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Deformation and Relaxation of Polymers Studied by Ultrarapid Scanning FT-IR Spectrometry

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ABSTRACT: A recently developed ultrarapid scanning Fourier transform infrared (URS-FTIR) spectrometer has been used to study the irreversible deformation of polymer films with a millisecond time resolution for the first time. The evolution of molecular orientation as a function of draw ratio and relaxation time was studied for films of amorphous poly(ethylene terephthalate) (PET) stretched above its glass transition temperature (T_g). Very good agreement was obtained between the results obtained by URS-FTIR and polarization modulation infrared linear dichroism (PM-IRLD) spectrometry. Reversible gauche-to-trans conversions were observed, indicating that the PET chains remain amorphous. The orientation and relaxation of polystyrene (PS) in films of pure PS and of blends of PS with poly(vinyl methyl ether) (PVME) were also studied above T_g . A method allowing the determination of the orientation function of PS using a single p-polarized spectrum is described. Results reveal a significant decrease in PS orientation during the first second following the end of deformation, emphasizing the importance of the experimental time resolution in the characterization of the relaxation behavior of polymers.

Introduction

Molecular orientation has a large impact on several properties of polymers and polymer blends, such as their modulus and gas permeability. For over three decades, efforts have been deployed to improve our understanding of the development of orientation during irreversible macroscopic and reversible microscopic deformations of polymers.¹ Several experimental techniques have been used to characterize the static orientation in samples quenched below their glass transition temperature (T_g) or in situ during slow deformations. Recently, interest has shifted toward the time-resolved determination of orientation during rapid deformation and to the direct determination of the relaxation kinetics following stretching.

Wide-angle X-ray diffraction (XRD) has recently been used to study the rapid deformation of poly(ethylene terephthalate) (PET) with a time resolution of 40–900 ms, but such an experiment requires a Synchrotron source.^{2–5} A simple dynamic birefringence setup has been used to follow deformation and relaxation kinetics in PET⁶ and polystyrene (PS)⁷ with a time resolution of 1 ms, but the technique suffers from a lack of selectivity since it only provides an averaged value of the orientation function, $\langle P_2(\cos \theta) \rangle$. In contrast, infrared linear dichroism (IRLD) can often discriminate between the orientation of the amorphous and crystalline phases in semicrystalline polymers and of the different species in multicomponent systems such as polymer blends or copolymers.^{1,8,9}

Several techniques have been developed to improve the time resolution of IRLD, which is usually of the

order of several seconds with the conventional rapid-scan approach. By using a step-scanning interferometer, time-resolved dynamic IRLD has allowed the study of the small-amplitude cyclic deformation of polymers with a time resolution of 1 ms.¹⁰ However, this technique is not useful for the study of the irreversible macroscopic deformation of polymers since a repeatable stimulus must be applied to the sample at each step of the moving mirror in order to record a complete scan. Polarization modulation IRLD (PM-IRLD), which makes use of a photoelastic modulator to switch the polarization plane of the infrared radiation from parallel (p) to perpendicular (s) at a high frequency, allows direct measurement of dichroic difference spectra in 400 ms.^{8,11} It was used to follow directly irreversible deformation and relaxation kinetics for films of PET,^{12,13} of PS,⁷ and of blends of PS with poly(vinyl methyl ether) (PVME)^{14,15} and with poly(phenylene oxide) (PPO).¹⁶

For conventional FT-IR spectrometers, the optical path difference is introduced by a moving optical element that travels with a reciprocating motion. The force required to retard the optical element and accelerate it in the reverse direction means that spectral data with a resolution of better than 8 cm⁻¹ cannot be measured at a rate of much more than 20 interferograms per second. The typical duty cycle efficiency of conventional FT-IR spectrometers operating at their highest scan speed is less than 20% and is usually much lower. Recently, Griffiths and co-workers have developed an ultrarapid scanning FT-IR (URS-FTIR) spectrometer that allows the measurement of infrared spectra in 5 ms.^{17,18} The optical path difference in this instrument is generated by a rotating wedged mirror, allowing operation at a duty cycle efficiency of approximately 70% at any angular velocity. As a result, spectra with a resolution of 6 cm⁻¹ can be generated at intervals of 5 ms. In fact, a time resolution of 1 ms would be possible, with no loss of duty cycle efficiency, if an analog-to-

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digital converter with a high enough data rate and dynamic range were commercially available. URS-FTIR spectrometry has been used to study the spark-initiated combustion of methane and ethane in air with a time resolution of about 12 ms.¹⁷

The aim of the current work is to evaluate the capability of URS-FTIR spectrometry to perform real-time orientation measurements during the irreversible macroscopic deformation of polymers and polymer blends and to follow the early part of their relaxation kinetics with a time resolution of the order of 20 ms. Films of three different systems have been studied: PET, PS, and a 70/30 PS/PVME miscible blend. Orientation results obtained by URS-FTIR and PM-IRLD were compared in order to validate the URS-FTIR measurements.

Experimental Section

Films of PET of 7 μm thickness were prepared by blow molding and were generously offered by Dr. K. C. Cole of the National Research Council of Canada. Monodisperse atactic polystyrene (Pressure Chemical) with $M_w = 942$ kg/mol and poly(vinyl methyl ether) (Polymer Scientific Products) with $M_w = 59$ kg/mol were used to prepare self-supported films of PS and of PS/PVME blends containing 70% w/w PS. They were cast on glass plates from 3% benzene solutions, air-dried at room temperature for 2 days, and then gradually heated under vacuum up to 80 °C for 48 h in order to remove the last traces of solvent and any residual stress. T_g of PET, PS, and PS/PVME blends were 78, 105, and 43 °C, respectively, as determined by differential scanning calorimetry using a Perkin-Elmer DSC-7 calorimeter at a scanning rate of 10 K/min.

All deformations were made using a custom-built mechanical stretcher fitted with ZnSe windows to allow the in situ recording of infrared spectra during the orientation and relaxation periods. The temperature was adjusted (± 0.1 °C) using an Omega temperature controller (CN 7600) and heating cartridges. Films were cut into 20 mm long and 6 mm wide strips and marked with ink lines to verify the draw ratio. Pyrotape (Aremco Products #546) was used to avoid the slippage of the films during the elongation. PET films were stretched at 90 °C and at a constant draw rate of 3.162 cm/s to a draw ratio of 1.5, while PS and PS/PVME films were stretched at 120 and 58 °C ($T_g + 15$ °C), respectively, and at a constant draw rate of 1.582 cm/s to a draw ratio of 2.

URS-FTIR spectra were measured using the spectrometer designed by Manning Applied Technology (Troy, ID).^{17,18} The radiation emerging from the interferometer was focused on the sample in the stretcher via a KRS-5 wire-grid polarizer. The output radiation was collected and detected using a liquid nitrogen-cooled photovoltaic mercury cadmium telluride (MCT) detector (Kolmar Technologies, Newburyport, MA). A four-channel 14-bit 4 MHz ADC was used to digitize the two signals coming from the infrared detector (low-gain amplification for the centerburst of the interferogram and high-gain amplification for the wings) and the signal from the laser photodiode at constant time intervals. Single-beam spectra were recovered from the output signal using a custom-built MatLab (MathWorks Inc., Natick, MA) program. Rotating speeds of the mirror and acquisition rate of the ADC were adjusted to acquire spectra in either 5 or 10 ms. For the PET experiments, the orientation function was calculated as¹

$$\langle P_2(\cos \theta) \rangle = \frac{2}{3 \cos^2 \alpha - 1} \frac{R - 1}{R + 2} \quad (1)$$

where $R = A_p/A_s$ is the dichroic ratio and α is the average angle between the transition moment of the vibration considered and the main-chain axis. For PS and PS/PVME experiments, the orientation function was calculated using a calibration curve as described in the Results and Discussion section.

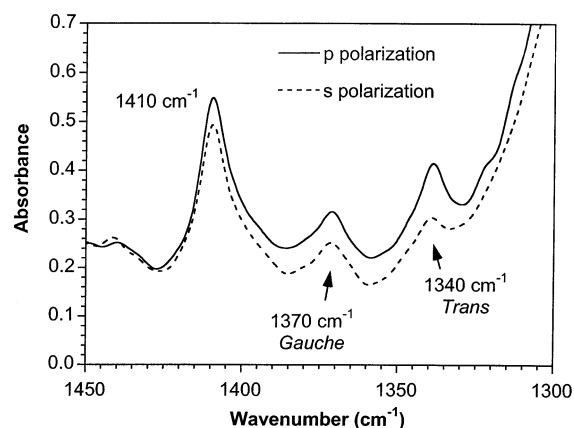


Figure 1. P- and s-polarized infrared spectra of PET recorded at the end of the deformation, at 90 °C, with a 10 ms acquisition time.

PM-IRLD difference spectra with a resolution of 8 cm^{-1} were obtained with a conventional FT-IR spectrometer (Michelson MB-100, ABB Bomem, Québec, PQ, Canada) using the optical setup and the two-channel electronic device previously described.¹⁹ A ZnSe photoelastic modulator (Hinds PEM-90 type II/ZS50, Hillsboro, OR) operating at 50 kHz, a lock-in amplifier (EG&G Princeton Applied Research, model 7260 DSP, Princeton, NJ) with a 40 μs time constant, two dual-channel electronic filters (Stanford Research Systems, model SR650, Sunnyvale, CA) and either a photoconductive or a photovoltaic MCT detector (Belov Technologies, New Brunswick, NJ, and Kolmar Technologies, respectively) were used to generate the double modulation and to isolate the experimental signals. For each deformation, 180 spectra of either one or four scans were recorded. The orientation function, $\langle P_2(\cos \theta) \rangle$, was calculated from the intensity of the dichroic difference ΔA as¹⁹

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

where λ is the draw ratio and A_0 the absorbance of the unstretched isotropic sample. This equation assumes incompressibility of the film during deformation. The A_0 values and conventional IRLD spectra were obtained using a Nicolet (Madison, WI) Magna 550 FT-IR spectrometer at a 4 cm^{-1} resolution.

Results and Discussion

Deformation of PET Films. Poly(ethylene terephthalate) can be prepared in either amorphous or semi-crystalline states, depending on its thermomechanical history. About 10–25% of the glycol groups of PET adopt a trans conformation in the amorphous state, while the crystalline phase is almost purely composed of trans conformers.^{20–22} Numerous studies have shown that the orientation of the trans conformers for an initially amorphous sample increases significantly during deformation above T_g , while the gauche conformers remain almost isotropic.^{3,4,21–24} The relative population of trans conformers first increases slightly with draw ratio and then more abruptly at draw ratios larger than about 2.5, for which stress-induced crystallization can occur.

In a first series of measurements, thin amorphous PET films were deformed at 90 °C, i.e., 12 °C above T_g , to a draw ratio of 1.5 at a nominal stretching rate of 3.162 cm/s. Considering the acceleration and deceleration necessary to reach this speed, the deformation time was 530 ms. Figure 1 shows the p- and s-polarized URS-FTIR spectra of two PET samples recorded at the end

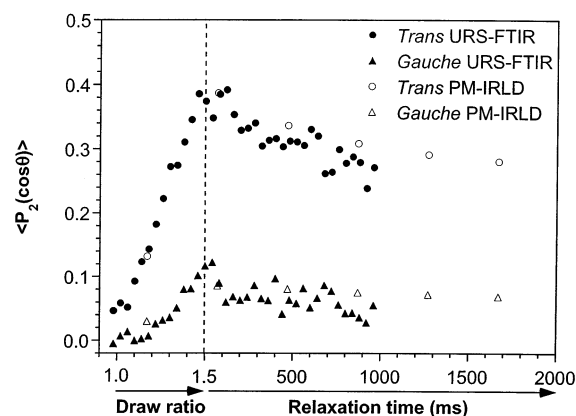


Figure 2. Orientation function of gauche (1370 cm^{-1}) and trans (1340 cm^{-1}) conformers of PET during and after deformation at 90°C , as determined from URS-FTIR and PM-IRLD measurements.

of the deformation, with an acquisition time of 10 ms. The bands observed at 1340 and 1370 cm^{-1} are assigned to the CH_2 wagging vibrations of the glycol group in trans and gauche conformations, respectively, while the 1410 cm^{-1} band has been assigned to the in-plane deformation of the phenyl ring.²² The weak shoulders appearing around 1322 , 1350 , 1380 , and 1397 cm^{-1} are due to imperfect background correction, most likely due to the presence of water vapor bands, and have no systematic effect on the measurement of the dichroic ratios. Significant differences can be observed between the two polarized spectra, especially for the 1340 cm^{-1} trans band, which is more intense in the p than in the s spectrum. A positive dichroism was expected for this band in the oriented sample since an α angle of 21° between its transition moment and the main-chain axis has been reported.²⁵ A weaker parallel dichroism can also be observed for the two other bands.

The 1410 cm^{-1} band has often been used as an internal thickness standard for deformation studies of PET because it was considered to be insensitive to orientation and conformation.^{21,24} However, it has recently been shown that the position of this band is slightly conformation dependent and that it exhibits a small positive dichroism in highly oriented samples.²² The results obtained here also point toward a positive dichroism for the 1410 cm^{-1} band, which could make its use as a thickness standard hazardous. Fortunately, the blow-molding process used to produce the PET samples yielded a film with a fairly constant thickness of $7\text{ }\mu\text{m}$, the standard deviation of the absorbance of any given infrared band before deformation being about 2% of its average. This sample-to-sample reproducibility allowed the direct comparison of films that were stretched with the radiation polarized p and s, without the requirement of using an internal reference band. The orientation functions for the 1340 and 1370 cm^{-1} bands were calculated using the dichroic ratios obtained from the URS-FTIR spectra and eq 1, assuming an α angle of 21° for both bands. Data points were obtained by averaging four consecutive 10 ms spectra in order to reduce scattering. Similarly, orientation functions were calculated using eq 2 from PM-IRLD dichroic difference spectra with a time resolution of 400 ms.

Figure 2 shows the evolution of $\langle P_2(\cos \theta) \rangle$ for the 1340 and 1370 cm^{-1} bands as a function of draw ratio during the deformation and as a function of time during the

relaxation period. An almost quantitative agreement is found between the URS-FTIR and PM-IRLD spectra for both types of conformers, which validates the ultrafast infrared measurements nicely. It can be observed in Figure 2 that trans conformers possess a small orientation before deformation, while gauche conformers are isotropic at first. This initial orientation is due to the blowing process; it was also observed by conventional IRLD. The orientation of both trans and gauche conformers increases more or less linearly as a function of draw ratio, after a small time delay that is due to the initial acceleration of the stretcher. As expected from Figure 1, the orientation developed by the trans conformers is much larger than that of gauche conformers, reaching a maximum $\langle P_2(\cos \theta) \rangle$ value of 0.38 as compared to 0.12 for the gauche conformers. This is in general agreement with the results obtained by Duchesne et al., who have recently been able to quantify the orientation and relaxation of the gauche conformers using PM-IRLD.¹²

A significant relaxation of orientation occurring in the first second following deformation can be observed in Figure 2, explaining at least in part why conventional IRLD experiments usually failed to provide a significant orientation for the poorly ordered gauche conformers. Long-time relaxation measurements by PM-IRLD show that the relaxation kinetics observed using the 1340 and 1370 cm^{-1} bands are rather similar. The orientation function of the 1410 cm^{-1} band is not reported here because no estimate of its α angle was found in the literature. However, a weak but significant positive dichroic difference peak appears for this band in the PM-IRLD spectra (not shown), and its intensity varies as a function of relaxation time in a way similar to the other bands studied.

Although the use of URS-FTIR spectrometry for the measurement of orientation in deformed polymer films is essentially an application of conventional IRLD, its speed allows measurements for which IRLD is unsuccessful because almost no relaxation of orientation occurs during the real-time data acquisition. In its current state of development, URS-FTIR experiments are limited to a total acquisition time of about 1.5 s, while PM-IRLD gives access to a much longer time range for the relaxation studies. Nevertheless, URS-FTIR spectrometry provides a greatly enhanced time resolution for measurements during the deformation and the early part of the relaxation, in this case a 10-fold increase as compared to PM-IRLD, which makes the two techniques complementary for studies of the time-resolved deformation and relaxation of polymers.

Another potential application of URS-FTIR spectrometry is the measurement of band shifts, conformational changes, etc., with millisecond time resolution. In the case of PET, it is well-known that gauche-to-trans conversion occurs when crystallization takes place,^{3,4,12,21–24} but the conformational rearrangements during deformation of amorphous PET are not as well documented, especially in the millisecond time scale. Figure 3A shows the evolution of the absorbance of the 1340 and 1370 cm^{-1} bands with p and s polarizations as a function of draw ratio and relaxation time, while Figure 3B shows the trans-to-gauche (T/G) intensity ratio calculated for both polarizations. To eliminate the thinning effect due to stretching, all band intensities were corrected by a factor $\lambda^{1/2}$, where λ is the draw ratio. Correction using the 1410 cm^{-1} band was avoided

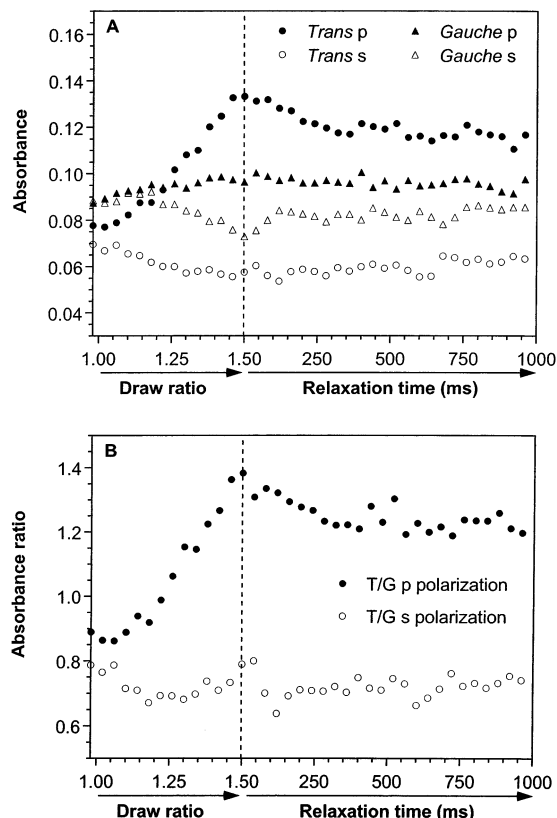


Figure 3. Evolution of (A) the absorbance bands due to the gauche (1370 cm^{-1}) and trans (1340 cm^{-1}) conformers with p and s polarization and (B) the trans-to-gauche (T/G) intensity ratios with p and s polarization, during and after deformation of PET at 90°C .

because of its slight dichroism, although both methods yield very similar results.

As expected from the results of Figure 2, the difference between p and s absorbances (A_p and A_s , respectively) increases during deformation and decreases during relaxation, and the amplitude of the change is much larger for trans than for gauche conformers, as this difference is directly proportional to orientation. A_p for the trans conformers increases by more than 70% during deformation while A_s decreases by only 20%, indicating that the large orientation functions observed in Figure 2 originate not only from the reorientation of disordered trans conformers but also from the conversion of gauche conformers into oriented trans conformers. This conversion is quite apparent when the evolution of the T/G ratio with p polarization is observed in Figure 3B, the proportion of trans conformers strongly increasing during deformation. A significant decrease in T/G ratio occurs during the first second of relaxation, indicating that the conformation rearrangement is reversible. In contrast, this conversion would be irreversible if strain-induced crystallization would occur because most of the trans conformers would then be included in the stable crystalline structure. The fact that the T/G ratio remains almost constant with s polarization could be indicative of a similar tendency for both gauche and trans conformers to orient when stress is applied to the sample.

The variations in T/G ratio reported in previous publications for a similar draw ratio were much smaller than those observed here with p polarization.^{4,12,21,23} This is explained in part by the fact that these mea-

surements were performed with unpolarized light, but it is most probably due to the significant reconversion of trans conformers back into disordered gauche conformers during the relatively long acquisition time necessary to measure the infrared spectrum. The URS-FTIR measurements thus indicate that the trans-to-gauche conversion is more important than expected when amorphous PET is deformed to small draw ratios.

In contrast to the observations for trans conformers, the results shown in Figure 3A indicate that the positive $\langle P_2(\cos \theta) \rangle$ values observed in Figure 2 for the gauche band at 1370 cm^{-1} originate from a decrease in A_s rather than from an increase in A_p . This could either mean that (1) initially disordered gauche conformers first orient but then rapidly convert into oriented trans conformers or (2) they directly convert into oriented trans conformers upon application of stress. The rapid increase in A_s for the gauche conformers observed in the earliest part of the relaxation period in Figure 3A, which is associated with a rapid decrease in A_p for the trans conformers, could suggest that a direct conversion from oriented trans to disordered gauche conformers takes place, but one should be careful not to overinterpret the rather scattered data.

Deformation of PS and PS/PVME Films. In a second example of the application of URS-FTIR spectrometry to the real-time determination of orientation in polymers, the deformation of films of polystyrene and of a miscible blend of PS with poly(vinyl methyl ether) (PS/PVME) was investigated. The orientation in this system has been studied by conventional IRLD by several groups^{26–28} and more recently by PM-IRLD.^{14,15} In contrast with PET, these samples were prepared by solution casting, yielding less homogeneous films. Furthermore, no internal reference band provides a means to correct for thickness differences between the films that are used to acquire the p and s series of spectra. It is nevertheless possible to follow the orientation of PS using a single polarized measurement by correlating the ratio of two bands possessing a vibrational dipole moment pointing in orthogonal directions with the orientation function of one of these bands. In the case of PS, no pair of completely orthogonal vibrational bands of appropriate intensity was present in the spectra, but the 1028 and 906 cm^{-1} bands (among others) can still be used for that purpose. They are assigned to the ν_{18a} in-plane and ν_{17b} out-of-plane vibrations of the phenyl ring and their reported α angles are 90° and 35° , respectively.²⁹

Figure 4 shows the conventional p-polarized infrared spectra of samples possessing an orientation function ranging from 0.00 to 0.26, as determined by conventional IRLD using the 1028 cm^{-1} band. The intensity of the spectra in Figure 4 was normalized with reference to the 1028 cm^{-1} band to highlight the absorbance variation of the 906 cm^{-1} band, which increases in intensity with orientation because its transition moment orients along the stretching direction. It is important to stress here that the normalization of the spectra in Figure 4 was performed only to emphasize the spectral changes and that unnormalized spectra were used in the calibration procedure described below, which is based on the absorbance ratio of two bands with orthogonal transition moments. For each spectrum, a corrected absorbance ratio, A_R , was determined as the difference between the absorbance ratio of the 906 and 1028 cm^{-1} bands (A_{906}/A_{1028}) in the oriented sample and

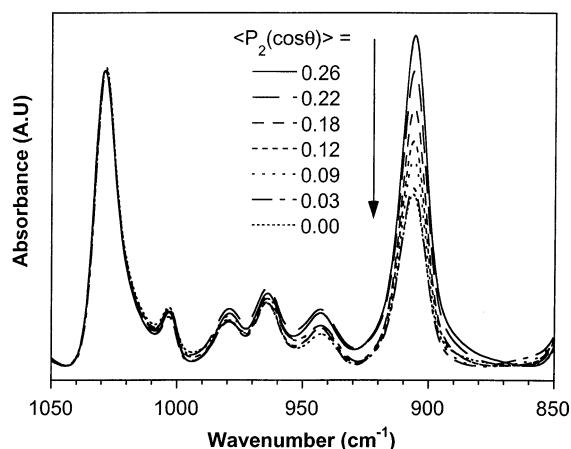


Figure 4. P-polarized conventional infrared spectra of PS for samples of different degrees of orientation. All spectra were normalized with respect to the absorbance of the 1028 cm^{-1} band.

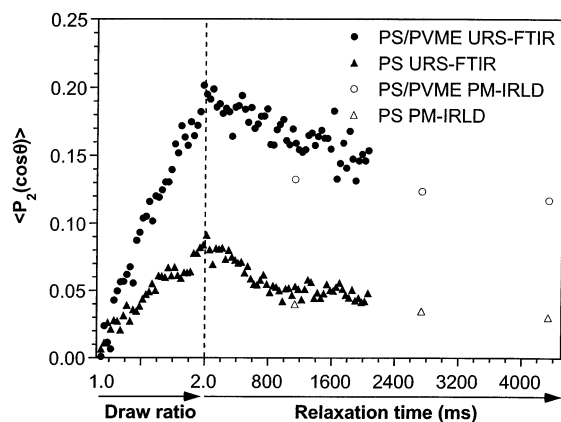


Figure 5. Orientation function of PS in films of pure PS and of a 70/30 PS/PVME blend, during and after a deformation at $T_g + 15\text{ }^\circ\text{C}$, as determined from URS-FTIR and PM-IRLD measurements.

that in the isotropic sample. Equation 3a shows the relation between $\langle P_2(\cos \theta) \rangle$ and A_R that was used to calculate orientation functions from a single p-polarized spectrum in the URS-FTIR measurements. Similarly, it is possible to follow the orientation of PS in the PS/PVME blend using the same band ratio with a slightly different calibration curve given by eq 3b. The correlation coefficients of the calibration curves for pure PS and for PS in the blend were 0.987 and 0.974, respectively. The orientation of PVME could not be followed because no orthogonal PVME bands are sufficiently isolated in the spectrum of the blend.

$$\text{pure PS: } \langle P_2(\cos \theta) \rangle_{\text{PS}} = -0.531A_R^2 + 0.783A_R \quad (3a)$$

$$\text{blend: } \langle P_2(\cos \theta) \rangle_{\text{PS}} = -0.519A_R^2 + 0.745A_R \quad (3b)$$

Films of pure PS and PS/PVME blends containing 70% PS were deformed at $T_g + 15\text{ }^\circ\text{C}$ to a draw ratio of 2 at a nominal stretching rate of 1.582 cm/s , for a total deformation time of 1360 ms. Figure 5 shows the evolution of the orientation function during deformation and the early part of the relaxation, as determined by URS-FTIR and PM-IRLD spectrometry. Because of the low orientation introduced during the deformation, especially for pure PS, four scans were necessary to generate PM-IRLD spectra with sufficient signal-to-

noise ratio, yielding a data point only every 1.6 s. This time resolution does not allow following the deformation curve and the shortest part of the relaxation curve with accuracy, while URS-FTIR spectrometry provides detailed data for these periods.

Figure 5 shows that the orientation measured by URS-FTIR spectrometry at the end of the deformation is significantly larger than that obtained using PM-IRLD. Nevertheless, the agreement between the two experimental techniques in the overlap range is good for the blend and excellent for pure PS, indicating that the higher orientation measured from the URS-FTIR spectra is not a mere artifact due to the technique or to the use of a single polarized spectrum to determine the orientation function. It can be observed that the orientation of PS in the blend is much larger than that in the pure polymer when T_g is used as the reference temperature and that the initial relaxation of PS is faster in the homopolymer than in the blend, in agreement with earlier results.^{15,27,28} We have recently proposed that this is due to the presence of concentration fluctuations in the miscible blends.¹⁴

In a previous paper, we have fitted hour-long relaxation curves of PS and PVME in their blends using a sum of three exponential functions.¹⁵ This procedure was based on the Doi-Edwards model, which predicts that the relaxation of an entangled polymer melt following a step deformation should follow a sum of exponential relaxation processes.³⁰ It is now interesting to evaluate the influence of the short-time relaxation data obtained by URS-FTIR spectrometry on the relaxation time constants. As expected, the second and third characteristic times and their preexponential factors do not change much when fitting the complete set of relaxation data. In contrast, the first relaxation time, which could be ascribed to the Rouse relaxation between entanglement points in the Doi-Edwards model, decreases from 3 to 1 s for pure PS while its preexponential factor, which characterizes the relative importance of the different relaxation times, increases by a factor of 3. The fit is not as good for the blend, in part due to the slightly inferior agreement between the URS-FTIR and PM-IRLD measurements, but the trends are similar to those observed for pure PS. These results confirm the existence and the significance of a short relaxation time of the order of a few seconds as well as the importance to perform sufficiently rapid measurements in order to fully capture the relaxation kinetics of a polymer following a rapid macroscopic deformation.

Conclusion

In this paper, we have demonstrated the value of ultrarapid scanning Fourier transform infrared spectrometry for the study of rapid polymer kinetics. This technique has allowed the determination of the orientation function of PET, of pure PS, and of PS in a blend with PVME, during both the deformation and the early relaxation periods, with a time resolution between 10 and 40 ms. The quantitative nature of the URS-FTIR results has been validated by comparison with those obtained using the established PM-IRLD technique. The gauche-to-trans conversion has also been followed for amorphous PET samples. The significantly enhanced time resolution of URS-FTIR spectrometry as compared to other infrared techniques that can be used to follow irreversible phenomena has allowed the observation of higher T/G ratios than in previous studies of amorphous

PET as well as larger orientation functions for PS at the end of the deformation. URS-FTIR spectrometry has the potential to shed a new light on the mechanisms of deformation and relaxation of polymers.

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