Quantitative orientational analysis of a polymeric material (Kevlar® fibers) with x-ray microspectroscopy

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It has previously been shown that x-ray linear dichroism microscopy can be utilized to image and determine orientation in a polymeric material at high spatial resolution. We have now expanded on this technique and extracted quantitative information about the orientation of specific functional groups in a polymeric system from submicron areas. This is accomplished by acquiring and analyzing spectral data sets rather than just images at specific energies. It has allowed us to compare the relative lateral orientation of various grades of Kevlar® fibers.

Near edge x-ray absorption fine structure (NEXAFS) spectroscopy has proven to be a valuable tool to study the electronic structure of a variety of materials, both in the bulk and near surfaces. This electronic structure is directly linked to the chemical bonding of the materials investigated and displays a rich spectral signature particularly for polymers and other organic materials. With a linearly polarized source, NEXAFS spectroscopy can also be utilized to determine the orientation of specific chemical bonds and has been employed to determine the orientation of small molecules adsorbed on surfaces, the orientation of Langmuir–Blodgett films, and the orientation of polymer surface molecules of technologically important polyimides films and the dependence of near surface orientation on buffing. The direct chemical sensitivity of NEXAFS spectroscopy has been exploited successfully as a microscopy technique. Electron energy loss spectroscopy (EELS) in an electron microscope is an alternative for transmission experiments. The main advantage of NEXAFS microscopy over EELS microscopy is that NEXAFS microscopy produces significantly reduced damage in radiation sensitive materials such as polymers and provides in general higher energy resolution. It is thus not surprising that NEXAFS microscopy has seen numerous applications in polymer science, biology, and organic geochemistry. These same advantages of low damage and good spectral sensitivity are also afforded by the combination of quantitative polarization dependent NEXAFS spectra with high spatial resolution (x-ray linear dichroism microscopy).

X-ray linear dichroism microscopy has previously been utilized to show that there is orientational sensitivity in images at a fixed photon energy. Here, we have performed a bulk orientational analysis of chemical functionalities in a polymer thin film at high spatial resolution. We have utilized the microspectroscopy capabilities of the scanning transmission x-ray microscope at Brookhaven National Laboratory for this work. We present quantitative NEXAFS spectra from a complex polymeric material and their polarization dependence as a function of sample location and analyze the orientational order of these materials.

The polymeric materials utilized here are various grades of poly (p-phenylene terephthalamide) Kevlar® fibers (for chemical structure see inset of Fig. 1). The internal structure of these technologically important, high crystallinity fibers is highly complex and certain aspects of its structure are still subject to debate. In particular, an accurate measure of the lateral orientational order of these fibers is still elusive. We utilize these fibers to demonstrate our technique of quantitative x-ray linear dichroism spectromicroscopy. The fiber grades investigated, Kevlar® 149, 49, and 29 form small microcrystallites and have a crystallinity of >90%, 90%, and 85%, respectively. Kevlar® 149 and 49 are known to have a radial lateral structure, and radial morphological features have also been observed for Kevlar® 29. Prior techniques can, however, not quantify the lateral orientational order and could not conclusively show that Kevlar® 29 is radially ordered in the same way Kevlar® 149 and 49 are. The crystallographic structure of the microcrystallites is also complex. The crystallites have a monoclinic (pseudoorthorhombic) lattice with \(a=0.787\) nm, \(b=0.518\) nm, \(c=1.29\) nm, and \(\gamma=90^\circ\). The \(c\) axis of these crystallites, \(n\)
corresponding to the polymer chain and covalent bonds, is pointing along the fiber axis in either direction. In addition, the orientation of the phenylene planes in crystallites had been estimated. The angle between the phenylene plane of the terephthalic segment ($-\text{CO- C}_6\text{H}_4\text{-CO-}$) and the (100) plane is $34^\circ$, while the angle between the phenylene plane of the $p$-phenylene diamine segment ($-\text{NH- C}_6\text{H}_4\text{-NH-}$) and the (100) plane is $234^\circ$.  

A representative NEXAFS spectrum of a Kevlar \textsuperscript{®} thin film is shown in Fig. 1. We have fitted the spectrum with 12 gaussian peaks and an arctangent stepfunction at 290.4 eV to achieve the best fit. An unambiguous spectral assignment for all features is difficult. However, for the purpose of the work presented here, an accurate assignment is not necessary for all these features. There is little ambiguity that the first three peaks near 285 eV correspond to the $p^*$ transitions of the phenylene, that the peak at 286.24 eV is due to the substituted carbon of $p$-phenylene diamine ($-\text{NH- C}_6\text{H}_4\text{-NH-}$), and that the feature at 287.8 eV is dominated by the carbonyl groups of the terephthalamide ($-\text{CO- C}_6\text{H}_4\text{-CO-}$).  

X-ray micrographs of thin sections (cut at 45° with respect to the fiber axis) of these fibers exhibit a “butterfly” pattern when imaged with linearly polarized photons at photon energies specific to certain chemical functionalities. All $p^*$ transitions are most absorbing at locations where the electric field is perpendicular to the radial position vector (as shown in the inset to Fig. 3). In order to account for small thickness variations we subtract the valence band background below the edge and scale all spectra to be equal to one at 318 eV. We show as examples spectra from parallel and perpendicular locations for one Kevlar \textsuperscript{®} 149 and one Kevlar \textsuperscript{®} 49 fiber in Fig. 3. The differences in the spectral intensities are extracted by simultaneously least squares fitting these spectra with coupled peak widths and peak energies. We define a “molecular orientation parameter” (OP$_f$) for a specific spectral feature as

![FIG. 2. X-ray absorption micrographs of thin fiber sections (cut at 45° with respect to the fiber axis) of (a) Kevlar \textsuperscript{®} 149, (b) Kevlar \textsuperscript{®} 49 and, (c) Kevlar \textsuperscript{®} 29 acquired at 285 eV, a photon energy corresponding to $\pi^*$ excitations of both phenylenes. The vertical bands are sectioning artifacts and predominantly thickness variations.](image1)

![FIG. 3. Spectra from perpendicular (solid) and parallel (dot) locations of Kevlar \textsuperscript{®} 149 (top) and Kevlar \textsuperscript{®} 49 (bottom) fiber thin sections. The larger difference between the Kevlar \textsuperscript{®} 149 spectra with respect to the Kevlar \textsuperscript{®} 49 spectra reflects the higher degree of radial orientation in Kevlar \textsuperscript{®} 149. (Spectra are scaled as described in the text and offset.) Inset shows locations of parallel and perpendicular data points within the cross section.](image2)
from the perpendicular position and oxygen value to study the dependence of the carbonyl group at the spectral peak dominated by the carbonyl functionality for the Kevlar® 149, 0.12 for Kevlar® 49, and 0.09 for Kevlar® 29 fibers. These variations are much larger than just a single functional group of the polymer and not all functional groups are laying in a single plane. For example, the sensitivity to the orientation of the two inequivalent phenylene groups is much reduced because they form an angle of 68° with respect to each other, yet both contribute to the peak near 285 eV. A rotation of the microcrystallites around their axis would also influence the measured OP. Nevertheless, ratios of the orientation parameter represent to first order the relative degree of orientational order for the specific functional groups in these fibers that contribute to that spectral feature. This is the case for variations within fiber grades as well as differences between the averages of the fiber grades. As all the geometric factors effect the analysis in the same way, these factors cancel out when one considers ratios of the degree of orientational order. Within the uncertainty due to variations within fiber grades, the ratios of the OP for the first three spectral features are essentially the same. Our numbers indicate that Kevlar® 149 is about 1.6 and 2.3 times as radially oriented as Kevlar® 49 and Kevlar® 29, respectively. These variations are much larger than those of the relative crystallinity.

Further developments of this technique might include extension to the oxygen and nitrogen K-edge as well as the development of a surface sensitive detection mode. For example, in order to more easily determine the absolute degree of lateral orientational order in Kevlar®, it would be of great value to study the dependence of the carbonyl group at the oxygen K-edge, where its associated spectral feature is well isolated compared to the carbon edge feature that has underlying spectral intensity from C–H σ* transitions and the π* (C–R) transition.

In summary, we have utilized for the first time quantitative polarization dependent NEXAFS spectroscopy from microscopic areas. As a demonstration, we have determined the relative orientational order of various Kevlar® fibers. Our analysis has shown that the orientational order in Kevlar® 149 is significantly larger than in the other fiber grades and we have directly observed the lateral radial orientation in Kevlar® 29. The technique presented should be useful to study orientation in a wide variety of materials that need not be restricted to polymers.

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TABLE I. Numerical values of orientation parameter for various spectral peaks.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Peak energy (eV)</th>
<th>Kevlar® 149</th>
<th>Kevlar® 49</th>
<th>Kevlar® 29</th>
</tr>
</thead>
<tbody>
<tr>
<td>1+2+3</td>
<td>285.0</td>
<td>0.09±0.03</td>
<td>0.06±0.02</td>
<td>0.06±0.03</td>
</tr>
<tr>
<td>4</td>
<td>286.2</td>
<td>0.14±0.05</td>
<td>0.11±0.03</td>
<td>0.06±0.04</td>
</tr>
<tr>
<td>7</td>
<td>287.8</td>
<td>0.20±0.03</td>
<td>0.12±0.01</td>
<td>0.09±0.04</td>
</tr>
</tbody>
</table>

\[ \text{OP}_i = \frac{I_i - I_\parallel}{I_i + I_\parallel}, \]

where \( I_i \) is the peak height (intensity) of the spectral feature from the perpendicular position and \( I_\parallel \) is the peak height from the parallel position.

We have found average values of \( \text{OP}_i \) of 0.20 for Kevlar® 149, 0.12 for Kevlar® 49, and 0.09 for Kevlar® 29 for the spectral peak dominated by the carbonyl functionality at 287.8 eV. We analyzed eight Kevlar® 149 fibers, seven Kevlar® 49 fibers, and five Kevlar® 29 fibers. A relatively wide range of OP values has been observed, reflecting the variation in orientational order within the same fiber grade. Additional values of this orientation parameter for other features in the Kevlar® spectrum can be found in Table I. Due to the uncertainty in spectral assignment we have evaluated the phenylene transitions near 285 eV as a single peak. We have also restricted our analysis to the main spectral features up to 287.8 eV, as these can be assigned and interpreted most clearly. The standard deviations reflect the variations found between fibers, rather than uncertainties of the fitting procedure. The OP values are not the same for the various spectral features because some features have contributions from more than just a single functional group of the polymer and not all functional groups are laying in a single plane. For example, the sensitivity to the orientation of the two inequivalent phenylene groups is much reduced because they form an angle of 68° with respect to each other, yet both contribute to the peak near 285 eV. A rotation of the microcrystallites around their c axis would also influence the measured OP. Nevertheless, ratios of the orientation parameter represent to first order the relative degree of orientational order for the specific functional groups in these fibers that contribute to that spectral feature. This is the case for variations within fiber grades as well as differences between the averages of the fiber grades. As all the geometric factors effect the analysis in the same way, these factors cancel out when one considers ratios of the degree of orientational order. Within the uncertainty due to variations within fiber grades, the ratios of the OP for the first three spectral features are essentially the same. Our numbers indicate that Kevlar® 149 is about 1.6 and 2.3 times as radially oriented as Kevlar® 49 and Kevlar® 29, respectively. These variations are much larger than those of the relative crystallinity.

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