An Analysis of Raman Spectra of Syndiotactic Polypropylenes. 2. Configurational Defects

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ABSTRACT: Raman spectra of syndiotactic polypropylenes of different stereoregularity are reported. Spectra for ordered and disordered structures of these polymers were simulated using a small number of parameters. The features that occur in the 300 and 400 cm^{-1} regions can be used to assess chain tacticity. A quantitative determination of the racemic content of polypropylene can be obtained from the Raman spectrum in the range of tacticity studied.

Introduction

Recent advances in catalyst design[1] allow synthesis of polyolefins with different structural defects. This advance in chemistry has raised interest in the study of polyolefin structure. The ability to control configuration precisely allows structural studies of syndiotactic polypropylene (sPP). Few studies have been undertaken to examine the structure of the syndiotactic isomer. Many questions regarding chemical and morphological structure and of the impact of structure on physical properties remain uninvestigated.

Configurational defects can cause significant differences in the crystallization behavior of polymers, reducing the degree of crystallinity and the size of crystallites.[2] NMR is often used to measure the number of configurational defects in individual chains. In this study, we intend to demonstrate the utility of Raman scattering and normal coordinate analysis to characterize the number of configurational defects described by the “syndiotacticity index”. In our laboratory, we are especially interested in the evolution of the ordered phase. This time-dependent process is extremely sensitive to changes in temperature. Many techniques, such as diffraction, can be used to characterize the crystalline phase. There are few techniques capable of characterizing the disordered phase, onset of order, and subsequent morphological evolution. Raman spectroscopy has proven to be particularly useful for studies of this type.[3]

A number of chain conformations and packing exist for syndiotactic polypropylene. The relative volume fraction of each state is highly dependent on thermal history, time, processing, and the type and number of configurational defects. There are at least three different crystalline forms associated with syndiotactic polypropylene. The helical form I, with *ggtt* chain conformation, is the most common.[4,5] Form II with an all trans sequence can be obtained by quenching the polymer from the melt followed by stretching.[5] Form III, with conformational features of both forms I and II, has also been proposed with the conformation $(g_2t_2g_2t_6)_n$.[6−8] It was recently found that the planar zigzag structure forms spontaneously over an extended length of time by quenching from the melt into ice water and storing the polymer at or below 0 °C.[9,10] Form III has also been observed when a drawn sample of form II is exposed to benzene, toluene, or xylene vapor.[6,7] Both forms II and III are stable at room temperature but revert to form I spontaneously with heating. Characterization of disordered structures of syndiotactic polypropylene may be divided into two interrelated analyses. The first deals with the disorder associated with chain conformations different from long regular sequences of *ggtt* or *tttt*, and the second deals with configurational defects, that is, with racemic or meso content.[3] A study in the first area has been reported.[11] We concentrate on the second in the work reported here.

Early spectroscopic studies of syndiotactic polypropylene configurations suggested defining a structural parameter called the “syndiotacticity index”.[12−14] The usefulness of Raman scattering was first demonstrated when the skeletal bending modes in the 300 cm^{-1} region of polypropylene were found to be indicative of chain configuration.[3,15] The broad, ill-defined bands in the 800 cm^{-1} region were also found sensitive to configurational differences and thermal history. These vibrations in the 300−400 cm^{-1} region have previously been assigned as skeletal motions in a number of normal-coordinate analyses.[3,11,16−18] Spectroscopic structural characterization depends on frequency and relative intensity, which depend on the relative concentrations of specific localized structures. For samples involving well-defined structures and dependable band assignments, the method works well. However, when a broad distribution of a large variety of conformations is present, the method is difficult to apply with confidence. Raman spectroscopy is ideal for studies involving disordered structures because the large polarizability changes associated with different carbon−carbon backbone conformations are directly reflected in the spectra.[19,20] Because Raman spectroscopy is a scattering phenomenon associated with a tensor, polarization data contain structural information for samples that are disordered in the melt or in solution.[19]

Unlike ordered chains with well-defined symmetry elements, disordered chains have a large number

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of totally symmetric vibrational modes. It takes considerable effort to simulate Raman spectra for all possible conformations associated with chain disorder. Computer programs such as DCNCA[21,22] have been introduced that attempt to consider structural defects. Instead of treating a specific structure, an ensemble of several thousand different but probable chain conformations is generated using the relative probabilities of the rotational isomeric states. Since the structural parameters and force fields for polyolefins are well-defined, once intensity parameters are included, surprisingly accurate Raman spectra can be generated.[3,17,18,23] The previous study considered syndiotactic polypropylene containing different chain conformations.[11] On the basis of that study, syndiotactic polypropylene's containing a number of different chain configurations were analyzed, and the results are reported here.

Experimental Section

A syndiotactic polypropylene sample containing 92% racemic content was furnished by Fina Oil Corp., Deer Park, TX, and several samples of syndiotactic polypropylene containing from 52 to 75% racemic content were synthesized at 3M. Isotactic polypropylene was purchased from Scientific Polymer Products, Inc., Ontario, NY. These materials were used as received.

Unpolarized Raman spectra of solid polypropylene samples were obtained using a Bruker FRA 106 Fourier transform Raman spectrometer equipped with a Nd:YAG laser that supplied 150 mW of 1064 nm excitation at the sample. Raman spectra were collected at 180°, and the resolution was maintained at 4 cm^{-1}. Any fluorescence these solid samples exhibited was largely suppressed by the use of the long wavelength excitation supplied by the Nd:YAG laser.

Polarized Raman spectra were collected at 90° with a dispersive instrument built around a 1 m *f*/6.8 Jobin-Yvon U-1000 double monochromator equipped with 1800 grooves/mm holographic gratings. Entrance and exit slits were set to constant widths of 210 μm and intermediate slits to twice this value. These mechanical slit width settings give an apparent spectral slit width of 2 cm^{-1} at 514.5 nm produced by a Spectra-Physics 165-08 Ar^+ ion laser adjusted to deliver 100 mW at the sample. The resolution slowly increases to somewhat less than 2 cm^{-1} as the spectrum is scanned. Thus, all dispersive spectra were obtained at resolutions of 2 cm^{-1} or better. A stepper motor controlled by a computer, which also counted and stored pulses delivered to photon counting electronics by the photomultiplier, drove the spectrometer.

A Polaroid filter and quartz polarization scrambler plate mounted before the entrance slit determined the state of polarization of Raman bands in the melt. The polarized and depolarized spectra are used to construct isotropic spectra of the molten phase. A heating cell similar to a Harney-Miller cell was constructed and could be used with both Raman instruments. Heated nitrogen gas was used to heat samples to as high at 190 °C. The isotropic intensity is given by

$$I(\mathrm{iso}) = I_{\|} - \frac{4}{3} I_{\perp} \qquad (1)$$

where $I_{\|}$ contains both isotropic and anisotropic scattering and $I_{\perp}$ contains only the anisotropic part.[24]

Simulation of Raman Spectra

Normal-Coordinate Analysis. Simulation of Raman spectra requires accurate structure, force field, and intensity parameters. Some aspects of a simulation for ordered and conformationally disordered structures of both isotactic and syndiotactic polypropylenes have been described previously.[3,11,25,26] In these simulations, the same bond lengths and valence angles were used for both isotactic and syndiotactic polypropylene. These structural parameters generate structures consistent with the helical parameters found with diffraction data.[17,18] Our studies are based on the analysis of the low-frequency Raman spectrum (below ~600 cm^{-1}) of isotactic polypropylene first carried out by Snyder and co-workers.[16] The force field includes the contribution of hydrogen nuclei omitted in earlier work in order to analyze bands with frequencies above ~600 cm^{-1}. The vibrational force fields for isotactic and syndiotactic polypropylene that are used here were first reported by Snyder[17] and Schachtschneider[18] and have since been confirmed.[23] In addition, the current study validates a set of intensity parameters used in the simulation.

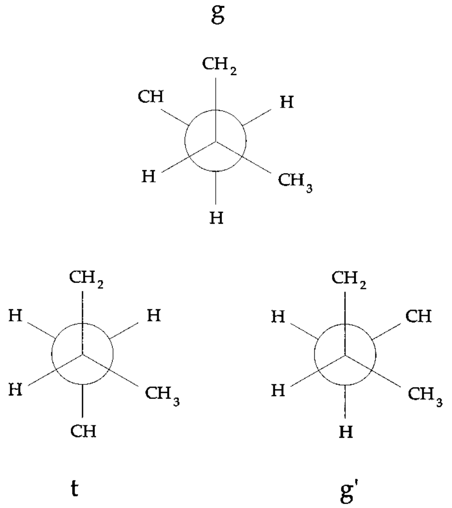

Figure 1. Three-state rotational isomeric state model for syndiotactic polypropylene.

A set of normal-coordinate programs first developed at the University of Michigan[26] was used to analyze ordered structures for both isotactic and syndiotactic polypropylene. These programs are specifically adapted for use with infinite chains which have well-defined chain conformations. Chains of finite length can also be analyzed with this set of programs. The vibrational spectrum of a collection of disordered chains is treated as a superposition of spectra of the individual members of an ensemble of several thousand chains, each with a statistically acceptable conformation.[21,22] The relative energy of each rotameric state was used to generate a conditional probability for each bond along the chain, using first- and second-order interaction rotational isomeric state (RIS) probabilities.

Our model assumes that the bonds can occupy three distinct conformations (trans, gauche, and gauche′: *t*, *g*, and *g*′) as shown in Figure 1.[27] The torsional angles are assumed to be 180° and ±60°. Deviation from these angles was not allowed. This model has also been applied to ethylene−propylene copolymers.[28] The force field used in the calculations was refined to the three-state model. The simplicity and convenience of this three-state model outweigh the possible advantage of higher accuracy associated with a five-state model.[29] For the isotactic and atactic polymer, C_∞ has been accurately calculated using the three-state model.[30]

To apply the rotational isomeric state models to building asymmetric chains, each chiral center must be specified in its *d*-form or *l*-form (Figure 2). On the basis of the conventions of Mattice and Suter[28] for an isotactic polymer in the *d*-form, the appropriate statistical weight-

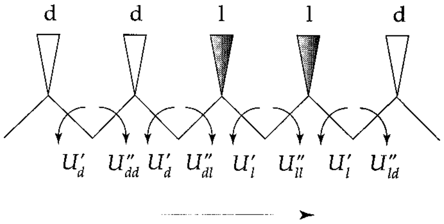

Figure 2. Illustration of both the *d*-form and the *l*-form for a polypropylene stereochemical sequence.

ing matrices are defined as

$$U'_d = \begin{pmatrix} \eta & 1 & \tau \\ \eta & 1 & \tau\omega \\ \eta & \omega & \tau \end{pmatrix} \quad \text{and} \quad U''_{dd} = \begin{pmatrix} \eta\omega'' & \tau\omega' & 1 \\ \eta & \tau\omega' & \omega \\ \eta\omega' & \tau\omega\omega'' & \omega' \end{pmatrix} \tag{2}$$

where η and τ represent first-order interactions dependent only on one bond rotation, and ω, ω', and ω'' represent second-order interactions. η represents the Boltzmann factor for the trans state, with the methyl side group 60° to the backbone, and τ is the Boltzmann factor for both the methyl side group and the backbone carbon at 60° to the backbone. The second-order interactions can be described as the pentane effect, which is the interaction of two atoms separated by four bonds. ω represents the second-order interaction of two backbone carbons, ω' represents the interaction of a backbone carbon with a side methyl, and ω'' represents the interaction between two side methyls.

The *l*-form of the statistical weight matrices for the meso pair is

$$U'_l = QU'_dQ \quad \text{and} \quad U''_{ll} = QU''_{dd}Q \tag{3}$$

where **Q** is the matrix transformation:

$$\mathbf{Q} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \tag{4}$$

which has the property $QQ = I_3$.

The chain conformation partition function for a meso (isotactic) chain is represented by

$$Z_m = J^*(U'_dU''_{dd})^{(n-2)/2}\ J = J^*(U'_lU''_{ll})^{(n-2)/2}J \tag{5}$$

where

$$J^* = [1 \ \ 0 \ \ 0] \quad \text{and} \quad J = \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix}$$

To simulate the random chains, it is necessary to apply the conditional probability matrices for each backbone conformer. Each element of the conditional probability matrix, q_{lm}, is obtained as follows

$$q_{lm} = \frac{J^*(\prod_{i=2}^{j-1} U_i)\tilde{U}_j \prod_{k=j+1}^{n-1} U_kJ}{Z} \tag{6}$$

where $\tilde{U}_j$ is obtained by replacing all the elements of matrix U_j in the partition function Z with zero, except for element u_{lm}, which remains unchanged.

Table 1. Calculated Populations of Most Common Conformers in Syndiotactic Polypropylene Based on the Flory Three-State RIS Model

conformation	expectation	SPP Monte Carlo
tttt	0.263	0.271
ttg′g′ + *ggtt*	0.395	0.385
ttg′t + *tgtt*	0.049	
g′ttt + *tttg*	0.041	
gg′tt + *ttg′g*	0.027	

For the racemic chain, the partition function statistical weight matrix sequence is $U'_dU''_{dl}U'_lU''_{ld}$, where

$$U''_{dl} = \begin{pmatrix} \eta & \omega' & \tau\omega'' \\ \eta\omega' & 1 & \tau\omega \\ \eta\omega'' & \omega & 0 \end{pmatrix} \tag{7}$$

and $U''_{ld} = QU''_{dl}Q$.

It is also desirable to understand what are other less probable conformations present in the disordered state. For syndiotactic polypropylene, we have analyzed combinations of *gg* and *tt* sequences. The primary model compound used was 2,4,6,8,10,12,14,16,18-nonamethylnonadecane $(CH_3{-}CCH_3H){-}(CH_2{-}CCH_3H)_8{-}CH_3$, NMN. This contains eight repeat units and is sufficiently long to achieve statistical accuracy yet small enough to allow simulations to be completed in a timely fashion. A skeletal model of NMN was first used by Hallmark et al.[16] for isotactic polypropylene using a skeletal force field. In addition, to analyze spectral features associated with conformational defects for syndiotactic polypropylene, we have analyzed the form II helical structure of varying length terminated with trans sequences. The total number of chemical repeats in the model structure was kept constant. The most common conformers of syndiotactic polypropylene are summarized in Table 1.

Intensity Considerations. To reproduce accurately the relative intensity of Raman bands, intensity parameters are needed. A number of normal vibrational analyses have used relative intensities, structures, and force fields to simulate successfully the Raman spectra of both syndiotactic and isotactic polypropylenes, and the details will not be repeated here. Aspects of the normal-coordinate analysis directly applicable to syndiotactic polypropylenes of various racemic content are discussed below.

It was first demonstrated by Snyder that it is possible to represent isotropic Raman intensity below ~1000 cm^{-1} by individual contributions of the skeletal components of the modes.[21,22] That study was based on the assumption that a linear combination of the amplitudes of displacement of the individual internal coordinates represented by the eigenvector for each mode is sufficient to represent the isotropic differential polarizability. Therefore, the isotropic scattering activity from this bond polarizability model for mode k can be represented as

$$S_k(\text{iso}) \sim (\sum_i d_iL_{ik})^2 \tag{8}$$

where L_{ik} represents the displacement amplitude of internal coordinate i, and d_i represents the relative contribution of the displacement to the isotropic differential polarizability. The skeletal components for polypropylene would then be the C−C stretch and C−C−C angle bending internal coordinates.[16] Components of the same type are assumed to give approxi-

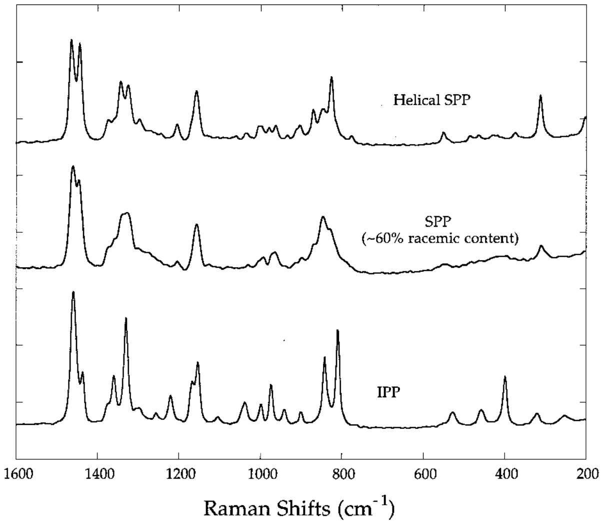

Figure 3. Experimental Raman spectra of helical syndiotactic polypropylene, polypropylene with 60% racemic content, and isotactic polypropylene.

mately the same contribution to the differential polarizability. A more specific relationship for either isotactic or syndiotactic polypropylene is

$$S_k(\text{iso}) \sim (D_R\sum_i L^R_{ik} + D_S\sum_j L^S_{jk} + D_\omega\sum_m L^\omega_{mk} + D_\zeta\sum_n L^\zeta_{nk})^2 \quad (9)$$

where L^R_{ik} and L^ω_{mk} represent the backbone C−C stretch and C−C−C angle bending components, and L^S_{jk} and L^ζ_{nk} represent the side group C−C stretch and C−C−C angle bending components of the eigenvector matrix for the normal mode k. The coefficients D represent the relative contribution to the total intensity of the four types of internal coordinates for a unit amplitude of the respective internal coordinate displacements.

The scattering activity at one frequency is given by

$$S(\nu) = \sum_k S_k(\text{iso}) \quad (10)$$

Equation 3 is then related to the isotropic Raman scattering intensity by

$$I(\nu) = S(\nu)/B(\nu) \quad (11)$$

where $B(\nu)$ is a Boltzmann factor

$$B(\nu) = \nu[1 - \exp(-h\nu/kT)] \quad (12)$$

For isotactic polypropylene, it was determined that $D_R = D_S = 1.0$ and $D_\omega = D_\zeta = D$ ($\sim$0.3).[16] It can be expected that meso (isotactic) and racemic (syndiotactic) structures have dissimilar differential polarizabilities. Consistent with previous studies, the C−C stretching coefficients are chosen as equal ($D_R = D_S = 1.0$). However, it is useful to differentiate between the parameters D_ω and D_ζ.

Results and Discussion

The Raman spectra of all polypropylene samples are shown in Figures 3 and 4. Some vibrations of polypropylenes are associated with differences in chain conformation, packing, or configurational disorder, and it is important to separate these features from one another. The Raman spectra of various crystalline forms of solid syndiotactic and isotactic polypropylene shown in Figure 3 have been reported previously.[3,19] The bands in the 800 and 300 cm^{-1} regions have been used for structural characterization of various polypropylenes.[3,11,15,23] The band at 870 cm^{-1} is assigned to long trans sequences.[10,11] In Figure 5, the experimental data are compared to the calculated spectrum for a *(ggtt)*$_4$ helix expected for an infinitely long syndiotactic polypropylene chain. In this figure, there are several bands typically observed for syndiotactic polypropylene, but only one dominant feature was calculated at 830 cm^{-1}. The Raman spectrum for ordered helical conformation [form I; (*ggtt*)$_4$] of syndiotactic polypropylene is typically characterized by a skeletal deformation band at 826 cm^{-1}. The broad band centered around 845 cm^{-1} is assigned to the amorphous portion. This band is the dominant feature observed for syndiotactic polypropylene in the molten state. The intensity of the band increases with decreasing racemic content, and the ordered bands decrease in intensity as shown in Figure 4A. Furthermore, as the racemic content decreases, the band shifts slightly to lower frequency, reflecting a changing conformational distribution.

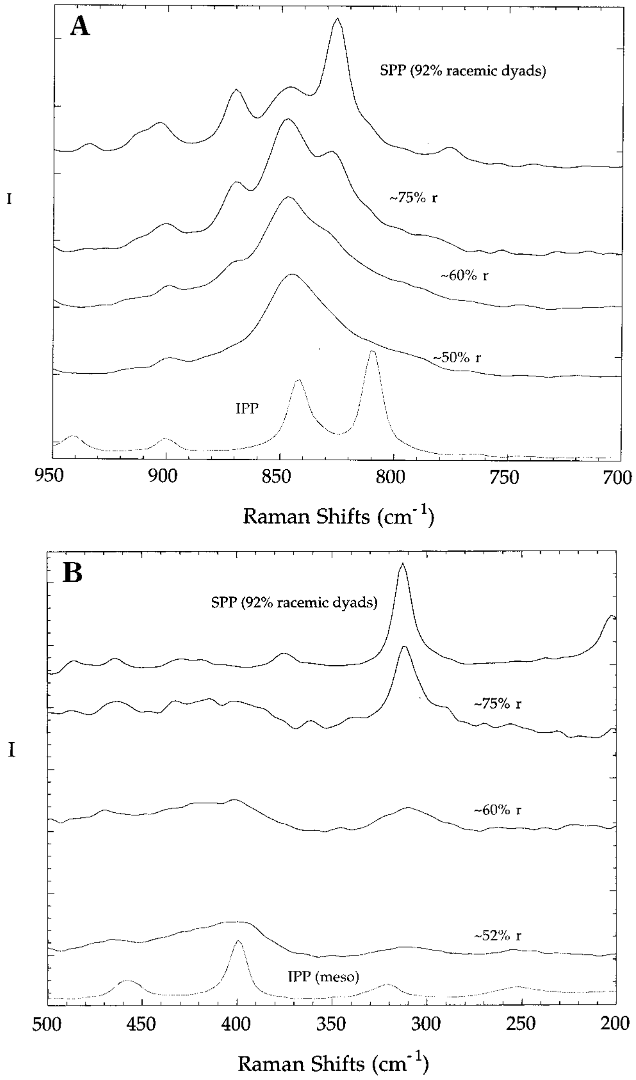

Figure 4. Raman spectra obtained for syndiotactic polypropylene of different stereoregularity: (A) 700−950 cm^{-1}; (B) 200−500 cm^{-1}.

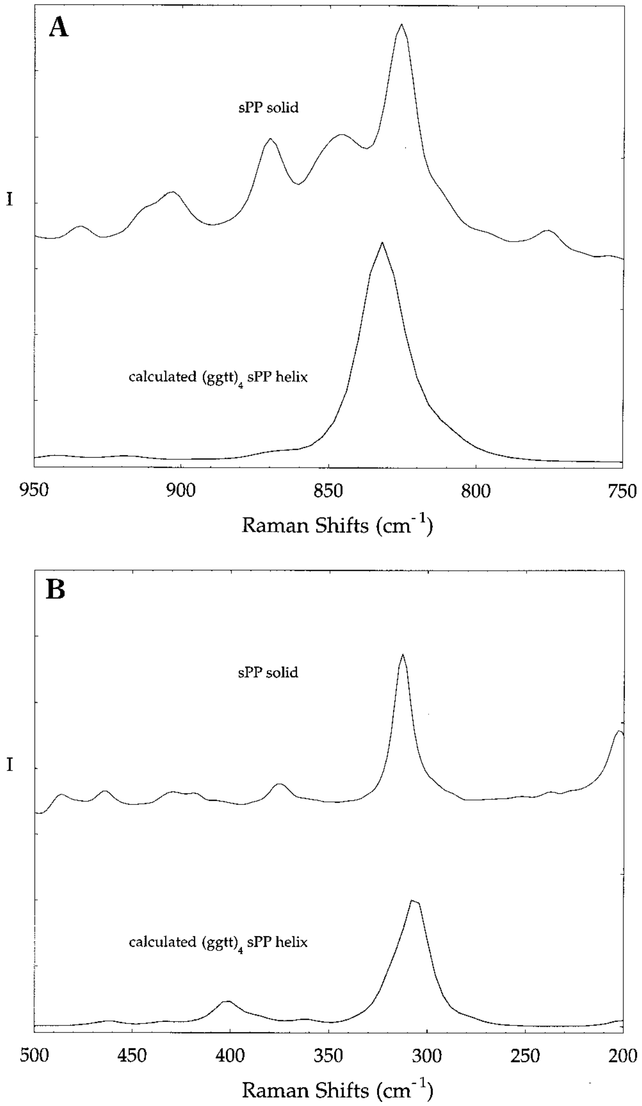

Figure 5. Measured Raman spectrum for solid syndiotactic polypropylene compared with $(ggtt)_4$ calculation: (A) 750−950 cm^{-1}; (B) 200−500 cm^{-1}.

The major bands of crystalline isotactic polypropylene are found at 842 and 809 cm^{-1}. The more intense component is at lower frequency. In the melt, the lower frequency component disappears and a strong broad band appears near 840 cm^{-1}. Because of band overlap, it is impossible to use the bands in the 800 cm^{-1} region to determine racemic content.

In the lower frequency region of the spectrum of syndiotactic polypropylenes, a band of very different nature appears. Figure 4B shows bands sensitive to configurational defects.[15] The 92% racemic sample spectrum shows an ordered helical band centered around 313 cm^{-1}, and the isotactic polymer shows an ordered helical band around 400 cm^{-1}. The presence of the 300 cm^{-1} band in 92% syndiotactic polypropylene is independent of conformational defects, and the band has high intensity. As shown in Figure 4B, as the racemic content decreases, the relative intensity of bands in the 300 cm^{-1} region decrease while a broad band in the 400 cm^{-1} region emerges. This band is found in the Raman spectrum of both crystalline and amorphous syndiotactic polypropylenes. The Raman spectra obtained for syndiotactic polypropylene and isotactic polypropylene in the molten state are shown in Figure 6A,B. Although the bands observed are quite broad, there is no question that the bands found in the 300 and 400 cm^{-1} regions are characteristic of syndiotactic polypropylene and isotactic polypropylene, respectively, even for chains completely lacking in conformational order. In the following it is shown that the 300 cm^{-1} band in syndiotactic polypropylene is independent of chain conformation and only depends on chain configuration, which makes an analysis of tacticity content possible.

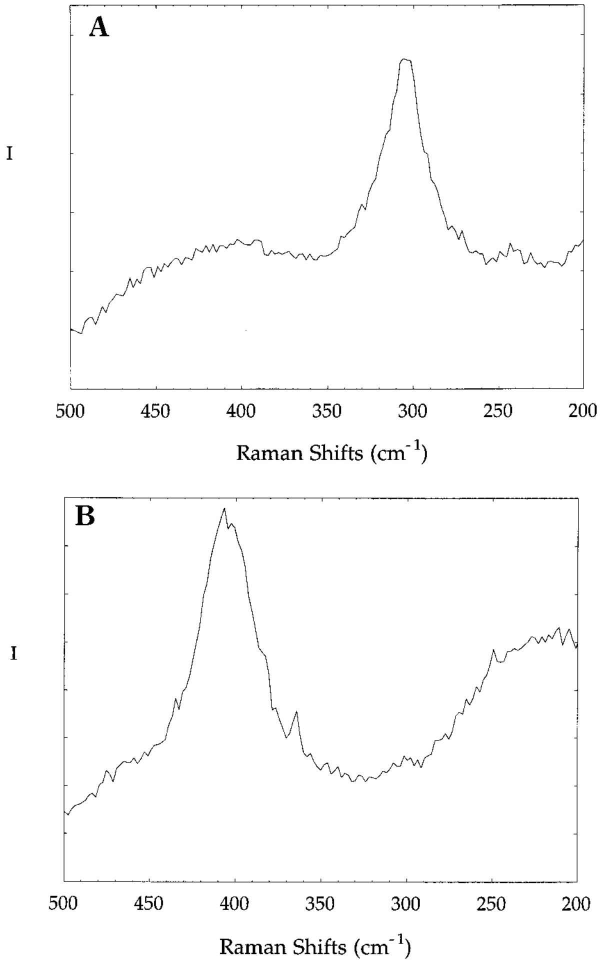

Figure 6. Raman spectrum of molten (A) syndiotactic polypropylene and (B) isotactic polypropylene.

The first step is to demonstrate that the 300 cm^{-1} band is independent of chain conformation. To establish this result, the simulated spectrum for a series of oligomers with *(ggtt)* chain conformation was calculated, since the conformer *(ggtt)* is the most favorable one according to several studies that characterized the conformational energy of syndiotactic polypropylene.[29,31,32] The energy contours reported by these investigators are all essentially the same, giving low-energy minima around the (*gg*) and (*tt*) pairs, with high-energy local minima around (135°, 60°) and (180°, 90°) and their complements.[32] Using normal-coordinate programs dimensioned for finite chains, it is possible to generate two full helical turns with the $(ggtt)_4$ sequence in a chain of 24 chemical repeats. The simulated results are compared with an all-trans simulation for a chain of the same length in Figure 7. The most prominent component calculated lies at about 310 cm^{-1}.

Molecules of various highly probable chain conformations such as $(g_2t_2)_2t_8g_2t_2g_2$, $(g_2t_2)_2t_4(g_2t_2)_2g_2$, or

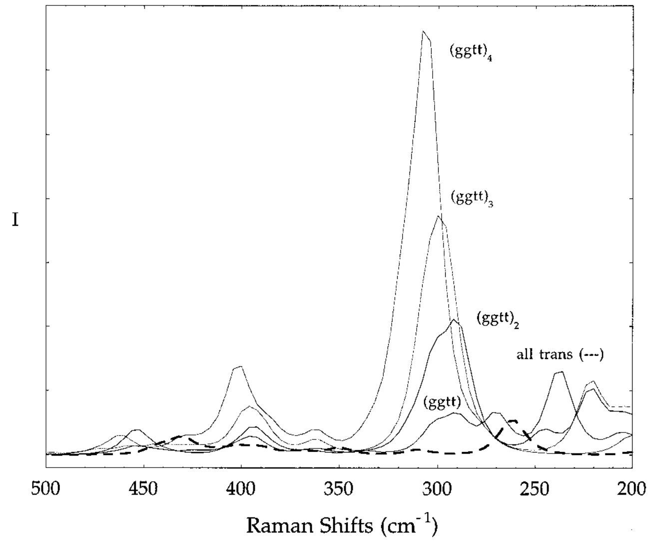

Figure 7. Isotropic Raman calculation for syndiotactic polypropylene for a range of helical lengths.

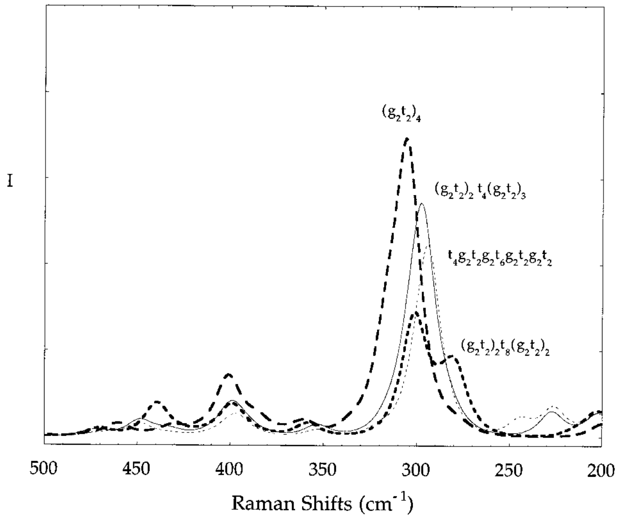

Figure 8. Isotropic Raman calculation for different chain conformations of syndiotactic polypropylene.

$t_4g_2t_2g_2t_6g_2t_2g_2$ which involve some local conformations other than *(ggtt)*$_4$ were then simulated. The calculated spectra for these short chain conformations are shown in Figure 8. As can be seen from the figure, all these chain conformations exhibit substantial intensity in the region around 300 cm^{-1}. As shown in Figures 5B and 6A, this 300 cm^{-1} band is found for both crystalline and amorphous chains. The calculations suggest that even disordered chains, including local chain conformations other than the *ggtt* or *tt* conformations, contribute intensity to this region.

The postulate that the 300 cm^{-1} band is only dependent on chain configuration can be further supported using other model analyses. Chains of different helical length, ranging from $n = 2$ to $n = 4$, were inserted with all trans segments while maintaining the total number of repeats at 24. The result of this calculation is shown in Figure 8. Although the simulated frequencies differ slightly, the bands cluster near 300 cm^{-1}. This calculation also suggests that the frequency of the 300 cm^{-1} band depends on chain length, as it varies from ~290 cm^{-1} for a short helix to ~310 cm^{-1} for a long helix. All syndiotactic polypropylene samples studied have a band at ~310 cm^{-1}. The minimum sequence length needed to display intensity around 300 cm^{-1} is either (*ggtt*) or (*ggtt*)$_2$. This calculation strongly supports the independence of the 300 cm^{-1} band of syndiotactic polypropylene chain conformation and suggests that it only depend on chain configuration.

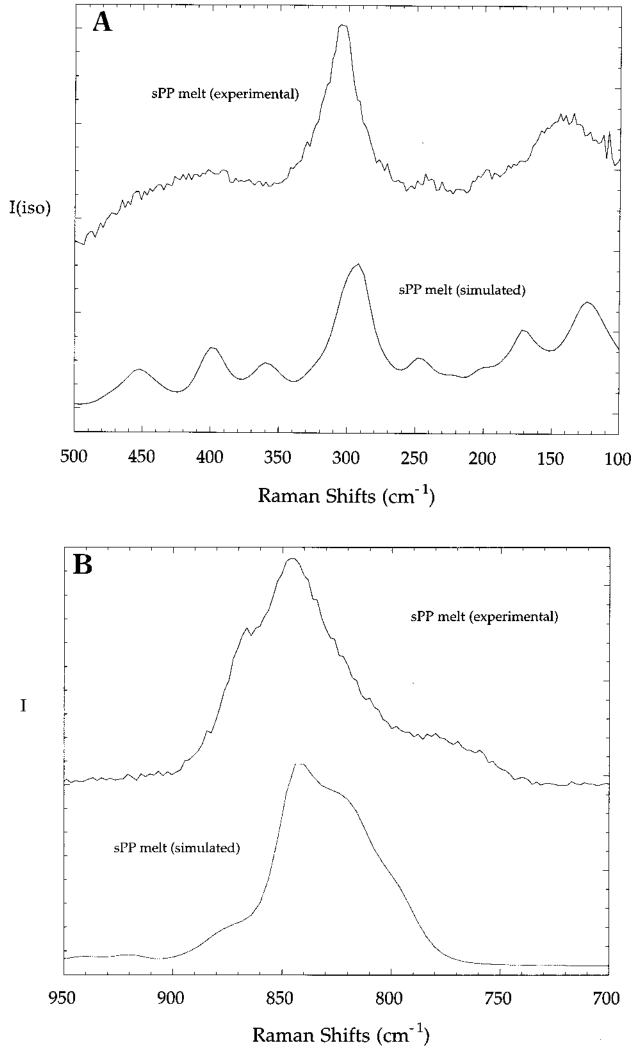

Figure 9. Observed Raman spectrum of syndiotactic polypropylene melt compared with syndiotactic polypropylene melt calculation using an ensemble of 2000 randomized chains: (A) 100−500 cm^{-1}; (B) 700−950 cm^{-1}.

The spectrum of a statistical ensemble of chain conformations was calculated next. The most commonly occurring rotational isomeric sequences in syndiotactic polypropylene are collected in Table 1, calculated using the relative energies and transition probabilities required by the Flory three-state rotational isomeric state theory. These results suggest that in the melt about 39% of the sequences be of the form *(ggtt)* or *(ttg′g′)*. The simulated spectrum of molten syndiotactic polypropylene was then calculated as a composite of simulated spectra calculated for each of 2000 randomly generated isomers of the polymer, each multiplied by its probability of occurrence.

The isotropic Raman spectrum of molten syndiotactic polypropylene is directly compared with a simulated spectrum in Figure 9. The simulated spectrum for the molten phase of syndiotactic polypropylene agrees well with the observed from frequency, bandwidth, and relative intensity considerations. Spectroscopic features of syndiotactic polypropylene below 500 cm^{-1} are sig-

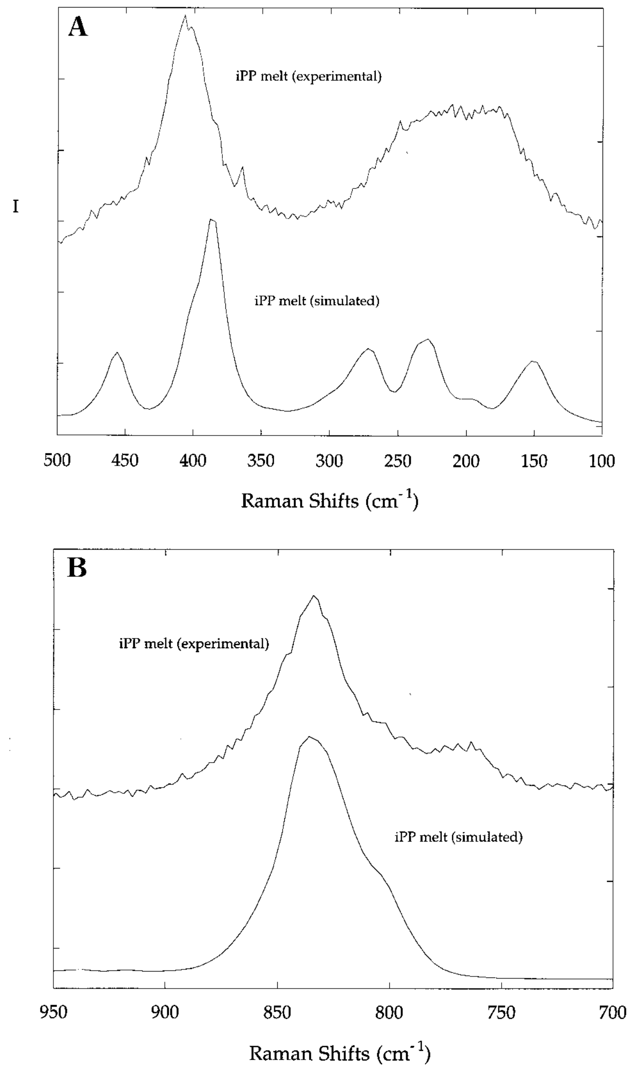

Figure 10. Observed Raman spectrum of isotactic polypropylene melt compared with isotactic polypropylene melt calculation using an ensemble of 2000 randomized chains: (A) 100−500 cm^{-1}; (B) 700−950 cm^{-1}.

nificantly different from those of isotactic polypropylene shown in Figure 10 in both the solid and the melt. The major difference is the presence of the band around 400 cm^{-1} in the isotactic polymer and the band around 300 cm^{-1} for the syndiotactic polymer, bands that are reproduced in the calculations. For syndiotactic polypropylene melt, the major peak around 305 cm^{-1} is represented by the calculation around 292 cm^{-1}, and the broad bands around 400 cm^{-1} and below 200 cm^{-1} are represented by multiple small peaks in the calculated spectrum. The spectra of both ordered and disordered isotactic polypropylene chains have been extensively discussed previously.[3,16,17] The main features calculated below 500 cm^{-1} are given in Figure 10. It is encouraging that the major components, including the bands characteristic of tacticity, are well reproduced for both syndiotactic polypropylene and isotactic polypropylene melt, although the frequency can deviate somewhat.

The slight variation in frequency of the 300 cm^{-1} band is suggestive of conformational order along the chain. For syndiotactic polypropylene samples of high crystallinity, the 300 cm^{-1} band is located in the upper region of the calculated range and is associated with a straight helical length of no fewer than 4 (*ggtt*) sequences. On the basis of the calculated trends shown in Figure 9,

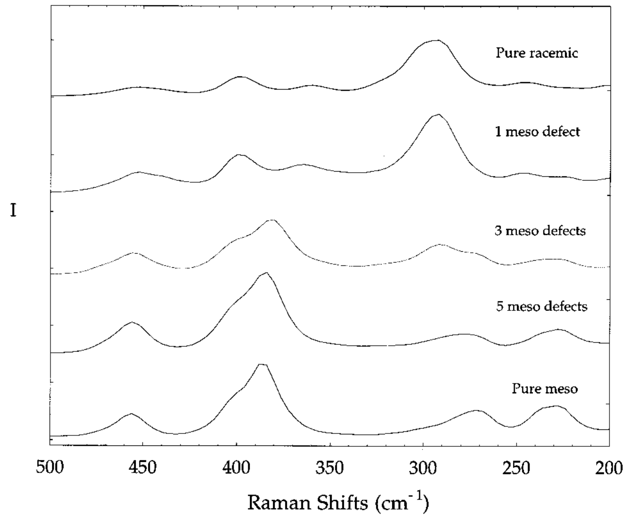

Figure 11. Calculated isotropic Raman spectra for a range of meso defects inserted into pure racemic chain.

when conformational disorder occurs, the band should decrease in frequency. In fact, at elevated temperatures this band does shift and is located at 307 cm^{-1} in the molten phase of syndiotactic polypropylene. In the simulation studies, we also observed strong intensity dependence on conformational order along the chain. When the helix reaches four repeats, the most intense band is calculated at 310 cm^{-1}, the frequency expected for the infinite chain. This suggests that the frequency and intensity of this polarized band are not only characteristic of the syndiotactic isomer but also can be indicative of the regularity in chain conformation.

The side group angle bending polarizability parameter (D) has little effect on the simulated relative intensity for the racemic chain, for D close to zero. The molten spectra for isotactic polypropylene have been extensively discussed previously.[16] In that case, the intensity parameters were chosen to match the parameters used by Snyder and co-workers.[16] Our analysis shows that this intensity parameter does not influence significantly the relative intensity of the skeletal modes.

To analyze the changing spectra associated with syndiotactic polypropylenes of different racemic content, the following calculation was made for model compounds with different defect populations. The simulated spectra for a model containing two, three, or five meso defects in the middle of the chain and a pure meso chain are shown in Figure 11. As seen in experiment, the disruption of chain configuration can cause significant changes in the Raman-active skeletal modes. This is well reproduced by the simulation experiment.

Below 500 cm^{-1}, the spectroscopic features are comparable to the measured spectra in the same region. Specifically, as the configuration progresses from mainly racemic to mainly meso, the intensity around 300 cm^{-1} decreases as intensity around 400 cm^{-1} increases. A quantitative comparison of both the calculated and experimental data was attempted by integrating all the bands between 350 and 500 cm^{-1}, integrating all the bands between 250 and 350 cm^{-1}, and taking the ratio of the integrated intensities (I_{400}/I_{300}). As Figure 12 shows, all the undeformed solid samples fall close to the line for racemic content. Typical errors are around 2−6%. Even the isotropic Raman spectrum of the syndiotactic melt falls close to the calculated line. The essentially atactic sample falls slightly below the line.

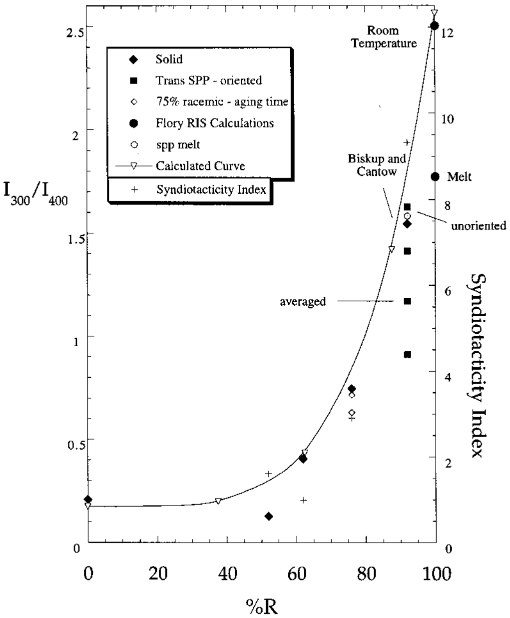

Figure 12. Ratio of intensities I_{300}/I_{400} (racemic/meso) against percent racemic content compared with the syndiotacticity index (SI).

However, this is not surprising since the model assumes that the features dominating the spectrum arise from having all the defects in blocks. The only sample that markedly deviates from the calculated intensity ratio curve is the 92% racemic sample that was stretched to induce the zigzag structure. This deviation is consistent with the simulated spectrum of the zigzag structure, in which intensity around 300 cm^{-1} is suppressed relative to the 400 cm^{-1} intensity region. The syndiotacticity index described by Boor et al.[14] was also measured for the racemic samples using attenuated total reflectance infrared spectroscopy. The results are scaled to best match the configuration curve for the simulated intensities. Our results suggest that tacticity determinations using Raman features are as accurate as infrared or NMR determinations.

Conclusions

It is possible to simulate the Raman spectrum of polypropylenes with different configurations. Both isotactic and syndiotactic ordered structure spectra may be simulated. The principal conformationally independent features occur in the 800 and 300−400 cm^{-1} regions. The intensity is dependent on the chain length for short sequences. This does not seem to be a significant issue for representing disordered chains. A quantitative representation of the configuration can be obtained from the Raman spectrum in the range studied. These observations are not dependent on the sample thermal history. The characteristic band of syndiotactic polypropylene around 300 cm^{-1} shifts slightly to higher frequency with increasing helix length. This observation is consistent with the frequency shift observed on going from the melt to the solid state. The combination of conformational mappings, analysis of the conformation distributions, and ordered band simulations is a useful tool for characterizing the Raman spectroscopic features. It can be used to characterize the configuration for polypropylenes, at least in the range studied here. Further, the tool makes possible a quantitative determination of the major conformations observed in the amorphous state.

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