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Surface analysis of partially crystalline and amorphous poly(ethylene terephthalate) samples by X-ray absorption spectroscopy (NEXAFS)

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Biaxially stretched poly(ethylene terephthalate) (PET) foils and spin-coated PET films were analysed by surface-sensitive X-ray absorption spectroscopy (NEXAFS). The surfaces of partially crystalline foils and amorphous films can be easily distinguished when the angle of incidence of the linearly polarized synchrotron light beam is varied relative to the surface normal of the respective sample. In contrast to the amorphous state, we found a strong angle dependence in the NEXAFS spectra of the surface of crystalline samples. Copyright © 1996 Elsevier Science Ltd.

(Keywords: poly(ethylene terephthalate); crystallinity; X-ray absorption spectroscopy)

Introduction

Recently, Boulanger *et al.*[1] reported attenuated total reflectance infra-red (i.r.-ATR) spectra, and core level and valence band X-ray photoelectron spectra obtained on amorphous powders and crystalline, 'bi-oriented' films of poly(ethylene terephthalate) (PET). The differences observed were interpreted as being of conformational origin. With i.r.-ATR, which essentially provides data representative of the bulk of the samples, the authors found well-distinguished conformation-related bands. With the surface-sensitive X-ray photoelectron spectroscopy (XPS) approach they found only small effects 'at the allowed sensitivity limit of the XPS technique' when an amorphous PET sample was compared with a crystalline one. The question of whether PET exists in different conformational states in amorphous and crystalline samples is of technological importance. For instance, in an adhesion-related study of the aluminium/PET interface, De Puydt *et al.*[2] emphasized the importance of the substrate crystallinity for the build-up of the metal–polymer interface.

In this communication we present near-edge X-ray absorption fine structure (NEXAFS) spectra which may reveal more insight into the situation at PET surfaces. NEXAFS spectroscopy is an analytical method providing molecular-specific information (the excitation of electrons into unoccupied molecular orbitals via dipole transition from core levels are probed) together with data on the orientation of macromolecules or parts of it[3]. It could be a useful approach for combining conformation with surface analysis.

Experimental

Biaxially stretched, 0.5 μm, Mylar PET foils (Du Pont) were used as test samples. The polymer is characterized by an average molecular weight of 250 000 g mol^{-1} (determined by size exclusion chromatography), a crystallinity of 60–65% (density measurement) and stretching ratios $\alpha_{\parallel}$ and $\alpha_{\perp}$ of 3.5. Thin PET films were spin-coated on silicon wafers employing a 0.5 wt% solution of PET in hexafluoroisopropanol at 2000 rev min^{-1}. The resulting film thickness was around 100 nm. No contributions of the substrate were detected in the XPS spectra. The samples were analysed by XPS to verify a sufficient purity for surface studies. In case of the spin-coated films we found fluorine impurities (<1 at%) which are residues of the solvent. In all cases, narrow XPS C 1 s and O 1 s scans resulted in spectra very similar to the reference spectra published elsewhere[4].

Partial electron yield X-ray absorption experiments were carried out on the HE-TGM 2 beam line at BESSY, with a resolution better than 0.8 eV at the C 1 s edge. The monochromator transmission function used for spectra normalization was obtained with a freshly sputtered Au sample. The energy scale was calibrated by setting the C–H* resonance peak of an octadecyltrichlorosilane (OTS) reference film to 287.5 eV (ref. 5). Characteristic features in the flux monitor signals were used to align the energy scales of all spectra relative to this value. Reproducibility of the spectra was carefully checked by multiple scanning. No indication of beam damage effects was found. To obtain difference spectra, all spectra were scaled to the same value before and far behind the absorption edge jump[3].

The information depth (95%) of the NEXAFS method in the electron yield mode can be estimated to be ≤ 30 Å for the C signal and ≤ 50 Å for the O signal[6],

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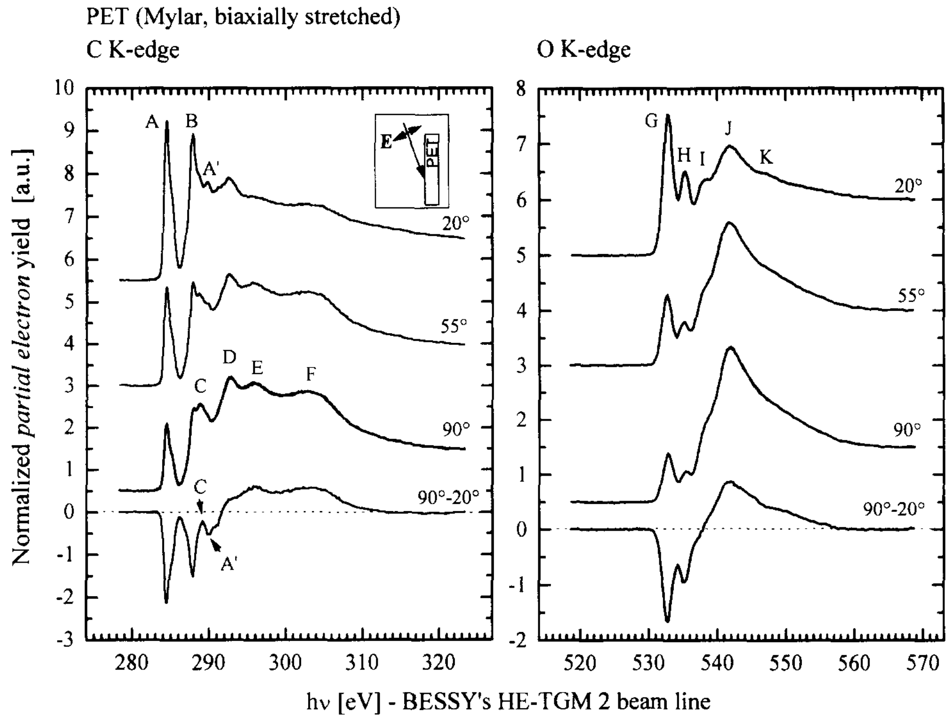

Energy reference OTS C-H* resonance with 287.5 eV

Figure 1 Angle-resolved partial electron yield C and O *K*-edge X-ray absorption spectra of a biaxially stretched PET foil (thickness: 0.5 μm) for different beam light incidence angles relative to the surface plane. The insert gives the geometry of the experiment for the 20° case. The most probable interpretations of the spectral features marked by capitals are given in the text. Additionally, a difference spectrum of normalized and energetically aligned 90° and 20° spectra is given. 90° spectra were measured at the beginning and at the end of an experiment to check for reproducibility. In the figure both 90° spectra were plotted together

assuming that these signals originate from C and O *KLL* Auger transitions including subsequent inelastic scattering events[3]. The kinetic energies of O *KLL* and C *KLL* Auger electrons are ≈510 and ≈270 eV, respectively. Low-energy electron contributions to the signals were discriminated by a retarding potential. This mode of measurement is called partial electron yield (PEY). In such mode only electrons with energies higher than a pre-set threshold energy (150 eV) may enter the channeltron detector.

To look for crystallinity effects, the polar angle of incidence of the linearly polarized synchrotron light was varied between 90° (i.e. the electric field vector **E** lies in the surface plane) and 20° (**E** nearly parallel to the surface normal). The 20° geometry is illustrated in the insert in *Figure 1*.

Fluorescence yield (FY) NEXAFS experiments were carried out on BESSY's HE-PGM 2 beam line at a resolution of ≈1.5 eV at the O *K*-edge. The spectra were divided by the monochromator transmission, scaled and aligned as in the former case. The oxygen and carbon fluorescence signals were detected with the help of a Ge detector (Explorer, Noran Instruments). The minimum information depth of FY mode NEXAFS can be estimated with the help of the maximum *K* shell X-ray absorption cross-section tables of low *Z* elements referred to in ref. 3. With 9.8 b and 5.1 b for C and O, respectively, primary photon free paths in the low μm range are evaluated for PET. The energies of the fluorescence photons (277 eV for C, 525 eV for O) detected in the experiment are below the respective *K* shell thresholds. Without doubt, bulk relevant information was obtained in the FY NEXAFS experiments with PET.

Results and discussion

Figure 1 presents a set of C *K*-edge and O *K*-edge NEXAFS spectra obtained in the surface-sensitive, angle-resolved PEY mode with the biaxially stretched, partially crystalline PET foil. Additionally, difference spectra '90° − 20°' are given. In a first approach, some of the spectral features marked with capitals will be interpreted in terms of the building block model for large molecules proposed by Stöhr[3]. Furthermore, the results of the relevant spectra simulations by Hitchcock *et al.*[7] are considered. Considering the C *K*-edge spectra we found dominating sharp C 1s $\rightarrow \pi^*_{\mathrm{ring}}$ (A) and $\rightarrow \pi^*_{\mathrm{C=O}}$ (B) resonances at 284.4 and 287.8 eV, respectively. The interpretation of feature B is supported by its angle dependence. Some smaller features, (C) at ≈289.1 eV and (A′) at ≈289.7 eV, can tentatively be attributed to a C 1s → C–H* resonance (C) and (relying on benzene results[3]) to a second, small $\rightarrow \pi^*_{\mathrm{ring}}$ resonance (A′). The assignment of the latter is supported by its angle dependence, which is identical to that of C 1s $\rightarrow \pi^*_{\mathrm{ring}}$. Finally, a shoulder on the high-energy side of A was obtained. This splitting of the π^*_{ring} resonance is due to symmetry reduction and chemical shifts associated with the ester ligands on the aromatic ring[3]. Features D, E and F are covering broad σ^* resonance contributions attributed to ring, $-CH_2-CH_2-$ sequence, C=O and C–O bonds.

The O *K*-edge spectrum is characterized by a relatively sharp O 1s $\rightarrow \pi^*_{\mathrm{C=O}}$ resonance at 532.9 eV (G). For the intense feature H at 535.4 eV, a splitting component of the O 1s $\rightarrow \pi^*_{\mathrm{C=O}}$ resonance is assumed to be the reason. Here we rely on results reported by Hitchcock *et al.*[7], who discussed the splitting to be a result of an interaction of C=O orbitals on the opposite sides of the aromatic ring with ethyl benzoate and dimethyl terephthalate. Consistently this feature shows an angle dependence correlated to the energetically lowest $\pi^*_{C=O}$ resonance (G). The features between 540 and 550 eV (J, K) are believed to be superimposed O 1s $\rightarrow \sigma^*_{C-O}$ and $\rightarrow \sigma^*_{C=O}$ resonance contributions. The most intense feature (J) at $\approx$541.8 eV is attributed to an O 1s $\rightarrow \sigma^*_{C-O}$ resonance whereas a broad O 1s $\rightarrow \sigma^*_{C=O}$ resonance is expected to occur with a maximum at $\approx$545 eV (ref. 7). The assignment given above is supported by the opposite angle dependence of $\rightarrow \sigma^*$ and $\rightarrow \pi^*$ features as verified by the difference spectrum. Finally, feature (I) at 538.2 eV probably represents the ionization potential of the C=O oxygen species. Hitchcock *et al.* assigned a very similar feature in their O 1s oscillator strength spectrum obtained with an ethyl benzoate model in the same way[7]. This interpretation can be supported by our experiment. Consistently feature (I) shows no angle dependence, as verified by the broad zero passage in the difference spectrum just at 538.2 eV.

Considering the angle dependence of the spectra, it should be noted that the NEXAFS method is a localized spectroscopy which probes the amplitude and directionality of unoccupied molecular orbitals on atoms characterized by a core hole[3]. Only the spatial orientation (direction of maximal orbital amplitude) of a selected orbital determines the angle dependence of *K*-edge absorption spectra. In this picture the π system of the PET ring can be represented by a vector which is orthogonal to the ring plane. Because the PET monomer unit is nearly planar[8] the vector representing the π bond of the C=O group is nearly parallel to that of the ring. The vectors representing σ bonds for the C=O and C–O groups can be found in the molecule's plane. Finally, the C–C σ bond vectors belonging to the benzene ring span a plane defined by the position of the respective C nuclei.

Considering the experimental results in *Figure 1* (see difference spectrum), we found the C 1s $\rightarrow \pi^*_{ring}$ (A) resonance and the $\rightarrow \pi^*_{C=O}$ (B) at 20° with maximum intensity. At this angle the orientation of **E** must be parallel to the vectors representing the benzene ring and C=O π bonds in the sample. The conclusion is that the monomer unit plane in the crystalline domains of the PET sample should be preferentially oriented parallel to the PET film surface plane. The NEXAFS signal intensity maxima correlated to the orthogonal σ_{C-O} and $\sigma_{C=O}$ bond vectors (features D, E and F) consistently occur at 90°. Considering the O *K*-edge results we found maxima for the O 1s $\rightarrow \pi^*_{C=O}$ (G) at 20° and for the O 1s $\rightarrow \sigma^*_{C=O}$ and $\rightarrow \sigma^*_{C-O}$ resonances at 90° (features J, K). All these cross-checking results support the conclusion given above. For further application of the NEXAFS method it should be mentioned that, for example the area of the C 1s $\rightarrow \pi^*_{ring}$ resonance feature A in the '90° – 20°' difference spectrum is correlated to the degree of crystallinity of the PET surface layer.

In a second experiment we were interested in the relative in-plane orientation of the molecular segments in the crystalline domains. For that aim we measured spectra after an azimuthal rotation by 90° of the PET sample. So we have two sets of spectra, one with an **E** projection parallel to the first stretch direction and the other with **E** parallel to the second stretch direction of the biaxially stretched PET foil. If there is a strong in-plane orientation, there should be an effect on the O 1s and C 1s $\rightarrow \sigma^*_{C-O}$ and $\rightarrow \sigma^*_{C=O}$ resonance intensities. Instead we found both sets of C and O *K*-edge spectra to

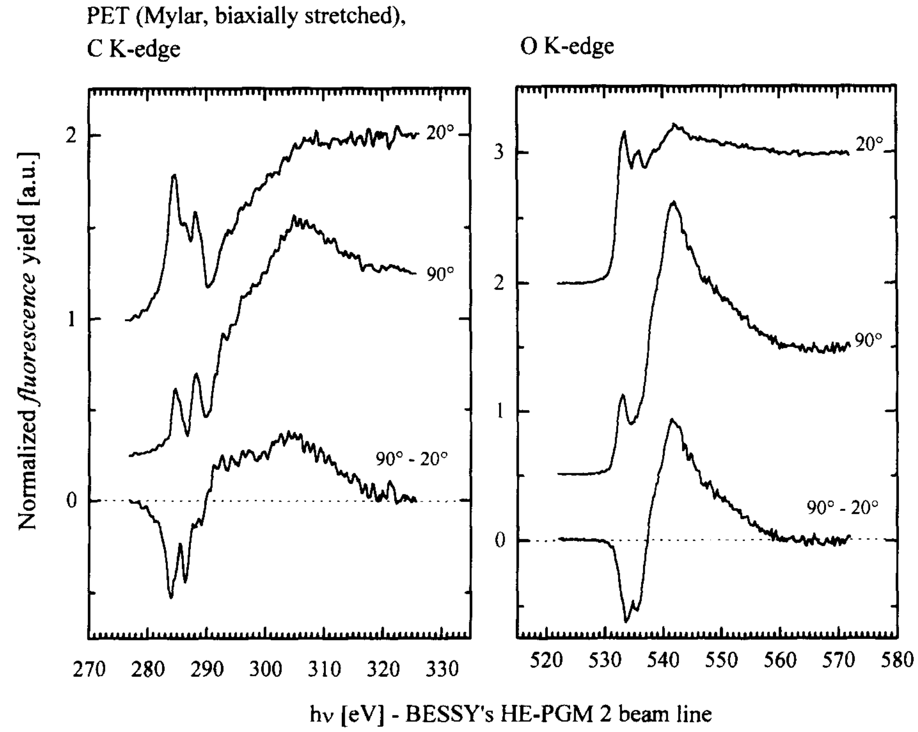

Figure 2 Angle-resolved fluorescence yield C and O *K*-edge X-ray absorption spectra of a biaxially stretched PET foil for different beam light incidence angles relative to the surface plane

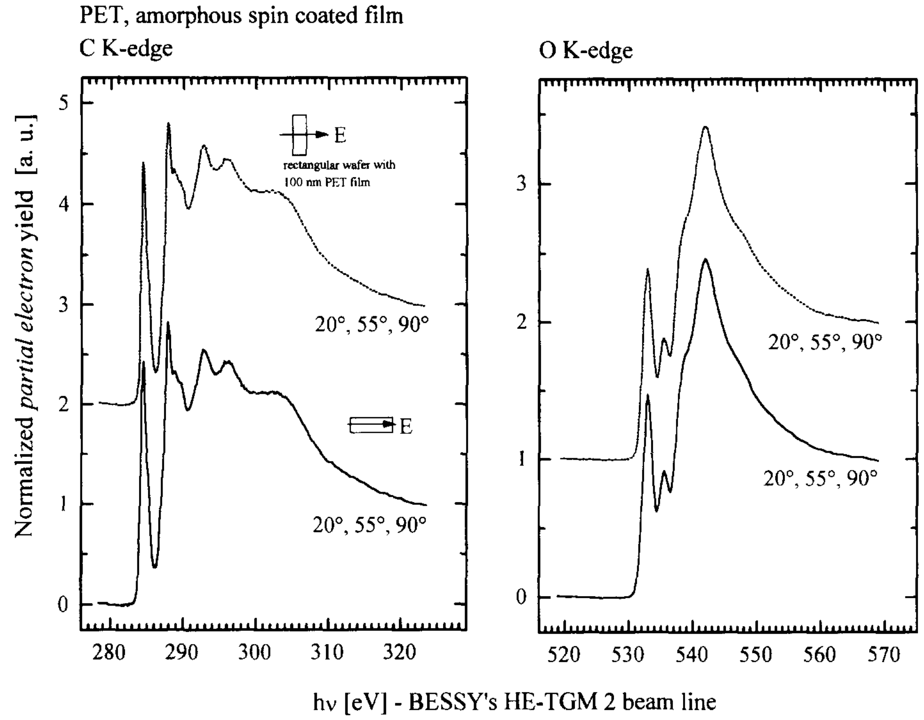

Figure 3 Partial electron yield C and O *K*-edge X-ray absorption spectra of an amorphous spin-coated PET film (thickness: ≈100 nm, substrate: silicon wafer) for different beam light incidence angles relative to the surface plane and orthogonal azimuthal angles of the **E** projection into the surface plane

be almost identical. Recently Castner *et al.*[9] verified an in-plane orientation for $-CF_2-$ chains at a skived poly(tetrafluoroethylene) surface with the help of azimuthal angle-dependent NEXAFS spectroscopy.

In a third experiment we analysed the biaxially stretched PET foils in the fluorescence yield (FY) mode. The respective results are presented in *Figure 2*. We measured bulk characteristic spectra which principally show the same features as obtained in the surface-sensitive PEY mode but at lower resolution. The angle dependence, illustrated by a difference spectrum '90° − 20°', verifies once again crystalline domains. However, in the FY mode the crystallinity effect is less pronounced. The negative elongations of the C $1s \rightarrow \pi^*_{ring}$ (A) and O $1s \rightarrow \pi^*_{C=O}$ (G) resonance related features in the difference spectrum are roughly three times higher in the respective PEY difference spectrum. One interpretation could be that there is an enhanced scatter in the 'alignment' of the crystalline domains at increasing thickness of the investigated layer. Thus a greater scatter of the directions of the vectors representing the PET ring π system or the C=O π bonds has to be expected. Another explanation could be a gradually increasing crystallinity towards the surface of the PET foils. In the discussion of their results Boulanger *et al.*[1] also considered this idea.

Finally we investigated a spin-coated PET film; the results are given in *Figure 3*. Variation of the polar angle (20°, 55° and 90°) yields fully identical PEY spectra for both the C and O *K*-edge regions. The spectra resemble those obtained at 55° in case of the biaxially stretched foil samples. This angle is near the 'magic angle' of 54.7° where the NEXAFS signals are independent of the respective molecular orientations[3]. Furthermore, *Figure 3* presents the results of measurements at two different, orthogonal azimuth angles. Obviously, there is also a good agreement between both sets of spectra. These results suggest a fully statistical distribution of the PET chains at the surface of this amorphous spin-coated film.

The results of this X-ray absorption study with PET samples show the potential of the method to differentiate precisely between partially crystalline and amorphous states at high surface sensitivity. In further experiments we will determine the response of the partially crystalline PET surface to metallization or plasma treatment using NEXAFS spectroscopy. Moreover, direct evidence was obtained for a preferential orientation of PET chain segments at the surface of partially crystalline, biaxially stretched foils, wherein the plane defined by the benzene ring of the PET monomer unit is parallel to the surface.

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Note added in proof

Recently, we re-investigated the spectral features in the C and O *K*-edge spectra of PET by a quantum mechanical approach considering the core holes produced by photoionization. As a result, the assignments of some minor features were changed (Petterson, L. G. M., Ågren, H., Shürmann, B. L., Lippitz, A. and Unger, W. E. S. *Int. J. Quantum Chemistry* submitted) without influence on the conclusions presented in this communication.