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Orientation and structure of drawn poly(ethylene terephthalate)

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Drawing of poly(ethylene terephthalate) (PET) films was performed from the amorphous state at different drawing rates and at 80°C. Crystallinity of the films was determined by thermal analysis and orientation of the different phases was determined by birefringence, Fourier transform infra-red (*FT*i.r.) specular reflection and wide angle X-ray diffraction. The mechanical properties of the oriented films were studied by dynamic mechanical analysis. *FT*i.r. and X-ray results showed large orientation of the different phases (*trans* conformers and crystalline phase), in contrast with refractive index measurements which showed unusually low birefringence results. The observed orientation was particularly high for draw ratios (λ) higher than 3. The orientation contribution of the non-crystalline phase was determined by combining *FT*i.r. and X-ray results. The *trans*-conformer contribution to the non-crystalline phase is shown to be very high for the high λ for which crystalline orientation was observed. A structural model consisting of a crystalline phase, a mesomorphic amorphous phase (constituted of *trans* conformers) and a purely amorphous phase (constituted solely of *gauche* conformers) is a possible representation of the observed results. Finally, the tensile modulus increased continuously with the overall orientation. Copyright © 1996 Elsevier Science Ltd.

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

INTRODUCTION

Properties of polymeric materials can be enhanced significantly through orientation processes, either in the solid state, in the rubbery state or from the melt. Substantial efforts have been directed to orientation of semi-crystalline polymers such as polyolefins, polyesters and polyamides[1-6]. In the case of polyesters, the most widely studied polymer is poly(ethylene terephthalate) (PET) because of its wide uses in fibres, films and bottles. However, many questions still remain unclear about its orientation. In fact conformational changes, the contribution of the interphase, relaxation and development of new characterization methods, are of great practical interest.

To understand the orientation behaviour of PET, it is necessary to start from a single phase structure, i.e. from the amorphous state, which is possible for this polymer because of its relatively high T_g (around 70°C), but not for polyolefins which have been studied extensively. It has been reported that orientation of amorphous PET above the glass transition temperature is mainly due to sliding of chains, denoted as flow drawing[7], and does not induce any birefringence in the films. However, these data were not compared with those from other techniques. In fact, many changes, such as conformation changes and strain induced crystallization, are involved when orienting PET.

On the other hand, crystallinity and orientation of

the crystalline phase play an important role in the determination of PET properties. Crystallinity may develop under different conditions. In a recent study, it was found that strain-induced crystallization (SIC) of annealed stretched PET can proceed by three different paths depending on the residual degree of orientation[8]. At a low degree of residual orientation, annealing of stretched PET leads only to molecular relaxation. At intermediate orientation levels, annealing causes an initial decrease in birefringence, followed by gradual increase and finally a levelling off after a fairly long time. At higher orientation levels, annealing causes a rapid increase in birefringence before levelling off. When stretching occurs at high extension ratios, leading to a high degree of orientation, all of the SIC occurs simultaneously during the stretching process. Further annealing at the temperature of stretch does not cause the crystallinity to increase further. Crystallinity development induced by SIC, as revealed by wide angle X-ray scattering (WAXS), occurs when samples are stretched to a strain below the strain hardening region.

Salem[9] studied the crystallization of PET during drawing at different temperatures and strain rates. He showed that decreasing strain rate shifts the onset of crystallization to higher draw ratios and reduces the rate at which crystallinity increases with draw ratio, an effect that becomes more pronounced as draw temperature increases. When the degree of crystallinity is plotted against draw time, it becomes apparent that the effect of changing strain rate is simply to shift the curves along the

log(time) axis. The shift factor and the strain rate were related by a power law, and the value of the exponent, which reflects the rate of molecular relaxation at the draw temperature, rises with temperature at an increasing rate. Due to strain-rate/draw-time superposition, empirical equations allow prediction of the degree of crystallinity and the crystallization rate at any strain rate or temperature in the range studied from knowledge of draw time or draw ratio. This study also revealed that increasing draw temperature does not necessarily increase the draw ratio for onset of crystallization λ_c.

Others studied the kinetics during the crystallization induction period by means of depolarized light scattering measurements[10]. The spinodal decomposition during this period[10] was shown to be caused by orientation fluctuations of polymer segments. Time evolution of these orientation fluctuations could be described by the spinodal decomposition kinetics in terms of transformation from the isotropic to nematic phase.

A detailed study was undertaken on the drawing behaviour of PET over the temperature range 20–80°C[11]. Homogeneous deformation was observed for samples drawn at 80°C. Birefringence measurements were carried out on all drawn samples and indicated non-negligible birefringence. The results were discussed in terms of continuum models for the deformation of polymers. In particular, the relevance of a simple molecular network model was considered. It was shown that many of the observations were consistent with the deformation of a molecular network. In a later study[12], combination of birefringence with X-ray and Fourier transform infrared (*FT*i.r.) spectroscopy measurements was performed. They characterized the drawn PET structure and orientation. They found also that the modulus related primarily to the molecular chains which were extended in the *trans*-conformation, irrespective of crystallinity.

The deformation of amorphous isotropic PET films drawn at temperatures slightly above the glass transition temperature (T_g) under constant load was described from a molecular point of view[13]. The deformation was qualitatively described by chain relaxation phenomena occurring before stress-induced crystallization, followed by the equilibration of a rubber-like network. The junction points include both trapped entanglements and crystalline units. The structure of the network was characterized by the number of segments between crosslinks. This parameter was calculated by comparing the predictions of the rubber elasticity theory (without Gaussian approximation) with the experimentally observed draw ratios under given conditions of temperature and loads. It was shown that small loads induce soft networks leading to high draw ratios. The predictions of molecular orientation derived from this treatment were in good agreement with birefringence data on a large variety of samples.

Others studied the deformation mechanism of amorphous PET also as a function of molecular weight and entanglement density in predrawn films[14]. The deformability was shown to be affected by the stress-induced crystals, which might act as network points. The tensile modulus and strength of drawn films were related to draw ratio and molecular weight. The higher the draw ratio and molecular weight, the higher were the tensile properties of drawn samples. The improved efficiency of draw with higher molecular weight was explained by the

suppression of disentanglement and relaxation of oriented amorphous molecules during deformation. Both are significant in the development of structural anisotropy and continuity along the draw direction.

In all these cases, the determination of orientation of the different phases using different techniques was not performed. In fact, determination of the molecular orientation is of critical importance in understanding the properties and structure of oriented materials. Many techniques such as infra-red (i.r.) spectroscopy, optical birefringence and X-ray diffraction for semi-crystalline polymers have been developed for the characterization of orientation in polymers[1,6]. For example, refractive index measurements along the three principal directions of uniaxial planar deformed PET films have been used to calculate the second moment of the orientation distribution function of the phenyl ring normal with respect to the three principal directions of the sample[15]. Under their stretching conditions, the phenyl rings showed a strong tendency to orient their plane parallel to the plane of the films. The orientation of the chain axis can also be evaluated from the same data. A good correlation was observed between this indirect measurement and i.r. dichroism, but no specific information on structure was obtained.

Others demonstrated that *FT*i.r. spectroscopy coupled with photoacoustic detection (PA-*FT*i.r.) is a useful tool for evaluating quantitative structural changes in solid materials[16]. For PET, the results indicated that the structural characteristics of the thermally treated samples are related to the fabrication process. Two different strata in the plates could be distinguished: a skin layer and the core. The correlation between the apparent degree of crystallinity of the surface and the percentage of *trans* conformer obtained by PA-*FT*i.r. allowed the latter parameter to be separated into crystalline and amorphous *trans*-conformer fractions and to follow its evolution with the annealing process. Amorphous *trans*-conformers vanish at the primary isomerization (100°C) while crystalline *trans* conformation shows an approximately linear increase at the expense of the *gauche* conformation. Finally, the ordered *trans*-conformer fraction was directly correlated with the apparent degree of surface crystallinity.

Reflection techniques have also been used to characterize orientation. For PET, polarized internal reflectance spectroscopy has been used to evaluate molecular orientation and crystallinity at the surface of films[17]. Measurements were made on samples stretched both uniaxially and biaxially. All bands of interest were normalized with respect to a reference band near 1410 cm^{-1}, resulting from phenylene ring vibrations. Normalization was performed in order to overcome problems with sample contact and effective thickness. Results from bands corresponding to *trans* and *gauche* rotational conformers, at 1340 cm^{-1} and 1370 cm^{-1} respectively, have been related to density and birefringence data. The polarized internal reflectance spectroscopy technique discussed is well suited for investigations of polymer orientation and crystallinity since it avoids limitations related to sample thickness and clarity imposed by polarized transmission i.r. spectroscopy. Parameters such as orientation functions, attenuation indices, dichroic ratios and structural factors have been determined from data collected in each of the

three spatial directions. The results were found to give good agreement with corresponding density, birefringence and refractive index values.

However, this technique also has limitations: quality of the sample-prism contact; and difficulties in making on-line measurements. In order to overcome these, we showed in previous work that a technique based on specular reflection can yield useful information on orientation and structure of oriented PET[18,19]. In particular, quantitative treatment of the specular reflection spectra obtained for uniaxially drawn PET films was performed. Corrections were made for surface inhomogeneities and the overall orientation function was calculated based on *trans* conformers. The results correlated with mechanical modulus and crystallinity[19].

A question that is becoming more and more important is the nature of the amorphous phase and the existence of a mesophase or third phase with different properties between those of the crystalline and amorphous regions. In a recent paper[20], the behaviour of drawn semi-crystalline PET films was investigated by d.s.c., X-ray diffraction and birefringence measurements. The comparison of the different results confirms the coexistence of two structures in the amorphous part of the material: a completely disordered amorphous phase and a mesomorphic one. Moreover, for the highest draw ratio, the calorimetric results showed that the drawing induces better orientation of the strain induced crystalline structure rather than nucleation and growth of new oriented crystallites.

Fluorescence on the other hand may yield specific information on amorphous and crystalline phases of PET[21–23]. PET contains two chromophores: a monomer (phenyl ring of the monomer unit) and an excimer (excited chromophore dimer). The monomer fluoresces mainly in the crystalline phase, whereas the excimer fluoresces in the amorphous phase. During deformation of crystalline PET film, the orientation coefficient followed approximately a superposition curve of crystal-lite-like orientation, separable in the initial range of stretching ratio ($\lambda < 2.5$), and of true-amorphous orientation of the affine network type that becomes noticeable at $\lambda > 3$[21]. For hot-drawing of noncrystalline films, the amorphous orientation data obtained from intrinsic fluorescence provided a consistent explanation of the influence of strain rate on the induction and development of crystallinity. Also, determination of intrinsic birefringences using the amorphous orientation data from the fluorescence method provided support for the argument that these values are not truly intrinsic but are dependent on the structural state of the crystalline and amorphous regions[22]. The relationship between the monomer–excimer fluorescence intensity ratio and the orientational deformation of PET films was established for structures obtained during isothermal uniaxial orientation of PET films[23]. The observed changes in fluorescence intensity ratio were assumed to result from changes in physical properties (e.g. degree of orientation and crystallinity) of structures that were obtained by isothermal uniaxial orientation. But no combination with other techniques was investigated.

The objective of the present study is to investigate the orientational behaviour and structure evolution of PET films. Amorphous and crystalline PET films were drawn to different draw ratios under various conditions. Their

behaviour was studied using crystallinity, orientation (via birefringence, *FT*i.r. and X-ray diffraction measurements) and dynamic mechanical properties data. The orientation of the non crystalline phase will also be discussed.

EXPERIMENTAL

The material used in this study was an extrusion grade PET (Selar PT 7086 from DuPont) having an intrinsic viscosity of 1 and not containing any nucleating agent. Its molecular characteristics as determined from gel permeation chromatography (g.p.c.) were $M_n = 28\,800$ and $M_w = 54\,600$. The material was first dried at 90°C for 24 h under vacuum and sheets were formed at 280°C by compression moulding using a laboratory press. Amorphous and crystalline sheets were prepared by changing the cooling history. Thin rectangular films (thickness 0.1–0.6 mm, 1 cm in width and 8 cm in length) were cut from the sheets for orientation and mechanical testing.

Drawing of the films was performed at 80°C in an Instron tensile tester equipped with an environmental chamber. The film length between the clamps was 4 cm. The draw rates used were 2, 5, 10 and 20 cm min^{-1}. The draw ratios ranged from 1.2 to 5, and the corresponding strain rates, although changing upon drawing, ranged from 0.0017 to 0.083 s^{-1}. The crystallinity of the films before and after orientation was determined from d.s.c. measurements. The crystallization exotherm enthalpy was subtracted from that of the melting endotherm 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. 24).

Birefringence measurements were made at room temperature using a refractometer in combination with a polarizer to measure the refractive index of the films in different directions. The contact liquid used was 1-bromonaphthalene, having a refractive index of about 1.63 (well above that of PET). The light source used was a sodium light having a wavelength of 0.5896 μm. I.r. dichroism measurements were made on a Nicolet 170SX *FT*i.r. spectrometer at a resolution of 4 cm^{-1} in the reflection mode using a specular reflection accessory. Each spectrum resulted from an accumulation of 128 scans. The angle of incidence used was 20°. The dichroic ratio was calculated from the specular reflection spectra[18,19].

X-ray diffraction data were obtained on a Rigaku RU200B rotating anode generator functioning at 55 kV and 120 mA, using the Cu Kα, Ni filtered radiation. Scattered X-rays were measured using a scintillation counter. Scans were taken along the equator and meridian in the $\theta - 2\theta$ geometry, with the draw direction of the samples placed vertically. For the crystalline phase, orientation scans were taken by fixing the 2θ angle at 42.7° and rotating the sample over 180°.

The dynamic mechanical properties, in the tensile mode, were measured using the PL-DMTA. The test frequency was 1 Hz. Due to large shrinkage of the oriented samples, only the results measured below the T_g (at 30°C) will be discussed.

RESULTS AND DISCUSSION

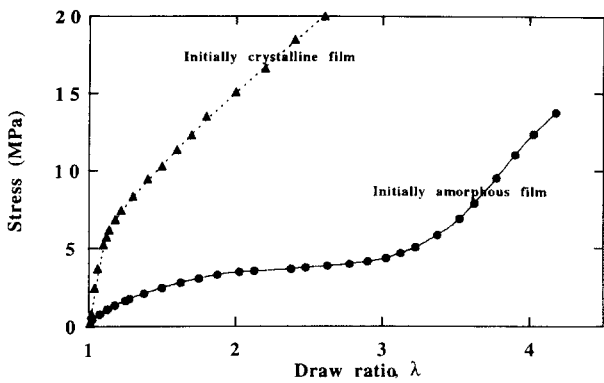*Figure 1* shows the stress–strain behaviour of initially

Figure 1 Stress–strain curve obtained for initially amorphous and crystalline films drawn at 80°C and 2 cm min^{-1}
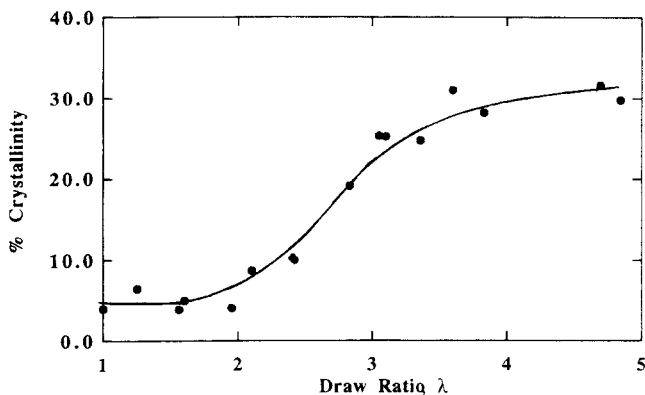

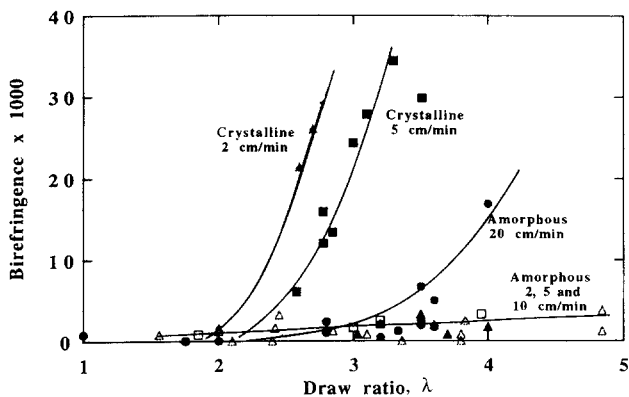**Figure 2** Crystallinity results for the amorphous PET films drawn at 80°C and 2 cm min^{-1}

Figure 3 Birefringence of the uniaxially drawn films at 80°C; drawing conditions as indicated

amorphous and crystalline films drawn at 2 cm min^{-1} and 80°C. For the amorphous film, three regions can be identified. First, a constant increase in stress is observed at low draw ratios, up to the rubbery plateau. Then, the stress remains essentially constant up to a critical draw ratio, corresponding to the onset of stress induced crystallization. The deformation scheme generally used for PET is a conformation change from *gauche* to *trans* conformers, which favours chain segment alignment, followed after a certain degree of order by the development of crystallinity. The size of the crystals formed will depend on temperature, deformation and deformation rate. For initially crystallized films, a constant increase of stress is observed. In this case there is no stress-induced

crystallization, and the increase in stress is due only to the energy needed to deform and align the crystallites.

Crystallinity of PET depends upon many parameters[8,25]. *Figure 2* shows the crystallinity results obtained for amorphous samples drawn at a rate of 2 cm min^{-1}. Up to draw ratios of about 2, the stress-induced crystallinity is negligible. As mentioned above, drawing the films causes conformation changes first, then chain segment alignment before crystallization occurs. In fact, the conformation of PET segments in the amorphous state is primarily *gauche* while crystalline PET is constituted solely of *trans* conformers. Deformation of amorphous PET results in alignment of the *trans* conformers in the draw direction. Further deformation converts *gauche* conformers into *trans* conformers and brings about their alignment. At a certain degree of local order, the aligned chains start to form crystals. The influence of drawing on the crystallinity of thermally crystallized samples seemed negligible for the draw rates used in this study. The data are therefore not reported here. For films drawn at higher drawing rate, the draw ratio for the onset of crystallization decreased with increasing draw rate, confirming other observations[8,9].

Orientation measurements were carried out on the different films to better understand the deformation and structure of PET. The birefringence results for samples drawn at 80°C and speeds of 2, 5, 10 and 20 cm min^{-1} are shown in *Figure 3*. These results reveal some puzzling features. In fact, for amorphous films drawn at 2, 5 and 10 cm min^{-1}, no birefringence was observed for draw ratios up to 3. Above this draw ratio, small birefringence values (maximum of about 5×10^{-3}) were observed. These results are surprising, even though highly reproducible; a more detailed discussion is given in the following paragraphs. For amorphous films drawn at 20 cm min^{-1}, a significant birefringence was observed starting at draw ratios around 3. For the thermally crystallized samples, non-zero birefringence was observed at all drawing rates and draw ratios studied. Experimental data for crystalline samples are not presented for draw ratios below 2 because of the difficulty in obtaining low draw ratios due to neck formation.

A number of studies have shown,[7,26–29] that if the temperature of drawing is relatively high (above T_g, e.g. 90°C) and the strain rates low, PET spun fibres and cast films will stretch without resultant orientation or crystallinity occurring; this is called flow drawing. It was suggested[26] that under these conditions, molecular relaxation processes predominate over the orientation process. Consequently the drawing tension drops to low levels and results in flow drawing. It has also been suggested[28] that above a critical temperature, the intermolecular linkages are broken down, and as a result the polymer molecules may slip past one another and flow individually, exhibiting a large deformation without inducing any molecular orientation and crystallization just like in flow of a simple liquid. Qian *et al.*[29] suggested that in such hot-drawn amorphous PET films, the macromolecular chains are in fact oriented to a significant extent in the global sense, while the local segments have random orientation as a result of the enormous differences in the relaxation times of chain segments and global chains. In flow drawing of PET films, the deformation process leading to chain orientation in the global sense mainly involves the

deformation of a rubber-like network in which molecular entanglements act as physical crosslinks.

The mechanism of orientation development is strongly dependent on deformation rate, temperature and total deformation, as mentioned above. In fact, there is a competition between alignment and relaxation of the chain segments. At low enough deformation rates, virtually no orientation of the amorphous phase will be observed, as mentioned above. The only orientation that can be observed is that originating from the crystals formed upon drawing and subjected to deformation. The very low birefringence in the initially amorphous films drawn at low deformation rates and showing significant, highly oriented, crystallinity is not understood yet. We are currently exploring the possibility of artifacts arising from the nature of the refractometry technique before attempting a molecular interpretation. In fact, many factors may alter the sensitivity of the refractometry technique; these include solvent evaporation and/or incomplete wetting of the surfaces, as well as unclearness of the extinction lines, particularly for the amorphous drawn films, which often made it difficult to determine their position reliably. These problems were not encountered for initially crystallized films followed by stretching.

Gupta et al.[30] used X-ray diffraction to study the degree of crystal perfection in semi-crystalline PET fibres and films produced under different conditions. Samples produced by low-speed melt extrusion followed by drawing in water at low strain rates in a low temperature environment had the lowest X-ray crystallinity and the most imperfect crystals. Evidence of large crystalline imperfection was provided by their X-ray intensity plots and their melting endotherms. The low X-ray crystallinity and high defect density have been attributed to the slow drawing at relatively low temperature, which does not provide the necessary environment for crystallization, and to the presence of very small nuclei which may be crystalline remnants that are retained at the low production speeds and which can act as seed crystals around which crystallization occurs with incorporation of defects. Heat setting of these samples at elevated temperatures improves crystal perfection significantly. On the other hand, samples produced by drawing at a higher temperature and velocity have higher crystallinity and more perfect crystals which crystallize further on heat setting without any significant enhancement of crystal perfection, except at very high temperatures. In another study on the uniaxial planar deformation of PET films under different levels of stress, a maximum crystal size of 6 nm and long spacing of 30–40 nm was obtained[31]. The crystals were shown to arrange in crystalline blocks (about 7–12 crystals per block) inside crystalline layers.

In order to clarify these results, and have a better idea of the orientation of the drawn films, i.r. dichroic ratio measurements were performed on these film samples by front surface specular reflection i.r. spectroscopy[18,19]. This technique was used because of its non-contact nature and its potential use for on-line monitoring of orientation. The questions arising about the correlation between surface and bulk orientation and structure have already been addressed[18,19,32–34]. In fact, the relative amounts of surface crystallinity and amorphous structure and their respective surface orientations were examined for PET (depths of 0.5 and 5 μm) using
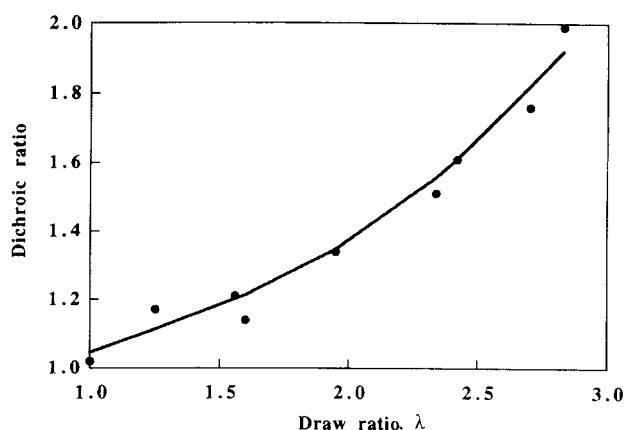

Figure 4 Dichroic ratio vs draw ratio for amorphous films uniaxially deformed at 80°C and 2 cm min^{-1}
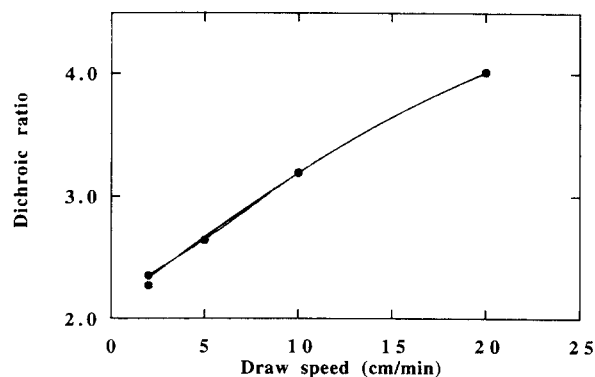

Figure 5 Effect of drawing rate at 80°C on dichroic ratio for a draw ratio of 2.7

attenuated total reflection (ATR)[34]. The surface orientation was determined using i.r. bands at 1340, 1370 and 1410 cm^{-1} (ref. 32). The results indicated a higher degree of extended *trans* segments and extended chain orientation near the surface in the drawing direction relative to the bulk of the film. An increased crystallinity at the surface was also observed.

The i.r. results obtained for the initially amorphous samples drawn at 2 cm min^{-1}, up to draw ratios of 3, are shown in *Figure 4* in terms of a dichroic ratio of a band corresponding to the *trans* conformer[19], as a function of draw ratio. For a non-oriented film, this ratio should be equal to 1. The results indicate a progressive increase of this ratio with λ, particularly for λs above 2. This increase is indicative of the orientation of the *trans* segments. It is thought that the number of these segments is still small and that a long range order has not developed yet, which may explain the non-birefringent nature observed for these films at low draw ratios. The effect of drawing rate on this dichroic ratio is shown in *Figure 5* for a λ of 2.7. It can be clearly noted that this ratio is very sensitive to the deformation rate. For the speed of 20 cm min^{-1}, this ratio is double that obtained for 2 cm min^{-1}, indicating much larger orientation. This may also explain the observation of non negligible birefringence for the films drawn at 20 cm min^{-1} and having some crystallinity.

Figures 6 and *7* show the orientation function and fraction of conformers as a function of λ for the *gauche* and *trans* conformers, as obtained by the i.r. specular
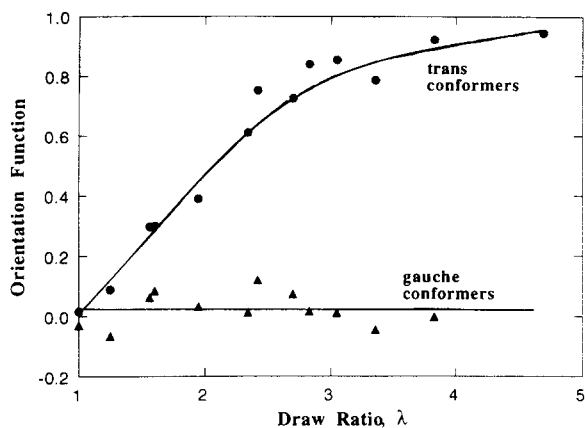
Figure 6 Orientation function of the *trans* and *gauche* conformers as function of draw ratio for amorphous films drawn at 80°C for 2 cm min⁻¹
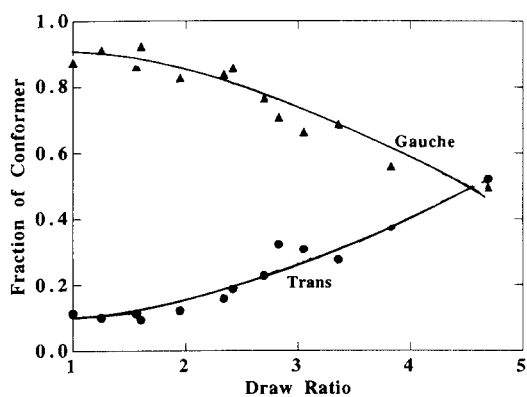

Figure 7 *Trans* and *gauche* conformers fraction as function of draw ratio for amorphous films drawn at 80°C and 2 cm min⁻¹
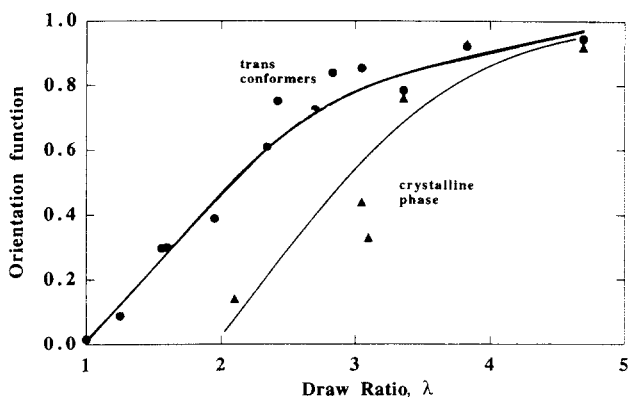

Figure 8 Orientation function obtained for the crystalline phase and the *trans* conformer for amorphous films drawn at 80°C and 2 cm min⁻¹

reflection technique. The details of the measurements and calculations are presented elsewhere[18,19]. The results clearly indicate an alignment of the chain's *trans* segments along the draw direction for all draw ratios. For the *gauche* conformers, no orientation is observed for all draw ratios, crystallinities and draw rates. Since this conformation is present only in the amorphous phase, this indicates that the amorphous phase is not significantly oriented. It is also observed that the *trans* conformer orientation saturates (very close to 1) at λ around 4. Concerning the structure of drawn films (*Figure* 7), a gradual conversion of the *gauche* to *trans*

conformers is observed. It is to be noted that the *trans* content is in all cases higher than the crystalline fraction (*Figure* 2).

In the cases where a crystalline phase was obtained, orientation of the crystalline phase was determined by wide angle X-ray diffraction (WAXD). The results obtained for the crystalline orientation function are presented in *Figure* 8 together with those obtained by i.r. for the *trans*-conformers' orientation. No crystalline orientation for λ below 2 was observed since the crystalline phase content in this region is negligible according to *Figure* 2. However, orientation of the *trans* conformers increases from the beginning of draw and it is to be noted that the crystalline orientation is lower than that of the *trans* conformers up to draw ratios of about 3.5. This may be attributed, as discussed above, to the presence of a certain number of imperfections[30]. In fact, the *trans*-conformers' orientation being measured by *FT*i.r. reflects the order of a specific group on the molecular level, whereas the crystalline orientation describes that of larger assemblies.

The overall orientation can be written as

$$f_{\text{overall}} = f_{trans}X_{trans} + f_{gauche}X_{gauche} \qquad (1)$$

or

$$f_{\text{overall}} = f_{\text{cryst}}X_{\text{cryst}} + f_{\text{non-cryst}}X_{\text{non-cryst}} \qquad (2)$$

where f designates the orientation function and X the volume fraction of the phase considered. The form contribution is neglected. The different contributions are, $f_{\text{cryst}}X_{\text{cryst}}$ for the crystalline phase and, for the non-crystalline phase, either $f_{\text{overall}} - f_{\text{cryst}}X_{\text{cryst}}$ when f_{cryst} is known or $(X_{trans} - X_{\text{cryst}})f_{trans} + X_{gauche}f_{gauche}$ when f_{cryst} is not known.

Figure 9 shows the overall orientation (the same as the *trans* contribution), the crystalline contribution and the calculated non-crystalline contribution. The non-crystalline orientation is observed to be lower than the other contributions above a draw ratio of 3, where a significant crystalline orientation is observed. At low draw ratios, the non-crystalline phase consists primarily of *gauche* conformations whose orientation is negligible. With the increase of deformation, the *trans* content, whose orientation is high, becomes larger and the contribution of the non crystalline phase starts to be non-negligible.
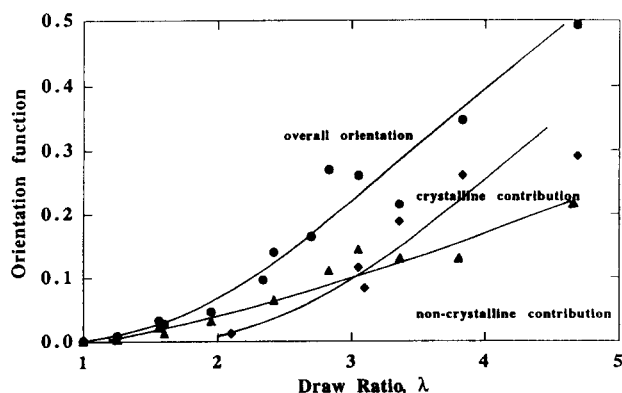

Figure 9 The orientation contributions of the *trans*, crystalline and non-crystalline phases to the overall orientation for amorphous films drawn at 80°C and 2 cm min⁻¹
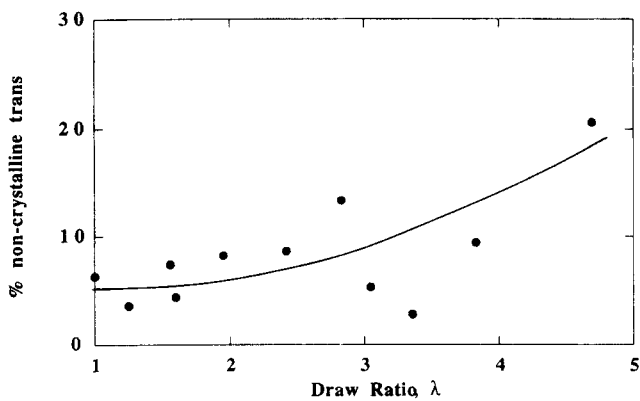
Figure 10 Fraction of the non-crystalline *trans* conformer as function of draw ratio for amorphous films drawn at 80°C and 2 cm min^{-1}
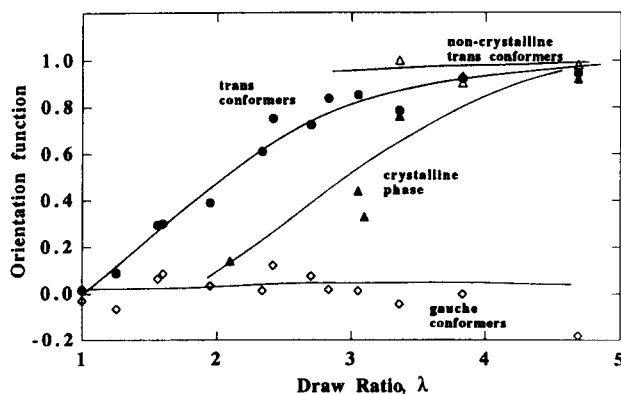

Figure 11 Orientation of the different phases as a function of draw ratio for amorphous films drawn at 80°C and 2 cm min^{-1}
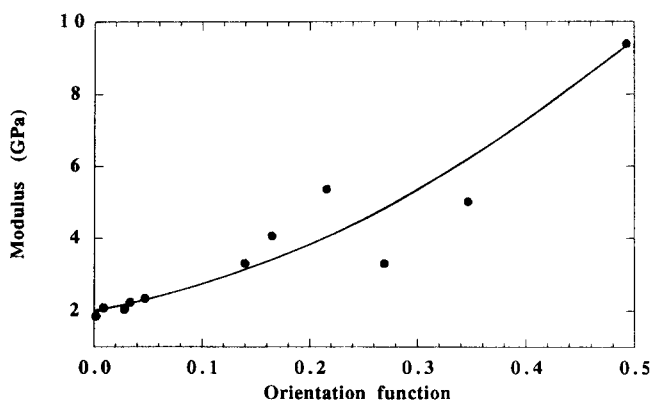

Figure 12 Modulus as a function of the overall orientation function for amorphous films drawn at 80°C and 2 cm min^{-1}

According to a recent work on the structural analysis of PET by PA-*FT* i.r. spectroscopy and d.s.c.[16] and to the results of Padibjo and Ward[12] a direct correlation between the ordered *trans* conformer and the apparent degree of surface crystallinity, measured by d.s.c., can be made. Applying this conclusion to our experimental results can allow the determination of the *trans* conformer present in the crystalline phase (which is the same as the crystalline content) and that present in the amorphous phase. The result of this determination is shown in *Figure 10*. Some scatter in the data is observed due to the cumulative errors in crystallinity and *trans* content determination. This non-crystalline *trans* content increases slightly up to λ around 3.5; above this range, a large increase is observed.

Knowing the *trans*-conformer content of the non-crystalline phase for the most crystalline films, a question may arise as to its specific orientation. Taking into account the fact that the *gauche* conformer orientation is negligible, the orientation of the non-crystalline phase of these films can be reduced to that of the *trans*-conformer present in this phase. In fact, the orientation of the non-crystalline phase can be written as

$$f_{\text{non-cryst}} = f_{trans \text{ non-cryst}} X_{trans \text{ non-cryst}} + f_{gauche} X_{gauche} \quad (3)$$

In this way, one can calculate the orientation of the non-crystalline *trans* conformers for the λs for which a significant crystalline orientation is known. The results are presented in *Figure 11*, together with those of the crystalline phase and the conformers. It is clearly observed that the orientation of the *trans* non-crystalline conformers is almost equal to 1, i.e. perfect orientation for the most crystalline samples. This observation will be further examined in future work.

Using these observations, one can speculate on the structural scheme for PET. One can assume that PET consists of three phases: i) a crystalline phase constituted solely of *trans* conformers arranged in small crystallites whose perfection increases with draw ratio and drawing rate; ii) a 'mesophase' constituted of *trans* conformers outside the crystalline phase; these can link the crystalline phase to the amorphous phase and have a high degree of orientation; and iii) a third phase completely disordered and constituted only of *gauche* conformers. The fraction of the mesophase would increase with draw ratio. However, it should be made clear that the data presented here do not provide direct evidence for this speculation. Further work is being conducted to gain more understanding of this particular aspect. However, this speculation is in agreement with recent work combining thermal, birefringence and X-ray analysis and which concluded the coexistence of two structures in the amorphous part of the material: a completely disordered amorphous phase and a mesomorphic amorphous one[20].

Finally, Young's modulus obtained from dynamic mechanical characterization, for a temperature of 30°C, is presented in *Figure 12* as a function of the overall orientation function. The results indicate a slight increase in the modulus for low draw ratios, up to 2.5 (where no significant crystallinity is present). For higher draw ratios, the increase in modulus is more pronounced. This is in agreement with the observations on crystallinity and orientation mentioned above. In fact, the contributions of the crystalline phase, as well as the contribution of the crystalline orientation, to the mechanical properties of semi-crystalline polymers have been shown to be the most important[2-6]. For the same draw ratio, films with higher crystallinity and/or drawn at a higher draw rate showed higher dynamic moduli, which is accounted for through the overall orientation.

CONCLUSION

FT i.r. and X-ray results showed significant orientation of the different phases in PET, particularly for λ higher than 3. The orientation contribution of the non-crystalline phase can be determined by combining *FT* i.r. and X-ray results. The *trans* conformer contribution to the non-crystalline phase is shown to be very high for the

high λs for which crystalline orientation was observed. A structural model consisting of a crystalline phase, a mesomorphic amorphous phase (constituted of *trans* conformers) and purely amorphous phase (constituted solely of *gauche* conformers) is a possible representation of the observed results.

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