Characterization of Surface Structure and Orientation in Polypropylene and Poly(ethylene terephthalate) Films by Modified Attenuated Total Reflection IR Dichroism Studies

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ABSTRACT: In order to characterize surface molecular orientation in three dimensions and to obtain other structural information such as the degree of crystallinity and the different conformer contents at the surface, a new ATR (attenuated total reflection) attachment was designed for FT IR ATR dichroism studies. This holder allows a wide range of well-defined incidence angles to the crystal, thereby allowing depth profiling, and when combined with an improved optical arrangement, provides increased sensitivity. In order to demonstrate the applicability of this new attachment, films of uniaxially drawn polypropylene (PP), poly(ethylene terephthalate) (PET), and biaxially drawn PP were characterized in this study, along with undrawn polypropylene for comparison. For uniaxially drawn polymers, the three-dimensional absorbances show that even though the major anisotropy exists between the draw direction (x) and the transverse direction (y) or between x and the thickness direction (z), the absorbance along the y or z direction is not identical in some bands, suggesting a certain extent of deviation from transverse symmetry. The surface degree of crystallinity in PP, averaging a depth of about 3 μm, has been estimated from the three absorbance values, after correction for the orientation effect, to be 0.62, 0.72, and 0.45 for uniaxially, biaxially, or undrawn films, respectively. These values agree favorably with their bulk crystallinity values obtained by other techniques. On the surface of uniaxially drawn PET, the amount of trans conformer in the ethylene glycol unit of PET is estimated to be at least 49%, and the surface degree of crystallinity to be 0.27. In equally biaxially drawn PP, surface orientation shows a slight imbalance in the two draw directions, while the orientation in the thickness direction is much smaller, as expected. The amorphous orientation functions calculated from our results always show smaller values than the crystalline orientation functions in both PP and PET regardless of whether they were uniaxially or biaxially drawn. Depth-profiling studies within the depth range 1–15 μm enable detection of the gradient in orientation as well as the changing degree of crystallinity near the surface. This technique therefore represents a new, rapid, nondestructive way to characterize surface structure and orientation in polymer films as a function of surface depth.

Introduction

IR spectroscopy by the attenuated total reflection (ATR) technique is one of the most useful techniques for characterization of polymer surfaces. Since a full characterization of polymer surfaces will undoubtedly require measurements of molecular orientation in all three spatial directions, crystallinity, and different conformer content (trans vs. gauche, for example), use of a polarized IR beam is preferred in ATR dichroism studies.

According to Flournoy and Schaeffers[1] and Hansen,[2] a polymer film surface will exhibit three spatial absorbance characteristics, A_x, A_y, and A_z, which are related to the ATR intensities for the transverse electric (TE) and the transverse magnetic (TM) waves, where the x axis is the axis of drawing in the case of uniaxial drawing and the y and z axes are parallel and normal to the film plane, respectively, as shown in Figure 1. Since both the polymer film and the polarizer can be rotated by 90°, one can obtain four reflection spectra from which only three spatial absorbances need to be calculated according to the equations

$$A_{\mathrm{TE},x} = \alpha A_x \tag{1}$$

$$A_{\mathrm{TM},x} = \beta A_y + \gamma A_z \tag{2}$$

$$A_{\mathrm{TE},y} = \alpha A_y \tag{3}$$

$$A_{\mathrm{TM},y} = \beta A_x + \gamma A_z \tag{4}$$

where α, β, and γ are constants determined by the refractive indices of the sample and the reflective crystal and the angle of incidence.[1]

In practice, when the sample is rotated (a necessary step even for two-dimensional orientation analysis) the sample must be remounted. After the remounting, reproducibility of optical contact between the crystal and the polymer film cannot be ensured. Since the intensities of ATR spectra are strongly dependent on such optical contact efficiency, the error could be substantial. In order to resolve this problem, a rotatable sample holder with a specially made square double-edged reflection crystal, which does not require remounting the sample for sample rotation, was recently designed in our laboratory.[3] With this modified holder, it was demonstrated that we can obtain two-dimensional molecular orientation information from polymer film surfaces.[3]

We have now extended our work to characterize molecular orientation in three dimensions by designing a new ATR attachment that allows a wide range of well-defined incidence angles to the crystal as well as increased sensitivity. With this holder/attachment arrangement, the effective surface depth being probed can be matched for TE and TM waves by choosing a proper incidence angle for each polarization. Three-dimensional orientation analysis[4] is, of course, important for a meaningful characterization of molecular orientation itself but is also a prerequisite for the estimation of other structural parameters (such as surface degree of crystallinity), because IR intensities characteristic of such structural parameters are dependent on orientation in drawn films.[5,6] The so-called structural factor (A_0), which is independent of orientation, can be calculated only with the knowledge of all three-dimensional absorbances as shown below.

$$A_0 = (A_x + A_y + A_z)/3$$

In addition, due to the strong dependence of penetration depth on the incidence angle, the capability for a wide range of well-defined incidence angles allows one to

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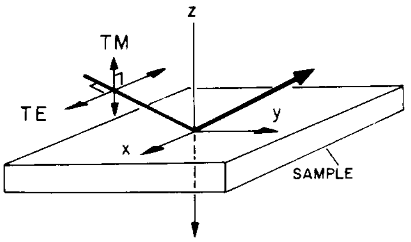

Figure 1. Definition of three spatial axes and two polarizations (TE and TM) for IR ATR dichroism studies on polymer samples.

Table I
Three Spatial Refractive Indices of Polymer Films

refractive index	polypropylene 1-PP[a]	2-PP[b]
n_x[c]	1.514	1.512
n_y	1.495	1.515
n_z	1.494	1.501

[a] Provided by Dr. de Vries for uniaxially drawn PP. [b] As reported in ref 7 for biaxially drawn PP (nominal draw ratio, 6 × 6). [c] x is the draw direction, y transverse to x in the film surface, and z is the thickness direction.

characterize surface orientation and structure as a function of depth.

Experimental Section

Materials. Experiments were carried out with polypropylene (PP) films and a poly(ethylene terephthalate) (PET) film. Uniaxially drawn PET was kindly provided by Dr. Willis at ICI. Polypropylene films (uniaxially and biaxially drawn) were kindly provided by Dr. de Vries of Rhône-Poulenc through Dr. Seferis of the University of Washington. Uniaxially drawn films had been prepared by drawing extruded sheets between a pair of rollers. The PP sheet was quenched in a water bath after drawing. This sample is similar to sample 1.04 as reported by de Vries[7] in its birefringence characteristics. In biaxially drawn PP, drawing in the x direction was immediately followed by drawing in the y direction with balanced draw ratios (6 × 6). This sample is sample 2.11 as reported by de Vries.[7]

To examine a sample with only a slight orientation, we heated highly drawn polypropylene sheets (Phillips Co.) above their melting point (at 375 °F) for 25 min between stainless steel molds to remove orientation, annealed them in air at 375 °F for 15 min, and then cooled them slowly to room temperature. We will refer to this sample as undrawn polypropylene.

Table I shows the three principal refractive indices of drawn polypropylene films used in this study. Other bulk characterization data on polypropylene samples can be found in ref 7.

ATR Apparatus. The symmetrical parallelogram KRS-5 crystal (25 mm × 25 mm × 2 mm, with 45° entrance and exit face angles) purchased from Harrick Scientific Corp. and the C-clamp sample holder have been described previously.[3] The advantages of using such a crystal were constant polymer/crystal contact and similar sampled areas when the sample was rotated.

For three-dimensional surface structural analyses, the polarizer needs to be rotated by 90° from the TE wave to the TM wave. The effective depth of penetration (d_e/λ_1) for the TE or the TM wave for isotropic materials is determined by eq 5 and 6, respectively,[8]

$$\frac{d_e(\mathrm{TE})}{\lambda_1} = \frac{n_{21}\cos\theta}{\pi(1 - n_{21}^2)(\sin^2\theta - n_{21}^2)^{1/2}} \qquad (5)$$

$$\frac{d_e(\mathrm{TM})}{\lambda_1} = \frac{n_{21}\cos\theta(2\sin^2\theta - n_{21}^2)}{\pi(1 - n_{21}^2)[(1 + n_{21}^2)\sin^2\theta - n_{21}^2](\sin^2\theta - n_{21}^2)^{1/2}} \qquad (6)$$

where $n_{21} = n_{\mathrm{polymer}}/n_{\mathrm{crystal}}$, $\lambda_1 = \lambda/n_{\mathrm{crystal}}$, and θ is the incidence angle. The effective depth for the TM wave is greater than for the TE wave as shown in Table II for isotropic PP and PET at a given incidence angle; this trend would also be valid even for anisotropic materials. It would be desirable to compare A_x, A_y, and A_z values at a similar depth, since structure and orientation may be a function of the surface depth. Fortunately, Table II shows that a 45° angle for the TE wave provides similar depth to that of a 51° angle for the TM wave, so this combination of angle and polarization was chosen for the three-dimensional analyses in this study.

Table II
Effective Penetration Depth $(d_e/\lambda_1)^a$ as a Function of Incidence Angle and Polarization

θ, deg	d_e(TE)	d_e(TM)
	Polypropylene	
45	0.737	1.474
51.2	0.514	0.823
	Poly(ethylene terephthalate)	
45	1.143	2.287
51.2	0.667	1.050

[a] $\lambda_1 = \lambda/n_1$, where λ is the wavelength and n_1 is the refractive index of the crystal.

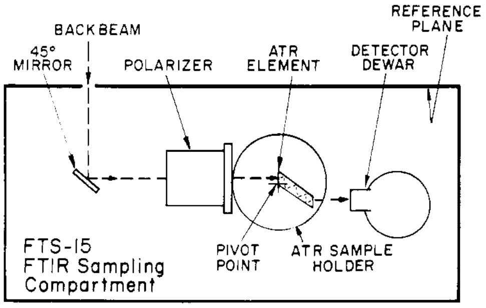

Figure 2. Schematic of new optical arrangement for IR ATR studies in FTS-15 sampling compartment. Dimensions of mirror, polarizer, and sample holder are not to actual scale.

The depth of the surface probed under these conditions is about 3 μm at 1000 cm^{-1} with KRS-5 as the crystal. Much shallower depths can be probed either at a higher incidence angle as described in depth-profiling studies or with a denser crystal such as germanium or through the use of an optical spacer.[8]

The ATR attachment (TMP-V00 from Harrick) used previously[3] was not adequate for this study since the angle of incidence could not be well defined for the specially made crystal, which is shorter than the conventional size crystal. Also the IR beam was not focused on the entrance plane of the crystal. In combination with beam divergence and reflectance losses this reduces the signal strength at the detector.

In order to solve these problems, a new ATR arrangement was developed, as shown schematically in Figure 2. In this arrangement, the Digilab FTS-15 Fourier transform IR spectrometer was used as a single-beam instrument. The back beam of the instrument was reflected by a mirror to travel parallel to the sample compartment wall, before being polarized by a Ge double-diamond crossed-plate polarizer (P00-1B, Harrick Scientific Corp.) and entering the ATR element. The ATR element was located so that its entrance face was in the focal plane of the IR beam. The angle the ATR element made with the beam was set by using the sample compartment wall as a reference plane. The ATR crystal and the C-clamp crystal holder were mounted in a new attachment, as shown in Figure 3. The zero-backlash worm gear drive for the attachment allowed reproducible settings of a wide range of the incidence angle to the crystal. Both the attachment and its worm gear drive were mounted on an X–Y stage that allowed adjustment of the ATR crystal entrance face position into the center of the IR beam's focal plane. This stage was mounted on a base plate, which also held the polarizer and mirror mounts and which could be locked into position in the sample compartment by set screws.

The liquid nitrogen cooled narrow-band mercury–cadmium telluride detector was placed on the base close to the exit face of the ATR crystal. This arrangement allowed an accurate determination of the crystal/beam angle and increased the measured signal by a factor of at least 10 in comparison to the previous

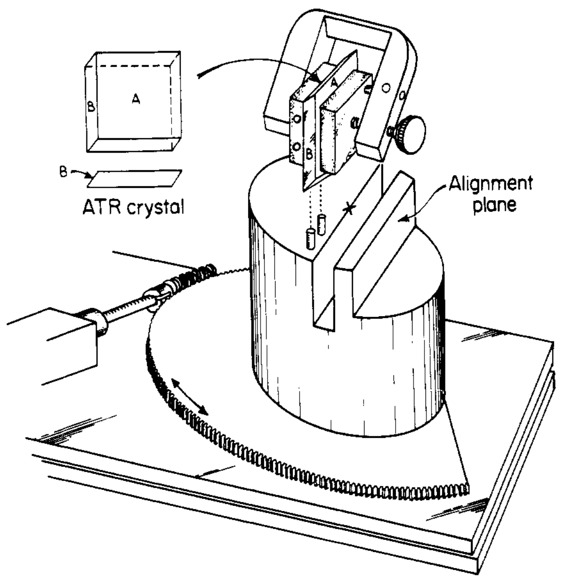

Figure 3. Drawing of new ATR sample holder, seen from detector, showing reflection crystal geometry and worm gear and drive, mounted on base plate. The IR beam enters the crystal from the back face of the crystal and exits from face B before entering detector.

Table III
α, β, and γ Values for Polypropylene and Poly(ethylene terephthalate) Films

	PP	PET
α at 45°	23.05	63.00
β at 51.2°	5.28	6.15
γ at 51.2°	15.23	28.04

arrangement.[3] In addition, adjustments for entrance face position needed after changing the incidence angle were minimized because the pivot point for the ATR crystal was now located near the entrance face of the crystal.

IR Analyses. ATR single-beam reflection spectra were collected with an FTS-15 (Digilab) instrument; typically 200 scans at a gain of 4–16×, with a resolution of 2 cm^{-1}, were taken. For characterization at a given depth, four ATR spectra of the sample film were collected, corresponding to $A_{\mathrm{TE},x}$ and $A_{\mathrm{TE},y}$ at a nominal 45° incidence angle and $A_{\mathrm{TM},x}$ and $A_{\mathrm{TM},y}$ at a nominal 60° incidence angle, to compare for a similar effective depth. Due to the beam refraction at the entrance face of the crystal, the actual effective angles of incidence were 45° or 51.2° rather than the nominal 45° or 60°. For depth-profiling studies, ten angles were studied from an effective angle of 39.5° to 55.2° to provide information covering a depth range of about 1–15 μm at 1000 cm^{-1}. The depth range is calculated based on eq 5 and 6, which assume ideal contact between the sample and the crystal and smoothness of both surfaces. The actual conditions may deviate from such ideal situations. Furthermore, the calculated depth is based on the refractive index for isotropic polymer, which introduces 5–10% error in the case of anisotropic, highly drawn polymer. Therefore, the depths given throughout this paper should be only regarded as approximate values.

The ATR spectra were calculated by ratioing the sample spectrum with the appropriate reference spectrum, which had been collected without the sample. Subtraction of water and CO_2 spectra was done from the ATR spectra for PET samples but deemed unnecessary for PP samples. Maximum noise was 3% in the ATR spectra.

Absorption values were assigned using peak height measurement and local base lines directly from ATR spectra. The values of α, β, and γ for eq 1–4 were determined following Flournoy[1] and are given in Table III for isotropic samples. For highly anisotropic samples such as 1-PP, the α, β, and γ values change at most 10%, which affects the A_x, A_y, and A_z values. However, it does not affect the dichroic ratio D_{xy}. Even its effect on the dichroic ratio D_{xz} is estimated to be relatively small, because A_x and A_z increase by similar extents.

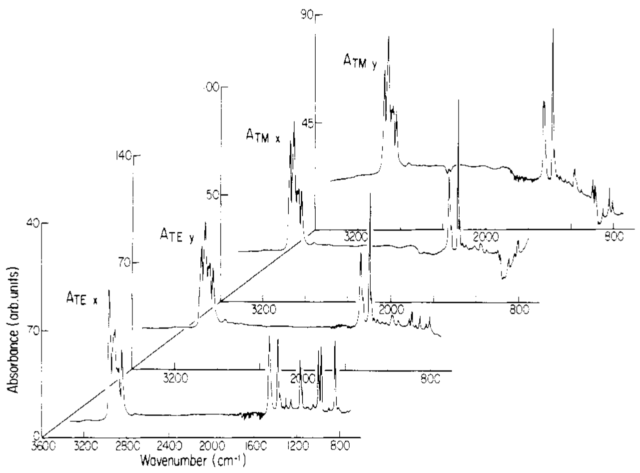

Figure 4. Four IR ATR spectra obtained from surface of uniaxially drawn polypropylene as a function of sample rotation and polarizer rotation.

Table IV
Three Spatial Absorbances in the Surface of Uniaxially Drawn Polypropylene (1-PP)

band, cm^{-1}	assignment	A_x	A_y	$A_z{}^a$	$A_z{}^b$	$\bar{A}_z$
841	∥, C	0.0197	0.0018	0.0007	0.0011	0.0009
973	∥, A, C	0.0172	0.0045	0.0028	0.0035	0.0032
998	∥, C	0.0162	0.0023	0.0023	0.0031	0.0027
1167	∥, C	0.0129	0.0030	0.0009	0.0013	0.0011
808	⊥, C	0.0007	0.0043	0.0036	0.0030	0.0033
899	⊥, C	0.0006	0.0045	0.0030	0.0021	0.0026
1102	⊥, C	0.0005	0.0016	0.0011	0.0008	0.0010
1376[c]	⊥, CH_3	0.0710	0.1285	0.2014	0.0896	0.1455

[a] Calculated from $A_{\mathrm{TM},x}$. [b] Calculated from $A_{\mathrm{TM},y}$.
[c] Absorbance values for 1376 cm^{-1} were obtained after deconvolution of the peaks and using peak area rather than peak height.

Results and Discussion

Uniaxially Drawn Polypropylene Film. Figure 4 shows the four IR ATR spectra obtained from the surface of a uniaxially drawn polypropylene film (1-PP) for the four possible combinations of sample and polarizer orientation. As explained in the Experimental Section, a similar effective depth from the surface was probed by using a 45° incidence angle for TE polarization and a 51.2° angle for TM polarization.

For IR dichroism studies of bulk PP samples, absorption bands at 1220 and 1256 cm^{-1} have been successfully used to represent crystalline and average orientation, respectively.[7,9] However, in our ATR dichroism studies, their intensities were too weak to yield accurate values. Instead, the absorption bands considered too strong in bulk analyses such as the 998-, 973-, and 1378-cm^{-1} bands were more useful in ATR analyses. Detailed assignments for these bands are discussed in ref 6 and 12.

From Figure 4, A_x, A_y, and two A_z values for bands strong enough for accurate measurement have been calculated based on eq 1–4 and are listed in Table IV, where parallel bands are grouped in the top half and perpendicular bands in the lower half. Since x is the draw direction, it is expected that A_x will be greater than A_y for parallel bands and A_y greater than A_x for perpendicular bands. Comparison of the A_x and A_y columns in Table IV shows that this is indeed the case for all the bands in polypropylene; this is more clearly shown in the dichroic ratio D_{xy} ($=A_x/A_y$), the second column in Table V.

Since the four spectra are obtained for only three unknown A values (eq 1–4), two A_z values have been esti-

Table V
Dichroic Ratios and Orientation Functions from the Surface of Uniaxially Drawn Polypropylene ($X_c = 0.62$)

band, cm^{-1}	D_{xy}	$D_{x\bar{z}}$	f_{xy}	$f_{x\bar{z}}$	$(f_{am})_{xy}$[b]	$(f_{am})_{x\bar{z}}$[b]
841	10.94	21.89	0.768[a]	0.874[a]	0.022	0.134
973	3.82	5.38	0.485	0.593		
998	7.04	6.00	0.668[a]	0.625[a]	0.185	0.541
1167	4.30	11.73	0.524	0.782		
808	0.16	0.21	0.778[a]	0.715[a]	0.006	0.395
899	0.13	0.23	0.817	0.691		
1102	0.31	0.50	0.597	0.400		
1376	0.55	0.49	0.353	0.410		

[a] Crystalline orientation function (f_c). [b] Amorphous orientation function, using $f_{973\text{cm}^{-1}}$ as f_{av} in eq 8.

mated from each of the $A_{\text{TM},x}$ and $A_{\text{TM},y}$ spectra. Comparison of the two A_z values in Table IV shows a general agreement between the two. Now we can compare A_y and $\bar{A}_z$ (the average of the two A_z values). In this sample, the refractive indices along the y and z directions are the same (see Table I), indicating that the overall transverse symmetry usually assumed for uniaxially drawn polymers is applicable, at least as measured by refractive indices. However, careful comparison of A_y and $\bar{A}_z$ values shows that while $\bar{A}_z$ values are close to A_y values, they are not identical. The difference between $\bar{A}_z$ and A_y values seems beyond the experimental error (~10%) in some bands such as the 1167- and 899-cm^{-1} bands. This suggests that transverse symmetry may not apply on a microscopic scale; i.e., different functional groups or parts of the polymer molecule may deviate to some extent from transverse symmetry. By using the tilting method, Hutchinson et al.[10] made a careful measurement of three-dimensional absorbances from the bulk of uniaxially drawn poly(ethylene terephthalate) and observed similar tendencies. de Vries[7] has also recently reported that uniaxially drawn polypropylene films exhibited deviation from perfect transverse symmetry even when refractive indices were used to measure overall orientation, except in very highly drawn films.

Since all three absorbances are determined, we can now estimate structural factors such as surface degree of crystallinity (X_c). In polypropylene, Quynn et al.[11] have shown that the ratio A_{998}/A_{973} is almost linearly correlated to density and thus can be used to measure crystallinity. In this sample, such a ratio after correcting for the orientation effect can be used to estimate crystallinity as follows:

$$\frac{A^0_{998}}{A^0_{973}} = \frac{\frac{1}{3}(A_x + A_y + A_z)_{998}}{\frac{1}{3}(A_x + A_y + A_z)_{973}} = 0.851 \qquad (7)$$

This value corresponds to a density of 0.904.[11] By assuming the density of the crystalline phase and of the amorphous phase of polypropylene to be 0.935 and 0.853 g/cm^3, respectively, and by assuming orientation to be independent of density,[11] the surface degree of crystallinity for this sample can be calculated, adopting the usual two-phase model:

$$X_c = \frac{d - d_{am}}{d_c - d_{am}} = 0.62$$

This value, averaging about 3 μm in depth, is similar to the bulk crystallinity value reported by de Vries[7] on similarly uniaxially drawn polypropylene based on density, X-ray, and DSC analyses.

In order to obtain more information on the surface structure of this polymer, two dichroic ratios ($D_{xy} = A_x/A_y$; $D_{x\bar{z}} = A_x/\bar{A}_z$) were calculated from the three spatial absorbances, and two corresponding orientation functions (f_{xy} and $f_{x\bar{z}}$) were calculated from such dichroic ratios by the equation

$$f = \left(\frac{D - 1}{D + 2}\right)\left(\frac{D_0 + 2}{D_0 - 1}\right)$$

where $D_0 = \cot^2 \alpha$, α being the angle between the transition moment vector for the vibration and the chain axis. f becomes unity for perfect alignment with the draw direction, −0.5 for transverse alignment, and zero for random orientation. The angle α for each absorption band is not accurately known. As a first approximation, we used 0° for all parallel bands and 90° for all perpendicular bands. If the angle is between 0° and 90°, the orientation functions calculated assuming 0° or 90° should be underestimated values, and therefore minimum orientation values.[7] Table V summarizes the dichroic ratios and orientation functions.

The following surface structural information can be derived from Table V

1. Even though f_{xy} and $f_{x\bar{z}}$ are not the same for a given band due to the deviation from transverse symmetry, the generally high values of the orientation function indicate that the chains on the surface are predominantly oriented toward the stretch (x) direction.

2. The surface orientation function of side-group methyl bending at 1376 cm^{-1}[12] is the smallest, while skeletal orientation functions at 841 or 998 cm^{-1}[12] are much greater toward the stretch direction.

3. Bands at 808, 841, and 998 cm^{-1} are characterized as crystalline bands.[12,13] In uniaxially drawn polypropylene, de Vries has shown that there is a good correlation between the orientation functions obtained by IR dichroism of these bands and the crystalline orientation function deduced from wide-angle X-ray diffraction studies.[7] Especially, the orientation function based on the band at 808 cm^{-1} gave values almost identical with the X-ray-deduced crystalline orientation function. Therefore, we may use f_{xy} and $f_{x\bar{z}}$ values for these three bands as representing the orientation of the chains in the crystalline phase. In contrast, the band at 973 cm^{-1} contains both crystalline and amorphous contributions,[12,13] and thus their orientation function would be close to f_{av}. By using the following equation, we can then estimate the amorphous chain orientation function (f_{am}) on the film surface:

$$f_{av} = X_c f_c + (1 - X_c) f_m \qquad (8)$$

where X_c is the surface degree of crystallinity. For example, when f_{av} of 973 cm^{-1} and X_c of 0.62 are used, f_{am} can be estimated from the above equation for the three crystalline bands, as listed in the last two columns of Table V. It is seen that the amorphous orientation function is always smaller than the corresponding crystalline orientation function. This trend is consistent with the bulk orientation studies reported by Samuels[9] and de Vries[7] on uniaxially drawn polypropylene film and can be explained as being due to molecular mobility and relaxation of orientation in the amorphous phase since its T_g is much lower than the melting temperature of the crystalline phase.

Uniaxially Drawn Poly(ethylene terephthalate) Film. For uniaxially drawn poly(ethylene terephthalate), analogous dichroic ratios and orientation functions are summarized in Table VI, assuming 0° for the transition moment angle for several parallel bands as a first approximation. We note that D_{xy} and $D_{x\bar{z}}$ are somewhat different in Table VI, suggesting again a deviation from transverse symmetry. Since this sample was processed

Table VI
Dichroic Ratios and Orientation Functions from the Surface of Uniaxially Drawn Poly(ethylene terephthalate) ($X_c = 0.27$)

band, cm^{-1}	assignment	D_{xy}	$D_{x\bar{z}}$	f_{xy}	$f_{x\bar{z}}$
1343	∥, C, CH$_2$ wagging	5.89	6.62	0.620	0.652
975	∥, C, trans	4.00	8.00	0.500[a]	0.700[a]
896	∥, A, gauche	1.29	1.83	0.088[b]	0.217[b]
795	∥, benzene	1.75	2.33	0.200[c]	0.308[c]

[a] Can be used for crystalline orientation function.
[b] Can be used for amorphous orientation function.
[c] Can be used for average orientation function.

between a pair of rollers after drawing, a slight biaxial orientation might have been introduced, which may account for such a deviation. It is seen that the values of orientation functions are quite different, depending on band position. For example, the orientation function for 975 cm^{-1} is always higher than for 795 cm^{-1}, and that for 896 cm^{-1} is the smallest of all. These tendencies can be explained in view of the following band assignments: the orientation at 795 cm^{-1} due to the benzene ring has been found to be linearly correlated with the average orientation (f_{av}) of PET.[14,15] The orientation at 896 cm^{-1} due to the gauche configuration of the $-OCH_2CH_2O-$ group[16] is largely associated with the amorphous orientation (f_{am}).[17] In comparison, the orientation at 975 cm^{-1} due to the trans configuration of the ethylene glycol unit is largely attributed to the crystalline orientation (f_c).[18] In view of the fact that the orientation for the crystalline region in PET has been shown to be greater than for the amorphous region,[9] the observed trends are reasonable.

In addition, we can estimate the surface degree of crystallinity based on these orientation functions by using eq 7. By substituting $f_{795\text{cm}^{-1}}$, $f_{975\text{cm}^{-1}}$, and $f_{896\text{cm}^{-1}}$ values for f_{av}, f_c, and f_{am}, respectively, into eq 8, one gets $X_c = 0.27$ for this PET film surface. We may attempt to estimate the concentration of trans conformer on the surface of this uniaxially drawn PET film. For bulk samples of uniaxially drawn PET, Cunningham et al. established a good correlation between orientation function as obtained by IR dichroism at the 975-cm^{-1} trans band and the trans/gauche conformer concentration.[15] Using their correlation (Figure 5 and Table 3 in ref 15) and assuming 0° for the transition moment angle for the 975-cm^{-1} band, we estimate the concentration of trans conformer on the surface to be about 49% when $f_{xy} = 0.5$ is used. This value, 49%, should represent a minimum value since f_{xy} can be greater than 0.5 if α is greater than 0°, leading to higher trans content. Undrawn PET is characterized as having about 24% trans conformer, at least in the bulk.[15] Therefore, the estimated trans content (at least 49%) on the surface of our drawn PET film shows a significant increase, due to the uncoiling of the amorphous chains as a consequence of drawing.

Comparison between Biaxially Drawn and Undrawn Polypropylene Films. Table VII summarizes the results on dichroic ratios and orientation functions obtained from several parallel bands at the surface of biaxially drawn polypropylene film (nominal draw ratio, 6 × 6). For comparison, analogous values from annealed polypropylene are compared. Annealed samples ought to possess only a small amount of orientation, since the sample was heated above the melting point of polypropylene and was annealed to remove orientation, followed by slow cooling. We will refer to this polypropylene as undrawn polymer.

The dichroic ratio D_{xy} on the surface plane of the undrawn polymer is very close to unity, which results in very small f_{xy} values, as shown in Table VII. On the surface of biaxially oriented polypropylene, D_{xy} deviates somewhat from unity, indicating that the orientation along the x direction is slightly higher than that along the y direction, as shown by corresponding f_{xy} values. This tendency toward an imbalance in orientation even in nominally balanced, sequentially stretched films has been observed to be representative of bulk structure in biaxially drawn polypropylene.[19] In spite of small differences in D_{xy} between undrawn and biaxially drawn polypropylene, D_{xy} or f_{xy} alone is insufficient to distinguish between biaxially drawn and undrawn polymers. However, in biaxially drawn polymer, the orientation along the z (thickness) direction is expected to be much less than that along either of the draw directions (x or y). This is borne out by large dichroic ratios $D_{x\bar{z}}$ and orientation function $f_{x\bar{z}}$, as shown in Table VII. For undrawn samples, much smaller values of $D_{x\bar{z}}$ and $f_{x\bar{z}}$ were obtained, indicating only a slight orientation. For isotropic samples, $D_{x\bar{z}}$ as well as D_{xy} is expected to be unity, and it would have been desirable to verify this with an isotropic polypropylene sample. Unfortunately, our attempts to cast isotropic polypropylene film from solution were not successful, owing to precipitation during the drying process. Nevertheless, the examples discussed above do illustrate the advantages of three-dimensional orientation analysis as opposed to two-dimensional analysis.

Following the procedure described for uniaxially drawn polypropylene, the degree of surface crystallinity was estimated to be 0.72 for biaxially drawn polypropylene and 0.45 for annealed polypropylene. It was interesting to find that de Vries reported the same degree of bulk crystallinity for the biaxially drawn sample[7] by other techniques.

Since the surface degree of crystallinity is known for both samples, we estimated the amorphous orientation functions $(f_{x\bar{z}})_{am}$ by using the two crystalline bands at 841 and 998 cm^{-1} and an average band at 973 cm^{-1} and listed them in Table VII. For biaxially drawn PP, again the amorphous orientation functions are smaller than the crystalline orientation function, a tendency observed in the bulk of biaxially drawn PP.[19] In comparison, the amorphous orientation functions $(f_{x\bar{z}})_{am}$ in undrawn polypropylene are similar to the crystalline orientation functions, as expected.

Characterization of Orientation and Structure as

Table VII
Dichroic Ratios and Orientation Functions from the Surface of Biaxially Drawn Polypropylene in Comparison to Undrawn Polypropylene

band, cm^{-1}	biaxially drawn polypropylene ($X_c = 0.72$)					undrawn polypropylene ($X_c = 0.45$)				
	D_{xy}	$D_{x\bar{z}}$	f_{xy}	$f_{x\bar{z}}$	$(f_{x\bar{z}})_{am}$	D_{xy}	$D_{x\bar{z}}$	f_{xy}	$f_{x\bar{z}}$	$(f_{x\bar{z}})_{am}$
841	1.28	9.87	0.086	0.816[a]	0.398	1.20	1.86	0.062	0.222[a]	0.158
973	1.21	5.64	0.066	0.699[b]		1.01	1.69	0.004	0.187[b]	
998	1.28	8.00	0.085	0.778[a]	0.496	1.06	1.76	0.018	0.203[a]	0.174
1167	1.26	6.22	0.079	0.723		1.02	1.63	0.005	0.172	

[a] $(f_{x\bar{z}})_c$. [b] $(f_{x\bar{z}})_{av}$.

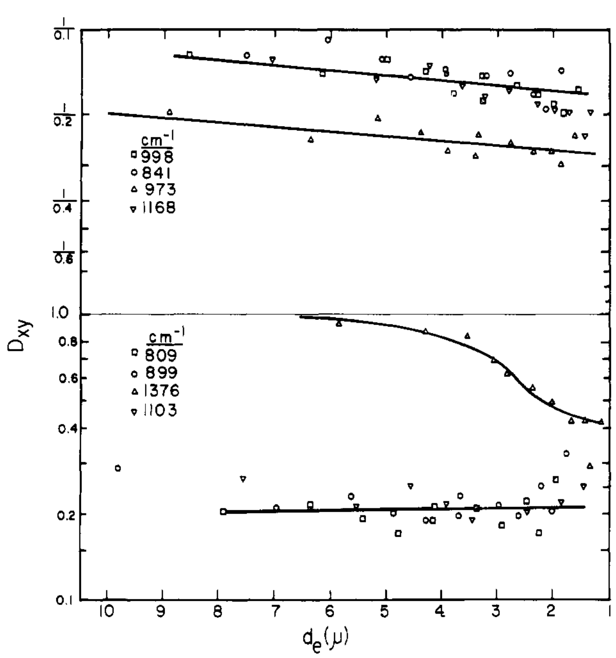

Figure 5. Dichroic ratio D_{xy} obtained from the surface of uniaxially drawn polypropylene as a function of surface depth (four parallel bands on the top and four perpendicular bands on the lower half).

a Function of Surface Depth. As shown in eq 5 and 6, the effective depth probed by the IR beam on the polymer surface is a strong function of the incidence angle, θ. Generally, this effective depth drops sharply at a higher incidence angle. Therefore we varied the incidence angle from an effective angle of 39.5° (which is just above the critical angle) to 55° (corresponding to a 70° nominal incidence angle), in order to characterize orientation and structure as a function of surface depth. This range of incidence angles corresponds to a depth of about 15 to 1 μm.

As an example of such depth-profiling studies, Figure 5 shows the plot of D_{xy} for four parallel bands and four perpendicular bands obtained with uniaxially drawn polypropylene film. It is seen that the planar orientation expressed by D_{xy} is amost constant when averaged in this range of depths except for 1376-cm^{-1} band. D_{xy} for this band is much lower in comparison to other bands, a tendency observed by Desper[20] in the bulk of ultrahighly drawn PP film. Nevertheless, for this band, orientation seems to increase, as the surface is approached. Since this band is assigned mostly for side-group methyl bending,[6,12] the results may suggest higher orientation of side groups on the surface in comparison to the bulk. The surface degree of crystallinity averaging for the first micron is calculated to be about 66%, showing a slight increase from 62% averaging for 3 μm in depth. Thus, the increasing orientation of the side group as the surface is approached may be a reflection of increasing crystallinity. More detailed three-dimensional orientation and structural analyses as a function of surface depth are in progress and will be reported in a later publication.

Summary

In order to characterize the surface molecular orientation in three dimensions and to obtain other surface structural information such as the degree of crystallinity and the different conformer contents, a new ATR sample holder was designed for FT IR ATR dichroism studies. This attachment allows a wide range of well-defined incidence angles to the crystal as well as increased sensitivity. For characterization at a given depth, we used a specially made, square double-edged KRS-5 crystal set to a nominal incidence angle of 45° and 60° for TE and TM polarization, respectively, to probe to a similar depth when the polarizer is rotated. Under these conditions, the surface depth being probed is about 3 μm at 1000 cm^{-1}. For depth-profiling studies, incidence angle was varied to probe the surface as a function of depth in the 1–15-μm range for the 1000-cm^{-1} region.

To demonstrate the applicability of this new setup, uniaxially drawn polypropylene, poly(ethylene terephthalate), and biaxially drawn polypropylene were characterized and compared with undrawn polypropylene in regards to their surface orientation and structure.

Since four spectra are obtained as a consequence of rotating the polarizer as well as the sample, the absorbance along the thickness direction (z) can be calculated independently from two sets of spectra. It was found that the two values agree reasonably well with each other. For uniaxially drawn polypropylene and poly(ethylene terephthalate) films, the three-dimensional absorbances show that even though the major anisotropy exists between x (draw direction) and y or x and z, the absorbances along the y and z directions are not always identical on some bands, meaning that there may be a certain extent of deviation from transverse symmetry.

The surface degree of crystallinity in polypropylene, averaging about 3 μm in depth, has been estimated from three absorbance values after correction for the orientation effect to be 0.62, 0.72, and 0.45 for uniaxial, biaxial, and undrawn films, respectively. These values of crystallinity are close to the bulk crystallinity values obtained by density, X-ray, or thermal analysis techniques.

On the surface of uniaxially drawn PET, the degree of crystallinity was estimated to be about 0.27, and the amount of trans conformer in the ethylene glycol unit of PET to be at least 49%.

In biaxially drawn polypropylene with nominally balanced draw ratio, the surface orientation was found to be slightly imbalanced in regards to two draw directions while the orientation along the thickness direction is smallest, as expected. In comparison, an undrawn polypropylene film surface shows no preferential planar orientation and only a small surface orientation in comparison to the z (thickness) direction.

The amorphous orientation functions calculated from our results always show smaller values than the crystalline orientation functions in both PP and PET regardless of whether they were uniaxially or biaxially drawn. In comparison, the values were similar to each other in undrawn PP.

As an example of the depth-profiling technique, uniaxially oriented polypropylene film was studied. It was found that the planar orientation is almost constant when averaged in the depth range 1–15 μm except for a band assigned to side-group methyl. For this band, higher orientation is observed near the surface, maybe due to the increasing surface crystallinity.

The results obtained in this study demonstrate that our new sample holder/attachment allows three-dimensional analysis, which provides a more detailed account of molecular orientation than two-dimensional analysis. This technique thus represents a new, rapid, nondestructive method of characterizing *surface* structure and orientation in polymer films as a function of surface depth. In films where the surface may be similar to the bulk, our technique can be used to estimate the average characteristics of bulk structure and orientation. This application should be an important one, since the thickness of most industrially processed polymer films (blown or drawn) is too great to allow transmission IR dichroism studies to probe bulk average characteristics. Comparing with the trirefringence technique,[21] where three spatial refractive indices can be measured by modifying an Abbe-type refractometer to estimate orientation, our IR ATR dichroism technique provides more detailed information on surface structure and orientation as demonstrated in this study.

Future Studies. For a surface depth greater than 10 μm, FT IR photoacoustic spectroscopy with a polarized IR beam was found useful to assess orientation.[22] A combination of FT IR ATR and photoacoustic dichroism studies will thus permit the probing of the surface structure and orientation as a function of a wider range of depths. For surface characterization in the range of a few thousand angstroms, a denser crystal such as Ge can be used. If one wants to limit the probing to hundreds of angstroms, a combination of a even denser crystal with a very high incidence angle should be used with longer scanning and improved optics (e.g., better focusing of the IR signal by a beam condenser).

Also, three-dimensional surface molecular orientation characterization in such polymers as liquid crystalline polymers, piezoelectric polymers, or chemically modified surfaces and correlating with surface-dependent properties will be interesting applications for this technique. We plan to continue our future studies in these directions.

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Structural Studies of Poly(ethylenimine). 3. Structural Characterization of Anhydrous and Hydrous States and Crystal Structure of the Hemihydrate

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ABSTRACT: A series of X-ray studies on the absorption of water vapor by poly(ethylenimine) revealed the existence of the hemihydrate, $(-CH_2CH_2NH-\cdot 0.5H_2O)_n$, besides the sesquihydrate and the dihydrate. It is therefore asserted that the anhydrate transforms into the hemihydrate, subsequently the sesquihydrate, and finally the dihydrate with increasing water content. The hemihydrate crystals are monoclinic, with cell dimensions a = 1.089 nm, b = 0.952 nm, c (fiber axis) = 0.731 nm, and β = 127.6°. The space group is $C2/c$, and the unit cell contains eight monomeric units (four chains) and four water molecules. The polymer chains are fully extended as in both the sesquihydrate and the dihydrate. All hydrogen bonds in the hemihydrate are of the N–H···O or N···H–O type: there exists no water···water hydrogen bond network, in contrast to the other two hydrates. The modes of hydrogen bondings in the anhydrate and the three hydrates are summarized and discussed. A variety of X-ray diffraction curves of poly(ethylenimine) are also presented for the use of identification of the crystal form (or forms) of a sample in question.

Previous X-ray studies[1-3] on linear poly(ethylenimine) (PEI) have revealed that the hygroscopic feature of this polymer is attributable to the formation of crystalline hydrates in which "water of crystallization" exists stoichiometrically. In practice, the PEI dihydrate contains a large quantity of water almost comparable to the weight of PEI itself. According to those studies, the polymer chains take the fully extended form in the sesquihydrate and the dihydrate,[1] while the double-stranded helical form in the anhydrate.[3] The striking difference in chain conformation between the anhydrate and the hydrates is the consequence of the full performance of hydrogen bondings in each crystal form; i.e., in all of the crystalline phases, every NH group and water molecule participate in hy-

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