

Observing molecular orientation in isotactic polypropylene films with polarized Raman spectroscopy

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Introduction

Engineering the properties of polymers and polymer composites requires the ability to control molecular orientation through the processing steps and in the final product. Molecular orientation can affect mechanical properties such as strength and flexibility as well as physical characteristics such as optical and thermal properties. Raman spectroscopy provides details on the chemical makeup of a polymer. Polarized Raman spectroscopy is ideally suited for characterizing molecular orientation.

Isotactic polypropylene (iPP) is a good example to illustrate the analysis of molecular orientation in polymers. It is a classic example of a stereo-regular polymer. iPP has a simple hydrocarbon backbone consisting of carbon-carbon single bonds with pendant methyl groups ($-CH_3$) arranged along one side of the polymer chain. This regular repeating structure leads to a high degree of crystallinity. iPP can be found in a variety of different polymorphic forms.

Several different crystalline phases have been identified (a, b, l) as well as a mesophase (smectic) and an amorphous state. The crystalline structures have a common helical conformation of the polymer chains but differ in the relative ordering and positioning of the helical chains.¹ It is interesting to note that a seemingly simple repeating unit can display such diversity in molecular structure which, in turn, determines the properties of the material.

There are many analytical techniques that can be used to study molecular structure and orientation of polymers. Some of the more commonly used techniques include; X-ray diffraction, wide angle and small angle X-ray scattering², solid state NMR³, birefringence⁴, and infrared and Raman spectroscopy. Polarized Raman spectroscopy is a quick and easy to use analytical method that readily provides detailed information on molecular structure and orientation. This information can be used to supplement or replace results from other techniques.

Experimental

Raman measurements for this report were made using two different Raman microscopes. The single point data was obtained using a Thermo Scientific™ DXR3 Raman Microscope and the imaging data was collected using a Thermo Scientific™ DXR3xi Raman Imaging Microscope. While both of these Raman microscopes can



Figure 1. DXR3 Raman Microscope and DXR3xi Raman imaging microscope.

collect single point data and both can collect Raman images, each is particularly suited to different types of applications. The data was collected using a 532 nm laser but the polarization option supports other laser excitation wavelengths (455 nm, 633 nm, and 785 nm) as well.

The polarization option provides software control to set the orientation of the plane polarized laser excitation that is focused onto the sample. It also gives control over the orientation of a polarization analyzer that is used to analyze the Raman light that is scattered from the sample. The plane polarized laser excitation can be oriented either parallel to the left and right movement of the microscope stage (defined as the x axis) or can be oriented perpendicular to this direction or parallel to the front and back motion of the stage (defined as the y axis) (Figure 1). The z axis is defined as the axis parallel to the incident laser beam.

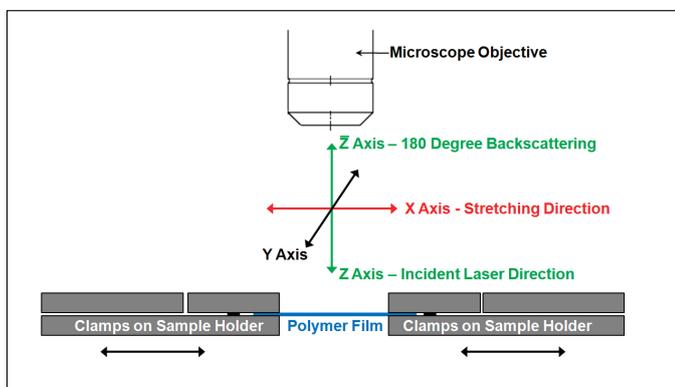


Figure 1. Defining the instrumental axes and the relationship to the mounted sample.

The orientation of the analyzer can also be controlled to be parallel or perpendicular to the incident plane polarized laser excitation orientation or can even be set at a user defined angle. If polarized Raman spectra are not required it is also possible to use the “depolarized” option to collect unpolarized Raman spectra. The instrument axes are defined in Figure 1 along with the relationship of those axes with respect to the way the samples were mounted.

Porto notation can be used to describe the different polarized states. $Z(XX)Z$ defines the state where both the plane polarized laser excitation orientation and the analyzer orientation are aligned parallel to the x axis (left and right motion of the stage). $Z(YX)Z$ defines the state where the plane polarized laser excitation orientation and analyzer orientation are aligned parallel to the back and front movement of the microscope stage.

Two different samples of isotactic polypropylene films were analyzed in this report to illustrate how polarized Raman spectroscopy can be used to evaluate molecular orientation. While visually similar these two iPP films displayed differences in their polarized Raman spectra as well as differences in their mechanical properties.

Both of the iPP samples were thin transparent films of similar thickness. However the tensile strengths of the two films were decidedly different. When a section of the first film was clamped in place between two jaws on the sample holder and stretched it continued to elongate to the limits of the sample holder. However, the second film, when subjected to the same conditions, required more force to move the jaws apart, elongating the polymer film. The second film also reached a point where the film did not elongate any further and instead it broke when additional stress was applied.

A MicroVice sample holder from S.T. Japan was used to hold and stretch the films. The samples were mounted on a rotatable stage insert that allowed the orientation of the sample to be varied with respect to the coordinate system defined by the instrument (see Figure 1).

Results

Distinguishing Oriented and Non-Oriented iPP Polymer Films

The polarized Raman spectra from the two isotactic polypropylene films showed some distinct differences. The first iPP film (Sample 1) showed no evidence of a preferred orientation. Equivalent spectra were obtained with the incident polarization and analyzer both oriented either parallel or perpendicular to the x axis (Figure 2). Rotating the film did not change the results.

The same type of analysis with the second iPP film (Sample 2) however, showed definite evidence of a preferred orientation (Figure 3). There were significant variations in the relative intensities of certain peaks when the polarization of the incident light and the analyzer were both oriented either parallel or perpendicular to the x axis. When the film was rotated 90 degrees and the analysis repeated, the opposite results were obtained, where the directions were just reversed. This is consistent with a distinct molecular orientation in the film. The observed orientation was very similar to what was observed for samples when they are stretched along the x axis. This induced orientation will be addressed in more detail later in this report.

This illustrates one of the advantages of using polarized Raman for the analysis of polymers. It can be used to observe differences in orientation that can correlate directly with differences in mechanical properties. As noted earlier, there was an obvious difference in the mechanical properties of these two iPP films and it is reflected in the differences in the polarized Raman spectra. While there were some subtle differences in the unpolarized spectra that might have given some indication of the differences in these materials it was much more obvious when polarized Raman spectra were used.

While there are many peaks in the spectra in Figure 3 that vary in relative intensity with the different polarization states, three sets of peaks were chosen to represent the differences.

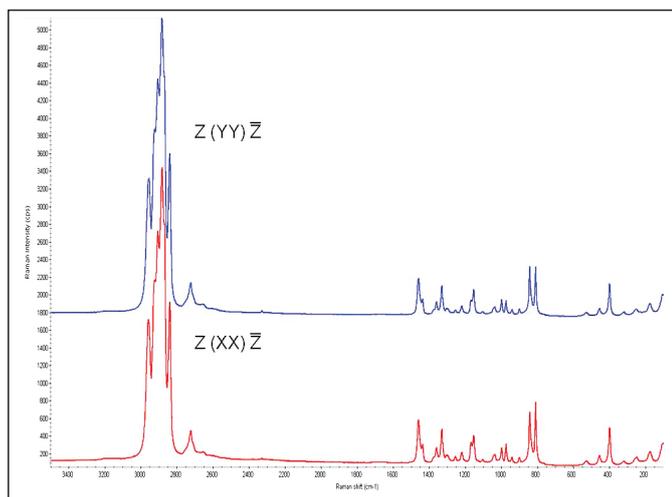


Figure 2. Polarized Raman spectra from Sample 1, the unoriented iPP film. There are no appreciable differences in the spectra.

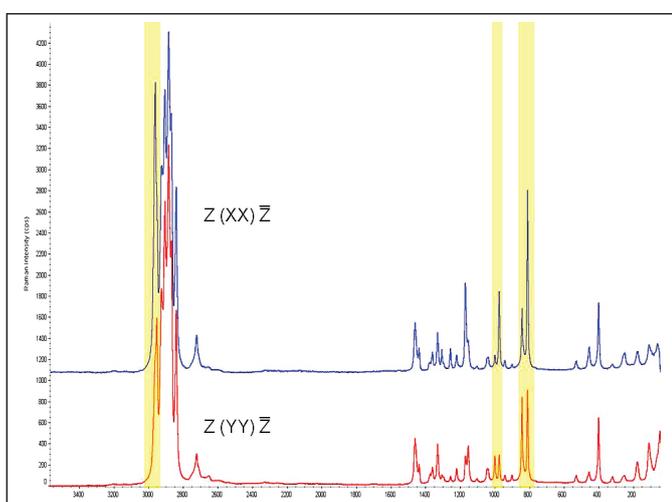


Figure 3. Polarized Raman spectra from Sample 2, the oriented iPP film. Colored areas (yellow) indicate 3 sets of peaks that are used to represent the differences.

The peaks at 2962 and 2953 cm^{-1} are associated with the asymmetric stretch of the methyl group of the isotactic polypropylene.⁵ The 2962 cm^{-1} peak is more intense in the spectrum obtained with the polarization of the incident light and analyzer parallel to the X direction ($Z(XX)\bar{Z}$). Where in the spectrum obtained with the polarization of the incident laser excitation and analyzer oriented perpendicular ($Z(Y\bar{Y})\bar{Z}$), the ratio of the two peaks is reversed and the 2953 cm^{-1} peak is more intense. This would seem to indicate a change in these peaks is associated with changes in molecular orientation and involves the orientation of the methyl groups.

The second set of peaks selected are the peaks at 998 and 973 cm^{-1} . The 973 cm^{-1} peak is associated mainly with asymmetrical stretching of the axial C-C bond and the 998 cm^{-1} peak is associated with the rocking of the methyl ($-\text{CH}_3$) lateral group. The ratio of these peaks has been used to evaluate molecular orientation and crystallinity.⁶ The peaks at 841 and 808 cm^{-1} are another set of peaks that have been used to evaluate crystallinity in iPP films. These two peaks

are associated with the 830 cm^{-1} peak that is observed in polypropylene melts but this peak splits into the 808 and 841 cm^{-1} peaks when it solidifies. These two peaks are clearly associated with the molecular structure including the molecular orientation.

Establishing sample orientation using polarization and sample rotation

The analysis can be taken one step further. Once it was clearly established that there was some initial molecular orientation in the iPP Sample 2 film the next logical step was to define the directionality of this molecular orientation with respect to the sample orientation. For many polarization measurements it is beneficial to be able to align or at least relate instrument polarization directions with sample axes. The mechanical properties are also likely to vary along directions in the sample associated with molecular orientation so it would be useful to have a way to define this direction. This can be done using polarized Raman spectra. Unpolarized spectra do not show a dependence on sample orientation and while that is an advantage in some situations, it is not, when trying to evaluate preferred sample orientations. Figure 4 shows that essentially equivalent Raman spectra were obtained from the orientated sample (Sample 2) regardless of the sample orientation when not using polarized light.

However, it is possible to define a preferred sample orientation or sample axis by using polarized Raman spectra. Figure 5 shows a plot of the ratio of the peak heights at 808 and 841 cm^{-1} from the oriented iPP film (Sample 2) as the sample is

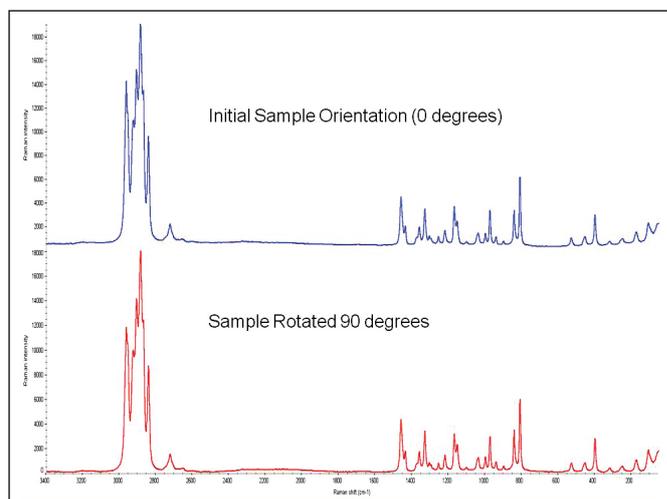


Figure 4. Unpolarized Raman spectra from Sample 2 show no sample orientation dependence.

rotated relative to the laser polarization. The maximum point is near the sample orientation defined as zero degrees. It is just a coincidence that the film was initially mounted with this orientation. It will not always correspond to 0 or 90 degrees. In this way, it is possible to orient the sample relative to the coordinate system defined by the Raman microscope. Similar results can also be obtained using the peak height ratio of the 973 and 998 cm^{-1} peaks.

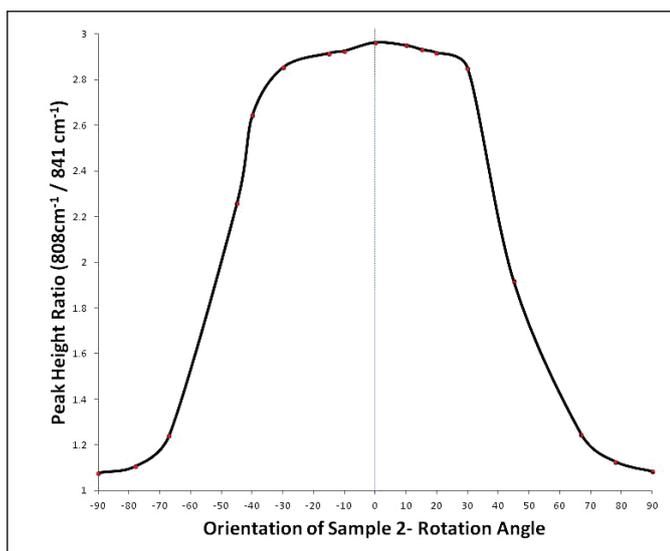


Figure 5. Determining Sample Orientation – Plot of the peak height ratio (808/841 cm^{-1}) from Z(XX)Z polarized Raman spectra as a function of sample orientation (rotation).

Inducing changes in molecular orientation – stretching the film

So far it has been shown that polarized Raman spectroscopy can be used to evaluate molecular orientation in iPP films to assess if a particular sample shows evidence of a preferred orientation or not. This is important in that it can correlate with mechanical properties. It is also possible to use polarized Raman spectra obtained at different sample orientations to define an axis of preferred orientation. Knowing what peaks change with molecular orientation can give some insight into what is happening on a molecular level. It is possible to study the process of molecular orientation by observing the transformations that take place in the Raman spectra as the molecular orientation change.

One example of this is to look at the changes that take place in the polarized Raman spectra as a polymer film is stressed. Sample 1 showed no preferred molecular orientation but if the same film is stretched along the x axis then it develops a preferred orientation similar to that observed in Sample 2. In this way it was possible to induce a preferred orientation aligned with the direction of the stress. It was also observed that applying stress to a sample with an established preferred orientation (Sample 2) can further effect the molecular orientation.

Figure 6 shows the changes that occur in the three sets of peaks, described previously, from polarized (Z(XX)Z) Raman spectra from Sample 2 as the film is successively stretched. The sample was oriented with the sample axis defined in Figure 5 along the y axis and this was perpendicular to the stretching direction (along the x axis). As the sample was successively stretched the peak ratios change to resemble those initially observed in the orthogonal orientation with the sample axis parallel to the x axis.

Figure 7 shows how the peak area ratios (808/841 cm^{-1} and 973/998 cm^{-1}) change with successively applied stress. Peak areas were used instead of peak heights because some small shifts in peak positions did occur when the films were stressed. The amount of stress was not measured quantitatively but with each step the jaws of the sample holder were moved further and further apart. This seems to imply that by applying stress to the film it is possible to alter the molecular orientation even in a sample that has a preferred orientation to begin with.

It also shows that it is possible to observe changes in molecular orientation that take place as the sample is stressed. Polarized Raman spectra could be incorporated into mechanical testing

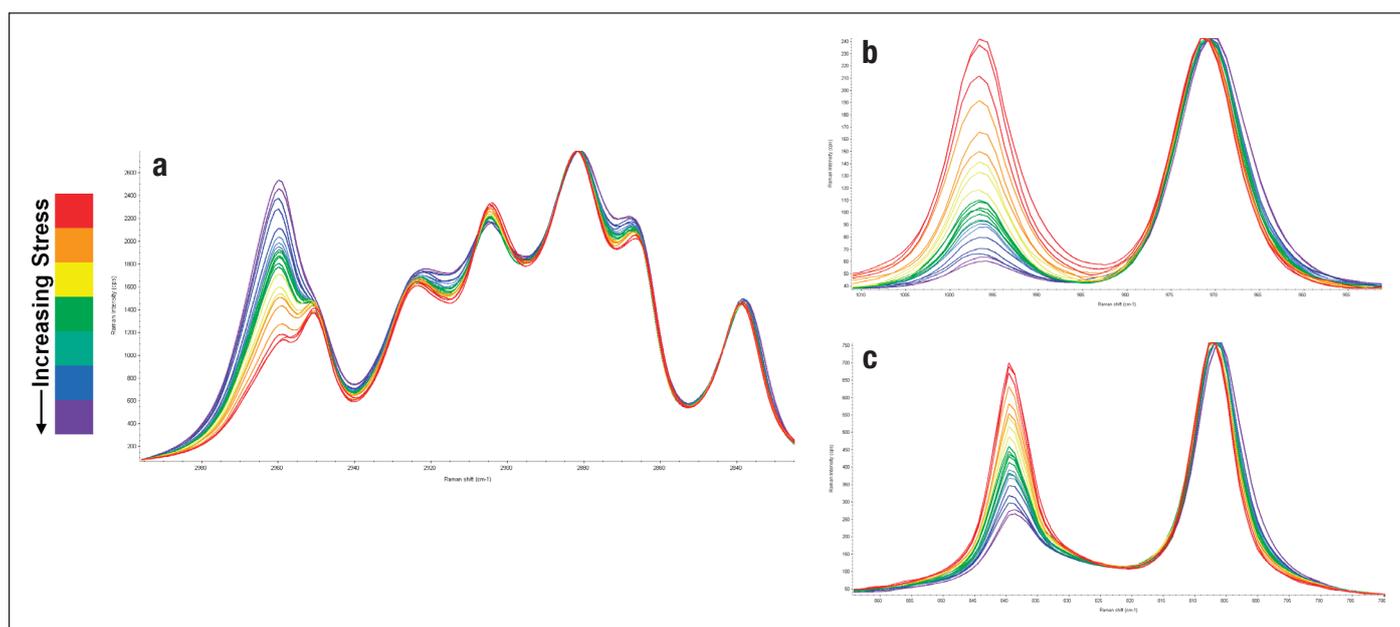


Figure 6. The effect that stretching the iPP film (Sample 2) has on the Raman polarized (Z(XX)Z) spectra (a) 2962 and 2953 cm^{-1} , (b) 998 and 973 cm^{-1} , (c) 841 and 808 cm^{-1} .

of polymers to provide additional information on what is changing at the molecular level during the test.

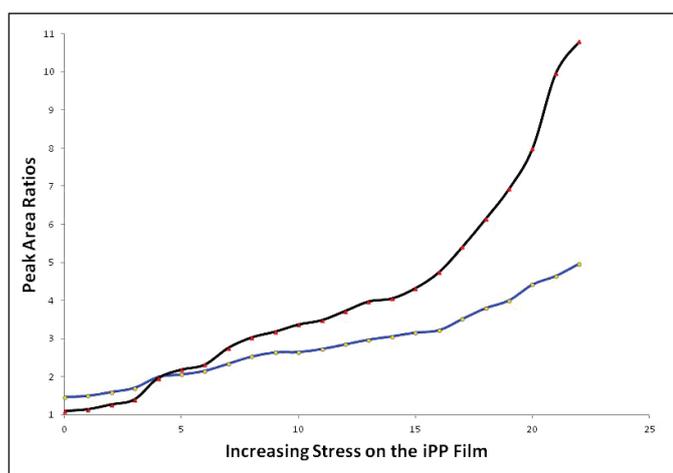


Figure 7. The effect of stress on the peak height ratios ($808/841\text{ cm}^{-1}$ and 973 and 998 cm^{-1}) from the Raman polarized (Z(XX)Z) spectra.

Imaging stress with polarized Raman

The evaluation of molecular orientation using polarized Raman micro-spectroscopy can be extended beyond just single points. Polarized Raman imaging can be used to provide views of differences or distributions of molecular orientations across a sample. This way a variety of different aspects of molecular structure including molecular orientation can be readily visualized.

Figure 8 shows the results of Raman imaging on Sample 1 when it is stretched. Sample 1 showed no orientation effects until it was stretched. The area represented by the image is $1.32 \times 1.16\text{ mm}$. The image pixel size is $10\text{ }\mu\text{m}$ and this results in an image consisting of 15,561 spectra. An exposure time of 0.2s was used along with 5 averaged scans of the area. The Raman image shown is based on the peak height ratio of $808/841\text{ cm}^{-1}$. The red color indicates a higher peak ratio which has been observed to be associated with greater molecular orientation while the blue color indicates areas that have a lower peak ratio and thus presumably lower molecular orientation. In the first image, (a), polarized (Z(XX)Z) Raman spectra were collected. In the second image, (b), unpolarized Raman spectra were collected over the same area. While the

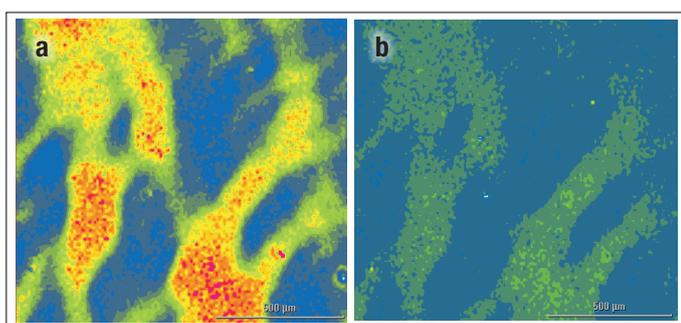


Figure 8. Raman images of stretched iPP film (Sample 1). The images are based on the peak height ratio, $808/840\text{ cm}^{-1}$, where the red color indicates a higher ratio (greater molecular orientation) and the blue color a lower ratio (lower molecular orientation). (a) image derived from polarized (Z(XX)Z) Raman spectra. (b) image derived from unpolarized Raman spectra.

unpolarized spectra still gave some indication of differences in molecular orientation, the differences are much smaller and the image does not have good contrast. The image produced using the polarized Raman spectra shows much more contrast and detail. This illustrates the potential for using polarized Raman imaging for these types of applications. It has the potential to significantly improve Raman images depicting differences in molecular orientation across large sample areas.

Conclusions

Isotactic polypropylene films were used to illustrate how polarized Raman micro-spectroscopy can be used to evaluate molecular orientation. The ability to detect molecular orientation in a material is important because it often correlates with physical properties and can provide information on the results of processing steps used to engineer specific physical properties into the product. Coupling polarized Raman spectroscopy with sample rotation was a way to determine a directionality of the sample itself based on molecular orientation. It was also shown that polarized Raman spectroscopy can be used to study molecular orientation induced as the result of applied stress and to observe what changes occur at the molecular level as the sample is stressed. While this report used isotactic polypropylene films to illustrate the concepts, this same type of analysis could be applied to many different types of polymer films. Whether the application calls for single point analysis or Raman imaging the Thermo Scientific DXR3 Raman Microscope and the Thermo Scientific DXR3xi Raman Imaging Microscope with the polarization options both provide easy access to molecular structure and orientation information. The data were collected using an older model instrument Antaris FT-NIR. Currently, Thermo Scientific offers an improved model, the Antaris II FT-NIR, which offers superior speed and performance over its predecessor model.

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