

Molecular Orientation and Relaxation of Poly(ethylene terephthalate) by Polarization Modulation Infrared Spectroscopy

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ABSTRACT: Molecular orientation and relaxation of the trans and gauche conformers of poly(ethylene terephthalate), during and after an uniaxial deformation above the glass transition temperature, between 85 and 100 °C, were investigated using polarization modulation infrared linear dichroism. At all temperatures, it was found that the trans conformers orient much more than the gauche conformers whereas their relaxation rates are comparable. Gauche–trans conformational changes were observed during both stretching and relaxation. At temperatures of 93 °C or below, the relaxation was exponential with time, whereas above 93 °C, the initial decrease was followed by an increase of the orientation function due to crystallization. A reorientation of the gauche conformers, driven by the movement of the trans conformers, was also observed during crystallization.

Introduction

Properties of polymeric materials can be enhanced significantly through orientation.¹ For example, orientation of poly(ethylene terephthalate) (PET) is induced during its processing via fiber spinning or blow molding. This polymer can be oriented in the amorphous or semicrystalline state because of its relatively high glass transition temperature (T_g). The draw temperature, draw rate, and draw ratio exert a profound influence on the orientation and crystallization of PET.

Several studies^{2–5} have shown that PET remains amorphous if the draw temperature and draw ratio are kept relatively low. However, Middleton et al.⁶ have recently suggested that, at relatively low strain rates ($<0.1 \text{ s}^{-1}$), crystallization occurs during the drawing process before significant gauche–trans conformational changes could be detected. For draw rates faster than the rate of chain retraction, Blundell et al.⁷ have shown that crystallization does not start until the end of the drawing process because the continuous network deformation frustrates any attempt by the chain segments to move into an ordered phase. Only when deformation has stopped can the oriented segments cooperatively align to form crystals. Finally, shrinkage experiments on oriented PET have demonstrated that, beyond a certain degree of orientation, shrinkage is hindered due to the development of crystallinity.^{8,9}

To investigate the orientation and relaxation of PET, several methods have been used such as birefringence, X-ray diffraction, and Fourier transform infrared (FTIR) spectroscopy.^{2–10} Ajji et al.^{2,3} have studied the development of molecular orientation of the trans and gauche conformers of PET, particularly at draw ratios larger than 3, using FTIR spectroscopy. Since the trans conformer contribution to the noncrystalline phase is high at draw ratios larger than 3.5, a structural model was proposed³ which consists of a crystalline phase (made of trans conformers), a mesomorphic amorphous phase (also composed of trans conformers), and a purely

amorphous phase (composed solely of gauche conformers). At low deformation, trans molecular segments possess a much higher orientation than gauche segments, whereas at high degrees of overall deformation, there is an appreciable alignment of both the gauche and trans segments.¹¹

In a previous article,¹² we have used birefringence to investigate the overall molecular orientation and relaxation of uniaxially stretched PET at different draw ratios and draw rates above T_g . From the relaxation curves, overall relaxation times have been calculated. However, different conformational segments are expected to relax at different rates. Such information can be obtained by using polarization modulation infrared linear dichroism (PM-IRLD),^{13–15} as has been done before for polystyrene¹⁶ and for blends^{17,18} where the two components were measured separately. In the present study, amorphous PET was drawn at different draw ratios and draw rates between 85 and 100 °C. The orientation and relaxation behavior of trans and gauche segments of PET was investigated using PM-IRLD. It will be shown that there is cooperativity between these two types of segments, in orientation and in relaxation, in both the amorphous and semicrystalline polymers.

Materials and Methods

The polymer used in this study was a commercial PET (Sellar PT 7086), kindly provided by DuPont. Differential scanning calorimetry (DSC) measurements showed that its glass transition temperature (T_g) at the mid-transition was 80 °C and its melting temperature (T_f) 254 °C. Its weight-average molecular weight (M_w), determined by size exclusion chromatography, was 54 600 and its polydispersity index 1.9.

Thin films of approximately 20 μm in thickness, suitable for infrared measurements, were produced by compression molding in a Carver Laboratory Press. PET pellets were grinded as a fine powder and then placed in the press between aluminum plates at 280 °C for 5 min. After compression molding, the sample assembly was quenched in an ice water bath. Under these conditions, the films were found to be amorphous by X-ray diffraction measurements and unoriented by PM-IRLD measurements. The resulting samples were cut into strips of 2.5 cm in length and 0.5 cm in width.

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The samples were stretched using two different mechanical stretchers, constructed in our laboratory,^{16,18} at a constant draw rate between 10 and 95 cm/min, at temperatures between 85 and 100 °C, and at draw ratios of 1.5 or 2.0. Ink marks previously made on the strips were used to determine the draw ratio after stretching. The two stretchers were equipped with ZnSe windows to allow in situ recording of the PM-IRLD and FTIR spectra during the orientation and relaxation periods.

DSC measurements were performed with a Perkin-Elmer DSC-7 apparatus at a heating rate of 10 °C/min. Calibration was performed with indium. The melting enthalpy of completely crystalline PET, used for the determination of the sample crystallinity, was 140 J/g.¹⁹

Polarization modulation infrared spectroscopy measurements (PM-IRLD) were performed on a Bomem Michelson MB-100 spectrometer equipped with a two-channel acquisition system, as described previously.^{13–15,20,21} The spectral resolution was 8 cm⁻¹, the speed of the moving mirror of the interferometer was 1.012 cm/s, and the time constant of the lock-in amplifier was 80 μs. The infrared beam was modulated between parallel and perpendicular directions using a Hinds modulator at a frequency of 100 kHz and detected with a MCT detector.

The procedure to obtain the second moment of the orientation function, $\langle P_2(\cos \theta) \rangle$, from the PM-IRLD spectra is described in detail in previous articles^{13–18} and is summarized, in the case of uniaxial deformations, by the following expression:

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

where ΔA is the dichroic difference, λ 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 angle α has been shown to have a value of 21° for the 1340 cm⁻¹ band.^{22,23} As discussed later in the Results section, the same angle value was used for the 1370 cm⁻¹ band.

The relaxation curves were recorded in three steps: in the first 100 s, spectra were recorded at every 0.4 s, in the second part (10 min) at every 4 s, and in the last part at every 30 s. Unless otherwise indicated, the draw rate used was 10 cm/min. Error bars are not reported for the calculated $\langle P_2(\cos \theta) \rangle$ values because they are very difficult to estimate. As seen in the figures, the scattering of the data points is quite low due to the use of the PM-IRLD technique. In fact, the main source of error is not on the measurements themselves but is due to the repeatability of the measurements. Our experience with the in situ determination of the orientation in thin polymer films has revealed that the repeatability of the measurements using different samples is of the order of 5–10%. We have, however, repeated each experiment several times and made sure that the reported curves are typical of the results obtained.

Unpolarized Fourier transform infrared measurements were performed with a Nicolet Magna 560 spectrophotometer (including the determination of A_0 in eq 1). The spectral resolution was 2 cm⁻¹, and 100 scans were recorded for each spectrum.

Wide-angle X-ray diffraction (WAXD) measurements were made with a Siemens/Bruker diffractometer equipped with a Kristalloflex-760 X-ray generator and a Hi-Star area detector. Scans were made in the transmission mode at 2θ angles between 2.5° and 50°, using Ni-filtered Cu K α radiation of 1.542 Å.

Results

Figure 1 shows an example of PM-IRLD spectra, recorded between 1300 and 1400 cm⁻¹, for a PET sample stretched to $\lambda = 2.0$, at 85 °C, recorded 0, 5, 30, 200, 3000 s, after stretching. Two bands are clearly visible;

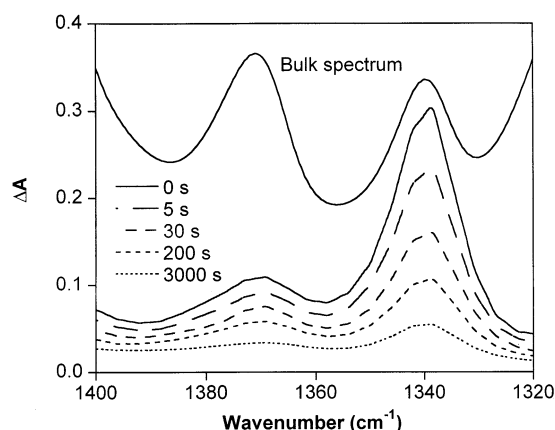


Figure 1. Dichroic difference (ΔA) spectra, between 1300 and 1400 cm⁻¹, of PET stretched to $\lambda = 2.0$ at 85 °C, immediately after stretching (0 s) and after 5, 30, 200, and 3000 s min of relaxation.

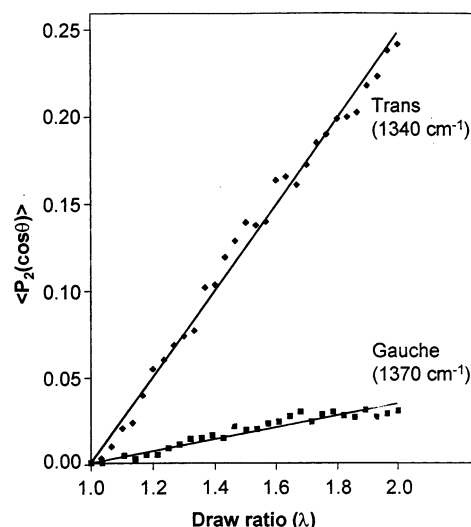


Figure 2. Orientation function of trans and gauche conformers for samples stretched to a draw ratio of 2.0, at 85 °C, at a constant draw rate of 10 cm/min.

the band at 1340 cm⁻¹ is assigned to the wagging mode of the glycol segments in the trans conformation and the band at 1370 cm⁻¹ to the gauche conformers.^{22,23} As seen in this figure, the intensity of the gauche band in the dichroic difference spectrum is much weaker than that of the trans band even though the intensity of the former is stronger in the spectrum of the unoriented sample (at the top of the figure). This result clearly demonstrates that the gauche conformers are much less oriented than the trans conformers. For the two bands, the highest intensity in the PM-IRLD spectra is seen at 0 min, and the intensity decreases with time, indicating the relaxation of orientation. To our knowledge, this is the first time that the relaxation of the gauche conformers of PET is directly measured. The observed ΔA values were then transformed into $\langle P_2(\cos \theta) \rangle$ using eq 1.

Figure 2 shows the orientation function $\langle P_2(\cos \theta) \rangle$ of trans and gauche conformers as a function of the draw ratio during the deformation, for samples stretched to $\lambda = 2.0$, at 85 °C. In both cases, the increase is linear with draw ratio, but the orientation function of the gauche conformers is much smaller than that of the trans conformers. Actually, the ratio between the

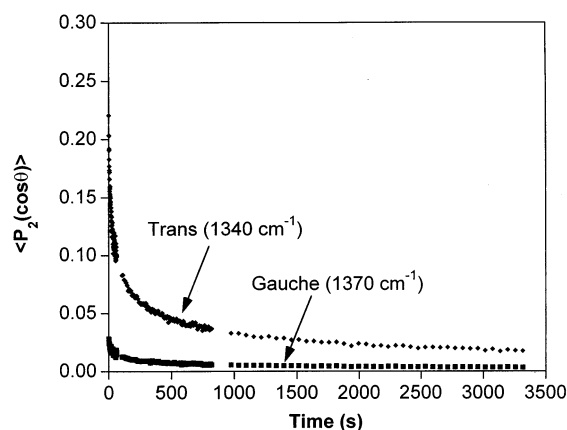


Figure 3. Relaxation of trans and gauche conformers for samples stretched to a draw ratio of 2.0, at 85 °C, at a constant draw rate of 10 cm/min.

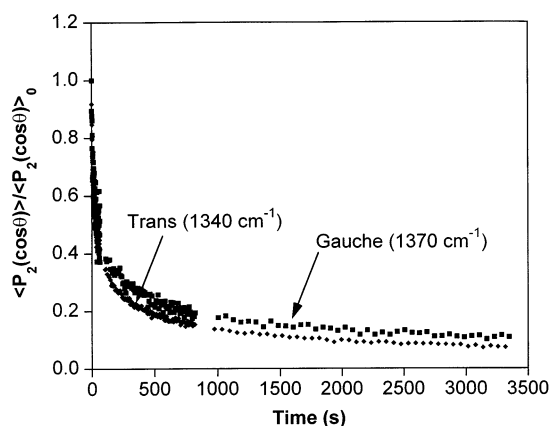


Figure 4. Normalized relaxation curves of trans and gauche conformers for samples stretched to a draw ratio of 2.0, at 85 °C, at a constant draw rate of 10 cm/min.

$\langle P_2(\cos \theta) \rangle$ of the two conformers is about 10, assuming that the angle α used for the gauche conformers is correct.

Indeed, we have assumed that the α angle of the 1370 cm^{-1} band is equal to 21°, but this value has never been determined in the literature. A value of 21° is, however, well established for the 1340 cm^{-1} band.^{22,23} To avoid making this assumption, we could have reported the orientation function of the transition moments, which does not involve an assumption about the angle α . This would have changed very little the curves shown and none of the conclusions, since several of the following figures are reported after normalization (Figures 4 and 5). On the other hand, Figures 2 and 3 would have been slightly modified with a correction factor equal to 1.239 applying both to the 1340 and 1370 cm^{-1} data, therefore not changing the ratio between the two. We feel that Figure 1 indicates clearly that the gauche conformers are much less oriented than the trans conformers. Equal values of $\langle P_2(\cos \theta) \rangle$ for the gauche and trans conformers would require an α angle close the magic angle (54.7°) for the gauche conformer, which is very unlikely.

Similarly, Figure 3 shows the relaxation curves of the trans and gauche conformers as a function of time, for a period of 1 h, for a sample stretched under the same conditions as in Figure 2, where $t = 0$ corresponds to the end of the stretching. In both cases, there is an exponential decrease of $\langle P_2(\cos \theta) \rangle$ with time, but the

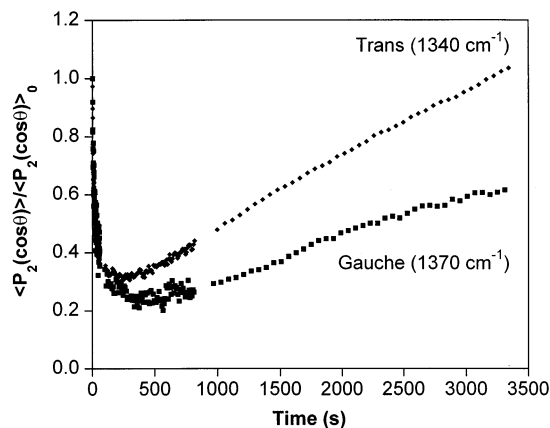


Figure 5. Normalized relaxation curves of trans and gauche conformers for samples stretched to a draw ratio of 2.0, at 100 °C, at a constant draw rate of 10 cm/min.

orientation function does not reach zero in the time period covered, as had already been observed for pure polystyrene^{16,17,24} (PS) and for poly(phenylene oxide)¹⁷ and poly(vinyl methyl ether)¹⁸ in blends with PS. The relaxation of the two conformers is different mainly because the orientation of the trans conformers is much higher than the orientation of the gauche conformers, which makes the comparison difficult. However, if the two curves are normalized relative to the maximum value of the orientation function, obtained at time zero, the relaxation of the two conformers is similar (but not exactly the same), as shown in Figure 4.

At higher temperatures, larger differences are observed in the relaxation curves of the trans and gauche conformers. For example, Figure 5 shows the normalized relaxation curves as a function of time for a sample stretched to $\lambda = 2.0$ at 100 °C. This temperature is 20 °C above T_g and 25 °C below the crystallization temperature determined (in the nonoriented state) by DSC measurements upon scanning at 10°/min. Under these conditions, the orientation function initially decreases and, subsequently, increases. This reorientation phenomenon is observed for both conformers, but it is more pronounced for the trans conformers, to the point where the final $\langle P_2(\cos \theta) \rangle$ values at 3500 s are larger than the initial values at $t = 0$ s. This phenomenon has also been observed for samples stretched at $\lambda = 1.5$ and 100 °C, but it then occurs at later times²⁵ than in Figure 5. DSC results indicate that, in contrast to the initial nonoriented samples and samples stretched at 85 °C (Figure 4), those stretched at 100 °C are semicrystalline. The estimated degree of crystallinity is 10%, but an accurate measurement can hardly be made since additional crystallization occurs during the DSC scan.

WAXD measurements were also performed to confirm that the increase in $\langle P_2(\cos \theta) \rangle$ observed in Figure 5 is really related to the presence of crystallinity. Figure 6 shows WAXD curves of PET samples stretched to $\lambda = 2.0$ at 85 and 100 °C. Crystalline peaks show up on the curve obtained at 100 °C, although of low intensity as compared to the amorphous halo, while at 85 °C, the diffraction curve is clearly amorphous. These results demonstrate the occurrence of crystallization after stretching at high temperatures, i.e., 100 °C.

Upon crystallization of PET in the above-mentioned conditions, there are important changes in the trans/gauche ratio, as demonstrated by the infrared spectra recorded during the heating and cooling processes. Figure 7 shows the intensity ratio of the 1340 and 1370

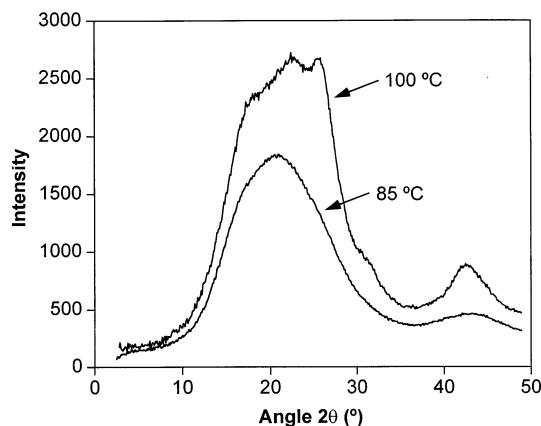


Figure 6. WAXD curves of PET after stretching to $\lambda = 2.0$, relaxation for 1 h at 85 °C and 100 °C, and quenching to room temperature.

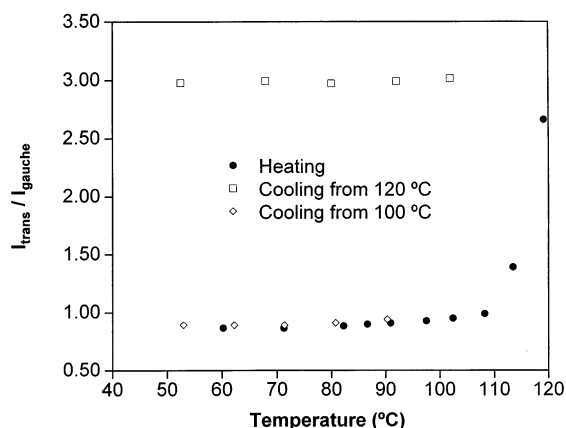


Figure 7. Intensity ratio of the 1340 cm^{-1} (trans)/1370 cm^{-1} (gauche) infrared bands during the heating of an unoriented sample (full circles), and its subsequent cooling after reaching 100 °C (empty diamonds) and 120 °C (empty squares). This series of measurements was done using FTIR spectroscopy (and not PM-IRLD).

cm^{-1} infrared bands ($I_{\text{trans}}/I_{\text{gauche}}$) upon heating an unoriented sample from 25 to 100 °C, and from 50 to 120 °C, and upon subsequent cooling. For these measurements, the samples were kept at each of the temperatures indicated by the data points during 15 min. It can be seen in Figure 7 that, above T_g , i.e., above 80 °C, the ratio of trans/gauche bands slightly increases upon heating, but it is reversible (empty diamonds) upon cooling, which indicates that the increase may stem from a change in absorbance coefficient and/or in trans/gauche conformer populations upon heating. However, at 120 °C, the ratio of trans/gauche bands increases substantially and never decreases back to its original value after cooling (empty squares). Changes in absorbance coefficients and in trans/gauche populations cannot explain this behavior. The irreversibility is, however, consistent with the occurrence of crystallization.

Similarly, Figure 8 shows the intensity ratio of the 1340 and 1370 cm^{-1} infrared bands upon heating the PET sample (left-hand side), immediately after stretching (vertical line), and during the relaxation period at 85, 90, and 100 °C (right-hand side). At each temperature, the intensity ratio slightly increases upon heating and decreases slightly after the stretching due to the elastic driving force that leads the extended chain (trans) to recover its initial coiled shape (gauche). At 85 and 90 °C, the intensity ratio remains constant

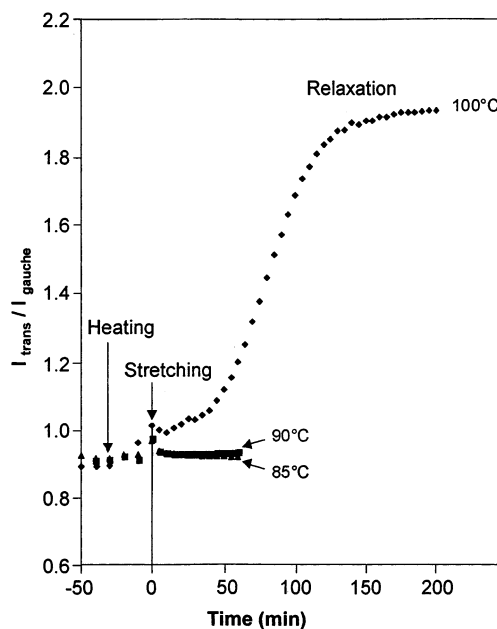


Figure 8. Intensity ratio of the 1340 cm^{-1} (trans)/1370 cm^{-1} (gauche) infrared bands during heating and subsequent relaxation at 85, 90, and 100 °C. The time "0 min" corresponds to the time where the stretching to $\lambda = 2.0$ stops. This series of measurements was done using FTIR spectroscopy (and not PM-IRLD).

during the relaxation process. On the contrary, at 100 °C, the intensity ratio increases 2-fold during the relaxation and becomes constant only after 150 min. These results are in good agreement with the above observation of PET crystallization at 100 °C, leading to an increase in the orientation function.

Discussion

In this study, the molecular relaxation of PET was followed in real time by polarization modulation infrared spectroscopy. It has been possible to distinguish between conditions where the polymer remains amorphous, at lower temperatures, and where it crystallizes, at 95 °C or higher, although the level of crystallinity was of the order of 10% only (at 100 °C) under the conditions used. Our measurements are in general agreement with those reported by Mahendrasingam et al.,^{4,5} since at $\lambda = 1.5$ and 2.0 and for a draw rate of 10 cm/min, no trace of crystallization could be detected by DSC, WAXD, or from the shape of the infrared relaxation curves at 93 °C or below (Figure 4).²⁵ However, the increase of the orientation with time at 95²⁵ and 100 °C (Figure 5), under the same conditions of stretching, is associated with the presence of some crystallinity. These measurements also suggest, again in agreement with Mahendrasingam et al.,^{4,5} that the crystallization begins after the completion of the deformation. There is no doubt that crystallization during drawing would be possible if the draw rate was reduced sufficiently to allow enough time for chain mobility.^{6,7}

Because of the sensitivity of the PM-IRLD measurements, the molecular relaxation curves of the gauche segments of PET have been recorded for the first time. It was found that the trans segments orient more than the gauche segments (Figure 2), but when the two relaxation curves are normalized to the maximum orientation, their relaxation rates are quite similar (Figure 4). At higher temperatures, where crystalliza-

tion occurs, larger differences are observed between the relaxation curves of the trans and gauche conformers (Figure 5). In both cases, there is an increase in the orientation function $\langle P_2(\cos \theta) \rangle$, driven by the crystallization, and this reorientation of the trans conformers is more important than that of the gauche conformers. The important reorientation of the gauche conformers is surprising because the only known crystal structure of PET includes trans conformers only.^{3,26} Furthermore, in FTIR spectroscopy, it was shown that the relative proportion of trans segments increases during relaxation.

These results suggest that, at high temperatures, the oriented trans conformers, or the general chain alignment, triggers crystallization, even if the degree of orientation is rather small, which in turn induces an increase in orientation of both the crystalline and amorphous parts of the sample, including the gauche conformers. The same general behavior has been seen by Zhao et al.²⁷ for the crystallization of polycaprolactone (PCL) in poly(vinyl chloride) (PVC) or poly(styrene-co-methacrylic acid) (SMA) matrices where a modest amount of orientation of PVC or SMA induces a very high orientation of PCL. Possible explanations for this behavior can be suggested. Either the crystallites that have already formed continue to grow during relaxation, inducing additional orientation in the neighboring amorphous interphase, or new crystallites form from amorphous material with a high orientation.⁶ Heffelfinger and Schmidt²⁸ have postulated that crystallization of PET occurs by one of the two following mechanisms: transformation of oriented gauche conformers into crystalline trans conformers or conversion of amorphous trans conformers into crystalline trans conformers. The FTIR results obtained in this work show that the conversion of gauche to trans conformers continues during the relaxation stage, which would indicate a major contribution from the former process. In that context, does the crystallization coincide with the increase in orientation of the trans segments? Radhakrishnan and Kaito²⁹ have suggested a three-stage process for the crystallization of PET, including (1) chain relaxation above T_g , (2) self-organization of the oriented amorphous structure in which the degree of orientation increases with time, along with a gauche to trans transformation, and (3) crystallization as such with the observation of WAXD peaks. Our measurements cannot confirm such a process, but they are certainly not in disagreement with this hypothesis.

In our previous work,¹² the same relaxation behavior has been observed using birefringence and PM-IRLD data for measurements made with exactly the same PET sample (which require the use of the 3336 cm^{-1} band because infrared measurements of thick samples with the 1340 cm^{-1} band are impossible).³⁰ In comparison, the shape of the relaxation curves obtained here by PM-IRLD is slightly different, even if the same stretcher was used, and measurements were made under the same conditions.

The main reason for this discrepancy is that the thermal history of the two PET samples is different. The thin films used in this work, which are required to suit the infrared measurements, were obtained by pressing the pellets at high temperatures, which induces some degradation. Actually, when a Goodfellow PET film (used in ref 12) of 350 μm thickness is pressed at high temperatures, its relaxation curve sets close to those

shown here. However, the average values of orientation function obtained by birefringence are always lower than those obtained from the 1340 cm^{-1} band by PM-IRLD, as expected, because the birefringence technique probes all chain segments in the sample whereas the 1340 cm^{-1} band probes only the trans segments. Even if the average sample orientation (as measured by birefringence) is low, a fraction of the chains with trans conformers may become highly oriented. Such a behavior was demonstrated in several studies,^{2,3} where it was shown that the fraction of trans segments increases and the fraction of gauche segments decreases by 8. It was also shown that the crystalline phase, composed only of trans segments, is much more oriented than the amorphous phase, principally composed of gauche segments. The chains in trans conformation can then act as crystal nuclei and contribute to the formation of stable crystals, causing $\langle P_2(\cos \theta) \rangle$ values of the trans segments to be higher than those of gauche segments.

In cases where no crystallization of PET occurs, the relaxation curves can be analyzed in a similar manner as previously done for polystyrene (PS),^{16,24} for PS/PPO blends,¹⁷ or for PS/PVME blends.¹⁸ It was assumed that the relaxation occurs in sequential steps as suggested by the Doi–Edwards theory.³¹ The basic model involves three interlinked mechanisms occurring over different time scale regimes. As a result of macroscopic deformation, the tubes whose topography is defined by entanglements are correspondingly deformed. The fastest relaxation motion, characterized by a relaxation time τ_a , involves the Rouse modes between two entanglements. These motions operate on a time scale in which the entanglements can be considered as fixed and enable the chain strands between the “fixed” entanglements to move toward equilibrium configurations. The second relaxation, characterized by τ_b , is enabled by the Rouse motions and involves a retraction of chains within the deformed tube in order to recover their equilibrium curvilinear lengths. This process results in a change in the length of strands between entanglements and, hence, a change in the effective Kuhn lengths. The third stage, characterized by τ_c , involves the reptation of the chains out of their original deformed tubes to form new undeformed tubes and results in chains attaining isotropic configurations. As done previously, attempts were made to fit the relaxation curves with the smallest possible number of exponential functions. It was found that a sum of three exponential functions is optimal (a sum of two exponential functions or a stretched exponential function were tried and found unsatisfactory¹⁶):

$$P_2(t) = \sum_{i=1}^n A_i \exp(-t/\tau_i) \quad (2)$$

where A_i is a weight factor, t is the time, and τ_i the relaxation time of the i th process. The fit was optimized with the Excel software. From this equation, three relaxation times were obtained for each curve.

The relaxation times thus calculated are summarized in Table 1 at four different temperatures, for samples stretched to $\lambda = 1.5$. In all cases, the first relaxation time τ_1 is of the order of 7 s, the second one τ_2 of the order of 100 s, and the third one τ_3 of the order of 2500 s. Each of them decreases with increasing temperature, in agreement with the chain mobility theory. In the context of the Doi–Edwards theory, τ_1 can be associated with the Rouse equilibrium relaxation time and τ_3 to

Table 1. Relaxation Times for PET Films Stretched to a Draw Ratio of 1.5, at a Constant Draw Rate of 10 cm/min

temp (°C)	relaxation time (s)		
	τ_1	τ_2	τ_3
85	8	130	2800
88	8	110	2300
90	7	100	2200
93	5	70	2100

the retraction time. The reptation time is not seen in our experiments since we stopped the measurements after 1 h; reptation times for polymers of this molecular weight and at a temperature of 85 °C would be of the order of several thousand seconds. The interpretation of the second relaxation time τ_2 remains unclear at this moment.^{16,17}

In the above analyses and experiments, it is assumed that the sample is stretched instantly and that there is no relaxation during the orientation; this cannot be entirely true with a stretching rate of 10 cm/s. In a previous article, Messé and Prud'homme¹⁷ approached this experimental condition by stretching uniaxially PS at a rate of 1800 cm/min. However, it is impossible to stretch PET at this rate because it crystallizes upon drawing when stretched above 95 cm/min.³² The linear behavior seen in Figure 2 suggests, however, that the amount of relaxation occurring during the orientation is minimal as compared to the relaxation curves that follow (Figures 3–5).

Conclusion

In practice, molecular relaxation always occurs during polymer processing, but it has been difficult to measure the details of the phenomenon. Nonetheless, it is important to be able to follow the polymer relaxation not only in terms of overall orientation but also in terms of the orientation of specific chain segments. Using the PM-IRLD technique, the relaxation of gauche and trans conformers of PET was followed in this study as a function of time, at temperatures between 85 and 100 °C. These measurements indicate (1) that the relaxation generally reduces the polymer orientation to a small fraction of its initial value, (2) that the orientation functions of the gauche and trans conformers are very different, and (3) that the rate of relaxation of the gauche and trans conformers is similar. For the first time, the relaxation of the gauche conformers of PET was measured along with that of the trans conformers. The relaxation behavior of these two conformers is very different in amorphous and crystallized samples. In the first case, the relaxation curves decrease exponentially at a similar rate. In the second case, there is an initial decrease, followed by an increase in orientation related to crystallization during relaxation, which is much more important for the trans than for the gauche conformers. However, surprisingly, the gauche conformers follow the same reorientation trend as the trans conformers.

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