

An Infrared Spectroscopic Study of Molecular Orientation in Heat-Set Poly(ethylene Terephthalate) Yarn Using Attenuated Total Reflection Technique

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Synopsis

The attenuated total reflection (ATR) technique has been used to obtain infrared spectra of heat-set poly(ethylene terephthalate) (PET) fibers. The *trans* and *gauche* content have been estimated from the absorbances of the *trans* band at 1342 cm^{-1} , the *gauche* band at 1370 cm^{-1} , and the internal standard band at 1410 cm^{-1} . The *trans* orientation, as calculated from the dichroic ratios of the absorption bands at 1342 , 972 and 846 cm^{-1} , shows a decreasing trend with an increase in heat-setting temperature. The overall molecular orientation, as calculated from the absorption bands at 1410 and 875 cm^{-1} , also decreases slightly with an increase in heat-setting temperature. The infrared data, in combination with X-ray data, have been used to calculate the amorphous orientation factor. The ATR technique is shown to give quite representative values of the amorphous orientation factor.

INTRODUCTION

It is generally accepted that synthetic fibers have a fibrillar morphology and that in the fibril the crystalline and amorphous regions are stacked vertically in series.¹ The crystalline regions, which can be studied by X-ray diffraction techniques as they give discrete reflections, are amenable to more precise characterization compared to the amorphous regions that are not so amenable.

Infrared spectroscopic measurements have shown considerable promise in providing direct measures of the parameters related to the amorphous regions and have been used extensively lately for this purpose. Edelmann and Wyden² used the attenuated total reflection (ATR) technique to measure the crystalline and amorphous content in PET, using absorption bands at 1342 cm^{-1} , with the band at 1410 cm^{-1} as an internal standard. Sabilia et al.³ suggested that the 846 cm^{-1} absorption band (*trans* CH₂-rocking) does not correlate well with crystallinity and that the *trans* conformation may exist outside the crystalline regions. They also showed for drawn ($\times 6$) and heat-set PET that *trans* (846 cm^{-1}) and *gauche* (1042 cm^{-1}) content as well as *trans* orientation do not vary much with heat-setting temperature. Statton et al.⁴ found a drop in *gauche* glycol units (895 cm^{-1}) on orientation of PET fibers. They observed that the

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tension pulling of the *gauche* structure in amorphous regions may result in *trans* conformation. They also found an increase in the regular chain folding band⁵ at 988 cm^{-1} on annealing. Read, Stein, and co-workers⁶⁻⁸ have made extensive measurements of molecular orientation in low-density polyethylene, oxidized polyethylene, ethylene-carbon monoxide copolymer, and crosslinked amorphous polyethylene. Gupta et al.⁹ studied the variation in dichroic function of 972 and 1578 cm^{-1} peaks using FT-IR spectroscopy to monitor orientational changes in PET films, during tensile stretching. Ward and co-workers¹⁰⁻¹² used transmission infrared measurements to get quantitative estimates of the *trans* content and the *trans* orientation in PET films, which, in combination with X-ray data, give a quantitative estimate of the amorphous orientation factor. Recently, Yazdanian et al.¹³ extended the above measurements to PET fibers using a special yarn-winding device to get a parallel layer of monofilaments suitable for recording transmission infrared spectra. They analyzed the infrared absorption peaks after resolving them, using a curve-resolution program. Heuvel and Huisman¹⁴ also used a similar approach to get a quantitative estimation of various parameters related to the infrared spectra of PET fibers.

In the present study, an attempt has been made to use the ATR technique to determine orientation parameters from the infrared spectra of PET fiber samples. The use of this technique avoids the difficulties associated with sample thickness limitation and losses due to reflection on filament surface in transmission spectroscopy.

EXPERIMENTAL

Material

Commercial multifilament PET yarn 76/36/0 (i.e., 76 denier, 36 filaments, and 0 twist) with draw ratio 3.92 was the starting material and will be referred to as the "control." The yarn was heat-set isothermally in a silicone oil bath maintained at temperatures of 100, 140, 180, 220, 230, 240, 250, and 258°C within $\pm 2^{\circ}\text{C}$. The heat-setting was done under two conditions, viz. when the yarn was (i) held taut at constant length (referred to as taut annealed or TA) and (ii) free to relax (referred to as free annealed or FA). After 5 min, the sample was taken out of the bath and allowed to reach ambient temperature before being washed thoroughly in carbon tetrachloride and allowed to dry in air.

Infrared Spectroscopy

Infrared spectra over the ranges of $750\text{--}1100$ and $1300\text{--}1500\text{ cm}^{-1}$ were recorded using the ATR technique.¹⁵ The yarn samples were carefully wound over two polished metal plates ($30 \times 25 \times 1\text{ mm}^3$) to form a parallel uniform layer of fibers. These sample plates were placed on both sides of the ATR element made of KRS-5 crystal, and sufficient pressure was applied to ensure intimate sample-to-crystal contact. The spectra were recorded at an incident angle of 45° with parallel and perpendicular polarization with respect to fiber direction, using a Shimadzu IR-440 ratio recording spectrophotometer. The scan speed of $40\text{ cm}^{-1}/\text{min}$ with a normal slit program was used. It was possible

to obtain good quality spectra with reasonably good reproducibility with careful sample preparation. Absorbances were calculated using the pseudo-base-line method¹¹ corresponding to internal standard absorption bands at 1410 and 875 cm^{-1} and the *gauche* absorption bands at 1370 and 896 cm^{-1} . The dichroic ratios (D) were then calculated¹⁶⁻²⁰ from these experimentally measured absorbances. The dichroic function DF, which is a measure of orientation, may be defined as^{9,11}

$$\text{DF} = \frac{D - 1}{D + 2} = P_2(\theta_m) \langle P_2(\theta) \rangle_{\text{ir}} \quad (1)$$

where $P_2(\theta_m) = 1/2(3 \cos^2\theta_m - 1)$ is a constant quantity determined by the angle θ_m between the transition moment of the absorbing group and the chain axis of the polymer, depending only on the molecular structure of the polymer. The quantity $\langle P_2(\theta_{\text{ir}}) \rangle$ is defined as the mean value of $P_2(\theta) = 1/2(3 \cos^2\theta - 1)$, as determined by the infrared method and is the absolute measure of the chain axis orientation. If the value of θ_m is known from other experiments or structural data, we can determine the absolute orientation factor $\langle P_2(\theta) \rangle$ from the measured infrared dichroic ratios.

X-Ray Measurements

The crystallinity of the sample was measured using the powder X-ray diffraction method as suggested by Farrow and Preston.²¹ For measuring crystallite orientation, f_c , azimuthal scans were obtained from a tilted bundle of parallel fibers corresponding to $(\bar{1}05)$ planes²² using a texture goniometer. The azimuthal scans were resolved to separate the contribution of $(0\bar{2}4)$ profile from the $(\bar{1}05)$ profile,²³ and the pure $(\bar{1}05)$ profile was used to calculate $\langle \cos^2\phi \rangle$, where ϕ is the angle between the plane normal and the fiber axis (azimuthal angle). From this, $\langle \cos^2\theta \rangle$ was determined,²⁴ where $\langle \cos^2\theta \rangle = \langle \cos^2\phi \rangle / \cos^2\rho$ and θ is the angle that a molecular axis makes with the fiber axis and ρ is the angle that the $\bar{1}05$ plane normal makes with the chain axis. This correction was necessary due to the off-meridional nature of the $(\bar{1}05)$ plane. Herman's orientation factor f_c was then determined using the expression

$$f_c = (3 \langle \cos^2\theta \rangle - 1) / 2 \quad (2)$$

where $\langle \cos^2\theta \rangle$ is the average value of $\cos^2\theta$.

RESULTS AND DISCUSSION

Typical ATR spectra of the "control" sample in the regions 750–1100 and 1300–1500 cm^{-1} are reproduced in Figure 1 for parallel and perpendicular polarization. The absorption bands are assigned as suggested by previous workers.^{11,25-32} The absorption bands at 1410 and 875 cm^{-1} represent total concentration of absorbing groups and, hence, can be used as the internal standard for the calculation of *trans*- and *gauche*-absorbing group concentrations. The absorption bands at 1342, 972, and 846 cm^{-1} have been assigned to the *trans*

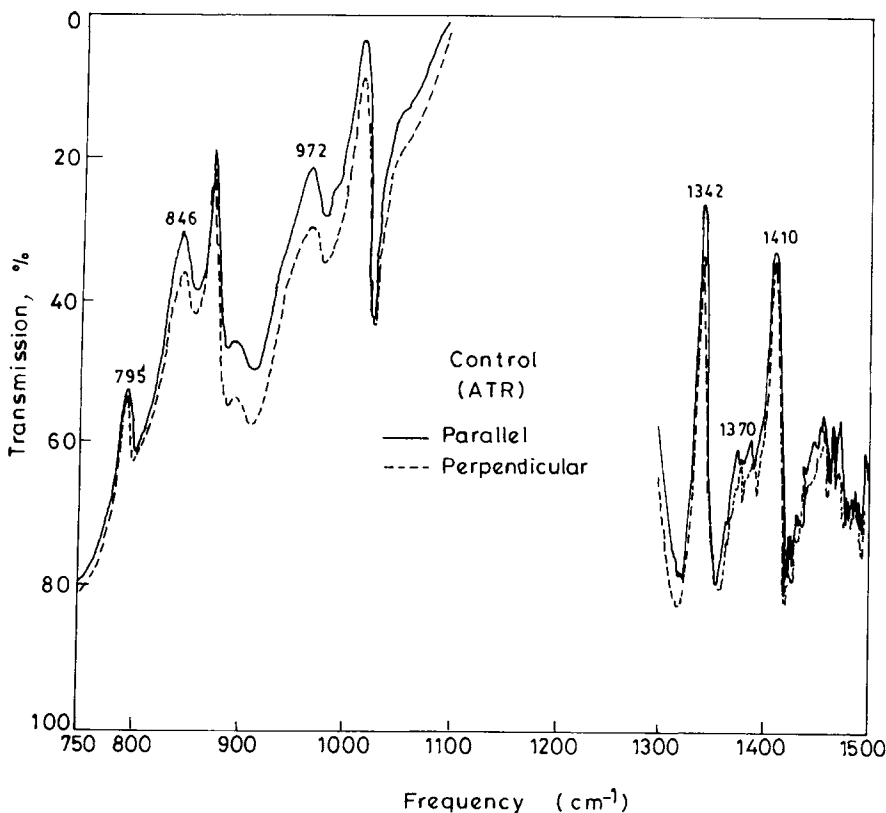


Fig. 1. Example of ATR spectra for the "control" PET sample for parallel and perpendicular polarization.

conformation of the PET molecule, whereas the absorption bands at 1370 and 896 cm^{-1} belong to the *gauche* conformation.

Trans and Gauche Content

The *trans* and *gauche* content have been determined from the total absorbance, $A_0 = (A_{\parallel} + 2A_{\perp})/3$, of the *trans* band at 1342 cm^{-1} and *gauche* band at 1370 cm^{-1} , taking the total absorbance of band at 1410 cm^{-1} as reference. The *trans* content of both TA and FA samples increases slightly with the heat-setting temperature as shown in Figure 2, whereas the *gauche* content shows a slight decrease. This is apparently due to an increase in the crystalline content as a result of the crystallization process during which some of the *gauche* conformers in the amorphous regions may be converted to *trans* conformers because of reorganization. Ward and co-workers¹¹⁻¹³ have used *trans* bands around 972 cm^{-1} (assigned to the $\text{CH}_2\text{—O}$ stretch of the *trans* $\text{—OC}_2\text{H}_4\text{O—}$ group) and *gauche* bands around 896 cm^{-1} (assigned to the CH_2 rocking of the *gauche* $\text{—OC}_2\text{H}_4\text{O—}$ group) for calculation of the *trans* content. In all these calculations, the underlying assumption is that for all *trans* and *gauche* bands the extinction coefficients are same. In this respect, the *trans* band at 1342 cm^{-1} (CH_2 wagging of the *gauche* $\text{—OC}_2\text{H}_4\text{O—}$ group) has been preferred for the

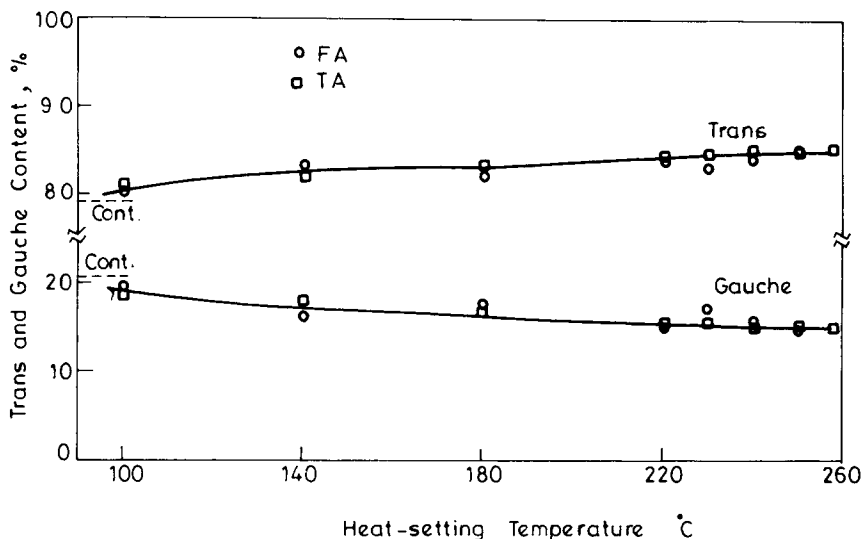


Fig. 2. The *trans* and *gauche* content in heat-set PET fibers as a function of the heat-setting temperature.

calculation of the *trans* content as they belong to the same kind of vibrational mode. Also, the absorbance measurement for the 1342 and 1370 cm^{-1} bands in the ATR spectra are expected to be more accurate without resorting to curve-resolution techniques because they appear to have very little overlapping. The *trans* band at 1342 cm^{-1} is quite well defined.

Trans Orientation

For both sets of samples (TA and FA), the dichroic functions for the *trans* band at 1342, 972, and 846 cm^{-1} are plotted in Figure 3. All three plots indicate a decreasing trend for the dichroic function with an increase in heat-setting temperature. Therefore, we may use any of these *trans* bands for the determination of *trans* orientation if we know the value of $P_2(\theta_m)$ corresponding to that particular absorption band as required in eq. (1) for determination of the orientation function $\langle P_2(\theta) \rangle_{ir}$. Unfortunately, the values of $P_2(\theta_m)$ for all the bands are not available. Padibjo and Ward¹² found $P_2(\theta_m)$ to be 0.48 in case of the single-stage and two-stage drawn PET films, whereas Yazdanian et al.¹³ estimated $P_2(\theta_m) = 0.55$ in case of the drawn PET yarns. The above values have been obtained by extrapolation of the measured value of the dichroic function $P_2(\theta_m)\langle P_2(\theta) \rangle$ to very high overall molecular orientation where $\langle P_2(\theta) \rangle$ may be assumed to be 1. A similar extrapolation for the heat-set samples led to a value of $P_2(\theta_m) = 0.48$. It may be noticed that the angle θ_m may vary for stretched and relaxed samples due to different degrees of bond-angle distortion. The calculated values of *trans* orientation $\langle P_2(\theta) \rangle^{tr}$ from the dichroic function of the 972 cm^{-1} *trans* band with $P_2(\theta_m) = 0.48$ are given in Table I. A plot between the dichroic function of the 1342 cm^{-1} *trans* band and the *trans* orientation obtained from the 972 cm^{-1} *trans* band shows a good correlation (Fig. 4), indicating the possibility of using the *trans* band at 1342 cm^{-1} for determination of the *trans* orientation.

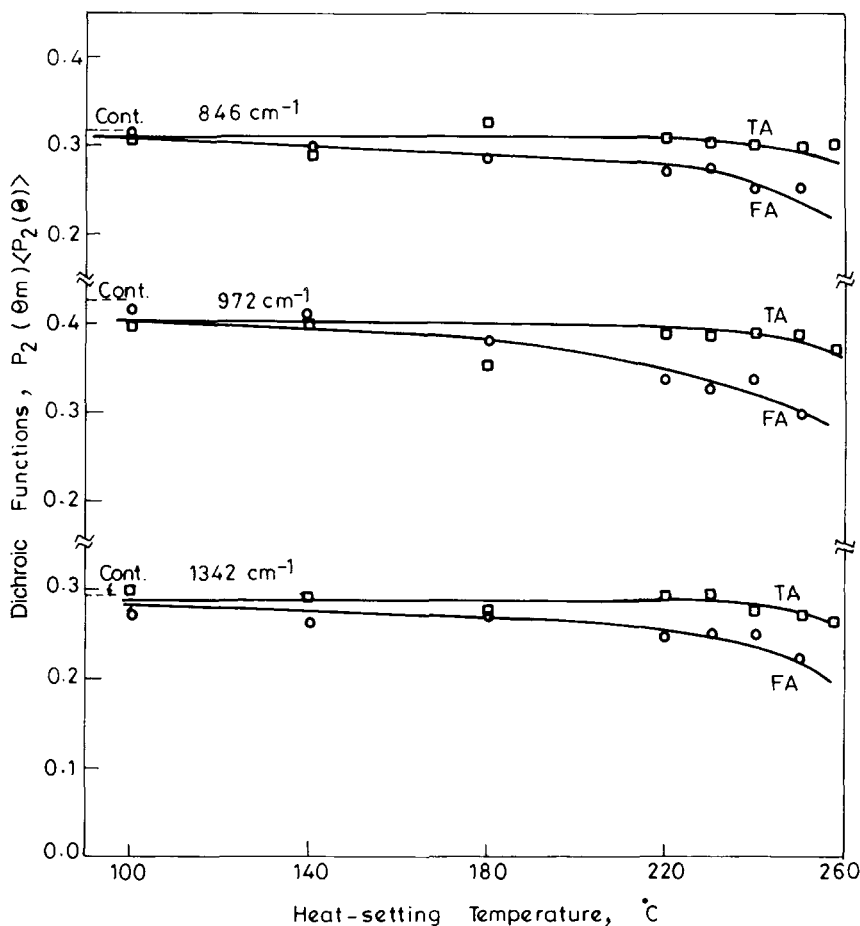


Fig. 3. The dichroic functions representing overall *trans* orientation as determined from the absorption bands at 1342, 972, and 846 cm^{-1} as a function of the heat-setting temperature.

In Figure 5, a plot of dichroic functions of the absorption bands at 1410 and 875 cm^{-1} representing the overall molecular orientation is shown. An expected decrease in overall orientation with the heat-setting temperature is indicated by the dichroic functions of both the bands. Cunningham et al.¹¹ have found excellent correlation between $\langle P_2(\theta) \rangle_{\text{ir}}$ and $\langle P_2(\theta) \rangle_{\text{optical}}$, which is a measure of the overall molecular orientation calculated from the refractive indices. Therefore, the bands at 1410 and 875 cm^{-1} may be used as representing overall orientation.

Amorphous Orientation

The fact that the *trans* conformation is present in both crystalline and amorphous regions and the *gauche* conformation only in the amorphous region enables one to write¹²

$$X^{tr} \langle P_2(\theta) \rangle^{tr} = X_{\text{cr}} \langle P_2(\theta) \rangle_{\text{cr}} + X_{\text{am}}^{tr} \langle P_2(\theta) \rangle_{\text{am}}^{tr} \quad (4)$$

TABLE I
The Various Structural Parameters Required for Calculation of Amorphous
Orientation Factor from Infrared Data

Sample	X_{cr}	$\langle P_2(\theta) \rangle_{cr}$	$X_{cr} \langle P_2(\theta) \rangle_{cr}$	X^{tr}	$\langle P_2(\theta) \rangle^{tr}$	$X^{tr} \langle P_2(\theta) \rangle^{tr}$	$X_{am}^{tr} \langle P_2(\theta) \rangle_{am}^{tr}$	f_{am}^{tr}
Control	0.341	0.940	0.321	0.795	0.885	0.704	0.383	0.582
TA 100	0.388	0.952	0.369	0.814	0.844	0.687	0.317	0.519
140	0.423	0.947	0.401	0.823	0.833	0.686	0.285	0.494
180	0.470	0.947	0.445	0.833	0.833	0.694	0.249	0.470
220	0.516	0.934	0.482	0.847	0.817	0.692	0.210	0.433
230	0.524	0.937	0.491	0.848	0.813	0.689	0.198	0.416
240	0.566	0.936	0.530	0.849	0.813	0.690	0.160	0.369
250	0.581	0.944	0.549	0.850	0.802	0.682	0.133	0.318
258	0.590	0.936	0.552	0.851	0.781	0.665	0.113	0.275
FA 100	0.400	0.944	0.378	0.805	0.858	0.691	0.313	0.522
140	0.445	0.952	0.424	0.824	0.854	0.704	0.280	0.505
180	0.470	0.922	0.433	0.835	0.792	0.661	0.228	0.430
220	0.520	0.912	0.474	0.844	0.708	0.598	0.124	0.258
230	0.553	0.877	0.485	0.846	0.679	0.575	0.090	0.200
240	0.567	0.859	0.487	0.848	0.654	0.555	0.068	0.156
250	0.589	0.860	0.507	0.850	0.615	0.522	0.016	0.039

and

$$\begin{aligned} X_{am} \langle P_2(\theta) \rangle_{am} &= (1 - X_{cr}) \langle P_2(\theta) \rangle_{am} \\ &= X_{am}^{tr} \langle P_2(\theta) \rangle_{am}^{tr} + X^{gauche} \langle P_2(\theta) \rangle_{gauche} \end{aligned} \quad (5)$$

On the assumption that the *gauche* component is disoriented, i.e., $\langle P_2(\theta) \rangle_{gauche} = 0$, the above equations can be rearranged to give the following expression for the amorphous orientation f_{am}^{tr} :

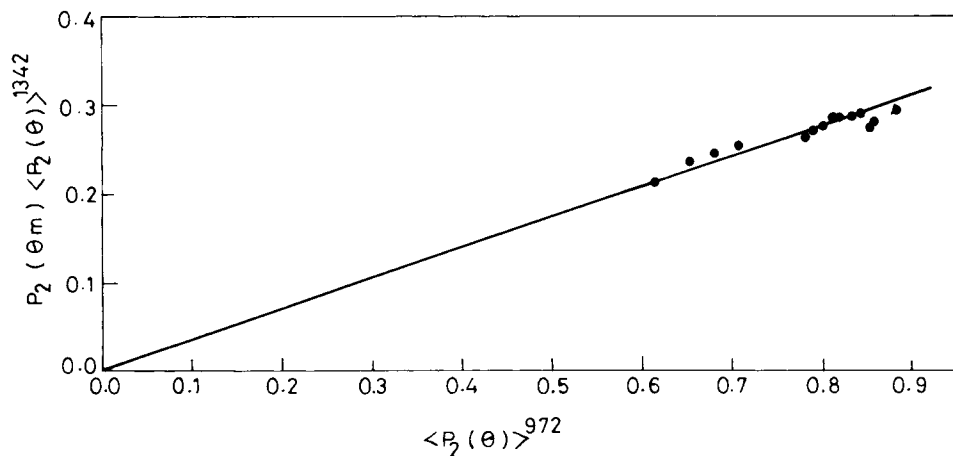


Fig. 4. Correlation between the dichroic function for the *trans* absorption band at 1342 cm^{-1} and the absolute *trans* orientation determined from the 972 cm^{-1} *trans* band.

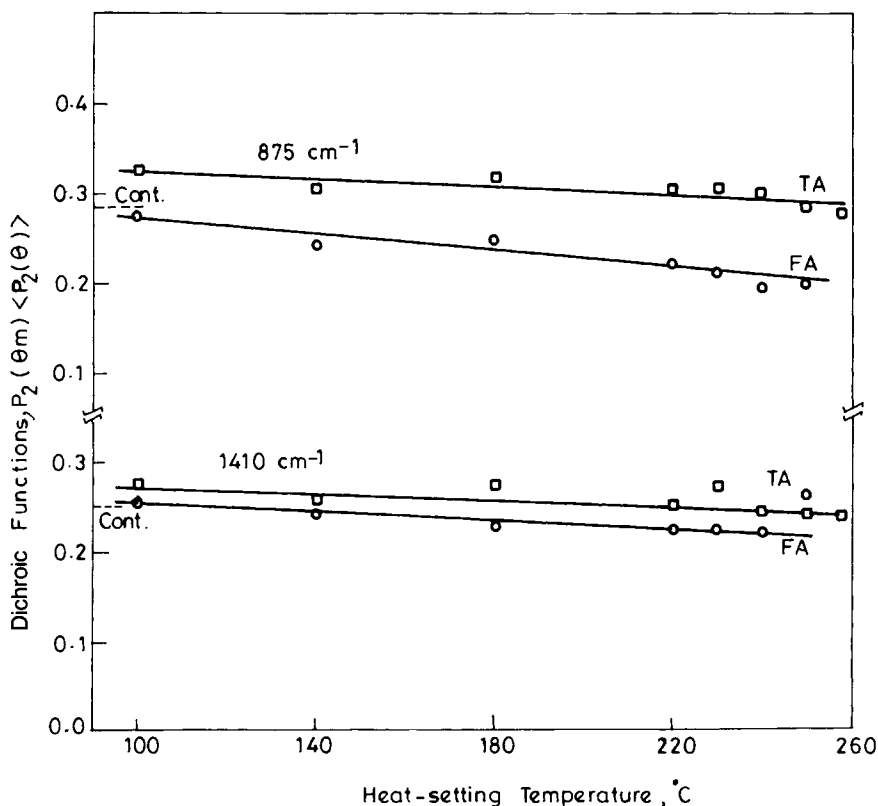


Fig. 5. The dichroic functions of the 1410 and 875 cm^{-1} bands, representing the overall molecular orientation as a function of the heat-setting temperature.

$$f_{\text{am}}^{\text{ir}} = \langle P_2(\theta) \rangle_{\text{am}} = (X^{\text{tr}} \langle P_2(\theta) \rangle^{\text{tr}} - X_{\text{cr}} \langle P_2(\theta) \rangle_{\text{cr}}) / (1 - X_{\text{cr}}) \quad (6)$$

Since X^{tr} and $\langle P_2(\theta) \rangle^{\text{tr}}$ can be determined from infrared and X_{cr} ($= \beta$) and $\langle P_2(\theta) \rangle_{\text{cr}}$ ($= f_{\text{c}}$) from the X-ray measurements, one can get an estimate of f_{am} , as shown in Table I, for the various samples examined.

The f_{am} values obtained from the present studies (Table I) are quite close to the values reported by other authors.^{12,13} Most of the authors who have measured f_{am} by infrared^{12,13} have reported values that came out to be lower than the sonic values³³ but quite close to those predicted by birefringence measurements.^{12,13} However, in calculating f_{am} from birefringence, the intrinsic birefringence values that have been used are not constant, e.g., Ward and co-workers used $\Delta n_{\text{co}} = 0.235$ and $\Delta n_{\text{amo}} = 0.275$ in their earlier paper¹² but $\Delta n_{\text{co}} = 0.22$ and $\Delta n_{\text{amo}} = 0.24$ in a later paper¹³. This aspect is of considerable significance in studies relating to structure-property correlation in fibers and might arise due to the morphology-dependence of intrinsic birefringence.³⁴

CONCLUSIONS

The ATR spectra of PET fibers in the regions 750–1100 and 1300–1500 cm^{-1} can be used for estimation of *trans* content, *trans* orientation, and amorphous

orientation factors. The amorphous orientation factor obtained from infrared, f_{am}^{ir} , is independent of the nature of coupling between the crystalline and the amorphous phases and also does not involve the use of intrinsic birefringence values, which are not known with certainty.

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