# A Comparison of the Determination of Macromolecular Orientation in Polypropylene by Attenuated Total-Reflection Fourier-Transform Infrared Spectroscopy and X-Ray Diffraction

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## Synopsis

Attenuated total reflection-infrared (ATR-IR) spectroscopy and wide-angle x-ray diffraction (WAXD) were used to determine the macromolecular orientation of a series of six uniaxially oriented polypropylene sheets with elongations of 0% to 500%. The orientation functions were expressed as fractions of chains oriented along the machine, transverse, and normal directions in the sheets. Good agreement was found between the orientation functions for the two techniques. Sources of potential difference between the two techniques were discussed. The ATR-IR technique is surface sensitive to a depth of about 5 or 10 $\mu$m into the surface while the WAXD technique is bulk sensitive. The ATR-IR technique is sensitive to both the crystalline and noncrystalline material while the XRD technique is sensitive only to the crystalline material.

## INTRODUCTION

The production of synthetic polymers with properties enhanced by processes that impose macromolecular orientation on these systems has yielded a wide range of products with unique properties. The characterization of the effects of such orientation processes has become a field of intense investigation in polymer science. The two primary areas of these investigations are: (1) the characterization of the molecular orientation and the supermolecular morphology imposed by deformation processes; and, (2) the relationship of the molecular orientation and morphological structure to physical properties. This area of investigation is particularly complex for semicrystalline polymers, which, in the most simplistic terms, have both a crystalline and noncrystalline phase.

The methods used to characterize the macromolecular orientation yield varying results according to the sensitivity of the methods to the orientation of macromolecular chains in each phase. The two most widely used methods are infrared spectroscopy (IR) and wide angle x-ray diffraction (WAXD). IR can be sensitive to both the crystalline and noncrystalline phase orientation, [1] while WAXD is sensitive to the crystalline phase only.[2] The purpose of this article is to compare these two methods.

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Measurements on a series of uniaxially oriented polypropylene sheets was used as the basis for this comparison. Since these sheets were quite thick (ca. 12 to 65 mils), IR measurements were made on the surfaces of the sheets by attenuated total reflection infrared (ATR-IR) spectroscopy.

## EXPERIMENTAL

### ATR-IR

All spectra were obtained on a Nicolet 6000 FTIR instrument at 4 cm$^{-1}$ resolution. ATR spectra were obtained with a variable-angle ATR accessory (TMP-MON, Harrick Scientific Co., Ossining, NY). Internal reflection elements of KRS-5 with especially cut 40° entrance aperture were used. Polarization was accomplished with a germanium polarizer (PSD, Harrick Scientific Co.). All ATR spectra were obtained at an incidence angle of 40° (normal to the entrance aperture). Other details of the spectroscopic experiments have been described previously.[3]

### WAXD

The diffraction patterns on isotactic polypropylene samples were obtained using an automated Siemens D-500 X-ray Diffraction System equipped with TX-500 texture goniometer. The diffraction experiments were performed using Ni-filtered Cu K$\alpha$ radiation and at 30 mA and 40 kV. The azimuthal scanning of the (040) and (110) reflections was performed using a step-scan method at an interval of 5 degrees.

### MATERIALS

A series of uniaxially drawn polypropylene sheets were drawn on a tenter frame at 300°F (148.9°C). Heating was by uniform convection. Extensions were ($= l/l_0$) 1X, 2X, 3X, 4X, 5X, and 6X or expressed as percent elongation 0%, 100%, 200%, 300%, 400%. and 500%. The crystallinities of the drawn specimens were previously reported.[4] The crystallinity of the undrawn (1 × ) material was 67%. The extension rates were 1 × (0 m/min), 2 × (23.8 m/min), 3 × (35.7 /min), 4 × (47.6 m/min), 5 × (59.5 m/min), and 6 × (71.4 m/min).

### RESULTS AND DISCUSSION

The experimental procedure and method of calculation of the ATR orientation functions have been described in detail elsewhere.[4, 5] The measurement is sensitive to a depth of about 5–10 $\mu$m into the surface of the specimen. The values of the ATR orientation function lie between 0.0 and 1.0. The value for perfect parallel orientation is 1.0, for perfect transverse orientation is 0.0, and for random orientation is 0.33. In this model, all chains are assumed to be aligned along one of the three orthogonal axes MD (machine), TD (transverse), and ND (ND is normal to the film plane). This ignores all intermediate orientations of molecules, however, $P_{MD}$, $P_{TD}$, and $P_{ND}$ represent the sum of the vector projections of each chain axis onto the principal orthogonal axes MD, TD, and ND. This function is called the fractional orthogonal orientation function. The variation in the ATR fractional orthogonal orientation
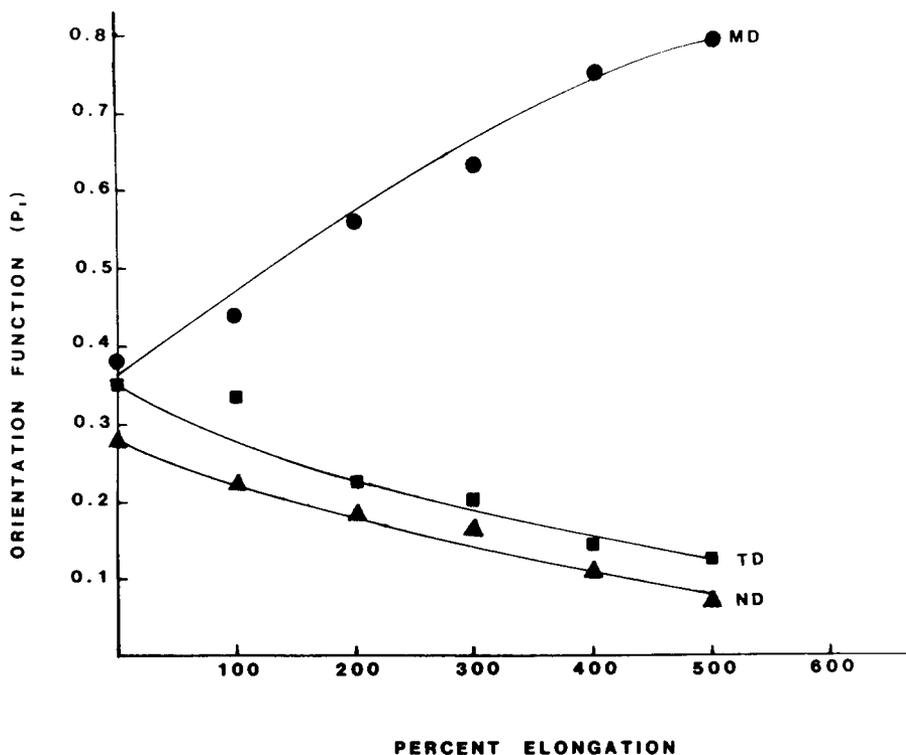
Fig. 1. ATR orientation function ($P_i$) as a function of elongation for uniaxially oriented PPOJ films. Orientation fraction in the (●) MD, (■) TD, and (▲) ND. The solid lines are simply arbitrarily fit lines to the points to suggest the trends.

function for a series of uniaxially drawn polypropylene films [($\lambda$ = 1X (0%) to $\lambda$ = 6X (500%)] is shown in Figure 1. It can be observed that $P_{MD}$ increases steadily and sharply as elongation increases and $P_{TD}$ and $P_{ND}$ decrease steadily. This indicates the reorientation of the macromolecular chains along the MD as elongation increases. Concomitantly, the chains are pulled away from the TD and ND as elongation increases.

The thicknesses of the films are plotted as a function of extension in Figure 2. The calculated thicknesses are plotted for the affine deformation model. For the affine deformation case for uniaxial extension, one dimension of an arbitrary unit cube is increased in the ratio $\lambda$ (where $\lambda$ = length after elongation/original length), while the other two dimensions are equally decreased by $1/\sqrt{\lambda}$ in order to maintain constant volume. It can be observed in Figure 2 that the thickness decreases more rapidly than predicted by the affine deformation model. The implications of this are that from 0 to 100% extension the deformation is affine but between 100 and 200% extension the deformation departs markedly from the affine model. This is supported by Figure 1 in which it is observed that the TD and ND orientation functions differ markedly between 0 and 200% extension, indicating some biaxiality of orientation. However, between 0 and 200% extension, the TD and ND orientation functions become nearly equal and remain so through 500% extension. This is an indication of a non-affine, that is a non-uniaxial process, occurring
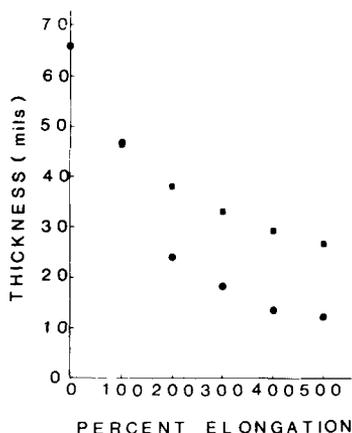
Fig. 2. Experimentally determined film thickness and film thickness calculated assuming affine, uniaxial deformation versus the percent extension. Affine (■) Experimental (●).

between 0 and 200% extension, thereby imparting unequal orientation in the TD and ND directions and resulting in an equalizing of the orientation functions in the TD and ND directions when 200% extension was reached.

In WAXD of polymers, it is conventional to assume that the c-axis of the unit cell is parallel to the polymer chain axis. Determination of average orientation of the c-axis with respect to the reference direction is thus a determination of the average orientation of the polymer molecules in the crystalline region. The average orientation of the crystallites can be formalized on a quantitative basis using the orientation functions $\overline{\cos^2\phi}_{c,\,\mathrm{MD}}$, $\overline{\cos^2\phi}_{c,\,\mathrm{TD}}$ and $\overline{\cos^2\phi}_{c,\,\mathrm{ND}}$, which represent the degree of alignment of the c-axis of the unit cell to the MD, TD, and ND, respectively, in the sample. Therefore, this function $(\overline{\cos^2\phi}_{c,\,\mathrm{MD,\,TD,\,ND}})$ must represent the fractional molecular orientation along the three orthogonal axes MD, TD, and ND, and is the same as the ATR fractional orthogonal orientation function.

Determination of $\overline{\cos^2\phi}_{c,\,\mathrm{MD}}$ requires the presence of pure c-axis (001) reflection in the diffraction pattern. In the case of isotactic polypropylene the three crystallographic axes are not mutually perpendicular and no pure c-axis reflection is present in the diffraction pattern. Therefore, Wilchinsky's[6] generalized approach to the determination of c-axis orientation must be used. From symmetry considerations, Wilchinsky derived the following expression relating the variation in intensity with azimuthal angle of (110) and (040) reflections to the $\overline{\cos^2\phi}_{c,\,\mathrm{MD}}$ parameter which characterizes the c-axis orientation in the MD:

$$\overline{\cos^2\phi}_{c,\,\mathrm{MD}} = 1 - 1.099\left(\overline{\cos^2\phi}_{110,\,\mathrm{MD}}\right) - 0.901\left(\overline{\cos^2\phi}_{040,\,\mathrm{MD}}\right) \tag{1}$$

In order to determine the c-axis orientation along the TD direction (1) can be rewritten as follows:

$$\overline{\cos^2\phi}_{c,\,\mathrm{TD}} = 1 - 1.099\left(\overline{\cos^2\phi}_{110,\,\mathrm{TD}}\right) - 0.901\left(\overline{\cos^2\phi}_{040,\,\mathrm{TD}}\right) \tag{2}$$

The quantities $\overline{\cos^2\phi}_{110,\,MD}$ and $\overline{\cos^2\phi}_{040,\,MD}$ can be determined experimentally from the azimuthal intensity distribution data using the procedure described elsewhere.[2,7] Mathematically the quantity $\overline{\cos^2\phi}_{hkl,\,MD}$ is defined by the expression:

$$\overline{\cos^2\phi}_{hkl,\,MD} = \frac{\int_0^{\pi/2} I(\phi)\sin\phi\cos^2\phi\,d\phi}{\int_0^{\pi/2} I(\phi)\sin\phi\,d\phi} \tag{3}$$

Similarly, the quantity $\overline{\cos^2\phi}_{hkl,\,TD}$ was determined using the following equation:

$$\overline{\cos^2\phi}_{hkl,\,TD} = \frac{\int_{\pi/2}^{\pi} I(\phi)\sin\phi\cos^2\phi\,d\phi}{\int_{\pi/2}^{\pi} I(\phi)\sin\phi\,d\phi} \tag{4}$$

Once $\overline{\cos^2\phi}_{c,\,MD}$ and $\overline{\cos^2\phi}_{c,\,TD}$ are determined using the above mentioned approach, $\overline{\cos^2\phi}_{c,\,ND}$ can be determined as follows:

$$\overline{\cos^2\phi}_{c,\,ND} = 1 - \left(\overline{\cos^2\phi}_{c,\,MD} + \overline{\cos^2\phi}_{c,\,TD}\right) \tag{5}$$

For an unoriented, totally random sample:

$$\overline{\cos^2\phi}_{c,\,MD} = \overline{\cos^2\phi}_{c,\,TD} = \overline{\cos^2\phi}_{c,\,ND} = 0.33 \tag{6}$$

For a sample in which the c-axes are aligned perfectly along the MD direction, the value of $\overline{\cos^2\phi}_{c,\,MD}$ is equal to unity and

$$\overline{\cos^2\phi}_{c,\,TD} = \overline{\cos^2\phi}_{c,\,ND} = 0 \tag{7}$$

Figure 3 contains the azimuthal intensity distribution scans of the (110) plane (i.e., the intensity as a function of angle of rotation $\phi$) from uniaxially oriented isotactic polypropylene specimens. It is evident from the figure that the angular distribution of the 110 planes along the MD direction increases with increasing draw ratio, thus illustrating the changes in molecular orientation as a function of deformation. One can also see a similar trend in the angular distribution of the (040) plane, a b-axis reflection, as a function of draw ratio (Fig. 4). Table I contains the $(\overline{\cos^2\phi}_{c,\,MD})$, $(\overline{\cos^2\phi}_{c,\,TD})$, and $(\overline{\cos^2\phi}_{c,\,ND})$ values for isotactic polypropylene specimens. The value of $(\overline{\cos^2\phi}_{c,\,MD})$ increases from 0.4 to 0.75 as the draw ratio increases from 1X to 6X. This suggests an increase in c-axis orientation (i.e., the orientation of the crystallites since c-axis is parallel to the polymer chain) along the MD direction as the draw ratio is increased from 1X to 6X. Figure 5 is a plot of $(\overline{\cos^2\phi}_{c,\,MD})$, $(\overline{\cos^2\phi}_{c,\,TD})$, and $(\overline{\cos^2\phi}_{c,\,ND})$ as a function of percent elongation. Again from this figure, it is obvious that the c-axis orientation along the MD increases with draw ratio while the crystallite orientation along TD and ND decreases with increasing elongation.

A comparison of the ATR-IR and WAXD data in Table I (or a comparison of Figures 1 and 5) reveals that there is good agreement of the absolute

PP  110  PLANE
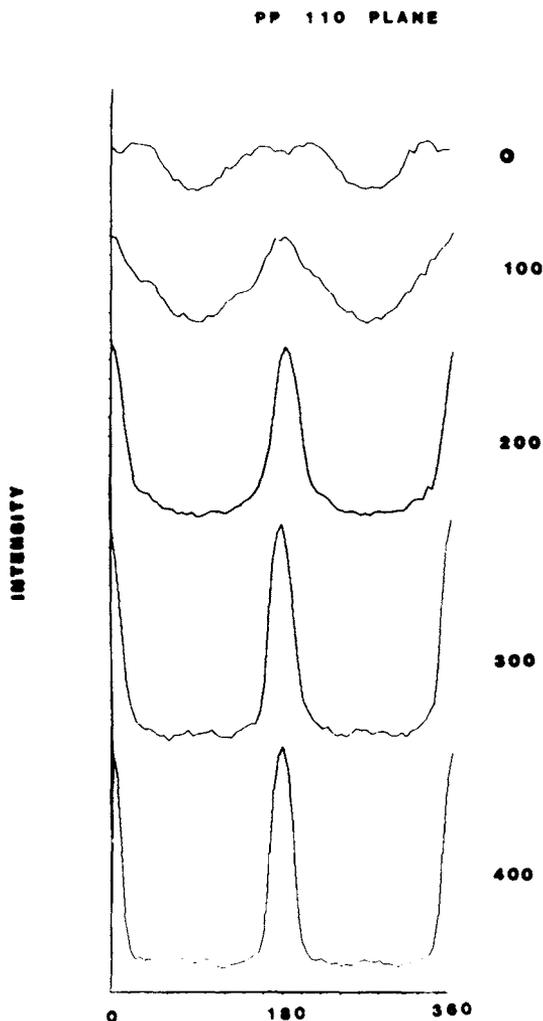


Fig. 3. [110] Azimuthal intensity distribution scans from oriented isotactic polypropylene specimens with 0, 100, 200, 300, and 400% elongation. The angles $\phi$ at $0°$, $180°$, and $360°$ refer to the MD while $90°$ and $270°$ refer to the TD.

orientation function values for the two techniques, as well as agreement of the qualitative trends in the data for the two techniques.

The agreement of the two methods indicates that the "surface" orientation at a depth of about 10 $\mu$m as determined by the ATR method is similar to the "bulk" orientation as determined by x-ray diffraction. It can be observed that the $P_{MD}$ values from x-ray diffraction are consistently larger than those from ATR until high elongation is attained (ca. 400%) when the ATR $P_{MD}$ become larger. This may be explained by the more rapid reorientation of the crystallites to which the x-ray diffraction measurement is solely sensitive, compared to the ATR method measurement which has major sensitivity to the crystalline, as well as minor sensitivity to the noncrystalline phase. Thus, as the crystalline orientation saturates the x-ray diffraction $\overline{\cos^2 \phi_{c, MD}}$ levels off

PP  040  PLANE
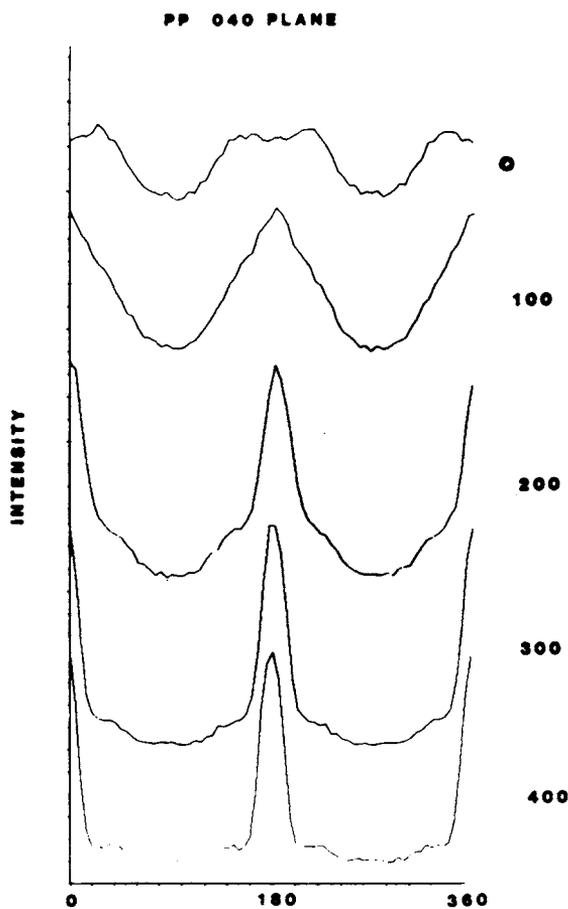


Fig. 4. [040] Azimuthal intensity distribution scans from oriented isotactic polypropylene specimens with 0, 100, 200, 300, and 400% elongation. The angles $\phi$ at $0°$, $180°$, and $360°$ refer to the MD while $90°$ and $270°$ refer to the TD.

TABLE I

ATR and WAXD Orientation Functions For A Series of Uniaxially Drawn Polypropylene Films

| Draw ratio | Percent elongation (%) | Film thickness (Mil) | ATR orientation functions | | | WAXD orientation functions | | |
|---|---|---|---|---|---|---|---|---|
| | | | PMD | PTD | PND | $\overline{\cos^2 \phi_{c,\,MD}}$ | $\overline{\cos^2 \phi_{c,\,TD}}$ | $\overline{\cos^2 \phi_{c,\,ND}}$ |
| 1 | 0 | 63 | 0.37 | 0.34 | 0.29 | 0.41 | 0.29 | 0.30 |
| 2 | 100 | 45 | 0.43 | 0.32 | 0.25 | 0.48 | 0.23 | 0.29 |
| 3 | 200 | 23 | 0.59 | 0.22 | 0.19 | 0.60 | 0.20 | 0.20 |
| 4 | 300 | 18 | 0.62 | 0.21 | 0.17 | 0.69 | 0.15 | 0.16 |
| 5 | 400 | 14 | 0.75 | 0.14 | 0.11 | 0.75 | 0.10 | 0.15 |
| 6 | 500 | 12 | 0.79 | 0.13 | 0.08 | 0.75 | 0.10 | 0.15 |
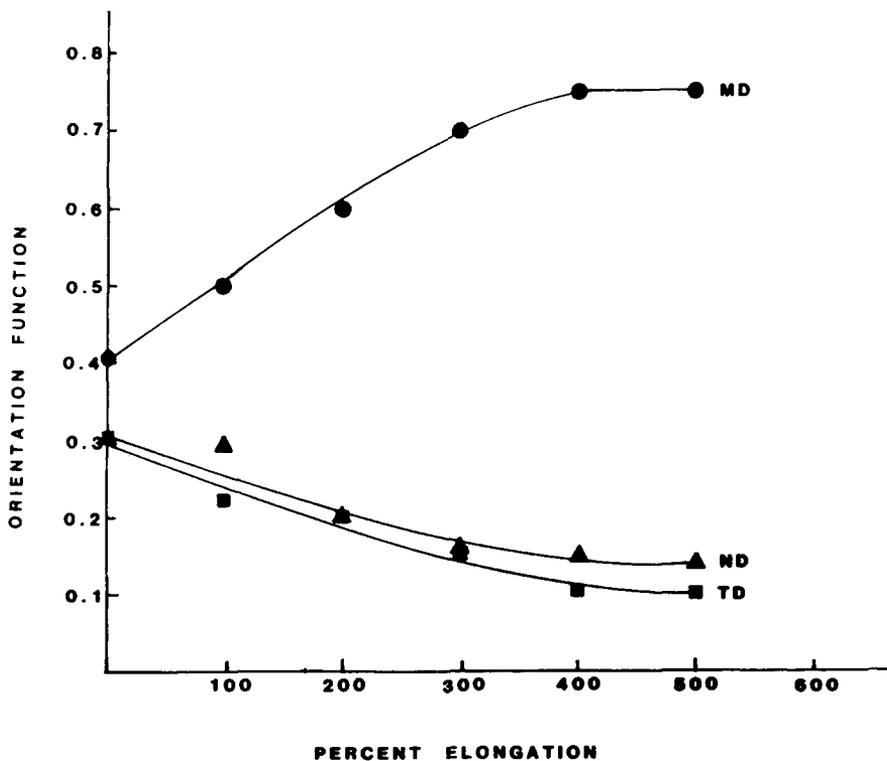
Fig. 5. WAXD orientation function $(\overline{\cos^2 \phi_c})$ as a function of elongation for uniaxially drawn PP films. Orientation function (●) MD, (■) TD, and (▲) ND.

while the ATR $P_{MD}$ goes on increasing due to partial sensitivity to the continuing reorientation of the noncrystalline phase.[1]

This orientation function, which is called the fractional orthogonal orientation function, appears to be a useful parameter to express the orientation data. It is readily comprehended and may be more comprehensible to a wide variety of users of the data than the Herman's orientation function.

These same oriented polyproplene sheets were analyzed by Pepper and Samuels[8] using polarized refractometry. These workers developed a similar fractional orthogonal orientation function (they called it the fractional orientation function) which was calculated from their polarized refractometric data. They found that the ATR-IR and polarized refractometry data for the 1X to 6X uniaxially drawn polypropylene sheets showed good agreement as to the trends of the data. Most of the data points for the two techniques had absolute values that agreed closely.

Pepper and Samuels repeated the ATR-IR and polarized refractometry measurements on a set of identical specimens taken from the same 1X to 6X uniaxially drawn polypropylene sheets.[9] They made measurements on each side of the sheets by each method. In this case they found excellent agreement between the two measurement techniques. The polarized refractometry technique is surface sensitive and is sensitive to both the crystalline and noncrystalline phases.

## CONCLUSIONS

It has been shown that similar orientation function data can be generated for uniaxially oriented polypropylene films by ATR-IR and WAXD techniques. These similar data are generated when the quantity being determined is the normalized fraction of macromolecular chain axes lying along the three principal, orthogonal films axes; MD, TD, and ND. This parameter is called the fractional orthogonal orientation function.
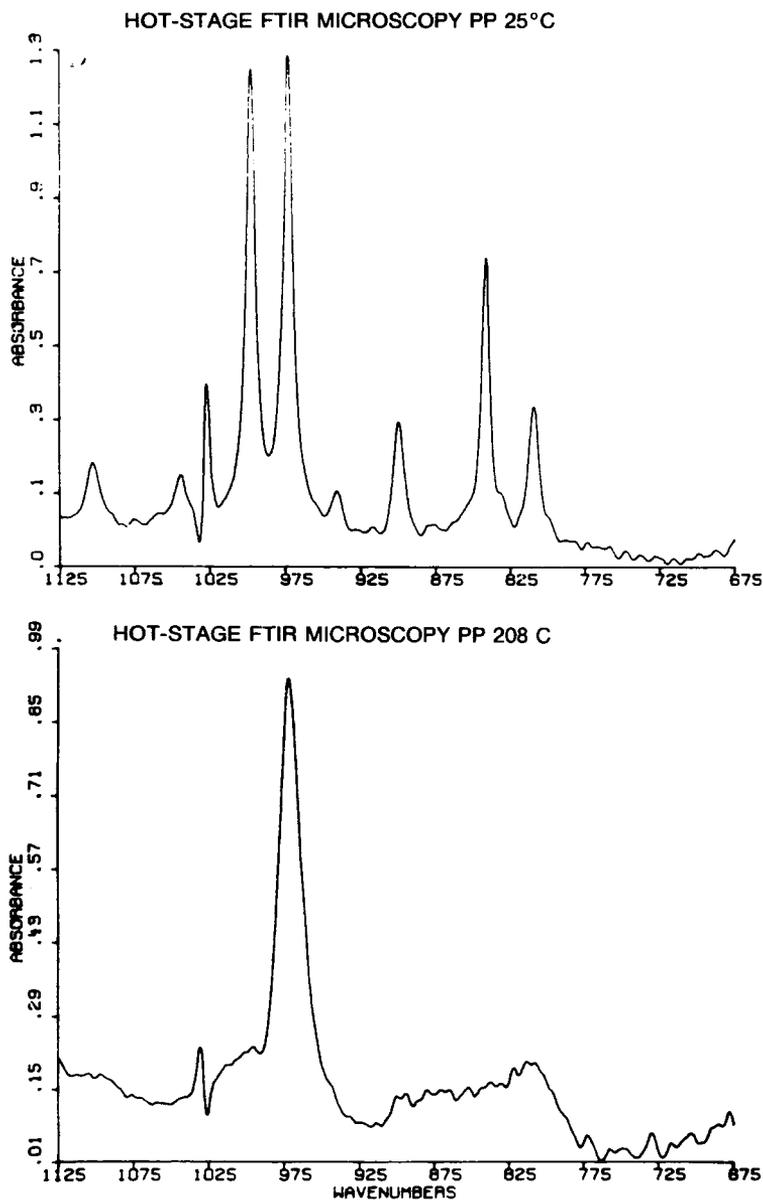


Fig. 6. Infrared spectra of isotactic polypropylene in the solid (25° C) and molten (208° C) states.

The data presented showed quite good agreement between the two techniques. However, there are several sources of variation between the two techniques. First, the ATR-IR method is surface sensitive to a depth of several micrometers, while the WAXD method involves a bulk measurement. Second, the WAXD method is sensitive to the crystalline-phase orientation, only. The ATR-IR method is sensitive to both the crystalline- and amorphous-phase orientation since the bands used at 841 and 809 cm$^{-1}$ arise from both the crystalline and amorphous phases. This can be appreciated by consulting Figure 6, which shows that as polypropylene is taken from the solid state (25°C) to the total melt state (208°C), there remains a minor contribution in the melt state to the bands at 841 and 809 cm$^{-1}$, while the band at 997 cm$^{-1}$ (crystalline sensitive band) totally disappears and the band at 971 cm$^{-1}$ (noncrystalline sensitive band) remains essentially unchanged. Thus, a small difference in the WAXD and ATR-IR data would be expected due to this partial sensitivity of the ATR-IR method to the noncrystalline phase.

Further, agreement between the ATR-IR data and previously published polarized refractometry data was noted. This indicates a general agreement of the fractional orthogonal orientation functions as determined by ATR-IR, WAXD, and polarized refractometry methods.

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