Spectromicroscopy of Poly(ethylene terephthalate): Comparison of Spectra and Radiation Damage Rates in X-ray Absorption and Electron Energy Loss


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The C 1s and O 1s X-ray absorption spectra of poly(ethylene terephthalate) (PET) have been recorded using transmission, fluorescence, and electron yield detection. The corresponding electron energy loss spectra (EELS) have been recorded in a scanning transmission electron microscope. These results are compared to the C 1s and O 1s spectra of gas phase 1,4-dimethyl terephthalate (the monomer of PET) recorded using EELS. The comparison of monomer and polymer materials in different phases and with different techniques has aided the understanding of the relative strengths and limitations of each technique as well as assisting the spectral interpretation. Good agreement is found in the overall shape and the energies of the spectral features. Relatively minor differences in intensities can be understood in terms of the properties of the individual spectroscopic techniques. The critical dose for radiation damage by 100 keV electrons incident on PET at 100 K is found to be $(1.45 \pm 0.15) \times 10^3 \text{ eV nm}^{-1}$. In contrast, the critical dose for radiation damage by 302 eV X-rays incident on PET at 300 K is $(1.2 \pm 0.6) \times 10^2 \text{ eV nm}^{-1}$. A figure of merit involving the product of critical energy dose and spectral efficiency (as expressed by the appropriate $G$ value) is developed. This indicates that, for near-edge studies involving a 20 eV spectral width, there is ~500-fold advantage of X-ray absorption studies on room temperature PET relative to electron energy loss studies of cooled PET.

1. Introduction

Near-edge core-excitation spectroscopy is an element specific probe of the local chemical environment of atoms in a material. Its basis is the excitation of inner-shell (core) electrons to unoccupied orbitals or bands. The core-excited state can decay by releasing X-rays (the basis for fluorescence yield (FY) detection) or by emitting Auger and secondary electrons (the basis for electron yield (EY) detection). Characterization of materials through their near-edge core-excitation spectra is useful for identifying specific functionalities in polymers,4,5 determining the orientation of small molecules or polymers,6 investigating biological systems,5 studying the d-states in metal alloys,7 and characterizing oxidation states in metal oxides,8 to name just a few applications. In order to obtain optimum results, it is necessary to understand the strengths and limitations of the various methods that can be used to acquire core spectra. In polymer applications, limitations associated with radiation damage must always be considered. Core excitation in a soft X-ray microscope is particularly promising for polymer microanalysis since it has the ability to obtain high-quality spectra and images, with fewer radiation damage problems than the analogous electron-based technique. In contrast, electron microscopy techniques have the potential for achieving much higher spatial resolution but require a significantly higher radiation dose to acquire equivalent data from the same sample volume.

When core-excitation spectra are measured using X-rays as the excitation source, the technique is called near-edge X-ray absorption fine structure (NEXAFS) spectroscopy.5 (Acronyms used in this paper are listed and defined in Table 1.) If they are measured using inelastic scattering of electrons, the technique is called electron energy loss spectroscopy (EELS). The methods are similar in that they determine aspects of the unoccupied electronic structure as sampled by core excitation, but they differ in the ways that the core-excited state couples to the incident probe and to the chosen detection methodology. These differences give rise to advantages and limitations for each technique.

The true X-ray absorption spectrum of a material is determined by measuring the incident and transmitted flux through a suitably thin sample (typically ~0.1 µm at the C 1s edge and ~0.5 µm at the O 1s edge for PET). NEXAFS can also be measured with electron yield detection (denoted EY-XAS) in which case the spectra are rather surface sensitive (~1–5 nm sampling depth for $h\nu \approx 1000 \text{ eV}$). Fluorescence yield detection (denoted FY-XAS) can also be used. It has a much greater sampling depth (~100 nm at 200–500 eV), and thus it is more sensitive to the bulk properties. Both EY-XAS and FY-XAS are based on recording signals associated with secondary processes. Thus, if the Auger/fluorescence branching ratio
TABLE 1: Acronyms

<table>
<thead>
<tr>
<th>acronym</th>
<th>meaning</th>
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<tr>
<td>ALS</td>
<td>Advanced Light Source (Berkeley, CA)</td>
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<tr>
<td>DMT</td>
<td>dimethyl terephthalate</td>
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<tr>
<td>EELS</td>
<td>electron energy loss spectra</td>
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<tr>
<td>EHMO</td>
<td>extended Hückel molecular orbital</td>
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<tr>
<td>EICVOM</td>
<td>equivalent ionic core virtual orbital model</td>
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<tr>
<td>EY-XAS</td>
<td>electron yield X-ray absorption spectroscopy</td>
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<tr>
<td>fwhm</td>
<td>full width at half-maximum</td>
</tr>
<tr>
<td>FY-XAS</td>
<td>fluorescence yield X-ray absorption spectroscopy</td>
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<tr>
<td>ISEELS</td>
<td>inner-shell electron energy loss spectra</td>
</tr>
<tr>
<td>LCAO</td>
<td>linear combination of atomic orbitals</td>
</tr>
<tr>
<td>NEXAFS</td>
<td>near-edge X-ray absorption fine structure</td>
</tr>
<tr>
<td>NSLS</td>
<td>National Synchrotron Light Source (Brookhaven National Lab, NY)</td>
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<tr>
<td>PET</td>
<td>poly(ethylene terephthalate)</td>
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<tr>
<td>STEM</td>
<td>scanning transmission electron microscope</td>
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<tr>
<td>STXM</td>
<td>scanning transmission X-ray microscope</td>
</tr>
<tr>
<td>STEM-EELS</td>
<td>electron energy loss spectrum recorded in a STEM</td>
</tr>
<tr>
<td>STXM-XAS</td>
<td>X-ray absorption spectrum recorded in a STXM</td>
</tr>
<tr>
<td>VMO</td>
<td>virtual molecular orbital</td>
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changes for different electronic states, this would cause differences between EY or FY and the true absorption spectra. By using highly monochromatic and intense synchrotron radiation sources, NEXAFS spectra can be recorded in moderately short acquisition times (several tens of seconds). The dependence of transition intensities on the polarization of the radiation also allows determination of the orientation of anisotropic systems, such as aligned polymers or molecular species on surfaces. Transmission X-ray spectromicroscopies have been developed recently which allow measurement of NEXAFS spectra on a submicron scale and the generation of chemically sensitive images with spatial resolution approaching 50 nm as well as the determination of the average orientation of specific functional groups with a similar resolution.

The primary process in EELS is inelastic scattering of a monoenergetic electron beam by a gas or solid target. It can be used to study atoms or molecules in the gas phase (inner-shell EELS or ISEELS) with moderate (~0.6 eV fwhm) to high (~0.1 eV fwhm) spectral resolution. EELS can also be recorded in a transmission electron microscope (TEM) with the potential advantage that exceptionally high spatial resolution (~1 nm) can be achieved. Appropriately thin (~0.1 μm) sections of materials can be prepared by various methods and studied with STEM-EELS. Early STEM-EELS studies of polymers were limited by the high electron beam damage associated with the long recording times required by serial detectors. However, recently developed parallel-detection electron energy loss spectrometers allow radiation sensitive polymers to be studied at much lower electron dose, as previously described for PET. Polyurethane model polymers, polycarbonates and poly(methyl methacrylate) (PMMA). The combination of STEM-EELS studies of polymers with studies of small molecule analogues using ISEELS and extended Hückel molecular orbital (EHMO) calculations has greatly aided the interpretation of the near-edge spectra of the polymers. Each of these techniques has advantages and limitations for studying polymers. We have explored these by an in-depth, multitechnique study of poly(ethylene terephthalate) (PET), a ubiquitous polymer often found in packaging applications, and a small molecule analogue, 1,4-dimethyl terephthalate (DMT), which is the repeat unit of PET. The basis for the use of small molecule (in this case monomer) species as standards for polymer spectra has been discussed and demonstrated previously. The combination of these techniques to study PET and DMT has helped further elucidate assignments for the spectral features of the polymer and monomer. Extended Hückel (EHMO) calculations of DMT are also used to aid interpretation of transitions in the C 1s near edge region. Radiation damage is a concern with both STEM-EELS and STXM-XAS of polymers. We have made a quantitative study of radiation damage to PET in both the spatially resolved EELS and transmission XAS experiments.

2. Experimental Section

The PET sample (density of 1.385 g/cm³) was obtained from Scientific Polymer Products. For the FY-XAS and EY-XAS measurements it was dissolved in hexafluoro-2-isopropanol (Kodak) to make a 0.01% solution which was spun-onto onto a single-crystal Si wafer which had previously been coated with 20 nm of Au. For the scanning transmission X-ray microscopy (STXM) experiments the sample was micromotated at room temperature to prepare sections of ~0.1 and ~0.5 μm thickness.

2.1. X-ray Absorption of PET. The EY-XAS and FY-XAS experiments were performed on the U1A beam line of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL). The apparatus has been described previously. The X-ray monochromator slits were such that the resolution at 300 eV was 0.6 eV full width at half-maximum (fwhm). The spectra were measured by both total fluorescence yield (FY) using a gas ionization detector operating in proportional mode and by partial electron yield (EY) using a channeltron detector with a bias on the entrance cone of ~150 eV relative to the sample substrate. The NEXAFS spectra of PET were collected with the sample at room temperature. All NEXAFS spectra were normalized to the incident photon flux by dividing by the Io spectrum measured as the total EY from a clean gold mesh placed before the sample.

At the C 1s edge the EY-XAS technique is best done on reasonably thin films (~100 nm) in order to minimize charging effects. For FY-XAS thicker films can be used since charging does not affect the detected signal. However, films that are thicker than several absorption lengths can give rise to distorted FY-XAS spectra on account of self-absorption of the fluorescence X-rays. The distortions in FY-XAS can be minimized by using grazing takeoff detection. The absorption length is inversely related to the transition intensity (oscillator strength). For intense features, such as the C 1s → π* peak of unsaturated species, the path length for 2 optical density (OD) units is ~80 nm, and thus sections less than 0.1 μm are required to measure spectra without absorption saturation effects. (One OD corresponds to a transmitted intensity of 1/e that of the incident intensity.) At the O 1s edge the absorption length and thus the optimal thickness increase to ~500 nm.

STXM-XAS measurements were made on room temperature samples both at the X-1A beamline at NSLS and at beamline 7.0 at the Advanced Light Source (ALS). In both systems the soft X-rays are focused by a Fresnel zone plate. The present generation of zone plates produces a spot about 50 μm fwhm in size. The flux transmitted through a thin sample is detected with a gas flow counter. For imaging, the transmission is recorded as a function of sample position by mechanically raster scanning the sample in the focal plane under computer control. Alternatively, the photon beam is left on the same sample position while the photon energy is scanned to acquire a spectrum. The natural logarithm of the ratio of the transmitted (Io) to the incident (I0) intensity yields the NEXAFS spectrum in true absorption mode. For this work the Io signal was obtained from a separate normalization scan recorded without a sample (typically through a hole in the thin film). Generally, data are acquired with an energy resolution of about 0.3 eV.
recording the spectrum. In order to achieve optimal energy
Spectra were acquired from 5 to 10 µ°-
scattering angle 2° were recorded using a final electron energy of 2.5 keV,
recording spectra of a mixture of DMT and CO₂. The gas phase
purity introduced from a small metal cell directly attached to the
these conditions electric dipole transitions dominate. Small
π* energy for PET is in agreement with that of 284.86(6) eV for the main
π*π C=C peak in the ISEELS of DMT. The O 1s NEXAFS
spectra were placed on an absolute scale by setting the main O
1s feature to 531.5 eV, the value obtained from the calibrated ISEELS spectrum of DMT.

2.2. Electron Energy Loss of 1,4-DMT. The gas phase
ISEELS spectrometer has been described previously.12 Spectra
were recorded using a final electron energy of 2.5 keV,
scattering angle 2°, and a resolution of 0.6 eV fwhm. Under
these conditions electric dipole transitions dominate. Small
angle rather than zero degree scattering is used in order to
prevent the main electron beam from entering the analyzer and
creating a large background. The solid DMT sample was
introduced from a small metal cell directly attached to the
collision cell. 1,4-DMT was obtained from Aldrich (stated purity >99%). Absolute energy scales were determined by
recording spectra of a mixture of DMT and CO₂. The gas phase
spectra were converted to an absolute oscillator strength scale using standard methods31 based on background subtraction and
normalization of the continuum intensity to atomic oscillator
strengths.32

In order to present the C 1s spectra of the polymer and
molecule from each technique on a common intensity scale, all
of the spectra have been processed by subtracting a linear or
polynomial background extrapolated from the signal below 283
eV and then setting the intensity at 300 eV to 0.0134 eV⁻¹. For
the C 1s spectra the normalization was carried out at 300 eV
rather than at higher energy where the continuum shape is more
atomic-like, because 300 eV is below the onset of the plural
scattering which distorts STEM-EELS spectra at higher energies.
Similarly, the O 1s spectra have been background subtracted and
normalized to the intensity at 545 eV to 0.0081 eV⁻¹.32 As
at the C 1s edge, the normalization is carried out at rather lower
energy than is normally the case,31 in order to allow comparison
to the STEM-EELS data without significant intensity distortion
associated with the plural scattering signal which begins around
550 eV.

2.3. Electron Energy Loss of PET. The STEM-EELS
spectra were recorded using a scanning transmission electron
microscope (STEM, VG Microscopes model HB501) equipped with a field emission source and a parallel detection electron
spectrometer (Gatan Model 666).33,34 The vacuum in the region
of the specimen was <5 × 10⁻⁹ mbar. Specimens were cooled
to 100 K during analysis in order to minimize radiation damage.
The spectrometer collection semiangle (α) was 2 mrad while the probe convergence semiangle (β) was 3 mrad. Suitable areas
for analysis were selected at low electron dose (∼10⁻⁶ e⁻ nm⁻²)
using the annular dark field image. By measuring the fraction
of transmitted electrons that suffered no energy loss,14 the
regions of the PET sample used for TEM-EELS analysis were
estimated to be 1.0—1.5 nm free paths or 100—150 nm thick.
Spectra were acquired from 5 to 10 nm square regions by
rastering the defocused 100 nm probe diameter beam while
recording the spectrum. In order to achieve optimal energy
resolution, it was necessary to descend movement of the spectrum
over the detector by applying a synchronized voltage to the spectrometer drift tube.35 Spectra were normalized by subtracting
the dark current and dividing by the spectrometer gain at
each channel. The instrumental energy scale of STEM-EELS is not accurate due to power supply drifts. For this reason
the main π* feature was calibrated to the NEXAFS of PET (for
the C 1s) or the ISEELS of DMT (for the O 1s). In order to isolate
the individual C 1s and O 1s core loss spectral signal, an AE⁻ background (with A and r as adjustable parameters) was
subtracted.

Spectral distortion associated with plural scattering can be a
problem if the sample is too thick. As noted earlier,13 sample
thickness does not affect the near-edge fine structure in PET
provided that the sample is thinner than one inelastic mean free path. With thicker samples plural scattering transfers intensity
from the lower energy C 1s (O 1s) to π* bands to the region
above 295 eV (550 eV), where it distorts the spectral normalization.
The region of the PET sample used for the STEM-EELS
measurements had a thickness of about 1.3 inelastic mean free paths, based on analysis of the low loss spectrum. From the
known density of 1.385 g/cm³ and the previously determined
value for total inelastic cross section per unit mass,36 the inelastic
mean free path in PET for 100 keV incident electrons is estimated as 100 nm. Thus, we estimate the PET sample to be
130 nm thick. Due to plural scattering the S/B ratio at the
carbon 1s edge drops by a factor of ∼5 as the specimen increases
into 1.3 inelastic mean free paths.37 Thus, plural scattering partly
accounts for the lower π*/σ* intensity ratio observed in the
STEM-EELS spectra. Fourier ratio deconvolution14 by the low
loss spectrum recorded under similar conditions provides an
accepted means to correct for plural scattering. It reduces
distortion of spectral shapes and increases the π*/σ* intensity
ratio. In addition, deconvolution provides a modest enhancement in energy resolution. For these reasons all of the STEM-
EELS spectra presented in this paper have been deconvoluted using low loss spectra.

2.4. Computational Procedures. Spectral assignments have
been assisted by comparisons to semiempirical extended Hückel
molecular orbital (EHMO) calculations48,39 of 1,4-DMT. The
molecular geometry (C₂h symmetry) was obtained from an ab
initio geometry optimization performed with a 3-21G* basis set.
This calculated structure is similar to the solid state crystal
structure of 1,4-DMT,49 except that the lowest energy gas phase
structure is planar whereas the methyl ester groups are nonplanar
by ∼5° in the solid state. The procedures used to apply EHMO
to core-excitation spectroscopy have been documented in earlier studies of organometallic,41—43 conjugated organic,44 and polymer analogue molecules.18,21

Predictions of core-excitation spectra were generated from
the EHMO output using the equivalent ionic core virtual orbital
model (EICVOM)45 procedures described previously.18,43,44
Briefly, a calculation is performed on a singly charged molecule
in which the core-excited atom is replaced with the Z + 1 atom;
for example, the C 1s spectrum of the ring-substitutional site
of DMT (denoted C 1s(C−R)) is derived from the EHMO
calculation for singly charged DMT, modified by replacing the
substituted ring carbon with a N atom. The energies of virtual
molecular orbitals (VMO) of this EICVOM species are assumed
to be related to the position of the core-excitation spectral lines.

Plots of the individual virtual molecular orbitals for DMT
are generated in which the radii of circles about individual atoms
are proportional to the 2p orbital contribution to the π* MOs,
as listed in the complete charge matrix given in the EHMO
output.44 These plots indicate the spatial distribution of the
Lippitz et al. 9b have recently published detailed studies of the dipole-dominated scattering conditions (2800 eV impact energy, 2terephthalate (1,4-DMT), recorded in the gas phase by ISEELS using The PET results are compared to the C 1s spectrum of 1,4-dimethyl deposed on a Si wafer, and transmission through a 200 nm thick film

PET.

Figure 1 plots the C 1s spectra of PET recorded using 3. Results and Discussion


coefficient and thus are a measure of the intensity of the core

core-excited atom are proportional to the square of the LCAO

molecular orbital in the core-excited species. They are related to the experimental spectra since the area of the circles on the core-excited atom are proportional to the square of the LCAO coefficient and thus are a measure of the intensity of the core → VMO transition.44 These plots are very helpful in relating spectral features to structural aspects of the molecule and in visualizing the effect of core hole relaxation on particular orbitals by comparison to the same orbital in the ground state.18,21

3. Results and Discussion

3.1. Technique Comparison. 3.1.1 Carbon 1s Spectra of PET. Figure 1 plots the C 1s spectra of PET recorded using electron energy loss (STEM-EELS), X-ray absorption with electron yield detection (EY-XAS), and true absorption (STXM-XAS), all in comparison with the C 1s spectrum of DMT recorded in the gas phase by ISEELS. The EY-XAS spectrum was collected at the so-called “magic” angle (55°) where orientation effects are minimal. Ouchi et al.9a and Lippitz et al.9b have recently published detailed studies of the polarization dependence of the C 1s spectrum of biaxially stretched, aligned PET. For this PET material, the intensities of specific transitions change dramatically with angle between the incident X-ray beam and the sample. The lowest energy π* bands (all those below 290 eV) all exhibit a linear dichroism effect that is opposite to that of the three broad σ* bands above 290 eV, consistent with the assignments we are proposing. In general, the assignments given by Ouchi et al.9a are similar but less detailed than those discussed in this paper. Lippitz et al.9b provide an in-depth discussion of the spectral features. Their polarization dependence observations fully support the assignments proposed earlier18 and in this work. In our study the EY-XAS of the PET films spun-cast on Si showed an angular variation of less than <5% (spectra not shown). This indicates the PET molecules in our films are mainly randomly oriented, as was found by Lippitz et al.9b in their studies of spun-cast amorphous PET.

Overall, there is very good agreement of the major features of the PET spectra recorded by all techniques, including the FY-XAS spectrum (not shown). The similarity of the STEM-EELS spectrum to the NEXAFS spectra demonstrates that, at low dose levels, the fine structure of polymer EELS spectra corresponds well with that in spectra obtained where radiation damage is of lesser concern (ISEELS, NEXAFS). There is also generally close agreement between the spectra of PET and DMT. These C 1s spectra are similar to those of several simulations derived from the spectra of small molecule analogues of PET (see Figure 12 of ref 18). DMT is a good model for PET since its structure is very close to that of the monomer repeat unit of PET. The main difference is replacement of two C–H bonds in DMT with a C–C bond in PET. This change should make little difference to the C 1s spectrum since the change is to only a small portion of the whole repeat unit, and it occurs in a region where the perturbation is expected to be localized and thus have minimal influence on the more highly structured electronic transitions associated with the unsaturated parts of the molecule.

Differences in the resolution provided by the various techniques are responsible for a large part of the differences in these spectra. The NEXAFS spectrum of PET, recorded in the NSLS STXM with about 0.3 eV resolution, displays additional features, in particular a fully resolved peak at 285.6 eV. This feature is detected as a shoulder in the EY-XAS and in the ISEELS of DMT (both recorded with 0.6 eV fwhm resolution), but it is not detected in the STEM-EELS spectrum. In principle, it is possible to achieve 0.3 eV fwhm at the zero-loss peak in STEM-EELS with a field emission gun in a dedicated scanning transmission electron microscope.33 However, this requires very low beam current which does not provide adequate signal in the core-excitation spectral region. For practical inner-shell studies higher beam current and larger analyzer acceptance angles are used, which degrade the energy resolution of STEM-EELS. In this work the measured fwhm of the zero-loss peak was ~0.45 eV, but the resolution achieved at the C 1s edge is clearly worse. When the STXM-XAS spectrum of undamaged PET is convoluted with a 1.2 eV Gaussian, it is a good match to the STEM-EELS spectrum. This suggests the effective resolution of the STEM-EELS is ~1.2 eV. From subsequent studies at least some of the resolution degradation appears to have been caused by not fully compensating for beam movement on the detector during the descending procedure. In any case, the net result is that the 285.6 eV peak, which is seen as a clear shoulder in the ISEELS of DMT and EY-XAS of PET (0.6 eV fwhm) and a fully resolved signal in the STXM (0.3 eV fwhm), is not at all visible in STEM-EELS. In addition, several transitions are clearly resolved between 288 and 290 eV in the
Methods provide a valuable complement to EELS. Resolution and numerous other imaging and microanalysis source instabilities, magnetic fields, radiation damage, etc.). Better understanding of these issues will facilitate the use of guidance for further minimization of troubling artifacts (e.g., resolution results. In the case of STEM-EELS, this can provide insights into the presence and identity of shoulders in the lower resolution spectra. Comparison of lower and higher resolution spectra can provide showing spectral features with less than 0.1 eV fwhm. 13,30 resolution, with many published examples of C 1s spectra of PET as a function of electron dose. Changes in the spectra are noticeable, but compared to saturated polymers46,47 the intensity of a specific spectral feature decreases to 1/e of its original value.14,22 In order to achieve meaningful analytical results with either technique, it is essential to use doses significantly lower than the critical dose for the specific polymer system under investigation. Thus, we have determined critical doses for radiation damage of PET in both STEM-EELS and STXM.

3.2. Radiation Damage Effects. Radiation damage can be a significant concern with both electron and photon impact based core excitation studies of polymers. Electron beam induced damage of various organic and inorganic materials has been reviewed recently.22,46 The nature and rate of damage is strongly dependent on the polymer being studied. Radiation damage induces chemical transformations (mainly reductions) and, in extreme cases, results in mass loss. These changes can be monitored by the decrease in the intensities of the spectral transitions associated with the chemically modified functional group(s). In addition, one may observe new spectral features associated with the products of radiation damage (e.g., the appearance of π\*C=C signal in radiation-damaged saturated systems). In PET the carbonyl bond is the most sensitive to radiation so carbonyl-related features are expected to be most affected. Radiation-modified spectra were recorded in both STEM-EELS and STXM-XAS measurements, and critical doses were determined. The critical dose is that dose at which the intensity of a specific spectral feature decreases to 1/e of its original value.14,22 In order to achieve meaningful analytical results with either technique, it is essential to use doses significantly lower than the critical dose for the specific polymer system under investigation. Thus, we have determined critical doses for radiation damage of PET in both STEM-EELS and STXM.

3.2.1. STEM-EELS: Damage with 100 keV Electron Impact. Figure 3 shows the first four in a series of STEM-EELS spectra of PET as a function of electron dose. Changes in the spectra are noticeable, but compared to saturated polymers46,47 the changes with the indicated beam doses are slight. This is likely due to the stabilizing effect of delocalization by the aromatic ring. As the dose increases, the intensity of the C 1s(C–H) → π\*C=C–C transition (285 eV) diminishes slightly while the intensity of the C 1s(C=O) → π\*C=O transition at 288 eV decreases more noticeably. In addition, a new signal appears at 286.7 eV. The 286.7 eV signal is visible only as a shoulder in STEM-EELS which is the carbonyl bond in PET. Radiation damage induces chemical transformations (mainly reductions) and, in extreme cases, results in mass loss. These changes can be monitored by the decrease in the intensities of the spectral transitions associated with the chemically modified functional group(s). In addition, one may observe new spectral features associated with the products of radiation damage (e.g., the appearance of π\*C=C signal in radiation-damaged saturated systems). In PET the carbonyl bond is the most sensitive to radiation so carbonyl-related features are expected to be most affected. Radiation-modified spectra were recorded in both STEM-EELS and STXM-XAS measurements, and critical doses were determined. The critical dose is that dose at which the intensity of a specific spectral feature decreases to 1/e of its original value.14,22 In order to achieve meaningful analytical results with either technique, it is essential to use doses significantly lower than the critical dose for the specific polymer system under investigation. Thus, we have determined critical doses for radiation damage of PET in both STEM-EELS and STXM.

3.1.2. Oxygen 1s Spectra of PET. Figure 2 compares the O 1s spectra of PET, measured by STEM-EELS; EY-XAS; and STXM-XAS (at the ALS), all in comparison with the O 1s spectrum of DMT, measured in the gas phase by ISEELS. As the C 1s edge, the O 1s spectra also show strong similarities in shape and number of transitions. Again, there are some resolution differences among the techniques, but the details of the O 1s spectra are less dependent than the C 1s spectra on the technique used. This is due to less spectral overlap at the O 1s edge because the natural line width is larger and the transitions are more widely spaced since there are only two different oxygen environments, as opposed to four different carbon environments. The resolution of STEM-EELS is sufficient to visualize all of the weaker transitions at higher energy than the main O 1s → π\*C=O transition. The similarity in shape of the spectra in Figure 2 demonstrates that there was relatively little radiation damage during acquisition of these spectra. This was particularly a concern since the STEM-EELS acquisition time for the O 1s spectrum is about 5 times longer than that for the C 1s edge.

Figure 2. Comparison of the O 1s spectra of PET recorded by STEM-EELS, glancing incidence EY-XAS, and transmission in the ALS STXM. The Figure also plots the O 1s spectrum of 1,4-DMT, recorded in the gas phase by dipole-regime ISEELS. In each case the as-recorded spectra have been subjected to background subtraction and normalized at 545 eV to the same oscillator strength value (0.0081 eV\(^{-1}\)). Offsets are used for clarity. The hatched lines indicate estimated core level ionization potentials of DMT.
characteristic critical doses are derived by fitting these curves to
\[ I(d) = Ae^{d\phi} + I_\infty \]
where \( I_\infty \) is the signal after the damage has ended (at low temperature, the main effect is chemical transformation rather than mass loss), \( A \) is an intensity scale factor, and \( d\phi \) is the characteristic critical dose. The characteristic critical doses derived from the dose dependence of the \( \pi^*(C=C) \) and \( \pi^*(C=O) \) signals are summarized in Table 2. The average value of 5400 electrons/nm\(^2\) corresponds to a charge dose of 0.086 C/cm\(^2\). Since the film thickness of 130 nm corresponds roughly to one inelastic mean free path, on average each 100 keV electron passing through the sample will be inelastically scattered once, with a mean energy loss of 35 eV.\(^22\) Thus, the average critical dose for reduction of the \( \pi^*(C=C) \) and \( \pi^*(C=O) \) intensities is equivalent to a critical energy loss of (1.9 ± 0.2) \times 10^5 eV nm\(^{-2}\) or (1.45 ± 0.15) \times 10^4 eV nm\(^{-2}\). The charge dose (0.086 C/cm\(^2\)) is almost an order of magnitude larger than that of 0.01 C/cm\(^2\) for loss of crystallinity in poly(butylene terephthalate), reported by Kumar and Adams.\(^47\) This is consistent with radiation affecting conformation and packing to a greater extent than chemical change. The critical energy dose we find for PET is similar to the values of (2.6 ± 0.7) \times 10^5 eV nm\(^{-2}\) or (6.5 ± 1.7) \times 10^4 eV nm\(^{-2}\) derived by Payne and Beamson\(^48\) from critical doses of (1.7−2.7) \times 10^4 electrons nm\(^{-2}\) determined by TEM-EELS for a 40 nm thick specimen of polyether ether ketone (PEEK). There was a range because the critical dose varied with the current density. Payne and Beamson predict the upper limit of usable current density is 5.8 \times 10^3 electrons nm\(^{-2}\) s\(^{-1}\), which they suggest will limit practical TEM-EELS studies of PEEK to areas greater than 140^2 nm\(^2\).\(^48\)

Our study shows that, although the EELS spectra recorded in the early stages are obtained at a small fraction of the critical dose and thus are characteristic of undamaged PET, measurements on the same region over a longer period result in readily detectible changes in the near-edge transitions of PET. Relative to previous STEM-EELS studies of PET,\(^17,18\) distortions associated with radiation damage are lower due to use of several techniques (cryogenic cooling and beam rastering) aimed at providing the lowest possible dose while still getting good signal/noise (S/N). There is good agreement between the edge shape in the first STEM-EELS spectrum of PET and that of the EY-XAS spectrum of PET (Figure 1), after taking resolution differences into account. This agreement strongly supports the argument that at very low dose STEM-EELS spectra can be obtained which truly reflect the chemical structure of PET.
**TABLE 2: Summary of Critical Dose (particles/nm²) and Critical Energy Dose (eV/nm² or eV/nm³) for Radiation Damage of PET Caused by 100 keV Electron Impact and 302 eV Photon Impact**

**a. 100 keV Electron Impact**

<table>
<thead>
<tr>
<th>feature</th>
<th>energy (eV)</th>
<th>critical dose (electrons nm⁻²)</th>
<th>Dₐ/area (eV nm⁻²)</th>
<th>Dₐ/volume (eV nm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>πᵣC=O</td>
<td>285.0</td>
<td>4.8(3) × 10²</td>
<td>1.7(2) × 10⁴</td>
<td>1.3(1) × 10⁵</td>
</tr>
<tr>
<td>πᵣC=O</td>
<td>288.5</td>
<td>6.0(3) × 10²</td>
<td>2.1(2) × 10⁴</td>
<td>1.6(1) × 10⁵</td>
</tr>
</tbody>
</table>

**b. 302 eV Photon Impact**

<table>
<thead>
<tr>
<th>feature</th>
<th>energy (eV)</th>
<th>critical dose (photons nm⁻³)</th>
<th>Dₐ/area (eV nm⁻²)</th>
<th>Dₐ/volume (eV nm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. πᵣC=O</td>
<td>284.8</td>
<td>11780</td>
<td>3.5(5) × 10⁶</td>
<td>1.7(2) × 10⁴</td>
</tr>
<tr>
<td>B. new feature</td>
<td>286.7</td>
<td>3500</td>
<td>1.0(2) × 10⁶</td>
<td>5.2(5) × 10⁵</td>
</tr>
<tr>
<td>C. πᵣC=O(1)</td>
<td>288.2</td>
<td>5435</td>
<td>1.5(2) × 10⁶</td>
<td>7.7(8) × 10⁵</td>
</tr>
<tr>
<td>D. πᵣC=O(2)</td>
<td>289.1</td>
<td>6490</td>
<td>1.8(3) × 10⁶</td>
<td>9.0(12) × 10⁵</td>
</tr>
<tr>
<td>E. πᵣC=O(3)</td>
<td>290.1</td>
<td>14500</td>
<td>4.3(9) × 10⁶</td>
<td>2.1(5) × 10⁴</td>
</tr>
</tbody>
</table>

*Derived from a series of STEM-EELS recorded from PET at 100 K. The measured sample thickness was 130 nm. The beam was rastered over an area of 10 × 10 μm. The dose rate based on 35 eV average energy loss per 100 keV incident electron was ~6 eV nm⁻³ s⁻¹. The G value for a 20 eV band at the C 1s edge is 0.0057 based on calculated energy loss cross sections of 100 keV electrons in atomic carbon and the experimental angular scattering range. *Error derived from the quality of the exponential fit. **Error derived from alternating higher intensity exposure and spectral scans of room temperature PET. The sample thickness was 200 nm as derived from the absorption coefficient at 310 eV. The beam was ~500 nm in diameter for both exposure and spectral acquisition. The dose rate from the experimental absorptivity was ~22 eV nm⁻³ s⁻¹.

Although radiation damage is far lower with the current version of parallel detection spectrometers for STEM-EELS and with the use of cryogenic techniques, one must always verify that radiation dose is not playing a role during each study. Comparison with other near-edge techniques can be helpful in this regard. This comparison of techniques demonstrates the value of using alternative techniques such as NEXAFS, and ISEEELS of molecular analogues, to verify STEM-EELS results on certain polymers and to understand the magnitude and mechanism of radiation damage.

3.2.2. NEXAFS: Damage with 302 eV Photon Impact. In order to assess radiation damage with soft X-rays, PET was exposed to high radiation dose with the NSLS STXM. Figure 4 plots a sequence of five NEXAFS spectra recorded with about 0.3 eV energy resolution from a ~500 nm diameter region, recorded after successive exposures of this region to monochromated 302 eV photons. The beam intensity was intentionally increased 8-fold during the radiation damage exposure by increasing the slit width and then decreased for spectral acquisition. Based on a film thickness of 200 nm (evaluated from the optical density) and a beam diameter of 500 nm, the analyzed volume is 3.9 × 10⁴ nm³. During radiation exposure, the transmitted intensity at 302 eV was about 200 kHz (detected by single photon counting). The optical density for the sample was 1.7 at 302 eV. Taking into account the estimated detector efficiency of 30%, the detected flux corresponds to 2.9 × 10⁸ photons/s absorbed in the irradiated volume. Thus, the dose rate per unit area was 2.9 × 10⁴ photons s⁻¹/2.0 × 10⁴ nm² or ~15 photons nm⁻² s⁻¹, or in terms of dose per unit volume, it was 2.9 × 10⁸/3.9 × 10⁴ nm⁻³ or ~0.08 photons nm⁻³ s⁻¹. The upper three panels of Figure 4 plot the intensity of five spectral features (πᵣC=O at 284.9 eV, the new signal at 286.7 eV, and the three πᵣC=O-related peaks around 288 eV) as a function of accumulated dose. The critical doses derived from the fit to the intensity decay or growth curves vary between 3 500 and 14 500 photons nm⁻² (see Table 2). This rather large spread in the critical doses may not reflect the true variation in damage rates at different chemical sites since peak heights rather than peak areas were used in the analysis, and there are definitely radiation-induced changes in peak shape. For X-ray absorption all of the photon energy is deposited into the sample. Thus, the critical dose averaged over all features is ~(8 ± 4) × 10³ photons nm⁻², which corresponds to an average critical energy dose of ~(1.2 ± 0.6) × 10⁴ eV nm⁻³.

In principle, the changes of the spectra with radiation dose can provide useful information about the radiation chemistry. Detailed NEXAFS studies of radiation damage of poly(methyl methacrylate) (PMMA) and poly(lactides) indicate that, in these species, loss of carbonyl functionality is accompanied by formation of C=O bonds. Qualitatively, the relative changes in peak area (see Figure 4) indicate that the carbonyl group of PET is more susceptible to radiation damage than the phenyl ring. Based on the spectral changes, the damage is localized in the region of the carbons and could involve expulsion of CO or CO₂. This would explain the decrease in πᵣC=O (288–290 eV), the decrease/change in πᵣC=O (285–286 eV), the appearance of the 286.7 eV peak (tentatively attributed to the C 1s(O=CH=CH=O) → πᵣC=O(t) transitions in the damage product), and eventual mass loss. The surprisingly small difference in damage rates between the aromatic πᵣ and carbonyl πᵣ signals in PET may be due to stabilization of the carbonyl group by extensive delocalization onto the phenylene in PET. Further high-resolution core-excitation and infrared spectral studies on heavily radiation-damaged PET may help identify the product(s) and mechanism(s) of damage.

Clearly, it is possible to damage PET with monochromated X-rays—in fact, the extent of spectral change is much larger in Figure 4 than in Figure 3. At the same time, STXM-XAS spectra of PET with S/N ratios only slightly worse than the ones presented in Figure 4 can be recorded under full-focus conditions (i.e., on 50 nm diameter regions) in less than 30 s, so useful results can be obtained without significant radiation damage. In cases where the ultimate spatial resolution is not required, the beam can be defocused, thus allowing longer exposure times before damage occurs. The critical dose of ~12 000 eV nm⁻³ for PET measured in this study is much larger that the critical dose of 63 eV nm⁻³ for PMMA measured by Zhang et al. and also using the NSLS STXM. Given that PMMA is much more radiation sensitive than PET, the 200-fold difference in critical energy dose is plausible.

3.2.3. Relative Capabilities of STEM-EELS versus STXM-XAS for Analysis of Radiation Sensitive Materials. How do these measured rates for electron and photon damage of PET compare? Superficially, when one directly compares the critical dose figures in terms of integrated flux of incident particles per unit area (~5400 electrons nm⁻² vs ~8000 photons nm⁻²), it appears that the situation is only slightly more favorable for photoabsorption than for STEM-EELS. However, the informa-
<table>
<thead>
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<th>EY-XAS</th>
<th>STXM</th>
<th>STEM-EELS</th>
<th>1,4-DMT</th>
<th>ISEELS</th>
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<td>284.86(6)*</td>
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a STXM calibration: −8.0(1) eV relative to C 1s → 3s (ν = 0) transition in CO2 (292.8 eV\textsuperscript{90}). Note that this uncertainty includes a contribution from nonlinearity in the photon energy scale. b Calibrated relative to CO2 (−5.88(6) eV relative to π* of CO2 (290.74 eV\textsuperscript{90}). c These letters refer to the results of EHMO calculations (Figure 5). d Estimated from the IPs of related species. e Estimated from the IPs of related species. f π* and σ* refer to the characteristic C 1s continuum resonances of phenyl rings.
<table>
<thead>
<tr>
<th>no</th>
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<th>STXM (eV)</th>
<th>p-EELS (eV)</th>
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<th>C=O</th>
<th>assignment</th>
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<td>1'</td>
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<td>π*&lt;sub&gt;C=O&lt;/sub&gt; (a)&lt;sup&gt;a&lt;/sup&gt;</td>
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<td>2</td>
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<td>533.9</td>
<td>534.0</td>
<td>534.0</td>
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<td>π*&lt;sub&gt;C=O&lt;/sub&gt; (b)</td>
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<tr>
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<td>536.4</td>
<td>π*&lt;sub&gt;C=O,C=C&lt;/sub&gt; (c)</td>
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<td>π*&lt;sub&gt;C=O&lt;/sub&gt; (e)</td>
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<tr>
<td>5 sh</td>
<td>546</td>
<td>546</td>
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<td></td>
<td>546</td>
<td>σ*&lt;sub&gt;C=O&lt;/sub&gt;</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Set to the value determined for the main π* of DMT: ISEELS calibration: -3.9 eV relative to π* of CO<sub>2</sub> (535.4 eV).<sup>b</sup> Letters refer to EHMO core excitation orbital pictures presented in Figure 5. <sup>c</sup> Estimated from the IPs of related species.<sup>53</sup>

4 are electrons

\[
10 \times 1.38 \times 10^{-18} \text{ e}^{-1} / (\text{A s} \times 35 \text{ eV/e}^{-1}) / (130 \text{ nm} \times 10000 \text{ nm} \times 10000 \text{ nm}) \sim 61 \text{ eV nm}^{-3} \\
(about 4% of the critical energy dose)
\]

4 are photons

\[
6 \times 4 \times 10^{18} \text{ photons/s} / (200 \text{ nm} \times 250 \text{ nm} \times 250 \text{ nm} \times \pi) \sim 180 \text{ eV nm}^{-3} \\
(about 2% of the critical energy dose)
\]

Thus, the first spectrum recorded by each technique was acquired using <5% of the critical dose. The area analyzed with STXM-XAS was smaller by a factor of 500. The ability of STXM to use a similar level of radiation damage to record a meaningful spectrum from a much smaller area than STEM is directly related to the analytical advantage of X-rays documented by the figure of merit described above.

In general, a useful way to compare the analytical capability of two spectromicroscopy techniques is in terms of the minimum sample size for which analytically meaningful spectra can be acquired. Many of the desired polymer applications of STXM or STEM-EELS involve characterization of dispersed phases where it is necessary to be able to identify chemical composition (speciation) of small regions or interfaces with submicron spatial resolution. Studies of damage rates of homogeneous systems (pure or mixed systems) such as the present work allow one to anticipate the applicability of either technique to specific problems, in terms of both quality of spectra and critical dose information. As one reaches the critical dose limits for radiation damage in either technique, one approach to extend the analytical utility without sacrificing spatial resolution is to sum spectra recorded for suitably brief periods over many identical particles. This can be done efficiently using a “mask” defined by an image recorded under low-damage conditions (e.g., an elastic image in STEM-EELS).<sup>35</sup> The actual minimum sample size achievable in either technique will depend on the desired energy range, energy resolution, and statistical precision. This comparative study of PET suggests that, when one takes into account the relevant factors, there is a difference of about 2 orders of magnitude between the two techniques in terms of the limitations imposed by radiation damage. This is in agreement with other published estimates.<sup>22</sup>

3.3. Spectral Assignments. 3.3.3. Carbon 1s Spectra of PET. The energies and proposed assignments for the C 1s spectral features are summarized in Table 3. These assignments are guided by our earlier study of an extensive set of molecular analogue species,<sup>18</sup> as well as extended Hückel calculations of DMT.<sup>18,52</sup> The detailed assignments of the 284–287 eV features (nominally π*<sub>C=C</sub>) and the 288–290 eV features (nominally π*<sub>C=O</sub>) are of particular interest since these features give insight into electronic delocalization. Also these are the features which reflect orientation and phase dependent effects.<sup>9</sup> While one can attribute the lower energy π* features to MOs of dominant π*<sub>C=C</sub> character and the higher energy π* features to MOs of dominant π*<sub>C=O</sub> character, in fact there are strong interactions among the ring and carbonyl π* levels such that the final state of the transitions actually have a mixed character. In addition, the nature of these interactions changes with location of the core hole. The EHMO calculations predict the orbital splitting caused by interactions of the π*<sub>C=O</sub> and π*<sub>C=C</sub> orbitals, as well as variations in molecular orbital character with variation in core hole position.

The results of EHMO calculations relating to the C 1s and O 1s spectra of DMT are presented in Figure 5. The EHMO predictions of the C 1s and O 1s spectra have been presented earlier, in comparison to STEM-EELS spectra of PET.<sup>18</sup> (Note that although the geometry employed in the earlier work differs slightly from that used in this study, the final spectral predictions are very similar.) Here we present pictures of the molecular orbitals in order to complement the earlier work by investigating the extent of delocalization in core excitation at each distinct site. The MO sketches show the contributions of each 2p<sub>(π*)</sub>
atomic orbital to the molecular orbital in the presence of the indicated core hole. Focusing first on excitations at the C–H ring carbons, EHMO predicts two main transitions separated by 1.2 eV, which are excitations to the orbitals depicted as (f, g) in Figure 5. These are C 1s(C–H) excitations to π* orbitals of mixed π*C=C and π*C=O character. They make up the majority of the intensity of the lowest energy π* band in the experimental spectra (Figure 1). The splitting of the transitions associated with C 1s(C–H) excitations to orbitals f and g has been resolved in small molecule analogues of PET,18 it is clearly detected in the transmission XAS spectrum, and it shows up as the shoulder at 285.6 eV in the EY-XAS and ISEELS spectra. The EHMO calculated value of 1.2 eV is somewhat larger than the observed separation of 0.7 eV.

Focusing next on excitations at the C–R ring carbons (those to which the methyl carboxylate groups are attached), there are two low-lying π* components, (d, e) with a mixed π*C=C and π*C=O character and with an even larger separation (~3 eV) than the (f, g) pair for C 1s(C–H) excitation. This large splitting, combined with the estimated ~0.5 eV chemical shift between the C 1s(C–H) and C 1s(C–R) IPks,53,54 places the first C 1s → π*C=C(π*)C=O transition (d) as part of the shoulder at 285.6 eV and the higher energy C 1s(C–R) → π* transition (e) at the leading edge of the 288 eV peak, where a shoulder is observed in the highest resolution XAS spectrum of PET as well as the ISEELS of DMT. This large splitting arises from a combination of the effect of symmetry reduction on the degenerate eπ orbital in benzene and the interaction of the π*C=C and π*C=O components. The delocalization interaction results in considerable mixing of excited state character which can generate a sizable splitting.

The third important aspect of the low-lying π* structure arises from excitations at the C 1s(C=O) carbon. Here three π* components (a–c) can be identified. The intense lowest energy component (a) corresponds to excitation to a π*C=O orbital which is quite localized on the C 1s excited carbonyl, but which otherwise is an in-phase combination of the π*C=O orbitals on the two methyl carboxylate groups (denoted π*C=O+(−) in ref 18). The next two components, (b, c) are considerably weaker and of more mixed π*C=C and π*C=O character. Peak b is the out-of-phase π*C=O combination (denoted π*C=O(−) in ref 18) while the third component (c) is very much delocalized over both the ring and carbonyl groups. Based on the alignment with the experimental spectrum, EHMO predicts that the (a), (e), and (b) components produce the three peaks at 288, 289, and 290 eV. Understanding the identity of these structures is important since the 288–290 eV region is the region which differs the most between the polymer and monomer. Also, this is the spectral region which is most readily affected by radiation damage. It is possible there could be a connection between the spatial distribution of the initial excitation and the subsequent bond breaking.55

3.3.2. Oxygen 1s Spectra of PET. The energies and tentative assignments of the O 1s spectral features of PET are summarized in Table 4. The main π* peak at 531.5 eV is attributed to O 1s(C=O) → π*C=O(+) while the second peak at 534.0 eV is attributed to O 1s(C=O) → π*C=O(−) and O 1s(C=O) → π*C=O(+) transitions. The peak at 536.4 eV is attributed to O 1s(C=O) → π*C=O(−) transitions. Some contributions of O 1s → Rydberg transitions may also exist between 534 and 540 eV in the ISEELS spectrum of gaseous DMT. However, these are generally expected to be rather weak in a molecule as large as DMT and are most likely absent in the spectrum of a polymer (but for a contrary viewpoint, see ref 56). The broad, intense peak at 540.8 eV is ascribed to O 1s (C=O) → σ*C=O transitions. There is also a broad, weak feature centered at about 547 eV. This is seen clearly in the ISEELS spectra of DMT, and it can be identified in most of the O 1s spectra of PET, with varying degrees of visibility (Figure 2). This broad signal is assigned to O 1s(C=O) → σ*C=O transitions. The weak intensity of σ*C=O relative to σ*C=O resonances has been noted in previous studies of the core spectra of ester species.18,57

The EHMO results generally support this interpretation of the O 1s spectrum of DMT. They predict there is extensive delocalization such that the final states of O 1s excitation at both the carbonyl and ether oxygen involve excitation to mixed π*C=O/π*C=O orbitals as presented in Figure 5. The three π* orbitals are rather similar for O 1s(C=O) (a–c) and O 1s(C–O) (d–f), although excitations from O 1s(C=O) are more intense than those from O 1s(C–O), as expected. The predicted splittings are almost 2 eV between each of the three components, which is somewhat smaller than that observed experimentally. Further discussion of the core spectra of 1,4-DMT is presented elsewhere, in the context of a comparison of the spectra and ab initio calculations of 1,2-, 1,3-, and 1,4-dimethyl phthalate isomers and their corresponding oligimers.58

4. Summary

The C 1s and O 1s spectra of poly(ethylene terephthalate) have been recorded by several techniques and have been compared to the spectra of the corresponding monomer (1,4-DMT). Once resolution differences have been taken into account, all of the polymer spectra recorded under low-dose conditions are generally in good agreement. This work demonstrates that, with a sufficiently high-performance system, STEM-EELS and STXM-XAS spectra of a relatively radiation sensitive polymer can be obtained with reasonable resolution and statistical precision before substantial radiation damage has occurred. Radiation damage was shown to be inducible by both electron and X-ray techniques, but it was also shown that spectra unaffected by damage could be acquired by both techniques. The quantitative analysis of the radiation damage rates produced a figure of merit indicating there is an ~500-fold advantage of STXM-XAS analysis of room-temperature PET relative to STEM-EELS of cryocooled PET. NEXAFS, particularly the high-resolution STXM-XAS spectra, confirmed the splitting of the C 1s(C=O) → π*C=O transitions predicted by earlier experimental studies and calculations of related systems,18 and provided information as to the damage mechanism.

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References and Notes

(48) Payne, R. S.; Beamson, G. Polymer 1993, 34, 1637.
(54) Beams, I.; Briggs, D. High Resolution XPS of Organic Polymers, The Scista ESCA300 Database; Wiley: New York, 1992. The narrowest line in their XPS spectrum of PET is 0.85 eV FWHM (C 1s(C=C=O)) whereas the C 1s(C=O) peak is 1.0 eV wide. Two 0.85 eV peaks separated by 0.5 eV in a 2:1 ratio gives a near symmetric peak 1.0 eV in width. From this we conclude that the C 1s(C=O) IP is ~0.5 eV above the C 1s(C=H) IP. A lower resolution XPS spectrum of PET, along with a discussion of the dependence of the XPS on conformation, is given in: Boulanger, P.; Pireaux, J. J.; Berbist, J. J.; Delhalle, J. J. Electron Spectrosc. 1993, 63, 53.