

X-ray absorption spectroscopy of ultraviolet-irradiated polyacetylene derivative

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1 Introduction

Poly(bis-alkylthioacetylene) (PATAc) [1-2] is one of the trans-PA derivatives, which is easily soluble in halogenated hydrocarbons and aromatic solvents. PATAc can be doped by only an ultraviolet (UV) / laser irradiation to become permanently conducting materials from initially insulating materials and produce micro-patterning of electrically conducting wires for integrated circuit designs. The electrical conductivity in PATAc is supposed to relate with the formation of a π -conjugated carbon chains linked by sulfur. However, there is little spectroscopic data about photoreaction products formed in UV-irradiated PATAc. In order to investigate the reaction process of poly[bis(methylthio)acetylene] (PATAc-Me), especially to clarify the production of sulfur compound by UV irradiation, we used sulfur *K*-edge X-ray absorption spectroscopy (XAS).

2 Experiment

Experiments were performed at beamline BL-27A with energy resolution of 0.9 eV. The XAS spectra were measured using monitoring sample drain current near the S *K*-edge (2465–2505 eV). Such energies were chosen to excite the S 1s core electron to unoccupied orbitals of PATAc-Me. PATAc-Me films were fabricated on silicon substrate by drop-casting from dilute solution (1.5 mg / g). All spectra were recorded at room temperature in the vacuum conditions. The XAS spectra were normalized to the incident X-ray flux measured by Al thin film. Photo-reaction process was measured with irradiation of UV light using a 100 W arc Hg lamp.

3 Results and Discussion

Figure 1 shows the S *K*-edge XAS spectra of PATAc-Me films at $\theta = \sim 55^\circ$ (magic angle) in various irradiation time of Hg lamp. A linear pre-edge was removed for each spectrum and the data were normalized by the height of the edge jump. There are one strong feature and three weak features in the XAS of PATAc-Me. The most intense peak 1 can be assigned mainly to S 1s $\rightarrow \sigma^*(\text{S-C})$ and partly to S 1s $\rightarrow \pi^*(\text{C=C})$ unoccupied states. The difference in both peak positions is ~ 1 eV or less. Thus, it is difficult to be separated from one another by peak-fitting method in the present energy resolution. A weak peak 2 can be attributed to S 1s $\rightarrow \sigma^*(\text{C-S})$ unoccupied state. The broad, higher-energy peaks 3 and 4 correspond to shape resonance states of $\sigma^*(\text{C-C})$ and $\sigma^*(\text{C=C})$, respectively. Only the intensity of the peak 1 decreases with increasing exposure time of UV irradiation. In

contrast, two new peaks A near peak 2 and B near peak 3 appeared, and increase with increasing exposure time of UV irradiation. It has been known that the sulfur *K*-edge XAS allows a determination of sulfur chemicals such as thiol, disulfide, sulfoxide and sulfone groups. The peaks A and B observed at ~ 2476.8 eV and ~ 2481.2 eV typically imply sulfone and sulfonate, respectively [3].

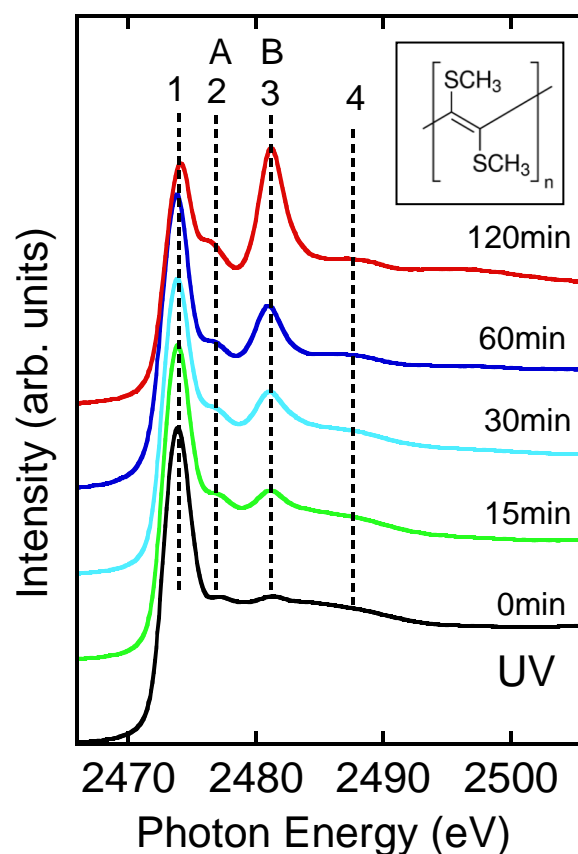


Fig. 1: XAS spectra of UV-irradiated PATAc-Me film near the S *K*-edge.

References

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