Molecular orientation and conformational changes due to uniaxial-planar deformation of poly(ethylene terephthalate) films

P. Lapersonne*, D. I Bower and I. M. Ward†
IRC in Polymer Science and Technology, University of Leeds, Leeds LS2 9JT, UK
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Conformational changes and chain axis orientation in poly(ethylene terephthalate) due to uniaxial-planar deformation (at constant width) at constant engineering stress in the range 1.2–5.5 MPa at temperatures in the range 85–105°C have been studied by means of infrared spectroscopy. For all samples the state of orientation was frozen just after the deformation reached the equilibrium value at a draw ratio λ_p. For a given temperature there are two stress regimes, a lower one where λ_p decreases with increasing stress, corresponding to 'stretching with flow', and a higher one where λ_p increases with increasing stress, corresponding to 'crystallizing stretching'. It is shown that the crystallinity of the samples is uniquely related to the content of *trans* conformers and that the overall chain axis orientation may be determined, to a good approximation, by determining the orientation of the *trans* conformers; the chain axes associated with *gauche* conformers are effectively randomly oriented. Under conditions of 'crystallizing stretching' the content of *trans* conformers and the chain axis orientation can be understood in terms of a rubber-like network extension if the drawing temperature is between 80°C (the glass transition temperature) and 95°C. At higher temperatures of drawing, relaxation occurs in the amorphous phase. For all samples there is an excellent correlation between the *trans* concentrations and the overall orientation, independent of whether relaxation or crystallization occurs.

(Keywords: orientation; deformation; poly(ethylene terephthalate))

INTRODUCTION

The overall aim of this research is to characterize the first drawing step of poly(ethylene terephthalate) (PET) flat-film processing. The main characteristics of this process for stretching isotropic PET film are that it is a uniaxial-planar deformation (at constant width) at constant force close to or above the glass transition temperature[1].

An analysis of the kinetic factors involved in the process[1], and initial measurements of the structure and crystallinity of the drawn film[2,3] have already been published, together with a general study of the orientation of the benzene ring normals on the basis of refractive index measurements[4]. Quantitative measurements by infrared and Raman spectroscopy of the benzene ring orientation in both crystalline and amorphous phases forms part of our recent research in this area and are reported separately[5].

The present paper is devoted to the characterization of conformational changes and of chain axis orientation by means of infrared spectroscopic measurements. Studies of molecular orientation and conformational changes have been presented in previous publications for thin uniaxially oriented films[6,7] and for fibres[8].

The infrared spectra have been analysed by means of a computer reconstruction[9] that enables us to associate some of the absorptions with the vibrations of *trans* and *gauche* conformational states of the glycol residue. The observed changes in molecular orientation and conformation will be compared with the predictions of a model deformation scheme for a rubber-like network. The amorphous contribution will be extracted by combining infrared data with those obtained previously from X-ray diffraction and crystallinity measurements[3].

EXPERIMENTAL

Films

The samples used in this work are the same as those used in earlier studies[3–5], and full details of their preparation are given in ref. 3. Briefly, wide samples were stretched by imposing a constant dead load, so that the central portion of the sample is characterized by a uniaxial-planar deformation produced at constant engineering stress. Twenty-four different samples were produced by varying the conditions of stretching load and temperature and were drawn 'with a short plateau'[1] (i.e. the state of orientation was frozen just after the deformation had reached the equilibrium value). The drawing temperatures were in the range 85–105°C, and the engineering stress varied from 1.23 to 5.52 MPa. The variation of the equilibrium plateau draw ratio $\lambda_p(\sigma_0, T)$ with initial stress σ_0 and temperature T is given in *Figure 1*. At a given temperature, λ_p goes through a minimum, the natural draw ratio, as the loading stress increases. The first regime, where the initial stress is smaller than σ_0 (natural draw ratio) and where λ_p decreases with increasing stress, corresponds to 'stretching with flow'

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* Present address: Rhone-Poulenc Recherches, Centre de Recherches des Carrières, 85 ave des Frères-Perret, BP 62-69192, Saint-Fons Cedex, France

† To whom correspondence should be addressed

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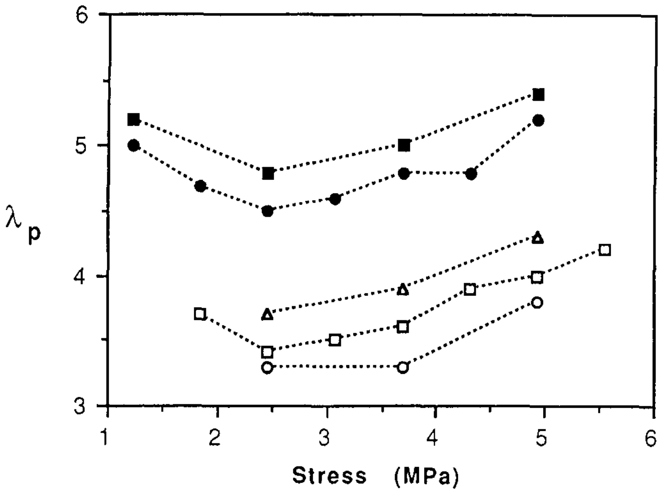

Figure 1 Plateau draw ratio $\lambda_p(\sigma_0, T)$ *versus* engineering stress σ_0 at different drawing temperatures T: ○, 85°C; □, 90°C; △, 95°C; ●, 100°C; ■, 105°C

and the second one to 'crystallizing stretching'[3]. The crystalline phase has already been characterized[3] for all these samples and moment averages of the benzene ring orientation distribution have been measured for eight of them[5].

Refractive index measurements

An Abbe refractometer equipped with a polarizer was used to measure the refractive indices for the three principal directions of the films.

Infrared measurements

The infrared spectra were obtained on a Perkin–Elmer 580B ratio recording spectrometer. Because our samples were biaxially oriented, it was necessary to make normal-film and tilted-film (45°) measurements. The samples were sandwiched with layers of nujol between two potassium bromide plates or prisms. The procedure for recording the spectra and for computer reconstruction is given in refs 8 and 9. The minimum number of Lorentzian peaks was used to obtain a good fit to the spectrum between 700 cm^{-1} and 1100 cm^{-1}. The positions and half-intensity widths of the peaks were allowed to vary freely for the study of the first sample and were subsequently kept fixed for all the samples. Good fits to all the spectra were obtained with this method.

In the regions near 889 and 972 cm^{-1}, it was necessary to use two and three Lorentzian peaks, respectively[8]. The first region corresponds to vibrations of *gauche* conformers and is the sum of two peaks at 889 and 899 cm^{-1}. The second region corresponds to vibrations of *trans* conformers and is the sum of three peaks at 961, 972 and 978 cm^{-1}.

THEORY

The procedure for obtaining quantitative information from the infrared spectra for biaxially oriented films has been described by Jarvis *et al.*[9], Cunningham *et al.*[6,10] and Lapersonne *et al.*[5].

A system of orthogonal axes $OX_1X_2X_3$ is defined within each sample, with OX_3 parallel to the draw direction and OX_1 perpendicular to OX_3 and lying in the plane of the film.

In each region of the spectra corresponding to *trans* and *gauche* conformer vibrations, k_i, the true absorbance for the electric vector parallel to OX_i ($i = 1, 2, 3$), can be calculated from the measurements of the experimentally observed absorbances for normal-film and tilted-film experiments described previously[5,9]. From the values of k_i and n_i (n_i being the refractive index for the electric vector parallel to the direction OX_i) it is possible to calculate quantities ϕ_i which relate to the conformer concentrations and, in the case of the 972 cm^{-1} absorption, to the orientation moment averages for the *trans* conformer.

The quantity $\phi_i = (4/3)\pi N\langle\alpha_i''\rangle$, where N is the concentration of absorbing species per unit volume and $\langle\alpha_i''\rangle$ is the imaginary part of the molecular polarizability, is given by[10]:

$$\phi_i = \frac{4\pi}{3}N\langle\alpha_i''\rangle = \frac{6n_ik_i}{[(n_i^2+2)^2 + (2n_i^2-4)k_i^2 + k_i^4]} \qquad (1)$$

In this study, where k_i is smaller than 0.1, equation (1) reduces to a good approximation to:

$$\phi_i = \frac{6n_ik_i}{(n_i^2+2)^2} \qquad (2)$$

The integrated intensity of each Lorentzian peak is given by:

$$\bar{\phi}_i = \int_{-\infty}^{+\infty} \phi_i(\lambda)\,\mathrm{d}\lambda = \frac{\pi}{2}\phi_i^{\mathrm{peak}}\,\Delta x_{1/2} \qquad (3)$$

with ϕ_i^{peak} the maximum value of ϕ_i for a given peak and $\Delta x_{1/2}$ the half-intensity width.

Calculation of conformational concentration

The concentration of any species is proportional to:

$$\phi_0 = \frac{1}{3}\sum_1^3 \bar{\phi}_i$$

As in previous work[6–8,11], the volume polarizability is assumed to be equal for all five absorption peaks corresponding to the *trans* and *gauche* conformers. Then the total *trans* content, χ_{trans}, is given by:

$$\chi_{trans} = \frac{\sum \phi_{0trans}}{\sum \phi_{0trans} + \sum \phi_{0gauche}} \qquad (4)$$

where $\sum \phi_{0trans}$ and $\sum \phi_{0gauche}$ are the summation over the various possible *trans* and *gauche* peaks respectively.

Calculation of the orientation averages

A system of axes $Ox_1x_2x_3$, fixed in the polymer chain, is chosen so that Ox_3 is parallel to the chain axis direction, Ox_2 is perpendicular to Ox_3 and the vibration moment vector μ_{trans} for the *trans* conformer is in the Ox_2x_3 plane.

A similar calculation to that described by Jarvis *et al.*[9] then leads to:

$$\frac{2\sum\bar{\phi}_{3trans} - \sum\bar{\phi}_{1trans} - \sum\bar{\phi}_{2trans}}{3\sum\phi_{0trans}} = 2P_{200}(\theta_m)P_{200}^{trans} - 4[1 - P_{200}(\theta_m)]P_{202}^{trans} \qquad (5)$$

and:

$$\frac{\sum \bar{\phi}_{1trans} - \sum \bar{\phi}_{2trans}}{3 \sum \phi_{0trans}} = 4p_{200}(\theta_\mathrm{m})P_{220}^{trans} - \tfrac{4}{3}[1 - p_{200}(\theta_\mathrm{m})]P_{222}^{trans} \quad (6)$$

where the quantities P_{2mn}^{trans} are the second moment averages of the orientation distribution function for the *trans* conformers. (See ref. 9 for a general definition of averages of the type P_{lmn}.) The angle θ_m ($= 32°$)[7,8] is the angle between the transition moment vector μ_{trans} and the chain axis Ox_3. The function $p_{200}(\theta)$ is simply the second order Legendre polynomial in $\cos\theta$, i.e. $\frac{1}{2}(3\cos^2\theta - 1)$, and P_{200}^{trans} is the average of this function over the distribution when θ is the angle between the axis of a *trans* conformer and the draw direction. It will be shown later that this is the only one of the four averages P_{2mn}^{trans} that can be evaluated from the present data.

Crystallinity

The density of the films can be obtained from the average refractive index $\bar{n}$, using the following expression derived for PET films[12]:

$$d = 4.047\frac{\bar{n}^2 - 1}{\bar{n}^2 + 2} \quad (7)$$

By assuming a two-phase model[13], a crystalline phase density $d_\mathrm{c} = 1.455$ and an amorphous density $d_\mathrm{a} = 1.335$, the crystallinity χ_c is given by:

$$\chi_\mathrm{c} = \frac{d - d_\mathrm{a}}{d_\mathrm{c} - d_\mathrm{a}} \quad (8)$$

RESULTS AND DISCUSSION

Concentration of trans *and* gauche *conformers*

The three *trans* absorption peaks can be divided into two groups[8]: one peak due to load-bearing *trans* conformers at 972 cm^{-1}, and two peaks due to non-load-bearing *trans* conformers at 961 and 978 cm^{-1}. These two different kinds of *trans* conformer have been ascribed to two types of crystallization[14]. The first type is due to the extension and orientation of 'backbone' molecules which carry the load. This crystallization can be associated with the 972 cm^{-1} peak. The second type of crystallization is the epitaxial crystallization onto this backbone and can be associated with the 961 cm^{-1} and 978 cm^{-1} peaks.

For the complete range of our samples, the total amount of 961 and 978 cm^{-1} *trans* conformers, $\phi_{0961} + \phi_{0978}$, represents less than 5% of the total amount of 972 cm^{-1} *trans* conformers, ϕ_{0972}. It can therefore be concluded that the crystallites in our films stretched at constant load are composed primarily of backbone crystals.

There is a good correlation between the crystallinity χ_c and the concentration of 972 cm^{-1} *trans* conformers. As in the study of fibres[8], this correlation is independent of the drawing temperature, as shown in *Figure 2*. Because ϕ_{0972} represents more than 95% of the total *trans* conformer content, a good correlation is also found between χ_c and the total *trans* content.

The variation of the total *trans* content with σ_0 and T is shown in *Figure 3*. At a given drawing temperature T, χ_{trans} increases with increasing stress. Under our stretching conditions, χ_{trans} increases with T at constant stress for a drawing temperature less than 100°C. These results can be understood in terms of the stretching of a network.

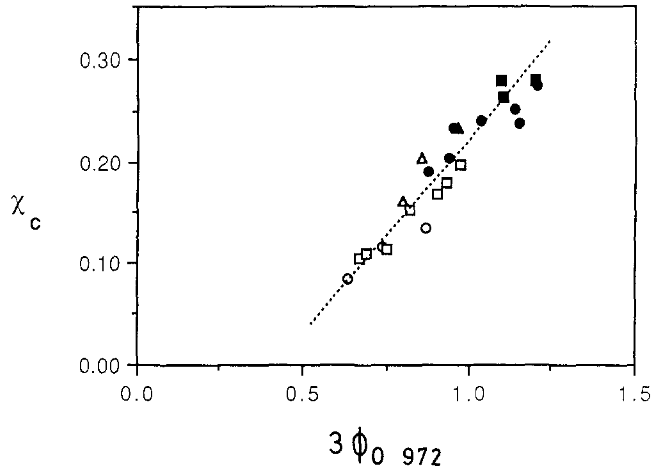

Figure 2 Crystallinity χ_c *versus* concentration of *trans* conformers related to 972 cm^{-1} *trans* band only (symbols as in *Figure 1*)

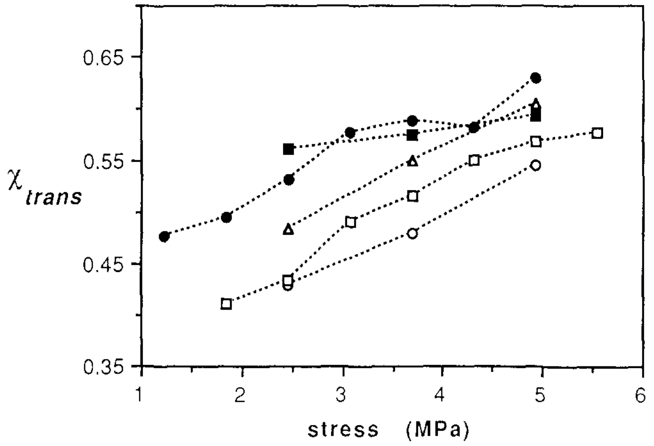

Figure 3 Total *trans* content χ_{trans} *versus* engineering stress σ_0 (symbols as in *Figure 1*)

Following Abe and Flory[15], if we assume an affine deformation of the chain end-to-end vectors within a network, the variation in the concentration of a particular conformer depends on the macroscopic draw ratio. For uniaxial deformation, the variation of the concentration of *trans* conformers is given by:

$$\Delta m_{trans} = \nu D_2\left[\frac{1}{3}\left(\lambda^2 + \frac{2}{\lambda}\right) - 1\right] \quad (9)$$

where ν is the total number of chains in the network, D_2 is a constant of proportionality and λ is the draw ratio. For uniaxial-planar deformation, a similar calculation leads to the following relationship:

$$\Delta m_{trans} = \nu D_2\left[\frac{1}{3}\left(\lambda^2 + \frac{1}{\lambda^2} + 1\right) - 1\right] \quad (10)$$

In the region of temperature and stress where 'stretching with flow' occurs, the equilibrium deformation increases with decreasing stress. It has been shown[1] that this behaviour can be attributed to a combination of chain slipping and relaxation, both of which are related to the rate of deformation. Under these circumstances the deformation process cannot be equivalent in a simple manner to the extension of a rubber-like network.

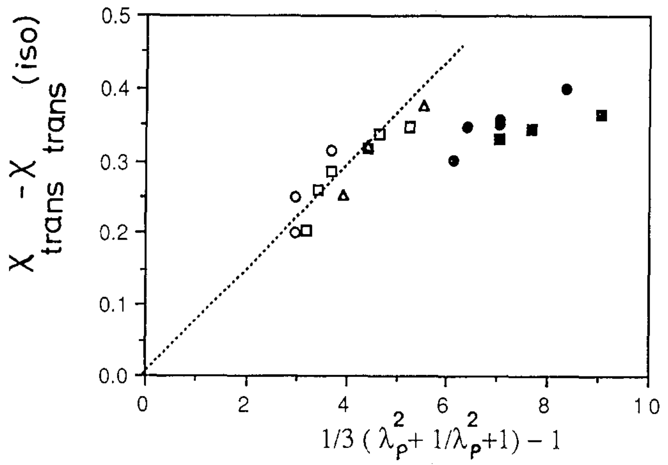

Figure 4 *Trans* content variation *versus* $[1/3(\lambda_p^2 + 1/\lambda_p^2 + 1) - 1]$ for 'crystallizing stretching' (symbols as in *Figure 1*)

A plot of

$$[\chi_{trans} - \chi_{trans}(\mathrm{iso})] \ versus \ [1/3(\lambda_p^2 + 1/\lambda_p^2 + 1) - 1]$$

is given in *Figure 4* for the films corresponding to different 'crystallizing stretching' conditions, where $\chi_{trans}(\mathrm{iso})$ is the initial concentration in the undrawn film. It is possible to distinguish two regimes of drawing temperature.

Regime 1. For a stretching temperature between the glass transition temperature ($T_g = 80°C$) and 95°C, a reasonable straight line relationship, independent of T and passing through the origin, is obtained. This shows that the deformation process can be considered as the extension of a rubber-like network. The slope of this straight line is 0.075 ± 0.01 and is in good agreement with the result of Cunningham *et al.*[6] for uniaxially drawn PET films (slope of 0.085 ± 0.005). In this low temperature range, the increases of χ_{trans} with temperature or stress, shown in *Figure 3*, are due to the fact that an increase of temperature or stress leads to an increase of the network draw ratio.

Regime 2. The points corresponding to films stretched with a drawing temperature equal to or greater than 100°C do not lie on that straight line, but lie significantly below it. This can be explained by the fact that significant relaxation occurs above 100°C, leading to a *trans* content almost independent of λ_p for higher values of λ_p. Since only *trans* conformers can crystallize:

$$\chi_{trans} = \chi_{trans}(\mathrm{amorph}) + \chi_c \qquad (11)$$

where $\chi_{trans}(\mathrm{amorph})$ is the concentration of amorphous *trans* conformers. In a previous investigation[3] it was shown that the crystallinity was uniquely related to the plateau draw ratio λ_p whatever the drawing temperature under 'crystallizing stretching' conditions. As a consequence, the deficit in the *trans* conformer concentration at higher temperature must be due to a reduction of *trans* conformers in the amorphous phase. A plot of $\chi_{trans}(\mathrm{amorph})$ from equation (11) *versus* λ_p is given in *Figure 5*. At a given draw ratio λ_p, a decrease of the *trans* concentration in the amorphous phase occurs with increasing temperature in each of the two domains, but for a given 5°C change in temperature the largest decrease occurs between 95 and 100°C.

It should be noted that in the present paper the crystallinity is calculated from the density assuming a two-phase model and $d_c = 1.455$. This is the minimum value published for the density of the crystalline phase of PET for stretching at a temperature around 100°C. The maximum value, $d_c = 1.484$, is given in ref. 16. The same pattern of behaviour is found for the amorphous *trans* conformer concentration when the crystallinity is calculated with this second crystalline density.

Molecular orientation

In the general case, it is impossible to solve equations (5) and (6). Fortunately for our system, however, certain simplifications arise which enable us to obtain quantitative information.

Lapersonne *et al.*[5] have obtained all the second moment averages P^r_{2mn} of the benzene ring orientation distribution for some of these samples. The value of P^r_{202} was found to be near 0.03 in either the amorphous phase or the crystalline phase and P^{trans}_{202} is expected to be very close to that value. For all the films involved, the value of

$$(2\sum\phi_{3trans} - \sum\bar{\phi}_{1trans} - \sum\bar{\phi}_{2trans})/3\sum\bar{\phi}_{0trans}$$

is between 0.7 and 0.9. The last term in equation (5) therefore represents less than 5% of the final result and can be neglected. Equation (5) then reduces to a good approximation to:

$$\frac{2\sum\bar{\phi}_{3trans} - \sum\bar{\phi}_{1trans} - \sum\bar{\phi}_{2trans}}{3\sum\phi_{0trans}} = 2p_{200}(\theta_m)P^{trans}_{200} \qquad (12)$$

Unfortunately equation (6) cannot be simplified to allow the calculation of P^{trans}_{220}.

Having calculated P^{trans}_{200} we can now consider the second moment average of the distribution function for the chain axis, P^c_{200}. In earlier studies[6–8], the orientation of the *gauche* conformers was assumed to be very low. Following that assumption, the second moment of the chain axis orientation P^c_{200} should be given by:

$$P^c_{200} = \chi_{trans}P^{trans}_{200} \qquad (13)$$

In related research[5], all the second moment averages of the benzene ring orientation, P^r_{2mn} were determined for some of the films stretched at 90°C and 100°C. Assuming that the orientation of the benzene ring C_1–C_4 axis in the polymer chain is the same as in the crystalline phase

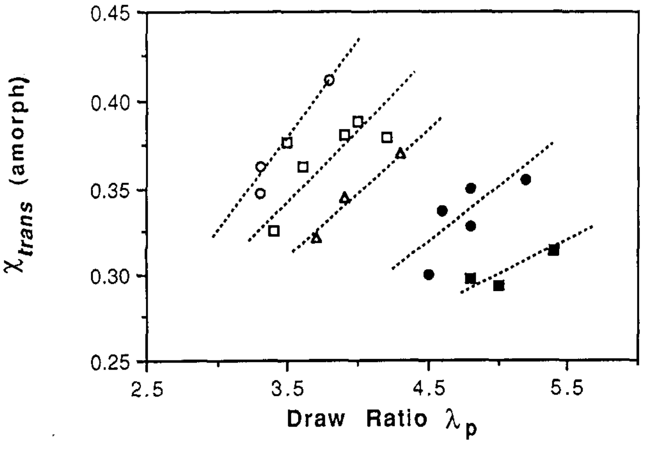

Figure 5 *Trans* content of the amorphous phase χ_{trans} (amorph) *versus* plateau draw ratio λ_p for the 'crystallizing stretching' (dotted lines are simply guides to the eye) (symbols as in *Figure 1*)

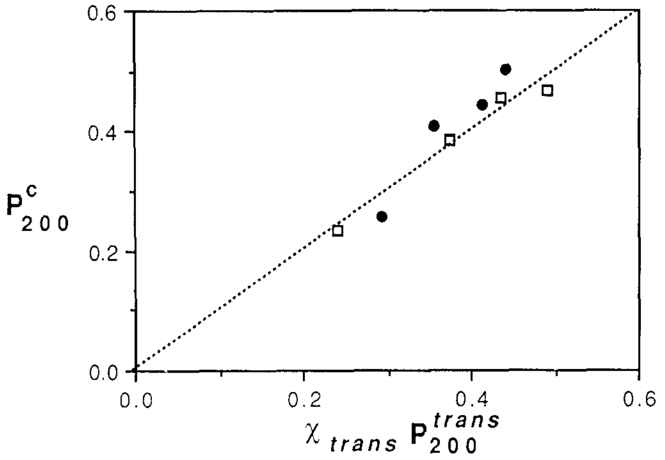

Figure 6 Orientation moment average of the chain axis P^c_{200}, given by the measurements of the 1616 cm^{-1} Raman line and the 875 cm^{-1} infrared peak, *versus* $\chi_{trans}P^{trans}_{200}$ (symbols as in *Figure 1*)

and that the crystalline unit cell is as described by Daubeny *et al.*[13], P^c_{200} can be calculated from these values of P^r_{2mn} (see ref. 17). *Figure 6* shows that the values of $\chi_{trans}P^{trans}_{200}$ and P^c_{200} are very similar, so that $\chi_{trans}P^{trans}_{200}$ is, to a good approximation, a measurement of the chain axis orientation with respect to the draw direction. As a consequence, it may be concluded that the orientation of the chain axes for the *gauche* conformers is effectively negligible. This conclusion implies that, for all the samples, the value of

$$(2\sum \bar{\Phi}_{3gauche} - \sum \bar{\Phi}_{1gauche} - \sum \bar{\Phi}_{2gauche})/3\sum \bar{\Phi}_{0gauche}$$

should be very small, as observed, but such a conclusion could not be inferred from this observation alone.

For a rubber-like network extension, it can be shown[18] that the second moment average of the orientation function of the random link $\langle P_{200}(\theta)\rangle_{\text{random link}}$ for a uniaxial-planar deformation is given by:

$$\langle P_{200}(\theta)\rangle_{\text{random link}} = \frac{1}{10N}\left(2\lambda^2 - \frac{1}{\lambda^2} - 1\right) \quad (14)$$

where N is the number of random links between the network junction points. A plot of $\chi_{trans}P^{trans}_{200}$ *versus* $(2\lambda_p^2 - 1/\lambda_p^2 - 1)$ is given in *Figure 7* for the films drawn under 'crystallizing stretching' conditions. The same two regimes of drawing temperature need to be considered as in the study of χ_{trans}.

Regime 1. For T less than or equal to 95°C, there is a good linear relationship between these two parameters for each drawing temperature and the slopes of the lines do not vary much with temperature. The value of N calculated from the slope of the best straight line through all the points is 6.5. This result is in good agreement with the previous stress-optical results obtained by Cunningham *et al.*[6] ($N = 5$) and Pinnock and Ward[19] ($N = 6$) for uniaxially drawn PET films with a drawing temperature less than or equal to 90°C and for melt spun fibres, respectively. As also found for these uniaxial samples, a linear relationship between the overall orientation and $(2\lambda^2 - 1/\lambda^2 - 1)$ is observed for higher values of λ (up to $\sim$4.5) than $N^{1/2}$ ($=2.5$) although the latter is actually the limit of applicability of the simple theory.

Regime 2. For T greater than 100°C, the results do not lie on the same curve and the drawing process can no longer be regarded as a simple rubber-like extension of the same network. The increase in orientation with increasing drawing stress is significantly smaller than at the lower temperatures.

In *Figure 8*, $\chi_{trans}P^{trans}_{200}$ is plotted *versus* true stress $\sigma_T = \lambda_p\sigma_0$ at the different drawing temperatures for the films drawn under 'crystallizing stretching' conditions. For small deformations, where the polymer behaves like an ideal rubber network, a linear relationship would be expected between these two variables, corresponding to a constant stress optical coefficient. Previous work on uniaxially oriented samples[20] has shown that for higher deformation ratios, this simple proportionality does not hold. Although the orientation continues to increase with increasing deformation, the stress shows a plateau region followed by a steeper rise again at higher deformation ratios. The present results are consistent with this behaviour, in that only a small increase in orientation is shown at the high drawing stresses employed here.

In an earlier study of the crystalline organization of these films[3], not only was a unique relationship, independent of the draw temperature, found to exist between the crystallinity and the draw ratio λ_p for 'crystallizing stretching' but also between the orientation moment averages and the draw ratio λ_p for the crystalline phase. The absence of any effect of draw temperature suggests

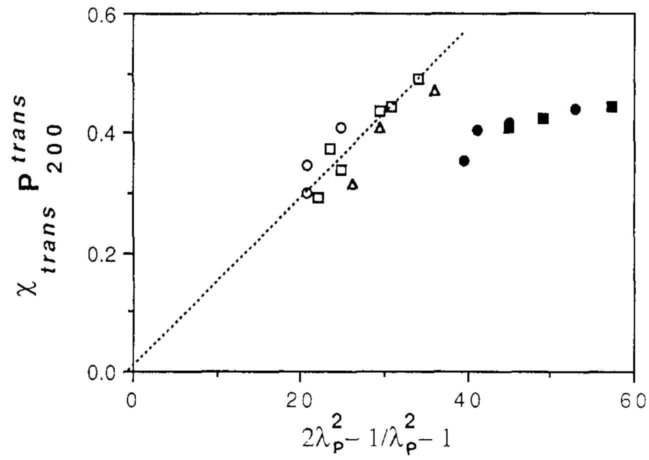

Figure 7 $\chi_{trans}P^{trans}_{200}$ *versus* $(2\lambda_p^2 - 1/\lambda_p^2 - 1)$ for 'crystallizing stretching' (symbols as in *Figure 1*)

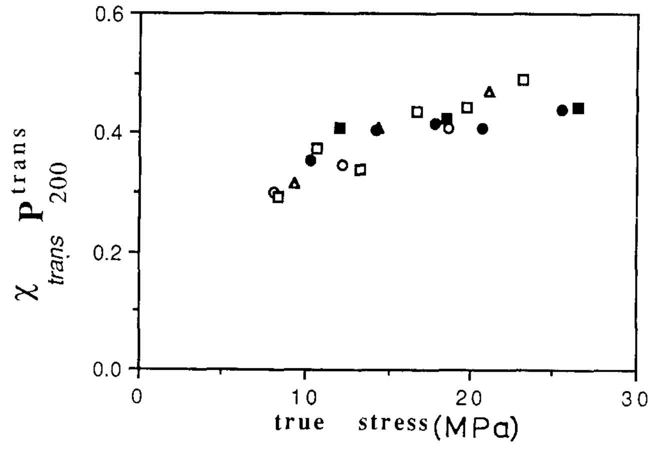

Figure 8 $\chi_{trans}P^{trans}_{200}$ *versus* true stress $\sigma_0\lambda_p$ for 'crystallizing stretching' (symbols as in *Figure 1*)

that there is no relaxation of the crystalline phase contribution to the average chain axis orientation. We can therefore conclude that this relaxation must take place in the amorphous phase. From the previous measurements of crystalline orientation[3], the second moment orientation averages of the distribution of the ($\bar{1}05$) and (100) plane normals are known. Assuming that the crystalline unit cell is that described by Daubeny *et al.*[13], the crystalline chain axis orientation P^c_{200}(crystals) can be calculated. The second moment of the amorphous chain axis orientation P^c_{200}(amorphous) is then given by:

$$P^c_{200}(\text{amorphous}) = \frac{1}{1-\chi_c}\left[P^c_{200} - \chi_c P^c_{200}(\text{crystals})\right] \tag{15}$$

In *Figure 9*, P^c_{200}(amorphous) is plotted against the plateau draw ratio λ_p for 'crystallizing stretching'. Below 100°C, there is a substantial increase in the amorphous orientation with increasing draw ratio and it is not greatly dependent on temperature. At higher temperatures, the amorphous orientation is much lower, due to relaxation effects which set in very significantly in the temperature range 95–100°C. As in the case of χ_{trans}(amorph), the crystalline density of 1.455 can be replaced by 1.484 for the calculation of the crystallinity χ_c without any changes in the general behaviour of these results.

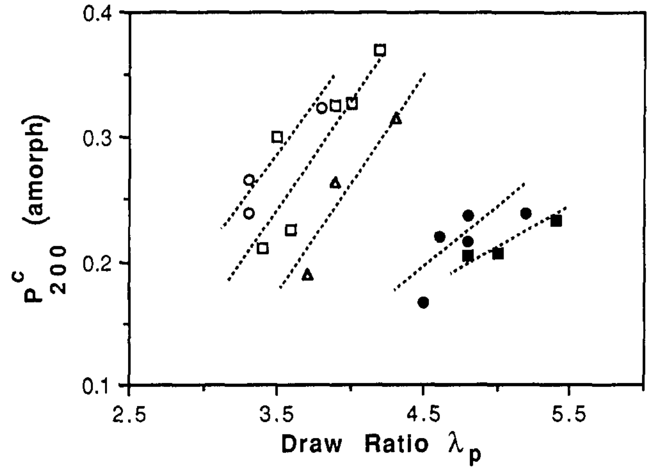

Figure 9 Orientation moment average of chain axis in amorphous phase P^c_{200} (amorph) *versus* λ_p for the 'crystallizing stretching' (dotted lines are simply guides to the eye) (symbols as in *Figure 1*)

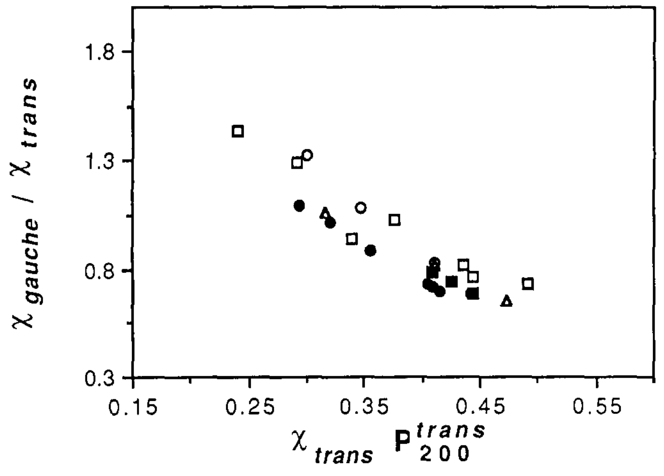

Figure 10 Ratio $\chi_{trans}/\chi_{gauche}$ as a function of the overall orientation determined by $\chi_{trans}P^{trans}_{200}$ (symbols as in *Figure 1*)

Conformational changes and molecular orientation

In the studies of uniaxially oriented PET films[6,7] and fibres[8], a unique relationship was found between the concentration of *trans* and *gauche* conformers and the overall orientation. This correlation was considered to be the consequence of a network-like extension. In the present research the overall orientation is given by $\chi_{trans}P^{trans}_{200}$; *Figure 10* shows a good correlation between the ratio $\chi_{gauche}/\chi_{trans}$ and $\chi_{trans}P^{trans}_{200}$ for all the samples, including those produced by 'stretching with flow' and by 'crystallizing stretching'. The correlation is not affected by either the existence of the two different temperature regimes or the nature of the stretching.

It is clear that the relationship between the conformational content and the overall orientation is retained during the relaxation process. It is to be noted that even for drawing temperatures higher than 95°C where relaxation occurs, or for 'stretching with flow', there is still no significant concentration of *trans* conformers corresponding to non-load-bearing conformers and the total concentration of *trans* conformers increases steadily with the overall orientation.

CONCLUSION

Infrared spectroscopy has been applied to study the chain axis orientation and the conformational changes in uniaxial-planar films stretched under constant load close to or above the glass transition temperatures. The main conclusions are as follows.

Only one major absorption peak due to *trans* conformers is observed, at 972 cm^{-1}, and this corresponds to a load-bearing conformation. The crystallinity is uniquely related to the content of *trans* conformers.

It has been shown that $\chi_{trans}P^{trans}_{200}$ is, to a good approximation, a measure of the chain axis orientation.

Studies of both χ_{trans} and $\chi_{trans}P^{trans}_{200}$ show the same two regimes of drawing temperature under 'crystallizing stretching' conditions. (1) If the drawing temperature is between the glass transition temperature ($T_g = 80$°C) and 95°C, the stretching process can be modelled by a rubber-like extension and the network parameters are in good agreement with earlier results for uniaxially oriented PET samples. The deviations of the points from the straight line in *Figure 7* imply, however, that the number N of random links between network junction points increases with temperature. Such an effect has been observed previously for PET[7] and also for poly(methyl methacrylate)[21]. An increase in N is also required to explain why the plateau draw ratio for a given stress increases with temperature, as shown in *Figure 1*. (2) When the drawing temperature is over 100°C relaxation occurs in the amorphous phase.

As found previously for uniaxially oriented PET films and fibres, there is an excellent correlation between the *trans* and *gauche* concentration and the overall orientation. It is perhaps surprising that this correlation is not affected either by relaxation processes or by crystallization.

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REFERENCES

1 Lebourvellec, G., Beautemps, J. and Jarry, J. P. *J. Appl. Polym. Sci.* 1990, **39**, 319
2 Lebourvellec, G. and Beautemps, J. *J. Appl. Polym. Sci.* 1990, **39**, 329
3 Lapersonne, P., Tassin, J. F., Monnerie, L. and Beautemps, J. *Polymer* 1991, **32**, 3331
4 Lapersonne, P., Tassin, J. F. and Monnerie, L. to be published
5 Lapersonne, P., Bower, D. I. and Ward, I. M. *Polymer* 1992, **33**, 1266
6 Cunningham, A., Ward, I. M., Willis, H. A. and Zichy, V. *Polymer* 1974, **15**, 749
7 Padibjo, S. R. and Ward, I. M. *Polymer* 1983, **24**, 1103
8 Yazdanian, M., Ward, I. M. and Brody, H. *Polymer* 1985, **26**, 1779
9 Jarvis, D. A., Hutchinson, I. J., Bower, D. I. and Ward, I. M. *Polymer* 1980, **21**, 41
10 Cunningham, A., Davies, G. R. and Ward, I. M. *Polymer* 1974, **15**, 743
11 Hutchinson, I. J., Ward, I. M., Willis, H. A. and Zichy, V. *Polymer* 1980, **21**, 55
12 De Vries, A. J., Bonnebat, C. and Beautemps, *J. Polym. Sci., Polym. Symp.* 1977, **58**, 109
13 Daubeny, R., Bunn, C. W. and Brown, C. J. *Proc. R. Soc. London* 1954, **226**, 531
14 Brody, H. *J. Macromol. Sci.* 1983, **B22**, 407
15 Abe, A. and Flory, P. J. *J. Chem. Phys.* 1970, **52**, 2814
16 Fakirov, S., Fischer, E. W. and Schmidt, G. F. *Makromol. Chem.* 1975, **176**, 2459
17 Bower, D. I., Jarvis, D. A. and Ward, I. M. *Polymer* 1986, **24**, 1459
18 Ward, I. M. *Adv. Polym. Sci.* 1985, **66**, 81
19 Pinnock, P. R. and Ward, I. M. *Trans. Faraday Soc.* 1966, **62**, 1308
20 Rietsch, F., Duckett, R. A. and Ward, I. M. *Polymer* 1979, **20**, 1133
21 Raha, S. and Bowden, P. B. *Polymer* 1972, **13**, 174