Systematic Oxidation of Polystyrene by Ultraviolet-Ozone, Characterized by Near-Edge X-ray Absorption Fine Structure and Contact Angle

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The process of implanting oxygen in polystyrene (PS) via exposure to ultraviolet-ozone (UV-O) was systematically investigated using the characterization technique of near-edge X-ray absorption fine structure (NEXAFS). Samples of PS exposed to UV-O for 10-300 s and washed with isopropanol were analyzed using the carbon and oxygen K-edge NEXAFS partial electron vields, using various retarding bias voltages to depth-profile the oxygen penetration into the surface. Evaluation of reference polymers provided a scale to quantify the oxygen concentration implanted by UV-O treatment. We find that ozone initially reacts with the double bonds on the phenyl rings, forming carbonyl groups, but within 1 min of exposure, the ratio of double to single oxygen bonds stabilizes at a lower value. Oxygen penetrates the film with relative ease, creating a fairly uniform distribution of oxygen within at least the first 4 nm (the effective depth probed by NEXAFS here). Before oxygen accumulates in large concentrations, however, it preferentially degrades the uppermost layer of the film by removing oxygenated low-molecular-weight oligomers. The failure to accumulate high concentrations of oxygen is seen in the nearly constant carbon edge jump, the low concentration of oxygen even at 5 min exposure (58% of that in poly(4-acetoxystyrene), the polymer with the most similarities to UV-O-treated PS), and the relatively high contact angles. At 5 min exposure the oxygen concentration contains ca. 7 atomic % oxygen. The oxygen species that are implanted consist predominantly of single O-C bonds and double O=C bonds but also include a small fraction of O-H. UV-O treatment leads a plateau after 2 min exposure in the water contact angle hysteresis, at a value of $67 \pm 2^\circ$, due primarily to chemical heterogeneity. Annealing above T_g allows oxygenated species to move short distances away from the surface but not diffuse further than 1-2 nm.

1. Introduction

The purpose of this study is to utilize NEXAFS to analyze the chemistry and bond structure of a systematically modified polystyrene (PS) surface, treated with ultraviolet-ozone (UV-O). Oxygen plasma and UV-O treatments are often used industrially for cleaning organic contaminants from inorganic surfaces (long exposure times) or introducing oxygen species to organic surfaces (short exposure times).¹ Short-time oxidation treatments can be extremely effective to improve the adhesion between hydrophilic polymer surfaces and other surfaces. UV-O is especially important for improving adhesion between multilayer films for packaging and modifying the surface of biologically compatible polymers.^{2–5} Without surface modification, PS culture dishes are only useful for the growth of nonaffixing cells such as bacteria; most other types of cells require a hydrophilic surface for growth. In the commercial arena for development of tissue cultures, oxidation via plasma or UV-O treatments have demonstrated universal suitability for surface modification of PS.³ Additionally, recent work in the area of artificial tissue engineering (e.g., for postsurgical wound healing) has shown the importance of precisely controlling adhesion and growth of cells

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on a structured substrate.⁴ Interfacial interactions have been fundamentally studied in many contexts, and it has been shown that physi- or chemisorption at interfaces is often the key mechanism⁶ for adhesion between surfaces, among the five routes to adhesion; the others being mechanical, rheological, entanglement, and electrostatic.^{7–9} The effect of plasma or UV-O treatment on a hydrophobic polymer is to introduce surface functional groups, whereby physi- or chemiadsorption is made possible.

Atactic PS is frequently used for fundamental studies because of the ease of spin-casting thin films from solution, the lack of crystallization, and a sufficiently high glass transition temperature to prevent dewetting. As mentioned above, it is also the most common material used for disposable cell culture dishes, due to its optical clarity, durability, and low cost.³ Here we modify PS by exposing thin films to UV-O for various times, thereby modifying the surface in degrees from a hydrophobic state to a more hydrophilic state. Near-edge X-ray absorption spectroscopy (NEXAFS) data were collected for the carbon and oxygen K-edges for multiple detector bias values. In addition, advancing, static, and receding contact angles were obtained to quantify the macroscopic modification. Limited results on the effect of annealing after UV-O exposure will also be discussed. UV-O exposure appears to lead to cross-linking, thereby preventing long-range diffusion of oxygen species into the bulk. The improvements of this study over previous studies of the surface

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chemistry of modified PS, primarily based on the advantages of NEXAFS and in-depth analysis of bonding peaks, will be enumerated in the summary.

Near-Edge X-ray Absorption Spectroscopy. NEXAFS is a unique technique for examining the surface of organic films, providing elemental, bonding, and structural information.¹⁰ The *K*-edges of carbon, nitrogen, oxygen, and fluorine, visible in the 250-750 eV range, are commonly studied. NEXAFS can also extend to higher energies and higher-order transitions of heavy elements, depending on the experimental setup. Within each *K*-edge, peaks appear on the basis of the electronic energetics of specific chemical bonds. It is possible to obtain both compositional depth and molecular orientation by varying the detector voltage bias and the angle between the excitation beam and the sample.

NEXAFS relies on a polarized beam of high-intensity X-rays from a synchrotron source, which excites a core electron to create a core hole.^{10,11} This hole is then filled by an outer-shell electron, and the excess energy causes the emission of a fluorescent photon or an Auger electron. For the K and L shells of low-Z elements, Auger decay is more probable than fluorescence and therefore has a much higher signal-to-noise ratio. Measurement of emitted Auger electrons proceeds by counting electron intensity as a function of incident X-ray energy, and separate peaks are observed that represent different electron binding energies, e.g., the bonding-to-antibonding transitions of $\sigma \rightarrow \pi^*$ or $\sigma \rightarrow \sigma^*$. The area of each peak is proportional to the concentration of bonds and the edge jump for any particular elemental K-edge is proportional to the total concentration of that element. Both of these quantities, the near edge and the edge jump, are dependent on the incidence and the emission angles, allowing for the determination of surface bond orientation.

NEXAFS was first pioneered by Stöhr, Jaeger, and Outka^{12,13} for the adsorption of small molecules on surfaces but was quickly extended to Langmuir-Blodgett monolayers¹⁴ and polymeric layers.¹⁵ The demonstration of quantitative curve-fitting of NEXAFS spectra greatly enhanced the power of NEXAFS as a tool to evaluate bonding in organic materials.¹⁵ Recent studies have examined a wider range of polymers and self-assembled monolayers. Koprinarov et al. utilized NEXAFS to track changes in polymer chemistry after oxygen plasma treatment.^{16,17} It was found that oxygen preferentially attacks phenyl rings in amorphous PS but preferentially avoids phenyl rings in crystalline poly-(ethylene terephthalate). The orientation of self-assembled monolayers was obtained through careful studies by Genzer et al.^{18–20} by varying the incident angle and bias voltage and tracking the intensity of specific transitions. Since the incident X-ray beam is strongly polarized and absorption by specific bonds is polarization dependent, the net orientation of molecules can be obtained. Utilizing partial electron yield variations as a function of detector gate high-pass entrance grid voltage bias allows for rough depth profiling, since Auger electrons escaping from deeper within the film experience multiple inelastic scattering events which decrease their energy. Depth profiling was also demonstrated for interpenetrating photoresist layers by Lenhart et al.²¹

2. Experimental Section

Material Preparation. Atactic PS ($M_n = 97$ kg/mol, PDI = 1.05, Polymer Source) was dissolved in toluene (99.9%, Fisher) to 3 wt % and filtered twice through 1 μ m Teflon filters. Silicon wafers were cleaned for 10 min by oxygen plasma etching and 2 min by UV-O treatment, followed by a toluene wash to remove residual dust. PS was then spun-cast into films ~150 nm thick and annealed at 120 °C for 16 h under vacuum. Exposure to UV-O, created from atmospheric oxygen and a high-intensity mercury lamp (Jelight, UVO-Cleaner), for specified times was followed by an isopropanol wash for 2 min. The mercury lamp output was 28 W/cm² at 254 nm, and the distance to the sample was ~4 cm. The relative humidity in the chamber was 10% ± 5%; it is expected that humidity should have a slight impact on UV–O modification, via incorporation of ambient water into the film as hydroxyls, although the precise impact of humidity is beyond the scope of this study.

The wash involved swirling the sample in a fresh solution of isopropanol, with no ultrasonication, followed by oven drying at 60 °C. Previous studies indicated washing to be effective in removing low-molecular-weight oxygen species and essential for increasing the reproducibility of surface compositions,^{3,5} although no measurement of the precise amount of material removed was undertaken in the present or referenced studies. As expected, washing with hydrophilic solvents preferentially removes the most oxidized species (carboxyls).³ When desired, temperature annealing was performed on a temperature-controlled metal heating plate with less than 1 °C deviation across the 10 in. square plate (Brewer Scientific, Inc.), under a positive N₂ pressure to prevent incidental oxidation from atmospheric oxygen.

Polymers used to produce calibration spectra included poly(4acetoxystyrene) (P4AS, $M_n = 21 \text{ kg/mol}$, PDI = 1.4, Polymer Source), poly(4-methoxystyrene) (P4MS, $M_n = 68$ kg/mol, PDI = 1.08, Polymer Source), poly(ethylene oxide) (PEO, $M_n = 100$ kg/mol, Acros), poly(4-*t*-butylstyrene) (P4tBS, $M_n = 132$ kg/mol, PDI = 1.04, Polymer Source), poly(4-hydroxystyrene) (P4HS, $M_n = 8.8$ kg/mol, PDI = 1.08, Polymer Source), poly(methyl methacrylate) (PMMA, $M_n = 15$ kg/mol, Acros), and poly(ethylene terephthalate) (PET, capacitor grade Mylar, DuPont). P4AS, P4MS, and P4tBS were spun-cast from toluene, PMMA from benzene, and P4HS from propanol, in a 3 wt % filtered solution and annealed under 120 °C vacuum overnight. PEO was cast from a 60:40 water/acetone solution into a thick film, dried at 50 °C, and annealed under 80 °C vacuum overnight. PET films were wiped with isopropanol and dried under 80 °C vacuum. Structures of the reference polymers are shown in Figure 1.

Characterization.²² NEXAFS measurements were performed at the U7A NIST beamline of the National Synchrotron Light Source at Brookhaven National Laboratory.¹¹ Partial electron yield spectra were collected at room temperature and $7 \times 10^{-5}-7 \times 10^{-6}$ Pa over the region 200–640 eV, as calibrated by the carbon *K*-edge π^* transition of graphite at 285.10 eV or the oxygen *K*-edge I_0 absorption dip at 531.2 eV. A monochromator with 600 lines/mm grating provided 0.15 eV resolution. After collection, the spectra were normalized to the incident beam intensity I_0 , which was obtained by collecting the total electron yield intensity from a gold-coated,

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Figure 1. Structures of the polymers utilized in this study.

90%-transmitting grid placed in the incoming X-ray beam path. The beam was incident to the sample normal at the magic angle of to remove any polarization dependence. In addition, a retarding adjustable entrance grid bias (V_{bias}) was placed across the electron detector in order to screen out electrons with kinetic energy less than V_{bias} , allowing for crude depth profiling. The voltage applied across the grid detector is set in V, and as it retards incoming electrons, may be interchangeably referred to in units of V or eV.

One advantage of synchrotron-based techniques such as NEXAFS is that far less spectral deconvolution is required due to the intense monochromatic source. For example, low-energy X-ray photoelectron spectroscopy (XPS) has been used previously to examine the effects of plasma or UV-O treatment on polymers by, e.g., Teare et al.,⁵ Callen et al.,³ Gerenser,²³ and Ton-That et al.²⁴ In all of these studies, however, five or more fitting peaks overlap at any particular incident X-ray energy. Synchrotron-based NEXAFS and XPS, on the other hand, can pinpoint individual excitations and typically only two peaks and the edge jump overlap at any energy. The additional advantage of NEXAFS also includes, as mentioned earlier, the ability to obtain orientational information.

Several bond types are examined here. The main carbon transitions are C 1s $\rightarrow \pi^*_{C=C}$, C 1s $\rightarrow \sigma^*_{C=C}$, and C 1s $\rightarrow \sigma^*_{C-C}$. In this discussion, the former transition is denoted by $\pi^*_{C=C}$; the latter two transitions cannot be separated by NEXAFS and are denoted by a single term $\sigma^*_{C=C, C-C}$. Carbon edge transitions also include C 1s $\rightarrow \sigma^*_{C-H}$, denoted σ^*_{C-H} . Similarly, the oxygen transitions consist of O 1s $\rightarrow \pi^*_{O=C}$, O 1s $\rightarrow \sigma^*_{O=C}$, and O 1s $\rightarrow \sigma^*_{O-C}$, denoted here by $\pi^*_{O=C}$ and σ^*_{O-C-C} .

Contact angle measurements were performed using a commercial setup (First Ten Angstroms, FTÅ200), whereby deionized water droplets were injected onto films placed on a horizontal, backlit stage. The syringe was computer-controlled for constant volumetric flow rate (~0.3 μ L/s), and images were recorded by a CCD camera horizontal to the drop. Sessile contact angles (advancing, receding, and static) were analyzed by directly measuring the angle between the liquid and surface at the air interface with an estimated error²⁵ of ±2 °C. Contact angles were measured on wafer pieces taken from regions adjacent to those used for NEXAFS measurements.

NEXAFS Analysis. Spectra were analyzed by first subtracting the pre-edge linear baseline, which, although a simple measure, is extremely important to proper analysis of the spectra. For the carbon

edge, a linear baseline was obtained for each spectra by finding the best linear fit to the data points from 210 to 260 eV. Following subtraction of this baseline, the spectra were shifted by a constant obtained as the average of the five points around 275.00 eV. This second step is necessary because the second-order oxygen K α edge manifests from 265 to 275 eV. The oxygen edge is simpler to baseline, and a single step was used to obtain a best-fit linear baseline from the points between 510 and 528 eV. Fitting minimized the residuals created by subtracting the summation of symmetric Gaussian functions with one or two error functions-decaying exponentials from linearly baselined spectra, according to methods established by Outka and Stöhr.^{10,15} The intensity of a Gaussian function is represented by

$$I_G = H_G \exp\left[-\frac{1}{2} \left(\frac{E - P_G}{W_G/c}\right)^2\right]$$
(1)

where *H*, *P*, and *W* are, respectively, the height, position, and width of the Gaussian peak *G*, *E* is the independent variable in eV, and $c = 2\sqrt{\ln 4}$. The intensity of an error function-decaying exponential is represented by

$$I_{\text{erf-exp}} = H_{\text{erf}} \left[\frac{1}{2} + \frac{1}{2} \text{erf} \left(\frac{E - P_{\text{erf}}}{W_{\text{erf}} / c^*} \right) \right], \text{ for } P_{\text{erf}} - W_{\text{erf}} < E < P_{\text{erf}} + W_{\text{erf}}$$
$$I_{\text{erf-exp}} = (H_{\text{erf}} - H_{\text{exp}}) \exp[\tau_{\text{exp}}(E - P_{\text{erf}} - W_{\text{erf}})] + H_{\text{exp}}, \text{ for } E > P_{\text{erf}} + W_{\text{erf}}$$
(2)

where the erf and exp subscripts denote separate parameters for *H*, *P*, and *W*, and $c^* = 2\sqrt{\ln 2}$.

For the oxygen edge, the width, height, and position of the Gaussians and exponentially decaying error functions were all allowed to vary (within limits) in the residual minimization algorithm. However, for the carbon edge, the presence of seven Gaussians and one exponentially decaying error function made it impossible to freely vary all parameters and still obtain physically meaningful parameters. Therefore, some parameters were fixed on the basis of estimates for their true values. The parameters for the carbon edge that remained fixed were P_G of the peaks at 285.25, 285.4, 286.8, and 287.5 eV; P_{erf} ; W_G of the peaks at 286.8, 287.5, ~289, ~293.5, and ~300 eV; and the time constant of the exponentially decaying error function.

The asymmetrically broadened Gaussian function described by Stöhr¹⁰ was avoided, as modifications to W_G are empirical. Rather it was found that two Gaussian functions could fit the asymmetric peaks with good precision, and the areas of two Gaussians were summed to define the total area of the asymmetric peak. This combination of two Gaussians was used in the fitting of the $\pi_{C=C}^*$ and $\sigma_{C=0,C=0}^*$ regions.

Positions (centers) of the fitted Gaussian functions and error functions are as follows. For the carbon edge: Gaussians at 285.3, 286.8, 287.5, 288.9, 293.5, and 299.5 eV, and the error function at 290.0 eV. For the oxygen edge: Gaussians at 532.8, 540.0, and 544.7 eV, and the error functions at 534.7 and 548.9 eV.

Values for the edge jumps were obtained from the magnitudes of I/I_0 at 315.0 eV for carbon and 570.0 eV for oxygen, averaged over ± 2.0 eV. Also note that although some polymers (such as PMMA) degrade under the synchrotron X-ray beam, PS exposed to the beam for less than 2 h is virtually unchanged.

NEXAFS Error Analysis. Previous investigations^{21,26} using the NIST U7a beamline at Brookhaven found that the error in the intensity at any particular energy is less than 2%, provided that the same sample is used, spectra are carefully baselined, and minimal sample degradation occurs under exposure to the synchrotron source. On the basis of these results, peak fitting of any individual spectrum is considered to be reliable and robust. However, because of the extreme sensitivity of NEXAFS to surface chemistry, much larger experi-

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mental errors may evolve from slight differences between the surfaces of different samples. Two spectra (on uniquely prepared samples) were collected for each condition examined in this study. It was found that the difference between evaluated peak areas or edge magnitudes may range from 1% to 15%, with errors on the higher end of the range more prevalent at longer exposure times. Approximate data ranges were calculated for individual exposure times on the basis of the differences between the two available points, although additional points would have been much more desirable to produce 95% confidence intervals. Error bars throughout the paper, unless otherwise noted, represent approximate errors estimated by this method.

3. Results and Discussion

NEXAFS peaks for PS and UV-O-modified PS were assigned on the basis of previous investigations, specifically those of Stöhr¹⁰ for the carbon edge and Koprinarov et al. and Stöhr for the oxygen edge.^{10,16} For the reference polymers, spectra taken by Ade et al.²⁷ were very helpful in interpretation. Examples of the fits achieved by regression are seen in Figure 2a, b, and c for the carbon *K*-edge of neat PS, the carbon *K*-edge of PS modified by 5 min exposure to UV-O, and the oxygen *K*-edge of PS modified by 5 min UV-O, respectively. The notations corresponding to the core electron-to-bonding electron transitions shown in the figures were described in the Experimental Section. The small residual values in Figure 2 indicate excellent fits, and equally small residuals are characteristic of all curve fits.

For a qualitative view of the changes with UV–O exposure, Figure 3 illustrates the carbon and oxygen NEXAFS spectra obtained at -150 and -450 V detector bias, respectively. With increasing UV-O treatment (10 s to 5 min), the peak representing $\pi_{C=C}^{*}$ at 285.3 eV decreases strongly and the peaks representing $\sigma_{C=C,C-C}^{*}$ at 293.7 and ~301 eV decrease weakly. The strong decrease seen in the $\pi_{C=C}^{*}$ peak is due to light-assisted oxidation (photo-oxidation)²⁸ of the double bonds by the UV light. The mercury lamp emits light at two primary wavelengths, 184.9 and 253.7 nm.¹ The former wavelength is absorbed by ozygen and results in ozone, whereas the latter is absorbed by ozone and most hydrocarbons.¹ UV–vis spectra for PS and polypropylene (PP) are seen in Figure 4: note the strong absorption region for PS extending from 275 nm to below 200 nm, which is absent for PP.

In Figure 3, there is a small peak centered at 286.7 eV that increases with UV-O exposure time. This arises from carbon with a double bond to oxygen, $\pi^*_{C=0}$, which appears at slightly higher energies²⁷ than $\pi_{C=C}^*$. Depending on the polymer structure under consideration, this peak may be located at energies between 286.5 and 289 eV;²⁷ due to the large increase in magnitude seen here with increasing UV-O time, this peak must arise from the presence of C=O. The small peak at slightly higher energy, 287.5 eV, representing C-H, simultaneously decreases significantly. This indicates that a significant fraction of the hydrogens, most of which are located on the phenyl rings, are being removed as the C=C bonds are broken. All of the oxygen K-edge peaks increase strongly with increasing UV-O time. A trace amount of oxygen is evident in the neat PS spectrum, which is likely due to silica dust from the substrate wafer after dicing samples. Note that the magnitude of the carbon spectra is an order larger than that of the oxygen spectra: while differences in quantum yield and instrument response at the respective C and O electron energies can contribute to intensity changes, these do not change



Figure 2. Fitted NEXAFS spectra for (a) the carbon *K*-edge of neat PS with a detector bias of -150 V; (b) the carbon *K* for PS exposed to UV-O for 5 min, at -150 V bias; and (c) oxygen *K*-edge spectrum for PS modified by 5 min UV-O with the detector at -450 V bias. Specific Gaussian positions for the assigned peaks are given in the text. The y axis indicates electron yield normalized by the incident X-ray beam intensity and baselined by subtracting the best-fit line through the preedge region 510-528 eV. Fits, consisting of Gaussian functions and an exponentially decaying error function, were obtained by minimizing the residuals. Peak assignments are made based on Stöhr's work.¹⁰

by an order of magnitude over this energy range. Therefore, the higher carbon *K*-edge jump indicates that there is significantly more carbon than oxygen present even after 5 min UV-O.

These chemical changes with UV-O exposure can be quantitatively analyzed through curve fitting. Two modes of analysis are possible. First, peak ratios can be obtained for peaks within the carbon and oxygen *K*-edges to examine the reactive selectivity of UV-O treatment for the carbon bonds present in PS. Second,

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Figure 3. NEXAFS spectra for the range of UV-O exposure times for (a) the carbon *K*-edge at -250 V bias, (b) a closer view of (a), and (c) the oxygen *K*-edge at -450 V bias. Solid arrows indicate the direction of increasing UV-O exposure time.



Figure 4. UV-vis spectra for PS and PP, indicating absorption of the wavelength at 253.7 nm by PS (one of the wavelengths emitted by the mercury lamp in the UV-O apparatus). The vertical axis gives absorption units per micron of film thickness.

the total edge jump magnitudes for a particular atomic species at a particular condition are proportional to the concentration of that atom in the material. Since all spectra at a particular bias were taken under the same conditions (same incident angle and baseline method) and assuming that the density of the material does not change significantly with UV-O treatment (density affects the inelastic mean free path of departing Auger electrons), the total edge jump magnitude is proportional to atomic concentration. The individual peak areas and edge jumps are given in Figures 5 and 6 for carbon and oxygen, respectively. Note the effect of bias voltage and the trends in magnitude of decreasing carbon and increasing oxygen bonds.

For carbon, the area ratio of π^* to the carbon edge jump decreases strongly with increasing UV-O exposure time (Figure 7), indicating a strong preference for ozone to react with double bonds of the phenyl rings rather than the single bonds in the backbone. Besides the evidence (Figure 4) indicating that C=C bonds are activated by absorbed UV light, oxygen addition to the conjugated ring is also more energetically favorable than the cleaving of C-C single bonds. This was found by Saito et al., who described the mechanism of ozone addition as occurring across a double bond on the ring and ultimately either forming two carbonyls on adjacent carbons or cleaving the ring to form reactive peroxides or carboxyls.²⁹ Preferential reactivity of the double bonds is likely accelerated by the initial breaking open of a phenyl ring, which would then destabilize the double bonds on that ring and promote the local formation of C–O bonds. Interestingly, the π^* to edge jump ratio is slightly larger for higher bias voltages (Figure 7). The probing depth at a retarding bias of -250 V cannot be precisely known, but calculations in the present work (discussed below) suggest -250 V probes 1.6 nm. The distance of a single PS monomer with sidegroups oriented normal to the surface is ca. 0.63 nm thick, so if the assumptions in the bias-depth model discussed below are correct, then -250 V probes approximately three monolayers of PS. The increase in the π^* to edge jump ratio at higher biases indicates that the phenyl sidegroups tend to orient perpendicular to the surface, and this is consistent with previous investigations using NEX-AFS^{30,31} and vibrationally resonant sum frequency generation.³²

For oxygen, the peak area ratio of π^* to σ^* decreases exponentially with increasing UV-O time (Figure 8). The shortesttime data points represent 10 s UV-O; neat PS is not represented because the oxygen peaks were both too small to fit reliably and not physically meaningful. Initial UV-O exposure results in significantly more C=O double bonds than single C-O bonds but at longer times this ratio stabilizes at a lower value. This indicates that (1) the reactivity of ozone with C=O-containing species is greater than C-O-containing species, and subsequent reactions break down carbonyls into ethers or hydroxyls; or (2) the high intensity ultraviolet light also present in UV-O treatments is absorbed by and degrades C=O groups.¹

The edge jump magnitudes for each bias voltage are normalized, using neat PS for carbon and PS exposed to 5 min UV-O for oxygen (Figure 9). Once normalized, data sets for all bias voltages overlap within experimental uncertainty. This means that the oxygen profile is constant over probing depth. While the total oxygen content increases steadily, the carbon content decreases by ca. 12% up to 1 min UV-O exposure, then stabilizes. The decrease in carbon content is caused primarily by the incorporation of oxygen, which both decreases the inelastic mean free path of escaping Auger electrons originating from carbon atoms by

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⁽³³⁾ Jablonski, A.; Powell, C. J. J. Electron Spectrosc. Relat. Phenom. 1999, 100, 137–160.



Figure 5. Areas of the fitted Gaussians and magnitude of the edge jump for the carbon *K*-edge as a function of UV-O exposure time. The peaks were centered at the energies in the NEXAFS spectra as follows. (a) $\pi_{C=C}^{e}$ at 285.3 eV, (b) σ_{C-H}^{e} at 287.5 eV, and (c) $\sigma_{C=C,C-C}^{e}$ at 293.5 and 300 eV; and the magnitude of (d) the carbon edge jump was evaluated at 315.0 \pm 2.0 eV. Lines are drawn to guide the eyes.



Figure 6. Areas of the fitted Gaussians and magnitude of the edge jump for the oxygen *K*-edge. The peaks were centered at the energies in the NEXAFS spectra as follows. (a) $\pi^*_{C=0}$ at 532.8 eV and (b) $\sigma^*_{C=0,C=0}$ at 540 and 545 eV; and (c) oxygen edge jump at 570.0 \pm 2.0 eV. Lines are drawn to guide the eyes.

increasing the overall density and decreases the density of carbon by "displacing" carbon atoms as oxygen atoms are implanted into the polymer backbone.

It was mentioned above that the detector bias voltage provides a crude method to probe different sample thicknesses. Since electrons deep in the sample undergo one or more inelastic scattering events, their kinetic energy is decreased from the initial energy of the Auger electron, which for carbon is 263 eV.²⁰ The following calculation, an oversimplified but typical approach in NEXAFS or XPS depth profiling,³³ builds from the method of Genzer et al.²⁰ for obtaining depth probed as a function of detector

⁽³⁴⁾ Zemek, J. Acta Phys. Slovaca 2000, 50, 577-589.

voltage bias. The photoelectron current dI emitted from a layer of thickness dz from a depth z is written^{10,34}

$$dI = I_0 A \mu_x(\theta, h\nu) \exp\left[\frac{-z}{\lambda_i \cos \alpha}\right] dz$$
 (3)

where I_0 is the incident flux of X-rays, A is the exposed area, μ_x is the material-dependent X-ray absorption coefficient, α is the angle between the surface normal and the emission angle (the takeoff angle), and λ_i is the inelastic mean free path (the mean distance between inelastic collisions,³⁵ IMFP). The absorption coefficient $\mu_x(\theta, h\nu)$ is composed of the atomic volume



Figure 7. Ratio of the π^{*1} area to the edge jump magnitude for the carbon edge as a function of UV-O exposure time, for various detector bias voltages.



Figure 8. Ratio of the area of the π^* to the area of σ^* for the oxygen edge as a function of UV-O exposure time, for two detector bias voltages. The line is drawn to guide the eyes.



Figure 9. Carbon and oxygen edge jump magnitudes for various detector bias voltages. For each bias voltage, edge jump magnitudes are normalized by the edge jump at 0 (carbon) or 5 min (oxygen). Lines are drawn to guide the eyes.



Figure 10. Schematic illustration of the incident and emission angles utilized by the NEXAFS instrumentation. PEY represents partial electron yield.

density n_v and absorption cross section $\sigma_x(h\nu)$, as well as the angle θ between the incident X-ray beam and the absorption dipole. n_v can be calculated from the mass density ρ , Avogadro's number N_A , the molecular weight, and the number of atoms of interest *n* contained in a molecular section:

$$\mu_x(\theta, h\nu) = \frac{n_v \sigma_x(h\nu)}{\sin \theta} = \frac{\rho N_A n \sigma_x(h\nu)}{\sin \theta M_0}$$
(4)

where for polymers the molecular weight M_0 is that of the repeat unit of the polymer, and the X-ray incidence angle θ is >10°, allowing us to neglect reflection and refraction.¹⁰ The arrangement of angles is illustrated in Figure 10.

In order to obtain the overall intensity I/I_0 , eq 3 must be integrated over all values of z. Subsequently, to introduce the effect of detector voltage bias V_{bias} , z is integrated from zero (the film surface) to a depth λ^* , which represents the effective depth probed at a particular detector bias. Typically this integral would be evaluated from zero to infinity to obtain the total electron yield from deep within the film,^{36,37} but by applying an external bias to the detector, the range of electron energies and thus the depth from which the electrons originate is reduced. Integration of eq 3 from zero to $\lambda^*(V_{\text{bias}})$ yields³³

$$I/I_0 = C_1 \lambda_i \left[1 - \exp\left(\frac{-\lambda^*}{\lambda_i \cos \alpha}\right) \right]$$
(5)

where C_1 is a constant describing the particular experimental conditions and material. I/I_0 will be a complex function of λ^* : Ashley³⁵ computed the average energy lost per unit path length and the inelastic mean free path for polyethylene (which closely approximates PS as considered by Tanuma),³⁸ and the result is given in the Supporting Information. As electrons experience inelastic collisions, they will lose energy and their average energy lost will change, following the curve computed by Ashley toward E = 0. The total intensity leaving the film will be a sum over the full thickness *z*, accounting for both varying electron loss over depth and Auger electrons escaping from different depths. Jablonski and Powell³³ discuss the complications in evaluating such an expression.

Before writing III_0 in terms of V_{bias} , it is first important to consider the relationship between escaping electrons and grid bias. Due to the discrete nature of electron shell changes, all electrons emitted at the carbon Auger energy possess a kinetic energy of 263 eV. If the grid bias is held slightly below this

⁽³⁵⁾ Ashley, J. C. J. Electron Spectrosc. Relat. Phenom. 1990, 50, 323–334.
(36) Briggs, D. Practical Surface Analysis: Volume 1- Auger and X-ray Photoelectron Spectroscopy; John Wiley and Sons Ltd.: New York, 1990; pp 201–255.

⁽³⁷⁾ Seah, M. P.; Dench, W. A. Surf. Interface Anal. 1979, 1, 2–11.
(38) Tanuma, S.; Powell, C. J.; Penn, D. R. Surf. Interface Anal. 1994, 21, 165–176.



Figure 11. Carbon edge jump magnitude, averaged across all samples, as a function of detector bias voltage. Error bars indicate 95% confidence intervals. The line indicates the best fit of $C_1\lambda_i\{1 - \exp[-C_2(263 + V_{\text{bias}})]\}$ to the data.

threshold of 263 eV, then only electrons that have escaped the film without undergoing inelastic collisions will be detected; but slightly above 263 eV, no carbon Auger electrons should be detected. Assuming that the average inelastic mean free path has a relatively sharp distribution, there should be a steplike transition at $V_{\text{bias}} = -263 \text{ eV}$, where electrons detected slightly below 263 eV will have traveled a distance equal to the inelastic mean free path. Experimentally, this transition is not sharp due to the distribution in the inelastic mean free path, the presence of valence electrons, and contributions due to higher order soft X-rays in the incident beam; but a slight drop in signal near 263 eV remains as evidence of this transition (Figure 11). A transition at 263 eV was also evident in plots of electron kinetic energy as a function of detector bias (not shown here). Note that the fact that this drop occurs at almost exactly the carbon Auger energy indicates that the energy to escape the film surface is less than 1 eV.

In order to proceed, a functional relationship between λ^* and V_{bias} must be constructed. We assume an arbitrarily linear form (thereby avoiding the difficulty in evaluating a form of λ^* that changes with energy and depth), restricted by the limit of $\lambda^*(V_{\text{bias}} \rightarrow 263 \text{ eV}) \rightarrow \lambda_i \cos \alpha$:

$$\frac{\lambda^*}{\lambda_i \cos \alpha} = C_2(263 + V_{\text{bias}}) + C_3 \tag{6}$$

where $-263 \ge V_{\text{bias}} \ge 0$ and C_2 and C_3 are constants. Figure 11 illustrates the fit of the combination of eqs 5 and 6 to a plot of carbon edge jump magnitude (averaged from the data sets in Figure 9) as a function of V_{bias} . Also incorporated into the plot at high bias fields are data taken at a later time for a self-assembled monolayer of octyltrichlorosilane, which as a hydrocarbon has a density approaching PS.

The resulting fit provides the parameters $C_1\lambda_i = 0.19 \pm 0.01$, $C_2 = 0.016 \pm 0.002$ V⁻¹, and $C_3 = 0.15 \pm 0.02$. Ideally, C_3 should equal unity, fulfilling the physical limit of $\lambda^*(V_{\text{bias}} \rightarrow 263$ eV) $\lambda_i \cos \alpha$; however, it is not possible within the confines of the data in Figure 11. Difficulties likely arise from the simplifying assumptions discussed above, and future work should attempt to improve upon eqs 5 and 6; but in the present case C_3 will be fixed at 1 and the fitted value for C_2 will be used.

The inelastic mean free path in PS was calculated to be 1.3 nm by Ashley and Tanuma,^{35,38} and α is 1° (see Figure 10).



Figure 12. Oxygen concentration calibration curve formed from the oxygen edge jumps of various reference polymers. Solid lines indicate best fits (-150 and -250 V were fit with the same line).

Therefore, a bias of 0 V probes a depth λ^* of 6.8 nm, and a bias of -250 V probes 1.6 nm. Comparing with predictions by Genzer et al.,²⁰ the present method gives slightly larger values at low biases but compares favorably as the bias nears -263 V (see the inset of Figure 11).

Examination of eqs 3 and 4 indicates that, provided the experimental conditions are the same, polymers with known elemental concentrations can be used to calibrate the NEXAFS intensity. The assumption must also be made that the absorption cross section remains unchanged, which is reasonable because the bond types (between carbon, oxygen, and hydrogen) are the same. Specifically, $I/I_0 \sim N_A \rho n/M_0$. Correlations with the carbon edge jump proved difficult because the data set contained a tightly grouped set of concentrations, but oxygen concentrations could be correlated in a linear fashion fairly well with oxygen edge jump. P4AS, P4MS, P4HS, PEO, PET, and PMMA were used to form the calibration curve seen in Figure 12. P4HS and PET are the outliers at low and high oxygen concentration, respectively. As expected for oxygen K-shell electrons emitted with energies of \sim 520 eV, biases of -150 and -250 V do not significantly perturb the quantity collected, but a bias of -450 V probes a much smaller depth into the film, collecting a fourth of the electrons as the -150 and -250 V biases.

Before examining values for the oxygen concentrations in UV-O-treated PS, it is revealing to locate specific peaks in the NEXAFS spectra of the reference polymers. For both carbon and oxygen, UV-O-treated PS most closely resembles P4AS in the sense that UV-O forms a high concentration of carboxyl groups, although an assortment of other chemical species is also present (Figure 13). A strong peak between 287 and 289 eV is typical in C=O-containing polymers,²⁷ and by virtue of the fact that P4AS is the only reference polymer to exhibit a peak at 533 eV, the UV-O-treated PS is composed of a significant fraction of C=O bonds. There is also a visible shoulder in the UV-O PS samples at 536 eV, which appears as a distinct peak in P4HS and P4MS, indicating the presence of O-CH₃ or O-H bonds in UV-O PS. The resemblance of UV-O PS to P4AS is confirmed by results from Ton-That et al.,²⁴ which indicated that carbonyls and carboxyls compose $\sim 2/3$ of the surface oxygen. Saito et al. obtained similar results,²⁹ concluding that carboxylic acids are the major products of ozonalysis of aromatics, although carbonyls, peroxides, and ethers also result. It is surprising that C-O-CH₃ species would result from UV-O treatment, since this would involve the breaking of a carbon single bond and the insertion of an oxygen atom, but there is a strong resemblance of UV-O PS to P4AS. The energy involved in the UV light and O₃ molecules



Figure 13. Comparison of baselined and normalized spectra for (a) the carbon edge and (b) the oxygen edge, both taken at -150 V bias.



Figure 14. Oxygen concentration in PS as a function of UV-O exposure time.

may be sufficient for this insertion, but the mechanism for such an insertion is unknown at this juncture.

Oxygen concentrations as a function of UV-O exposure time are shown in Figure 14, obtained from the calibration curve of Figure 12. The trend naturally follows the same seen in Figure 9, since edge jump magnitude is proportional to concentration. Importantly, the concentrations seen in UV-O PS are significantly smaller than those in the reference polymers, e.g., the oxygen concentration ranges from 2% to 42% that of P4AS between 10 s and 5 min exposure, respectively. A plateau in the oxygen concentration is reached between 2 and 5 min exposure, as confirmed by the washed PS UV-O plots of Teare et al.,⁴ which reach a plateau at 3 min. Callen et al.³ claim that oxygen concentration continues increasing up to 30 min exposure, although close examination of their data shows that at 5 min the maximum oxygen concentration is obtained within the error of the measurement. Assuming that UV-O-treated PS has approximately the same bonding composition as P4AS (a good



Figure 15. Advancing, static, and receding contact angles for water on PS exposed to UV-O. Error bars indicate 95% confidence intervals.

assumption by inspection of Figure 13), at 5 min UV-O exposure the atomic oxygen fraction is 7%. This is significantly lower than the values of 16% and 25% reported by Callen et al. and Teare et al., respectively. Such a large discrepancy likely arises from XPS curve deconvolution and incorrect peak assignment in these previous studies, although the UV-O equipment (lamp intensity, humidity, and oxygen pressure) and the method of washing (solvent, time, and intensity) may also affect oxygen concentration significantly. Further insight into the differences between these studies can be found in the contact angle measurements, discussed below.

Interestingly, annealing PS after UV-O exposure produced mixed results. It was expected that above T_{g} the high-energy, oxygenated species would diffuse away from the surface. The oxygen concentrations of PS exposed to 10 and 30 s UV-O, probed using the oxygen edge at a bias of -450 V, decreased at most by only a factor of ~2, even after annealing at 125 °C for 30 min. However, static sessile contact angles increased substantially after the same treatment, from 60° to 85°. Contact angles in general sample the outermost 0.5 nm.^{28,39} Therefore, annealing above T_g allowed oxygenated segments to diffuse a short distance away from the surface but not diffuse deeply into the film. The lack of a concentration gradient resists this diffusion of oxygen species: several prior studies^{5,28} indicate that UV-O penetrates deeply into the film, as far as several hundred nanometers. Of course, the oxidative impact still falls off with depth. Other factors resisting diffusion may include a mild crosslinking effect for polymers in the presence of ozone and photooxidation or the immiscibility (large χ of mixing) of the oxygenated PS and the neat PS. There is no specific evidence from NEXAFS implicating either mechanism, but both are likely given the strong chemical changes caused by UV-O exposure and the slow interpenetration of polymers that do not possess specific intermolecular interactions. It should be further noted that since the impact of annealing above $T_{\rm g}$ for extended times was minimal beyond a depth of 1-2 nm, the impact of the short isopropanol rinse at room temperature did not allow for significant reorganization of the oxygenated PS.

Finally, a complementary analysis of the surface changes can be obtained from sessile contact angle (CA) measurements. Figure 15 provides the advancing, static, and receding CAs measured for water on UV-O-treated PS. As expected, the CA decreases sharply after short UV-O exposure times and then plateaus at longer times. Values for the static CA closely match those of Callen et al.,³ starting from for neat PS and reaching a plateau

⁽³⁹⁾ Morra, M.; Occhiello, E.; Garbassi, F. Adv. Colloid Interface Sci. 1990, 32, 79–116.



Figure 16. Contact angle hysteresis between advancing and receding measurements. Error bars indicate 95% confidence intervals.



Figure 17. Contact angle as a function of oxygen concentration [O], calculated as described in the text. Lines represent best linear fits to the [O] and [π^* O] data.

near after long UV-O exposure times. This is significantly higher than the plateau of found by Teare et al.,⁵ corresponding to the higher oxygen content found by the same study. Although the static CA plateaus near, however, the receding CA is depressed much further by the UV-O treatment, to $\sim 20^{\circ}$. The difference between the advancing and receding CAs (seen in Figure 16), or the CA hysteresis, provides crucial information as to the chemical heterogeneity and roughness of the surface.^{40,41} In particular, Decker et al. found the CA hysteresis of organic surfaces modified with UV-O to be dependent primarily on chemical heterogeneity.⁴² Teare et al. similarly demonstrated by atomic force microscopy that UV-O exposure results in grains of oxidized material that are easily washed off (of low molecular weight), and therefore, the surface roughness only increases slightly between 0 and 5 min UV-0 exposure for the washed films. In fact, both the CA hysteresis (Figure 16) and the inverse of the dynamic CA (Figure 15) closely mirror the oxygen content observed by NEXAFS (Figure 9).

The surface energy measured by the CA can be directly correlated to oxygen concentration, and this is shown in Figure 17. It is expected that CA would linearly decrease with increasing oxygen concentration: in a study of self-assembled monolayers (SAMs) of various functionality, Ukiwe et al. found that the fraction of carbonyls to methyls at the SAM end is proportional

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A. W. Colloids Surf., A: Physicochem. Eng. Aspects 1998, 142, 219–235.
(42) Decker, E. L.; Garoff, S. Langmuir 1997, 13, 6321–6332.



Figure 18. Contact angles of the UV-O PS in context of the reference polymers. Values for UV-O PS were obtained using the oxygen edge magnitudes at -450 V bias.

to CA.⁴³ CA is therefore plotted against three data sets in Figure 17: (1) bulk oxygen concentration [O], where values of [O] were obtained from NEXAFS edge jumps taken at -150 and -250 V (see Figure 13); (2) surface [O], obtained from edge jumps taken at -450 V; and (3) surface [π^* O], obtained as the product of π^* bond fraction and the surface [O]. CAs as a function of bulk [O] form a nonlinear trend, but as a function of surface [O] we find a much more linear correlation. This is expected as surface tension probes a very shallow distance into the film surface, demonstrated in particular by the annealing experiments detailed above. Utilizing the π fraction does not increase the R^2 value of the linear fit, indicating that a single type of oxygen bond is not alone responsible for decreases in CA but that both singly and doubly bonded oxygens contribute.

UV-O PS can be put in the context of the reference polymers using the same contact angle to oxygen concentration correlation. Figure 18, constructed from the surface [O] data in the previous figure and the theoretical [O] concentrations of Figure 12, displays a fairly linear trend. Certainly scatter in the data arises from the various chemical functionalities contained in the variety of polymers selected and the degree that oxygen species point toward the surface. The UV-O-treated PS data fills out the region of low oxygen concentration between PS and P4HS.

4. Summary

A nearly complete picture of the steps in UV-O interaction with PS emerges from the evidence. Ozone begins by reacting primarily with the double bonds on the phenyl rings, forming carbonyl groups (Figure 10). Double bonds are more susceptible to oxidation due to more favorable chemical energetics and stronger absorption at the UV wavelengths. Within 1 min of exposure the ratio of double to single oxygen bonds stabilizes at a lower value. Depending on the exposure time and strength, oxygen may penetrate the film to several hundreds of nanometers,^{5,28} and within the limits of the NEXAFS (4 nm), a fairly uniform distribution of oxygen within PS is implanted (Figures 7 and 9). Before oxygen accumulates in large concentrations, however, it preferentially degrades the uppermost layer of the film by removing oxygenated low-molecular-weight oligomers. This is confirmed by the significant impact that washing has on removing low-molecular-weight species and decreasing the oxygen content of the polymer surface.^{3,5} The failure to accumulate high concentrations of oxygen is seen in the nearly constant carbon edge jump (Figure 9), the low concentration of oxygen even at 5 min exposure (58% of that in P4AS), and the

⁽⁴⁰⁾ Chibowski, E.; Ontiveros-Ortega, A.; Perea-Carpio, R. J. Adhes. Sci. Technol. 2002, 16, 1367–1404.

⁽⁴³⁾ Ukiwe, C.; Mansouri, A.; Kwok, D. Y. J. Colloid Interface Sci. 2005, 285, 760–768.

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relatively high contact angle (Figure 15). In addition, at 5 min exposure, the oxygen concentration reaches a plateau of 7 atomic % oxygen. The oxygen species that are implanted, by comparison with the reference polymers, are composed of O–C, O=C, and O=C–O, but also include a minor amount of O–H. It is surprising to find evidence for C–O–C species following UV-O treatment, since it would require a large amount of energy to break the carbon single bonds, but there is sufficient similarity to the reference polymer spectra to confirm the presence of such species. The CA hysteresis reaches a constant value of $67^{\circ} \pm 2^{\circ}$ at 2 min, and this hysteresis arises more from chemical heterogeneity than surface roughness.⁴²

Annealing above T_g allows oxygenated species to diffuse a short distance away from the surface but not further than 1-2 nm; the relatively high concentrations of oxygenated species deep within the sample prevents significant diffusion away from the surface.

Curve fitting of the NEXAFS spectra, depth profiling via a series of retarding voltage biases, and application of calibration standards to obtain absolute oxygen concentrations all proved successful. NEXAFS edge jump magnitudes and sessile contact angles generally produced consistent results, although NEXAFS, even at relatively high retarding bias fields, still probes much deeper into the surface than water surface tension. The results presented here provide a more complete picture than the previous studies of surface chemistry changes upon UV-O exposure by Callen et al. and Teare et al. due to the advantages of the synchrotron technique, quantitative peak analysis, and comparison with reference polymers. There is far less peak deconvolution in NEXAFS spectra than when using XPS, thereby distinguishing chemical changes more easily, and with comparison to reference polymers it is possible to assign the shift and growth of peaks to specific chemical environments (e.g., UV-O-modified PS is most similar to P4AS). The development of calibration curves for both oxygen content, based on reference polymers, and depth probed as a function of bias is crucial for understanding the impact of UV-O on PS. The discussion of the impact of oxygen bond character (the presence of double versus single bonds) on contact angle also distinguishes this study from prior literature.

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Supporting Information Available: Average energy lost per unit path length *S* and inelastic mean free path λ_i for electrons traveling through polyethylene, which closely approximates PS. Values are taken from the work of Ashley.³⁵ This material is available free of charge via the Internet at http://pubs.acs.org.

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