Core Electron Absorption Spectra of Poly(ethylene terephthalate) and Poly(ethylene 2,6-naphthalate) Films

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ABSTRACT: Absorption spectra by means of the transmission method and total electron yield method were obtained for poly(ethylene terephthalate) (PET) and poly(ethylene 2,6-naphthalate) (PEN) films in the soft X-ray region by use of synchrotron radiation. The absorptions at 285.6 and 289.3 eV were due to C1s $\rightarrow\pi^*$ transitions, showing stronger intensities for obliquely incident light than for normal. Broad absorptions consisting of humps at 293.5, 296.9, and 304.5 eV were originated in C1s $\rightarrow\sigma^*$ transitions, having stronger intensities for an incident beam normal to the film plane than for obliquely incident light. The strong absorption of core electrons of oxygen appeared near 540.5 eV and was attributed to an O1s $\rightarrow\sigma^*$ transition; a neighboring peak at 532.3 eV was sensitive to the incident angle and was assigned as O1s $\rightarrow\pi^*$ transition. Oscillator strength and other optical features are briefly discussed.

KEY WORDS Polarized Absorption Spectra / Synchrotron Radiation / Poly(ethylene terephthalate) / Poly(ethylene naphthalate) / Biaxially Oriented Films / Total Electron Yield / Transmission / Carbon K Edge / Oxygen K Edge / Oscillator Strength /

Absorption and emission spectra of the valence electrons of poly(ethylene terephthalate) (PET) have been studied for the clarification of photochemical and photophysical features.^{1–10} The polarized absorption and reflection spectra of uniaxially drawn PET films were analyzed in detail in the ultraviolet region down to 190 nm (or up to about 6.5 eV); the transition energies observed therein were compared with theoretical values from molecular orbital calculations.^{8–10} The emission spectra were measured and their origins were discussed.^{4–8,10} Furthermore, X-ray photoelectron spectrum of the valence band of PET in the binding energy up to about 30 eV was obtained by use of synchrotron radiation, together with simulation calculations^{11,12}; conformational effects were revealed in the spectra.¹²

The spectroscopy related to the core electrons, whose energy corresponds to far ultraviolet or soft X-ray, has been studied for PET by means of X-ray photoelectron spectroscopy (XPS); whereby, assignments were given for three kinds of carbon (carbonyl, aromatic, and aliphatic) and two kinds of oxygen (carbonyl and ester).^{12–15} Recently, electron energy loss spectroscopy (EELS) was applied to PET¹⁶; spectral features of this polymer were discussed with the aid of core excitation spectra of small molecule analogues and extended Hückel molecular orbital calculations of dimethylterephthalate.

Absorption spectra of core electrons of polymers were first obtained by Seki *et al.*¹⁷ for very thin oriented syndiotactic 1,2-polybutadiene films. By use of a synchrotron radiation, they observed anisotropic absorp-

tion spectra with an incident beam normal or near parallel to the film plane and identified 284.9 eV peak as a $\text{Cl}1s \rightarrow \pi^*$ transition. Since then, studies of core electron absorption spectra of polymers gradually increased in number: polyethylene,^{18,19} polytetrafluoroethylene,¹⁸ poly(vinylidene fluoride),¹⁸ polyimide,²⁰ poly(dimethyl phenylene oxide),²⁰ poly(vinyl methyl ketone),²⁰ etc. have been made for various purposes. According to the literature,¹⁶ X-ray near edge absorption spectra of PET is under investigation, in addition to EELS spectra. However, so far, no work has been reported on the polarized absorption spectra of core electrons of PET or poly(ethylene 2,6-naphthalate) (PEN) to our knowledge. PEN has a similar chemical structure as PET except that it has a naphthalene ring instead of a benzene in the main chain. Comparison of these polymers often provided helpful information for the elucidation of their structures and properties.²¹

In this study, measurements were made for obtaining the absorption spectra of core electrons of thin films of PET and PEN by the transmission mode and also by the total electron yield method, at the UVSOR facility of the Institute for Molecular Science. The transmission method offers direct absorption data if the film is sufficiently thin, but it is not necessarily easy to hold a thin film sample so as to make an incident beam nearly parallel to the film plane. On the other hand, in the total electron yield method, the film plane can be held in any direction since the rear side of the specimen can be supported by a conductive plate. However, total electron yield is proportional, but not necessarily equal, to the product of the absorption coefficient and the electron escape depth. Therefore, it is rather difficult to obtain the absolute value of absorbance. Electron escape depth is not constant but slightly depends on the material and wavelength; nevertheless, overall spectra have been shown to be almost identical to the absorption spectra by the transmission method in many

samples.²² Furthermore, details in fine structures are better obtainable by electron yield spectra than by transmission.^{23–25} With these complementary two methods, it was intended in this work to see general features of core electron absorptions and to give assignments of peaks in thin films of PET and PEN.

EXPERIMENTAL

Samples

Film grade polymers of PET and PEN were used for sample preparation. Similar procedures as utilized previously for measuring ultraviolet absorption spectra of PET⁸ were employed: 1.5 and 2.5% hexafluoroisopropanol solution of PET and PEN were made and a clean slide glass plate was dipped into each solution. After the glass plate was dried in nitrogen atmosphere, films were peeled off from the plate in a water bath. Each piece of film was carefully fixed between a pair of supporting frames made of amorphous PET films about 100 μm thick and then dried. For obtaining uniaxially drawn film, the undrawn film was stretched together with thick PET frame by use of an Instron tensile tester at 90°C for PET and 110°C for PEN, at a speed of 50 mm min⁻¹. Biaxially stretched films of about 0.7 μm thickness were fabricated by sequential drawing method at the Research Plant of Film Research Laboratories, Teijin Limited.

Thickness of the films was measured by the interference of transmitted light.⁸

Light Source and Monochromator

Measurements were carried out at BL-2B1 of UVSOR facility of the Institute for Molecular Science; the storage ring of UVSOR has a circumference of 53.2 m, the energy at normal operation is 750 MeV and the beam current after injection is 200 mA. This current decreases gradually and resumes the original magnitude by reinjection after 4 h. The light is horizontally polarized. The BL-2B1 is equipped with a Grasshopper grazing inci-

dence monochromator of a Roland circle diameter of 2 m, whose wavelength range is 1.3–20 nm (60–1000 eV).²⁶

Measurements were made with a grating of 1200 lines mm⁻¹ except for earlier measurements of 600 lines mm⁻¹. Output signal was counted at each position at a certain interval (normally 0.05 eV).

Transmission Measurements

A film sample was held between a pair of copper frames and fixed on a copper mount which had several openings; one of the openings was for a reference and the rests were attached with 3 or 4 samples. The film plane of the beam was made either normal to the incident beam or at 25° incidence. The sample chamber was evacuated overnight; measurements were made under a vacuum of 2–4 × 10⁻⁷ Pa.

Transmitted light through the sample hit an Au target; emitted photoelectrons were measured by use of a Keithley programmable electrometer. In order to compensate the fluctuation of beam intensity and contaminations piled on the monochromator mirrors and slits, transmitted light intensities were normalized by simultaneous detection of the photoelectrons from an Au mesh placed in front of the sample chamber. The grating and mirrors were likely to be contaminated by carbonaceous materials; therefore, one had to be careful in examining the absorption near the carbon edge.

The absorbance of the sample was obtained from the ratio of the normalized blank intensity and normalized transmitted intensity. However, these two measurements could not be done simultaneously; therefore, some error was unavoidable, although that caused from beam fluctuation was eliminated by normalization by use of an Au mesh.

The photon energy of the incident beam was calibrated by the dips of the Au mesh spectra at 284.7 and 291.0 eV originating from carbon contamination, as described by Stöhr *et al.*²⁷

Total Electron Yield Measurement

Each film sample was pasted on a molybdenum disk by use of a piece of two-sided carbon adhesive tape so that the entire surface of the tape would be covered by the sample film. This disk was mounted on a holder which was rotatable around an axis normal to the disk, or film plane. The holder itself was rotated about a vertical axis and fixed at a certain angle with incident beam; thereby, the film plane was placed to the beam either normal or with a certain angle.

The total electrons ejected into a vacuum were measured by use of a Keithley programmable electrometer; the yield was normalized by the Au mesh yield simultaneously obtained as in the case of the transmission mode. No bias voltage was applied to the sample.

RESULTS AND DISCUSSION

Wide Scan Spectra

Absorption spectra of biaxially drawn PET and PEN, taken by transmission mode, are shown in the wavelength range from 260 eV to 660 eV in Figure 1, where the thicknesses were 0.74 μm for PET and 0.78 μm for PEN. Typical shape of absorption spectra at C and O absorption edges was clearly revealed. From similarities in chemical structure and thickness of these polymer films, it is natural that their spectra resemble each other in gross features.

Absorption Spectra near Carbon K-Edge

The absorption spectra of biaxially drawn PET film near carbon K-edge, by the transmission mode, are shown in Figure 2. A remarkable peak is seen at 285.6 eV. This peak "A" exists also in the spectra of PEN as shown in Table I. This corresponds to the absorption maximum at 285.5 eV in the spectra of C₆₀,²⁸ the strong absorption of benzene adsorbed on Pt(111) peaking at 286 eV with a broad tail,²⁹ the peak at 285.5 eV of polycrystalline and microcrystalline graphite,³⁰ amorphous

Figure 1. Wide scan absorption spectra of PET and PEN biaxially oriented films between 260 and 660 eV. Thicknesses of the films were 0.74 μm for PET and 0.78 μm for PEN, respectively. Measurements were made by the transmission mode using a monochromator with a grating of 600 lines mm^{-1} .

Figure 2. Absorption spectra near carbon K-edge of a biaxially oriented PET film of 0.74 μm thickness. Measurement was made by the transmission mode.

carbons,³¹ and carbon films made by CVD.³² All these peaks have been assigned to the $\text{C}1\text{s} \rightarrow \pi^*$ transitions in the aromatic rings; therefore, the absorption peak "A" at 285.6 eV of PET and PEN can be similarly assigned. Peak "A" corresponds to that at 284.7 eV in the EELS spectrum of PET.¹⁶

$\text{C}1\text{s} \rightarrow \pi^*$ transition occurs when the electric vector of the incident beam is perpendicular to the ring plane, as clearly demonstrated in extremely thin films of a series of aromatic hydrocarbons, including benzene and naphthalene, formed on Ag(111) and Cu(100).³³ The

aromatic ring planes of PET and PEN tend to become parallel to the film plane when the films are stretched, particularly when biaxially drawn, as revealed by X-ray diffraction.^{34,35} Peak "A" at 285.6 eV should thus be more intense when the film plane makes a smaller angle with incident beam, as long as the skin portion of the film has similar molecular orientation as the interior. This is actually observed in the total electron yield spectra in Figure 3; the intensity of peak "A" grows as the incident angle becomes larger, where the incident angle is defined as the angle between the incident beam and normal of the irradiated surface. On the other hand, the orientation of the molecules of PET and PEN is not perfectly aligned and distributes to some degree; therefore the $\text{C}1\text{s} \rightarrow \pi^*$ transition has finite intensity even when the beam is incident normal to the film.

In the total electron yield method, the front layer corresponding to the electron escape depth, which is estimated to be of in the order of 10 nm,²² is responsive to absorption spectra. From the incidence angle dependence of peak "A" described above, the surface region of the film within an order of 10 nm depth has similar molecular orientation as the bulk of the film.

There is another distinct peak "B" at

Table I. Assignments and polarization

Sample	Peak "A"	Shoulder	Peak "B"	Shoulder	Peak "C"	Peak "D"	Peak "E"
PET undrawn	285.7 eV	287.8 eV	289.2 eV		293.5 eV	297.2 eV	305 eV
PET $\times 3.5$ (oblique)	285.4		289.3		293.5	296.6	303.5
PET biax. drawn	285.6		289.1		293.5		304.7
PEN undrawn	285.8		289.3	291.4	293.6		ca. 303.7
PEN $\times 3.5$ Y	285.5		289.5		294.3		
PEN $\times 3.5$ (oblique)	285.7		289.4		ca. 293.5		ca. 305
PEN biax. drawn	285.5	287.7	290.5		293.3		
Average	285.6	287.8	289.3	291.4	293.5	296.9	304.5
Polarization ^a	(z)		(z)		(x, y)	(x, y)	(x, y)
Assignment	1s $\rightarrow$ π^*		1s $\rightarrow$ π^* + 1s $\rightarrow$ σ^*		1s $\rightarrow$ σ^*	1s $\rightarrow$ σ^*	1s $\rightarrow$ σ^*
	C=C	O-C	C=C C=O C-H		C-C	C-C	C-C

^a z is normal of film plane; x and y are parallel to the plane.

Figure 3. Total electron yield spectra of a biaxially drawn PET film 0.74 μm thick at normal and at 45° incidence. Intensities of these spectra are adjusted at 360 eV.

289.3 eV in Figure 2. This may be related to the C1s $\rightarrow$ π^* transition in the aromatic ring, corresponding to the second absorption peak of benzene around 288.5 eV.³⁷ However, this peak of benzene is not so intense as the lower energy transition at 285.6 eV, and it is not resolved as a single peak when benzene is adsorbed on Mo or Pt.³⁷ As seen in Figure 3, the intensity growth of peak "B" at 289.3 eV for oblique incidence is less remarkable than for peak "A" at 285.6 eV. Therefore, there must be some additional contribution to peak "B".

Poly(methyl methacrylate) (PMMA) shows an intense peak at 288 eV originating in the C1s $\rightarrow$ π^* transition associated with the C=O orbital. Furthermore, C1s $\rightarrow$ σ^* transitions in the CH bond are reported for polyethylene at 287.4 eV, polarized perpendicular to the chain.^{18,19} and for benzene in the 286–290 eV range, polarized in the ring plane.³⁷ The peak at 287.9 eV in the EELS spectrum would correspond to the peak "B" because the difference of energy with the lowest energy peak is 3.2 eV for EELS and 3.7 eV for the present case. The peak at 287.9 eV is more sensitive to radiation damage and related to $\pi^*(\text{C}=\text{O})$ resonance.¹⁶

Therefore, the absorption peak "B" at 289.3 eV of PET and PEN is attributed to contribution from $\pi^*(\text{C}=\text{O})$, $\pi^*(\text{C}=\text{C})$, and $\sigma^*(\text{C}-\text{H})$ transitions. C–H absorption is expected to occur for light whose electric vector is parallel to the film plane, while C1s $\rightarrow$ π^* transitions associated with C=O and C=C would become intense for the electric vector perpendicular to the plane. Therefore, the peak "B" at 289.3 eV has mixed polarization.

There were 3 broad peaks ("C", "D", "E") above 290 eV in the total electron yield spectra of PET in Figure 3. These peaks are assigned

as $\text{C}1\text{s} \rightarrow \sigma^*$ transitions, as in other carbonaceous materials; graphite has humps at 291.7, 295, 302.4, and 306 eV,³⁰ diamond has such at 291.7, 296.6, and 303.8 eV,³¹ C_{60} is shown to have a broad peak with humps at 291.7, 294.5, 297.5, and 299.5 eV,²⁸ and amorphous carbon has a very broad, structureless band ranging from 290 to 300 eV, composed of many different bonding configurations superposed on each other.^{31,32}

These broad peaks of the PET film, "C" at 293.5, "D" at 296.9, and "E" at 304.5 eV, decrease their intensity relative to $\text{C}1\text{s} \rightarrow \pi^*$ transitions with increasing incidence angle as shown in Figure 3. This is consistent with the interpretation that $\text{C}1\text{s} \rightarrow \sigma^*$ transitions may occur when the electric vector is parallel to the molecular plane. Spectra of undrawn films, having rather isotropic nature, are actually insensitive to the incident angle of the light.

There seems to exist an extra hump at 299.3 eV in PEN films. Benzene and naphthalene thin films deposited on Ag(111) and Cu(100) are mostly alike,³³ whereas their EELS spectra are different in minute features.^{37,38} Difference of spectra between PET and PEN are yet to be elaborated in future.

Absorption above 290 eV would be due to $\text{C}1\text{s} \rightarrow \sigma^*$ transitions and not involve π^* . According to the Pariser-Parr-Pople molecular orbital calculation,^{8,9} there are 5 unoccupied π orbitals in a repeat unit of PET, of which the difference between the highest and the lowest is 4.61 eV. This would provide an approximate estimate of the energy range of $\text{C}1\text{s} \rightarrow \pi^*$ transitions. Since the lowest $\text{C}1\text{s} \rightarrow \pi^*$ is 285.6 eV, the highest would be 290.2 eV; hence, major absorption above 290 eV would not be related to $\text{C}1\text{s} \rightarrow \pi^*$ transitions. The assignments of peaks are listed in Table I.

From the absorption spectra by the transmission mode, the oscillator strength of each peak should be obtainable. As described above, however, accurate calculation was not possible in our case, partly because incident and transmitted intensities were not measured

simultaneously and peaks were not resolved well, particularly for those related to σ^* . Nevertheless, the overall oscillator strength would be estimated roughly from the absorption curves such as those shown in Figure 1, by use of formula (1) which is valid for isotropic materials. Namely, the molar extinction coefficient ϵ was obtained from absorbance, thickness of the film, molecular weight per repeat unit, and density of the films. The values used for the density here were 1.39 g cm^{-3} for PET and 1.36 g cm^{-3} for PEN.³⁹ Then, the oscillator strength f was calculated from⁴⁰

$$f = \frac{10^3 \times \ln 10 \times mc^2}{\pi e^2 N_A} \int \epsilon(\sigma) d\sigma$$

$$= 4.32 \times 10^{-9} \int \epsilon(\sigma) d\sigma \quad (1)$$

where m is the mass of an electron, c the light velocity, N_A Avogadro's constant, and σ wave number. For simplicity, the integral was taken between 280 eV and 520 eV for carbon. The integrated values of f thus obtained from the curves shown in Figure 1 were 9.1 for PET and 12.2 for PEN, per repeat unit; namely, for both films, the sum of oscillator strengths per carbon atom, between 280 and 520 eV, was 0.9. These films are biaxially drawn and not isotropic three dimensionally. However, error caused in the calculation for the π^* and for the σ^* transitions would be canceled out to some extent from the consideration of their relative directions. Therefore, obtained f would be valid within the crudeness of the estimation.

According to literature,³⁰ the maximum optical density of microcrystalline graphite film of 250 nm thickness was approximately 1.2 (converted from the value of 2.8 read from the original figure, taking account of their use of the natural log in the definition of optical density). Assuming the density of the graphite to be 2.25 g cm^{-3} , the corresponding sum of the oscillator strength of the graphite was calculated as 0.8 per carbon atom. Obtained values for PET and PEN described above were

Figure 4. Total electron yield spectra of a uniaxially drawn PEN film of 3 times at normal, 30°, 45°, and 60°. The ordinate is adjusted at 360 eV.

almost the same as this value of graphite. Considering the degree of precision of the estimation, these values would be reasonable although somewhat smaller than the value expected from the sum rule.

Figure 4 shows the total electron yield spectra of uniaxially drawn PEN films of 3 times at normal, 30°, 45°, and 60° incidence, where the intensity was normalized at 360 eV; the multiplication factors therein were 1, 0.86, 0.75, and 0.67 respectively. These values are nearly equal to the cosine of the incident angles except for the last one: 1, 0.87, 0.71, and 0.5. Since the electrons ejected into vacuum should be generated within an electron escape depth, and the path of the light before reaching this depth is proportional to the inverse of the cosine of the incident angle, the above factors are reasonable, considering various factors that cause error at larger incident angle. A more detailed account of the angle dependence is given in Stöhr's book.²² After taking account of this geometrical angle effect, the tendency that the π^* -related peak at 285.6 eV grows and σ^* -related peaks above 290 eV decrease with incident angle conforms to the orientation of the aromatic rings in these films.

Absorption Spectra near Oxygen K-Edge

Oxygen K-edge spectra of biaxially drawn

Figure 5. Absorption spectra, by the transmission mode, near the oxygen K-edge of a biaxially oriented PET films of 0.74 μm thickness.

Figure 6. Absorption spectra, by the total electron yield method, near the oxygen K-edge of a uniaxially drawn PEN film of 3 times. The ordinate is adjusted at 580 eV.

PET by the transmission mode are shown in Figure 5 and those of PEN by the total electron yield mode in Figure 6. There are peaks "OA" around 532.3 eV and "OB" around 540.5 eV and a broad shoulder "OC" around 551 eV. These peaks change in relative height with the orientation of the films; peak "OA" is small for the normal incidence and large for the oblique incidence. Therefore, peak "OA" is attributed to $\text{O}1s \rightarrow \pi^*$ transition. Contrary to this, peak "OB" decreases in height for oblique incidence and is assigned to an $\text{O}1s \rightarrow \sigma^*$ transition.

In EELS spectrum,¹⁶ peak "OA" appears

around 532 eV and "OB" around 541 eV, although they are noisier than carbon K-edge spectrum.

In the O1s XPS spectra of PET, peaks due to carbonyl ($\text{O}=\text{C}-$) and ether group ($-\text{O}-\text{C}-$) carbons appear at about 533 eV and *ca.* 2 eV higher binding energy, respectively, with a shake-up structure at still higher energy side.^{11,13} However, considering the small separation of these peaks and width of the presently observed peak "OA", and comparing the shapes of our carbon K edge spectra with that of XPS, our $\text{O1s} \rightarrow \pi^*$ peak "OA" at 532.3 eV would correspond to the doublet at 533–535 eV in XPS, and peak "OB" at 540.5 eV would be σ^* shape resonance.

The oscillator strengths of these peaks were estimated as in the case of carbon K-edge spectra. Integrated *f* of biaxially oriented PET and PEN films was 0.8 per O atom, which is comparable to 0.9 for the C atom described above.

CONCLUSION

Absorption spectra of oriented PET and PEN films were obtained by the transmission method and total electron yield method. The peaks at 285.6 and 289.3 eV were attributed to $\text{C1s} \rightarrow \pi^*$ transitions and those at 293.5, 296.9, and 304.5 eV were assigned to $\text{C1s} \rightarrow \sigma^*$. Absorption at 532.3 eV was due to $\text{O1s} \rightarrow \pi^*$ transition and at 540.5 eV, to the $\text{O1s} \rightarrow \sigma^*$ transition.

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