

An analysis of the Raman spectrum of syndiotactic polypropylene.

1. Conformational defects

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Abstract

Spectroscopic features in the Raman spectrum of both crystalline and amorphous syndiotactic polypropylenes are reported which characterize different chain conformations. A normal coordinate analysis was conducted to assist in identifying conformationally sensitive bands in the experimental spectra. Based on a force field transferred from smaller molecules, and on a rotational isomeric state model, the conformational distribution associated with the amorphous phase is obtained. Changes in the spectrum due to sample deformation are identified. In the calculation of simulated Raman spectra, only two polarizability parameters associated with C–C stretching and C–C–C angle bending were needed to duplicate the spectroscopic features observed. Conformationally sensitive bands occur in the 300 and 800 cm⁻¹ regions. The bands at 865, 845 and 826 cm⁻¹ are assigned to all-*trans* (*tttt*), amorphous and helical (*ggtt*) structures in syndiotactic polypropylene. The band near 300 cm⁻¹ shifts from 290 cm⁻¹ for a short helix to 310 cm⁻¹ for a long helix, and is highly dependent on chain configuration. These features have been correlated with changing chain conformation distributions. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Recent developments in catalyst design have allowed synthesis of highly-ordered polyolefins with few defects and control of the defect distribution [1]. These advances in polyolefin chemistry have enhanced interest in the study of polyolefin structure and in the development of diverse applications. The ability to control configuration has sparked interest in structural studies of syndiotactic polypropylene. Isotactic polypropylene is one of the most frequently used polymers and is well studied, but the properties of syndiotactic polypropylene are not as well known. Far fewer structural studies have been undertaken of the syndiotactic isomer than of the isotactic. Doubtless, many of the properties of syndiotactic polypropylene remain to be discovered.

Syndiotactic polypropylene crystallizes in at least three different forms. Helical form I, with iterated *ggtt* chain conformation is the most common [2,3]. Form II has an all-*trans* sequence that can be obtained by quenching the

polymer from the melt and then stretching [3]. The conformations of forms I and II are shown schematically in Fig. 1, and were recently confirmed and refined [4–13]. Form III (conformation $(g_2t_2g_2t_6)_n$) assumes some of the conformational features of both forms I and II, and has been proposed recently [14–16]. It was recently found that the planar zigzag structure forms spontaneously over an extended length of time by quenching from melt into ice water and then storing at or below 0°C [17,18]. Form III has also been observed when a drawn sample of form II is exposed to benzene, toluene or xylene vapor [14,15]. Forms II and III are metastable at room temperature, and revert to form I spontaneously on heating. The richness in the number of seemingly stable chain conformations of syndiotactic polypropylene is intriguing. The relative volume fraction of each of the aggregation states is highly dependent on the thermal history, time, and processing conditions, and in many cases, on the type and number of configurational defects.

The degree of crystallinity, size of crystallites, and their interconnectivity are crucial parameters in the consideration of phenomenological models of deformation. Therefore, it is important to characterize the various morphological units

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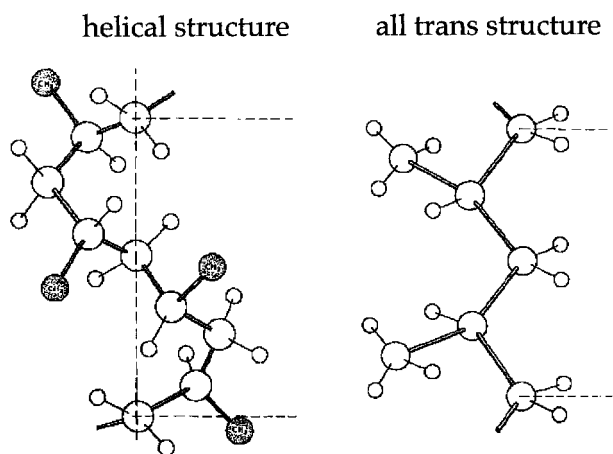


Fig. 1. Primary chain conformations associated with syndiotactic polypropylene.

both ordered and disordered. Most structural characterization studies have employed diffraction methods, and these have yielded considerable insight into structures with long-range order. However, there is little information regarding one crucial part of polypropylene morphology, namely, the amorphous phase. This is particularly important since the degree of crystallinity of polypropylenes is usually not high. It is well established that the presence of even a small number of configurational defects can significantly decrease the degree of crystallinity and crystallite size [19]. These facts suggest that characterization of disordered structures of syndiotactic polypropylenes may be divided into two separate types of analysis. One deals with the disorders associated with chain conformation. The other deals with configurational defects. In the work described here, only conformational order is considered.

Localized polymer structures can be measured by infrared spectroscopy, by ^{13}C NMR spectroscopy and by Raman spectroscopy. Additionally, isotropic Raman spectra can be simulated by a minimal normal coordinate analysis of a statistical ensemble of calculated polymer conformations. The earliest method used to characterize the configuration in fact was infrared spectroscopy resulting in the structural parameter referred as “syndiotacticity index” [20–22]. Configuration and its distribution studies were carried out with ^{13}C NMR [23]. It is also possible to characterize chain conformations present and their distribution using NMR. However, substantial sample preparations and long measurement times were needed to obtain sufficient signal-to-noise for analysis. In addition, the amorphous conformational features could not be completely separated from the crystalline features by NMR, except at high temperatures. More recently, a number of infrared spectroscopic analyses have been carried out for the elucidation of syndiotactic polypropylene structures [24–26]. In our laboratory, we have concentrated on Raman studies. The usefulness of Raman spectroscopy was first shown when the skeletal bending modes in the low frequency Raman

spectra of polypropylenes were found sensitive enough to differentiate between racemic (syndiotactic) and meso (isotactic) sequences in characterizing the overall chain configuration [27]. The band around 400 cm^{-1} in isotactic polypropylene was observed both in the melt and in the solid, and likewise the band around 300 cm^{-1} in syndiotactic polypropylene was present both in the melt and in the solid. These authors suggested that these bands are dependent on sample tacticity and might be persistent due to the presence of trapped helical structure in the molten state. But later work noted that the broad ill-defined bands in these regions are extremely sensitive to differences in configuration and that these bands change as a function of thermal history. These differences suggest that structures in various syndiotactic polypropylenes are complex and include at least all the various known chain conformations.

Vibrational spectroscopy exhibits particular sensitivity for the measurement of localized polymer structures. Raman spectroscopy allows analysis of extremely small samples, permits measurement of individual segmental orientation, and provides descriptions of the entire conformational distribution in both ordered and disordered structures. Experimental Raman spectra of polymeric species have been compared with computed simulations of isotropic Raman spectra that describe an ensemble of conformational distributions even in the absence of long-range order [28–32]. Spectra of polymers in the solid state and in the melt have been successfully simulated both for linear chains and crosslinked ones [28–32]. Considerable interest attaches to using Raman spectroscopy to follow the structural changes during deformation of polypropylenes.

In the work reported here, simulated Raman spectra for both ordered and disordered structures were generated utilizing computer program that uses four different input parameters to generate disordered states. First, a model oligomer of sufficient length is needed to represent the polymer adequately; second, a suitable vibrational force field is needed to execute the normal coordinate analysis and obtain characteristic frequencies; third, intensity parameters need to be introduced; and fourth, Monte Carlo simulation of an ensemble of disordered chains is necessary to generate a conformation distribution that is representative of the disordered state. Both the structural parameters and force fields were transferred from previous studies [33–35]. The chain conformational distribution can be generated by using the rotational isomeric states (RIS) generated in earlier work [36–38]. The energy contours calculated in previous experimental and theoretical studies have yielded low energy minima around the *gg* and *tt* pairs. Lastly, only two intensity parameters are needed to generate the isotropic Raman spectra for syndiotactic polypropylenes containing various configurations and conformations. In the work reported here, the analysis is described. It is also indicated how the results can be used for structural characterization of syndiotactic polypropylenes of different thermal histories.

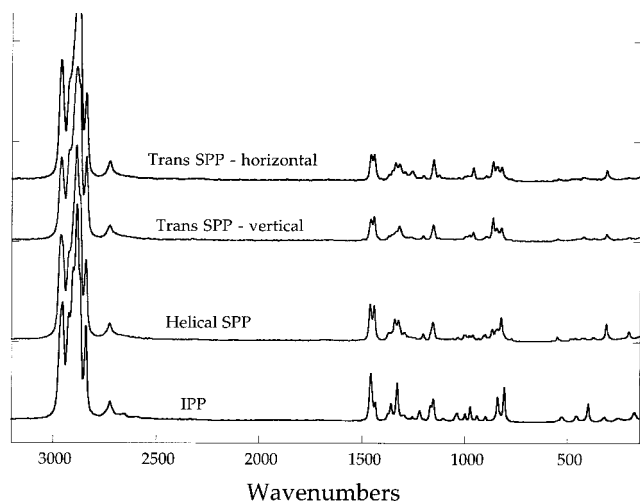


Fig. 2. Raman spectra obtained for syndiotactic and isotactic polypropylenes; horizontal and vertical refers to the orientation of the deformation axis relative to the laser polarization.

2. Experimental section

A syndiotactic polypropylene sample with 92% racemic content was obtained from Fina Chemical. Several samples containing 52–75% racemic content were supplied by 3M Company, St. Paul, MN. Isotactic polypropylene was purchased from Scientific Polymer Products, Inc., Ontario, NY. To prepare a syndiotactic polypropylene sample containing mostly *trans* conformation, the sample from Fina Chemical was heated to 180°C under N₂ gas. The molten sample was maintained at elevated temperatures for 10 min., then quenched in ice water. This sample was subsequently drawn at room temperature to a draw ratio of 5.

Dispersive Raman spectra were obtained using an Instruments SA U-1000 double monochromator equipped with a thermoelectrically cooled RCA C31034A photomultiplier and photon counting electronics. A Spectra Physics Model 164-08 Ar⁺ ion laser oscillating on the 5145 Å green line provided Raman excitation. Spectrometer drive and data acquisition electronics were interfaced with a small personal computer used for data collection and storage. The laser power at the sample was 100 mW and the slit width was set to give a spectral resolution of 2 cm⁻¹ at the exciting line. For these measurements, 90° scattering geometry was used. In order to minimize fluorescence associated with solid isotactic or syndiotactic polypropylene samples, some Raman spectra were obtained using a Bruker Fourier transform Raman spectrometer (model FRA 106). This instrument achieved substantial reduction in fluorescence due to the use of a 1064 nm Nd:Yag laser for excitation of Raman scattering. The collection geometry was 180° and the resolution was set at 4 cm⁻¹ throughout the spectrum. Laser power at the sample was 150 mW in these experiments. Several heating cells were built to be used with both Raman instruments. Heated nitrogen gas was

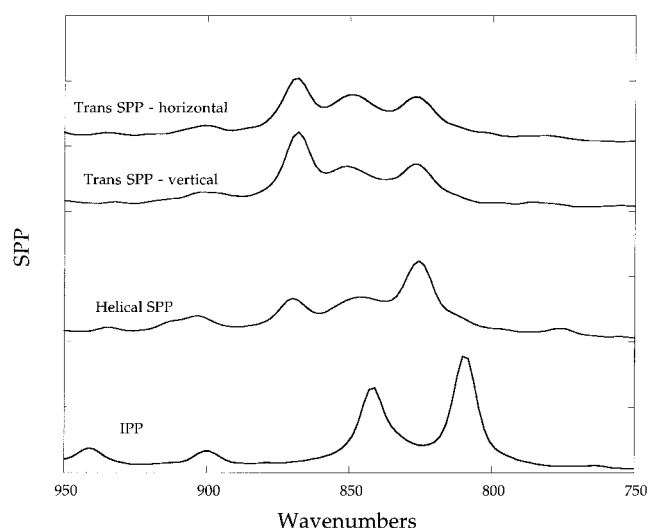


Fig. 3. Raman spectra obtained for syndiotactic and isotactic polypropylenes in the 800 cm⁻¹ region; horizontal and vertical refers to the orientation of the deformation axis relative to the laser polarization.

used in these cells to heat samples to 190°C, allowing Raman spectra to be obtained in the molten state. The Raman spectrum (uncorrected relative intensity) of a mostly syndiotactic polypropylene (Fina sample) in helical form I and all-*trans* form II and of isotactic polypropylene is shown in Fig. 2. Bands in the 800 and 300–400 cm⁻¹ regions are shown in greater detail in Figs. 3 and 4, respectively.

3. Theoretical normal coordinate analysis

3.1. Structural aspects

3.1.1. Ordered chains

In all 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 [33,34]. A set of normal coordinate programs first developed at the University of Michigan [39] 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. Infinite chains considered include 3₁ helix for the isotactic isomer and both the *ggtt* helix and the all-*trans* structure for the syndiotactic isomer. Conformational defects may involve well-defined chain conformations extending over only a finite number of chemical repeats. In order 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 at 11 chemical repeat units.

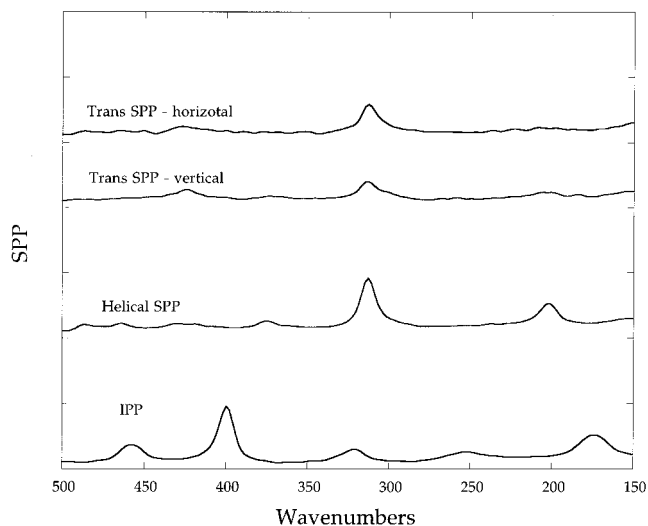


Fig. 4. Raman spectra obtained for syndiotactic and isotactic polypropylenes in the 400 cm^{-1} region; horizontal and vertical refers to the orientation of the deformation axis relative to the laser polarization.

3.1.2. Disordered chains

Rather than analyzing one specific chain conformation, the analysis of disordered chains requires the analysis of the vibrational spectrum of an ensemble of chains with randomized conformational content. This problem is complex, even in relatively short chains. In order to treat polymers lacking long-range order, an approximate method was developed [40]. The isotropic Raman spectrum $S(\nu)$ for the disordered state was simulated as a composite of contributions from an ensemble of chains generated by a *Monte Carlo* procedure that assigned both a conformation and a

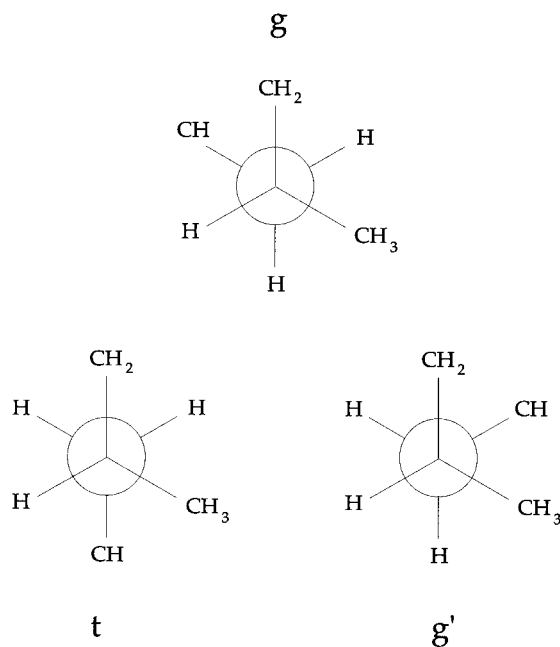


Fig. 5. Rotational isomeric units associated with syndiotactic polypropylenes.

corresponding probability of occurrence for each chain. 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 RIS probabilities. The spectrum of each conformation generated was calculated from force constant and intensity data transferred from smaller molecules. These individual data spectra were then weighted by the probability of occurrence of the chain and combined into a composite spectrum. With a small number of structural and intensity parameters, it has been possible in this way to reproduce experimental IR and Raman spectra of some *n*-alkanes surprisingly accurately [40–43]. The same method has been applied to more complicated polymers lacking long-range order [44]. The original code was designed for *n*-alkanes. Program modifications were later introduced that allowed non-equivalent bonds along the chain [28,44].

Typically, an ensemble of 2000 chains was used, generated at random as described above. This model assumes that the bonds can occupy three distinct conformations (*trans*, *gauche*, and *gauche'* — *t*, *g*, *g'*) as shown in Fig. 5 [45]. These torsional angles are assumed to be 180° , and $\pm 60^\circ$. This model has also been applied to ethylene–propylene copolymers [46]. The force field used in the calculations was refined to the three-state model. The simplicity and convenience of this three-state model outweighs the possible advantage of higher accuracy associated with the five-state model [37]. For the isotactic and atactic polymer, C_∞ has been accurately calculated using the three-state model [47]. The model compound, 2,4,6,8,10,12,14,16,18-nona-methylnonadecane $(\text{CH}_3\text{--CCH}_3\text{H})\text{--}(\text{CH}_2\text{--CCH}_3\text{H})_8\text{--CH}_3$, containing 8 repeat units, is sufficiently long to achieve statistical accuracy, yet small enough to allow simulations to be completed in a timely fashion. The statistical weight matrices and the generation of conditional probability of each bond along the chain follow the procedure first presented by Flory [48].

3.1.3. Force field

A requisite for accurate normal coordinate analysis is the availability of a reliable force field. In general, only intramolecular potential energies are needed. The vibrational force field parameters used were specifically optimized for the three backbone torsional angles that are associated with the three-state model. The force constants were originally derived from smaller molecules and have been successfully used to calculate vibrational spectra of both isotactic and syndiotactic polypropylenes [27,33,34,49,50].

3.1.4. Intensity parameters

It has recently been shown that only very few parameters are needed to calculate the isotropic Raman scattering intensities below $\sim 1000\text{ cm}^{-1}$ [40,41,51]. Additivity in bond polarizability is always assumed. The isotropic scattering

activity for mode k can be represented as:

$$S_k(\text{iso}) \sim \left(\sum_i d_i L_{ik} \right)^2 \quad (1)$$

where L_{ik} is the internal coordinate displacement amplitude of component i for eigenvector L_k , and d_i represents the mean polarizability derivative for internal coordinate i . The summation in Eq. (1) is a representation of the polarizability derivative, described in terms of the internal coordinates. The most important derivatives for n -alkanes are associated with C–C stretch and C–C–C angle bending internal coordinates [43]. These derivatives were applied to isotactic polypropylene [42].

$$S_k(\text{iso}) \sim \left(D_R \sum_i L_{ik}^R + D_S \sum_j L_{jk}^S + D_\omega \sum_m L_{mk}^\omega + D_\zeta \sum_n L_{nk}^\zeta \right)^2 \quad (2)$$

where the elements of the eigenvector matrix, L_{ik}^R and L_{mk}^ω , represent the backbone C–C stretch and C–C–C angle bending components, and L_{jk}^S and L_{nk}^ζ represent the C–C stretch and C–C–C angle bending components containing the methyl side groups for the normal mode k . The D coefficients represent the relative contribution to the total intensity of the four types of internal coordinates, and $D_R \approx D_S$ and $D_\omega \approx D_\zeta$. In n -alkanes the ratio of the bend to the stretch D 's is 0.295 [40]. Additional complexity is found for vinyl polymers when C–C bonds of the side group may need to be considered. Backbone and side group intensity contributions were not differentiated for isotactic polypropylene [42], but this can depend on polymer tacticity [52]. We have evaluated the relative magnitude of the intensity parameter associated with the side group angle bending polarizability parameter (D). From our analysis, it was found that this parameter has little effect on the simulated relative intensity for the racemic chain, for D close to zero. Therefore the intensity parameters in our calculation in fact are identical to the parameters developed earlier for isotactic polypropylene [42].

4. Results and discussion

Raman spectra obtained for polypropylenes with different conformational distributions can be simulated accurately in order to characterize morphology development. The identification of specific features, such as those in the 800 and 400 cm^{-1} regions, allow changes of polypropylene from a completely disordered state to a more ordered one to be followed. Secure assignment of spectroscopic features also allows the onset of disorder at elevated temperatures to be dependably characterized. The structure of syndiotactic polypropylene is capable of significant change as a function of time [17]. Time-dependent issues are important in evaluation of the effect of morphology changes on deformation behavior in polypropylenes. Skeletal deformation

modes are extremely useful in providing information regarding both the chemical and physical structures of syndiotactic polypropylenes.

Raman spectra obtained from syndiotactic polypropylenes with different thermal histories generally exhibit similar features except for the skeletal deformation bands in the 400 and 800 cm^{-1} regions. These bands have been related to the stereoregularity of the samples [27]. Although the changing features in the spectra generally are associated with differences in chain conformation, these same features may also be dependent on differences in configurational disorder since a few defects along the chain can significantly influence the crystallization behavior [19]. It is important to separate features strictly dependent on configurational differences from those due to purely conformational differences.

There are three bands found in the 800 cm^{-1} region at 865, 845 and 826 cm^{-1} that have been designated as “regularity” bands but have never been accurately assigned. It has been suggested that the band at approximately 826 cm^{-1} is characteristic of form I (helical) syndiotactic polypropylene [27,35]. The broad band centered around 845 cm^{-1} has been assigned to amorphous polypropylene [35], and is the dominant feature observed in this region in the spectrum of polypropylene melt. The ordered bands at 826 and 865 cm^{-1} decrease in intensity relative to the composite amorphous band at 845 cm^{-1} and the peak position of the amorphous band shifts slightly to lower frequency as conformational order decreases.

The 826 and 845 cm^{-1} bands can be assigned based on normal coordinate analysis. Fig. 6 compares the Fourier transform Raman spectrum of solid syndiotactic polypropylene to the simulated spectrum for an ordered helical structure of form I ($ggtt$)₄. The results of a normal coordinate calculation for an infinite chain consisting solely of ($ggtt$)₄ conformation repeats showed only one dominant isotropic component at 830 cm^{-1} . To confirm this result, the simulated spectrum for a series of oligomers with ($ggtt$) _{n} chain conformation was calculated. The conformer, ($ggtt$)₄, has the largest number of helical turns (2) that can be simulated with the available finite chain programs. In these calculations, a specified helical length is embedded between sequences of *trans* structures at each end. The simulation results are shown in Fig. 7 as a function of chain length. It is clear that helical structures of various lengths contribute in the 845 cm^{-1} region. As the length of the helical segment increases, the frequency decreases toward 830 cm^{-1} , strongly suggesting that the 830 cm^{-1} frequency is a limiting value associated with long helical chain structures. Shorter helical structures contribute to the intensity in the middle 850 cm^{-1} region flanked by bands associated with long helix and all-*trans* conformations. As the chain length increases, the simulation shows that the 830 cm^{-1} band increases in intensity relative to all others. Therefore the assignment of this band to the two-fold $ggtt$ helix is firm. There are also a number of weak features

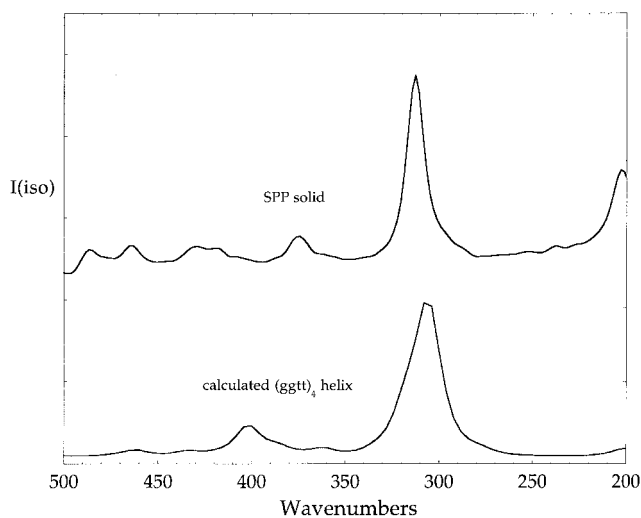
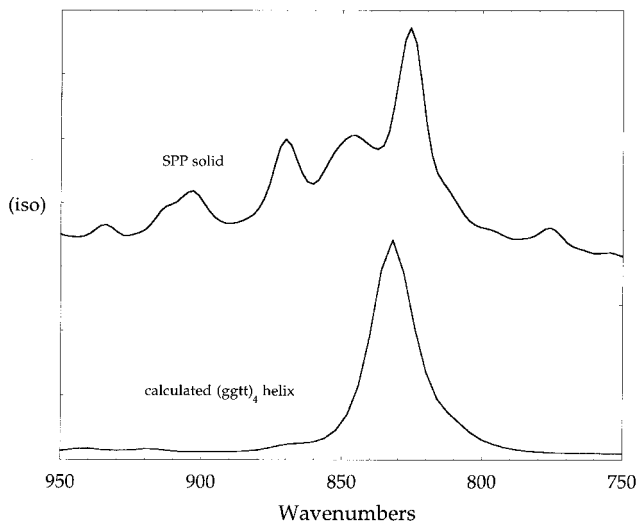


Fig. 6. Measured and calculated isotropic Raman spectrum for solid syndiotactic polypropylene in the *ggtt* conformation: (a) the bands in the 800 cm^{-1} region; and (b) the bands in the $300\text{--}400\text{ cm}^{-1}$ region.

calculated in this region of interest, but these do not appear to have dependable conformational origin and are therefore not further considered.

The Raman spectrum of form II (*all-trans*) syndiotactic polypropylene produced by stretching the film is shown in Fig. 2, for comparison with simulations of *all-trans* structures with different chain lengths ranging from $n = 6$ to $n = 11$. Raman bands were observed at 868 and $849\text{--}851\text{ cm}^{-1}$ depending on the orientation of the laser polarization relative to the stretching direction. The most intense of these bands was found at 868 cm^{-1} . Two isotropic components were calculated at 850 and 870 cm^{-1} for the *all-trans* structure. In the simulated spectrum of oligomers consisting of 6, 8, 10 or 11 *trans* units (Fig. 8), the higher frequency component is less intense than the lower one. However, the intensity of the 870 cm^{-1} component increases as the length of the *trans* chain increases. The relative intensity of the two simulated

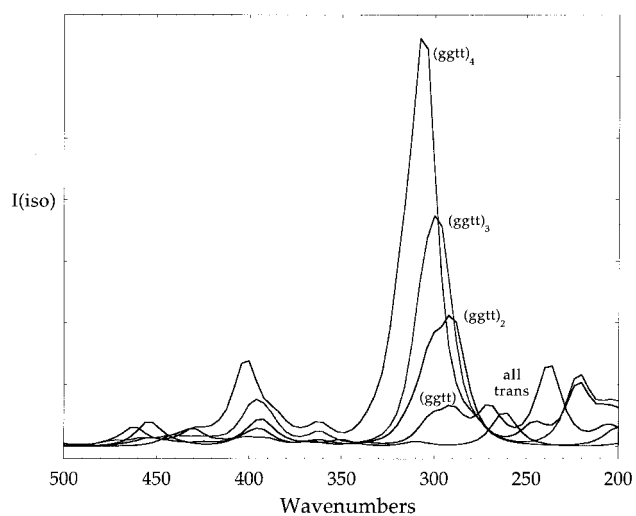
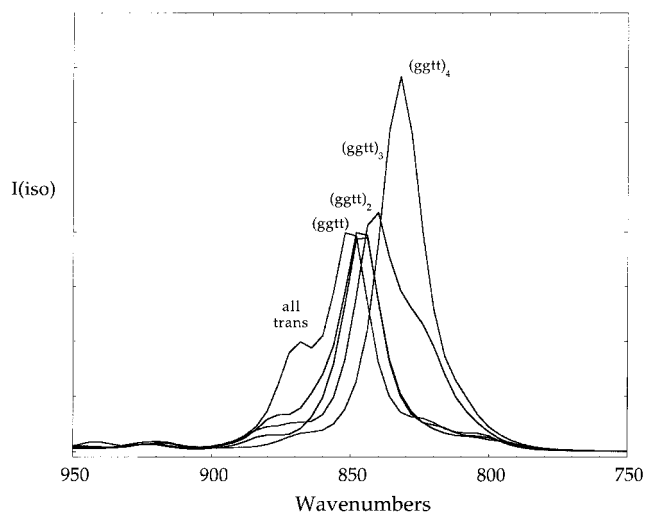


Fig. 7. Calculated spectra of different helical lengths for model syndiotactic polypropylene. The exact chain conformation is described in text: (a) the bands in the 800 cm^{-1} region; and (b) the bands in the $300\text{--}400\text{ cm}^{-1}$ region.

bands is shown as a function of chain length in Fig. 9. Based on the relationship calculated, the higher frequency component would have equal or higher intensity than the lower component when $n = 13$. This higher frequency component is then assigned to *all-trans* structures of fairly long length. If there are conformational defects along the chain, it is natural then to assume that the intensity of the 845 cm^{-1} amorphous component would increase as observed. If the chain conformation is helical in nature, the 826 cm^{-1} band dominates the region. Conversely, if the *all-trans* structure is present, the 868 cm^{-1} band is strong.

In the lower frequency region of the spectrum of syndiotactic polypropylene simulated for various chain conformations and different helical lengths, a band of very different nature appears. This is shown in Fig. 10. Similar to effects of the conformational differences calculated for the bands in the 800 cm^{-1} region, the band in the 300 cm^{-1} region

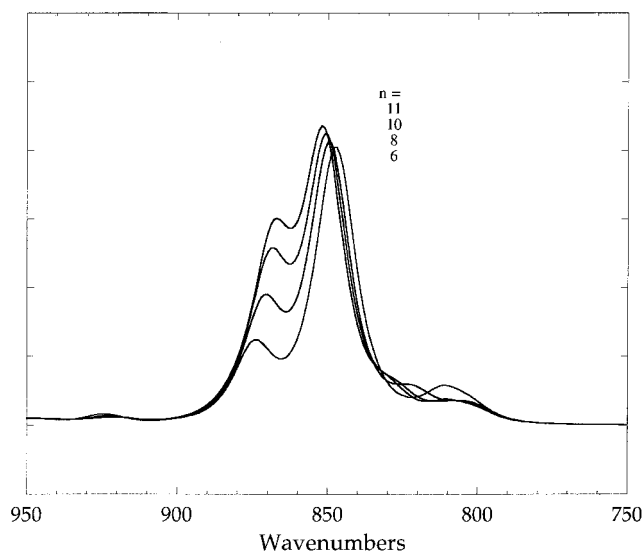


Fig. 8. Calculated Raman spectra in the 800 cm^{-1} region of different all-trans chain length for model syndiotactic polypropylene.

depends on the chain length. The frequency varies from $\sim 290\text{ cm}^{-1}$ for a short helix to $\sim 310\text{ cm}^{-1}$ for a long helix. But this band in the 300 cm^{-1} region is characteristic of all syndiotactic polypropylenes studied. Actually all syndiotactic polypropylene samples studied have a band at $\sim 310\text{ cm}^{-1}$. As shown in our calculations, it is a configuration band as well as a conformationally sensitive band. In syndiotactic polypropylene this band can be found in both crystalline and amorphous states. In contrast, for isotactic polypropylene a strong band is found at about 400 cm^{-1} . It has been suggested that the relative intensity of the two bands in the $300\text{--}400\text{ cm}^{-1}$ region can be used as an indicator of configuration [27].

The variation in frequency of the 300 cm^{-1} band can also be indicative of conformational order along the chain. For syndiotactic polypropylene samples of high degree of crystallinity, the 300 cm^{-1} band is located in the upper region of the calculated range and can only be associated with a straight helical length of no less than four (*ggtt*) sequences. Based on these calculated trends, we would expect that when conformational disorder occurs, the band would 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 our 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. These facts suggest that the frequency and intensity of this polarized band is not only characteristic of the syndiotactic isomer but also can be indicative of the regularity in chain conformation.

The spectra of both ordered and disordered isotactic polypropylene chains have been extensively discussed

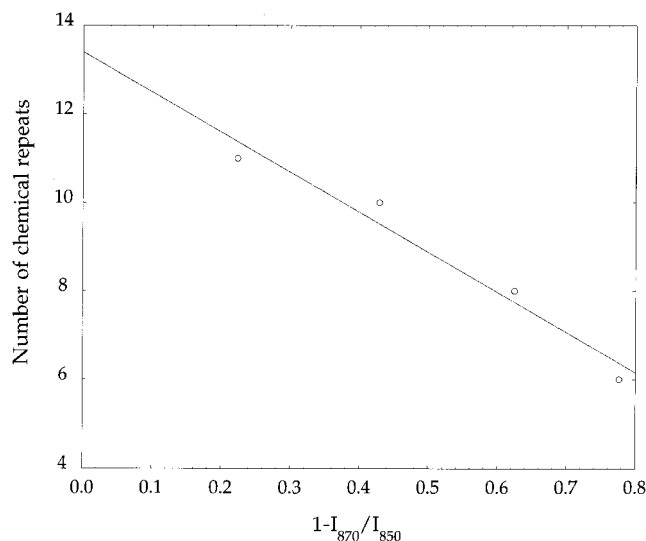


Fig. 9. Relative intensity of $870/850\text{ cm}^{-1}$ bands as a function of chain length.

previously [34,42]. The Raman spectrum observed for isotactic polypropylene shows an ordered helical band around 400 cm^{-1} . The main features calculated to occur below 500 cm^{-1} are given in Fig. 11. The length dependence is seen with the chains of length $n = 6$ and $n = 9$, which have two and three complete turns of the helix, respectively. In this plot, it is evident that as the length of the chain increases, the intensity of the band around 400 cm^{-1} increases more than the other two major bands in this region. It is anticipated that the intensity of these bands will fall in line with the experimental observations for sufficiently long calculated chains. The calculations for both isotactic and syndiotactic polypropylene show that the presence of the 400 cm^{-1} band is dependent on chain configuration only.

4.1. Simulation of disordered structures

Two types of normal coordinate analysis were conducted in analysis of the spectroscopic properties of disordered chains. First, calculations were conducted using the models mentioned above. Second, the spectrum of a statistical ensemble of chain conformations was calculated. Several studies have characterized the conformational energy of syndiotactic polypropylene [36–38]. 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 $(135^\circ, 60^\circ)$ and $(180^\circ, 90^\circ)$ and their complements [38]. The effects of conformational disorder were examined using model molecules of various possible conformations such as $(g_2t_2)_2t_8(g_2t_2)g_2$, $(g_2t_2)_2t_4(g_2t_2)_3$, or $t_4g_2t_2g_2t_6g_2t_2g_2t_2$ which involve some local conformations other than the (*gg*) and (*tt*) minima found in the conformational search. Each of these chain conformations clearly also contains

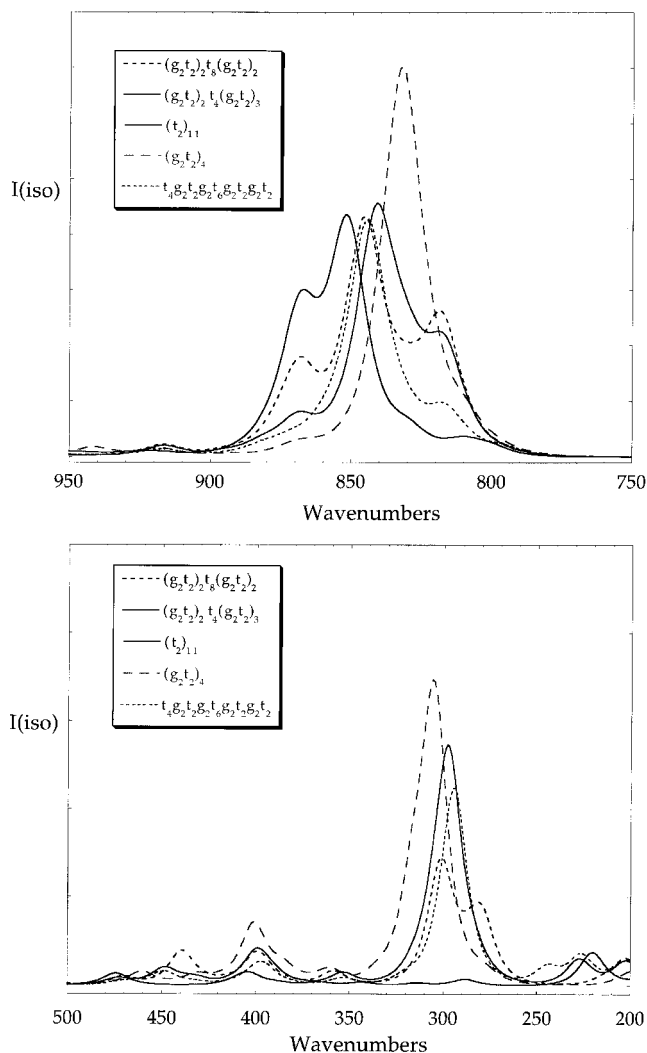


Fig. 10. Calculated Raman spectra for syndiotactic polypropylenes of different chain conformational distributions: (a) the bands in the 800 cm^{-1} region; and (b) the bands in the $300\text{--}400\text{ cm}^{-1}$ region.

large fractional contributions from the most probable sequences of (gg) and (tt) . The calculated spectra for these short chain conformations are shown in Figs. 7 and 10. All these regular chain conformations exhibit intensity in the region around 850 cm^{-1} , except the twofold $tggttg'g't$ helix. Presumably a disordered chain would include local chain conformations other than the $ggtt$ or tt conformations, and these other structures would then contribute intensity to this region. Attribution of the 845 cm^{-1} band to the amorphous structure is thus supported by this calculation. Indeed, the 845 cm^{-1} band does not appear in any normal coordinate analysis of long ordered chains, which lends further credence to the assignment.

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 RIS theory. These results suggest that in the melt, about 39% of the

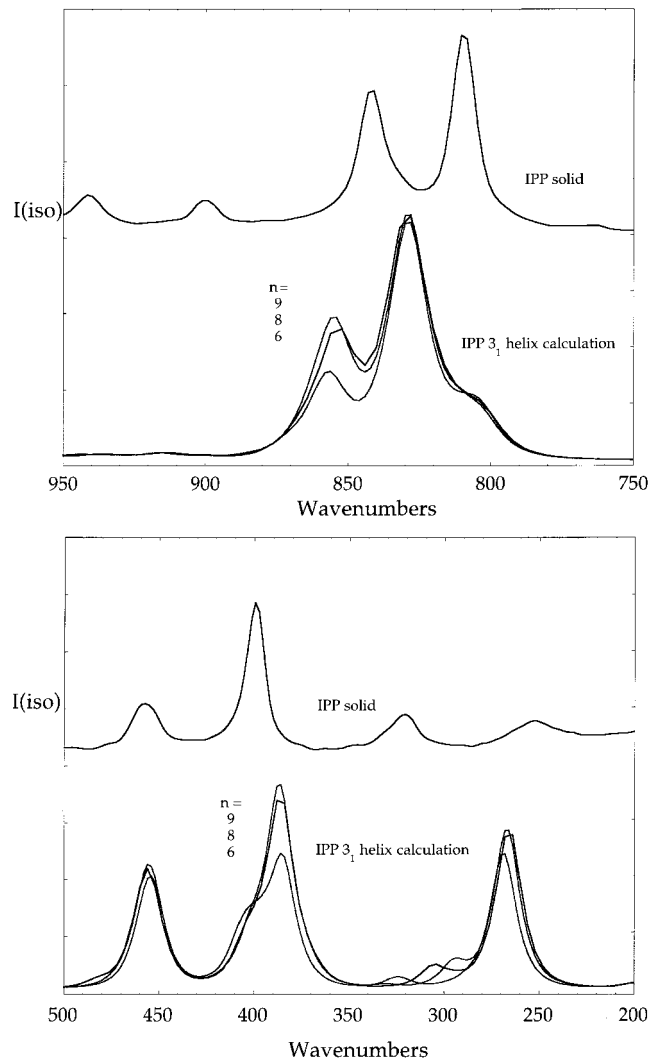


Fig. 11. Comparison of Raman spectra obtained for isotactic polypropylene solid with the calculated one: (a) the bands in the 800 cm^{-1} region; and (b) the bands in the $300\text{--}400\text{ cm}^{-1}$ region.

sequences be of the form $(ggtt)$ or $(tg'g')$. 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

Table 1
Calculated populations of most common conformers in syndiotactic polypropylene based on the Flory three-state RIS model

Conformation	Expectation	SPP Monte carlo
ttt	0.263	0.271
$tg'g + ggtt$	0.395	0.385
$tg't + tggt$	0.049	
$g'ttt + ttgg$	0.041	
$gg'tt + ttg'g$	0.027	

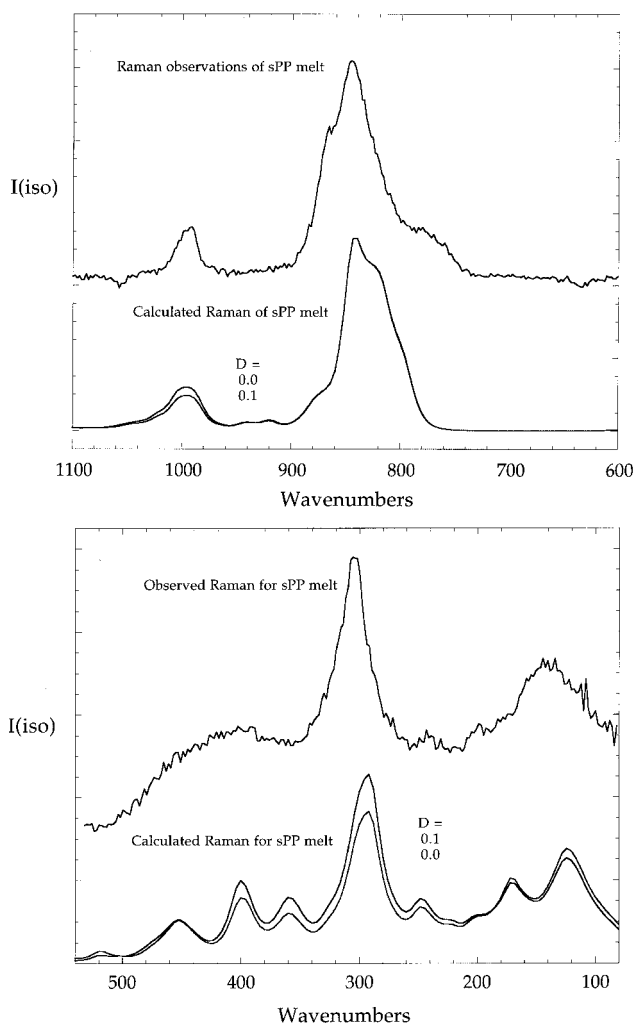


Fig. 12. Comparison of Raman spectra obtained for syndiotactic polypropylene melt with the calculated one: (a) the bands in the 800 cm^{-1} region; and (b) the bands in the $300\text{--}400\text{ cm}^{-1}$ region.

polypropylene is directly compared with simulated spectra in Fig. 12. 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 significantly different from those of isotactic polypropylene shown in Fig. 13, 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, which is reproduced in the calculation. In the 800 cm^{-1} region, the 845 cm^{-1} band is accurately reproduced. The weaker features are sharper in the simulation than expected. This can be attributed to the bandwidth assumed for each component. If a bandwidth larger than 8 cm^{-1} is allowed, or if the shape of the potential well is included by varying the torsion angles randomly over ranges corresponding to vibrational amplitudes in the potential energy minima, the bandshape can be reproduced even more accurately.

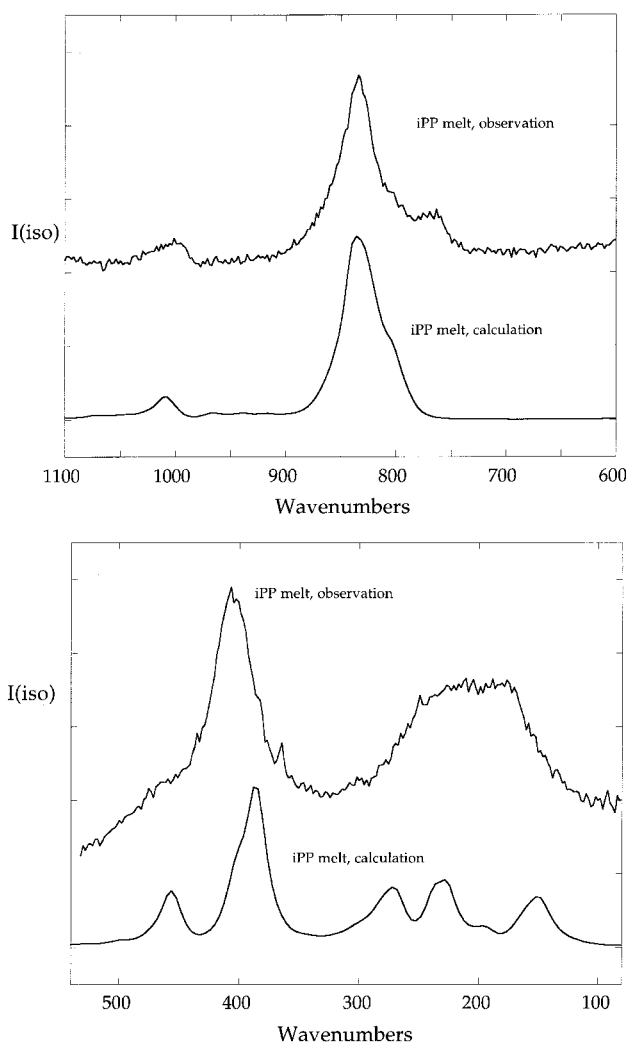


Fig. 13. Comparison of Raman spectra obtained for isotactic polypropylene melt with the calculated one: (a) the bands in the 800 cm^{-1} region; and (b) the bands in the $300\text{--}400\text{ cm}^{-1}$ region.

5. Conclusions

Conformational mapping of both the 800 and $300\text{--}400\text{ cm}^{-1}$ regions show the minimum helical length required to observe the characteristic ordered bands. The band around 826 cm^{-1} requires a minimum sequence length of $(ggt)_4$. Likewise, the band around 300 cm^{-1} shifts to higher frequency with increasing helix length. This observation is consistent with the frequency shift observed on melting. The combination of conformational mappings, analysis of the conformation distributions and ordered band simulations is a useful tool for characterizing the features of the Raman spectrum. Further, the analysis makes possible a dependable estimate of the major conformational content observed in the amorphous state. These observations may be expected to support studies of time-dependent phenomena such as conformational ordering, packing, and physical aging of polypropylene.

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