

The Use of Infrared Spectroscopy for Determination of Polypropylene Stereoregularity

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Synopsis

This study examines the application of infrared (IR) spectrometry to the determination of polypropylene (PP) stereoregularity. The use of the absorption bands at 998 cm^{-1} and 841 cm^{-1} as indices of isotacticity and bands at 1167 cm^{-1} and 973 cm^{-1} as internal references have been explored. Calibration curves relating various absorption ratios to isotacticity as measured by ^{13}C nuclear magnetic resonance are reported. The ratios A_{998}/A_{973} and A_{841}/A_{973} are the most useful and provide linear correlations with isotacticity. The effect of instrument type on the calibration has been investigated for both dispersive and Fourier transform type IR spectrometers. For samples annealed at room temperature the average of measurements on the same set of PP films by five instruments provide the calibrations: $A_{998}/A_{973} = 1.08 \pm 0.02 (\text{mm}) - 0.15 \pm 0.03$; and $A_{841}/A_{973} = 0.84 \pm 0.06 (\text{mm}) - 0.04 \pm 0.02$. High temperature annealing increases the crystallinity of the samples and the corresponding value of the absorption ratio but is not necessary for obtaining reproducible calibration curves.

INTRODUCTION

Polypropylene (PP) is an important commercial polymer whose synthesis and properties have been actively researched for more than three decades. An interesting aspect of the PP chain structure is the existence of distinct configurational isomers resulting from the presence of a *pseudo* asymmetric carbon atom. The actual polymer stereoregularity or tacticity, as it is termed, is quite variable, being dependent on the nature of the catalyst, the presence or absence of additives, and other parameters such as temperature or reaction medium. Since the polymer morphology and hence physical properties are crucially dependent on the PP tacticity, the measurement of the same is of considerable moment both in commercial production and fundamental investigations.

Various methods have been developed over the years to measure the stereoregularity of PP and these methods, which have been briefly reviewed,¹⁻³ include: solvent extraction; IR spectrometry; X-ray diffraction; calorimetry and density measurements. All these techniques, however, provide only an indirect assay of stereoregularity since the parameters are actually measures relating to the crystallinity or conformational arrangement of the PP macromolecule and not tacticity per se.

A major breakthrough in PP characterization was made possible with the application of high resolution ^1H and ^{13}C nuclear magnetic resonance (NMR) which allows the absolute determination of tacticity. These methods, which have been comprehensively reviewed,⁴⁻⁷ are of paramount importance since

they permit not only quantification of tacticity but also elucidation of stereo-sequences. However, although NMR characterization provides the most fundamental information about stereostructure, secondary methods based on IR spectroscopy or solvent extraction are still very widely employed. The continuing use of these secondary methods is a direct consequence of simplicity, speed, and low equipment cost which are particularly important for routine or screening analysis.

As has been discussed elsewhere,² the solvent extraction technique is not a reliable method since the degree of extraction is dependent on molecular weight as well as stereoregularity. Measurement by IR spectroscopy is potentially more promising and semiquantitative evaluations are possible. However, the IR methods currently employed suffer from two main drawbacks: the absence of suitable calibration and the problem of thermal history effects. Thus the earliest calibration data of Luongo,⁸ which is still quoted, predates the development of NMR analysis and consequently is based on physical mixtures of atactic and isotactic PP, of assumed stereoregularity, as the reference standards. Even if the calibration standards prove correct there is no reason to suppose that the IR behavior of heterogeneous physical mixtures corresponds to the response of homogeneous polymer of varying stereoregularity. The second limitation is the change induced in the IR spectra by thermal history effects. Thus the IR bands used to measure isotacticity are actually bands sensitive to the formation of regular isotactic helices rather than isotacticity itself. As such the IR absorbance will be dependent on pretreatment and annealing which determine the conformation and morphology of the polymer chains.

Since IR analysis is a relatively simple, fast, and potentially quantitative approach, we have reinvestigated the use of IR spectroscopy for the determination of PP isotacticity. In this paper we report IR calibration curves based on NMR triad tacticity values. The problem of thermal history effects has been investigated, and a simple procedure proposed for obtaining reproducible results.

EXPERIMENTAL

Materials

Polypropylene samples spanning the isotacticity range $m = 0.35$ to 1.00 were of varying molecular weight and were obtained from a variety of sources including both laboratory and commercial plant preparations. Methods for laboratory syntheses have been described or referenced in earlier publications.^{9,10} Certain samples were fractionated by hot heptane extraction² into a heptane insoluble (HI) and heptane soluble (HS) fractions.

Characterization

Polymer isotacticities were determined by ¹³C-NMR measurements using a JEOL FX-200 spectrometer on 15-30 w/v% dichlorobenzene solutions at 413 K, as described earlier.^{11,12}

Samples were prepared for IR examination by hot pressing 50 mg samples between aluminium foil at temperatures in the range 120–200°C. The lower

temperatures were used for samples of low stereoregularity which tended to form very thin films at higher temperatures. Samples were pressed for approximately 5 s, immediately removed from the press, and allowed to air cool to ambient temperatures. Films for certain of the HS samples were prepared by casting from hot toluene solutions onto glass plates and removing solvent under high vacuum. When required, samples were annealed at elevated temperatures by heating the film, sandwiched between aluminium foil, in an evacuated glass tube (10^{-2} mmHg) which was thermostated in an oil bath. The samples were annealed at temperatures approximately 5–10 K below the melting point as determined by differential scanning calorimetry (DSC). After annealing for 3 h, the samples were then allowed to cool slowly in the oil bath for a further 2 h, while maintaining a vacuum environment. Samples of very low isotacticity which did not form a coherent film were examined and annealed after casting onto a sodium chloride disc.

Two distinct mounting procedures were used for IR examination, namely: (i) use of a film holder; and (ii) sandwiching between NaCl discs. The prepared samples were analyzed by representative IR instruments of both conventional dispersive and Fourier transform types in six different laboratories in Malaysia, the United States, and Japan. For these comparative instrument studies a set of samples was employed which had been pressed and annealed for at least 7 days at ambient temperatures.

Absorbance ratios were found to be influenced by the computerized data processing available with certain of the Fourier transform infrared (FTIR)

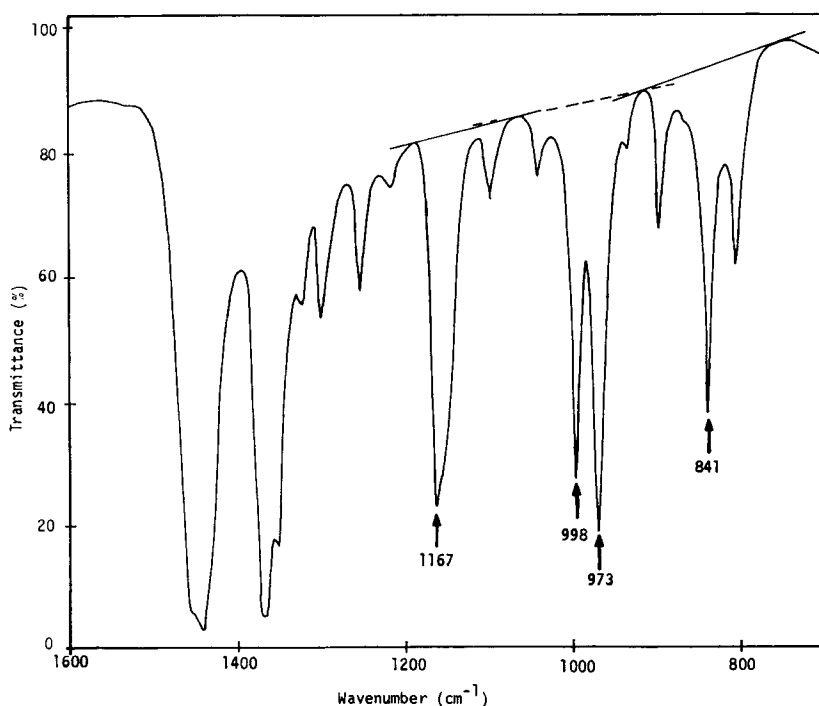


Fig. 1. IR spectrum of isotactic ($m = 0.82$) polypropylene in the 1600 cm^{-1} to 700 cm^{-1} region, showing positioning of measurement baselines.

instruments. In particular, *smoothing* of the IR spectrum and *flattening* of the data to give a common baseline introduced considerable differences compared to untreated data. To avoid data processing-induced differences, all spectra were evaluated manually using the following baselines for the denoted peak absorptions: A_{840} (910 cm^{-1} to 760 cm^{-1}); A_{970} and A_{995} (1060 cm^{-1} to 910 cm^{-1}) and A_{1160} (1180 cm^{-1} to 910 cm^{-1}) as shown in Figure 1. Errors were minimized by optimizing the film thickness so as to obtain % transmission values in the region of 20 to 30 for the peaks of interest. The spectrum from the dispersive instruments were obtained as % transmission plots, whereas the FTIR output was plotted as absorbance with expansion to full scale for the relevant peaks.

RESULTS AND DISCUSSION

Quantitative IR Studies of Stereoregular Polypropylene

IR spectroscopy has been widely used in the elucidation of PP stereostructure ever since Natta et al.¹³ first reported the spectrum of the crystalline polymer. Most studies have concentrated on identifying suitable bands to measure tacticity and to correlate with other indices of stereoregularity. The bands apparently associated with isotactic helices absorb at 1220, 1168, 998, 900, 841, and 809 cm^{-1} and of these the bands at 841 and 998 cm^{-1} have been principally used for the derivation of calibration curves. Since it is difficult to prepare films of a standard thickness, it is customary to use an internal reference band and the absorptions at 1460, 1168, and 973 cm^{-1} have been generally used for this purpose. It is perhaps worth noting that the origin of the reference band at 973 cm^{-1} , which is observable both in the melt of isotactic samples^{8,14} as well as in purely atactic material,¹⁴ is disputed. Thus the band, which has been attributed^{14,19} specifically to the polypropylene head-to-tail sequence of repeating units, has also been associated with the presence of short isotactic helices apparently still present in the melt or atactic material.¹⁵

Although quantitative IR studies of stereoregular polypropylene have been carried out by several authors, much of the published work is concerned with the determination of polymer crystallinity rather than isotacticity. Thus, in a comprehensive study Quynn et al.¹⁶ have shown that the absorbance ratios A_{997}/A_{972} , A_{840}/A_{972} , and A_{808}/A_{972} are all linearly related to polymer density and hence may be used as measures of polymer crystallinity. At the same time Heinen¹⁸ showed that the absorbance ratio A_{841}/A_{1168} bore a similar relationship with crystallinity.

The earliest study seeking to provide an IR calibration for isotacticity determination appears to be the work of Luongo⁸ who indexed the ratio A_{974}/A_{995} against physical mixtures of supposedly atactic and isotactic polymers. This calibration was later modified by an annealing procedure, initially in air²⁰ and subsequently under argon,²¹ the purpose of which was to ensure that all of the isotactic segments were converted to IR active isotactic helices. Hughes²¹ suggested that for annealed highly stereoregular PP, the numerical value of the ratio A_{995}/A_{974} was very close to the isotactic fraction (I). Subsequently, the most extensive studies relating to IR characterization were

carried out by Kissin and co-workers and much of this work has been summarized.^{3,15,22} Essentially, three indices for measurement of isotacticity were proposed. These included the ratio A_{998}/A_{973} earlier proposed by Luongo,⁸ which was now designated as the macrotacticity (M). Two further ratios: A_{973}/A_{1460} [known as the spectral degree of isotacticity (α)] and A_{841}/A_{973} were also proposed. The significance of utilizing three distinct indices lies in the observation that the appearance of these helix bands is sensitive to the length of the isotactic sequences.³ Thus the critical sequence lengths for the appearance of these bands are: 998 cm^{-1} (11–12 units); 973 cm^{-1} (5 units); 841 cm^{-1} (13–15 units). The advantage claimed for using the 973 cm^{-1} band is its sensitivity to even low levels of isotactic units and its apparent insensitivity to thermal history effects. However, the use of this band is complicated by the uncertainty of the assignment and the reduced sensitivity for highly isotactic polymers.

The quantitative measurements proposed by Kissin et al. are based on calibration with supposedly completely isotactic samples and require the assumption that there is a linear relationship between the absorption ratios and isotacticity.^{15,23} Thus, for example, the degree of isotacticity α is given by the relationship:¹⁵

$$\alpha = (A_{973}/A_{1460}) : N$$

N is a normalizing factor obtained by calibration with a highly isotactic sample and is sensitive to instrument type. (Values of $N = 0.265$ and 0.300 were observed for two different dispersive instruments.)

It is quite clear from the above discussion that none of the numerical values derived from the above methods can be easily equated to numerical tacticity values determined by more fundamental NMR measurements. Furthermore, there are considerable uncertainties with respect to: sample pretreatment, instrument effects, and calibration standards. In light of these deficiencies the current work has been conducted in an attempt to establish an empirical IR method based on an absolute NMR calibration, with standardized sample preparation methods and applicable to a wide range of instrumentation.

Designation of Peak Wavenumbers and Choice of Absorbance Ratios

The literature accounts of the IR spectra of tactic PP samples indicate a range of wavenumber values associated with the peaks of interest. The range may in part be due to differences in instrument calibration or to shifts associated with changes in polymer stereoregularity. In this study four absorption bands have been selected for measurement of isotacticity or as an internal reference, and these are designated as: 1167, 998, 973, and 841. The actual observed wavenumbers associated with these bands, as measured by two FTIR instruments, are summarized in Table I. It may be seen that only the 1167 band shows a significant dependence of wavenumber on tacticity.

Various absorption ratios have been proposed in the literature, *vide supra*, as indices of isotacticity. The ratios examined in this study are: A_{998}/A_{1167} ; A_{998}/A_{973} ; A_{841}/A_{1167} ; and A_{841}/A_{973} . The helix peak at 809 cm^{-1} was

TABLE I
Observed Peak Wavenumbers for Selected Absorption Bands as a Function of Polymer Isotacticity

Sample	NMR isotacticity (mm)	1167 band		998 band		973 band		841 band	
		I	II	I	II	I	II	I	II
PP52HS	0.54	1158.0	1158.1	998.0	997.4	973.0	972.8	841.0	840.9
PP52	0.82	1167.0	1166.5	998.0	997.6	973.0	972.8	841.0	840.9
PP52HI	0.95	1167.0	1167.1	998.0	997.6	973.0	973.1	841.0	840.9

I — Measurement with a Perkin-Elmer Model 1710 FTIR.

II — Measurement with a Mattson Sirius 100 FTIR.

TABLE II
Reproducibility of IR Absorbance Ratios at Different Peak Intensities

Transmittance range	Absorbance ratios			
	A_{998}/A_{973}	A_{841}/A_{973}	A_{998}/A_{1167}	A_{841}/A_{1167}
90–10%	0.839 ± 0.019	0.757 ± 0.015	0.936 ± 0.005	0.844 ± 0.004
90–20%	0.827 ± 0.007	0.739 ± 0.002	0.929 ± 0.009	0.830 ± 0.002
90–30%	0.820 ± 0.007	0.722 ± 0.007	0.919 ± 0.006	0.809 ± 0.006
90–40%	0.813 ± 0.016	0.707 ± 0.006	0.948 ± 0.013	0.825 ± 0.010

Perkin-Elmer Model 1330.

generally found to give a rather weak absorption, whereas the reference band¹⁷ at 1460 cm^{-1} was generally too intense to provide accurate absorption values, hence the use of these bands was not considered.

Preliminary Studies

Various preliminary studies were carried out as a prelude to the determination of the empirical calibration curves. The effect of the film thickness on the reproducibility of IR absorption measurements was first determined. Films of different thickness were prepared which provided for the bands of interest to be in the transmittance range from 90% (baseline) to 10, 20, 30, or 40% (maximum intensity). The reproducibility of measurement, of samples measured in triplicate, at each film thickness is shown in Table II. The best reproducibility, within $\pm 1\%$, was observed for films of such a thickness so as to provide a peak intensity equivalent to a transmission in the 20–30% region and such samples were employed in this study.

The effect of sample mounting on absorbance ratios was also investigated. Samples were mounted either directly in a suitable film holder or cardboard mount, or alternatively sandwiched between sodium chloride plates. The latter procedure is necessary for samples of very low isotacticity which do not form a coherent film, and has the advantage of ensuring the film is perpendicular to the sample beam. Unfortunately, the method of mounting does appear to have a significant effect on the quantitative value of the absorbance ratios. For a series of 4 samples run in a dispersive IR instrument (PE 1330) the value of the A_{998}/A_{973} ratio was approximately 4–5% higher when sandwiched between sodium chloride plates. There appear to be two possible explanations for this phenomenon: irregularities in the baseline due to the presence of sodium chloride plates and/or temperature effects. Direct observation of the baseline in absence of the sample does in fact show some absorption by the sodium chloride but the effect is small. However, monitoring the temperature of the film with a thermocouple reveals a rapid temperature rise after placing in the IR beam. Thus within 30 seconds the temperature rises from 20 to 45°C and by 2 minutes has reached 54°C . It seems likely that this significant temperature rise could influence the equilibrium polymer conformation and hence the absorption derived from the isotactic helices.

The relatively massive sodium chloride plates thus probably act as an effective heat sink, reducing the film temperature and hence increasing the absorption coefficient.

TABLE III
Effect of Instrument Type, Mounting Procedure,
and Reference on Absorption Ratios

Sample mounting	Reference or ^a	A_{998}/A_{973}	A_{841}/A_{973}	A_{841}/A_{1167}	A_{998}/A_{1167}
	baseline subtraction				
Dispersive IR ^b					
Direct	Air	0.82	0.74	0.83	0.91
NaCl	NaCl	0.88	0.80	0.85	0.96
NaCl	Air	0.87	0.76	0.83	0.95
FTIR ^c					
Direct	Air	0.86	0.77	0.88	0.98
NaCl	NaCl	0.88	0.79	0.88	0.98
NaCl	Air	0.86	0.75	0.84	0.97

Sample is DRB5HI ($mm = 0.89$).

^aIndicates reference used in second beam for dispersive instrument or, baseline subtraction for FTIR.

^bPerkin-Elmer model 1330.

^cMattson Sirius 100.

The above suggestion was further tested by comparing the IR absorption of a particular sample measured with both dispersive and FTIR instruments. Monitoring the film temperature in the FTIR instrument immediately revealed significant differences since the film temperature after 10 min was only 25°C compared to an ambient temperature of 20°C. The absorbance ratios measured in the two instruments, while employing the two mounting procedures, are summarized in Table III. The absorption ratios based on the 998 cm^{-1} band show the clearest trend. Thus the lowest ratio is shown by the film mounted directly in the dispersive instrument. Films mounted between sodium chloride plates or mounted directly in the FTIR instrument show significantly higher values. Compensation by using a sodium chloride reference cell in the double beam instrument or by reference baseline subtraction in the FTIR instrument does not show very marked differences. It may be concluded that temperature effects rather than reference imbalance is the main cause for the observed sample mounting variations, and that sample temperature rise is minimized by the use of FTIR instrumentation.

Another aspect of film mounting was the possible influence of orientation effects. Films of approximately 6 cm diameter were examined with the center or edge of the films being placed in the sample beam. Although small variations in absorbance ratios were observed these were generally within the reproducibility of the measurement and hence no significant orientation effects were detected.

The Effect of Sample Annealing

Previous authors^{20,21} have emphasized the need for high temperature annealing of samples in order to obtain reproducible results. The purpose of annealing is to develop fully the crystallinity of the sample and to destroy the previous thermal history. However, such annealing is time-consuming and requires specialized techniques to circumvent sample oxidation. Since hot-

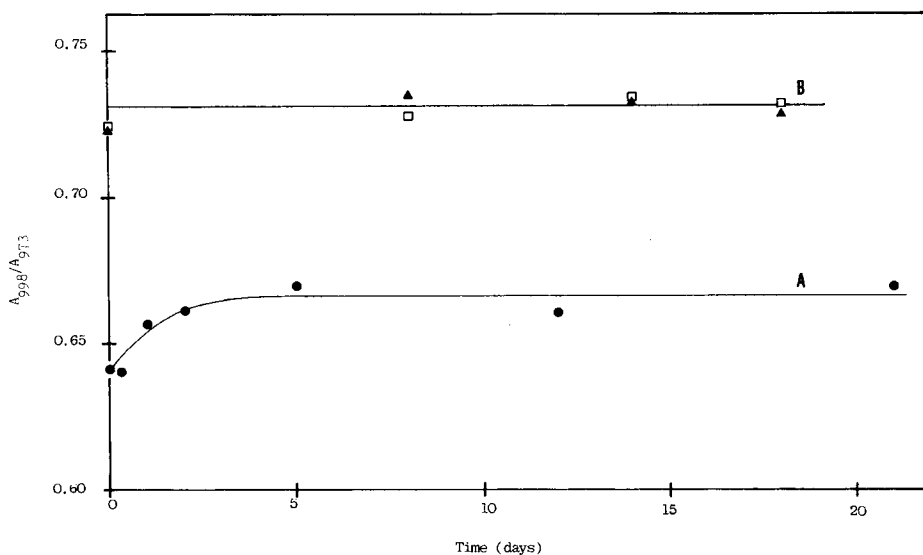


Fig. 2. The effect of sample annealing on the absorption ratio A_{998}/A_{973} . Curve A: ambient temperature annealing. Curve B: high temperature annealing.

pressing of the sample films should provide rather similar thermal histories it appeared pertinent to investigate whether further annealing was actually necessary in attempts to obtain reproducible results.

Initially, samples were hot-pressed and IR measurements were made at regular time intervals while storing the samples at ambient temperatures (ca., 25°C). Figure 2 (Curve A) illustrates the typical effect of room temperature annealing on the absorption ratio A_{998}/A_{973} . The effect, which is quite similar for the other absorption ratios, involves a slow increase of about 4% in the value, reaching a maximum after about 5 days at ambient temperatures. Storage, for periods of up to 75 days, provide no additional changes in the absorption ratio.

The results of high temperature annealing under vacuum are displayed in Figure 2 (Curve B). The figure records the effect of the annealing of a freshly pressed sample and one aged for 75 days before annealing. In both cases the annealing process significantly increases the absorption ratio by about 18% for the aged sample. However, after annealing the absorbance values for the two samples are indistinguishable and no further long-term changes occur on room temperature storage.

There would appear to be three possible approaches to sample preparation for IR measurement in order to obtain reproducible results:

1. Hot-press and run immediately within 1 or 2 hours
2. Hot-press and allow to anneal at ambient temperatures for > 5 days
3. Hot-press and anneal at high temperatures

All three approaches are technically feasible and have been employed in this study. The reproducibility of calibration curves obtained by the different techniques are discussed below.

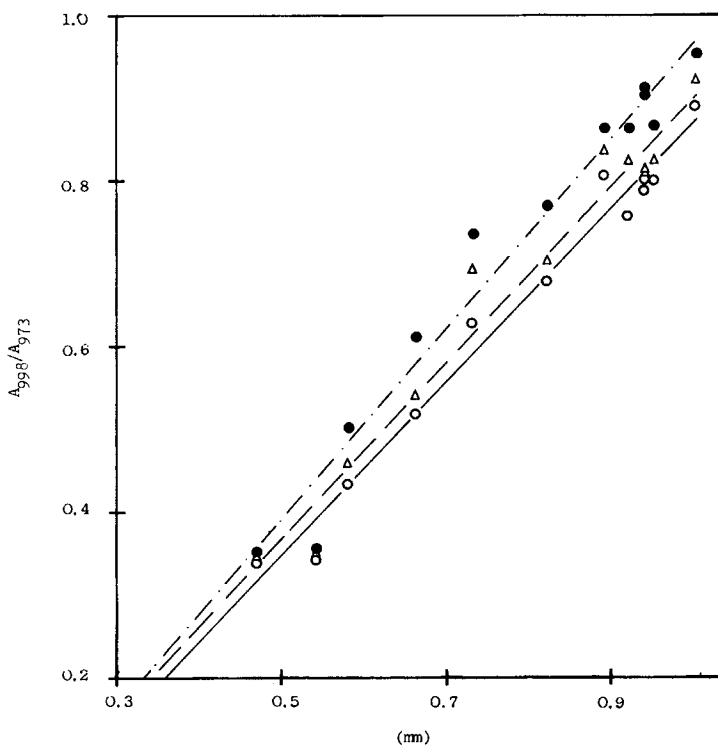


Fig. 3. Calibration curve for IR absorbance ratio A_{998}/A_{973} versus NMR triad isotacticity. (●) High temperature annealed; (○) hot-pressed only; (Δ) ambient temperature annealed.

IR Calibration Curves

Four possible calibration curves of absorption ratio versus NMR tacticity were investigated and these are: the absorption at 998 cm^{-1} referenced to bands at 973 cm^{-1} or 1167 cm^{-1} and the absorption at 841 cm^{-1} with the same reference bands. The forms of the calibration curves so obtained are shown in Figures 3–6. The use of the 973 cm^{-1} band as reference provides effectively linear calibration curves for both ratios and this was found to be true for all of the instruments employed and for all sample treatment conditions. However, calibrations based on the 1167 cm^{-1} reference are curves the form of which provides rather low sensitivity in the important high isotacticity ($mm > 0.8$) region. For this reason we consider the 973 cm^{-1} band as the most appropriate reference and consequently data for this band will be most fully described. A further advantage of calibrations involving the 973 cm^{-1} reference is the possibility of representation as the simple linear equation:

$$\text{Absorption ratio} = m(mm) + c \quad (1)$$

where mm is the NMR triad isotacticity and m and c are constants depen-

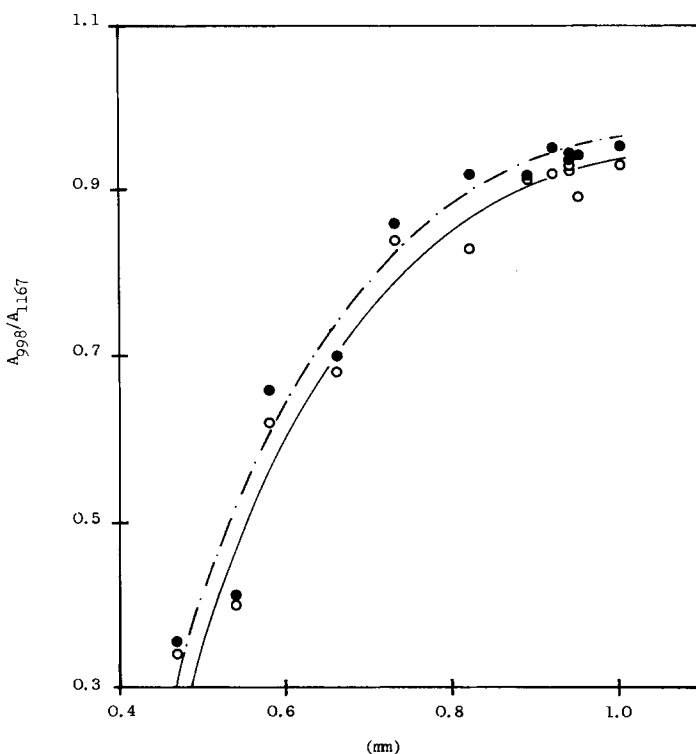


Fig. 4. Calibration curve for IR absorbance ratio A_{998}/A_{1167} versus NMR triad isotacticity. (●) High temperature annealed; (○) hot-pressed only.

dent on the measurement band and sample thermal history. Such representation aids statistical treatment.

The effect of high temperature annealing on the calibration curves is to shift the absorption ratios to higher values and is similar for all cases as shown in Figures 3-6. Room temperature annealing has a less pronounced, but nevertheless significant, effect. Comparison of these calibrations is made in Table IV where the gradient (m) and intercept (c) values are summarized. Although sample treatment does give rise to shifts in the calibration curves, there is only limited variation in the fit of the data. This contrasts with the much earlier publication²¹ where it was claimed that high temperature annealing was a prerequisite of good reproducibility. Since high temperature annealing is time-consuming, requires prior knowledge of the PP melting point, and has no demonstrable advantages over the other sample preparation techniques, it was decided to concentrate on these latter approaches. What does appear to be important is to use a consistent and uniform approach, that is, to either measure samples almost immediately after hot-pressing or after an extended period of approximately 5 days when annealing is effectively complete.

In earlier studies¹⁵ it has been suggested that calibration curves may be somewhat instrument dependent. This is a serious consideration in any attempt to prepare universally applicable calibrations; consequently it was

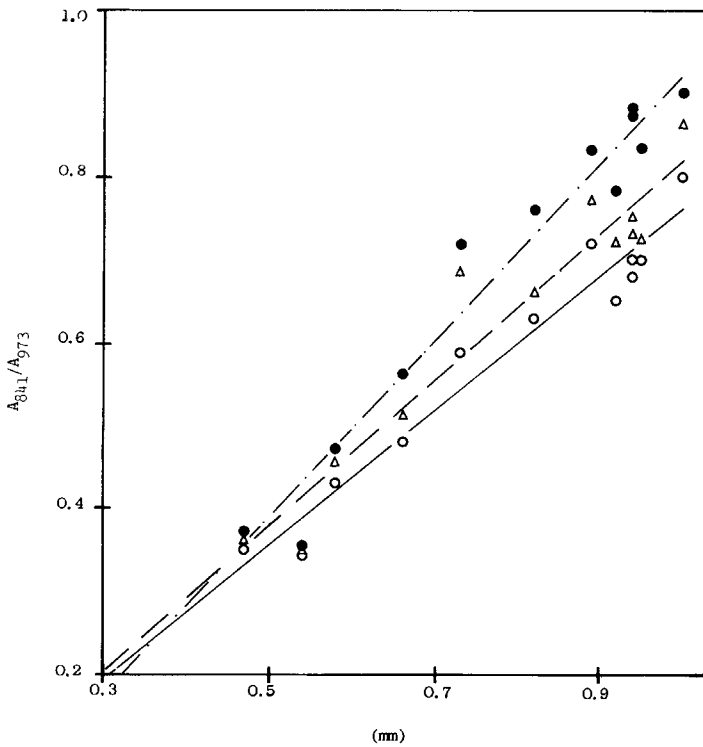


Fig. 5. Calibration curve for IR absorbance ratio A_{841}/A_{973} versus NMR triad isotacticity (●) High temperature annealed; (○) hot-pressed only; (△) ambient temperature annealed.

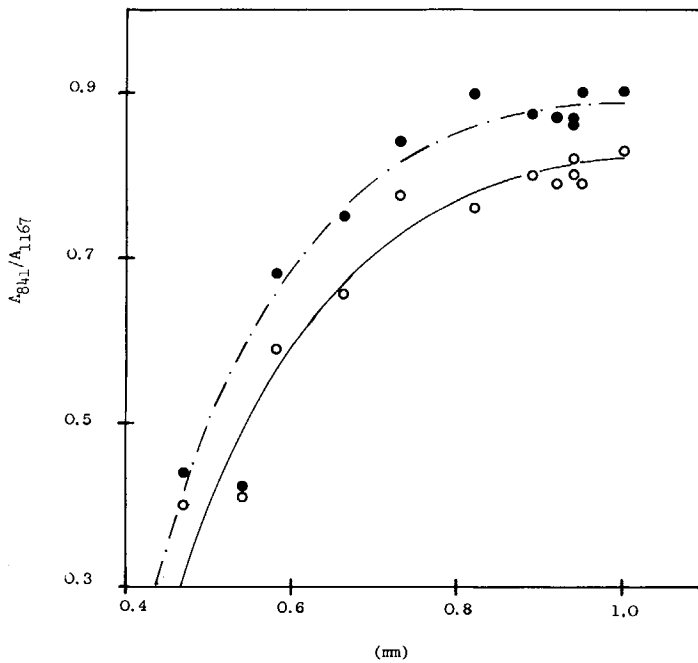


Fig. 6. Calibration curve for IR absorbance ratio A_{841}/A_{1167} versus NMR triad isotacticity. (●) High temperature annealed; (○) hot-pressed only.

TABLE IV
Effect of Ambient and High Temperature Annealing on Isotacticity Calibration Curves

Sample treatment	A_{841}/A_{973}		A_{998}/A_{973}	
	<i>m</i>	<i>c</i>	<i>m</i>	<i>c</i>
As pressed	0.81 ± 0.07	-0.05 ± 0.06	1.05 ± 0.06	-0.18 ± 0.05
Ambient temperature annealing	0.88 ± 0.10	-0.06 ± 0.09	1.07 ± 0.09	-0.17 ± 0.07
High temperature annealing	1.06 ± 0.08	-0.14 ± 0.06	1.15 ± 0.08	-0.19 ± 0.06

Instrument: Perkin-Elmer Model 1330; Direct mounting, air reference.

TABLE V
Dependence of Calibration Curves on Instrument Type

Instrument	A_{998}/A_{973}		A_{841}/A_{973}	
	<i>m</i>	<i>c</i>	<i>m</i>	<i>c</i>
Dispersive				
Perkin Elmer 1330	1.07 ± 0.09	-0.17 ± 0.07	0.88 ± 0.10	-0.06 ± 0.09
Perkin Elmer 782	1.07 ± 0.06	-0.15 ± 0.05	0.87 ± 0.06	-0.07 ± 0.05
FTIR				
Nicolet 5MX	1.10 ± 0.04	-0.17 ± 0.04	0.78 ± 0.03	-0.01 ± 0.03
Perkin Elmer 1710	1.10 ± 0.06	-0.17 ± 0.05	0.77 ± 0.05	-0.03 ± 0.04
Mattson Sirius 100	1.05 ± 0.09	-0.11 ± 0.08	0.88 ± 0.10	-0.04 ± 0.08
Mean value	1.08 ± 0.02	-0.15 ± 0.03	0.84 ± 0.06	-0.04 ± 0.02

Samples annealed at ambient temperatures minimum of 7 days; Direct mounting, air reference.

decided to prepare calibrations with several IR spectrometers of both conventional dispersive and FTIR design. For this purpose a set of 13 PP film samples, spanning the tacticity range $mm = 0.47 - 1.00$, were prepared and annealed for a minimum of 7 days before measurement. The results of this study are summarized in Table V for the calibrations based on the 973 cm^{-1} reference band. Generally the calibrations show reasonable agreement but indicate that there may be some slightly instrument bias. It is perhaps pertinent to point out that even with the same instrument, variation in instrument adjustment or condition or factors such as "warming" time do have small but measurable effects on values of absorption ratios.

Comparison with Literature Calibrations

A direct comparison of the present results with Luongo's⁸ widely used calibration is shown in Figure 7. It is apparent that the agreement is rather poor if the % atactic values are compared against the NMR triad readings. However, if Luongo's atactic and isotactic samples are assigned values of $mm = 0.35$ and $mm = 1.00$, respectively, then a good agreement is obtained.

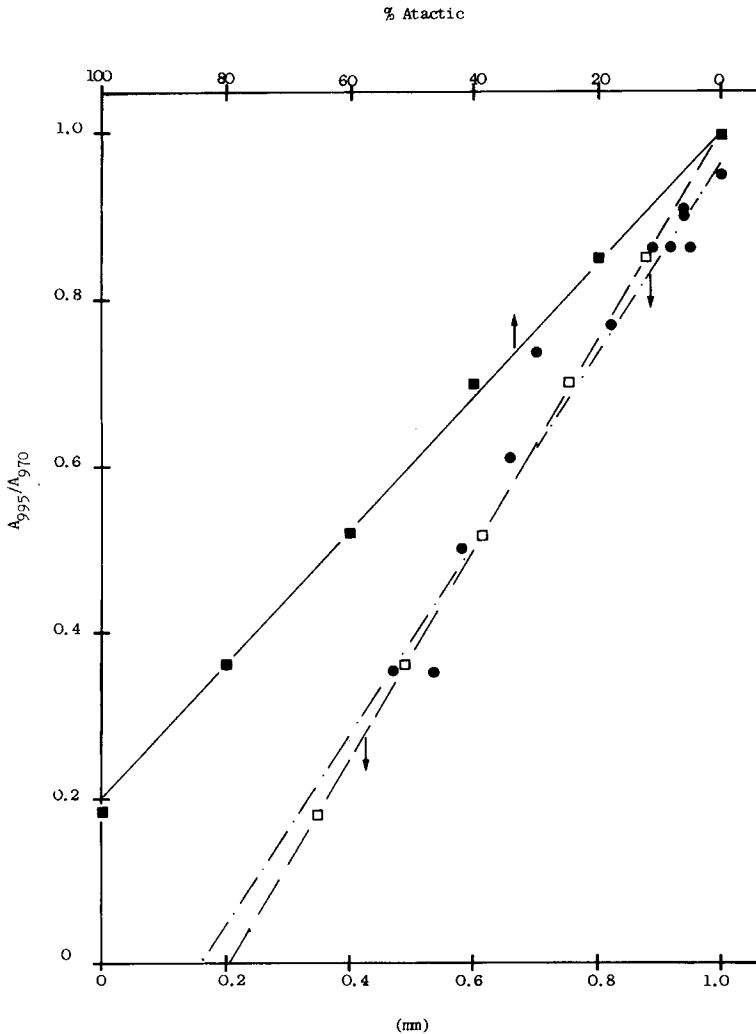


Fig. 7. Comparison of present calibration data with literature results. (■) Original data from Luongo; (□) Luongo data recalculated using $mm = 0.35$ and $mm = 1.00$ for atactic and isotactic polymers; (●) this work, high temperature annealing.

CONCLUSION

Infrared measurements provide a simple and reasonably precise determination of the isotacticity of polypropylene films. The preferred procedure is the measurement of the A_{998}/A_{973} absorption ratio on hot-pressed film samples. For PP samples annealed at ambient temperatures for 5 days the calibration curve is defined by the relationship $A_{998}/A_{973} = 1.08 (mm) - 0.15$. These values are significantly different from earlier calibration results.

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