Integrated Infrared Band Intensity Measurement of Stereoregularity in Polypropylene

J. L. KOENIG* and A. VAN ROGGEN,† *Plastics Department, E. I. Du Pont De Nemours and Company, Inc., Wilmington, Delaware*

Synopsis

An infrared band asymmetry method involving use of integrated infrared band intensities was devised for the measurement of stereoregularity differences in polypropylene resins. A simple digital readout apparatus was attached to a high resolution infrared spectrophotometer, and a computer program was written to calculate the integrated band intensities from the digital data. Comparison of this method with others based on crystallinity measurements of the isotactic portion and on solvent extraction techniques for measurement of the atactic portion demonstrated its sensitivity for the stereoblock portion of the polypropylene resin. A polypropylene resin which was fractioned by a temperature-controlled sequential extraction was examined by this band asymmetry method and the results reported.

INTRODUCTION

Stereospecific polymerization has led to a class of polymers characterized by an exceptional regularity of structure. For example, isotactic polypropylene has high crystallinity and very good mechanical properties relative to the atactic and stereoblock components; the proportions of these polymers can be varied within wide limits by varying the polymerization conditions. Thus, polypropylenes having physical properties variable over a wide range can be obtained according to their stereoisomeric composition.

A variety of methods are reported for measuring stereoregularity differences in polypropylene. Since for most commercial polypropylenes the isotactic polymer predominates, and since this is the material lending the excellent mechanical properties, a measure of crystallinity is particularly useful. Crude correlations between crystallinity and physical properties are available. However, exceptions are noted, and polypropylene samples with the same crystallinity may have different melting points and solubilities.

Another simple, but time-consuming, method of characterizing the polymer from the viewpoint of the stereoisomeric composition is the extrac-

tion of the raw polymer with boiling heptane or boiling benzene, the weight fraction of residue being taken as a measure of the isotactic character. The limitations of this method are due primarily to the presence of stereo-block polymer which may or may not be extracted and to the poor repro-ducibility of the results.

Realizing a need for a better method of characterizing the polymer, the present study was undertaken. The basis of the method and a description of the digital apparatus designed for this method are given in this report.

DISCUSSION

Effect of Stereoisomers on Infrared Spectra

Peraldo[1] first observed the effect of stereoregularity on the 998 cm.$^{-1}$ skeletal vibration of polypropylene. Quynn[2] related the density of the polymer sample to the absorbance of certain bands in the infrared spectrum of isotactic polypropylene using the 974 cm.$^{-1}$ mixed carbon-hydrogen mode as an internal thickness band. This was followed by similar methods by Luongo[3] and Brader.[4] Luongo used the ratio of the absorbances of the 974 cm.$^{-1}$ and 995 cm.$^{-1}$ bands as a measure of the atactic fraction in the sample. Brader used the ratio, $A_{1167 \text{ cm.}}{}^{-1}/A_{974 \text{ cm.}}{}^{-1}$ to measure the degree of helical structure (as he terms it) as opposed to the per cent isotacticity. The need for a different terminology results from the observation of positive deviations from a linear relationship between the absorption and per cent crystallinity. The reason for such deviations is the failure of all of the isotactic polymers to crystallize. For 100% isotactic polymer, only 80–85% crystallinity is found. In addition, the presence of stereoblock polymer further limits the attainable crystallinity. For example, the n-heptane-soluble polypropylene fraction contains stereoblock material pos-sessing a degree of order corresponding to 20–40% isotactic polypropylene.[5] The crystallinity that this stereoblock polymer can attain depends on the steric arrangement and the temperature of annealing. If extremely short sequences of isotactic units are present, the polymer chain will not be able to assume the helical conformation necessary for crystallization.[6] For intermediate sequence lengths, the crystallization and annealing conditions must be different due to the lower melting points of stereoblock polymers.[7] Thus, the linear relationship between the ratio of the intensity of the ab-sorption bands and density is a useful measure of the "effective" isotacticity from a crystallization point of view, but is not useful at either end of the isotacticity scale. The failure of these procedures was illustrated by Sibilia,[8] who obtained three different values for per cent isotacticity for three different infrared bands, the disagreement being greatest for low tacticity. One serious drawback in the low tacticity range is the failure of the 974 cm.$^{-1}$ band to behave as a true "internal" thickness band.

A measurement of the absolute isotactic content must measure the helical content of the polypropylene sample independent of the crystallinity. Three methods are available in principle to accomplish this objective.
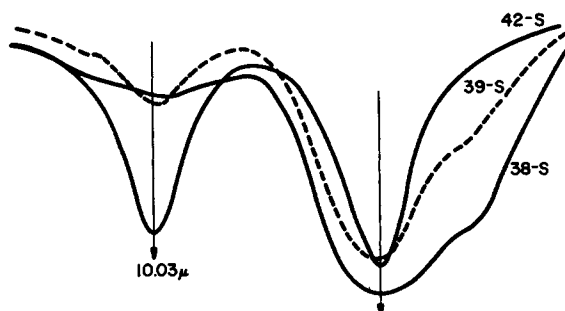
Fig. 1. Portion of infrared spectra of polypropylenes demonstrating effects of stereo-regularity differences: (38-S) *n*-pentane-soluble; (39-S) *n*-hexane-soluble; (42-S) *n*-heptane–*n*-octane-soluble.

First, the measurements can be made on an isolated band which is sensitive to the helical regions. The 1155 cm.$^{-1}$ band has been given such an assignment[9] but has not been used to make any measurements to date. A second expedient, which has been championed by the Russians,[10] is to determine the degree of tacticity on the basis of the ratio of the dichroism of the 2926 cm.$^{-1}$ band to that of the 2845 cm.$^{-1}$ band. This ratio depends on the tacticity but is independent of the degree of crystallinity and elongation of the specimens. However, it is difficult to make this method quantitative. Finally, one can use the broadening of an infrared band which is caused by the slightly different frequencies associated with configurational isomers or differences in sequence length.

The stereochemical difference due to the presence of configurational isomers is reflected in a broadening of the infrared bands in the spectrum.[11] This is illustrated for the 972 cm.$^{-1}$ (10.28 μ) band of polypropylene in Figure 1. The soluble (highly atactic) portions successively extracted by *n*-pentane, *n*-hexane, and a mixture of *n*-heptane and *n*-octane are illustrated. As the atactic fraction decreases, the band becomes narrower. The differences in the 995 cm.$^{-1}$ (10.03 μ) band are a reflection of the differences in crystallinity of the fractions. The 972 cm.$^{-1}$ band has been assigned to a CH_3 rocking mode. The CH_2 rocking mode for paraffins has been reported to have a frequency which is dependent on the number of consecutive methylene groups in the molecule.[12] The number of carbons in the side chain of polyethylene is reflected in a frequency shift of the CH_2 rocking mode.[13] By analogy, this would suggest that the broadening of the 972 cm.$^{-1}$ band is a consequence of different numbers of consecutive isotactic methyl groups in the polypropylene chain. Of course, above a certain number of consecutive methyl groups, the energy shift is too small to be reflected in the frequency. This number seems to closely coincide with the minimum number of consecutive isotactic methyl groups which can form a crystallite. This is apparent in the increased intensity of the 995 cm.$^{-1}$ band for the sample giving the sharpest 972 cm.$^{-1}$ band in Figure 1. The molecules giving rise to the broadened portion of the 972 cm.$^{-1}$
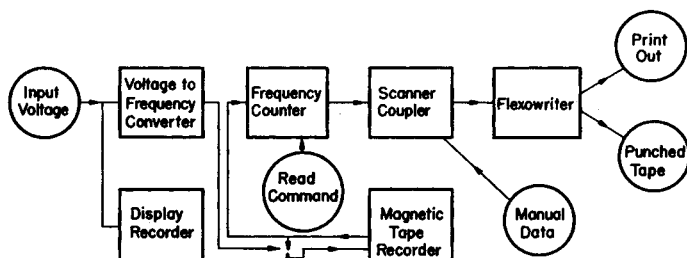
Fig. 2. Block diagram of digital readout system.

band apparently cannot crystallize. This is probably due to the lack of a helical configuration for these very atactic molecules.

Thus, the 972 cm.$^{-1}$ band of the infrared spectrum is sensitive to the number of consecutive isotactic methyl groups in the polypropylene chain. It is interesting to note that apparently interactions with more than the nearest neighbor are being observed. Recent highly successful NMR measurements[14] of stereoregularity of polymers are based only on nearest neighbor interactions. The volume fraction of long isotactic sequences is reflected in the intensity of the 995 cm.$^{-1}$ band. The intensity of this band is sensitive not only to the helical configuration but also to the long-range lateral packing. The smectic phase of polypropylene results in a slight decrease in the intensity of the 995 cm.$^{-1}$ band although the chain configuration is helical in this phase.

It would appear that a very sensitive method exists for measuring stereoregularity differences in polypropylene if these changes in the infrared spectrum can be accurately measured. It was concluded that these small differences could only be observed by making accurate band asymmetry measurements. A digital readout system was used since digital computers allow more flexibility in programming.

Digital Readout Apparatus

The infrared spectrophotometer, a Beckman IR-7 instrument, records per cent transmission as a function of wave number linearly with time. The block diagram of the digital apparatus is shown in Figure 2. The input voltage to the recorder is fed simultaneously to a Dymec voltage-to-frequency converter that produces a pulse train with repetition rate proportional to the absolute value of the input voltage. These pulses are sampled over 1 sec. intervals by a counter with binary coded digital output. This parallel (simultaneous) output is converted into series (consecutive) output by a suitable scanner-coupler and is fed to an 8-channel Frieden Flexowriter typewriter-tape punch. Recorded data are available both on the spectrometer chart, in typed form, and on punched paper tape during the measurement. Additional information such as starting wavelength, sample number, and computer directions can be punched in the Flexowriter before the run. The tape recorder can be used for storage of spectrograms before digitizing.

An interlock between Flexowriter and counter prevents the start of a new count until the previous count has been punched. The shortest time interval between successive counts is 0.5 sec., and the rate of scanning of the spectrometer is so adjusted that the optimum performance is obtained. As many as 100 counts per wave number were possible, but 10 counts per wave number gave the necessary precision. A 2% variance was observed, and this was attributed to day-to-day variations in the performance of the spectrophotometer. It is felt that the error introduced by the digital apparatus was an order of magnitude smaller. The variations were minimized by running a daily standard measurement to which all the measurements were normalized.

Digital Computer Technique for Infrared Band Intensities

The punched paper data were converted to cards for input into an IBM 650 computer. The program deck preceded the experimental data, so many successive experimental runs could be calculated easily. The additional input to the computer were the starting and final wave numbers so that a base line could be drawn by the computer using the initial and final data points. The number of counts in the wavelength increment was given so that the number of data points could be properly accounted for. The computer was instructed to interpolate from the base line to the per cent transmission of the increment and calculate the optical density, average over three increments, multiply by the increment and sum the total area. Since band asymmetry measurements are required, the wave number around which the area was to be taken was read as additional input. A typical example of the computer output is shown in Figure 3. The case column gives the data and sample number. The XO, Xmax and XN columns give the initial wave number, maximum wave number, and final wave number for the sample. The LEFT, RITE, and TOT columns record the respective areas. The final column subtracts the left from right and gives the percentage of the total area on the left side of the band maximum. The final three runs are of the standard and reflect the precision of the measurement.

Method of Measurement and Calibration

The first moment technique of band asymmetry was used, and an asymmetry factor was obtained from the following:

$$R = \frac{\text{Area on right of band maximum}}{\text{Area on left of band maximum}}$$

A highly atactic fraction and a highly extracted isotactic were selected as standards. Mixtures of these two samples were prepared and examined. The results are shown in Figure 4. The linear relationship is an indication that the volume fraction of atactic (or isotactic) material is being measured. The melting points of these mixtures were only slightly depressed, as expected of such mixtures.[7]

IR CALCULATIONS

| CASE	XO	XMAX	XN	LEFT	RITE	TOT	DIF	PERCENT ON LEFT
*92300 00001	950.001	971.001	985.001	611.71991	672.07794	1283.79785	- 60.35804	47.64924
*92300 00002	950.001	971.001	985.001	604.13299	680.05441	1284.18745	- 75.92142	47.04399
*92300 00003	950.001	971.001	985.001	611.96419	612.57196	1224.53615	- 0.60777	49.97519
*92300 00004	950.001	971.001	985.001	612.83714	608.01691	1220.85405	4.82023	50.19741
*92300 00005	950.001	971.001	985.001	625.07497	601.79526	1226.87025	23.27971	50.94374
*92300 00006	950.001	971.001	985.001	776.06235	1013.60235	1789.66465	- 237.54001	43.36356
*92300 00007	950.001	971.001	985.001	752.04701	1015.64985	1767.69685	- 263.60281	42.54389
*92300 00008	950.001	971.001	985.001	770.65246	996.63375	1767.28625	- 225.98131	43.60655

Fig. 3. Computer readout data.
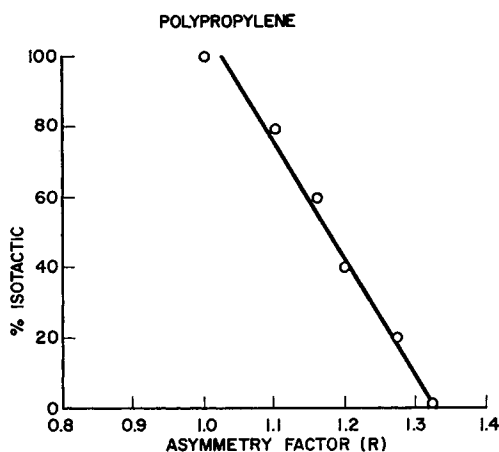
POLYPROPYLENE

Fig. 4. Relationship of asymmetry factor to per cent isotacticity for synthetic mixtures of atactic and isotactic polypropylene.

Having established that the volume per cent of atactic material could be measured, the method was calibrated by examining a series of fractions of a polypropylene sample. The fractionation procedure was sequential column extraction at progressively increasing solvent temperature. As a solvent system, a mixture of xylene with 10% by volume of carbitol was selected. The addition of carbitol broadens the dissolution temperature range and so increases the selectivity in fractionation. The fractionation was carried out stepwise at increasing temperature intervals from 55°C. to the temperature of complete polymer dissolution. Such a fractionation procedure separates mainly according to structural features and only to a limited degree on the basis of the molecule weight. The data on the fractions are given in Table I.

With the use of similar data of Natta[7] as a calibration, the melting point of the fraction was used to calculate a per cent irregularity. An essentially linear correlation of the asymmetry factor with the per cent isotacticity is obtained. Hence, a measurement of the asymmetry factor gives a volume average measure of the stereoregularity of the polymer.

Conclusion

The relationship between per cent crystallinity and stereoregularity has found much favor in the past. However, the crystallinity level has a definite limit. This is probably due to the entanglement of the extremely long chain resulting in a limit to the crystallizable portion of the chains. These chains are, however, capable of assuming the helical form and are crystallizable theoretically if annealed for a sufficiently long period of time However, despite the fact that crystallinity is, in reality, an expression of the isotacticity of the molecule, nevertheless, as a result of the annealing required, under normal conditions a divergence between crystallinity and

TABLE I
Physical Data for Sequentially Fractionated Polypropylenes

Fraction	Experimental temp., °C.	Melting point (DTA), °C.	Crystal- linity, %[a]	Asymmetry R	Isotactic content, %[b]
1	55	102	19	1.26	68
2	65	132	42	1.11	81
3	75	—	55	1.04	—
4	85	143	61	1.05	86
5	95	147	—	—	—
6	105	155	81	1.05	91
7	110	155	80	1.08	91
8	112	—	—	0.99	—
9	114	—	79	—	—
10	116	167	77	1.02	95
11	118	167	79	0.93	96
12	120	—	77	—	—
13	125	169	79	0.91	97

[a] Measured by infrared analysis.
[b] 100% irregularity.

isotacticity is observed. In the ranges of isotacticity of 80–100%, crys-tallinity measurements do not necessarily reflect the inherent tacticity of the polymer. The infrared asymmetry method described in this paper detects stereoregularity differences in this range as the high molecule weight fractions in Table I illustrate. For lower levels of isotacticity, a crystal-linity measurement is adequate.

References

1. Peraldo, M., *Gazz. Chim. Ital.*, **89**, 798 (1959).
2. Quynn, R. G., J. L. Riley, D. A. Young, and H. D. Noether, *J. Appl. Polymer Sci.*, **2**, 166 (1959).
3. Luongo, J. P., *J. Appl. Polymer Sci.*, **3**, 302 (1960).
4. Brader, J. J., *J. Appl. Polymer Sci.*, **3**, 370 (1960).
5. Russell, C. A., *J. Appl. Polymer Sci.*, **4**, 219 (1960).
6. Liang, C. Y., and W. R. Watt, *J. Polymer Sci.*, **51**, S14 (1961).
7. Natta, G., *J. Polymer Sci.*, **34**, 531 (1959).
8. Sibilia, J. P., and R. C. Wincklhofer, *J. Appl. Polymer Sci.*, **6**, S56 (1962).
9. Folt, Y. L., J. J. Shipman, and S. Krimm, *J. Polymer Sci.*, **61**, S17 (1962).
10. Volchek, B. Z., and Zh. N. Robberman, *Vysokomol. Soedin.*, **2**, 1157 (1960).
11. Novak, A., and E. Whalley, *Trans. Faraday Soc.*, **55**, 1490 (1959).
12. McMurry, H. L., and V. Thornton, *Anal. Chem.*, **24**, 318 (1962).
13. Bryant, W. M. D., and R. C. Voter, *J. Am. Chem. Soc.*, **75**, 6113 (1953).
14. Bovey, F. A., and G. V. D. Tiers, *J. Polymer Sci.*, **44**, 173 (1960).

Résumé

On a imaginé une méthode basée sur l'assymétrie des bandes infra-rouges utilisant l'intensité intégrée de ces bandes pour la mesure des différences de stéréorégularité des résines de polypropylène. On complète un spectrophotomètre infra-rouge de haute résolution par un simple appareil à lecture directe et un calcul programmé afin de calculer les intensités intégrées des bandes en partant de ces données Lorsqu'on compare cette méthode avec d'autres basées sur des mesures de cristallinité de la fraction isotactique et sur des mesures d'extraction par solvant pour la mesure de la fraction atactique, on peut se rendre compte de sa sensibilité pour mesurer la fraction stéréobloc des résines de polypropylène. On a étudié par cette méthode d'asymétrie des bandes une résine polypropylène qui a été fractionnée par une extraction successive controlée par la température, et on rend compte des résultats obtenus.

Zusammenfassung

Eine Infrarotbandenasymmetriemethode mit Benützung integrierter Infrarotbandenintensitäten wurde zur Bestimmung von Stereoregularitätsunterschieden bei Polypropylenharzen angegeben. Ein einfacher Digitalableseapparat wurde an einem Hochauflösungsinfrarotspekrophotometer angebracht und ein Computerprogramm zur Berechnung der integrierten Bandenintensitäten aus den digitalen Daten aufgestellt. Ein Vergleich dieser Methode mit anderen, auf der Kristallinitätsmessung des isotaktischen Anteils und auf Lösungsmittelextraktionsverfahren zur Messung des ataktischen Anteils beruhenden, zeigte ihre Empfindlichkeit für den Stereoblockanteil der Polypropylenharze. Ein mittels einer temperaturkontrollierten Extraktionsfolge fraktioniertes Polypropylenharz wurde nach dieser Bandenasymmetriemethode untersucht und die Ergebnisse mitgeteilt.