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Isotacticity determination of polypropylene using *FT*-Raman spectroscopy

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We have studied the applicability of Fourier transform (*FT*)-Raman spectroscopy to the determination of isotacticity in polypropylene. We have compared *FT*-Raman and Fourier transform infra-red (*FT*i.r.) spectroscopy as isotacticity determination methods and used ^{13}C nuclear magnetic resonance (n.m.r.) spectroscopy as a reference method. Calibration curves relating Raman scattering and i.r. absorption ratios to the ^{13}C n.m.r. results are presented. We found that the repeatability for both *FT*-Raman and *FT*i.r. measurements is comparable to that of ^{13}C n.m.r. analysis and that there is a good correlation between ^{13}C n.m.r. and *FT*-Raman/*FT*-i.r. results. The reliabilities of the three methods are statistically evaluated and compared. Copyright © 1996 Elsevier Science Ltd.

(Keywords: *FT*-Raman spectroscopy; isotactic polypropylene; ^{13}C n.m.r.)

INTRODUCTION

The determination of stereoregularity in polypropylene is of great importance when evaluating the properties and performance of commercial polypropylene materials and of the catalysts used for their manufacture. This study was made to define the possibility of using Fourier transform (*FT*)-Raman spectroscopy in polymer analysis and especially in making tacticity determinations in polypropylene.

The Raman effect arises from inelastic photon scattering. The exchange of energy between the molecule and the incident photon gives the scattered photon a new energy that is different from the initial one and therefore measurable. For some molecules, many of the observable Raman shifted frequencies are identical to the frequencies observed by infra-red (i.r.) spectroscopy. The frequency matching between the spectra obtained by the two different techniques suggests that Raman spectroscopy could be used to provide fundamental information on the architecture of molecules[1].

In this contribution, sample characterization was focused on isotacticity determination. Like solvent extraction, differential scanning calorimetry, X-ray diffractometry and *FT*i.r. spectroscopy, *FT*-Raman spectroscopy provides an indirect measure of the tacticity of polypropylene samples. These methods actually measure parameters relating to the crystallinity or conformational arrangement of the polypropylene macromolecule and not taciticity itself. High resolution ^{1}H and ^{13}C nuclear magnetic resonance (n.m.r.) analysis allows absolute determination of tacticity and, therefore, ^{13}C n.m.r. has been used as a calibration method in *FT*-Raman measurements. Raman light scattering bands at seven and i.r. absorption bands at four different wavenumbers were used as indices of tacticity, and bands at two different wavenumbers as internal references. *FT*i.r. and *FT*-Raman bands used to measure isotacticity are actually bands which are sensitive to the formation of regular isotactic helices, rather than to the isotacticity itself[2].

EXPERIMENTAL

Materials

As all commercial grade polymers have about the same isotacticity, the samples in these measurements have been chosen partly from laboratory-scale and partly from pilot-scale production samples to allow a wide range of isotacticity to be investigated. A broad range of tacticity was achieved by fractionating polypropylene with n-heptane, xylene and solvent gradient extraction. The fractionations were made at Borealis Polymers Oy, using procedures described elsewhere[3]. The ^{13}C n.m.r. isotacticity of the fractions ranged from 44.5 to 95.4% and molecular weight (M_w) ranged from 23000 to 382000[4].

Methods

FT-*Raman measurements.* The *FT*-Raman measurements on fractions of polypropylene were made using a metallic sample holder with a conic hole of ~2 mm in diameter. Pellets were measured with a slightly modified

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sample holder of the same type. To keep the absorbance peaks in the *FT*-i.r. spectra below 1.5–2.0 units, films with a thickness of ~ 80 μm were pressed at 230°C. The amount of sample was 70–80 mg. The samples were softened for 1 to 2 min, kept at high temperature for 3 min in normal atmosphere and then kept under pressure for 1 min. The samples were then cooled in a cooling chamber for 5 min, from 230°C to 40–50°C. The films were annealed at room temperature for a minimum of 5 days before measuring the spectra.

The *FT*-Raman spectra were recorded with a Bruker FRA 106 *FT*-Raman spectrometer with a resolution of 4.0 cm^{-1}. The laser power was varied between 150 and 320 mW, the number of scans was between 200 and 2000, and the scanner velocity ranged from 2000 to 10 000 scans per second. The baseline was drawn between the minima at approximately 950 and 990 cm^{-1} for the reference peak, respectively 775 and 825 cm^{-1} for the isotacticity peak. The peak heights at 809 and 974 cm^{-1} were used to calculate the intensity ratio which was calibrated with ^{13}C n.m.r. triad isotacticity.

FT*i.r. measurements.* The *FT*i.r. measurements were performed on the same films as in the *FT*-Raman experiments. The films were scanned on a Nicolet magna-IR spectrometer 550, with data analysis by Nicolet Omnic software. Scanning was made both on fresh films immediately after pressing, and on aged films, annealed at room temperature for 7 days. The baseline was drawn between the minima at approximately 1070 and 925 cm^{-1}. The height of the peak at 998 cm^{-1} was used for calibration. The peak at 841 cm^{-1} was also tested but no improvement in the calibration was achieved. The height of the peak at 973 cm^{-1} was used as an internal reference. The ratio A_{998}/A_{973} was compared with ^{13}C n.m.r. isotacticity values.

^{13}*C n.m.r. measurements.* The samples were dissolved at ~ 150°C in a mixture of 1,2,4-trichlorobenzene and hexadeuterobenzene (10%). The spectra were recorded at 150°C with a JEOL GSX400 spectrometer. The analysis parameters were 9.3 μs pulses, 2000 scans with 9.5 s relaxation delay in a frequency range 25 000, resulting in 32 768 data points. The triad tacticities were determined from the methyl carbon resonances.

RESULTS AND DISCUSSION

FT-*Raman measurements*

The most critical step for *FT*-Raman and *FT*i.r. analyses is sample preparation. Every factor, other than isotacticity which influences the formation of crystalline helices in the sample, will also influence the *FT*-Raman scattering intensities. The difficulty is to prepare samples in a standard crystalline state by eliminating the thermomechanical history of the materials and moulding them under reproducible conditions. An annealing step after moulding may improve the preparation by allowing the sample to develop full crystalline structure. Factors which influence the crystallization behaviour of the polymer and its Raman scattering intensities include choice of polymerization catalyst, form of raw material (powder, pellets, etc.) and additives (e.g. nucleating agents).

The following peaks in the *FT*-Raman spectra were studied as a measure of the isotactic/(syndiotactic + atactic) helix content of the sample: ~ 310 cm^{-1}, ~ 398 cm^{-1}, ~ 809 cm^{-1}, ~ 841 cm^{-1}, ~ 900 cm^{-1}, ~ 998 cm^{-1} and ~ 1168 cm^{-1}. These peaks have been used in the literature for isotactic and syndiotactic polypropylene[5–7]. The CH_3 rocking peaks at ~ 974 cm^{-1} and at ~ 1160 cm^{-1} were studied as reference peaks. When ^{13}C n.m.r. isotacticity was used as calibration method, the best correlation and reproducibility were achieved with the ratio of the 809 cm^{-1} peak to the 974 cm^{-1} reference peak. Baselines were drawn between the minima at ~ 950 and 990 cm^{-1} for the reference peak and ~ 775 and 825 cm^{-1} for the isotacticity peak. The peaks at 310 and 398 cm^{-1} are probably situated too far away from the reference peak to give good, reproducible results. Both peak heights and peak areas were investigated.

The peak heights and peak areas were integrated using several different methods offered by the operating system. Overall, the peak heights were found to correlate better to the ^{13}C n.m.r. results than the peak areas. All *FT*-Raman measurements in this study have been made using 180° (back-scattering) *FT*-Raman light collection.

To achieve better resolutions on the *FT*-Raman spectra of the tested polypropylenes, some test runs were performed on the dispersive *FT*-Raman instrument of the Department of Physical Chemistry at the University of Helsinki. This instrument is capable of higher resolution, revealing the fine structure of the peaks. A homogenized powder sample was measured with 0.1 and 0.25 cm^{-1} resolution. With 0.1 cm^{-1} resolution, the signal/noise ratio was too low to allow interpretation of the spectra. With 0.25 cm^{-1} resolution the signal/noise ratio was acceptable. The fine structure of the interesting peaks at 809 and 974 cm^{-1} showed that they consist of only one peak.

When measuring fractions the *FT*-Raman light scattering from the sample is greatly dependent on the packing density of the sample. This is an uncertainty factor in the experiments. Films cannot be made from these low isotacticity fractions, they are too sticky due to low degrees of crystallinity and low molecular weights. *Figure 1* presents the averaged results from the measurements, I_{809}/I_{974} *versus* ^{13}C n.m.r. tacticity. The standard deviation of the I_{809}/I_{974} ratio between separate measurements for the same fractions was between 2 and 10% depending on the fraction. The deviation was higher for

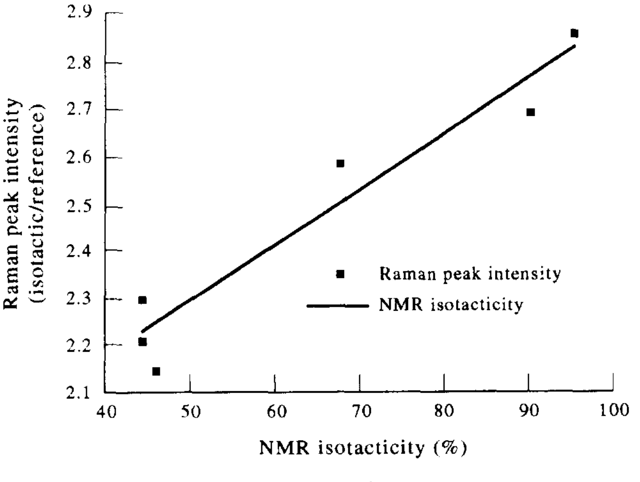

Figure 1 *FT*-Raman tacticity *versus* ^{13}C n.m.r. tacticity for polypropylene fractions

the lower isotacticity (softer) fractions. The r^2 value, which is a measure of the linear correlation between the experimental points (measured I_{809}/I_{974} ratio) and the actual isotacticity (^{13}C n.m.r. isotacticity), was 0.936.

The great advantage of *FT*-Raman spectroscopy in tacticity determinations of polypropylene is the possibility to measure pellets directly. Several measurements on polypropylene pellets of different isotacticity have been made using different measuring methods including constant laser power, constant scattering intensity, and constant reference peak height. The thermodynamic and physical background of the pellets has great bearing on the results obtained. Comparison of different pellet isotacticity values should be made between pellets with similar morphology achieved by similar homogenization, pelletization and cooling processes.

Measurements have been made both on the 'normal' surface of the pellets and on freshly cut surfaces, in order to find out if storage or exposure to air has any effect on the results. Smaller deviations in the separate measurements were achieved with freshly cut surfaces than with normal surfaces. The standard deviation of the I_{809}/I_{974} ratio between separate measurements for the same kind of pellets was between 1 and 3% for the freshly cut pellet surfaces. A standard deviation of 2% in the *FT*-Raman measurements corresponds to approximately 0.75% deviation in the actual (^{13}C n.m.r.) isotacticity. Nucleating agents added to the polymer during the production stages change the crystallization behaviour of the polymer and thereby the Raman scattering behaviour. Due to this fact separate calibration curves are required for polymers prepared with different kinds and amounts of nucleating agent. *Figure 2* shows the results for freshly cut pellet surfaces.

When measuring the *FT*-Raman or *FT*i.r. spectra on films the ageing of the film can be of great importance to the results. It is essential that the films are subjected to similar treatments (temperature, pressure, cooling time, etc.) during and after film pressing. As experienced earlier, samples in powder form are not the best for film preparation because of variations in the bulk density and other possible inhomogeneities. A storage time of 5 days minimum has been found to be enough to achieve stabilized morphology in the samples[8].

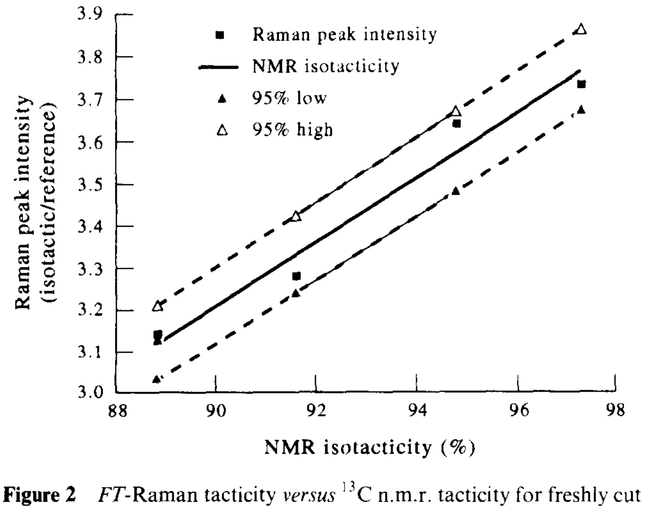

Figure 2 *FT*-Raman tacticity *versus* ^{13}C n.m.r. tacticity for freshly cut polypropylene pellets

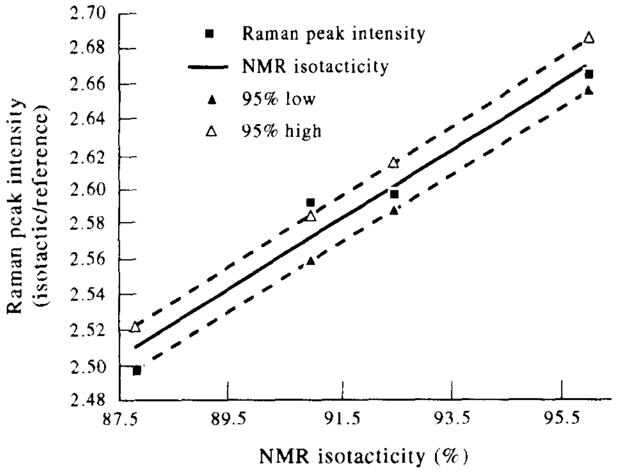

Figure 3 *FT*-Raman tacticity *versus* ^{13}C n.m.r. tacticity for polypropylene films

The standard deviation of the intensity ratio (809/974 cm^{-1}) for separate measurements was between 0.1 and 0.4% using the *FT*-Raman technique. The reproducibility of the *FT*-Raman measurements is not as good as for *FT*i.r. measurements. This may be due to low intensities of the peaks in the *FT*-Raman spectra, making determination of *FT*-Raman peak heights rather complicated (compare the peak height of 0.015 units for the reference peak in the *FT*-Raman spectra with the absorbances in the *FT*i.r. spectra, between 1.5 and 2.0). *Figure 3* shows the results for the *FT*-Raman measurements on films.

FT *i.r. measurements*

The *FT*i.r. spectral bands at 1168, 998, 973 and 841 cm^{-1} are related to the formation of regular isotactic helices. The most widely used bands for calibrating the isotacticity (or crystallinity) are the ones at 998 and 841 cm^{-1}, corresponding to sequence lengths of 11–12 and 13–14 repeat units in crystalline, or mesomorphic, regions. The band at 973 cm^{-1}, corresponding to five units, can be attributed to both crystalline and amorphous chains in helical conformations and is often used as an internal reference[2].

Calculation of the A_{998}/A_{973} ratio from the scanned spectra is fairly straightforward. After measuring the first three films discrepancies in the A_{998}/A_{973} ratio appeared between the films of the same material, especially for reactor powders. Although powders were ground before pressing, no real improvement was obtained. An increased time in the melt and a slow cooling rate (<10°C min^{-1}) achieved only marginal improvements. The reproducibility was improved by making films from extrudates obtained from the melt-indexer. This was not due to the mixing effect of the melt-indexer, which has low shearing and mechanical action. The extrudates are simply more appropriate for film compression than the reactor powders because they do not contain micropores and the polymer has passed through the molten state during its history.

Annealing increased the A_{998}/A_{973} ratio by 17–25%, due to increase in crystallinity. Slow cooling from the melt led to a 26–37% higher A_{998}/A_{973} ratio than for normal cooled films. After annealing, the slow cooled films had A_{998}/A_{973} ratios that were 25% higher than those of the normal annealed films.

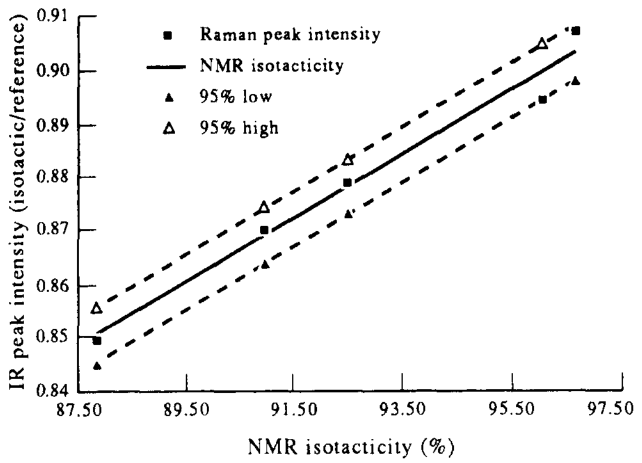

Figure 4 *FT*i.r. tacticity *versus* ^{13}C n.m.r. tacticity for polypropylene films

Heterogeneity within a film was checked by scanning through three distinct locations of each film and calculating the average A_{998}/A_{973} ratio from the three spectra. Scattering of the A_{998}/A_{973} ratio within a film was 0.2–0.4% for fresh films and 0.1–0.3% for annealed films. This indicates that annealing has a positive but a small effect on heterogeneity. Film-to-film heterogeneity was also checked and standard deviations were found to be below 0.0035 units, corresponding to less than 0.4% of the *FT*i.r. ratio ($0.8 < A_{998}/A_{973} < 0.9$). Annealing did not overcome this effect. The results were better for pelletized samples that exhibited a more homogeneous crystallization behaviour and therefore a better film-to-film reproducibility of the A_{998}/A_{973} ratio. Calibration curves for annealed films are shown in *Figure 4*.

^{13}*C n.m.r. measurements*

^{13}C n.m.r. spectroscopy is considered to be the most reliable method of determining the tacticity of polypropylene. ^{13}C n.m.r. directly determines the stereochemical structure of the polymer chain, usually sequences relating to three repeating units (triads) are measured. The *meso–meso* (*mm*) triad represents the isotactic content while the *meso–racemic* (*mr*) and *racemic–racemic* (*rr*) are used to determine the atactic and syndiotactic content, respectively[9].

The ^{13}C n.m.r. results are presented in *Table 1*, which also includes solvent extraction and ^{13}C n.m.r. isotacticity determinations measured with a JEOL GSX400 spectrometer in a second laboratory. *Table 1* shows that differences between separate measurements do occur in ^{13}C n.m.r. tacticity determinations. Sample preparation and treatment are critical in ^{13}C n.m.r. measurements since the polymer is in solution and separation of fractions with different densities, molecular weights and isotacticities may occur. It is clear that a single ^{13}C n.m.r. experiment is not sufficient and that an average of several measurements is needed for determination of isotacticity. The main disadvantage of the ^{13}C n.m.r. technique is that it is a time-consuming method.

Evaluation of the measurements

Statistical evaluation of the separate measurements for films show the repeatability of the method. The standard deviation for the *FT*-Raman isotacticity ratio varies between 0.05 and 0.06 units, corresponding to a 95% confidence interval of ±0.024 to ±0.029 units. Linear equation fitting to experimental data in the 95% confidence interval corresponds to ^{13}C n.m.r. isotacticity values between ±1.0 and ±1.2%. By comparison, the ^{13}C n.m.r. measurements have standard deviations of ±1.0 to ±2.0%, indicating that *FT*-Raman measurements have equal or superior reproducibility to ^{13}C n.m.r. For pellets, the 95% confidence interval of separate measurements varies between ±0.028 and ±0.073 units, corresponding to ^{13}C n.m.r. isotacticity values of ±0.4 to ±1.0%. For fractions and powder samples the

Table 1 ^{13}C n.m.r. and solvent extraction isotacticity determinations on polypropylene samples

Sample	Laboratory 1 n.m.r. isotacticity (%)	Laboratory 2 n.m.r. isotacticity (%)	n-Heptane extraction (%)	95% Confidence interval
PP 1	94.8			
PP 2	91.6			
PP 3	88.8			
PP 4	97.3			
PP 5	93.5, 95.8 (94.6)[a]	93.7, 89.9, 92.7, 93.4, 92.9 (92.5)	95.4	91.0–93.9
PP 6	94.5	94.7, 95.4, 96.1, 97.0, 97.0 (96.0)	98.8	95.1–97.0
PP 7		90.0, 87.1, 87.1, 88.5, 86.4 (87.8)	88.3	86.4–89.2
PP 8		93.5, 90.3, 89.7, 90.4 (91.0)	92.2	88.9–93.0
PP 9		97.2, 97.4, 96.1 (96.9)		

[a] Values in parentheses are averages of the reported measurements

repeatability of separate measurements is significantly poorer due to the inhomogeneities, density and morphology variations in the samples.

Statistical evalution of the method shows how well the *FT*-Raman measurements correspond to ^{13}C n.m.r. results. For films, linear regression analysis gives an r^2 value of 0.985. The *F* statistic shows whether the observed relationship between the *FT*-Raman and ^{13}C n.m.r. values occurred by chance. The observed *F* value for films was 134.2 compared with a critical *F* value of 18.5. The greater the observed *F* compared with the critical *F*, the more reliable is the r^2 value. The *t*-statistics show if the dependent variables, in this case the *FT*-Raman isotacticity ratios, have statistical significance when estimating the actual isotacticity values. Again, an increase in the observed *t* value compared with the critical *t* value indicates a more useful dependent variable in predicting the actual value. For films, the observed *t* was 11.6 compared with the critical *t* of 2.92 (corresponding to a 95% confidence interval). For films the 95% confidence interval for the method ends up at ±0.025 units, corresponding to ±1.1% ^{13}C n.m.r. isotacticity. *Figure 3* also shows the 95% confidence interval for the method for films.

For pellets, with a freshly cut surface, the statistical values were as follows: the r^2 value was 0.960, calculated *F* was 48.6 compared with the critical *F* of 18.5 and the calculated *t* value was 7.0 compared with the critical *t* value of 2.92. The 95% confidence interval for pellets is ±0.091 units which corresponds to ±1.2% ^{13}C n.m.r. isotacticity. *Figure 2* shows the 95% confidence interval for pellets with freshly cut surfaces.

The standard deviation of the *FT*i.r. technique, both pressing and scanning the sample, can be considered small. For the *FT*i.r. measurements, the statistical evaluation gives the following results: r^2 was 0.976, calculated *F* was 122.3 compared with critical *F* of 18.5 and calculated *t* was 11.1 compared with critical *t* of 2.92. The 95% confidence interval for the *FT*i.r. method is 0.005 units which corresponds to ±0.84% ^{13}C n.m.r. isotacticity. The statistics for the *FT*i.r. analyses are based on rather few (five) measurements/sample compared with the 15 measurements/sample statistics for the *FT*-Raman analyses. *Figure 4* shows the 95% confidence interval for the *FT*i.r. measurements.

CONCLUSIONS

The great advantage of *FT*i.r. and *FT*-Raman techniques compared with ^{13}C n.m.r. analysis is that they are much less time consuming and simpler to perform. The thermodynamic and physical background of the polymer samples should be similar in order to achieve reliable results. The best reproducibility and best correlation to n.m.r. measurements were found for polypropylene film samples. When films are measured, *FT*i.r. spectroscopy gave better reproducibility than *FT*-Raman spectroscopy, while the correlation to n.m.r. results is better for *FT*-Raman measurements. When measuring soft samples (fractions), the results are greatly dependent on the packing density of the sample. For pellets, freshly cut surfaces seem to give better results than an 'aged' pellet surface.

In theory, *FT*-Raman measurements can be made directly on the homogenized polymerization products (pellets) without any additional sample preparation. In this case, the total analysis time for a sample is < 5 min. *FT*-Raman spectroscopy could be used as a fast method for tacticity determination of pellets in industrial processes where the thermodynamic background is known and fairly constant. In laboratory applications, accurate sample preparation methods (i.e. film pressing) are needed for reliable results.

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