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ORIENTATION MEASUREMENTS FROM POLYMER SURFACES USING FOURIER TR--ETC(U)
SEP 81 K KRISHNAN, S HILL, J P HOBBS N00014-78-C-0676

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Orientation Measurements from Polymer Surfaces
Using Fourier Transform Infrared Photoacoustic Spectroscopy,

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Abstract

Fourier Transform IR Photoacoustic (FTIR-PAS) dichroism studies have been applied to determine molecular orientation from the surface of one-way drawn poly(ethylene terephthalate) film. When compared with ATR dichroic spectra obtained with a modified, rotatable sample holder on the same sample, PA spectra show saturation effects in strong absorption bands near 1730, 1250 and 1100 cm^{-1} , probably due to the greater penetration depth in the PA technique. The dichroic ratios (k_x/k_y) on the plane of the sample film have been calculated from PA spectra, only on bands which do not show saturation and compared with the analogous ratios determined from ATR dichroic spectra. For three well-known parallel bands at 1335, 975 and 795 cm^{-1} the dichroic ratio is greater than unity in both ATR and PAS, as expected from the drawing process. In general, somewhat lower dichroic ratios are observed by PA spectra than by ATR spectra with this sample. Possible reasons for this trend are discussed. This study demonstrates the potential of FTIR-PAS dichroism as a complementary technique to ATR dichroism, especially on samples with rough or brittle surfaces.

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Photoacoustic spectroscopy (PAS) has been shown to be a very useful experimental technique for the study of the spectra of gases, liquids, and solids. Rosencwaig(1) has recently reviewed the theoretical and experimental aspects of PAS and has shown its applicability especially for the study of solids. In the PAS experiments the solid under study is placed in a sealed cell containing an inert gas and a highly sensitive microphone. Pulsed or chopped radiation is focussed on the sample by means of suitable optics. If the sample absorbs radiation at any particular frequency, the absorbed radiation is converted into thermal energy by non-radiative processes. This thermal energy is transmitted to the surrounding gas and sets up a pressure wave in the cell. This pressure or acoustic wave is detected by the microphone resulting in the PA signal. This signal is proportional to the incident energy, and is also dependent on the thermal and optical properties of the sample. The thickness or the depth of the sample from which the PA signal emanates is also dependent on the chopping frequency. Rosencwaig(1) has shown that this depth can be of the order of 10 to 100 micrometers at low (~ 5 KHz) chopping frequencies and of the order of 0.1 to 1 micrometer for high (~ 100 KHz) chopping frequencies. The PA technique has been recently extended to the mid-infrared region of the electromagnetic spectrum by several investigators using dispersive(2) or Fourier transform(3,4) spectrometers. Krishnan(5) has shown that under normal operating conditions of the Fourier transform infrared (FT-IR) instruments, the PA signal can arise from a layer of thickness around 10 micrometers for typical polymers at 1000 cm^{-1} . This thickness would then represent an intermediate case when compared to infrared surface measurement techniques such as attenuated total internal reflectance (ATR) and bulk measurement

techniques such as transmission. One of us (Sung,6) has recently shown that the dichroic ratios and hence the surface orientation of polymers could be studied using a modified polarized IR-ATR technique. In this note we show that good quality dichroic spectra can be obtained for polymers using the PA method. The results obtained from PA spectra will be compared with the dichroic ratios obtained for the same sample by the modified polarized ATR technique.

The sample used in the present study was a sheet of poly(ethylene terephthalate), one-way drawn between a pair of rollers. The surface studied was that facing the hot roller. All the spectra presented here were recorded at 4 cm^{-1} spectral resolution using a Digilab FTS-15 Fourier transform infrared spectrometer. The polarized ATR spectra were recorded using a specially designed accessory with a symmetrical KRS-5 crystal, as described in Reference 6, and a liquid nitrogen cooled mercury cadmium telluride detector. The polarizer in the ATR accessory (a germanium double diamond crossed-plate type from Harrick) was set at perpendicular polarization (TE wave), and two spectra were recorded for the sample oriented with its draw axis perpendicular and parallel to the incident plane. The ratio of peak heights in the two spectra will then yield the dichroic ratio k_x/k_y , where x is the stretch direction and y is transverse to x. The PA spectra were recorded using a Digilab PAS cell and a gold wire grid polarizer (Perkin-Elmer). Two PAS spectra were recorded, this time by keeping the sample orientation constant but by changing the polarizer orientation by 90 degrees. The ratio of the peak heights in these two spectra will also yield the dichroic ratio k_x/k_y .

Figure 1 shows the k_x spectra from the PA (top) and the ATR (bottom) measurements. One can see the qualitative similarity in the appearance of the two spectra. Figure 2 shows the corresponding k_y spectra.

It can be seen in Figures 1 and 2 that the positions of the strongest bands in the PA and ATR spectra are at different frequencies. This is particularly noticeable for the bands at around 1730, 1250 and 1100 cm^{-1} . Krishnan(5) has shown that these differences arise due to saturation effects in the PA spectra. When the sample absorption at a particular frequency is very strong, most of the incident radiation at this frequency is absorbed within a sample thickness that is small compared to the thermal diffusion length of the sample and the PA spectrum will show saturation at this frequency(1). The weaker absorptions, however, will not show this effect and will exhibit an apparent increase in intensity relative to the saturated ones. Thus in the PA spectra of the PET sample, the satellite absorbances of the strongest bands in the sample are enhanced, leading to an apparent shift in the strongest bands in the PA spectra. The weaker bands in the PET spectra do not show these saturation effects and appear at the same frequencies in the PA and ATR spectra.

Table 1 summarizes the dichroic ratios k_x/k_y derived from the PA and the ATR experiments for PET, after excluding saturated bands. It can be observed that for three well known parallel bands(7), at 1335, 975 and 795 cm^{-1} , the dichroic ratio is greater than unity in both ATR and PAS, as expected from one-way drawing. In hot-rolled samples such as the one used in the present study, the surface may be expected to show a slightly greater degree of orientation than the bulk of the sample. If as was postulated by Krishnan(5), the depth of penetration is greater in the PA experiments than in the ATR experiments, then one would expect the dichroic ratios from the PA spectra to be closer to unity when compared to the ratios from the ATR spectra. The results shown in Table 1 show that this may indeed be the case generally. The results presented here would thus indicate the potential

that polymer orientation as a function of sample depth can be studied by a combination of ATR and PA experiments. Furthermore, if ATR crystals of different refractive indices and effective angles could be used, then a complete depth profiling of the orientation might be achieved.

In conclusion, we have shown that good quality dichroic spectra which give reasonable dichroic ratios can be achieved using the FTIR-PAS technique. As far as the authors are aware, this is the first such study of the dichroic FTIR-PAS spectra. Since the PA technique does not depend on a good contact of the sample with the reflection crystal as in ATR, the PA technique can be used to determine orientation in films with rough or brittle surfaces.

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Table 1.

Comparison of Dichroic Ratio (k_x/k_y) on the PET Surface
by FTIR-ATR and FTIR-PAS Techniques

Bands (cm^{-1})	Dichroic Ratio (k_x/k_y)	
	ATR	PAS
1335	6.08	2.56
975	4.09	2.78
795	1.73	1.39

Figure Captions

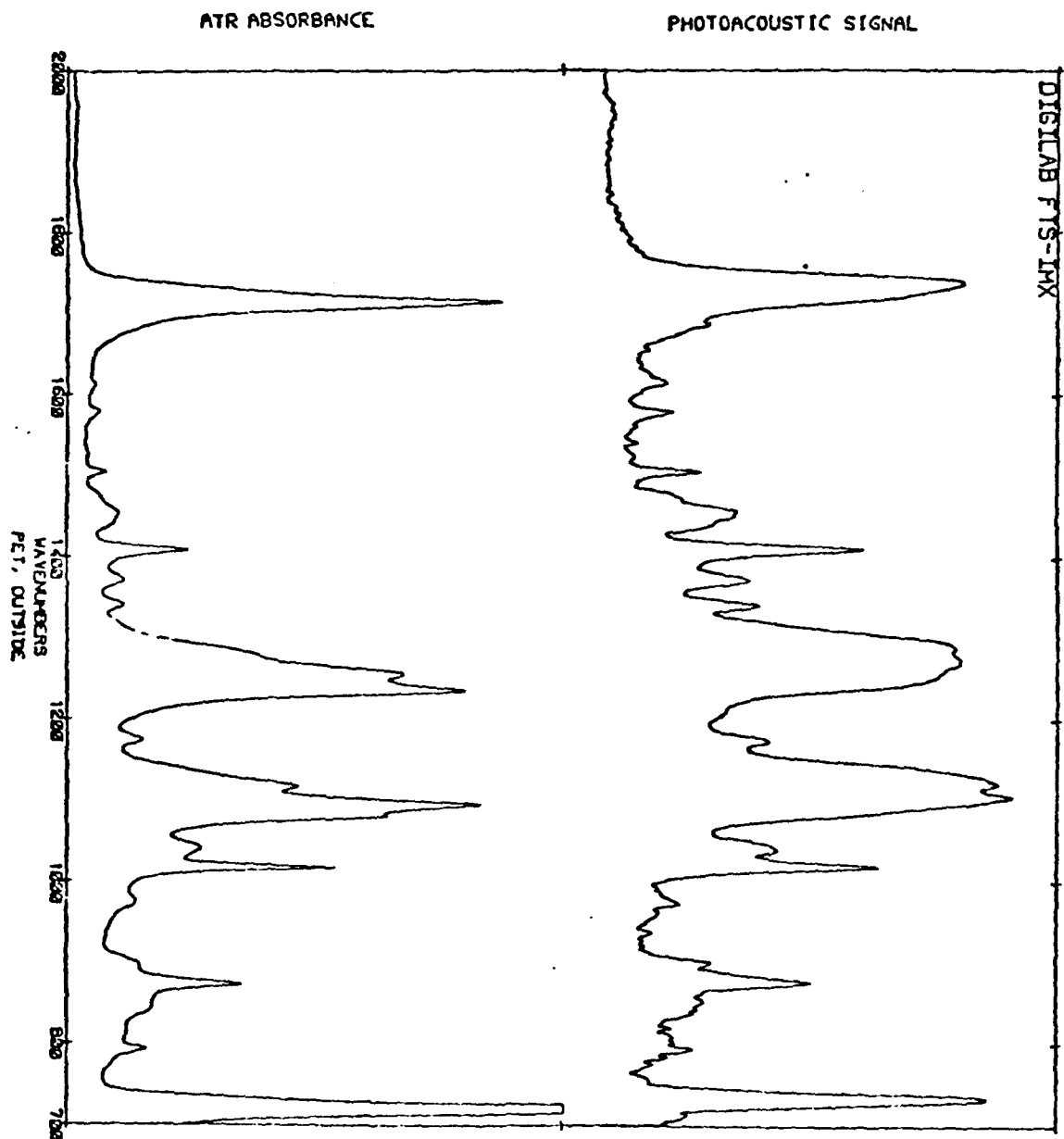
Figure 1. (Top) Photoacoustic spectra of PET surface.

(Bottom) Polarized ATR spectra of PET surface.

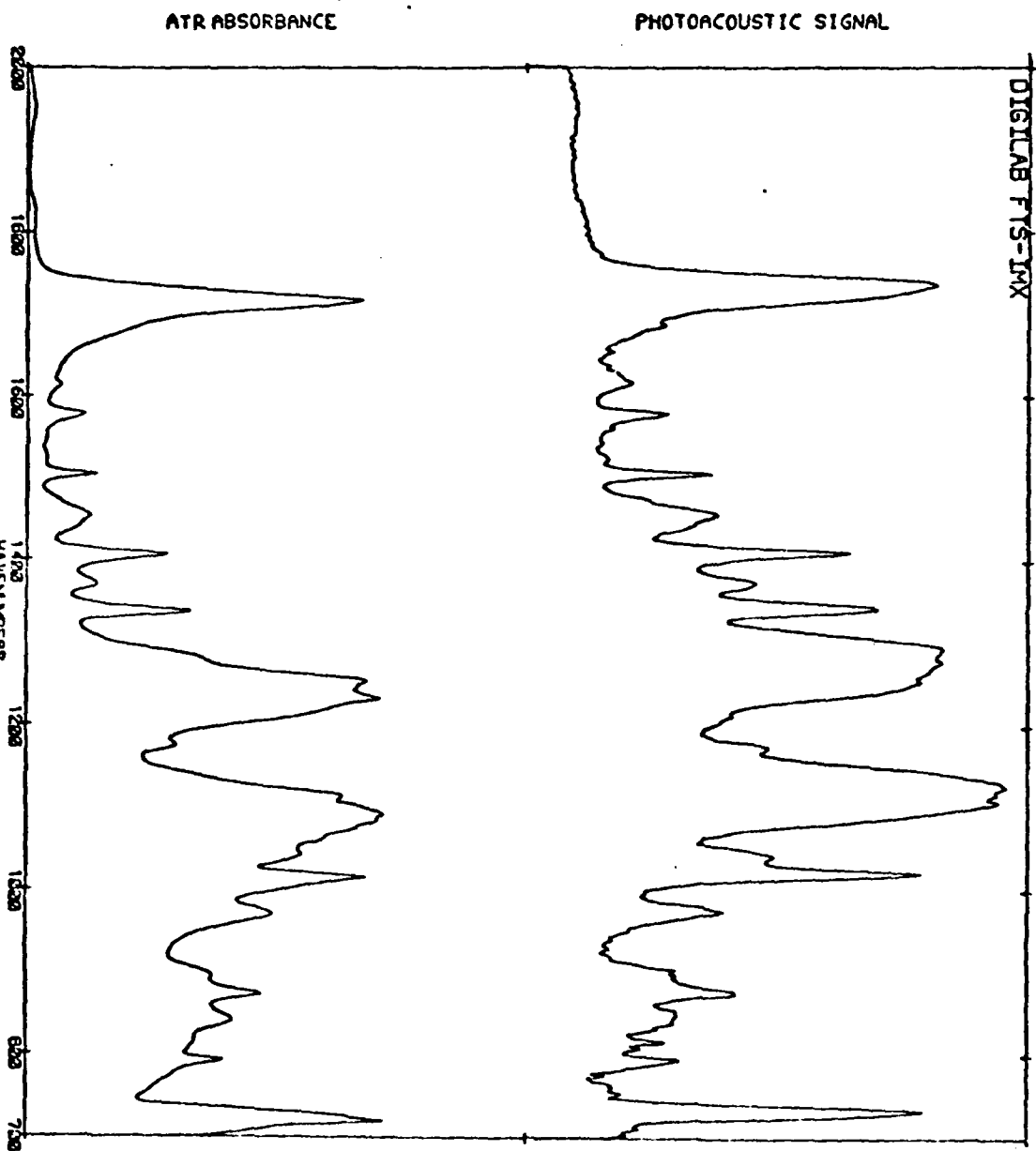
In both spectra, polarization was parallel to x (draw direction) and thus k_x is obtained.

Figure 2. (Top) Photoacoustic spectra of PET surface.

(Bottom) Polarized ATR spectra of PET surface. In both spectra, polarization was perpendicular to x (draw direction), and thus k_y is obtained.



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Figure 1



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Figure 2

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