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New Analysis Method for Three-Dimensional Orientation of PEN Using Polarized FTIR-ATR Spectroscopy: Multiple Peak Reference Method

Ki Ho Park, Yongri Liang, Seung Hyun Kim, and Han Sup Lee*

Department of Textile Engineering, Inha University, 253 Yong-Hyun-Dong, Incheon, 402-751, Korea

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ABSTRACT: The FTIR-ATR technique has been used to obtain structural information for thick polymer samples to which the conventional FTIR method using transmitted infrared radiation could not easily be applied. This technique coupled with polarized radiation has also been used to obtain three-dimensional orientation information for many segments comprising the polymer chain simultaneously. To obtain quantitative orientation values with the FTIR-ATR method, all of the infrared intensity should be normalized with the absorbance of a known reference band, whose absorbance is not affected by any change in structural factors such as the orientation, conformation, and crystallinity. However, this method cannot be applied to polymer samples whose FTIR-ATR spectrum does not include such a reference band. In this work, a new analysis method, called the multiple peak reference (MPR) method, is proposed, which provides a means of obtaining a new reference peak by linearly combining two existing infrared bands. The appropriateness of this new method was tested by comparing the results obtained from the MPR method with the corresponding results from the well-known method (single peak reference (SPR) method) in the case of uniaxially stretched PET and PTT films. A three-dimensional analysis was successfully carried out for a uniaxially stretched PEN film whose three-dimensional orientation information could not be obtained using the polarized FTIR-ATR method, due to the lack of any known single reference peak.

Introduction

Infrared spectroscopy is a very useful method of analyzing the orientation of various polymeric materials in thin films, since it can provide orientation information on the multiple segments constituting the long polymer chains simultaneously. The transmission infrared method using normal incidence can provide orientation information only in the two directions in the film plane. However, the FTIR-ATR method can provide orientation information not only along the machine and transverse directions (MD, TD) in the film plane but also along the normal direction (ND) of the film because the electric field of the incident infrared radiation exists in all three directions (MD, TD, ND) when total internal reflection occurs at the interface between the ATR crystal and sample.[1,2]

To obtain the three-dimensional orientation information with the FTIR-ATR method, however, four different infrared spectra have to be obtained using four different experimental setups, as shown schematically in Figure 1. The two different polarization directions (TE, TM waves) shown in Figure 1 can be obtained by rotating the infrared polarizer. For the TE wave mode, the electric field direction of the incident radiation is perpendicular to the plane of incidence, which is itself perpendicular to the film plane (MD, TD plane). Therefore, the electric field component of the TM wave lies in the plane of incidence. In Figure 1, there are also two different sample positions (MD, TD). For the MD sample positions (first and second setups in Figure 1), the MD direction (uniaxially stretched direction) of the sample is set to be parallel with the *x* direction of the laboratory coordinate. For the TD sample positions (third and fourth setups in Figure 1), the TD direction in the sample is parallel with the *x* direction of the laboratory coordinate.

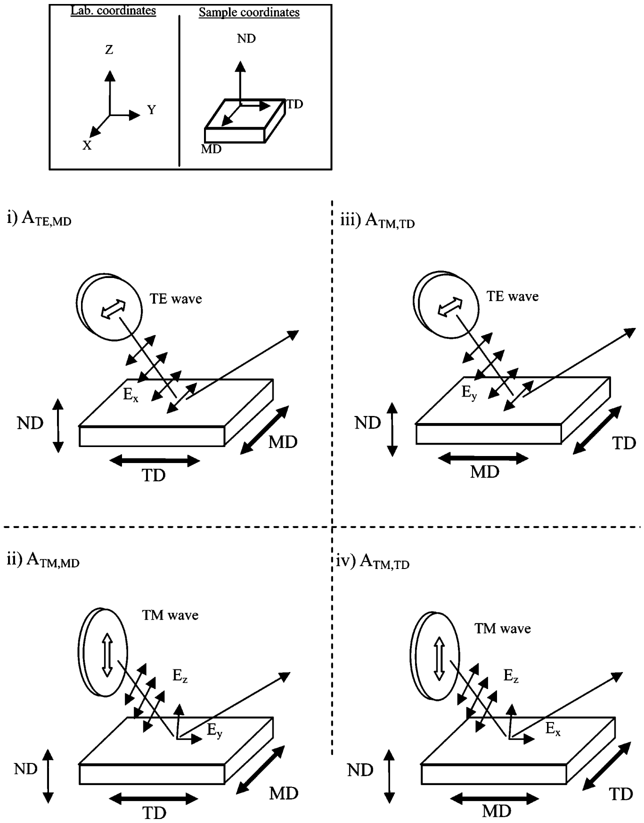

Figure 1. Coordinate systems of the ATR measurements used for 3D-orientation analysis. The polarizer direction determines either the transverse electric (TE) or transverse magnetic (TM) component of the incident IR radiation. The sample was stretched along the machine direction (MD) for uniaxial deformation.

Once four absorbances have been obtained for a certain infrared peak, the three spatial attenuation indices (k_x, k_y, k_z),

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* To whom all correspondence should be addressed. E-mail: hslee@inha.ac.kr.

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which correspond to the absolute absorbances along the MD, TD, and ND directions, respectively, can be calculated using eq 1.[3,4]

$$\begin{aligned} A_{\mathrm{TE},x} &= \alpha k_x \\ A_{\mathrm{TM},x} &= \beta k_y + \gamma k_z \\ A_{\mathrm{TE},y} &= \alpha k_y \\ A_{\mathrm{TM},y} &= \beta k_x + \gamma k_z \end{aligned} \tag{1}$$

Here, α, β, γ are constants which are determined by the refractive indices of the ATR crystal (n_{crystal}) and polymer sample ($\bar{n}_{\mathrm{polymer}}$) and the angle of incidence (θ), as shown in eq 2.

$$\begin{aligned} \alpha &= \frac{4n^2\cos\theta}{(\sin^2\theta - n^2)^{1/2}(1-n^2)} \\ \beta &= \frac{4n^2\cos\theta(\sin^2\theta - n^2)}{(\sin^2\theta - n^2)^{1/2}(\sin^2\theta - n^2 + n^4\cos^2\theta)} \\ \gamma &= \frac{4n^2\cos\theta\sin^2\theta}{(\sin^2\theta - n^2)^{1/2}(\sin^2\theta - n^2 + n^4\cos^2\theta)} \\ n &= \frac{\bar{n}_{\mathrm{polymer}}}{n_{\mathrm{crystal}}} \end{aligned} \tag{2}$$

Using the three attenuation indices obtained with eq 1, the structure factor (K_0) and three orientation parameters (f_x, f_y, f_z) along the MD, TD, and ND directions can also be obtained (eq 3).

$$\begin{aligned} K_0 &= k_x + k_y + k_z \\ f_x = k_x/K_0, &\quad f_y = k_y/K_0, \quad f_z = k_z/K_0 \end{aligned} \tag{3}$$

For a certain vibration mode, whose transition dipole moment direction is perfectly parallel with the direction of the main chain, the orientation parameter along the uniaxial stretching direction of that band approaches unity as the orientation of the polymer chains becomes perfect, while the orientation parameters along the y and z directions approach zero. For a randomly distributed sample, all three orientation parameters get the value one-third.

Even though the polarized FTIR-ATR method appears to be convenient to obtain the three-dimensional orientations of most infrared bands, it has not been extensively used for that purpose due to several experimental difficulties. When a conventional (one-dimensional) ATR crystal is used, the contact between the sample and the crystal has to be changed during the measurement of the four infrared spectra with the setups shown in Figure 1, as follows. After the measurement of the MD spectra using the first and second setups shown in Figure 1, the contact between the sample and ATR crystal has to be broken. The sample is then rotated by 90° and remounted again to obtain the TD spectra using the third and fourth setups shown in Figure 1. This makes it very difficult to ensure that the optical contact during the measurement of the MD and TD spectra is identical. As a result, since the infrared absorbance of the ATR spectrum is extremely sensitive to the quality of the optical contact, quantitative analysis using eq 1 cannot be carried out.

One method of alleviating the optical contact problem is to use a two-dimensional ATR crystal (a rotatable, double-edged crystal), four of whose sides are cut to allow the beam to travel along two orthogonal paths. With such a two-dimensional ATR crystal, the optical contact between the sample and the crystal can be maintained during the measurement of all four infrared spectra.[5−7] In subsequent studies, however, it was demonstrated that the use of this rotatable double-edged crystal cannot resolve the optical contact problem completely because the two beam paths showed different optical contacts.[8] Furthermore, this difference in the optical contact was even more significant if there was a preferred direction, as in the case of a uniaxially stretched sample.[9]

It is possible to overcome the optical contact problem completely if there exists an infrared band which is not affected by such structural characteristics as the orientation, conformation, and crystallinity. Since the absorbance of such a band is determined only by the quality of the contact, the variation in the optical contact can be successfully removed by normalizing all of the infrared bands in the ATR spectra with respect to this reference band.[8−14] This method is referred to as the “single peak reference (SPR) method” and has been successfully used to obtain three-dimensional orientation information for selected samples, including uniaxially stretched PET[10−14] and PTT.[15−17] However, it is impossible to apply the SPR method to a sample which does not have such a reference infrared band.

In this study, we propose a new method which allows three-dimensional orientation information to be obtained for samples to which the SPR method cannot be applied, due to the absence of any reference band. We refer to this new method as the “multiple peak reference (MPR) method” because the new reference peak is synthesized by linearly combining multiple peaks.

Experimental Section

Sample. The PTT sample used in this work was synthesized with 1,3-propanediol and terephthalic acid. The intrinsic viscosity (I_v) of the PTT measured in dichloroacetic acid at 30 °C was 0.84 dL/g. PEN (I_v = 0.46 dL/g, T_m = 280 °C) and PET (I_v = 0.8 dL/g, T_m = 270 °C) were supplied by Hyosung and SKC Co. (Korea), respectively. The three polymer samples were heated to the temperature 20 deg above the corresponding melting temperature for melt pressing and maintained at that temperature for 2 min. The samples were then quenched in ice water to form the melt-quenched amorphous films. The amorphous films were then uniaxially stretched at 150 °C (PEN, T_g = 120 °C), 90 °C (PET, T_g = 75 °C), or 55 °C (PTT, T_g = 45 °C) with a drawing speed of 10%/s inside a temperature-controlled uniaxial stretcher. The sample width during uniaxial stretching was allowed to contract. It should be noted that, whereas two samples (PET, PTT) were stretched at a temperature 10−15 deg higher that their T_g, the PEN sample was stretched at a temperature which was 30 deg above its T_g. At this temperature, the PEN sample was able to be successfully stretched, without any occurrence of the necking phenomenon.

Measurement of the Three Principal Refractive Indices. The three principal refractive indices of the drawn films were measured with a polarized refractometer (Atago, Abbe refractometer 4T) using a sodium lamp (λ = 589 nm). Methylene iodide (n = 1.74) was used as the contact liquid to provide a continuous path for the light by excluding the presence of air between the prisms and the sample.

ATR Measurement. For the ATR measurement, a double-edged parallelogram-shaped ATR crystal (GaAs 25 × 25 × 3 mm, 45° cut, Crystaltec Ltd.) was used, along with a rotatable sample holder initially designed by Sung and co-workers.[6] Using a variable angle ATR attachment (Nicolet Corp.), the angle of incidence (θ) of the infrared radiation at the interface between the ATR crystal and the polymer film was set to 45°. When mounting the polymer film to the ATR crystal, a torque wrench was used to maintain a constant pressure (40 oz/in.^{2}) between them. All ATR spectra were obtained at a resolution of 4.0 cm^{-1} using a Bruker IFS 66V/S FTIR

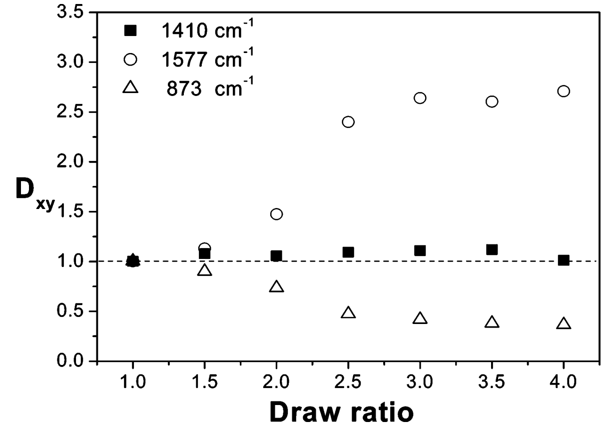

Figure 2. Change in the dichroic ratio as a function of the draw ratio for uniaxially stretched PET films.

spectrometer equipped with a liquid nitrogen cooled mercury−cadmium−telluride (MCT) detector, and 32 scans were averaged. The polarization of the infrared radiation was achieved by inserting a wire-grid polarizer (KRS-5, Specac. Corp.) between the ATR setup and the detector. All absorbance was the peak height from the local baseline.

Results and Discussion

Multiple Peak Reference (MPR) Method. As mentioned in the Introduction, the only practical method of solving the optical contact problem is to normalize all of the ATR spectra with the absorbance of a known reference peak. In Figure 2, the dichroic ratios (D_{xy}) of three selective infrared bands of PET are plotted as a function of the uniaxial draw ratio (DR). Since it is calculated from the infrared spectra obtained using the transmission method, the dichroic ratio is related to the orientation in the film plane (*xy* plane). As the DR increases, the dichroic ratios of the 1577 and 873 cm^{-1} bands vary continuously, whereas that of the 1410 cm^{-1} band remains almost constant over the entire DR range studied. From this result, it can be concluded that the absorbance of the 1410 cm^{-1} band is not affected by the orientation of the polymer chains in uniaxially drawn films.

The three refractive indices (n_x, n_y, n_z) along the three orthogonal directions of the PET, PTT, and PEN samples were also measured during the uniaxial deformation process, and the results are shown in Figure 3. As expected, the three refractive indices show identical values for the unstretched samples (DR = 1). As the DR increases, the refractive index along the stretching direction (*x* direction) increases continuously, whereas the remaining two indices (n_y, n_z) show a steady decrease. It is also to be noted that the values of the latter two indices (n_y, n_z) remain almost identical over the entire DR range.

These results indicate that these samples maintain cylindrical symmetry around the stretching direction during the uniaxial deformation process. On the basis of the results shown in Figures 2 and 3, we can conclude that the absorbances of the 1410 cm^{-1} band along all three orthogonal directions remain almost constant during the uniaxial deformation process. Therefore, the band at 1410 cm^{-1} can act as a reference band for the intensity normalization process used to obtain the three-dimensional orientation information for uniaxially drawn PET using eq 1. The existence of a similar band which can be used for the normalization process for uniaxially deformed PTT has also been confirmed.[15−17] However, no such infrared bands have been suggested thus far for many other polymers, including PEN and poly(trimethylene naphthalate) (PTN).

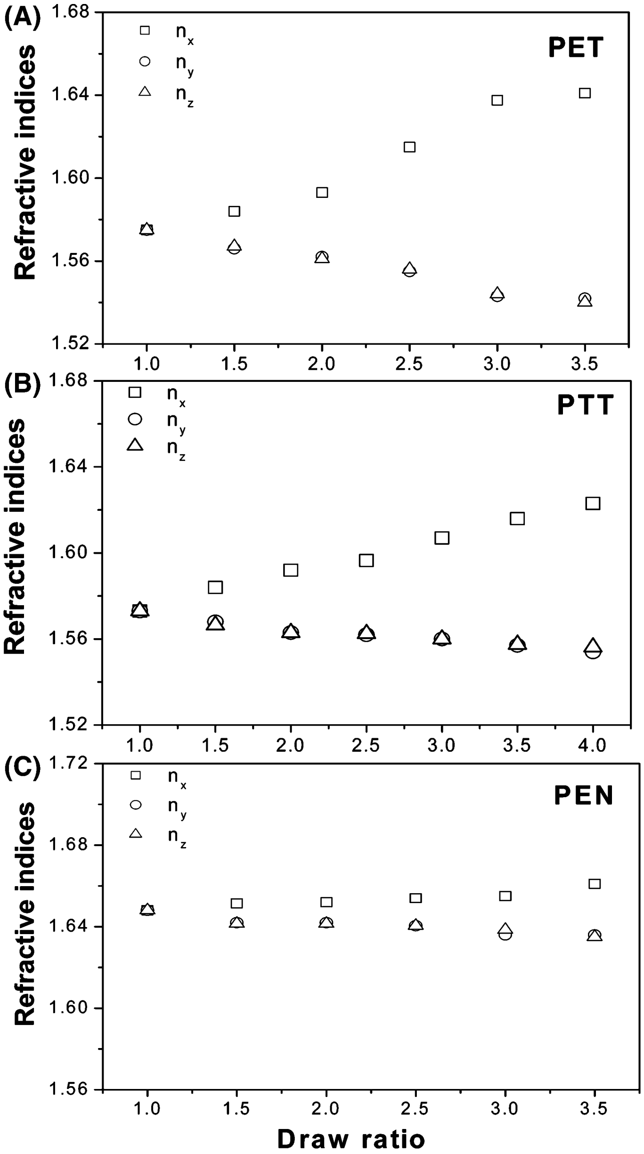

Figure 3. Three refractive indices (n_x, n_y, n_z) along the MD, TD, and ND directions of uniaxially stretched PET (A), PTT (B), and PEN (C) films.

To be used for the purpose of intensity normalization, it is obvious that the dichroic ratio of a reference band should retain its initial value of one during the entire deformation process. Therefore, it might be possible to generate a new reference band by combining the existing multiple infrared bands. If two infrared bands are to be used to make a single new reference band, the new band generated by linearly combining two existing infrared bands using a “combination constant” “*c*” should satisfy the relationship described in eq 4.

$$D_{xy} = \frac{A_1(\|) + cA_2(\|)}{A_1(\perp) + cA_2(\perp)} = 1 \tag{4}$$

Here, $A_1(\|)$ and $A_1(\perp)$ are two absorbances of one of the infrared bands obtained with the polarization direction of the incident infrared radiation parallel and perpendicular to the deformation direction, respectively, $A_2(\|)$ and $A_2(\perp)$ are the corresponding values of the other infrared band, and “*c*” is a constant. It is clear from eq 4 that if $A_1(\|)$ is larger than $A_1(\perp)$, then $A_2(\|)$ should be smaller than $A_2(\perp)$. Thus, if one (A_1) is the “parallel” band, then the other band (A_2) should be the “perpendicular” band.

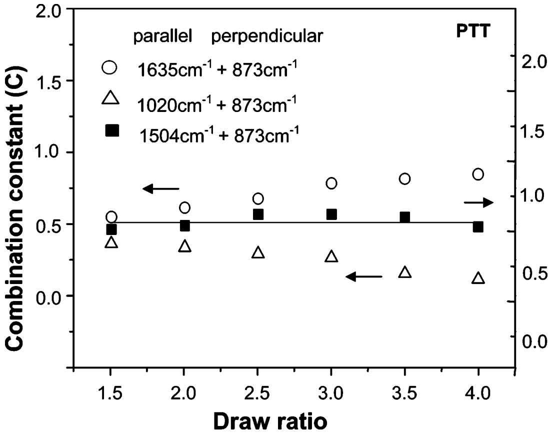

Figure 4. Constant *c* in eq 1 of three combined peaks obtained from one perpendicular peak (873 cm^{-1}) and three parallel peaks (■, 1504 cm^{-1}; ○, 1635 cm^{-1}; □, 1020 cm^{-1}).

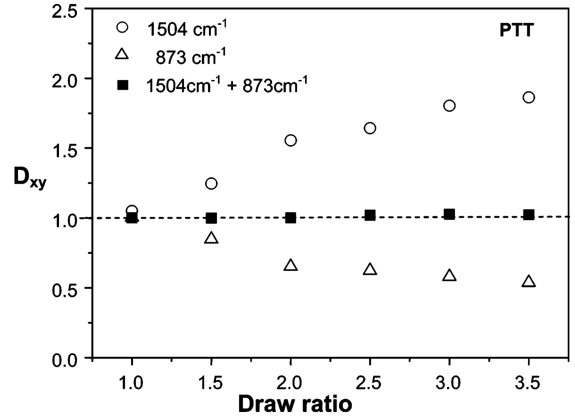

Figure 5. Change in the dichroic ratio of the 1504 cm^{-1} (parallel peak), 873 cm^{-1} (perpendicular peak), and combined peak from 1504 and 873 cm^{-1} (MPR method) peaks as a function of the draw ratio for uniaxially stretched PTT films.

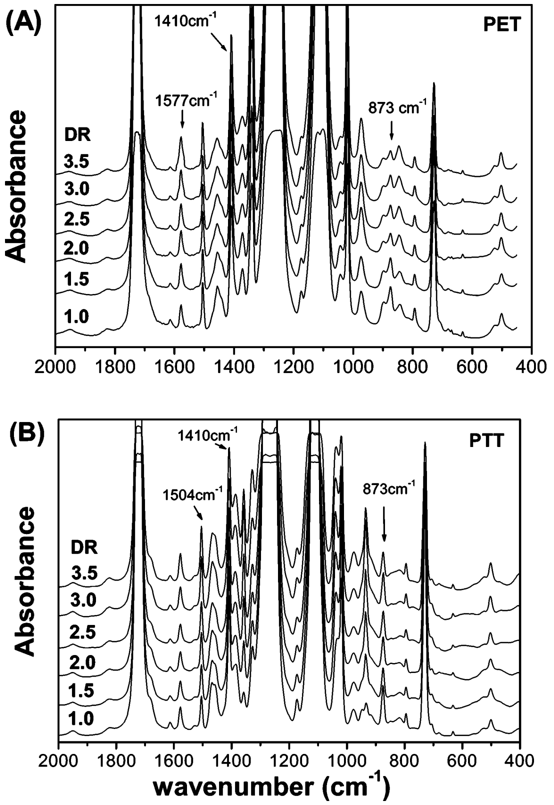

Figure 6. Polarized FTIR-ATR spectra of uniaxially stretched PET (A) and PTT (B) films along the drawing direction. (The polarization direction is parallel to the draw direction.)

To experimentally obtain the new reference band by combining the two existing infrared bands, eq 4 is rearranged into the following relationship for the sake of convenience.

$$\frac{A_1(\|) - A_1(\perp)}{A_2(\|) - A_2(\perp)} = -c \qquad (5)$$

The combination constant, *c*, in eq 5 is determined by the ratio of the difference in absorbance between the parallel and perpendicular spectra of one band (A_1) to the corresponding value of the other band (A_2). The value of the constant, *c*, obtained from four experimentally determined absorbance values should remain the same over the entire deformation range studied. In this study, the constant, *c*, was calculated for three different combinations of infrared band pairs for PTT, and the results are shown in Figure 4 as a function of the DR. Of these three combinations, only one combination of infrared bands, viz. 1504 and 873 cm^{-1}, shows an almost identical value of the combination constant over the entire DR range. These results indicate that the new peak generated with the 1504 and 873 cm^{-1} bands using a combination constant of about 0.82 can be used as a reference band for the intensity normalization process. Since these two bands are predominantly related to the vibration of the aromatic ring,[18] their absorbances should not be sensitively affected by any changes in the chain conformation or crystallinity.

The dichroic ratio of the new band generated using the 1504 and 873 cm^{-1} bands was calculated, and the results are plotted in Figure 5 as a function of the DR. The dichroic ratios of the two individual bands are also plotted to demonstrate the difference in behavior of the individual bands and the newly generated reference band. It is clear from the results shown in Figure 5 that the new reference band obtained from the two existing infrared bands does not show any dependence on the orientation during the entire uniaxial process studied, whereas the two individual bands at 1504 and 873 cm^{-1} are dependent on the chain orientation. Since this sample showed cylindrical symmetry during uniaxial deformation (Figure 3), we can conclude that the new reference band obtained with the MPR method can be used for the purpose of normalizing the intensity to remove the variation in the optical contact which occurs during three-dimensional orientation analysis with polarized FTIR-ATR spectroscopy.

Comparison between SPR and MPR Methods (PET and PTT). Figure 6 shows the infrared spectra of PET and PTT, obtained with the electric field direction of the incident radiation set to be parallel with the stretching direction, as a function of DR. As mentioned above, the band at 1410 cm^{-1}, which is related to the vibrations of the aromatic ring, does not show any dichroic behavior during the uniaxial stretching process and has previously been used as a reference band (SPR method) for the three-dimensional orientation analysis of uniaxially stretched PET[10−14] and PTT[15−17] samples.

To test the applicability of the new method of analysis proposed in this study, the three orientation parameters were recalculated using a new reference band generated from two existing bands (MPR method). For PET, the two bands at 1577 and 873 cm^{-1} were used to generate the new reference band. As can be seen from the spectra shown in Figure 6A, the absorbance of the band at 1577 cm^{-1} (“parallel” band) increases, while that of the band at 873 cm^{-1} (“perpendicular” band)

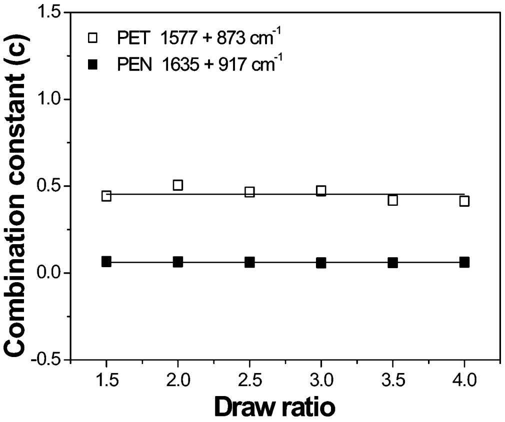

Figure 7. Combination constant as a function of the draw ratio for the uniaxially stretched PET and PEN films.

decreases with increasing DR. The "parallel" and "perpendicular" characteristics of the 1504 and 873 cm^{-1} bands of PTT can also be confirmed from the spectra shown in Figure 6B. The combination constant, *c*, obtained with the two bands of PET is shown in Figure 7, and it is noted that its value remains almost constant during the entire uniaxial deformation process. The results shown in Figure 7 indicate that the new combination band generated with the two bands at 1577 and 873 cm^{-1} might be able to be used for the purpose of intensity normalization.

The orientation parameters along all three directions during the uniaxial process were calculated for a few selected infrared bands of PET and PTT using two independent methods, i.e., the SPR and MRP methods, and the results are shown in Figures 8 and 9.

In Figure 8, the orientation parameters of the 1337 and 1358 cm^{-1} bands that are associated with the wagging vibration of the CH_2 groups in the crystalline phases of PET (Figure 8A) and PTT (Figure 8B) are shown with filled (SPR) and open (MPR) marks.[18,19] Both of these are "parallel" bands whose transition dipole moment vectors are close to the direction of the main chain. Before stretching (DR = 1), all of the orientation parameters showed an almost identical value of one-third, which indicates the isotropic distribution of the corresponding dipole moments.

As the draw ratio increases, the orientation parameter along the *x* direction (f_x) increases, whereas the other two orientation parameters (f_y, f_z) decrease. Furthermore, the orientation parameter values obtained with the MPR method are almost identical to the values obtained from the SPR method. This result clearly indicates that the MRP method can be used as an alternate method of conducting three-dimensional orientation analyses in conjunction with polarized FTIR-ATR spectroscopy, provided that there is no preconfirmed reference peak. It is interesting to note that the overall behavior of the orientation parameter values in Figure 8 is comparable with that observed in Figure 3. The detailed structural analyses of these polymers have already been published.[15,16]

In Figure 9, the orientation parameter values of the 873 cm^{-1} band are plotted as a function of the DR for PET (A) and PTT (B). Since this infrared band is associated with the out-of-plane (oop) bending vibration of the C−H bonds in the aromatic ring, its transition dipole moment is "perpendicular" to the direction of the main chain.[18] The orientation parameter values of this band are also close to one-third for the undrawn samples, which is another clear indication of their macroscopically isotropic state. As the DR increases, the orientation parameter along the *x* direction (f_x) slowly decreases, whereas the other two parameters (f_y, f_z) increase. Considering the "perpendicular" direction of the transition dipole moment vector of this band, the variations in Figure 9 can be easily understood in terms of the uniaxial orientation of the main chains. Once again, the results obtained with the SPR and MPR methods show no noticeable difference.

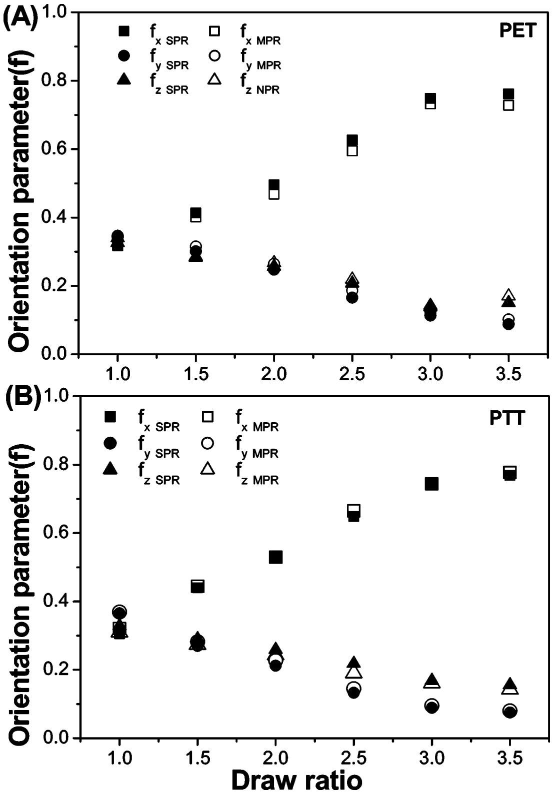

Figure 8. Orientation parameters along the three orthogonal directions for the 1337 cm^{-1} band (CH_2 wagging of trans conformer) of uniaxially stretched PET (A) and the 1358 cm^{-1} band (CH_2 wagging in crystalline phase) of uniaxially stretched PTT (B) films calculated using the conventional SPR method (1410 cm^{-1}, filled symbols) and the new MPR method (open symbols) developed in this work.

Three-Dimensional Orientation Analysis of PEN. Since no single reference peak has so far been found for PEN, it has not been possible to conduct a three-dimensional orientation analysis using polarized FTIR-ATR for this polymer. In this study, it was demonstrated for the PET and PTT samples that the MPR method can be successfully used to conduct a three-dimensional analysis. Therefore, the MPR method might also be able to be used for the three-dimensional analysis of substances such as PEN that do not show any single reference infrared band. For a combination of two bands to be used as a newly generated reference band for the purpose of intensity normalization, they should have a combination constant that does not change during the uniaxial deformation process (refer to eq 4). The "parallel" band at 1635 cm^{-1} and "perpendicular" band at 917 cm^{-1} were used to generate a new peak, and the corresponding combination constant is shown in Figure 7. Since its value of about 0.062 appears to remain almost constant during the entire uniaxial deformation process, the orientation parameters along all three directions were calculated using the new reference band obtained with the MPR method.

In Figure 10A,B, the orientation parameters of the 1600 and 917 cm^{-1} peaks, which are mainly associated with the C=C aromatic ring and aromatic C−H oop bending vibrations, respectively,[18,20] are plotted as a function of the DR. For the "parallel" band at 1600 cm^{-1}, the orientation parameter along

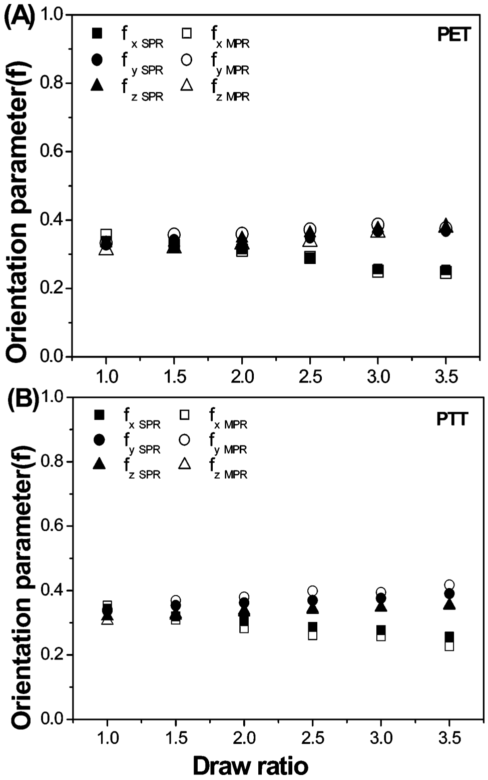

Figure 9. Orientation parameters along the three orthogonal directions for the 873 cm^{-1} band (aromatic ring C−H oop) of uniaxially stretched PET (A) and PTT (B) films calculated using the conventional SPR method (1410 cm^{-1}, filled symbols) and the new MPR method (open symbols) developed in this work.

the *x* direction (f_x) increases slowly with increasing DR, whereas the two remaining orientation parameters (f_y, f_z) decrease. In the case of the "perpendicular" band at 917 cm^{-1}, the behavior of the orientation parameters is totally reversed. Compared with the results shown in Figure 8, the maximum orientation parameter values in Figure 10 are appreciably smaller. The low degree of orientation of the PEN sample used in this experiment can also be confirmed from the refractive indices values shown in Figure 3. The refractive index value at the highest DR was only slightly higher than that before drawing. This is presumably due to the high drawing temperature (30 °C higher than the T_g of PEN) that was used to preclude the possibility of the necking phenomenon occurring, which would otherwise have prevented us from obtaining a uniform orientation.

The stretched PEN chain appears to have sufficient mobility at this drawing temperature to ensure orientation relaxation during stretching as well as during the cooling period. Since the major purpose of this work is to demonstrate the applicability of the MPR method to the three-dimensional analysis of PEN films for which such an analysis could not normally be conducted due to the lack of a single reference peak, the detailed structural changes occurring during the uniaxial deformation process of the PEN film will be treated in a separate paper that will be submitted shortly.

Conclusions

The FTIR-ATR technique is a very useful infrared spectroscopic method which can be used for the characterization of thick samples such as fibers, fabrics, coatings, and thick films to which conventional the FTIR method using transmitted infrared radiation cannot easily be applied. It is also possible to obtain three-dimensional orientation information with this technique using polarized radiation. However, the dependence of the ATR absorbance on the quality of the optical contact has hindered the application of this technique to a wider range of polymer samples. One method which has been used to overcome the optical contact problem is to normalize all of the infrared absorbances with respect to that of a known reference band whose infrared intensity is not affected by any structural factors, such as the orientation, conformation, and crystallization. In the case of PET and PTT polymers, for example, this method has been successfully employed to obtain three-dimensional orientation information. However, it cannot be applied to polymers such as PEN that do not have a suitable reference infrared band.

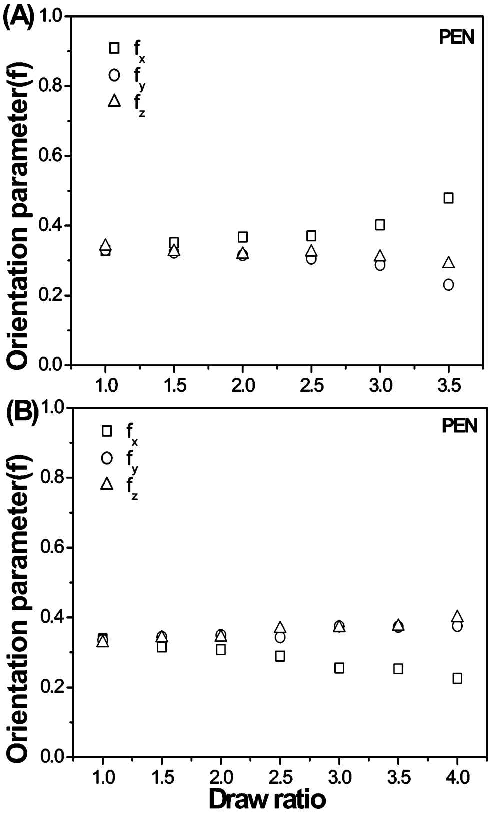

Figure 10. Orientation parameters along the three orthogonal directions for the (A) 1600 cm^{-1} band (C═C aromatic ring vib) and (B) 917 cm^{-1} band (oop bending of C−H in aromatic ring) of uniaxially stretched PEN calculated using the new MPR method developed in this work.

In this work, we propose a new MPR method of carrying out the three-dimensional analysis of any polymer sample to which the conventional SPR analysis technique cannot be applied due to the lack of a known reference peak. Both methods (SPR, MPR) were used to obtain the orientation parameters of PET and PTT, with no significant difference being observed between the two results. We used the MPR method to investigate PEN film, which has not previously been studied by three-dimensional orientation analysis using the polarized FTIR-ATR method, and were able to demonstrate that the orientation parameters along all three directions could be successfully obtained.

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