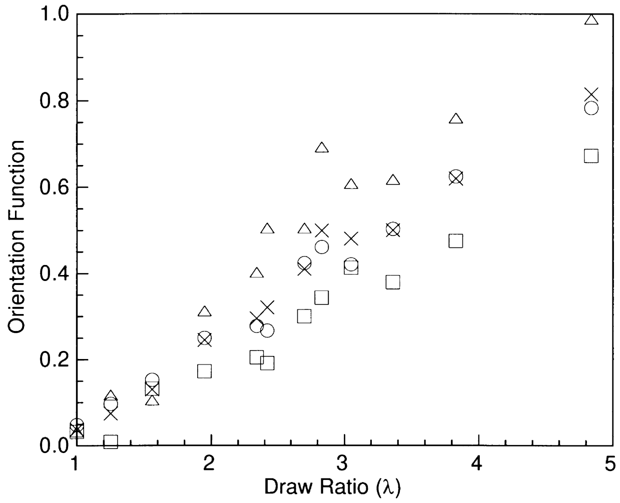

Fig. 4. Orientation function as a function of draw ratio for the set of uniaxially drawn PET samples, based on the dichroism of different peaks in the IR spectrum: 730 cm$^{-1}$ (○); 875 cm$^{-1}$ (△); 1018 cm$^{-1}$ (□); average of all three ( × ).

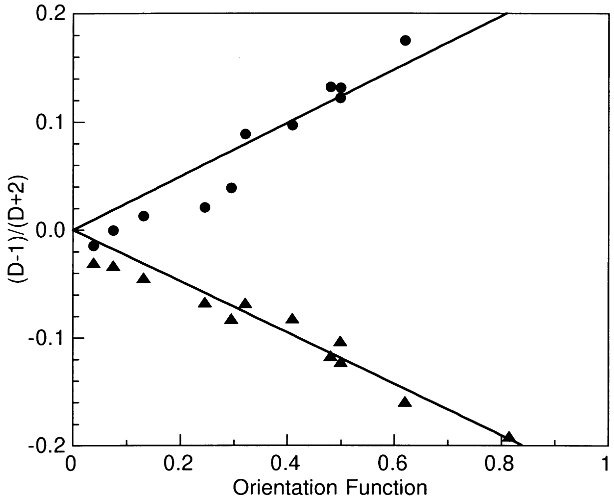

Fig. 5. Relationship between $(D-1)/(D+2)$ and the orientation function for the complex ester peak at 1330–1240 cm$^{-1}$ (●) and the carbonyl peak at 1729 cm$^{-1}$ (▲).

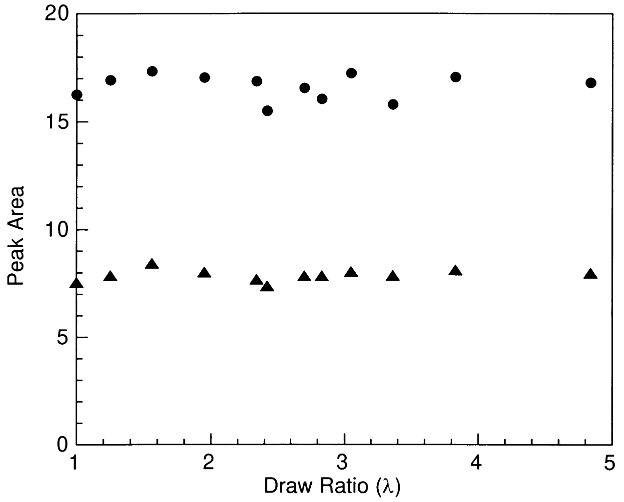

Fig. 6. Variation of peak area in the structural factor spectrum as a function of draw ratio, for the complex ester peak at 1330–1240 cm$^{-1}$ (●) and the carbonyl peak at 1729 cm$^{-1}$ (▲).

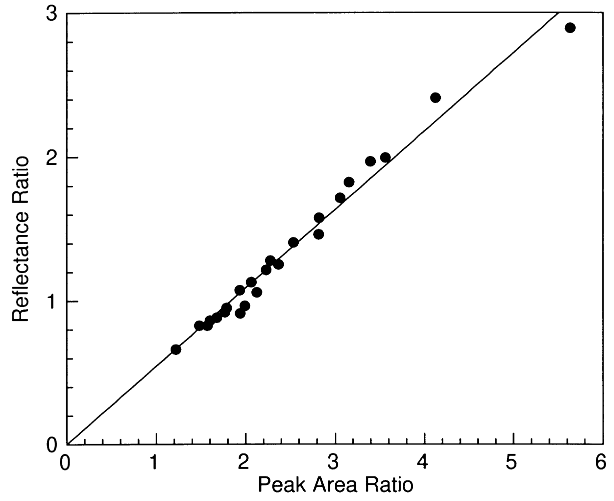

Fig. 8. Relationship between the ratio of the areas of the ester and carbonyl peaks in the molecular polarizability spectrum and the ratio of peak heights in the reflectance spectrum.

values in the numerator and denominator of Eq. (9) will be different. Thirdly, the ratio $R_0$ should be constant. This may not be the case if the bands are related to specific molecular conformations whose concentrations change upon drawing. In the present case, although the shape of the complex ester band in the structure factor spectrum changes somewhat upon drawing (Fig. 3), its area remains constant, as does that of the carbonyl band (Fig. 6). Thus, the ratio $R_0$ is constant and Eq. (10) should be valid.

It remains to test its validity and determine the values of the different parameters. For the set of uniaxially drawn samples, the values of $f_{cM}$ have already been determined as described previously. From these the values of $f_{cT}$ were calculated as $f_{cT} = -1/2 f_{cM}$. The values of $f_{cM}$ and $f_{cT}$ were then correlated with the corresponding values of the ratio $R$ of the areas of the bands at 1330–1240 and 1729 cm$^{-1}$ in the individual $\phi$ spectra, recorded in both the $M$ and $T$ directions. The relationship is shown in Fig. 7 and the solid line represents the fit obtained by nonlinear regression with Eq. (10). The best fit parameters are $R_0 = 2.086$, $\alpha$ (ester peak) $= 44.5°$, and $\alpha$ (carbonyl peak) $= 66.4°$. The fit is reasonably good and the $\alpha$ values are in excellent agreement with those determined by the more conventional approach. Hence, Eq. (10) appears to be valid.

It would be simpler if, instead of having to perform the Kramers–Kronig transformation and calculate the $\phi$ spectra, the original reflectance spectra could be used. Because of the dispersion-type shape of the peaks [Figs. 1(a) and 2(a)], it is difficult to calculate peak areas. However it is reasonable to consider the use of the maximum reflectance of each peak as a measure of its intensity. The general theoretical relationship between the reflectance $R$ and the imaginary molecular polarizability $\phi$ depends on the Fresnel

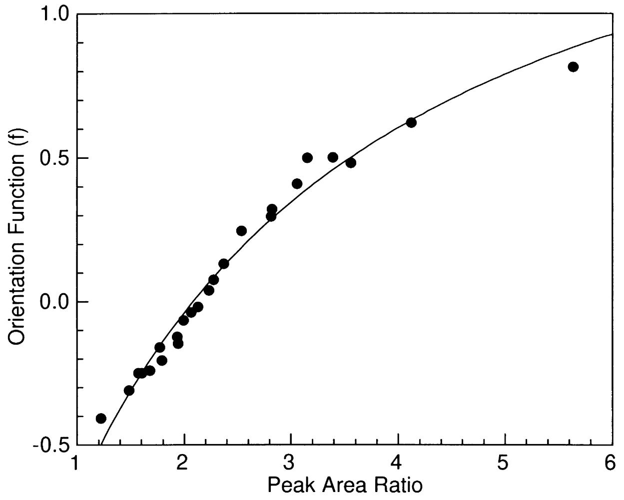

Fig. 7. Relationship between the orientation function and the ratio of the areas of the ester and carbonyl peaks in the molecular polarizability spectrum.

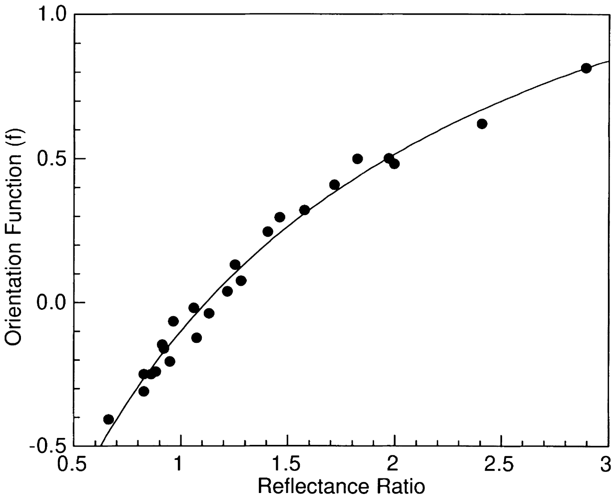

Fig. 9. Relationship between the orientation function and the ratio of the heights of the ester and carbonyl peaks in the reflectance spectrum.

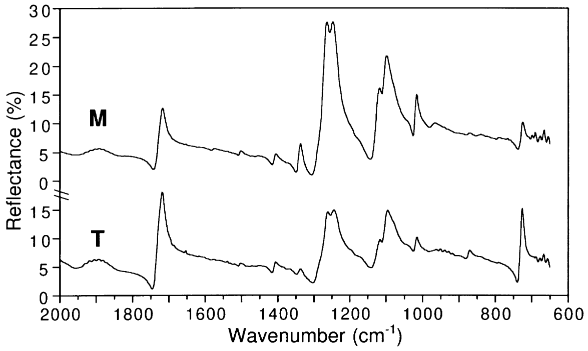

Fig. 10. Front-surface reflection spectra measured at the surface of the uniaxially oriented PET sample (λ = 2.8) with polarization in the *M* and *T* directions.

equations and is quite complex. However, at least for the present case, the relationship is empirically quite simple. Fig. 8 shows a plot of the ratio calculated from the peak maxima in the reflectance spectra versus the ratio calculated from the band areas in the $\phi$ spectra. The relationship can be described very well by a simple proportionality with a factor of 0.54. Fig. 9 shows a plot of the orientation function versus the ratio calculated from the heights of the peaks in the reflectance spectra. It can be seen that Eq. (10) applies just as well as in the previous case (Fig. 7). In this case, the relevant equation is:

$$f_{cJ} = \frac{R_J - 1.12}{0.657 + 0.528 R_J} \qquad (11)$$

where $R_J$ is the ratio of the heights of the reflectance peaks at 1243 and 1717 cm$^{-1}$ in a spectrum measured with polarization in the direction *J*. It should be noted that the peak maxima in the reflection spectrum occur at somewhat different frequencies from those of the polarizability spectrum. It should also be noted that the good results obtained with the reflectance peak heights may be fortuitous and only obtainable in certain cases, like the present one, whereas the method based on peak areas in the $\phi$ spectra has a more sound theoretical basis and should be more generally valid. The coefficients in Eq. (11) correspond to the following values of $\alpha$: 43.3° for the ester band and 66.6° for the carbonyl band.

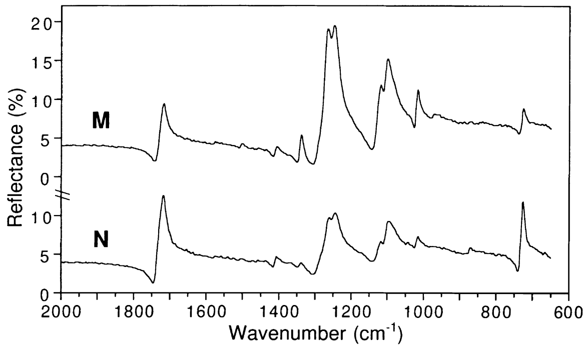

Fig. 11. Front-surface reflection spectra measured by IR microscopy for a cross-section in the *MN* plane of the uniaxially oriented PET sample, with polarization in the *M* and *N* directions.

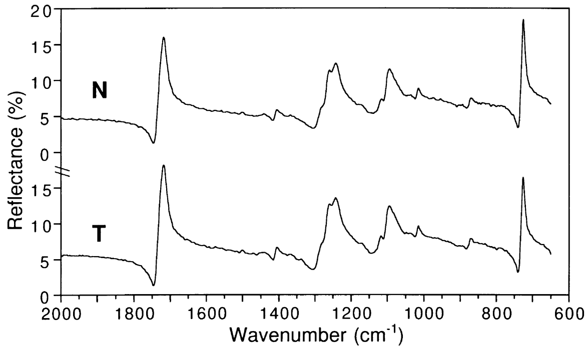

Fig. 12. Front-surface reflection spectra measured by IR microscopy for a cross-section in the *TN* plane of the uniaxially oriented PET sample, with polarization in the *T* and *N* directions.

Eq. (11) provides a very simple means for determining the orientation at the surface of PET. It was derived from the spectra recorded for a set of uniaxially drawn samples. To further test it, it was applied to a different uniaxially drawn sample (λ = 2.8) and to a biaxially oriented sample obtained from a blow-moulded bottle. Details on the origin and the characterization of these specimens were given in the experimental section.

Fig. 10 shows the front-surface reflection spectra measured at the surface of the uniaxially drawn sample with polarization in the *M* and *T* directions. Figs. 11 and 12 show the spectra obtained from the polished cross-sections of the same sample with the use of an infrared microscope. The *M*-direction and *T*-direction spectra measured in the *MN* and *TN* planes respectively are in excellent agreement with those measured on the surface (*MT* plane). Likewise, the two *N*-direction spectra are in good agreement and both closely resemble the *T*-direction spectrum. The similarity between the *N* and *T* spectra confirms the uniaxial orientation of the sample. It should be noted that while the two spectra measured in any given direction resemble each other in shape, their overall intensity is different. Taking the ratio of peak heights eliminates this problem.

Eq. (11) was used to estimate the orientation function for each of the spectra shown in Figs. 10–12 and the results obtained are summarized in Table 1. The quantitative results agree with the qualitative description. The orientation function $f_{cM}$ was found to have a high and positive value (0.54), while the other functions $f_{cT}$ and $f_{cN}$ are negative and

Table 1
Orientation functions for the uniaxial PET specimen calculated from the spectra of Figs. 10–12 by means of Eq. (11)

| Surface | $f_{cM}$ | $f_{cT}$ | $f_{cN}$ |
|---|---|---|---|
| MT plane | 0.54 | − 0.30 | ( − 0.24) |
| MN plane | 0.54 | ( − 0.30) | − 0.24 |
| TN plane | (0.62) | − 0.32 | − 0.30 |

Values in parentheses were calculated by difference based on Eq. (2).

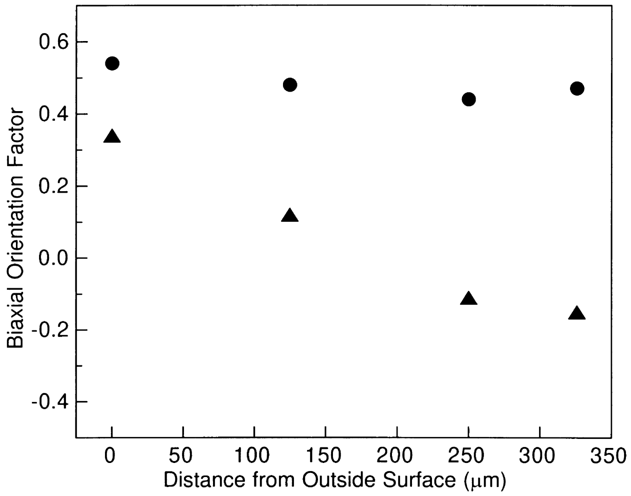

Fig. 13. Variation of the biaxial orientation factors of the blow-moulded sample as a function of distance from the outside surface, as measured in the transverse, or hoop, direction *T* (●) and the machine, or axial, direction *M* (▲).

approximately equal, confirming that the polymer molecules in the specimen are uniaxially oriented in the *M*-direction. Further, good agreement is observed for the values of a given *f* as measured in the different planes. The small differences noted are an indication of the experimental error involved in the process. Thus, the usefulness of Eq. (11) has been confirmed and it can be considered to give an adequate measurement of the degree of molecular orientation in the uniaxially oriented specimen of PET.

For the biaxially oriented (blow-moulded) sample, spectra were initially measured in the *MT* plane for both the inside and outside surfaces. A significant difference was observed, suggesting the presence of an orientation gradient across the thickness direction. Because of this, spectra were not measured in the cross-sectional *MN* and *TN* planes. Instead, to further investigate this phenomenon, the orientation was measured at different distances across the thickness direction by mounting the sample in epoxy and polishing it to different depths. At each depth, reflection spectra were measured in the *M* and *T* directions and Eq. (11) was used to calculate the corresponding orientation functions. In order to more easily compare the results with those obtained from birefringence measurements, the biaxial orientation factors defined by White and Spruiell were calculated according to Eq. (3a), Eq. (3b). The variation of these factors as a function of the distance across the thickness is shown in Fig. 13, which confirms that there is a significant gradient of molecular orientation in the thickness direction. The inside surface was found to be much more strongly oriented in the hoop direction *T* than in the axial or length direction *M*, whereas on the outside surface the axial orientation approaches that of the hoop direction, so the orientation is closer to equibiaxial. The intermediate surfaces situated at 125 $\mu$m and 250 $\mu$m from the outside surface were found to have intermediate orientations. Results showing a similar gradient were reported by Cakmak et al. [23]. They found that polymer molecules at the inside and outside surfaces of stretched blow-moulded bottles of PET are biaxially oriented with a preferential orientation in the hoop direction. Moreover, it was noted that the inside surface of the bottle is much more oriented than the outside one. These results are somewhat different from those obtained in the present study, probably because of the difference in the shape of the bottles used in the two cases, but they clearly show the presence of a significant gradient of molecular orientation in the thickness direction of the blow-moulded bottles of PET.

Table 2
Average biaxial orientation factors for the biaxially oriented specimen

| Method | $f^B_{cM}$ | $f^B_{cT}$ |
|---|---|---|
| Infrared Reflection | 0.10 | 0.47 |
| Birefringence | 0.14 | 0.43 |

The orientation factors shown in Fig. 13 were used to calculate average values across the thickness direction. In Table 2, these are compared with the values obtained from birefringence measurements [19]. Basically, both techniques indicate that the specimen under investigation is biaxially oriented with a preferred orientation in the hoop direction. Moreover, both techniques give almost the same average degree of orientation in the *M* and *T* directions. The small differences observed are undoubtedly caused by the experimental error involved in the measurements. Overall, the equation proposed in this study (Eq. (11)) can be considered to provide adequate characterization of molecular orientation in biaxially oriented specimens of PET. Its main advantage is that the biaxial orientation can be characterized by making measurements in only the MT plane.

## 4. Conclusions

It was demonstrated that it is possible to characterize the orientation in both uniaxially and biaxially oriented PET samples by measuring front-surface reflection infrared spectra with polarization in two mutually perpendicular directions, normally the machine (*M*) and transverse (*T*) directions. The ratio of the intensity of the complex ester band at 1330–1240 cm$^{-1}$ with respect to that of the carbonyl band at 1729 cm$^{-1}$ can be used to determine the orientation function with respect to the measurement direction and an equation was derived for this purpose. The validity of the equation was confirmed by tests on uniaxially and biaxially oriented samples and by comparison with birefringence results. For PET, the method can be applied with the use of either the peak heights in the measured reflectance spectra, or the peak areas in the imaginary molecular polarizability spectra obtained by Kramers–Kronig transformation. However the latter approach is more theoretically sound and should be valid for general application to other polymers that possess suitable infrared absorption bands.

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