FTIR Spectroscopic Investigation of Thermal Effects in Semi-Syndiotactic Polypropylene*

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ABSTRACT: The temperature-dependent behavior of individual components within metallocene-catalyzed semisyndiotactic polypropylenes (semi-sPP) with a wide range of stereoregular content (26 to 96% rr) is studied using Fourier transform infrared (FTIR) spectroscopy and temperature-modulated differential scanning calorimetry (DSC). Changes in sensitive, high-resolution absorbance spectra are observed as melt-slow-cooled thin films are subjected to stepwise temperature increases. In general, spectral bands previously identified as being sensitive to ordered structures (e.g., conformed chains, crystal morphs) appear to follow overall trends of shifting to lower wavenumbers (energies), broadening, and decreasing in peak area intensity as temperature increases. Peaks that appear due to “splitting” (observed in more stereoregular materials) show a trend toward coalescence as temperature increases; this corresponds to a gradual loss of chain conformational order. Gauche-gauche-trans-trans (ggtt)ₙ helical and all-trans (tttt)ₙ planar zigzag-conformed chains that participate in the crystalline-amorphous interfacial region (“mesophase”) appear to be more stable (i.e., they do not lose their conformational order as easily) with increasing temperature in materials with a greater degree of syndiotacticity. Moreover, IR data correspond well with modulated DSC endotherms located near 50 °C and 70 °C. At each transition temperature—thought to represent, respectively, a thermally driven chain conformation from planar zigzags to helices, and a dynamic disorder of helices marked by rapid gauche ↔ trans isomerization—the IR absorbance ratio, A978/A963, which represents the relative population of helical chains, undergoes an accelerated decrease.© 2005 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 43: 439 – 461, 2005

Keywords: syndiotactic polypropylene (PP); FT-IR; thermal properties; structure-property relations; metallocene catalysts

INTRODUCTION

The introduction of metallocene catalysts into olefin polymerization¹,² chemistry has generated re-

newed interest in research on many well-known polymers. Syndiotactic polypropylene (sPP) is a good example of this. There are many studies in the literature, both theoretical and, to a lesser degree, experimental, concerning sPP; however, the ability to synthesize, and thus to study experimentally, highly stereoregular sPP was only realized around 1990.³,⁴ Since then, much has been learned regarding the crystal morphology,⁵–⁷ chain conformations,⁸–¹⁰ blend compatibility,¹¹–¹⁳ elastomeric behavior,¹⁴–¹⁶ and many
other physical properties of sPP. Vibrational spectroscopy has certainly contributed to the experimental progress. Infrared (IR) absorbance and Raman scattering have been used to identify the presence and relative populations of gauche-gauche-trans (ggtt) helical and all-trans (tttt) planar zigzag-conformed chains as sPP undergoes a variety of thermal and mechanical processing conditions. Recently, infrared linear dichroism (IRLD) spectroscopy was used to measure structure formation and viscoelastic component orientation in tensile-deformed sPP. Simultaneously collected absorbance and IRLD spectra reveal and quantify both a helical-to-planar-zigzag conformation change and “mesophase” formation that accompany tensile yielding. The specific technique, rheo-optical FTIR spectroscopy, provides a means of sensitively measuring stepwise changes in sPP morphology while en route to completing a crystal–crystal transformation at high strains (~600%).

This work focuses on the characterization of the IR absorbance spectrum of sPP as stereoregularity is decreased. The effects of varying tacticity alone have been investigated recently. Increasing syndiotacticity is found to cause intensity change, wavenumber shift, and “splitting” in certain characteristic IR peaks. These phenomena can be linked to an overall change in the local molecular environment of vibrational dipole moments, specifically in the degree of configurational and conformational order in sPP chains. It is hypothesized here that varying temperature will also have some effect on molecular order, and thus, on the IR spectrum of sPP as well.

The impetus of this work is two-fold:

1. Semisyndiotactic polypropylene (semi-sPP) with such a broad range of stereoregular content (26 to 67% rr) has, to date, not been analyzed with FTIR spectroscopy. The microstructural consequences of stereoregularity could be manifested in the IR spectrum.

2. The spectral changes listed above have also been observed in the course of rheo-optical FTIR dichroism experiments on highly stereoregular sPP. Results from the present work can be helpful in distinguishing thermal effects from other factors that may influence IR spectra in a similar fashion.

Thus, a thorough investigation of semi-sPP becomes necessary to distinguish between tacticity, thermal, and mechanical effects on IR spectra, and thus, to analyze and interpret spectral effects in dichroism studies accurately. In general, the variations observed (intensity change, broadening, shifting, and splitting) are small with respect to the overall magnitude of the spectra measured. Thus, high-resolution IR spectroscopy must be employed. The following work investigates six materials, each with a different degree of stereoregularity. As temperature is varied, subtle changes in absorbance spectra are detected sensitively, and careful analysis is performed, in light of what has been learned from a previous study where tacticity alone was varied.

**EXPERIMENTAL**

**Materials**

Five semisyndiotactic polypropylenes with various degrees of stereoregularity, synthesized using an unsymmetrical anza-fluorenyl metallocene catalyst, are analyzed: aPP, s-sPP32, s-sPP49, s-sPP65, and s-sPP67. A highly stereoregular material (sPP), obtained from the Fina Oil and Chemical Company, is also studied. 13C-NMR spectroscopy and high-temperature GPC triple-detection are used to determine stereoregularity and molecular weight distributions, respectively, of each material. These properties are reported in Table 1. Thin film samples are obtained by compression molding melted material, followed by slow cooling. Bulk material is heated to 180 °C inside a hot press (Hydraulic Unit model 3912, Carver, Inc.) and held for 20 min to ensure complete melting. Melts are then sandwiched between...
between polytetrafluoroethylene sheets and compression molded into films of nearly uniform 150-μm thickness. The pressing load is then removed, and films are maintained at 180 °C for 30 min to allow relaxation of any processing stresses.53 Samples are then allowed to air-cool slowly to ambient temperature (~ 30 °C) over a period of 4 h. This step encourages the formation of any thermodynamically favorable ordered structures (e.g., conformed chains, aggregates, crystallites). It is expected that any structural order in each material will be composed mostly of chains adopting a \((ggtt)_n\) helical bond sequence, a portion of which may arrange to create crystalline Form I domains in the more stereoregular species.7,9,11 Each sample film is maintained at ambient conditions for at least one month of residence prior to testing. Under these processing conditions, it is unlikely that a majority of macromolecular chains will adopt the less stable \((tttt)_n\) planar zigzag conformation. Nevertheless, it is also unreasonable to expect that this conformation will be absent entirely, especially in more stereoregular samples.

FTIR spectroscopy

Transmission mode IR absorbance spectra are collected using a Bio-Rad model FTS 6000 FTIR spectrometer operating under rapid-scan (continuous) interferometry. A silicon carbide source provides broadband excitation in the wavenumber range from 4000 cm\(^{-1}\) to 400 cm\(^{-1}\). The Michelson-interferometer-modulated beam is redirected to an external chamber that contains a custom modified tensile rheometer (MiniMat 2000, Rheometric Scientific, Inc.) capable of near isothermal temperature control from ambient conditions to 200 °C. The rheometer is fitted with potassium bromide windows in an aluminum block housing to provide both a transparent medium for the mid-IR beam and good control of the sample chamber temperature. Spectra are collected with a resolution of 0.5 cm\(^{-1}\) and 1024 scans coadded (i.e., averaged) using a liquid-nitrogen-cooled fast mercury-cadmium-telluride (MCT) detector. Between loading a sample film and spectral acquisition, 45 min are allowed to elapse in order for samples to equilibrate thermally and for ambient carbon dioxide and moisture to be purged from the external chamber. Spectra are acquired at 30 °C and at increasing intervals of 20 °C until the film can no longer stand freely under gravity (i.e., it “sags” out of the beam path). Thus, more spectra are collected for certain materials than for others. In general, the maximum temperature achievable for scanning films using this experimental setup increases with syndiotactic content, with the exception of aPP—probably due to its noticeably greater molecular weight. Including the allotment for thermal equilibration and chamber purging, spectral acquisition requires approximately 3 h.

Differential scanning calorimetry

Specimens are analyzed using either a TA Instruments 2920 or a TA Instruments Q1000 Modulated® Differential Scanning Calorimeter (MDSC). A linear heating rate of 5 °C/min is applied with a perturbation amplitude of \(± 0.796 °C\) every 60 s. Samples are subjected to a heat-cool-heat profile using a temperature range from either –60 °C or –80 °C to ~ 200 °C. \(n\)-Decane, indium, and tin standards are used for temperature calibration. Calorimeters are also calibrated for modulated work using a sapphire standard for heat capacity calibrations. Thermogram baselines are normally examined and corrected for curvature if present using manufacturer-suggested methods during calibration; however, these are not included in the data presented. Sample amounts of 10 to 14 mg are used for analysis; sample mass does not change appreciably over the course of the DSC experiments.

RESULTS AND DISCUSSION

FTIR spectroscopy

IR absorbance spectra of all six materials at different temperatures are reported in Figures 1 through 6. Peak assignments, summarized in Table 2, are compiled from three sources: valence force calculations and observations of sPP vibrational spectra54; rheo-optical infrared linear dichroism studies of sPP44; and a recent work, complementary to the present work, characterizing the effects of stereoregularity on sPP vibrational spectra.50 Since each spectrum contains many peaks over the wavenumber range scanned (1300 cm\(^{-1}\) to 800 cm\(^{-1}\)), the analysis to follow will focus more narrowly on those peaks exhibiting greatest change with temperature. Each figure (Figs. 1–6) consists of:
Figure 1. High-resolution FTIR absorbance spectra of aPP, reported over various wavenumber ranges and at different temperatures: (a) fully measured spectrum (1300 cm\(^{-1}\) to 800 cm\(^{-1}\)) at 30 °C; (b) 905 cm\(^{-1}\) to 800 cm\(^{-1}\), from 30 °C to 150 °C; (c) 1000 cm\(^{-1}\) to 967.5 cm\(^{-1}\), from 30 °C to 150 °C; (d) 1265 cm\(^{-1}\) to 1150 cm\(^{-1}\), from 30 °C to 150 °C.
a. The full spectrum acquired at 30 °C. Significant peaks are labeled with center wavenumber and, parenthetically, peak area magnitudes relative to the conformation-insensitive reference peak near 1157 cm\(^{-1}\).  
b. the region from 920 cm\(^{-1}\) to 800 cm\(^{-1}\) at various temperatures.

Figure 1. (Continued from the previous page)
Figure 2. High-resolution FTIR absorbance spectra of s-sPP32, reported over various wavenumber ranges and at different temperatures: (a) fully measured spectrum (1300 cm\(^{-1}\) to 800 cm\(^{-1}\)) at 30 °C; (b) 915 cm\(^{-1}\) to 800 cm\(^{-1}\), from 30 °C to 90 °C; (c) 1005 cm\(^{-1}\) to 967.5 cm\(^{-1}\), from 30 °C to 90 °C; (d) 1270 cm\(^{-1}\) to 1150 cm\(^{-1}\), from 30 °C to 90 °C.
c. the region from 1010 cm\(^{-1}\) to 920 cm\(^{-1}\) at various temperatures.

d. the region from 1270 cm\(^{-1}\) to 1010 cm\(^{-1}\) at various temperatures.

In approximately atactic materials (aPP in Fig. 1, s-sPP32 in Fig. 2), the region from 850 cm\(^{-1}\) to 800 cm\(^{-1}\)
Figure 3. High-resolution FTIR absorbance spectra of s-sPP49, reported over various wavenumber ranges and at different temperatures: (a) fully measured spectrum (1300 cm\(^{-1}\) to 800 cm\(^{-1}\)) at 30 °C; (b) 920 cm\(^{-1}\) to 800 cm\(^{-1}\), from 30 °C to 110 °C; (c) 1010 cm\(^{-1}\) to 930 cm\(^{-1}\), from 30 °C to 110 °C; (d) 1270 cm\(^{-1}\) to 1150 cm\(^{-1}\), from 30 °C to 110 °C.
cm$^{-1}$ is dominated by a broad, nearly featureless plateau. Two very weak peaks appear around 828 cm$^{-1}$ and 843 cm$^{-1}$, and have been assigned to planar zigzag and helical chains, respectively, in the interfacial mesophase using rheo-FTIR spectroscopy.$^{44}$ These peaks are understandably weak due to:  

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**Figure 3.** (Continued from the previous page)
Figure 4. High-resolution FTIR absorbance spectra of s-sPP65, reported over various wavenumber ranges and at different temperatures: (a) fully measured spectrum (1300 cm$^{-1}$ to 800 cm$^{-1}$) at 30 °C; (b) 920 cm$^{-1}$ to 800 cm$^{-1}$, from 30 °C to 110 °C; (c) 1010 cm$^{-1}$ to 930 cm$^{-1}$, from 30 °C to 110 °C; (d) 1270 cm$^{-1}$ to 1150 cm$^{-1}$, from 30 °C to 110 °C.
1. Low stereoregularity, and therefore, the inability to form helices and planar zigzags.
2. The complete absence of a crystalline phase (confirmed using X-ray diffraction), and thus, of a crystalline-amorphous interface.
Figure 5. High-resolution FTIR absorbance spectra of s-sPP67, reported over various wavenumber ranges and at different temperatures: (a) fully measured spectrum (1300 cm\(^{-1}\) to 800 cm\(^{-1}\)) at 30 °C; (b) 910 cm\(^{-1}\) to 800 cm\(^{-1}\), from 30 °C to 110 °C; (c) 1010 cm\(^{-1}\) to 930 cm\(^{-1}\), from 30 °C to 110 °C; (d) 1270 cm\(^{-1}\) to 1150 cm\(^{-1}\), from 30 °C to 110 °C.
These peaks remain relatively weak, even for more stereoregular samples (Figs. 3–6). This behavior is curious, especially considering that the strongest mesophase response in IR dichroism (in sPP) occurs at 838 cm$^{-1}$ (a band to which 828 cm$^{-1}$ and 843 cm$^{-1}$ contribute). With increasing
Figure 6. High-resolution FTIR absorbance spectra of sPP, reported over various wavenumber ranges and at different temperatures: (a) fully measured spectrum (1300 cm$^{-1}$ to 800 cm$^{-1}$) at 30 °C; (b) 910 cm$^{-1}$ to 800 cm$^{-1}$, from 30 °C to 150 °C; (c) 1010 cm$^{-1}$ to 930 cm$^{-1}$, from 30 °C to 150 °C; (d) 1270 cm$^{-1}$ to 1150 cm$^{-1}$, from 30 °C to 150 °C.
temperature (Figs. 1b and 2b), these peaks simply decrease in intensity, coalescing into the broad plateau.

Peaks representing crystalline helices ("Form I") appear at 812 cm$^{-1}$ and 867 cm$^{-1}$ as tacticity increases. As temperature increases, these two
peaks decrease in relative intensity and grow broader, as observed in Figures 3b through 6b. Also, the 867 cm\(^{-1}\) peak, which has been characterized as most sensitive to Form I crystals,\(^5^6\) undergoes a wavenumber shift from 867.3 cm\(^{-1}\) to 866.6 cm\(^{-1}\) in Figure 6b. This is a common feature that is observed to some extent in each material. As thermal energy is added, intramolecular and intermolecular forces will be overcome gradually. Thus, less energy is required to excite corresponding vibrational dipoles, and spectral peaks will appear at lesser wavenumbers as thermal energy drives materials toward increasing disorder. This trend does not always hold, however, as will be demonstrated for peaks that split with increasing tacticity.

A weak peak at 898.4 cm\(^{-1}\) in aPP (Fig. 1b) simply diminishes in peak area intensity (from 0.040 to 0.024) with temperature increase. At more moderate levels of stereoregularity (s-sPP32 and s-sPP49), this peak shifts to greater wavenumbers with additional shoulder peaks appearing on either side (e.g., 908.6 cm\(^{-1}\) and 888.8 cm\(^{-1}\) in Fig. 3b). It has been suggested that this “split” of 900 cm\(^{-1}\) is caused by some as yet unidentified, perhaps highly disordered, modification of Form I crystals that is generated only in moderately stereoregular sPP.\(^5^0\) A more thorough

### Table 2. Characteristic Infrared Peak Assignments for Syndiotactic Polypropylene\(^a\)

<table>
<thead>
<tr>
<th>Position (cm(^{-1}))</th>
<th>Vibrational mode(s)(^b)</th>
<th>Morphology</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>812 (\gamma(CH_2))</td>
<td></td>
<td>Helical (crystalline)(^e)</td>
<td></td>
</tr>
<tr>
<td>828 (\nu(C-CH_3))</td>
<td></td>
<td>Planar (mesophase)(^e)</td>
<td>Very weak in absorbance; strong in dichroism(^e)</td>
</tr>
<tr>
<td>843 (\gamma(CH_2))</td>
<td></td>
<td>Helical (mesophase)(^e)</td>
<td>Very weak in absorbance; strong in dichroism(^e)</td>
</tr>
<tr>
<td>867 (\gamma(CH_2))</td>
<td></td>
<td>Helical (crystalline)(^e)</td>
<td>Shoulder(^d) of 900 cm(^{-1})</td>
</tr>
<tr>
<td>889 (\gamma(CH_3))</td>
<td></td>
<td>Amorphous(^d)</td>
<td>Shoulder(^d) of 900 cm(^{-1})</td>
</tr>
<tr>
<td>900 (\gamma(CH_3))</td>
<td></td>
<td>Helical (crystalline)(^d)</td>
<td>Split(^d) from 972 cm(^{-1}); helical population index with 977 cm(^{-1})</td>
</tr>
<tr>
<td>909 (\gamma(CH_3))</td>
<td></td>
<td>Amorphous(^d)</td>
<td>Parent(^d) of 963, 977 cm(^{-1})</td>
</tr>
<tr>
<td>936 (\gamma(CH_3), \gamma(C-C))</td>
<td>Helical (crystalline)(^d)</td>
<td>Split(^d) from 972 cm(^{-1}); helical population index with 963 cm(^{-1})</td>
<td></td>
</tr>
<tr>
<td>963 (\gamma(CH_3), \gamma(C-C))</td>
<td>Planar zigzag (interfacial)(^c)</td>
<td>Parent(^d) of 963, 977 cm(^{-1})</td>
<td></td>
</tr>
<tr>
<td>972 (\gamma(CH_3), \gamma(C-C))</td>
<td>Planar zigzag (interfacial)(^c)</td>
<td>Parent(^d) of 963, 977 cm(^{-1})</td>
<td></td>
</tr>
<tr>
<td>977 (\gamma(CH_3), \gamma(C-C))</td>
<td>Helical (interfacial)(^c)</td>
<td>Parent(^d) of 963, 977 cm(^{-1})</td>
<td></td>
</tr>
<tr>
<td>992–997 (\gamma(CH_3), \gamma(C-C))</td>
<td>Helical (amorphous)(^d)</td>
<td>Parent(^d) of 963, 977 cm(^{-1})</td>
<td></td>
</tr>
<tr>
<td>1005 (\nu(C-CH_3), \gamma(CH_3))</td>
<td>Helical (crystalline)(^e)</td>
<td>Parent(^d) of 963, 977 cm(^{-1})</td>
<td></td>
</tr>
<tr>
<td>1035 (\nu(C-C), \phi(CH_2))</td>
<td>Helical (crystalline)(^d)</td>
<td>Parent(^d) of 963, 977 cm(^{-1})</td>
<td></td>
</tr>
<tr>
<td>1061 (\nu(C-CH_3))</td>
<td>Helical (crystalline)(^d)</td>
<td>Parent(^d) of 963, 977 cm(^{-1})</td>
<td></td>
</tr>
<tr>
<td>1085 (\nu(C-C), \delta(C-H))</td>
<td>Helical (crystalline)(^d)</td>
<td>Parent(^d) of 963, 977 cm(^{-1})</td>
<td></td>
</tr>
<tr>
<td>1131 (\gamma(CH_3), \omega(CH_2))</td>
<td>Planar zigzag (amorphous)(^d)</td>
<td>Parent(^d) of 963, 977 cm(^{-1})</td>
<td></td>
</tr>
<tr>
<td>1153 (\gamma(CH_2), \gamma(CH_3))</td>
<td>Planar zigzag (amorphous)(^d)</td>
<td>Parent(^d) of 963, 977 cm(^{-1})</td>
<td></td>
</tr>
<tr>
<td>1157 (\gamma(CH_3), \gamma(CH_3))</td>
<td>Planar zigzag (amorphous)(^d)</td>
<td>Parent(^d) of 963, 977 cm(^{-1})</td>
<td></td>
</tr>
<tr>
<td>1157 (\nu(C-C))</td>
<td>Non-conformed</td>
<td>Parent(^d) of 963, 977 cm(^{-1})</td>
<td></td>
</tr>
<tr>
<td>1161 (\nu(C-C))</td>
<td>Helical (amorphous)(^d)</td>
<td>Parent(^d) of 963, 977 cm(^{-1})</td>
<td></td>
</tr>
<tr>
<td>1169 (\nu(C-C))</td>
<td>Helical (amorphous)(^d)</td>
<td>Parent(^d) of 963, 977 cm(^{-1})</td>
<td></td>
</tr>
<tr>
<td>1201 (\delta(C-H))</td>
<td>Helical</td>
<td>Parent(^d) of 963, 977 cm(^{-1})</td>
<td></td>
</tr>
<tr>
<td>1201 (\delta(C-H))</td>
<td>Helical</td>
<td>Parent(^d) of 963, 977 cm(^{-1})</td>
<td></td>
</tr>
<tr>
<td>1232 (\delta(C-H), \omega(CH_2))</td>
<td>Planar zigzag +</td>
<td>Parent(^d) of 963, 977 cm(^{-1})</td>
<td></td>
</tr>
<tr>
<td>1232 (\delta(C-H), \omega(CH_2))</td>
<td>Planar zigzag +</td>
<td>Parent(^d) of 963, 977 cm(^{-1})</td>
<td></td>
</tr>
<tr>
<td>1249 (\phi(CH_2))</td>
<td>Amorphous(^d)</td>
<td>Parent(^d) of 963, 977 cm(^{-1})</td>
<td></td>
</tr>
<tr>
<td>1264 (\delta(C-H), \omega(CH_2))</td>
<td>Helical (crystalline)(^d)</td>
<td>Parent(^d) of 963, 977 cm(^{-1})</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Assignment taken from valence force calculations (Ref 54), unless otherwise noted.

\(^b\) Key: \(\gamma = \) rock, \(\nu = \) stretch, \(\phi = \) twist, \(\delta = \) bend, \(\omega = \) wag.

\(^c\) Assignment taken from rheo-FTIR spectroscopy of sPP (Ref 44).

\(^d\) Assignment suggested based on results in vibrational spectroscopic studies (Ref 50 and the present work).
crystallographic analysis is required to compose a more definite picture of what is happening. The fact that the shoulders do not coalesce with the parent peak at 900 cm$^{-1}$ as temperature increases (Fig. 3b) suggests that the shoulders are not formed from true “splitting.” That is, the peaks at 889, 900, and 909 cm$^{-1}$ are distinct, and do not represent sPP chains that participate in a common domain or microstructure, as is the case with peak splitting at 972 cm$^{-1}$ and 1157 cm$^{-1}$.

1010 cm$^{-1}$ to 920 cm$^{-1}$

A weak band appears near 936 cm$^{-1}$ in s-sPP49 (Fig. 3c) and grows slightly more intense with increasing tacticity. This peak behaves very much like 812 cm$^{-1}$ with temperature increase, diminishing in intensity and broadening, but not shifting its position very much. This behavior most likely corresponds to helices found in Form I crystallites. The strong peak near 972 cm$^{-1}$ in aPP (Fig. 1c) does not change much with temperature. Even at high temperatures, this peak shows only a minimal shift from 971.9 cm$^{-1}$ to 971.3 cm$^{-1}$. This peak also increases gradually in magnitude as temperature increases. For s-sPP32 (Fig. 2c), this peak also grows with temperature, but does not shift its position. This is interesting to note since, although both materials are approximately atactic—certainly both are unable to form conformed chains or crystals$^{50}$—the peak appears at a position in s-sPP32 1 cm$^{-1}$ greater than in aPP. Even with similar morphologies, the subtle difference in configurational order (i.e., stereoregularity) between these two materials is detected with FTIR. As discovered previously,$^{50}$ this peak splits into two peaks at 963 cm$^{-1}$ and 978 cm$^{-1}$ as syndiotacticity increases (see Figs. 4a–6a). Rheo-FTIR analysis assigns these bands to planar zigzag and helical chains, respectively, that participate in the crystalline-amorphous interface, which transforms into the planar-rich mesophase, upon application of sufficient tensile strain.$^{46}$ As can be observed in the more stereoregular materials (Figs. 4c–6c), these split peaks do not simply diminish and shift to lesser wavenumbers with temperature increase as do other IR bands. Rather, each peak broadens and changes its intensity to match that of the other. To varying extents in each material, the peaks noticeably shift toward each other, as if coalescing to form the parent peak at 972 cm$^{-1}$. This behavior also agrees well with the assignment of the absorbance ratio of these two split peaks ($A_{978}/A_{963}$) as an index of overall helical content in sPP.$^{37}$ As temperature increases, the value of this ratio steadily decreases, as illustrated in Figure 7. It also appears that tacticity affects the extent to which the split peaks shift as temperature varies. Table 3 lists the extent of shift for both 978 cm$^{-1}$ and 963 cm$^{-1}$ peaks in the three most stereoregular samples. The lesser degree of shifting ob-

![Figure 7](image-url)

**Figure 7.** Ratio of the absorbance at 978 cm$^{-1}$ to the absorbance 963 cm$^{-1}$—indicative of the overall relative population of helical chains to planar zigzag chains—for highly syndiotactic materials as temperature varies.
Table 3. Extent of Temperature-Induced Shifting of the 978 cm\(^{-1}\) and 963 cm\(^{-1}\) Peaks (Split from 972 cm\(^{-1}\)) as a Function of Tacticity

<table>
<thead>
<tr>
<th>Material</th>
<th>Maximum temperature achieved (°C)</th>
<th>978 cm(^{-1}) peak shift (cm(^{-1}))</th>
<th>963 cm(^{-1}) peak shift (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>s-sPP65</td>
<td>110</td>
<td>-1.4</td>
<td>+0.4</td>
</tr>
<tr>
<td>s-sPP67</td>
<td>110</td>
<td>-1.1</td>
<td>+0.7</td>
</tr>
<tr>
<td>sPP</td>
<td>150</td>
<td>-0.6</td>
<td>0.0</td>
</tr>
</tbody>
</table>

served in sPP suggests that conformed chains (certainly helices) are more stable in materials of greater syndiotacticity. This is similar to behavior of the parent 972 cm\(^{-1}\) peak in the approximately atactic materials. The minimal amount of splitting observed in s-sPP49 (Fig. 3c) quickly coalesces into the parent peak at greater temperatures.

The moderately strong peak at 994 cm\(^{-1}\) shows splitting behavior similar to 972 cm\(^{-1}\) for more stereoregular samples, but behaves quite differently at lower stereoregularities. In aPP (Fig. 1c), this peak decreases in intensity and broadens slightly. The same peak, which appears near 997 cm\(^{-1}\) in s-sPP32 (Fig. 2) (again, the more energetic position stemming from configurational order), also decreases in peak area intensity and broadens with increased temperature. However, its center position shifts from 996.9 cm\(^{-1}\) at 30 °C to 995.9 cm\(^{-1}\) at 90 °C. We suggest that this peak shifts to a greater extent in s-sPP32 than in aPP (from 993.9 cm\(^{-1}\) to 993.7 cm\(^{-1}\)) because the helical chains it represents experience a greater loss of order with temperature increase than do the more disordered helices in aPP. Unlike 978 cm\(^{-1}\), which represents interfacial helices and undergoes a lesser degree of wavenumber shift with temperature, this peak most likely represents helices present in amorphous domains. 994 cm\(^{-1}\) does not undergo as pronounced a wavenumber shift in aPP as it does in s-sPP32 (where it appears at 997 cm\(^{-1}\)) simply because it has less conformational order to lose to thermal effects. In s-sPP49 (Fig. 3a), this peak appears to split into two bands centered around 992 cm\(^{-1}\) and 1005 cm\(^{-1}\). For a given temperature, as tacticity increases, the relative intensities of 992 cm\(^{-1}\) and 1005 cm\(^{-1}\) decrease and increase, respectively, until the former peak disappears entirely in sPP (Fig. 6a). This behavior supports a previously proposed assignment of 992 cm\(^{-1}\) and 1005 cm\(^{-1}\) to helical chains present in amorphous and Form I crystalline domains, respectively.

1270 cm\(^{-1}\) to 1010 cm\(^{-1}\)

Several weak bands appear around 1035, 1061, 1085, and 1264 cm\(^{-1}\) in the more stereoregular samples (Figs. 4–6). All four peaks decrease in intensity and shift to lesser wavenumber positions as temperature increases (Figs. 4d–6d). These results help to support the assignment of each band to helices present in Form I crystalline domains. Yet another weak band that grows with stereoregular content appears at 1131 cm\(^{-1}\). While it behaves similarly to the four bands mentioned above, both valence force calculations and rheo-FTIR dichroism experiments confirm that 1131 cm\(^{-1}\) is sensitive to planar zigzag present in amorphous domains.

The principal feature in this range of the spectrum is the strong peak centered near 1157 cm\(^{-1}\). This is the well-characterized conformation-insensitive reference peak of sPP. 1157 cm\(^{-1}\) retains its general shape, with some shifting to lesser wavenumbers as syndiotacticity increases, for all semi-sPP materials (Figs. 1a–5a). This behavior can be explained using the split peaks that appear and surround this reference peak in sPP (Fig. 6a). Valence force calculations clearly place bands sensitive to helical and planar zigzag chains at 1167 cm\(^{-1}\) and 1153 cm\(^{-1}\), respectively (near the observed split peaks). The successively greater populations of nonconformed (1161 cm\(^{-1}\)) and planar zigzag (1153 cm\(^{-1}\)) chains can be described best by assigning all three split peaks (and the parent peak) to chains that are absent from any ordered domain or microstructure (i.e., in amorphous domains). In highly stereoregular sPP, it is intuitive to suggest that the majority of helices are populating either the crystalline–amorphous interface or Form I crystallites. By this reasoning, it is conjectured that amorphous domains contain a greater relative population of planar zigzags than both nonconformed chains (due to the high level of configurational order in sPP) and helical chains (due to their participation in ordered structures). Furthermore, these three peaks exhibit true splitting behavior, as they coalesce completely into the parent peak as temperature increases (Fig. 6d).

The broad, weak peak at 1201 cm\(^{-1}\) remains relatively unchanged with temperature. In fact,
its only significant changes, an intensity increase and shift to greater wavenumbers, accompany an increase in syndiotacticity. This suggests that the horizontal shift of 1201 cm$^{-1}$ may function as a syndiotacticity index because of its low degree of sensitivity to temperature change. Figure 8 illustrates the overall increase in wavenumber position for this peak as tacticity increases. While some decrease in position is observed as tacticity increases, the variance is within the 0.5-cm$^{-1}$ resolution of spectral measurements. The overall position change, however, clearly exceeds this parameter (e.g., 1201.0 cm$^{-1}$ to 1202.8 cm$^{-1}$) at 30 °C. A pair of peaks at 1232 cm$^{-1}$ and 1249 cm$^{-1}$ also seems to function as a good syndiotacticity index. The absorbance ratio, $A_{1232}/A_{1249}$ (Fig. 9), agrees well qualitatively with $^{13}$C-NMR tacticity measurements. The relative intensities of these

![Figure 8](image1.png)

**Figure 8.** Center wavenumber position of peak near 1201 cm$^{-1}$, suggested to be a qualitative index of syndiotacticity, as both tacticity and temperature are varied.

![Figure 9](image2.png)

**Figure 9.** Ratio of the absorbance at 1232 cm$^{-1}$ to the absorbance 1249 cm$^{-1}$—indicative of the overall syndiotactic content in sPP—at different temperatures for lower syndiotactic materials.
Figure 10. DSC thermograms of syndiotactic polypropylene materials (aPP, s-sPP49, s-sPP65, and sPP): (a) heat flow versus temperature. (b) Modulated® thermograms, showing both reversible and irreversible components of heat flow.
peaks change steadily with tacticity until 1232 cm$^{-1}$ is dominant and 1249 cm$^{-1}$ is only a shoulder (in s-sPP65, Fig. 4a). These peaks do undergo a slight shift to lesser wavenumbers as temperature increases, but no greater than 0.6 cm$^{-1}$, observed in aPP (Fig. 1d). This suggests that each is sensitive to some chain conformation; rheo-FTIR firmly assigns 1232 cm$^{-1}$ to amorphous planar zigzags.

Differential scanning calorimetry

Intramolecular forces that hold the dominant population of helical chains in their conformation are progressively overcome as thermal energy is added. This conformational disorder in sPP helical regions has been observed using variable temperature $^{13}$C-CP/MAS NMR, in addition to the aforementioned IR analysis. Modulated DSC thermograms (Fig. 10) illustrate how s-sPP49 and s-sPP65 possess thermal transitions at temperatures intermediate to those observed for transitions in highly atactic and highly syndiotactic materials. The intermediate tacticity materials show two endothermic nonmelting transitions near 50 °C and 70 °C, which are above the glass transition temperature of aPP (near 0 °C) and below the classical melting region observed for crystalline sPP (at 129 °C; see Fig. 10a). The former is attributed to a thermally-driven trans-to-gauche isomerization, causing planar zigzag chains to re-conform as more thermodynamically stable helices. The latter transition is thought to be due to helices that exist in a “dynamically disordered” equilibrium, characterized by rapid trans $\leftrightarrow$ gauche conversion of bond angles along the main chain. The reversing and nonreversing heat flow signals summarized in Figure 10b also support the interpretation that the lower temperature endotherms are due to a thermally driven trans-to-gauche isomerization and the motion of the helices as described above. Note that above the 50 °C and 70 °C endothermic transitions, the nonreversing signal for the highly syndiotactic polymer evolves into the typical exothermic crystal rearrangement/crystal perfection behavior normally observed prior to melting in other slowly ordering semicrystalline materials (e.g., PET). It is also interesting to note that the characteristic absorbance ratio, $A_{978}/A_{963}$ (Fig. 7) decreases in value at an accelerated rate near the two aforementioned transition temperatures. This observation reinforces the assignment of the $A_{978}/A_{963}$ ratio as proportional to the population of Form I helical crystals.

CONCLUSIONS

This work continues the first-ever experimental FTIR investigation of metalloocene-catalyzed semisyndiotactic polypropylenes with a broad range of stereoregular content (26 to 96% rr). With the spectral effects of tacticity characterized and understood, this work examines spectral results for melt-slow-cooled semi-sPP films as temperature is varied. These measurements help to confirm the splitting behavior of 972 cm$^{-1}$ and 1157 cm$^{-1}$ that occurs as syndiotacticity increases. The trend of split peaks to coalesce gradually as temperature increases corresponds nicely to the thermally induced conformation loss of planar zigzags and helices described using Modulated DSC and $^{13}$C-NMR spectroscopy. Also, results suggest that peak behavior around 900 cm$^{-1}$ at moderate syndiotacticity levels is not true peak splitting, due to the lack of thermally driven coalescence. Rather, peaks at 889 cm$^{-1}$ and 909 cm$^{-1}$ are most likely caused by some heretofore-unidentified disordered crystal morph that is able to form at moderate tacticities. New assignments are proposed for peaks at 1201, 1232, and 1249 cm$^{-1}$. These peaks exhibit a much greater sensitivity toward tacticity change than toward temperature change, and are thus suggested to be good qualitative indices of syndiotactic content.

The spectral phenomena observed in our experimental studies thus far—peak area intensity change, broadening, shifting, and splitting—have also been observed in rheo-FTIR linear dichroism measurements. To be sure, a mechanical perturbation imposed on sample films can cause a slight variation in the local environment of vibrational dipole moments, thus causing one or more of the peak behaviors listed above. Having gained more insight into the roles tacticity and temperature play in the IR spectrum of sPP, we now move forward to characterize the anisotropic orientation behavior of these novel semi-sPP materials using rheo-FTIR spectroscopy.

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55. Peak area intensities for the peak near 1157 cm\(^{-1}\) are absolute values.


57. Siedle, A. R. submitted for publication.