

The Determination of the Isotacticity of Polypropylene in the 90–100% Range by Infrared Spectroscopy*

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Synopsis

An infrared method has been developed for the determination of the isotacticity of polypropylene in the 90–100% range. The method requires the annealing of thin films at 165–167°C. for 3 hr. in an inert atmosphere, followed by slow cooling to room temperature. For approximate answers the ratio of the intensity of the 10.00 μ band to that of the 10.27 μ band can be reported as the fraction of isotactic material. Better results are obtained, however, by using Figure 2 as a calibration curve and reading the values from it.

Introduction

The purpose of this paper is to describe the infrared method used in the polymer section at this laboratory for estimating the isotacticity of highly isotactic polypropylene. This infrared method is generally more useful, rapid, and accurate than other methods. The method based on differences in solubility of isotactic and atactic materials does not always give clear separations and requires from 6 to 24 hr of extraction in a Soxhlet extractor.¹ As the infrared method uses no solvent separations, it is not plagued with differences in solubilities of materials of different molecular weights. The determination of isotacticity by density is subject to error from the presence of catalyst residues. Some evidence has been accumulated that these impurities cause no inaccuracy in the infrared method.

The infrared spectra of isotactic and atactic polypropylene are shown in Figure 1. The spectrum of molten isotactic material is the same as that of the atactic material. Studies of a fundamental nature made by Brader² and by McDonald and Ward³ strongly indicate that the extra bands in isotactic polypropylene are caused by the helices that the isotactic material can form in the solid state. The presence of helices has been shown by x-ray diffraction.^{4,5} The interactions between the closely spaced atoms in

* Presented as a paper before the Meeting of the American Chemical Society Division of Polymer Chemistry, September 1963, in New York City. At that time this laboratory was the Research Center of the Spencer Chemical Company.

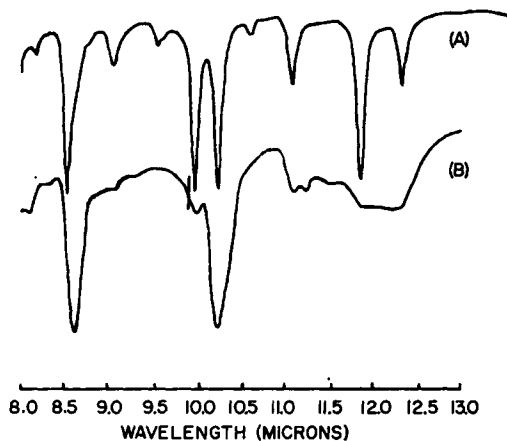


Fig. 1. Spectra of (A) isotactic propylene and (B) atactic propylene, both at room temperature.

the helix give rise to the new absorption bands. As atactic material cannot form helices, it does not show these bands.

Before the work in this paper was started, methods for the measurement of polypropylene isotacticity by infrared spectroscopy had been published by Heinen,⁶ Luongo,⁷ Brader,² and Volchek and Robberman.⁸ The methods of Heinen, Luongo, and Brader depend upon the measurement of the intensity of a band from the isotactic material in the crystalline state relative to that of a band occurring in both isotactic and atactic materials. The methods require calibration with materials of known isotacticity. The method of Volchek and Robberman utilizes the difference in polarization between isotactic and atactic polypropylene of certain short-wavelength bands. Since the work in this paper was completed, several other infrared methods have appeared in the literature. Sibilia and Winckhofer⁹ presented data they obtained by using both Luongo's and Brader's methods besides melting point and infrared methods of their own. Kissin et al.¹⁰ have presented a method that has been criticized by Volchek.¹¹ Koenig and Van Roggen¹² described a novel method depending upon the increase, with increasing atactic content, of the width of the $10.27\text{ }\mu$ infrared band. Koenig et al.¹³ have published the spectrum of syndiotactic polypropylene and compared the spectra of isotactic, atactic, and syndiotactic polypropylenes.

Brader,² from work done at this laboratory, decided that the ratio of the intensity of the $8.57\text{ }\mu$ band to that of the $10.27\text{ }\mu$ band is directly related to the helical content. He annealed the samples by placing them directly in a Carbowax bath at 160°C for 15 min. He states that the helical content is a measure of isotacticity when all of the isotactic material has been converted into the helical form by annealing.

According to Luongo,⁷ crystalline isotactic polypropylene absorbs at $10.00\text{ }\mu$ (995 cm^{-1}), and all forms absorb at $10.27\text{ }\mu$ (974 cm^{-1}). He uses

the ratio of the intensities of these two bands to measure the isotacticity of a polypropylene sample, employing closely controlled, reproducible conditions of sample preparation and a calibration curve prepared by using mixtures compounded of known reference materials. He states that this is actually measuring the crystallinity of the sample but that under reproducible conditions crystallinity is a measure of isotacticity.

At this laboratory a study has been made of the temperature dependence of the infrared bands. Because of the fact that all of the bands unique to the isotactic form disappear at the same temperature, the melting point, we are of the opinion that no distinction can be made between crystallinity and helical content by infrared spectroscopy. It is felt that Luongo and Brader are measuring the same parameter.

We have found that Luongo's method does not work well for highly isotactic samples when his sample preparation technique is used. He has confirmed this by private communication. On the other hand, it works quite well with the addition of a careful annealing procedure. We have adopted his method but with the addition of an annealing procedure developed at this laboratory.

The sample must be carefully annealed so that all isotactic molecules are converted into helices. A further study of Brader's annealing procedure,² placing the samples directly into a Carbowax bath without protection from

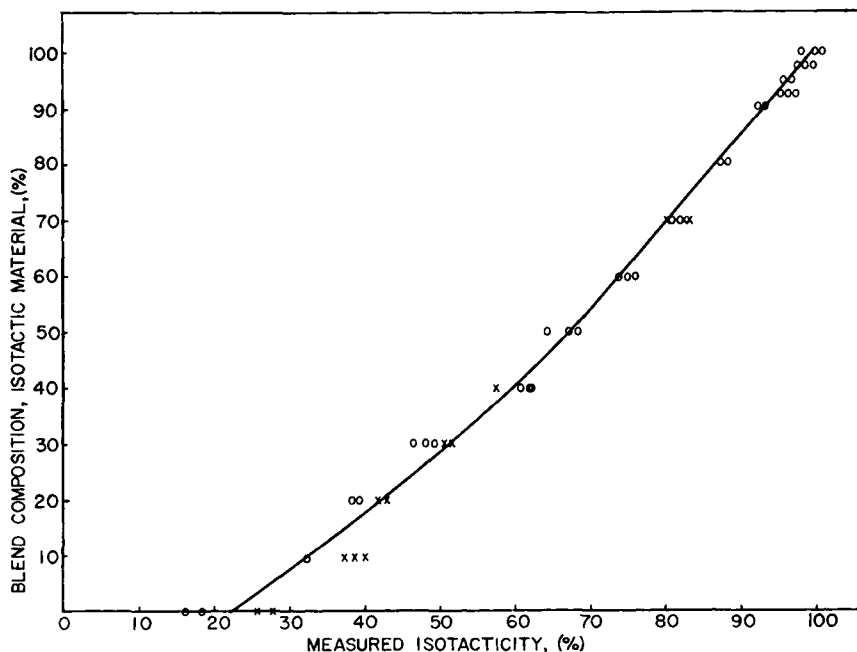


Fig. 2. Measured isotacticity of polypropylene blends: (O) blends of Profax 6511 with laboratory-prepared atactic polypropylene; (X) blends of Profax 6511 with Eastman amorphous polypropylene, Epolene X-3259.

the oil, showed that annealing was occurring but that there was also oxidation of the samples. New bands caused by the oxidation appeared between 9 and 10 μ . These interfere with the bands used for isotacticity measurements. It is thought that this degradation of the material was also giving some change in its isotacticity. Therefore, a bomb with an inert argon atmosphere was designed to hold the samples during annealing. Numerous experiments were performed on annealing conditions before the final ones were chosen. A temperature a few degrees below the melting point of polypropylene was finally chosen, since this seemed to give the most rapid annealing, and a period of annealing was chosen that seemed to give the highest isotacticity without being extremely time-consuming.

When this work was started, relative isotacticity values of highly isotactic materials were needed, not absolute values. It was assumed that the 10.00 μ band of the atactic material would have negligible intensity and thus the intensity ratio of the 10.00 to 10.27 μ band for atactic material would be zero. It was also assumed that when atactic and isotactic materials were mixed, the band intensities would be additive. Under these assumptions the isotacticity would be equal to the measured band ratio. A very large number of samples were measured under these assumptions and the results reported as percent isotacticity, even when the accuracy was not known. All numbers in the tables are given on this basis. After the routine samples had been measured, measurements of mixtures of the best atactic and isotactic materials available were made to determine the accuracy of the method. This curve, Figure 2, can be used as a calibration curve to give accurate isotacticity values from the band ratio values of samples.

Method

The samples are prepared by pressing between 10 \times 10 in. Mylar sheets in a South Bend press with 10 \times 10 in. platens. Small piles of polymer powder, each containing enough polymer to give a film about 2.5 in. in diameter (0.03 g), are placed at spacings of 3 in. in a geometrical arrangement on the bottom Mylar sheet. The amount of material in an individual pile must be such that the films made in pressing do not run together. The top sheet is placed on the bottom one and the sandwich placed in the press, which had been heated to 400°F. A pressure of 30 tons is then applied to the platens. After the polymer has fused and spread, the platens are water-cooled to room temperature while the pressure is still applied. The sheets are removed from the press and the polymer samples peeled from the Mylar. The samples should be between 0.01 mm and 0.02 mm thick. They are trimmed to approximately 1.5 \times 1.5 in.². These are then placed between pairs of pieces of Mylar about 2 in.², and the Mylar is stapled, so that the samples are rigidly held. The samples are then placed in the annealing bomb.

The bomb was made from a 4 in. length of schedule 40, 1.5 in. pipe with pipe threads on both ends. The ends were sealed with regular 1.5 in pipe caps. Teflon pipe-joint sealing tape was used to make the threads gas-

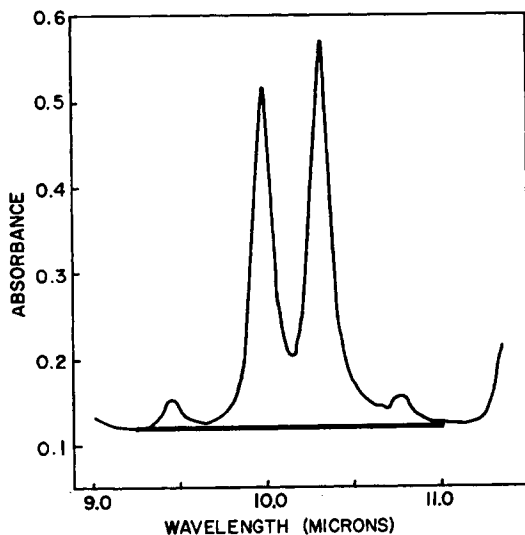


Fig. 3. Absorption between 9.0 and 11.0 μ for polypropylene sample 1196, unannealed. Baseline for isotacticity shown.

tight. One of the caps was drilled in the center and tapped to receive a Swagelok fitting. A copper tube in the fitting was connected to a T fitting, one arm of which was connected to a 100-lb pressure gauge and the other to a Hoke valve and fitting for connection to an argon gas cylinder. The bomb is opened by removing this cap with a pipe wrench.

After the desired number of samples are in the bomb, the cap is screwed back on, after the Teflon tape is put on the joint. The bomb is evacuated with a vacuum pump, to remove the air, and then filled with argon to atmospheric pressure. The evacuation process is repeated several times, to remove all of the air. Then the bomb is filled with argon to a pressure of 60 psi. The gauge is watched several minutes for leaks. The bomb is then placed in the previously heated annealing bath.

The annealing bath consisted of a baking pan 6 in. wide, 12–15 in. long, and 4 in. high, about 7/8 full of silicone oil. It was provided with a tubular heating coil and a thermostat, which regulated to $\pm 0.1^\circ\text{C}$. The oil was stirred with an oil-bath circulating pump. The bath temperature should be between 165 and 167°C.

The bath is allowed to remain at the annealing temperature with the bomb in it for 2.5–3 hr. The heat is then turned off and the bath allowed to cool to room temperature with the bomb in it, which requires about 3 hr. The bomb is then removed from the bath and the oil wiped off. The cap is unscrewed, and the samples are removed. The Mylar sheets are removed from the samples.

The samples should be inspected visually. Samples should have a corrugated appearance but should show no signs of fusion. Films showing fusion are deformed, lose their corrugated appearance, and show thick

areas. If this occurs, they should be discarded and new ones prepared. The annealing is then repeated on the new films but at a temperature several degrees lower.

The spectra are run on the Perkin-Elmer 221 Infrared Spectrophotometer under quantitative conditions with a resolution setting of 990, response of 600, gain of 4.0, and a speed setting of 16 min. These settings give sufficient resolution, little noise, and quite good reproducibility. Only the necessary portion of the spectrum is recorded, 9.0–11.0 μ . An example is given in Figure 3. A baseline is drawn tangent to the lowest absorbance values, as in Figure 3. The intensities of the two bands are measured with respect to this baseline and the ratio of the intensity of the 10.00 μ band (995 cm^{-1}) to that of the 10.27 μ band (974 cm^{-1}) is calculated. This fraction is multiplied by 100 and reported as percent isotacticity, if approximate results are desired. Subsequent data will show that this figure is close to the actual isotacticity, if the sample is in the 90–100% range. More accurate results will be obtained by using Figure 2 as a calibration curve. The actual isotacticity is read from the ordinate scale for the apparent measured isotacticity value located on the abscissa scale.

Effect of Annealing

The results for measurements of the band ratios of eight samples of one of our laboratory polypropylene materials, both before and after annealing, are given in Table I. This material is known to be almost 100% isotactic from solubility behavior and mechanical properties. It will be noted that the annealing procedure gives an average increase of 12.2% in the apparent isotacticity value. Similar results have been noticed with many other samples. These results show that high isotacticity material must be annealed, if accurate isotacticity values are to be obtained.

Precision

The data in Table I gives a fine estimate of the standard deviation of the results for multiple testing of a single material, which is 0.84%. The

TABLE I
Effect of Annealing on Polypropylene 1196

Sample	Apparent isotacticity before annealing, %	Apparent isotacticity after annealing, %
1	85.7	97.8
2	87.6	98.1
3	85.7	99.4
4	86.4	99.2
5	88.6	97.3
6	82.9	98.1
7	87.3	99.6
8	86.9	99.3
Average	86.4	98.6
spread	5.7	2.3

standard deviation for a series of eighteen measurements made from six films of the same material at another time was 0.88%. By this measure the 95% confidence limits are $\pm 2\%$.

Isotacticity as measured for a set of typical samples is shown in Table II. Three places on each film were measured, and for most samples the values fall within a 2% range. A few samples give a much wider spread; there is indication that these materials are actually inhomogeneous. For one material in the table that gave a wide spread ten samples were measured both before and after thorough mixing. The mixing was accomplished by dissolving the samples in toluene, driving off the solvent, pressing, and annealing. There was a spread of 7% in the individual readings before mixing and a spread of only 2.1% after mixing. From consideration of all of these data the precision of the method is believed to be $\pm 2\%$.

TABLE II
Isotacticity Measurements of Laboratory Polypropylene Samples

Sample	Measurements at three positions, %			Spread, %	Reported value, %
1187-A	98.8	97.0	99.3	2.3	98.3
1191	102.2	100.4	101.3	1.8	101.3
1196	93.8	99.3	99.1	5.5	99.2 ^a
1197-A	100.3	102.3	100.4	2.0	101.0
1198	98.7	98.1	100.0	1.3	98.9
1198-A	100.7	101.1	102.0	1.3	101.3
1199	100.0	98.9	99.0	1.1	99.3
1199-A	99.4	98.5	102.7	4.2	99.0 ^a
1200	91.9	95.2	95.3	3.4	95.2 ^a
1236	92.5	92.0	93.5	1.5	92.7
1237	93.2	90.5	86.3	7.2	90.0 ^b
1238	90.0	90.5	88.2	2.3	89.6
1240	86.0	85.1	85.4	0.9	85.5
1241	86.9	86.7	85.2	1.7	86.3

^a The reported value is the average of the two closest values, the two falling within a 2% range.

^b All three values were averaged; there were no two close values.

Absolute Isotacticity Values

To test the hypothesis that the intensity ratio of the 10.00 μ band to the 10.27 μ band is a reasonable measure of isotacticity throughout a wide range, measurements were made on accurately prepared blends of isotactic and atactic materials. Hercules Profax 6511 was the isotactic material used. Two atactic materials were used: atactic material extracted from polypropylene produced at this laboratory and Epolene X-3259, an amorphous polypropylene sold by Eastman. Mixtures were prepared containing from 0 to 100% isotactic material by increments of 10% and also 92.5, 95.0, and 97.5%. These samples were then annealed under the previously described annealing conditions. As the samples of less than 50% isotactic-

ity made with commercial amorphous material melted when annealed at 165°C for 2.5 hr, these samples were annealed at 105°C for 18 hr.

The results of measuring the isotacticity of these blends are shown in Figure 2. The curve is not an ideal one, a straight line going through the origin, but on the other hand it is not unreasonable. The fact that the curve does not go through the origin can be explained by the apparent isotacticity of the atactic materials. The spectrum near 10 μ of the atactic material extracted from the polypropylene produced at this laboratory is shown in Figure 4. This material has an apparent isotacticity of about 20%. The shoulder of the 10.27 μ band causes an apparent absorption at 10.00 μ , which would lead to an apparent isotacticity of about 10% for this sample. The other 10% apparent isotacticity is caused by the definite peak at 10.00 μ . This peak possibly indicates that the material is not 0% isotactic. However, it is not definitely known that 0% isotactic material should not have a small peak at 10.00 μ . The Eastman amorphous material

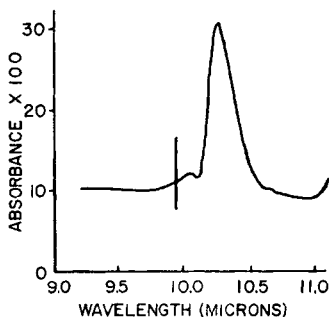


Fig. 4. Absorption of atactic polypropylene near 10 μ .

had a stronger peak on the background at 10.00 μ and thus probably did contain some isotactic material.

The reason for the greater slope of the line for the points from 50 to 100% than for the points below 50% isotacticity is not known. There may be some kind of cooperative action by the isotactic molecules in lining up isotactic segments of the atactic molecules, which increases as more isotactic material is present.

The bias in computing isotacticity as the ratio of the 10.00 μ band to the 10.27 μ band as compared with the calibration curve in Figure 2 is zero at 100%. For 90% isotactic samples the bias is about +3.5%. Therefore, the ratio of the infrared bands of carefully annealed samples is a fairly adequate measure of the isotacticity of the system if the material is in the 90–100% isotacticity range; better results, however, would be obtained by using the calibration curve. As the error continually becomes worse on going below 90% isotacticity, the use of a calibration curve such as that in Figure 3 is mandatory for samples having less than 90% isotacticity.

Conclusions

A decided improvement in measuring the isotacticity of polypropylene by infrared spectroscopy has been made by employing a careful annealing procedure, which converts all the isotactic material into helices and does not oxidize the samples. The precision is believed to be $\pm 2\%$ or better. The accuracy in the 90–100% range is $\pm 2\%$ when the isotacticity values are read from the calibration curve.

The author is indebted to C. Maurice Stephens and to Charles Harris for their assistance with the equipment and measurements and to H. D. Anspen and C. F. Feldman for their advice.

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Received January 26, 1968