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Application News

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Spectrophotometric Analysis

Polarized ATR Measurements of Uniaxially Drawn PET Film

In the process of forming film by the melting method, uniaxial or biaxial drawing of the film is typically conducted to improve the film properties according to the intended application. The orientation of molecules in drawn film changes according to the direction(s) in which the film was drawn, and the molecules will assume a specific orientation. The orientation can be evaluated using the transmission method to obtain the dichroic ratio, an absorbance ratio of the spectra obtained by irradiating the sample with polarized light parallel to and perpendicular to the draw axis of the sample. In contrast to this method, in which evaluation can only be conducted two-dimensionally, polarized light measurement by the ATR method permits evaluation along the Z-axis (thickness direction), in addition to the X-axis and Y-axis.
Here, we present an example of evaluation of uniaxially drawn polyethylene terephthalate (PET) film using the polarized ATR measurement technique.

Polarized ATR Measurements

When using the transmission method, peak saturation may prevent measurement if the film is too thick. However, one advantage of the ATR method is that measurement can be conducted regardless of the film thickness. Furthermore, with single reflection ATR, the prism size is small compared to that used in multiple reflection ATR, thus allowing the sample to be easily rotated. Also, thanks to the excellent contact that can be obtained with single reflection ATR, highly repeatable spectra can be acquired.
As shown in Fig. 1, the polarized ATR method allows molecular orientation information to be obtained for any of the X, Y, and Z axial directions of a sample having biaxial symmetry (film-like sample). In this figure, the Y-axis shows the draw direction, the X-axis shows the in-plane transverse direction, and the Z-axis shows the thickness direction perpendicular to the sample surface. The measurement must be conducted four times—that is, the sample needs to be irradiated with parallel polarized light and perpendicular polarized light with the light travelling in the draw direction of the sample and then with the sample rotated by 90 °. Here, parallel polarized light refers to linearly polarized light having an electrical field parallel to the plane that includes the incident and reflected light, and perpendicular polarized light refers to linearly polarized light having an electrical field on a plane perpendicular to the above-mentioned plane (that is, one parallel to the sample surface). The evanescent wave at the reflection point, as shown in Fig. 2, has a vector in the X-axis direction in the case of perpendicular polarized light. In addition, in the case of parallel polarized light, it has vectors in the Y-axis and Z-axis directions.
Therefore, a spectrum obtained using the above procedure includes information on molecular vibrations in the X-, Y-, and Z-axis directions.

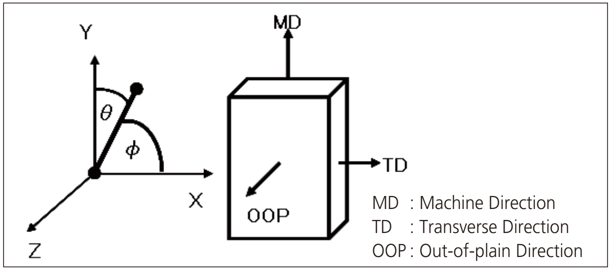

Fig. 1 Expression of Molecular Orientation

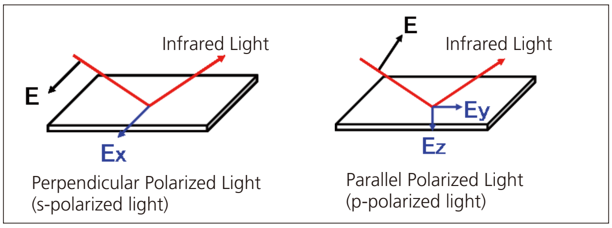

Fig. 2 Evanescent Electric Field in s- and p-Polarized Light

Instrument and Samples

Measurement was conducted with a wire grid polarizer (GPR-8000) and a single reflection ATR accessory (DuraSamplIR Ⅱ, diamond prism) mounted in the FTIR sample compartment. The analytical conditions are shown in Table 1.
The samples used consisted of uniaxially drawn PET film (Elongation: 1, 2, 3).

Fig. 3 Photograph of Single Reflection ATR (DuraSamplIR Ⅱ)

Table 1 Instruments and Analytical Conditions

Instruments	: IRPrestige-21 DuraSamplIR Ⅱ (diamond/KRS-5)
Resolution	: 4 cm^{-1}
Accumulation	: 32
Apodization	: Happ-Genzel
Detector	: DLATGS

Calculations

Here, the absorption coefficients (*kx*, *ky*, *kz*) and orientation parameters (*fx*, *fy*, *fz*) were calculated according to the published literature of P. A. Flournoy[1] and K. Palm[2], assuming the drawing axis as being in the X-axis direction.
The required values used for the calculations were the refractive index of the diamond prism: 2.38, refractive index of the sample (PET film): 1.57, and angle of incidence: 45 °.

Results

Fig. 4 shows the polarized ATR spectra of un-drawn PET film, and Fig. 5 shows the polarized ATR spectra of triple-drawn PET film. In the case of the un-drawn sample, almost no difference in intensity is seen among the four spectra, indicating the absence of orientation. On the other hand, in the case of the triple-drawn film, large differences are seen among the spectra. Table 2 shows the orientation parameter values calculated from the CH_2 wagging vibration peak at 1337 cm^{-1}. The CH_2 wagging vibration is parallel to the molecular axis. The *fx* value indicates how great the orientation is in the axial draw direction along with the increase in elongation.

Here, the 1337 cm^{-1} peak was used, but for an evaluation peak, it is important to select a peak with a large dichroic ratio in which the angle formed by the molecular axis and the transitional vibration moment is 0 ° or 90 °.

Table 2 Calculated Absorption Indices and Orientation Parameters

	Absorption Coefficients			Orientation Parameters		
Draw Rate	*kx*	*ky*	*kz*	*fx*	*fy*	*fz*
1	0.00704	0.00694	0.00500	0.375	0.345	0.280
2	0.01789	0.00623	0.00557	0.678	0.149	0.173
3	0.03707	0.00636	0.00789	0.778	0.064	0.138

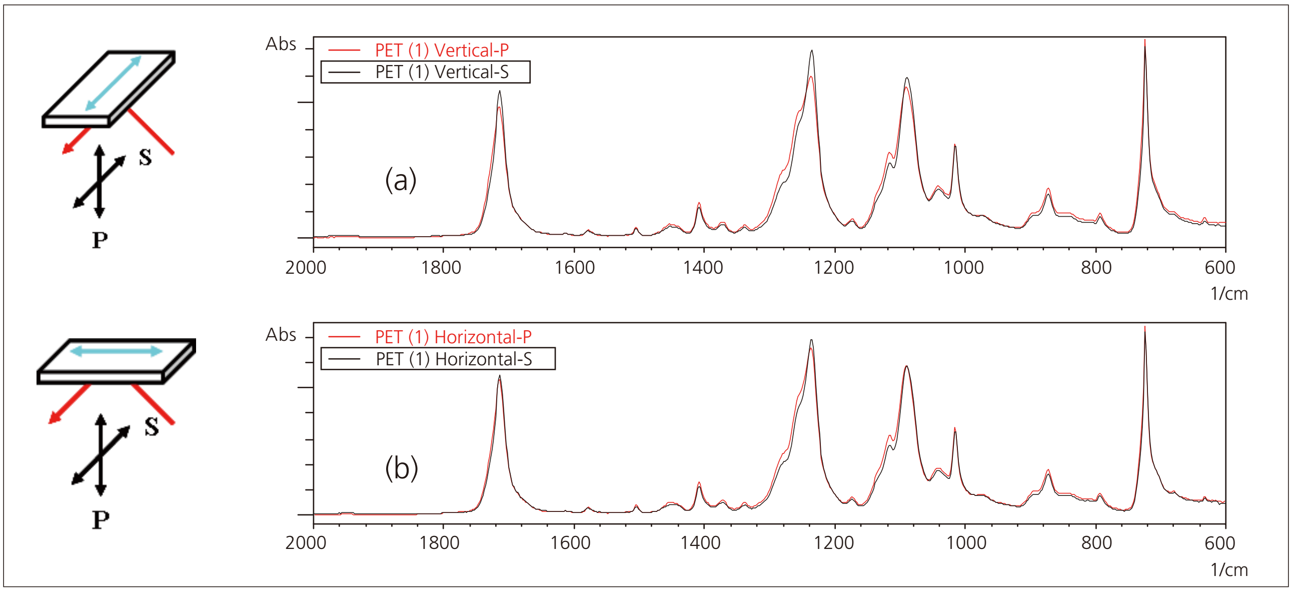

Fig. 4 Polarized ATR Spectra of PET Film with Draw Ratio × 1.0 in Vertical Position (a) and in Horizontal Position (b)

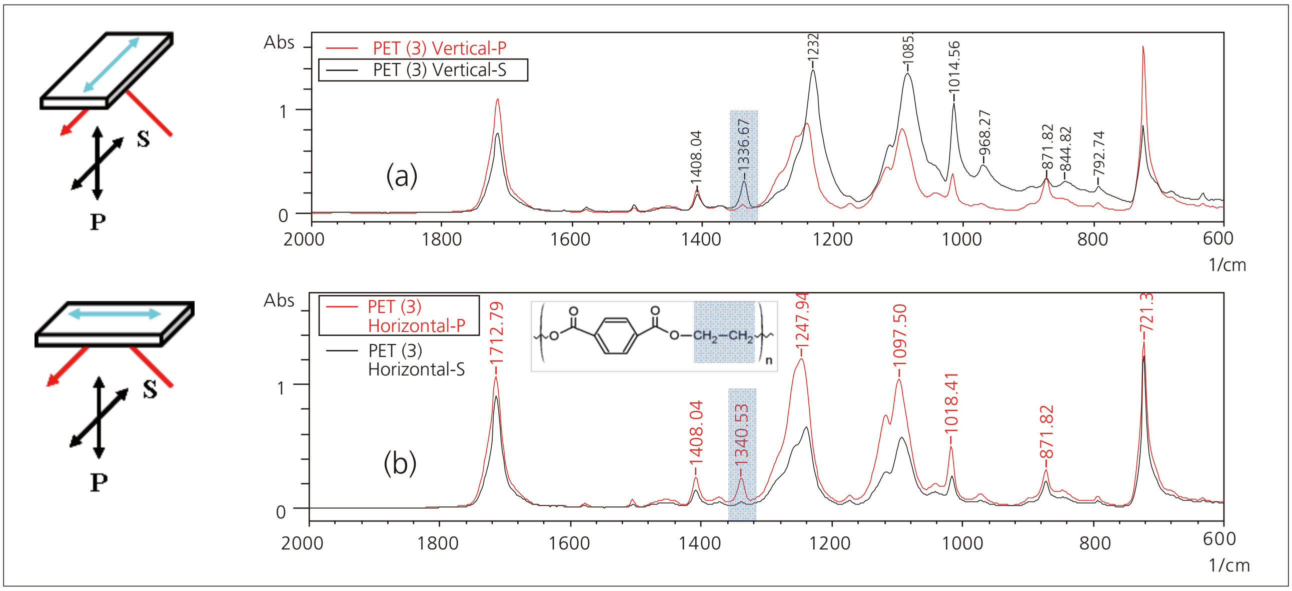

Fig. 5 Polarized ATR Spectra of PET Film with Draw Ratio × 3.0 in Vertical Position (a) and in Horizontal Position (b)

[References]
1) P. A. Flournoy, W. J. Schaffers, Spectrochim. Acta, 22, 5-13 (1966)
2) K.Palm, Vibrational Spectroscopy, 6, 185-191, (1994)

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