

Radiation-induced degradation of polydiene sulfones as obtained by sulfur K-edge XANES

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Poly(hexadiene-1,3 sulfone), PHS, is a polymer which has demonstrated potential as an X-ray resist material for microfabrication based on X-ray lithography. Sulfur K-edge XANES measurements were performed on PHS after various dosages of exposure to synchrotron-generated X-rays to assess the role of sulfur atoms in the degradation. The effects of irradiation are assessed and compared to those in poly(butene-1 sulfone), PBS, a commercially used e-beam resist.

Keywords: XANES; sulfur; poly(hexadiene-1,3 sulfone); poly(butene-1 sulfone); X-ray lithography; resist

1. Introduction

Due to its high sensitivity, good film-forming capabilities, and high glass transition temperature (T_g), poly(hexadiene-1,3 sulfone), or PHS, has been proposed as a potential X-ray resist for application in microfabrication (Davies, 1996). For the development of more effective X-ray resists, it is desirable to gain an understanding of the mechanism by which the polymer degrades during irradiation. Of unique interest in the case of sulfone resists like PHS (compared to PMMA, for example) is the role played by sulfur atoms in the degradation process. The current study was performed to assess the ability of sulfur K-edge XANES to elucidate possible reaction channels and their relative quantification. This ability is suggested by its sensitivity to changes in the first and higher (e.g. Hitchcock et al., 1988; Chauvistré, et al., 1997) coordination shells. For this study,

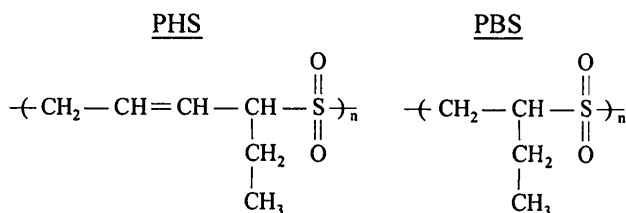


Figure 1
Structures of poly(hexadiene-1,3 sulfone), labeled PHS, and poly(butene-1 sulfone), labeled PBS.

XANES spectra of PHS exposed to various doses of radiation (of equal spectral distribution) have been measured. In addition, similar measurements were made on poly(butene-1 sulfone), or PBS, a commercially used e-beam resist, for comparison. The structures of PHS and PBS are presented in Figure 1.

2. Experimental

Thin films (~ 3 μm) of PHS and PBS were spin-coated on 4" silicon wafers and exposed to bending magnet radiation at beamline XRLM3 (Vladimirsky, et al., 1995) at the CAMD synchrotron operating at 1.3 GeV. Various exposure times were used, which are reported in terms of dosage in units of J/cm².

X-ray absorption near-edge structure (XANES) spectra were collected in total electron yield (TEY) mode at the DCM1 beamline at the CAMD synchrotron facility at Louisiana State University. The maximum of the sharp spectral white line of ZnSO₄ at 2481.44 eV was used for energy calibration (Chauvistré, et al., 1997). XANES spectra were recorded using a TEY detector (Tourillon et al., 1987) to measure the signal and an ionization chamber to monitor I₀, both operating at 100 mbar He. Data reduction involved background removal based on a linear pre-edge subtracted from the TEY/I₀ spectrum and normalization to an edge jump based on a post-edge linear fit extrapolated back to E₀ (set to the position of the sulfone white line).

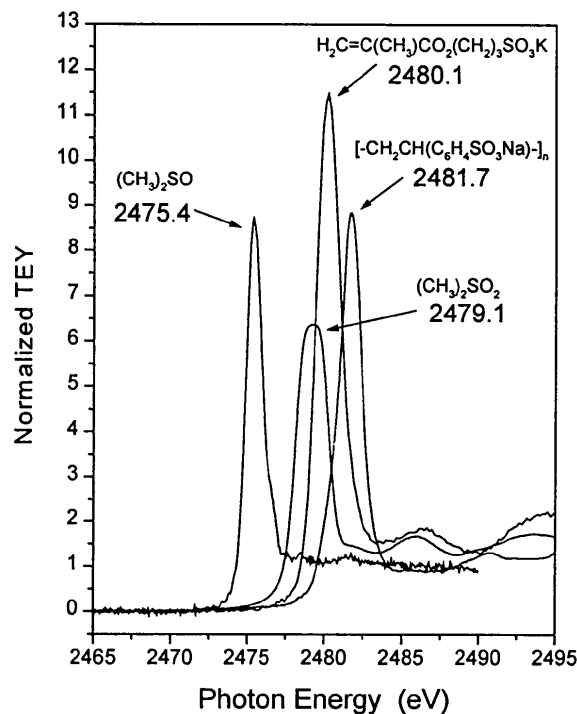


Figure 2
S K edge XANES of reference compounds.

3. Results and Discussion

Sulfur K-edge XANES of reference compounds dimethyl sulfoxide, (CH₃)₂SO; dimethyl sulfone, (CH₃)₂SO₂; 3-sulfopropyl methacrylate potassium salt, H₂C=C(CH₃)CO₂(CH₂)₃SO₃K; and poly(sodium 4-styrenesulfonate), [-CH₂CH(C₆H₄SO₃Na)]_n; are shown in Figure 2. The spectra for PHS and PBS samples exposed at various doses are presented in Figures 3 and 4, respectively.

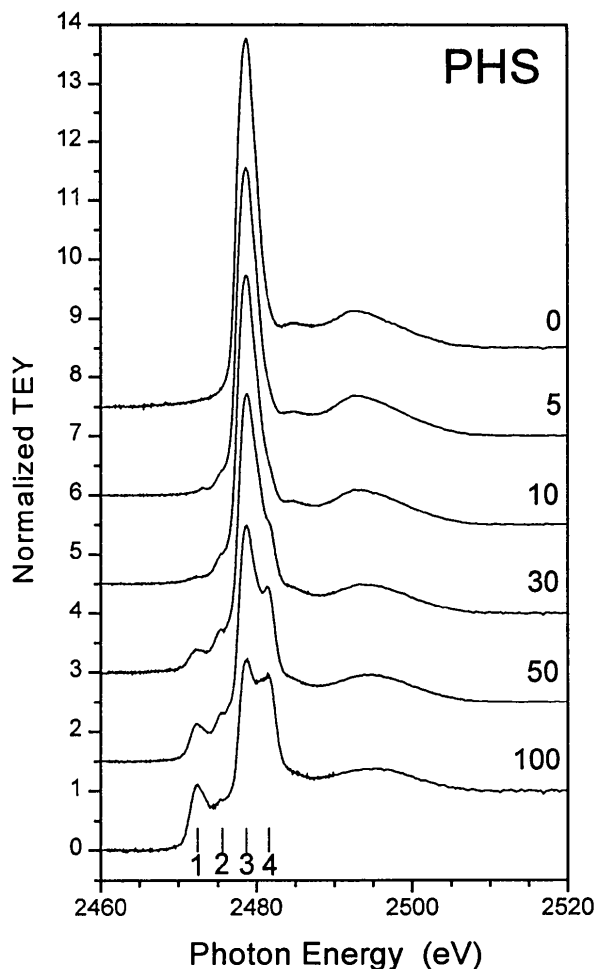


Figure 3
Sulfur K edge XANES of PHS. Spectra are for unexposed PHS (labeled 0), and PHS exposed to give doses of 5, 10, 30, 50, and 100 kJ/cm².

It is apparent from the spectra in Figures 3 and 4 that dramatic changes occur in the sulfur environment upon irradiation. Strong new features arise indicating the presence of various functional groups. The main features in the PHS spectra are labeled 1-4 in Figure 3, with feature number 3 representing the white line of PHS before irradiation. The energy positions for features 1-4 in the PHS spectra (based simply on positions of local maxima) are approximately 2472.5 eV, 2475.5 eV, 2478.7 eV, and 2481.6 eV respectively (relative to the white line maximum of ZnSO₄ at 2481.4 eV).

The first three peaks can be assigned in a straightforward manner. Peak number 3 at 2478.7 eV is obviously the sulfone peak, which can be followed from the initial structure. Peaks 1 and 2 represent reduced sulfur species. Peak number 2 at 2475.5 eV indicates the presence of a sulfoxide group (similar to dimethyl sulfoxide as in Figure 2 and in the study by Sze et al., 1988). Similarly, peak number 1 can be interpreted as representing the presence of a sulfide group (similar to dimethyl sulfide as in Dezarnaud, et al., 1990). Feature number 4 at 2481.6 eV represents a shift to a more oxidized state (e.g. sulfonate or sulfate) from the initial sulfone, which would involve the breaking of a S-C bond. A sulfate peak (for example the ZnSO₄ peak at 2481.4 used for calibration) would be expected at this position. Two organic sulfonate compounds were measured as references for this functional group (see Figure 1), H₂C=C(CH₃)CO₂(CH₂)₃SO₃K produced a white line at 2480.1 eV

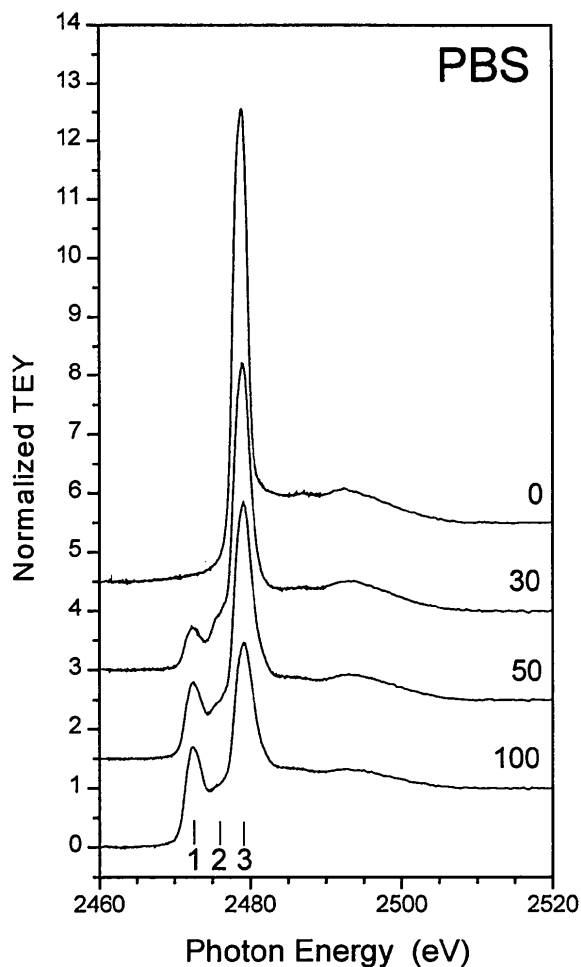


Figure 4
Sulfur K edge XANES of PBS. Spectra are for unexposed PBS (labeled 0), and PBS exposed to give doses of 30, 50, and 100 kJ/cm².

which is consistent (after adjusting for different calibration methods) with spectra of several sulfonates reported by Vairavamurthy, et al. (1994). In contrast, [-CH₂CH(C₆H₄SO₃Na)-]_n, produced a white line at 2481.7 eV. The difference between these two lies in the presence of a phenyl ring bonded directly to sulfur in the latter, causing a surprisingly large chemical shift. This peak (like the sulfate peak) is in close agreement with peak 4 in the irradiated PHS. It is not clear whether the π -system associated with the double bond in the PHS chain could cause a large enough shift to interpret this feature as being due to the presence of a similar sulfonate group. However, in the PHS sample irradiated at a dose of 100 kJ/cm² (see Figure 3), there appears to be evidence of another peak between peaks 3 and 4, in the energy range of these sulfonate compounds. It is thus difficult to specify the functional group(s) responsible for feature number 4. However, it results from a more oxidized state of sulfur (sulfonate or sulfate), and to form either of these requires the breaking of S-C bonds and consequently the scission of the polymer chains. This is generally the critical factor in the sensitivity of positive X-ray resists (e.g. PMMA).

The main features in the spectra from the irradiated PBS are labeled 1-3 in Figure 4. These can be interpreted in a manner identical to peaks 1-3 in PHS. A distinct difference is observed in the PBS spectra compared to PHS in the absence of the strong feature labeled as number 4 in the PHS spectra. This difference is very interesting considering the similarity of the sulfur

environment in the two polymers. The presence of the C=C double bond in the chain apparently has a strong influence on the behavior of the resist. While the presence of peak 4 in the irradiated PHS is clear evidence of chain scission at the sulfur site, its absence in the PBS spectra cannot be interpreted to the contrary. An alternative reaction channel is the formation of SO₂, as reported by Yates, et al. (1993) for PBS irradiated over the photon energy range 20–1000 eV. This species, even if trapped in the sample, would be difficult to distinguish in the XANES spectra due to the overlap of its main features (see Bodeur & Esteva, 1985) with those of the sulfone and reduced species already identified.

In both PHS and PBS, the structural changes can be clearly followed as a function of radiation dosage, with the sulfone white line decreasing in intensity and the peaks representing the newly formed sulfide, sulfoxide, and (in the case of PHS) sulfonate/sulfate increasing with increasing dosage. This demonstrates that S K-edge XANES spectroscopy exhibits great potential as a means to correlate resist sensitivity to structural changes.

4. Conclusions

The sulfur K-edge XANES of irradiated PHS and PBS show strong changes in the local sulfur environment. The unirradiated spectra of both have one strong white line representing the sulfone group. After irradiation, the PHS spectra reveal the formation of sulfide, sulfoxide, and a more oxidized sulfonate or

sulfate group. The irradiated PBS spectra display evidence of sulfide and sulfoxide groups, but no strong feature for the more oxidized sulfur species. In both cases, the changes can be correlated to the absorbed dosage. The potential for S K-edge XANES as a tool in characterizing this system is evident and more detailed studies are in progress, including correlation of spectral changes to resist development and the effect of spectral distribution.

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