Rheooptical Fourier Transform Infrared Spectroscopy of the Deformation Behavior in Quenched and Slow-Cooled Isotactic Polypropylene Films*

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Received 8 May 2002; revised 12 August 2002; accepted 12 August 2002

ABSTRACT: Emerging technological applications for complex polymers require insight into the dynamics of these materials from a molecular and nanostructural viewpoint. To characterize the orientational response at these length scales, we developed a versatile rheooptical Fourier transform infrared (FTIR) spectrometer by combining rheometry, polarimetry, and FTIR spectroscopy. This instrument is capable of measuring linear infrared dichroism spectra during both small-strain dynamic deformation and large-strain irreversible deformation over a wide temperature range. The deformation response of quenched and slow-cooled isotactic polypropylene (iPP) is investigated. In quenched iPP, under dynamic oscillatory strain at an amplitude of ~0.1%, the dichroism from the orientation of the amorphous chains is appreciably less than that from the crystalline region. At large irreversible strains, we measured the dichroic response for 12 different peaks simultaneously and quantitatively. The dichroism from the crystalline peaks is strong as compared to amorphous peaks. In the quenched sample, the dichroism from the crystalline region saturates at 50% strain, followed by a significant increase in the amorphous region dichroism. This is consistent with the notion that the crystalline regions respond strongly before the yield point, whereas the majority of postyielding orientation occurs in the amorphous region. Our results also suggest that the 841 cm⁻¹ peak may be especially sensitive to the 'smectic' region orientation in the quenched sample. The response of the slow-cooled sample at 70 °C is qualitatively similar but characterized by a stronger crystalline region dichroism and a weaker amorphous region dichroism, consistent with the higher crystallinity of this sample, and faster chain relaxation at 70 °C. © 2002 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 40: 2539–2551, 2002

Keywords: structure-property relations; FT-IR; isotactic poly(propylene) (PP)

INTRODUCTION

In complex polymer systems, the macroscopic mechanical and rheological behaviors have distinct underlying contributions from individual chemical moieties, the microstructure, and/or the nanostructures that may be present. For example, in a semicrystalline polymer the macroscopic mechanical behavior may have distinct contributions from the amorphous and crystalline regions. In a microphase-separated block copolymer, the individual blocks and the nanostructure may contribute differently to the macroscopic behavior. Therefore, isolating the response at each of these length scales is vital for understanding not only the structure–property relationships but also the impact of processing on the structure. A combination of mechanical, scattering (neutrons, light, and X rays), diffraction, and spectroscopic meth-
ods have been developed to gain insight into responses at these length scales. Although scattering can reveal structure and orientational direction, time resolution and quantitative orientation of multiple length scales are a challenge, in addition to the labeling requirements in some methods.

In this work, we illustrate the ability of Fourier transform infrared (FTIR) spectroscopy to reveal quantitative, simultaneous, real-time orientational responses of multiple vibrational modes. A state-of-the-art rheooptical FTIR spectrometer has been developed by combining step-scan FTIR spectroscopy, polarization modulation, and rheometry. Infrared absorbance has been used to characterize and quantify tacticity, crystallinity, and to identify crystalline and amorphous domains in semicrystalline polymers. IR dichroism is the anisotropic attenuation of IR radiation by an absorbing vibrational moment and can be used to quantify the orientation of the dipole moment. Hence, an IR linear dichroism (IRLD) spectrum can present a quantitative picture of the average spatial orientation of several IR-absorbing species simultaneously. Therefore, in contrast with other rheooptical techniques (e.g., X-ray scattering, birefringence, and IR dichroism using a diode laser), measurement of IRLD spectra can be sensitive to the orientation and relaxation responses of both amorphous and crystalline regions of a semicrystalline polymer undergoing mechanical deformation.

Early work by Stein and coworkers, Siesler, Hayes and coworkers, and Zawada and coworkers as well as recent work by Nakashima and coworkers, Wang and coworkers, and Pellerin and coworkers have explored the various aspects of the use of FTIR spectroscopy to characterize orientation in complex polymers. Noda et al. were the first to incorporate polarization modulation with dynamic sample perturbation for direct measurement of dynamic infrared linear dichroism (DIRLD). DIRLD data were later used in the development of a two-dimensional FTIR correlation technique. This triple-modulation scheme, however, used a monochromator and required much time to compile spectra over an appreciable range of IR wave numbers. Wang et al. showed the use of step-scan mode Fourier transform (FT) spectroscopy to make time-resolved DIRLD measurements on isotactic polypropylene (iPP). This led to the elimination of so-called “Fourier frequencies” that arise with the use of continuous-scan FT spectroscopy and add to the difficulty of signal demodulation. Data collected from these experiments suffer from baseline noise because spectral arithmetic must be performed on two separate measurements to generate a DIRLD spectrum. Furthermore, previous IRLD measurements (using diode lasers) on polymer films and fibers subjected to large draw ratios (~20:1) exhibit very strong, yet insensitive, responses with no appreciable dichroism signal appearing until high strain values. The apparatus described in this work incorporates features from each of its predecessors, combining step-scan FTIR spectroscopy, polarization modulation, and dynamic sample perturbation into a single instrument. When coupled with a single external lock-in amplifier and digital signal processing (DSP) electronics, a wide variety of IRLD experiments can be performed on this single instrument.

iPP is a widely used, commercially important semicrystalline polymer that exhibits a complex mechanical behavior in the solid state. There is strong interest in improving the properties of polypropylene with copolymerization, processing, or composite fillers. The deformation behavior of polypropylene has received renewed attention with recent developments in metalloocene catalyst technology, which allows for tacticity control and biaxially oriented polypropylenes, resulting in superior properties. iPP is a richly polymorphic material that exhibits three well-documented crystalline forms (monoclinic, hexagonal, and triclinic) as well as a paracrystalline “smectic” phase (generated via rapid quenching from the melt), each contributing differently to the physical properties of the material. The deformation behavior and the role of the crystalline phase on the tensile properties during deformation are addressed in great detail by Baltá-Calleja and Peterlin and others. A majority of these studies used wide-angle X-ray scattering (WAXS) and wide-angle X-ray diffraction (WAXD) to characterize the crystal structure before and after deformation. Small-angle X-ray scattering (SAXS) and WAXD have been used to characterize the complex crystallization response of this polymorphic material. In this study, we indicate that rheooptical FTIR spectroscopy can provide complementary information regarding the orientation of amorphous and crystalline regions of the material. In the following sections, data are pre-
sent on iPP samples with varying crystalline content formed by quenching and slow cooling. Both small-strain DIRLD and large-strain IRLD data are presented at different temperatures.

**EXPERIMENTAL**

**Materials**

Small-strain DIRLD experiments were performed on iPP films provided by Manning Applied Technology. These films were heated (below their melting point) and biaxially drawn (10× in one direction, 5× in the orthogonal direction) and then quenched. Consequently, we did not expect this material to possess a large crystalline content. Films were cut to dimensions of 3 × 1 cm and were 40 μm thick. Changes in the spacing of interference fringes, caused by reflections at the film surface, can introduce large artifacts into DIRLD signals. We used a simple solution by gently roughing the film surface with fine (600-grit) sand paper.

For large-strain IRLD experiments, sample films were formed from a commercial iPP powder (Scientific Polymer Products, Inc.). A small amount of powder (~1 g) was transferred onto an acetone-cleaned glass slide (50 × 75 × 1.2 mm thick), heated to 193 °C, and held for 20 min, allowing the powder to melt completely. A second clean glass slide was placed atop the melt, and the ensemble was mechanically pressed (model 3912, Carver, Inc.) until the melt was a film of nearly uniform thickness. The pressing load was subsequently removed, and the sample was allowed to anneal (also at 193 °C—above its melting temperature) for 30 min. This step allows for the relaxation of any orientation anisotropy within the sample caused by melt-pressing. This preparation procedure results in films with a thickness of between 80–150 μm. Upon annealing, solid-state films of varying crystallinity are prepared by choosing one of the following two sample-preparation routes:

1. The melt (still contained between the glass slides) is suddenly quenched into liquid nitrogen, where rapid cooling to sub-glass-transition temperatures effectively arrests the formation of appreciable crystalline domains. However, these quenched samples are not entirely amorphous and have been shown to consist of smectic crystals.

2. The heating elements of the melt-press blocks are deactivated, and the sample is allowed to cool to ambient temperature slowly within the blocks. These slow-cooled samples require about 4 h to attain a temperature of 30 °C. Solid films are then easily extracted from between the glass slides by an ordinary straight razor blade. This sample is expected to form monoclinic α crystals as shown previously.

**Instrument**

The rheo-FTIR apparatus combines step-scan FT interferometry with polarization modulation, dynamic mechanical testing, and high-speed digital signal-processing electronics, providing the ability to measure both small and large dichroism responses rapidly, directly, sensitively, and quantitatively. Source light is passed sequentially through a Michelson interferometer, low-pass filter, linear polarizer, photoelastic modulator (PEM), and sample stretcher before it is selectively absorbed by the sample (Fig. 1). The resultant intensity is gathered and converted into an electrical signal by a liquid-nitrogen-cooled fast mercury–cadmium–telluride detector. The detected signal has imposed upon it three modulations by the optical train (phase modulation in the interferometer, polarization modulation via PEM, and dynamic deformation in the stretcher, sequentially) that need to be demodulated appropriately to extract raw dichroism and absorbance spectra (Fig. 2). As a final step, raw data need to be appropriately normalized by background and calibration spectra to get quantitative results.

The FTIR spectrometer (model FTS 6000, Bio-Rad) essentially serves as a polychromatic mid-IR radiation source. As mentioned previously, step-scan interferometry is advantageous for experiments involving other modulations imposed on the IR source. Amplitude modulation of the broadband source, caused by operation in continuous-scan mode, would prove difficult to distinguish from dynamic sample perturbation during signal processing. Step-scan operation effectively eliminates this problem because the interferometer’s moving mirror is stationary during data collection. A zinc selenide photoelastic modulator (PEM-90/ZS37, Hinds Instruments, Inc.) induces broadband polarization modulation of the linearly polarized source, causing the electric field to alternate its polarized state rapidly. This allows for direct measurement of IRLD that is found by
demodulating the detected signal at twice the PEM fundamental frequency. Additionally, PEM provides a high-frequency “carrier” signal for the source light as well as an improved signal-to-noise ratio because of multiplicative noise suppression as a result of averaging. Depending on how we wish to deform sample films, one of two rheometers is used. For DIRLD experiments, a PZT-controlled microrheometer (TC-100 Polymer Modulator, Manning Applied Technology) is used to apply small-amplitude, reversible oscillatory deformation. An external function generator (Hewlett–Packard 33120A) is used to trigger a 20-Hz sinusoidal waveform deformation. The polymer modulator can be operated from room temperature up to 75 °C. To apply large irreversible deformations, a tensile tester (Minimat 2000, Rheometric Scientific, Inc.) is used. The Minimat can be operated from room temperature up to 250 °C. The use of IR-transparent KBr windows allows for simultaneous measurements of rheology and FTIR dichroism spectra. In the large-strain, static deformation mode, IRLD and absorbance spectra are acquired at each strain step. The demodulated raw spectra are converted to the quantitative dichroism spectra with appropriate calibration and background spectra (details are described elsewhere). Three of the following sets of normalization spectra are obtained:

1. A second linear polarizer is used in place of the sample—its polarization axis is aligned with that of the first polarizer \(P_B\) and \(P_D\). (“B” subscripts denote dichroism spectra, and “D” represents absorbance.)
2. A second polarizer is used, as before, but with its polarization axis perpendicular to that of the first polarizer \(Q_B\) and \(Q_D\).

**Figure 1.** Diagram of rheooptical FTIR optical and signal processing train. Optical and electronic signals are represented by dashed and solid lines, respectively.

**Figure 2.** Diagram of signal-processing electronics. Static and dynamic dichroism signals are extracted from the detector signal after being demodulated by electronics with appropriate reference signals.
These first two scenarios simulate ideally oriented samples.

3. No sample is placed in the stretcher (\(M_B\) and \(M_D\)). This considers the anisotropic and optical throughput properties of the instrument itself.

The raw dichroism spectra (\(V_B, V'_C\): dynamic inphase, and \(V''_C\): dynamic quadrature) are also normalized by their raw static absorbance counterpart (\(V_D\)). This step considers changes in sample thickness and corrects the spectra to make it quantitative, analogous to the approach by Noda et al.\(^{34}\) For dynamic deformation, the inphase (\(\Delta A'\)) and quadrature (\(\Delta A''\)) dichroism are calculated by

\[
\Delta A' \text{ or } \Delta A'' = \frac{(V_C \text{ or } V''_C)}{V_D} \left( \frac{P_B}{P_B} \right) \left( \frac{M_B}{M_D} \right)
\]

For static irreversible deformation, the dichroism (\(\Delta A\)) is calculated by

\[
\Delta A = -\log \left( \frac{T_1}{T_2} \right);
\]

where

\[
T_\parallel = \frac{P_B V_D - P_B V_B}{P_B M_D - P_B M_B}
\]

and

\[
T_\perp = \frac{Q_B V_D - Q_B V_B}{Q_B M_D - Q_B M_B}
\]

are static transmittances of light polarized parallel and perpendicular to the strain direction, respectively.

**IR Spectrum of iPP**

Before venturing into a physical interpretation of IR dichroism spectra, we discuss the static absorbance spectrum of iPP (Fig. 3). As a reference, the spectrum of a slow-cooled iPP sample is shown. The spectrum is characterized by several peaks where multiple vibrational modes contribute to the absorption peak. The considerable task of as-
assigning vibrational moments to each absorbance frequency has been masterfully accomplished by Snyder and Schachtschneider\textsuperscript{73} and McDonald and Ward\textsuperscript{2} through comparison of theoretical absorbance peaks (determined via valence-force calculations) to experimental observations. Much effort has also been spent on labeling IR peaks as characteristic of crystalline, paracrystalline, or amorphous activity. These findings are summarized in Table 1. The main peaks, their associated vibrational modes, associated microstructures, and dipole moment orientation angles with respect to the main chain are listed as gathered from the literature. The peaks at 809, 841, 998, and 1165 cm\textsuperscript{-1} are representative of the helical chains in iPP. Thus, the amount of crystalline character in the material is gauged by the presence of certain “helical” peaks because crystallites are formed over helical chains of sufficient regularity. These peaks arise as a result of coupled vibrations that are due to the complex nature of the helical chain structure. The 841 cm\textsuperscript{-1} peak is an especially strongly absorbing peak, whereas 998 and 1165 cm\textsuperscript{-1} are somewhat weaker. Previous studies on molten iPP and atactic polypropylene suggest that the 973, 1153, 1377, and 1459 cm\textsuperscript{-1} peaks represent segments residing predominantly in the amorphous region. From the vibrational mode assignments of the low wave number range (<1165 cm\textsuperscript{-1}), several peaks have contributions from the C–C stretching mode and can be sensitive to backbone orientation.

### RESULTS AND DISCUSSION

As previously mentioned, a central feature of the rheo-FTIR spectrometer is its ability to track dichroism at several vibrational modes simultaneously. A high-resolution absorbance spectrum, given in Figure 3, clearly shows 19 distinct peaks that characterize iPP. iPP is characterized with respect to three principal variables—initial morphology, temperature, and extent of deformation. To review, it is expected for quenched samples to be mostly amorphous, with a small quantity of smectic crystallites as shown by WAXS\textsuperscript{60,63,66} and for the slow-cooled samples to possess a greater

### Table 1. Characteristic Infrared Absorbance Peaks of Isotactic Polypropylene\textsuperscript{2,3,25,73,80,81}

<table>
<thead>
<tr>
<th>Wave Number (cm\textsuperscript{-1})</th>
<th>Vibrational Mode(s)</th>
<th>Associated Microstructure</th>
<th>Dipole Moment Orientation</th>
</tr>
</thead>
<tbody>
<tr>
<td>809</td>
<td>C–C stretching</td>
<td>Helical (α crystalline)</td>
<td>Perpendicular (⊥)</td>
</tr>
<tr>
<td></td>
<td>Coupled C–H deformation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>841 (s)</td>
<td>C–C stretching</td>
<td>Helical (α crystalline and mesophase)</td>
<td>Parallel (∥)</td>
</tr>
<tr>
<td></td>
<td>CH\textsubscript{2} rocking</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH\textsubscript{3} rocking</td>
<td></td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>C–C stretching</td>
<td>Helical (α crystalline)</td>
<td>Perpendicular (⊥)</td>
</tr>
<tr>
<td></td>
<td>Coupled C–H deformation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>941 (w)</td>
<td>C–C stretching</td>
<td>Helical (α crystalline)</td>
<td>Perpendicular (⊥)</td>
</tr>
<tr>
<td></td>
<td>Coupled C–H deformation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>973</td>
<td>C–C stretching</td>
<td>Amorphous</td>
<td>Parallel (∥)</td>
</tr>
<tr>
<td></td>
<td>CH\textsubscript{2} rocking</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH\textsubscript{3} rocking</td>
<td></td>
<td></td>
</tr>
<tr>
<td>998 (s)</td>
<td>C–C stretching</td>
<td>Helical (α crystalline)</td>
<td>Parallel (∥)</td>
</tr>
<tr>
<td></td>
<td>CH\textsubscript{2} rocking</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH\textsubscript{3} rocking</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1153 (sh)</td>
<td>CH\textsubscript{3} wagging</td>
<td>Amorphous</td>
<td>Parallel (∥)</td>
</tr>
<tr>
<td>1167 (s)</td>
<td>C–C stretching</td>
<td>Crystalline</td>
<td>Parallel (∥)</td>
</tr>
<tr>
<td></td>
<td>CH\textsubscript{3} wagging</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1257 (w)</td>
<td>C–H wagging</td>
<td>Parallel (∥)</td>
<td></td>
</tr>
<tr>
<td>1305</td>
<td>C–H bending</td>
<td>Parallel (∥)</td>
<td></td>
</tr>
<tr>
<td>1359</td>
<td>C–H bending</td>
<td>Crystalline</td>
<td>Perpendicular (⊥)</td>
</tr>
<tr>
<td>1377 (s)</td>
<td>Symmetric C–H bending</td>
<td>Amorphous</td>
<td>Perpendicular (⊥)</td>
</tr>
<tr>
<td>1436</td>
<td>CH\textsubscript{2} bending</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1459 (s)</td>
<td>Asymmetric, inplane CH\textsubscript{3} bending</td>
<td>Amorphous</td>
<td>Perpendicular (⊥)</td>
</tr>
</tbody>
</table>

s: Strong peak, w: weak, and sh: shoulder.
degree of well-defined monoclinic crystals, also shown by WAXS. In this article, we discuss the responses of the amorphous and crystalline regions.

**Dynamic Oscillatory Strain Measurements**

**DIRLD Spectra**

The dynamic small-amplitude (~0.1%) oscillatory strain IRLD spectral response of quenched, prestretched iPP at room temperature indicates the sensitivity of the rheo-optical FTIR apparatus (Fig. 4). The same experiments at an elevated temperature of 45 °C (not shown here) demonstrate a qualitatively similar response. Even at this small strain, we are able to measure dichroism signals on the order of 10^{-5}–10^{-4} at several wave numbers, indicated in Table 1. This suggests the sensitivity of our instrument. At all wave numbers, the quadrature dichroic response (ΔAq) is much smaller than the inphase dichroism (ΔA^p). This indicates that the orientation response of the film is predominantly inphase with the applied strain, as may be expected at this temperature. Results have been presented over wave numbers of 800–1500 cm^{-1}, a broader range as compared with previous studies on iPP. This allowed this work to explore both the responses of the amorphous and the crystalline regions. Over the wave number range where comparison was possible, the magnitude of the dichroic response and the qualitative nature of the results agree with the frequency-domain results of Budevska et al. and the time-resolved results of Wang et al. From Figure 4, it is apparent that the dichroism at 1167, 973, 841, and 809 cm^{-1} shows a bimodal nature manifested by a positive and a negative dichroism response with the zero response centered at the aforementioned wave numbers. This is consistent with a small wavelength shift in these vibrational modes as a result of the dynamic deformation.

Among the peaks revealing a strong response, the peak-to-peak magnitude of the dichroism arising from amorphous chain orientation is lower than that from the crystalline region (|ΔA(1377, 1459 cm^{-1})| ≈ 3 × 10^{-4} vs |ΔA(1167 cm^{-1})| ≈ 8 × 10^{-4}). This magnitude is related to the amount of chains residing in the particular region, the strength of the vibrational moment, and the extent of the orientation. However, considering that the prestretched, quenched sample is likely to have appreciably less crystalline than amorphous content, the higher dichroism values of the crystalline region suggest that at small strains, the vibrational moments associated with
the crystalline region indicate a much stronger net orientation as compared with those from the amorphous region. A possible reason for the relatively reduced net dichroism at the two main amorphous peaks may be the fact that this dipole moment is oriented perpendicular to the main chain. For this dipole moment to show a strong response, there would have to be significant main-chain orientation. This is unlikely at small strains. This is more evident in the next section.

**Large Irreversible Strain Measurements**

**Stress-Strain Behavior**

The engineering stress-strain behavior of the iPP films, obtained simultaneously with the IRLD spectra, shows responses typical of semicrystalline polymers (Fig. 5). Because of its high crystallinity, the slow-cooled sample is very brittle and hence fails at a rather low strain value at room temperature. Therefore, large-strain tests for these samples were performed at 70 °C. At this temperature, the slow-cooled sample has a yield stress and a yield strain of 6 MPa and ~15%, respectively. The quenched iPP sample tested at room temperature has a yield stress and a yield strain of 11.5 MPa and 12%, respectively. In the Hookean region, the crystallites are thought to support the stress, resulting in a high modulus. Beyond the yield point, the crystallites commence irreversible deformation via slip and dislocation movements. Concurrently, the chains in the amorphous domains begin to undergo chain elongation and continue to do so until material failure.75 No strain-hardening or other mechanical phenomena are observed in the plastic deformation region. We present the stress-strain data to establish the yield strains so that we can compare the orientation response differences before and after the yield point.

**Static IRLD Spectra**

IRLD spectra obtained during large irreversible deformation are depicted in Figure 6. For the idealized case, one would expect a perfectly flat baseline of \( \Delta A(\nu) = 0 \) at 0% elongation. This is because an ideal sample would initially possess no orientational anisotropy. To avoid any residual orientation, the sample is annealed above its melting temperature before the subsequent cooling. Regardless, there is a small amount of residual orientation. Therefore, we subtract the IRLD spectrum at 0% from the spectra at higher strains [insets of Fig. 6(a,b)]. First, it is important to note

![Figure 5. Tensile behavior of iPP with approximate yield point labeled. Quenched and slow-cooled films have a gauge length of 14.7 mm and a thickness of ~ 150 μm. Elongation rate: 0.5 mm/min.](image)
Figure 6. Static IRLD spectra of iPP. Peaks are labeled with their predicted moment orientation upon tensile strain (i.e., parallel or perpendicular to the strain direction). Spectra at 0% strain (representing "residual" orientation) are shown as insets. (a) Quenched iPP at room temperature (8 cm$^{-1}$ resolution, 10 scans coadded). (b) Slow-cooled iPP at 70 °C (4 cm$^{-1}$ resolution, 25 scans coadded).
the sign of the dichroism signal is at each wave number. As pointed out in Table 1, previous researchers have assigned the orientation of each of the 12 dipole moments. If a dipole moment is oriented parallel to the chain and the chain is oriented in the direction of strain, then one would expect positive dichroism. On the other hand, if the dipole moment is oriented perpendicular to the chain backbone and the chain is oriented in the direction of strain, one would expect negative dichroism. All of the peaks for both quenched and slow-cooled samples exhibit dichroism signs that are entirely consistent with the orientation direction assigned in Table 1. As the strain increases, the parallel dipole moments are positive and increasing, whereas the perpendicular dipole moments are negative and decreasing.

The crystal structure of quenched iPP films is discussed by Seguela et al. Their WAXS data suggest that these samples form somewhat ill-defined smectic crystals that do not transform to the more-stable monoclinic α crystals, even at 250% strain at room temperature. Our quenching procedure is the same as that of these researchers. Therefore, we suggest that our sample also contains a small amount of smectic crystals that do not transform into the monoclinic form. This sample would be expected to be highly amorphous. Therefore, if the amorphous chains and the crystalline regions were to show the same extent of orientation, then the peaks associated with the amorphous chains would be significantly greater in magnitude than those associated with the crystalline regions. For quenched iPP, IRLD spectra have been measured at strains of 10, 25, 50, 75, 100, 150, 200, and 250% (Fig. 6(a)). The residual dichroic spectrum at 0% strain is shown in the inset. Although the residual dichroism is relatively small at most wavelengths, there appears to be some transverse orientation of the amorphous chains (1377 and 1459 cm⁻¹) in the film. Before the yield point (strain ≈ 15%), there is an increase in the dichroism magnitude for iPP helix chain peaks (809, 841, 900, 998, and 1167 cm⁻¹), whereas the orientation of the amorphous chains is relatively small (1377 and 1459 cm⁻¹). The most notable change in the crystalline dichroism response is from the 841 cm⁻¹ peak. When the strain is increased beyond the yield point, there is a strong response from the helical chains associated with the crystalline region until a strain of 50%. At this strain, the dichroism associated with the 841 cm⁻¹ peak reaches 0.035, whereas those associated with the other three crystalline peaks reach approximately 0.01. Beyond 50% strain, the orientation associated with the crystalline region saturates, accompanied by a continued increase in the orientation associated with the amorphous region (1377 and 1459 cm⁻¹). At 200% strain, these two strong amorphous peaks show nearly equal dichroism of 0.025. This is consistent with the idea that beyond the yield strain, the dominant contribution to orientation comes from the amorphous chains. The crystalline orientation is expected to reach a maximum near the yield point, beyond which there is a gradual breakup of the crystallites by slip and dislocation motion, leading to a gradual saturation of crystalline orientation.

Amorphous peaks are generally broader than their crystalline counterparts. The relatively gradual change in amorphous peak area with strain gives an idea of the deformation process that occurs. Considering the high amorphous content, one would expect a much stronger dichroism response than what we observe. However, because the dipole moments are perpendicular to main-chain orientation, the bonds may not be truly representative of main-chain orientation until high strains, that is, they may still have a ‘near random’ net orientation until high strains are reached. Another reason could be that there may have been some relaxation of the amorphous chain orientation even during the measurement. Dynamic strain measurements in the previous section, at a faster timescale of 20 Hz, showed appreciable dichroism associated with the amorphous regions even at small strain. On the other hand, at each step, the data-acquisition time for large strains takes about 5 min in which time some orientation relaxation can occur.

The dichroism spectrum of slow-cooled iPP at 70 °C (Fig. 6(b)) is somewhat similar and consistent with that of the quenched sample, except that the crystalline peaks give a much stronger orientational response. The residual orientation in the film, as measured by the dichroism at 0% [inset, Fig. 6(b)], is appreciably small as compared with that at higher strains. Previous WAXS data have shown that these samples would be expected to form monoclinic crystals. The stronger dichroism response is consistent with the higher degree of crystallinity. In contrast with the quenched sample, the saturation in the crystalline orientation occurs well beyond 50%. In this sample, the dichroism values at 841 and 809 cm⁻¹ are nearly the same (0.06 at a strain of 100%).
The dichroism at 900 cm\(^{-1}\) is 0.04. We note that at the same strain, the dichroism of the quenched sample at 841 cm\(^{-1}\) is only slightly lower, whereas dichroism values at 900 and 809 cm\(^{-1}\) are appreciably lower. This is notwithstanding the fact that all of them are representative of the helical chains that are expected to be part of the ‘crystalline’ region. The appreciably stronger response of the 841 cm\(^{-1}\) peak as compared with the 900 and 809 cm\(^{-1}\) peaks perhaps suggests that the 841 cm\(^{-1}\) peak is more sensitive to the helical chains, whether present in the smectic (quenched sample) or monoclinic (slow-cooled sample) form. On the other hand, the 809 and 900 cm\(^{-1}\) peaks may be more sensitive to the orientation of the helical chains that are part of monoclinic crystals.

The orientation of the amorphous chains (1377 and 1459 cm\(^{-1}\)) in the slow-cooled sample at 200% strain is much lower than that of quenched iPP at comparable strains. This could be because of the smaller fraction of the amorphous chains in the slow-cooled sample and the faster orientation relaxation of the amorphous chains during measurement at 70 °C. On deforming the material beyond the yield point, a distinct behavior is observed in the strong crystalline peaks. The 841, 998, and 1167 cm\(^{-1}\) peaks reveal a sign change (i.e., a flip from negative to positive values). This was observed in repeated measurements on different quenched and slow-cooled samples, but is more clearly evident in the slow-cooled samples. At this time, it is not clear why there is a change in the sign of dichroism. Although further experiments are needed, we offer the following preliminary hypothesis. This may be attributed to the tilting of crystalline lamellae beyond the yield point as suggested by Peterlin.\(^{78}\) On the basis of transmission electron microscopy and WAXS data, he offers that lamellar tilting involves a shift of the \(a\) axis and later of the \(b\) axis, away from the draw direction. This is accompanied by a gradually increasing orientation of the \(c\) axis in the draw direction. This explanation of lamellar tilting is disputed by the work of Flory and Yoon.\(^{79}\) This alternative viewpoint that suggests lamellae melt at the yield point has been supported by Wignall and Wu.\(^{79}\) If the lamellae melt and reform, we may expect to see a diminished crystalline-phase dichroism, followed by an increase. Unless this melting and recrystallization happen rapidly as compared with the timescale of the measurement, our data would not support this explanation. The results produced in this work appear to agree with a scenario involving flipping of the crystalline domains, as evidenced by the change in sign of the dichroism; however, we are unable to verify the reason for the flip. Flipping of the lamellae also gives us an idea of the amount of crystalline character present in a particular IR peak. The 841 cm\(^{-1}\) peak represents ‘crystalline’ behavior the best with the strongest orientation before the yield point, followed by the 998 and 1165 cm\(^{-1}\) peaks. These three bands also disappear in the melt,\(^{3}\) thereby affirming their representation of the crystalline phase.

**CONCLUSIONS**

We have developed a versatile rheooptical FTIR spectrometer that is capable of simultaneous, quantitative measurements of both stress and the dichroism spectrum over a wide range of temperatures. This is achieved by combining a step-scan spectrometer with a PEM-based polarization modulation, a dynamic stretcher (or a rheometer), and a lock-in amplifier DSP demodulation scheme. The ability of this instrument to provide quantitative orientation of several vibrational modes in complex polymers is illustrated by studying iPP films. The orientation behavior was explored at both small and large strains at different temperatures.

First, under small-amplitude (~0.1%) oscillatory strain, we were able to measure the dichroism at several wave numbers, demonstrating the sensitivity of the instrument. Under dynamic strain, the peaks at 809, 841, 1167, 1359, and 1459 cm\(^{-1}\) appear show a small shift in wave number characterized by a bimodal response. The dichroism associated with the crystalline region is much higher than those associated with the amorphous chains. This may be due to the perpendicular orientation of the vibrational modes associated with the amorphous region, thereby making them less sensitive to chain orientation at small strains.

Second, under large irreversible strain, we were able to measure the dichroism at 12 different peaks simultaneously and quantitatively. The responses at different peaks associated with the crystalline and the amorphous regions are self-consistent in their orientational response. Each peak exhibits a dichroism sign that is consistent with its dipole moment orientational assignment.

Third, in a quenched sample expected to contain a small amount of ‘smectic’ crystals, the orientation of the crystalline region is much stronger.
than that of the amorphous region. Although the dichroism of the crystalline region saturates just beyond the yield point, the amorphous chains appear to continue to orient until 200% strain. However, the measured dichroism of the amorphous chains may be diminished partly because of the fact that the dominant dipole moments are oriented perpendicular to the chain backbone and partly because of relaxation of orientation. The 841 cm\(^{-1}\) peak appears to be more sensitive to the ‘smectic’ region orientation as compared with the other ‘crystalline’ peaks.

Fourth, in the slow-cooled sample at 70 °C, the dichroism associated with the crystalline regions is much higher as compared with the quenched sample resulting from the higher crystalline content, whereas that of the amorphous chains is lower because of faster relaxation at the higher temperature. Future work will explore the role of tacticity on the mechanical and orientation behavior in syndiotactic and semisyndiotactic polypropylenes. The rheo-FTIR data will be complemented by WAXD and WAXS measurements.

The authors acknowledge funding from NSF-CAREER (DMR 9876221) (RMK), NSF-IGERT (MSS), and the Wayne State University Institute for Manufacturing Research (GP).

REFERENCES AND NOTES

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