

Orientation and Relaxation in Thick Poly(ethylene terephthalate) Films by Transmission Infrared Linear Dichroism

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Infrared spectroscopy is a powerful tool for the study of the orientation in amorphous and semi-crystalline polymers, but it is generally limited to thin samples. In this study, we have used transmission infrared linear dichroism to study the orientation of thick poly(ethylene terephthalate) (PET) films. To overcome the saturation problem of the intense bands of PET, overtones and combination bands in the high-frequency region of the mid-infrared spectrum were used. Using polarization-modulation infrared linear dichroism (PM-IRLD), it was possible to follow in real-time the relaxation of orientation of uniaxially oriented PET films up to 500 μm thick. It was observed that between 30 and 500 μm , the thickness of the films has no effect on the orientation relaxation dynamics. It should, therefore, be possible to use thick films, which are much easier to prepare than thin films, for future infrared studies of the deformation of PET. A very good correlation was also observed for the relaxation curves obtained using high- and low-frequency bands related to *gauche* and *trans* conformers in thin and thick films. An example of the application of these high-frequency bands to obtain orientation and structural information is also given in the case of a commercial PET bottle showing a biaxial orientation.

Index Headings: Poly(ethylene terephthalate); Thick films; Infrared linear dichroism; Polarization modulation; Orientation; Relaxation.

INTRODUCTION

Poly(ethylene terephthalate) (PET) is a semi-crystalline polymer of major industrial importance because of its good physical properties. It is widely used in different commercial applications such as textile fibers, films, and bottles. It is possible to significantly enhance the physical properties of PET, such as its tensile modulus or gas permeability, by introducing a preferential orientation of the macromolecular chains through processing.¹ For instance, roll drawing of PET has been shown to introduce uniaxial orientation of the chains along the machine direction, while blow molding leads to biaxial orientation. Several studies have dealt with the deformation mechanisms and the phase structure of PET.²⁻¹⁸

In the amorphous state, PET contains only 10% *trans* conformers, but in the crystalline phase, only *trans* segments are present.^{2,3} During deformation above T_g of an initially amorphous sample, the orientation of the *trans* conformers increases significantly while the *gauche* conformers remain almost unoriented, and the relative population of *trans* conformers increases gradually with increasing draw ratio.³⁻⁶ At draw ratios higher than about

2.5 (depending on stretching rate and temperature), it was shown that stress-induced crystallization occurs.⁶⁻⁸ The highly oriented crystals so produced can act as pseudo cross-links and hinder most of the relaxation of the amorphous chains. In contrast, if the stretching is stopped at smaller draw ratios, a rapid relaxation of orientation occurs.

X-ray diffraction (XRD) has been widely used for the characterization of the orientation of the crystalline phase of PET because it gives access to the complete distribution of orientation of all diffraction planes and provides information about the crystallinity level and size of the crystals.^{1,9} However, its application to amorphous samples is restricted, and it can hardly be used to follow the kinetics of relaxation of PET without using a synchrotron source.^{7,10} Optical birefringence can be used efficiently for such dynamic experiments,^{1,11} but it only measures the overall orientation of the sample, without discrimination between the amorphous and crystalline phases. On the other hand, infrared spectroscopy is an interesting tool for orientation characterization because bands specific to different phases or molecular conformations can be found in the infrared spectra. The most straightforward approach for the determination of orientation in PET by infrared linear dichroism (IRLD) is transmission spectroscopy, but most of the interesting infrared bands of PET are very strong and cannot be used quantitatively for films thicker than 2 μm .¹² However, by using weaker bands, this technique has been applied for films up to 50 μm thick.^{13,14} Clayden et al. have studied thicker samples, but microtoming of the samples to a thickness of less than 10 μm was required in order to obtain accurate results.¹⁵ Furthermore, the authors reported that this procedure introduced a slight level of orientation in the samples. Attenuated total reflection (ATR) has also been used to study the surface orientation of thick PET films but is limited by the sample-prism contact.¹⁶ Cole et al. have shown that polarized front-surface reflection infrared spectroscopy can be used efficiently to determine the orientation and structure of thick and even opaque PET films.^{12,17,18} For instance, they were able to determine the orientation of the strongly absorbing carbonyl band in 500- μm -thick films.

While conventional IRLD is well suited for static measurements, it suffers from a limited time resolution for dynamic deformation-relaxation experiments. To overcome this limitation, the polarization-modulation (PM) technique has been coupled to the conventional trans-

Received 22 June 2001; accepted 21 August 2001.

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mission IRLD measurements. With this technique, the dynamics of strain-induced orientation of polymers and the light-induced orientation of azopolymers have been studied with a time resolution on the order of one second.^{19–21} Recently, PM-IRLD has been used to study the deformation of PET films,²² but the technique was limited to thin films, thus requiring a difficult sample preparation and excluding measurements on most “real-life” samples. In the current study, PM-IRLD has been used in the transmission mode to study the relaxation of orientation of uniaxially oriented thick PET films. To overcome the saturation problem, overtones and combination bands in the high-frequency region of the mid-infrared spectrum were used. The orientation of *gauche* and *trans* conformers in thin and thick films will be compared. Finally, an example of the use of such high-frequency bands will also be given in the case of a commercial PET sample.

EXPERIMENTAL

The polymer used in this work was an extrusion grade PET (DuPont Selar 7086) containing no nucleating agents. Its molecular weight was $M_w = 54\,600$ g/mol with a polydispersity index of 1.9, as previously determined by gel permeation chromatography relative to polystyrene standards.⁸ The initial polymer, in the form of crystalline pellets, was first reduced to a powder and then dried under vacuum at 90 °C for 24 h. Films with a thickness ranging from 30 to 500 μm were formed by compression molding in a Carver press. The films were held during 4 min at 280 °C, above the melting point of PET, under an applied load of 2 tons for thick films and 5 tons for thin films. Films were then rapidly quenched in an ice water bath to avoid crystallization. A T_g of 78 °C was obtained for PET, as determined by the mid-point of the heat capacity jump by differential scanning calorimetry (Perkin–Elmer DSC-7) at a scanning rate of 10 K/min. The crystallinity level of the samples was also obtained by DSC by subtracting the crystallization endotherm from the melting exotherm, assuming a melting enthalpy of 140 J/g for completely crystalline PET.²³ The initial samples were all amorphous (below 5% crystallinity), which was confirmed by X-ray diffraction (Kristalloflex 760 generator with Bruker/Siemens Hi-Star bidimensional detector).

For the deformation experiments, the films were cut into strips 20 mm in length and 6 mm in width and marked with ink lines to verify the real draw ratio. A pyrotape (Aremco Products #546) was used to avoid any slippage of the films during the elongation. The films were stretched uniaxially at 90 °C to a fixed draw ratio of 1.5 at a constant draw rate of 10 cm/min with a mechanical stretcher fitted with ZnSe windows to allow the *in situ* recording of the PM-IRLD spectra during the orientation relaxation. The temperature was adjusted (± 0.1 °C) using an Omega temperature controller (CN 7600) and heating cartridges. Dichroic difference spectra with a resolution of 8 cm^{-1} were recorded with a Bomem Michelson MB-100 spectrophotometer using the optical setup, two-channel electronic processing, and calibration procedure previously described.^{24,25} An InSb detector (EG&G Judson), a ZnSe photoelastic modulator (Hinds PEM-90 type II/ZS50) operating at 50 kHz, a lock-in

amplifier (EG&G 7260 DSP) with a 40- μs time constant, and two dual channel electronic filters (Stanford Research Systems SR650) were used to generate the double modulation and to isolate the experimental signals. For the low-frequency measurements with thin films, the InSb detector was replaced by an MCT detector (Belov). All experiments were conducted in three consecutive acquisition steps: the first series of 180 spectra of 4 scans was followed by 90 spectra of 30 scans and by a final series of 80 spectra of 75 scans, for a total measurement time of about one hour.

The orientation function $\langle P_2(\cos \theta) \rangle$ in the case of uniaxial deformations was calculated from the dichroic difference ΔA using the following expression:²⁵

$$\langle P_2(\cos \theta) \rangle = \frac{2}{(3 \cos^2 \alpha - 1)} \frac{\Delta A}{3A_0} \sqrt{\lambda} \quad (1)$$

where λ is the draw ratio, A_0 the absorbance of the unstretched isotropic sample, α the angle between the transition moment of the vibration considered and the main chain axis, and θ the average angle between the chain axis and the stretching direction. The A_0 values were determined from transmission spectra recorded with either Nicolet Magna 560 or 750 spectrophotometers.

Static IRLD measurements on samples cut from a commercial PET bottle were performed using a Nicolet Magna 560 spectrophotometer equipped with an InSb detector with a 4 cm^{-1} resolution. A wire-grid KRS-5 polarizer was rotated to acquire sequentially the spectra in the machine direction (MD), along the bottle long axis, and in the transverse direction (TD). To generate the spectrum in the normal direction (ND), the polarizer was set parallel to the machine direction and the sample was rotated by 30° around the axis parallel to the transverse direction. It was shown that the absorbance in the normal direction, A_{ND} , is given by:²⁶

$$A_{\text{ND}} = \frac{A_{\beta} \left(1 - \frac{\sin^2 \beta}{n^2} \right)^{1/2} - A_{\text{MD}}}{\frac{\sin^2 \beta}{n^2}} + A_{\text{MD}} \quad (2)$$

where A_{β} is the absorbance of the tilted sample, β the angle between the incident electric vector and the sample plane, and n the refractive index of the sample. The refractive index of the samples was determined using the tilt angle method, as described by Koenig et al.²⁷ A mean value of 1.67 was found for the PET bottle in the machine direction, in agreement with previously reported results on stress-crystallized PET.²⁸

RESULTS AND DISCUSSION

The transmission infrared spectrum of a 30- μm -thick PET film is shown in Fig. 1A. Even for such a thin film, several bands like the 1725 cm^{-1} band due to the carbonyl stretching vibration are saturated. Nevertheless, several weaker bands can be used for transmission IRLD measurements. For instance, Pearce et al.¹³ have used the 970 and 1340 cm^{-1} bands, both associated with *trans* conformers, while Lorentz et al.¹⁴ have used the 1020 and 875 cm^{-1} bands to characterize the orientation of the

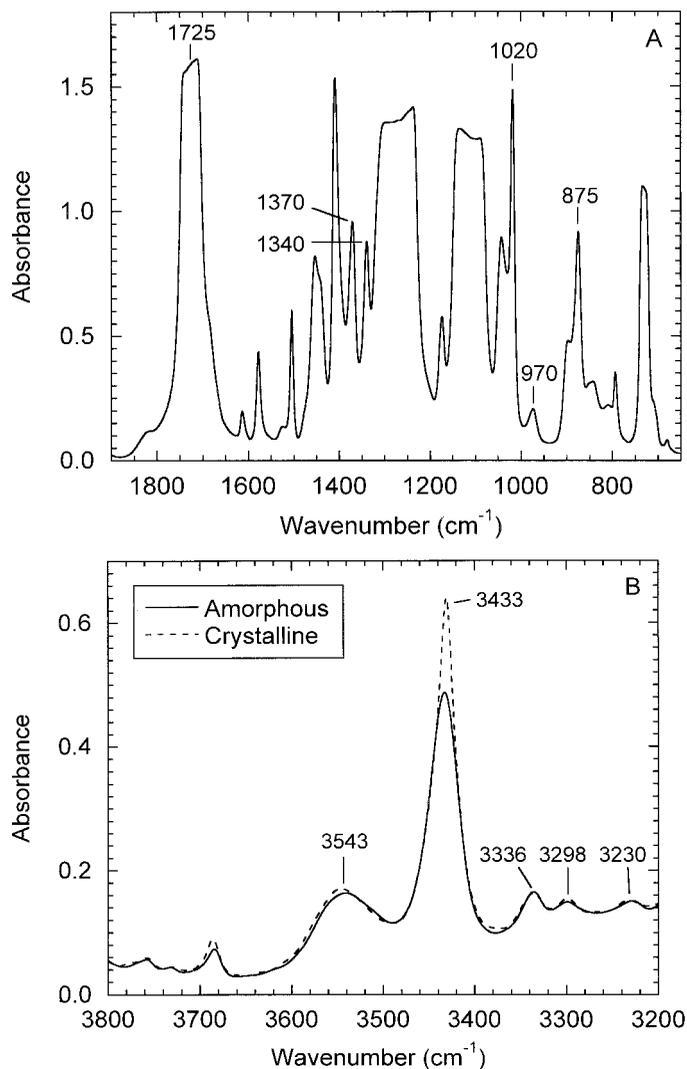


FIG. 1. Infrared spectra of (A) an amorphous 30- μm -thick PET film in the low-frequency region, and (B) amorphous and crystalline 150- μm -thick PET films in the high-frequency region.

chain axis and of the normal to the phenyl rings, respectively. Although very useful for relatively thin films, all these bands become completely saturated and thus, useless for thick PET films.

A direct and simple approach to determining the orientation in thick films by transmission infrared spectroscopy is to take advantage of the weaker bands in the spectrum. It is well known that overtones and combination bands observed in the near infrared (NIR) region are often very weak and allow the study of thick samples.^{29–31} As shown in Fig. 1B, such bands are present and are relatively well isolated in the 3200–3800 cm^{-1} region of the spectrum of a 150- μm -thick film of PET. The most intense band, around 3433 cm^{-1} , is assigned to the overtone of the C=O stretching band, while the band near 3543 cm^{-1} has been ascribed to the stretching of the O–H groups present at the chain ends of PET.³² A clear assignment for the small bands at 3336, 3298, and 3230 cm^{-1} was not found in the literature, but they most likely arise from the combination of the C=O stretching vibration with the ν_{8B} , ν_{8A} , and ν_{19A} phenyl deformations appearing at 1613, 1578, and 1504 cm^{-1} , respectively.

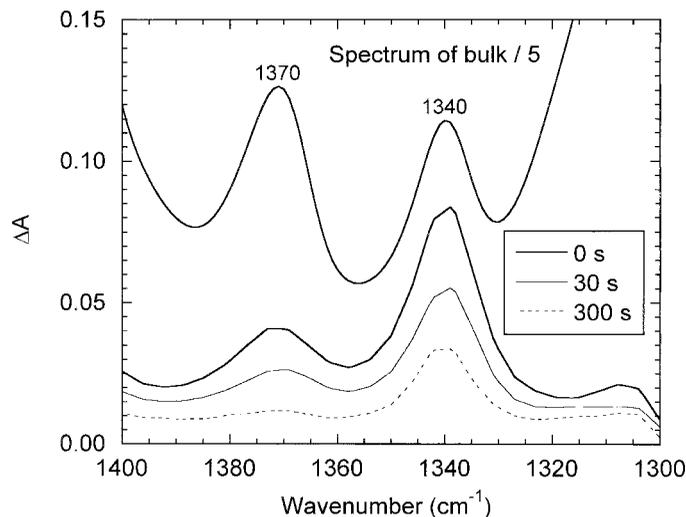


FIG. 2. Infrared spectrum of an undeformed 30- μm -thick PET film in the low-frequency region, and dichroic difference spectra recorded by PM-IRLD at the end of the deformation (0 s) and after 30 and 300 s of relaxation.

The initially amorphous 150- μm -thick film was crystallized overnight at 140 $^{\circ}\text{C}$ in a vacuum oven, leading to a degree of crystallinity of 31%, as determined by DSC. The most striking change in the spectra of Fig. 1B is observed on the 3433 cm^{-1} band. Upon crystallization, the band gradually shifts to lower frequencies by about 2 cm^{-1} , its peak height increases by 30%, and its width at half-height decreases significantly from 36 to 26 cm^{-1} . In contrast, the area of the 3336 cm^{-1} band decreases slightly, by about 12%, during crystallization. Such results demonstrate that these two high-frequency bands, and several others not discussed here, can be used to obtain structural information on thick PET films. Even if these bands are not strictly related to the ethylene glycol moiety of PET, the behavior of the 3336 cm^{-1} band is similar to that observed under the same conditions for the 1370 cm^{-1} band, assigned to the CH_2 wagging vibration of the *gauche* conformers. On the other hand, the 3433 cm^{-1} band, which is present in both the amorphous and crystalline PET, could be correlated with the *trans* conformers, although the increase in intensity of this band is smaller than that observed for the all-*trans* band at 1340 cm^{-1} after an identical treatment on thin films.

In order to compare the orientation measurements obtained with the use of the high-frequency bands to those obtained in the well-characterized low-frequency region, we have performed a series of reference experiments using 30- μm -thick PET films. Samples were deformed at 90 $^{\circ}\text{C}$ ($T_g + 12^{\circ}\text{C}$), up to a draw ratio of 1.5 at a drawing rate of 10 cm/min . It was verified by X-ray diffraction that the samples remain amorphous under these stretching conditions. Figure 2 shows the unpolarized infrared spectrum (divided by 5) of the initial PET film in the 1300–1400 cm^{-1} region, as well as three dichroic difference spectra recorded by PM-IRLD immediately at the end of the deformation process (time = 0 s) and after 30 and 300 s of relaxation. The two bands observed in the spectra at 1340 and 1370 cm^{-1} are assigned to the main chain CH_2 wagging vibrations of *trans* and *gauche* conformers, respectively.⁵ They appear as positive peaks because their

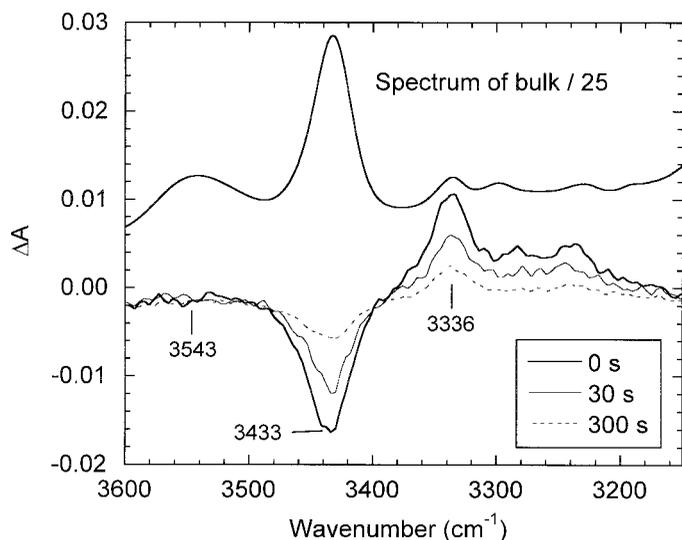


FIG. 3. Infrared spectrum of an undeformed 300- μm -thick PET film in the high-frequency region, and dichroic difference spectra recorded by PM-IRLD at the end of the deformation (0 s) and after 30 and 300 s of relaxation.

transition moment is mostly parallel to the main chain axis, with a reported α angle of 21° .¹⁷ The two bands show a maximum dichroic difference at 0 s because the orientation is larger immediately at the end of the deformation process. The dichroism then decreases as a function of time, as the amorphous PET chains relax toward their isotropic state. The signal-to-noise ratio of the dichroic difference spectra is very good, even if the acquisition time was less than 2 s for the spectra recorded after 0 and 30 s of relaxation. This shows the efficiency of PM-IRLD in following the relaxation kinetics of amorphous polymers. It is interesting to compare the relative intensity of these two bands in the spectrum of the unstretched sample and in the dichroic difference spectra. In the first spectrum, the *gauche* band at 1370 cm^{-1} is stronger than the 1340 cm^{-1} band, which reflects the larger amount of *gauche* conformers in the amorphous phase. On the other hand, the *trans* band at 1340 cm^{-1} is much more intense than the *gauche* band in the dichroic spectra. Considering that the α angle between the main chain axis and the transition moment of the vibration is the same for these two bands, this means that the orientation of the *trans* conformers is much higher than the orientation of the *gauche* conformers. The orientation function $\langle P_2(\cos \theta) \rangle$ of the *trans* conformers is actually about three times larger than that of the *gauche* segments.

Series of deformation-relaxation experiments were then performed with thicker films, using the high-frequency bands for the orientation determination. PET samples with thicknesses of 150, 300, and 500 μm were stretched uniaxially at 90°C to a draw ratio of 1.5 at a drawing speed of 10 cm/min. The unpolarized infrared spectrum (divided by 25) of a 150- μm -thick PET film in the $3150\text{--}3600\text{ cm}^{-1}$ region is shown in Fig. 3, along with three dichroic difference spectra recorded immediately at the end of the deformation process (time = 0 s) and after 30 and 300 s of relaxation. The signal-to-noise ratio in Fig. 3 is not as good as that obtained in Fig. 2, but it must be stressed that the dichroic difference is very small

in these difference spectra, less than -0.02 a.u. for the strongest band as compared to 0.08 a.u. in the low-frequency region. The two strongest bands in the dichroic difference spectra are observed at 3433 and 3336 cm^{-1} . The first one shows a negative dichroism, indicating that the transition moment associated with this band is mostly perpendicular to the chain axis. Since this band is the overtone of the carbonyl stretching, our result is in qualitative agreement with the α angle of 65° reported by Cole et al. for the carbonyl band.¹⁸ The 3336 cm^{-1} band gives a positive peak and thus possesses a transition moment relatively parallel to the chain axis. At first sight, the intensity ratio of these two bands in the dichroic difference spectra as compared to the absorbance spectrum is somewhat surprising. For the bulk sample, the intensity of the 3433 cm^{-1} band is about 5 times larger than that of the 3336 cm^{-1} band, while the intensities are similar in the dichroic difference spectra. Considering that the 3433 cm^{-1} band is partly due to the *trans* conformers, which are much more oriented than the *gauche* conformers, the opposite intensity ratio would have been expected.^{4,22} The difference between the α angle associated with these bands is most likely at the origin of this result. Since the reported angle between the chain axis and the transition moment of the 3433 cm^{-1} band is close to 54.7° , the magic angle, a small dichroism is expected for this band even if the orientation of the macromolecular chains is large in the sample. On the other hand, the 1340 cm^{-1} *trans* band and even the 1370 cm^{-1} *gauche* band show a much larger dichroic difference in the low-frequency spectra because their α angle is 21° , far from the magic angle.

Another interesting feature of Fig. 3 is the absence of any dichroism for the band at 3543 cm^{-1} , even if it is quite strong in the absorbance spectrum of the bulk sample. This band was assigned to the O-H stretching of the chain end groups.³² Even at the end of the mechanical deformation, at time 0 s, no PM-IRLD signal is detected, which either means that no orientation is introduced, or that the chain ends have completely relaxed during the 6 s needed to stretch the sample. It has often been proposed that the chain ends of a macromolecule possess a greater mobility and thus relax at a faster rate than the other parts of the chain, which is in agreement with our results.^{21,33,34} Block copolymers of polystyrene (PS) in which either the center or the end blocks were deuterated have been used to compare the relaxation of the different parts of the chain.^{34,35} It was observed that the end blocks exhibit less orientation and relax at a faster rate than the rest of the chain. Decreasing the length of these end blocks should reduce the observed orientation and increase the relaxation rate. The complete absence of dichroic difference for the 3543 cm^{-1} band in PET could thus be explained by the fact that the end groups of PET, as revealed by the O-H band, are a single motif (as compared to about 365 repeat units in the end blocks for PS) that can relax at a very high rate.

Figure 4 compares the orientation relaxation curves obtained from the 3336 and 3433 cm^{-1} bands for the 300- μm -thick films. The data were normalized with respect to the first relaxation data measured at 0 s. The dispersion in the data of the 3433 cm^{-1} band is relatively large, due to the fact that the absorbance is above unity for this band

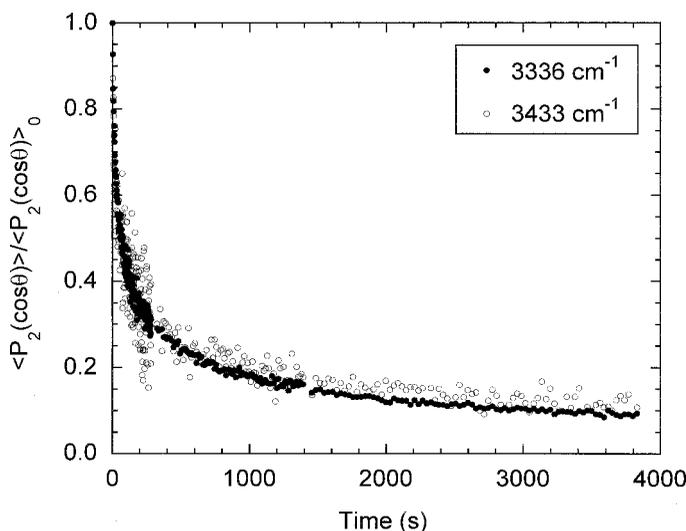


FIG. 4. Normalized relaxation curves of a 300- μm -thick PET film in the high-frequency region as a function of time after a deformation at 10 cm/min at 90 °C.

in the absorbance spectrum of thick films. Nevertheless, Fig. 4 shows that the relaxation kinetics for the two bands are very similar. Since the 3336 cm^{-1} band appears to be related mostly to the *gauche* conformers while the 3433 cm^{-1} band could be influenced by both *gauche* and *trans* segments, Fig. 4 reveals that the relaxation rate in amorphous PET does not depend on the nature of the conformers, even if the absolute value of the orientation function does. This result is in agreement with the observations of Duchesne et al., who have recently demonstrated with the use of PM-IRLD, that the relaxation rate of the 1370 and 1340 cm^{-1} bands is similar in thin 20- μm amorphous PET films.²²

Since the two high-frequency bands relax with the same kinetics, either one can be used to compare the relaxation of PET in thin and thick films. Figure 5 shows the normalized relaxation curves of 30- and 300- μm -thick films after a similar deformation to a draw ratio of 1.5, at 90 °C and using a stretching rate of 10 cm/min. The 3336 and 1340 cm^{-1} bands have been used for the thick and thin films, respectively. As seen in Fig. 5, the two curves display a very low level of dispersion and are clearly superimposable. The relaxation is thus totally independent of the thickness of the samples, even if there is a tenfold difference between the thickness of the two samples displayed. For clarity, the relaxation curves of the 150- and 500- μm -thick films are not shown on Fig. 5, but they are in complete agreement with those obtained for the 300- μm -thick films. This clearly demonstrates that samples of any thickness can be used to follow the deformation and relaxation kinetics in amorphous PET. To further prove the validity of this method to determine the orientation of PET, it was recently shown that the relaxation dynamics of a 350- μm -thick PET film obtained using PM-IRLD and dynamic birefringence are in excellent agreement within experimental error.¹¹

A further step would be to quantify the absolute orientation functions obtained in thick films using the 3336 cm^{-1} band, but a value of the α angle is needed for that purpose. Since the band appears to arise mostly from

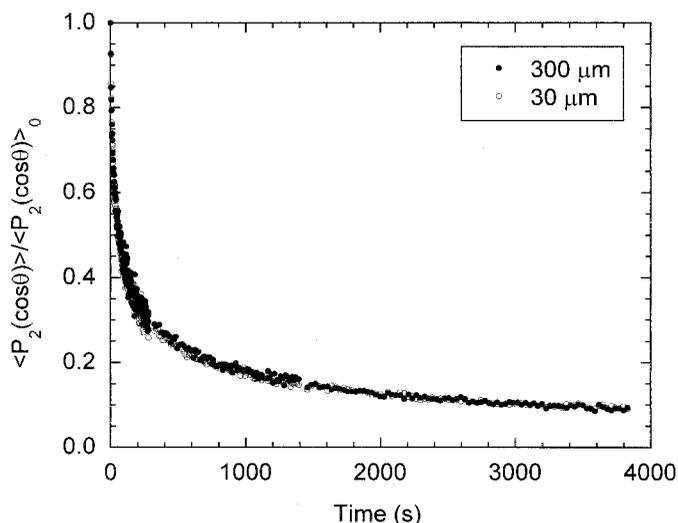


FIG. 5. Comparison of the normalized relaxation curves of PET for 30- and 300- μm -thick films, recorded using the 1340 and 3336 cm^{-1} bands, respectively, after a deformation at 10 cm/min at 90 °C.

gauche conformers, the $\langle P_2(\cos \theta) \rangle$ values obtained from this band should be identical to the orientation function determined for thin films using the 1370 cm^{-1} *gauche* band. According to Eq. 1, it is possible to determine the angle α by plotting the values of $(\Delta A/3A_0)\sqrt{\lambda}$ for the 3336 cm^{-1} band as a function of $\langle P_2(\cos \theta) \rangle$ for the 1370 cm^{-1} band. Such a plot is shown in Fig. 6, in which an α angle of 21° is used for the 1370 cm^{-1} band. As can be seen, a linear relation is obtained with a regression coefficient (R) of 0.984, a slope of 0.444, and an intercept equal to 0. This yields a value of 38° for the α angle for the 3336 cm^{-1} band of PET. However, it must be noted that this determination depends on the validity of the 21° angle used for the 1370 cm^{-1} band.

Although PM-IRLD offers undeniable advantages for the dynamic study of the uniaxial orientation in polymers, conventional infrared linear dichroism is still a valuable

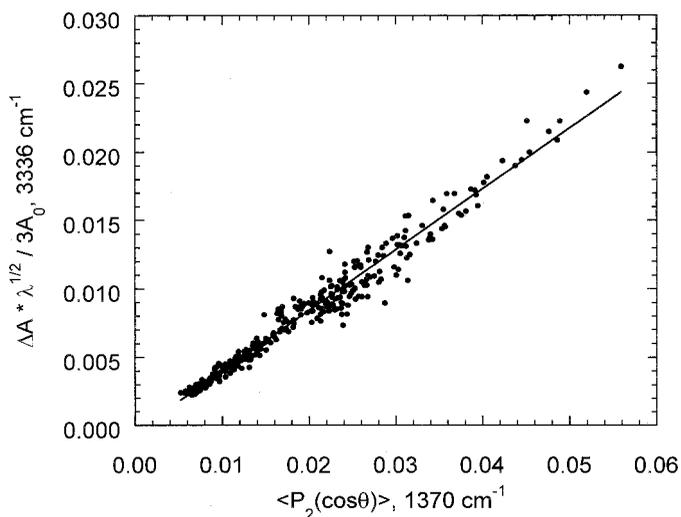


FIG. 6. $(\Delta A/3A_0)\sqrt{\lambda}$ calculated from the 3336 cm^{-1} band of a 300- μm -thick PET film plotted as a function of the orientation function $\langle P_2(\cos \theta) \rangle$ obtained from the 1370 cm^{-1} band of a 30- μm -thick PET film. The line is a least-square plot giving a correlation coefficient of 0.984.

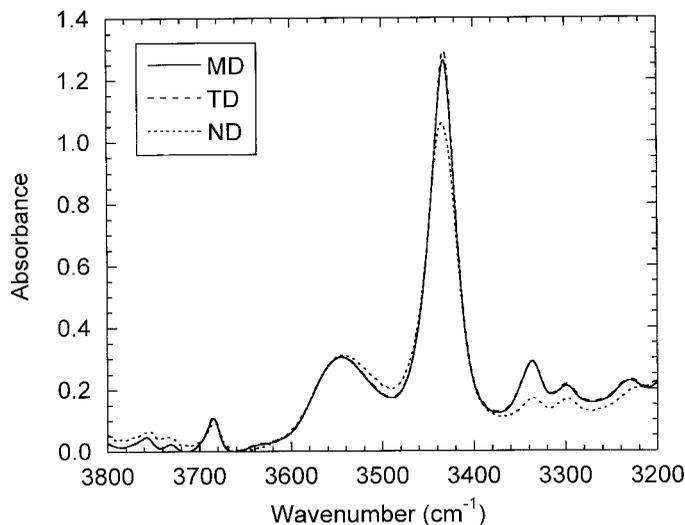


FIG. 7. Polarized infrared spectra of a commercial PET bottle recorded in the machine (MD) and transverse (TD) directions and calculated for the normal (ND) direction using Eq. 2.

tool for the static determination of orientation in PET. With IRLD, it is possible to determine the spectra of the sample in the three principal directions, which is an essential feature for the determination of the orientation in biaxial samples. To demonstrate that the high-frequency infrared bands can be used for such determination with thick films, we have studied a series of samples cut from a commercial PET bottle. The thickness of the films was about 270 μm , far from the usual range used for transmission infrared spectroscopy. The spectra in the machine and transverse directions are easily obtained by rotating the polarizer, but the spectrum in the normal direction cannot be determined directly. However, it can be calculated if a polarized spectrum is recorded with oblique incidence, as described in the Experimental section. Figure 7 shows the experimental MD and TD spectra of the PET bottle, as well as the ND spectrum as calculated using Eq. 2 with a refractive index of 1.67. The sample clearly shows a biaxial orientation; the ND spectrum is less intense than the MD and TD spectra, indicating that the chains are preferentially oriented in the plane of the film. On the other hand, the absorbances in the machine and transverse directions are very similar. The intensity of the 3433 cm^{-1} band is slightly higher in the transverse direction, indicating a small orientation of the chains along the machine direction, but the opposite effect was observed for other samples. This shows that the blow molding process used to produce the bottle introduces a generally balanced orientation of the chains within the plane of the film, with slight deviations depending on the position of the sample in the bottle.

It is possible to characterize the orientation of biaxial samples more quantitatively using a set of two orientation functions, f_θ and f_ϕ , as described by Kaito et al.:³⁶

$$f_\theta = \frac{A_{\text{MD}}/A_0 - 1}{2} \quad (3)$$

$$f_\phi = \frac{A_{\text{TD}} - A_{\text{ND}}}{A_{\text{TD}} + A_{\text{ND}}} \quad (4)$$

where the isotropic absorbance is given by $A_0 = (A_{\text{MD}} +$

TABLE I. Orientation functions of a commercial PET bottle.^a

	f_θ	f_ϕ
3433 cm^{-1}	0.04 ± 0.03	0.07 ± 0.04
3336 cm^{-1}	0.11 ± 0.03	0.5 ± 0.1
Perfectly equibiaxial	0.25	1

^a Mean values of four determinations on samples cut from the sides of the bottle.

$A_{\text{TD}} + A_{\text{ND}})/3$. The function f_θ describes the orientation of the transition moment of a given infrared band with respect to the machine direction. Its maximum value is 1 if all transition moments are along the machine direction and -0.5 if they are all oriented in the transverse and/or normal directions. On the other hand, f_ϕ compares the orientation of the transition moments in the transverse and normal directions. Maximum values of 1 and -1 are obtained if all the transition moments are along the transverse and normal directions, respectively. Both functions are equal to zero if the sample is isotropic. Table I lists the values of f_θ and f_ϕ for the 3433 and 3336 cm^{-1} bands, as well as the theoretical values for a perfect equibiaxial orientation of the transition moments in the plane of the film. From this table, it is apparent that the transition moments of the 3336 cm^{-1} band are strongly oriented in the plane of the film. Since the α angle between this transition moment and the chain axis is about 38°, mostly parallel to the main chain, the macromolecular chains are also highly oriented in the plane of the film. The orientation functions for the 3433 cm^{-1} band are much smaller, but they are positive. This indicates that transition moments associated with this band are oriented preferentially in the plane of the film, although their reported α angle is 65°, mostly perpendicular to the main chain axis. To account for these results, i.e., a preferential orientation of the PET chains and of the carbonyl groups in the plane of the film, we have to consider a non-cylindrical symmetry of the chains. The chains would be oriented more or less randomly in the plane of the film, but with a restricted rotation along their main axis, the carbonyl groups being preferentially oriented in the machine and transverse directions. Since the carbonyl transition moment lies almost parallel to the plane formed by the phenyl groups, this would further indicate that the aromatic rings are also stacked in the plane of the sample. Such an organization is in agreement with results reported for biaxial and planar deformation of PET samples,^{37,38} as well as with our own XRD measurements on the same PET bottle.

It is also possible to extract structural information from the infrared spectra in the high frequencies. As mentioned earlier, we have observed that upon thermal crystallization at 140 °C, the 3433 cm^{-1} band decreases in width and is shifted to lower wavenumbers. Such behavior is also observed in the case of stress-crystallized samples and could be used to qualitatively probe the presence of crystallinity in the sample. For the PET bottle, a degree of crystallinity of 30% was obtained by DSC. The mean width of the band in the MD and TD spectra for four samples (Fig. 7 gives a representative example) was evaluated to be 31 cm^{-1} , while it was 35.5 cm^{-1} for the ND spectrum calculated using Eq. 2, as observed for the amorphous sample. Because this band is assigned to the

carbonyl overtone, this would indicate that the crystallites are oriented with their 010 plane parallel to either the machine or the transverse direction, while the infrared absorption in the normal direction would mostly come from amorphous regions. This is in complete agreement with the conclusions derived from the orientation functions of Table I. In a second example (not shown), a PET film was stretched uniaxially to a draw ratio of 4 in order to provoke stress-induced crystallization, which was confirmed by DSC and X-ray diffraction. Polarized infrared spectra have revealed a broader band in the MD than in the TD, while an intermediate value was obtained from the calculated ND spectrum. These results indicate that the carbonyl groups in the crystalline domains are oriented perpendicular to the stretching axis, as expected, but also that they have a tendency to align in the plane of the film, even for an uniaxial orientation.

CONCLUSION

In this work, we have shown that the high-frequency bands of the mid-infrared spectrum can be used efficiently to characterize the orientation of thick PET films. The use of transmission IRLD with thick films is advantageous because little or no sample preparation is required, which allows the characterization of samples without affecting their orientation or thermal history. This measurement is also experimentally easier to perform than other infrared techniques such as front-surface reflectance or ATR, and it provides information about the orientation of the whole sample instead of its surface only. Furthermore, it allows coupling with a photoelastic modulator to determine relaxation kinetics following a deformation. Using PM-IRLD, it was demonstrated that the thickness of the sample, between 30 and 500 μm , has no effect on the relaxation rate and that the relaxation kinetics of the *gauche* and *trans* conformers are similar in the amorphous state. This should reduce the need for thin films, which are much more difficult to prepare than thick films, for future infrared studies of the deformation of PET. A method for the quantitative determination of the orientation function of PET using the 3336 cm^{-1} band has also been proposed. Finally, it was shown that the high-frequency bands can be used to determine the orientation in biaxially oriented thick films using conventional IRLD and to provide qualitative information about the crystallinity of the sample.

ACKNOWLEDGMENTS

This work was funded by NSERC of Canada and Fonds FCAR of the Province of Québec. C.P. also expresses his thanks to NSERC for a post-graduate scholarship.

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