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Polymer Vol. 36 No. 17, pp. 3385–3392, 1995
Elsevier Science Ltd
Printed in Great Britain
0032-3861/95/$10.00+0.00

Orientation and conformation in poly(ethylene terephthalate) with low draw ratios as characterized by specular reflection infra-red spectroscopy

J. Guèvremont, A. Ajji, K. C. Cole* and M. M. Dumoulin
National Research Council Canada, Industrial Materials Institute, 75 Boulevard de Mortagne, Boucherville, Québec, Canada J4B 6Y4
(Received 12 September 1994; revised 24 February 1995)

A quantitative treatment of the specular reflection spectra obtained from the surface of uniaxially drawn poly(ethylene terephthalate) samples has been performed. A procedure for correcting for the effect of surface irregularities is presented, and an overall orientation function based on the orientation and content of *trans* conformers is calculated. The results are correlated with mechanical modulus and crystallinity values. In addition, an unconventional dichroic ratio parameter based on a combination of two major bands is proposed. Results obtained from the Kramers–Kronig analysis and directly from the reflection spectra are discussed. Both are compared with the overall orientation function obtained before.

(Keywords: poly(ethylene terephthalate); orientation; specular reflection *FT*i.r.)

INTRODUCTION

General

Infra-red (i.r.) spectroscopy has been used extensively over the years for polymer characterization. In particular, the determination of molecular orientation from dichroic ratio measurements has attracted the interest of many researchers. Poly(ethylene terephthalate) (PET) has received much attention because of its practical applications and its complex and interesting behaviour. A quantitative relationship has been established between directional absorption measurements and the distribution of the molecular chain-axis orientation[1]. Several studies followed, focusing on overall molecular orientation, conformational changes and crystallinity as determined from infra-red spectra[2–5]. These and other analyses have contributed much to the understanding of the drawing and structural behaviour of PET[6].

In those studies, absorption measurements were carried out in transmission. Since infra-red radiation can be strongly absorbed by the polymer molecular groups, the studies were limited to fibres and films less than 50 μm thick. Even for such films, the strongest absorption bands are often saturated and an extensive examination was done only for the less intense bands.

Other authors used the attenuated total reflection (a.t.r.) method for the determination of surface molecular orientation in PET[7,8]. Although the method is successful in determining surface orientation, it should be noted that a prism is needed at the surface of the sample and that the results depend greatly on the quality and reproducibility of contact between the prism and the sample. In addition, the more intense absorption bands show saturation even when a.t.r. is used.

External specular reflection spectroscopy can also be used for the determination of molecular orientation and other properties at the surface of a polymeric material[9–14]. The obvious advantages of this method are that it is non-contact and that it enables orientation measurements on thick or opaque samples. Another point of interest is that the specular reflectance spectrum clearly shows the most strongly absorbing bands. These bands, as mentioned above, are often saturated when other methods are used. Therefore, specular reflection gives access to new information about the structure and orientation mechanisms to complement that obtained by transmission or a.t.r. spectroscopy.

Care must be exercised, however, since the physical state of the polymer surface may influence the dichroic ratio measurement if the irregularities are directional. Also, the relationship between surface and bulk orientation, which will depend on the process and on the extent of deformation, should also be considered if a correlation with bulk properties is needed.

Only recently have there been some reports on the use of polarized specular reflection spectroscopy in studying surface molecular orientation. Orientation functions have been calculated for PET and a liquid-crystal polymer from dichroic ratios in the ultra-violet range[9,10]. The orientation function and its distribution have also been determined from the i.r. spectrum for moulded sheets of liquid-crystal polymer[11–13]. The i.r. spectrum of PET as measured by specular front-surface reflection has been presented and analysed in a previous

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* To whom correspondence should be addressed

work[14]. In the present paper two main issues are considered: (i) the quantitative determination of conformational changes and an overall orientation function from the front-surface specular reflection spectrum of PET; and (ii) the use of some of the major bands in the reflection spectrum for the determination of molecular orientation in opaque PET samples.

Theory

The theory related to infra-red dichroism and its use to determine molecular orientation is well known[15,16] and will be discussed here only to the extent needed to define certain quantities used in this work. Dichroism depends on the fact that electromagnetic radiation can be absorbed by a molecule when the frequency is equal to that of a normal mode of vibration of the molecule (usually corresponding to the infra-red region of the electromagnetic spectrum). The efficiency of the absorption depends on the angle between the electric vector of the incident radiation and the direction of the transition moment of the vibrational mode being considered. In the case of a uniaxially drawn polymer, by making measurements with radiation polarized so that the electric vector is either parallel or perpendicular to the draw direction, it is possible to characterize the degree of molecular orientation. The quantity generally used for this purpose is the dichroic ratio D, defined as the ratio of the absorbance measured with the electric vector polarized parallel to the draw direction with respect to that measured perpendicular to the draw direction.

The reflectance from the surface of a thick polymer sample is related to the polymer's optical constants and the angle of incidence through the well known Fresnel equations. The optical constants are the real and imaginary parts of the complex index of refraction, defined as:

$$n^* = n - \mathrm{i}k \tag{1}$$

where the real part n is the refractive index and the imaginary part k is the absorption index. These two quantities can be interrelated through the Kramers–Kronig relationship, based on the classical approach of dispersion analysis[9]. In order to obtain a quantitative dichroic ratio from the reflection spectra, the contribution of the absorption index must be separated out. In the present study, this was done with the aid of the software Spectra Calc$^{\mathrm{TM}}$ from Galactic Industries Corp.; the Maclaurin series algorithm was used to perform the integration. The absorption index k is closely related to the absorption coefficient α obtained from transmission measurements, and the k spectrum obtained from the Kramers–Kronig analysis resembles the absorbance spectrum obtained in transmission[14]. The dichroic ratio can thus be defined in terms of the absorption index k:

$$D = k_{\parallel}/k_{\perp} \tag{2}$$

This ratio can be related to the average orientation of the main polymer chain. For comparing results obtained by different methods it is useful to define this in terms of an orientation function. Infra-red spectroscopy gives access to the second moment of the orientation function of the polymer chain, described by the second-order Legendre polynomial of $\cos\theta$:

$$f = \langle P_2(\cos\theta)\rangle = \tfrac{1}{2}(3\langle\cos^2\theta\rangle - 1) \tag{3}$$

where the angle brackets indicate averaged values and θ is the angle between the polymer chain axis and a defined reference direction (usually the draw direction). For uniaxially drawn material, the orientation function f is related to the dichroic ratio D by:

$$f = \frac{D-1}{D+2}\,\frac{D_0+2}{D_0-1} \tag{4}$$

where D_0 is the dichroic ratio of a perfectly oriented sample. The latter is related to the angle α between the polymer chain axis and the transition moment direction of the particular vibrational mode under consideration by:

$$D_0 = 2\cot^2\alpha \tag{5}$$

In cases where no structural information is available (i.e. the angle α is not known), it is convenient to describe the orientation in terms of the following quantity, which is proportional to the orientation factor f:

$$\frac{D-1}{D+2} = \frac{D_0-1}{D_0+2}f = P_2(\cos\alpha)\langle P_2(\cos\theta)\rangle \tag{6}$$

The above approach is based on the molecular-gas approximation and thus does not consider any interactions between the molecules. In actual fact, the electric field at a given dipole will be influenced by neighbouring dipoles, and a model has been developed to correct for this 'local field effect'[1]. In certain circumstances this correction can be significant, but in the present work, where the orientation and birefringence are relatively low, it was not deemed necessary to take it into account.

EXPERIMENTAL

Sample preparation

The polymer used in this study was an extrusion-grade PET from DuPont, without any nucleating agent. The material was dried at 90°C for 24 h under vacuum. Sheets were formed at 280°C by compression moulding in a laboratory press, then quenched in an ice bath to give an amorphous product (crystallinity $<5\%$). Thin rectangular films (6 cm long by 1 cm wide by 0.1–0.6 mm thick) were cut from the sheets for orientation and mechanical testing.

Oriented samples were prepared by stretching this amorphous material, except for one sample that was thermally crystallized (15 min at 200°C) prior to stretching in order to evaluate the effect of thermally induced crystallinity on the dichroic response. The crystallinity of this sample was about 28%. Drawing of the films was performed at 80°C and 2 cm min^{-1} in an Instron tensile tester equipped with an environmental chamber. The draw ratios ranged from 1.2 to 2.8.

Modulus and crystallinity measurements

The dynamic mechanical properties were measured in the tensile mode at 1 Hz on a d.m.t.a. instrument from Polymer Laboratories. Because of significant shrinkage of the oriented samples, we will discuss only the results measured below the glass transition temperature.

The crystallinity of the films before and after orientation was determined by differential scanning calorimetry. The area of the crystallization exotherm peak was subtracted from that of the melting endotherm peak to determine the amount of crystallinity initially present in the samples. The enthalpy of melting of completely crystalline PET was taken as 140 kJ kg^{-1} (ref. 17). Comparison with density measurements was also made, using values of 1.335 g cm^{-3} for the amorphous phase and 1.455 g cm^{-3} for the crystalline phase[18].

Infra-red measurements

Details of the set-up and procedure are given elsewhere[14], so only a brief account will be given here. The measurements were made in the external reflection mode with a resolution of 4 cm^{-1} on a Nicolet 170SX *FT*i.r. spectrometer using a specular reflection accessory with an angle of incidence of 20°. Each spectrum was the result of an accumulation of 128 scans.

The Kramers–Kronig software used is based on normal incidence, which was not the case here. Thus it was necessary to correct the measured reflectance for each polarization before applying the analysis. Based on a refractive index n of 1.58 and an absorption index k of 0.5, the correction factors were found to be as follows[14]: $R_{\parallel}(0°) = 1.16R_{\parallel}(20°)$ and $R_{\perp}(0°) = 0.870R_{\perp}(20°)$. Although n and k will vary somewhat with wavelength and orientation, the effect on the factors is not large.

All dichroic ratios were calculated by integrating peak areas and taking the ratio.

RESULTS AND DISCUSSION

Typical spectra

Figure 1 shows the spectra obtained for the sample corresponding to a draw ratio of 2.7. The reflectance spectra (*Figures 1a* and *1b*) show the dispersion-shaped peaks characteristic of Fresnel reflection, but the absorption index spectra obtained from the Kramers–Kronig treatment (*Figures 1c* and *1d*) resemble absorbance spectra obtained by transmission. In both cases, however, the dichroism is obvious for certain peaks. Some (for example, 1340 and 1265 cm^{-1}) show parallel dichroism, while others (for example, 1725 and 729 cm^{-1}) show perpendicular dichroism.

Surface correction

As mentioned before, surface irregularities can influence the measured values of reflectance. Even if both the parallel- and perpendicular-polarized spectra are measured without repositioning the sample, the effect may be different for the two cases if the surface irregularities have a directional nature. This seemed to be the case for some of our samples, and obviously must be taken into account in calculating dichroic ratios. One way of doing this is to select a reference band that does not show significant dichroism, as would be the case for a molecular group whose transition moment makes an angle α of 55° with the main chain (see equations (5) and (6)). The apparent dichroic ratio calculated for such a band, if not equal to unity, would represent the correction factor needed to take into account the effect of surface irregularities. However, the loss of reflection due to the irregularities may also depend on the radiation frequency, so, in order to obtain an accurate value of the dichroic ratio of a particular band, the frequency difference between that band and the reference band should be as small as possible.

Orientation and content of conformers

Some molecular groups of PET, such as the ethylene glycol moiety, have the interesting particularity of having rotational conformers. These conformers are linked with both crystallinity and stretching. It has been proposed[6] that, in the amorphous phase, both *gauche* and *trans* conformers are present, while only *trans* conformers exist in the crystalline phase. Also, several studies[6] showed that the *gauche* conformers are only poorly oriented even for high draw ratios, whereas the *trans* conformers are highly oriented, suggesting that there is a transformation from *gauche* to *trans* conformers in the alignment

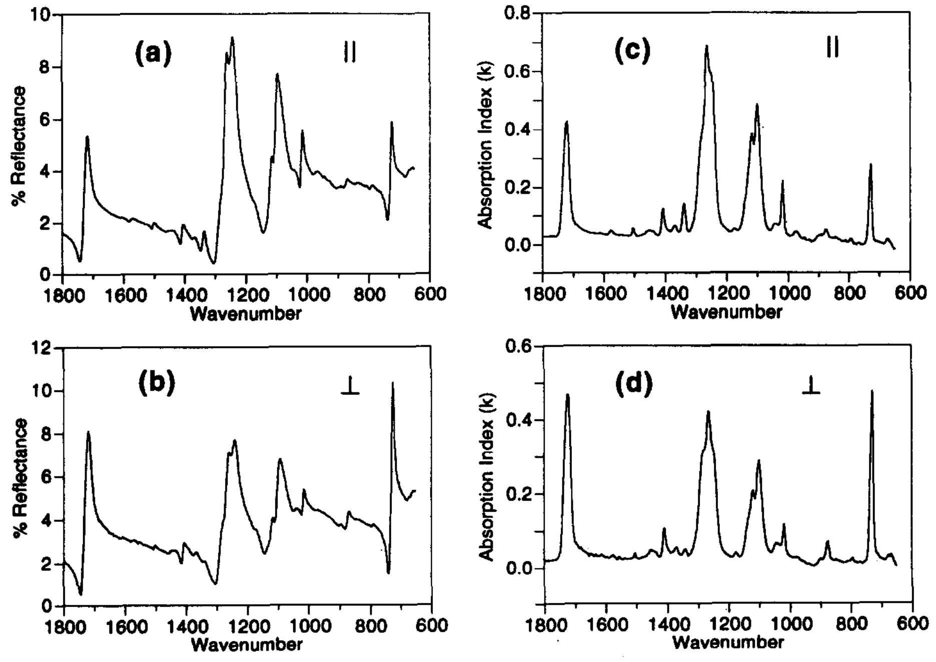

Figure 1 Spectra obtained for the sample with a draw ratio of 2.7: (a) measured reflectance, parallel polarization; (b) measured reflectance, perpendicular polarization; (c) calculated absorption index, parallel polarization; (d) calculated absorption index, perpendicular polarization

process. Thus, it is relevant to study both the orientation and the concentration of these conformers in order to understand and characterize the orientation mechanisms of a semicrystalline polymer such as PET. In this regard, infra-red spectroscopy can give useful information since it is possible to assign some of the observed bands specifically to either *trans* or *gauche* conformers. For example, the bands at 1340 and 1370 cm^{-1} are assigned to CH_2 wagging modes of the glycol segments possessing the *trans* and *gauche* conformations respectively[5]. We have followed the dichroic behaviour of these two bands taking the nearby band at 1410 cm^{-1} as a reference band to correct for the surface effect mentioned above. Walls *et al.*[7] have demonstrated that this band has a low sensitivity to orientation and have used it to correct for contact artefacts that arise in using the a.t.r. method. The corrected dichroic ratio of a particular band *i* is thus calculated from the formula:

$$D_i = (k_{i\parallel}/k_{i\perp})/(k_{1410\parallel}/k_{1410\perp})$$

The correction factors $k_{1410\parallel}/k_{1410\perp}$ ranged from 1.01 to 1.53. In the case of the unoriented sample, all dichroic ratio values, after correction, were very close to unity. This indicates that the correction is valid over a wide range of frequencies, i.e. the effect is not highly dependent on the frequency.

Figure 2 shows the results obtained both before and after the correction. The quantity plotted as a function of the draw ratio λ is $(D-1)/(D+2) = P_2(\cos\alpha) \times \langle P_2(\cos\theta)\rangle$. It is seen that the correction results in a somewhat lower degree of scatter (the correlation coefficient for the *trans* peak increases from 0.9806 to 0.9883) and also brings the values for the unoriented sample closer to the expected value of zero. *Figure 2* shows that, while the *trans* conformers present a degree of orientation proportional to the draw ratio, the *gauche* conformers show negligible orientation over the range of draw ratios used. The results obtained by the specular reflection method are thus similar to those obtained for the same bands by Spiby *et al.*[5] from transmission measurements on very thin films and also by Walls and Coburn[8] using a.t.r.

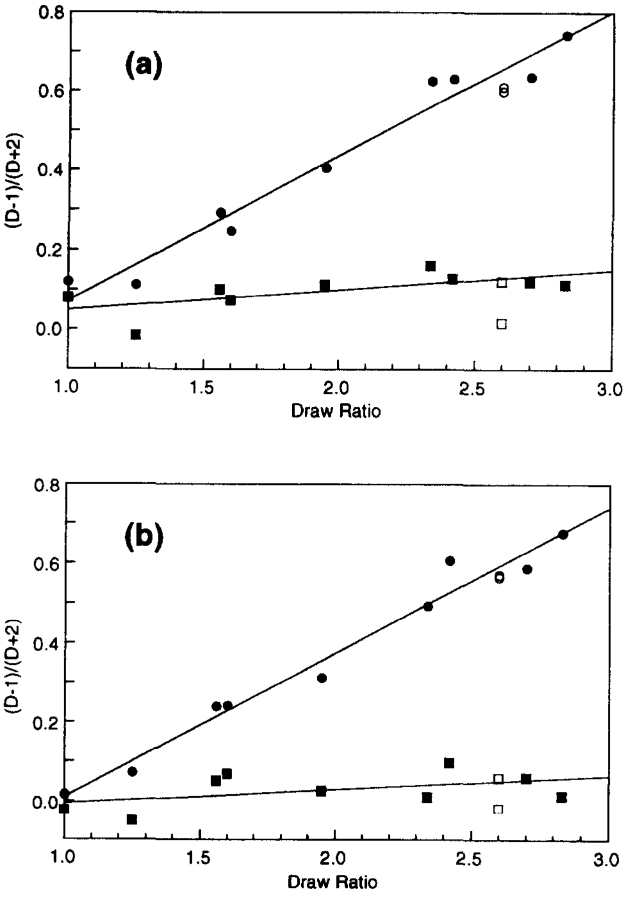

Figure 2 The quantity $(D-1)/(D+2) = P_2(\cos\alpha)\langle P_2(\cos\theta)\rangle$ as a function of draw ratio for the *trans* peak at 1340 cm^{-1} (●) and the *gauche* peak at 1370 cm^{-1} (■). Filled symbols represent initially amorphous material; open symbols represent the sample crystallized before drawing. The graphs represent the data (a) before and (b) after correction for reflection losses, as discussed in the text

In order to follow the conformational changes from the i.r. spectrum, it is necessary to determine the relative concentrations of both conformers. This was done by a method similar to that used by Edelmann and Wyden[19]. First it is necessary to calculate the 'structural factor' spectrum representing an isotropic sample. For a uniaxially oriented sample, this can be calculated as $k_0 = (k_\parallel + 2k_\perp)/3$. The structural factor spectra were used to measure the heights *H* of the reference, *gauche* and *trans* peaks at 1410, 1370 and 1340 cm^{-1} respectively. When the quantity H_{1340}/H_{1410} is plotted against H_{1370}/H_{1410}, a straight line with negative slope is obtained whose *x* and *y* intercepts may be considered to correspond respectively to 100% *gauche* and 100% *trans* conformer. By applying these factors to the spectrum of a given sample, the fractions of *gauche* and *trans* conformers χ_{gauche} and χ_{trans} can be estimated. These should add up to unity. For the set of spectra analysed, the sum ranged from 0.95 to 1.05, so the estimated error is at most 5%.

Figure 3 shows the results of these calculations as a function of draw ratio. Unlike the orientation, which appears to increase linearly up to $\lambda = 3$, χ_{trans} changes very slowly up to $\lambda = 2$, then more rapidly between 2 and 3. Again the results are similar to those obtained by Spiby[5], except that in our case the samples with small draw ratios show a lower percentage of *trans* conformers. This is most probably due to the different thermal histories of the two materials.

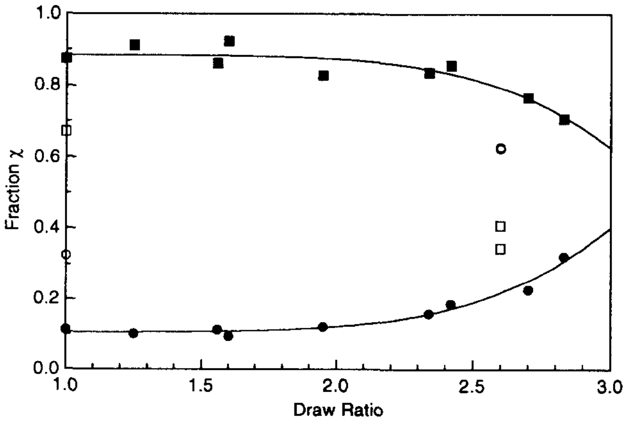

Figure 3 The fractions of *trans* (●) and *gauche* (■) conformers as a function of draw ratio. Filled symbols represent initially amorphous material; open symbols represent the sample crystallized before drawing

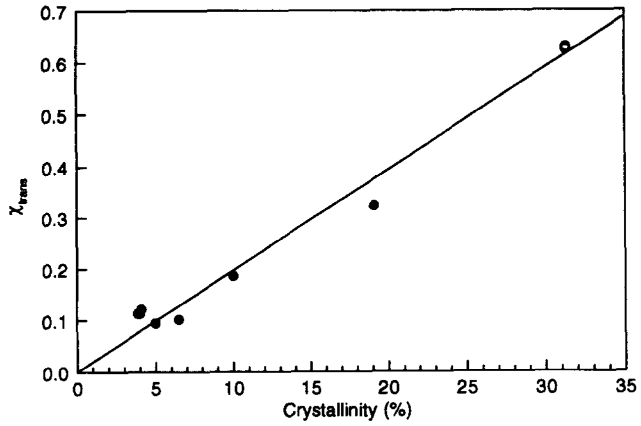

Figure 4 The relationship between the fraction of *trans* conformer and the crystallinity. Filled symbols represent initially amorphous material; open symbols represent the sample crystallized before drawing

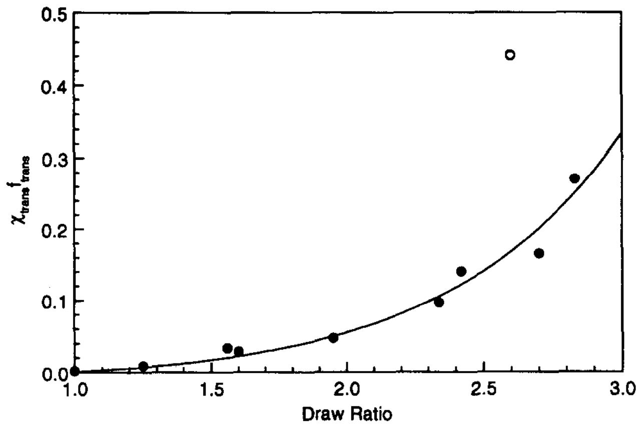

Figure 5 The 'overall' orientation factor $\chi_{trans}f_{trans}$ as a function of draw ratio. Filled symbols represent initially amorphous material; open symbols represent the sample crystallized before drawing

An interesting aspect of these results is the behaviour of the sample that was partially crystallized prior to drawing. From the points in *Figure 3* corresponding to undrawn samples (draw ratio = 1), it can be seen that the energy supplied by the thermal treatment increases the *trans* conformer content from 11% to 32%, but these *trans* conformers have no preferred direction. When the crystallized sample is stretched to a draw ratio of 2.6 (the two points correspond to two spectra measured at different points on the same sample), molecular rearrangement and alignment brings about a conversion of *gauche* conformers to *trans* and the *trans* content increases to about 62%. These conformers will show a directional nature. *Figure 2* shows that the degree of *trans* orientation in the drawn material is the same as in an initially amorphous sample drawn to the same extent, although the *trans* content is about three times higher. The *trans* segment content is strongly related to crystallinity, whether induced thermally or by stretching. *Figure 4* shows the relationship between *trans* content and crystallinity as measured by d.s.c.; the proportionality is evident.

Overall orientation

The infra-red bands discussed above give information on the orientation of specific conformers, either *gauche* (found only in the amorphous phase) or *trans* (found in both amorphous and crystalline phases). Techniques such as birefringence give an overall orientation representing an averaging over both amorphous and crystalline phases. Certain infra-red bands, such as those associated with benzene ring vibrations, can also give an overall orientation. For specimens drawn from the amorphous state, several workers[2-5] have related the overall orientation function to the concentration and the orientation function of the *trans* conformers:

$$f_{overall} = \chi_{trans} f_{trans} \quad (7)$$

This assumes that the orientation of the *gauche* conformers is negligible and does not contribute significantly to the overall orientation. The results obtained here confirm this assumption, at least to a first approximation (*Figure 2*).

To calculate the absolute value of the overall orientation function from our data, we then need to know the angle α for the 1340 cm^{-1} band of the *trans* conformers. This was determined by examining the spectra of a highly oriented sample ($\lambda = 5.18$), not shown here. Assuming that $f = \langle P_2(\cos\theta)\rangle$ is close to unity for this high draw ratio, we obtain a value of $\alpha = 21.3°$. This is in agreement with the value of $\alpha = 21°$ found by Spiby *et al.*[5] from a correlation of the 1340 cm^{-1} band with the band at 975 cm^{-1} and with birefringence results. *Figure 5* shows the values of $\chi_{trans}f_{trans}$, calculated with $\alpha = 21.3°$, as a function of the draw ratio. For the initially amorphous samples, this represents $f_{overall}$, and we observe a relatively smooth increase as a function of the draw ratio. This curve includes the effects of increased crystallinity induced by stretching. However, the sample that was partially crystallized before drawing gives a much higher value of $\chi_{trans}f_{trans}$. This is almost entirely due to the higher value of χ_{trans}, since f_{trans} is the same as for the initially amorphous samples. In other words, the *trans* chain segments are oriented to the same degree, but because there are more of them in the thermally crystallized sample, the overall orientation (averaged over all chain segments) is higher. However, a preliminary analysis of other bands in the spectrum such as the benzene ring band at 875 cm^{-1} does not provide clear confirmation of this. Further investigation is planned in order to determine whether, in the case of a thermally crystallized sample, the overall orientation as defined by equation (7) is consistent with that determined from other infra-red bands or by other techniques.

The degree of orientation of the main chain is related to the mechanical properties of the sample. It has been shown[3] that there is a good correlation between the modulus and the overall orientation $\chi_{trans}f_{trans}$, irrespective of the crystallinity (induced by stretching). *Figure 6* shows a plot of the elastic modulus as obtained by d.m.t.a. *versus* the overall orientation function. A reasonably good correlation is obtained, considering the error associated with the modulus measurement. It is interesting to note that the correlation seems to hold for the initially crystallized sample as well. This would mean that the quantity defined by equation (7) is related to the mechanical modulus irrespective of the crystallization process. Again the results obtained here suggest that this aspect needs to be explored in more depth.

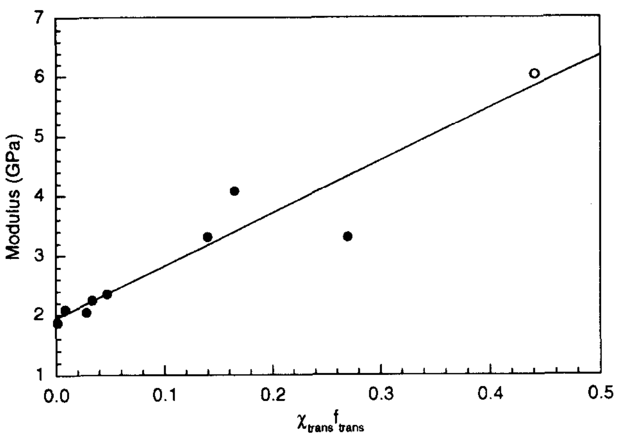

Figure 6 The relationship between the mechanical modulus and the 'overall' orientation factor $\chi_{trans}f_{trans}$. Filled symbols represent initially amorphous material; open symbols represent the sample crystallized before drawing

As mentioned in the Introduction, the relationship between surface and bulk orientation must be considered, since the orientation function is measured here at the surface while the modulus is representative of the whole volume. The relationship between surface and bulk orientation for uniaxially oriented PET films has been studied by Walls and Coburn[8]. They observed that the orientation and content of the *trans* conformers at the surface are higher than in the bulk and that the difference increases with draw ratio. Nevertheless, the difference was shown to be small for draw ratios below 2.5, which is the case for most of our samples. Furthermore, the correlation observed between the i.r. measurements (representative of the surface) and both crystallinity and mechanical modulus (representative of the bulk) indicates also that the relation between surface and bulk properties is constant for the draw ratios considered here. In this paper it is assumed that the measured orientation and concentration at the surface are not significantly different from those present in the bulk.

The above analysis shows that the results obtained from specular reflection are, in general, in excellent agreement with those obtained from transmission measurements[5,8]. This provides confidence in the determination of the overall orientation function by the specular reflection method.

Orientation behaviour of some of the major bands

A significant advantage of the specular reflection method is that it allows measurement of the more intense bands in the spectrum, which are often saturated when measured by other methods. Two of these will be considered here. The first is the band at about $1725\,\mathrm{cm}^{-1}$, assigned to the carbonyl stretching mode[20]. It appears to consist of two main components, one around $1730\,\mathrm{cm}^{-1}$ and the other around $1718\,\mathrm{cm}^{-1}$, both of which show perpendicular dichroism[14]. The second strongly absorbing band is at $1265\,\mathrm{cm}^{-1}$, assigned to stretching of the C(O)–O bond. This is a complex band with several components. On the whole it shows parallel dichroism[14]. There have been no detailed studies made, to our knowledge, on the orientation behaviour of these bands.

As mentioned previously, because of the imperfect surfaces of the samples studied in this work, the specular reflection spectra are subject to a general intensity attenuation. One way of overcoming this problem in quantitative treatments is to use ratios of two bands in the same spectrum, in the manner that the $1410\,\mathrm{cm}^{-1}$ band has already been used in this work. To amplify the effects of orientation, it is better to use two bands showing opposite dichroism. This approach has been applied by Mirabella to polypropylene spectra measured by attenuated total reflection, where a problem arises because of variations in sample–prism contact[21]. In this work, we have taken the ratio of the peaks at 1265 and $1725\,\mathrm{cm}^{-1}$ as a measure of the orientation. However, the surface irregularities may also cause a wavelength dependence that may vary from sample to sample. To reduce such effects, we take the ratio of the results for parallel and perpendicular polarized spectra of the same sample. Thus we define the double ratio based on integrated peak areas in the k spectra:

$$D_k^* = \frac{k_{1265\|}/k_{1725\|}}{k_{1265\perp}/k_{1725\perp}} \tag{8}$$

It can be seen that this is equivalent to taking the ratio of two dichroic ratios, the first of which is greater than one and the second less than one:

$$D_k^* = \frac{k_{1265\|}/k_{1265\perp}}{k_{1725\|}/k_{1725\perp}} \tag{9}$$

This 'double dichroic ratio' is thus more sensitive to orientation effects than a simple ratio, but at the same time less sensitive to the errors caused by surface irregularities and related effects. The ratio D_k^* has shown coherent results in all our investigations, which have included measurements of biaxially deformed samples and samples featuring high draw ratio, up to 5.5 (not included in the present study). *Figure 7* shows the relationship between D_k^* (calculated from peak areas in the absorption index spectra) and the 'overall orientation function' $\chi_{trans}f_{trans}$ for the samples studied in this work. Although there is no theoretical basis for it, the relationship can be described reasonably well by a straight line, which seems to apply also to the sample that was thermally crystallized prior to drawing.

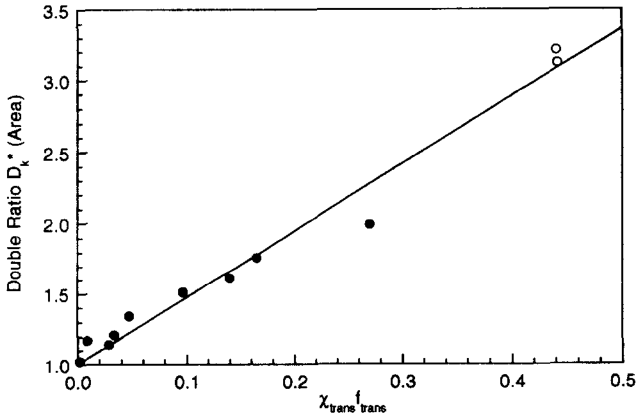

Figure 7 The relationship between the 'double dichroic ratio' D_R^* (based on peak areas in the absorption index spectra) and the quantity $\chi_{trans}f_{trans}$. Filled symbols represent initially amorphous material; open symbols represent the sample crystallized before drawing

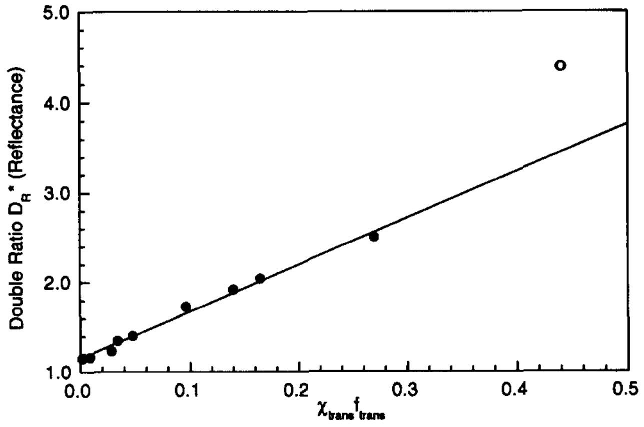

Figure 8 The relationship between the 'double dichroic ratio' D^*_R (based on peak heights in the reflectance spectra) and the quantity $\chi_{trans}f_{trans}$. Filled symbols represent initially amorphous material; open symbols represent the sample crystallized before drawing.

Determination of the orientation directly from the reflectance spectrum

It may furthermore represent a significant advantage to determine the orientation directly from the reflected radiation, i.e. without applying the reflection analysis and the Kramers–Kronig transformation. The strong bands at 1725 and 1265 cm^{-1} are easily detected in reflection. We have thus calculated a second 'double ratio' D^*_R based on the reflectance values R obtained from the peak maxima (not areas) in the original reflectance spectra:

$$D^*_R = \frac{R_{1265\parallel}/R_{1725\parallel}}{R_{1265\perp}/R_{1725\perp}} \qquad (10)$$

(In the reflectance spectra, the peak maxima actually occur at 1242 and 1718 cm^{-1}, somewhat shifted with respect to the absorption index spectra.) *Figure 8* shows the relationship between D^*_R and $\chi_{trans}f_{trans}$. For the initially amorphous samples, the relationship is again well described by a straight line, but the thermally crystallized sample lies somewhat above it. This may be attributed to the complexity of the 1265 cm^{-1} band, which comprises at least three components arising mainly from vibrations of the ester groups. For the initially amorphous samples, this band shows a single maximum at 1265 cm^{-1} in the k spectra, but two maxima (1260 and 1242 cm^{-1}) in the reflectance spectra (see *Figure 1*). For the thermally crystallized sample (see *Figure 1* of ref. 14), the band shape differs as a result of changes in molecular conformation and ordering, and the reflectance spectrum shows only a single maximum at 1244 cm^{-1}. The ratio D^*_R, which is based only on the band maximum, is more sensitive to these effects.

The direct relationship between reflectance and orientation is particularly interesting from a practical standpoint because the quantity $\chi_{trans}f_{trans}$ has been shown to correlate very well with the mechanical modulus (*Figure 6*). This means that the orientation/crystallinity properties that determine the modulus can be characterized directly from measurements of the specular reflectance at two discrete frequencies. This could represent a considerable advantage for on-line orientation measurement.

CONCLUSION

The orientation function of PET has been calculated from front-surface specular reflection spectra by using the Kramers–Kronig transformation and by considering a uniaxial deformation model. The results have been shown to be consistent if the dichroic ratios are corrected, using the 1410 cm^{-1} band as a reference, to compensate for the effects of surface irregularities.

An analysis of both orientation and content of *trans* segments has shown that *gauche* conformers show poor orientation and decrease in number with increasing draw ratio, while *trans* orientation and content both increase with draw ratio, as expected. This is in agreement with a model in which the *gauche* segments are transformed into *trans* segments while the deformation occurs. Furthermore, the *trans* conformation is more favourable to an ordering of the molecular chains, leading to crystallization induced by the alignment process. This is confirmed by a comparison of the *trans* segment content, calculated from the spectra, with the crystallinity as measured by the d.s.c. method.

The overall orientation function has been determined as the product of the *trans* content with the *trans* orientation function. This function shows a good correlation with the mechanical modulus as measured by the d.m.t.a. method.

The behaviour of the initially crystallized sample is interesting. It shows the same *trans* orientation function as the initially amorphous sample, when stretched to the same extent, but the *trans* segment content is about three times higher both before and after drawing. It has also been shown that the relationship between *trans* content and crystallinity holds for both crystallization processes. Furthermore, the overall orientation as defined here will be affected if the *trans* content changes, so the orientation function is higher for the initially crystallized sample. The significance of this overall orientation function in the case of an initially crystallized sample is not clear. Nevertheless, the correlation between the overall orientation function as defined here and the mechanical modulus is valid irrespective of the crystallization process. The actual value of the orientation function of a sample stretched from the crystallized state requires further investigations. These studies are important in the case of the orientation determination of thick samples since the process usually involves some thermal crystallization.

The orientational behaviour of two major bands has been explored. A dichroic parameter has been defined based on a combination of the 1725 and 1265 cm^{-1} bands. Both k and R ratios have been calculated and compared to the overall orientation function as calculated previously. In both cases the relationship is seen to be linear when the samples are stretched from the amorphous state. In the case of initially crystallized samples, more extensive investigations are planned.

As a general conclusion of this work, the reflection method is shown to give consistent results concerning the molecular conformation and orientation at the surface of a polymeric material (PET). Furthermore, the examination of two major bands as done here could lead to a fast and economical on-line method for the determination of molecular orientation and mechanical properties of thick samples.

ACKNOWLEDGEMENTS

The authors wish to express their gratitude to Dr Paolo Cielo for helpful discussions and to Michel Carmel for the mechanical modulus measurements.

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