

Soft X-Ray Characterization of a Polymerized Self-Assembled Monolayer

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Abstract No. Mars8612

Beamline(s): U7A

Introduction: Self-assembled monolayers are used in applications ranging from sensor design to photolithography. Incorporation of a polymer backbone within the monolayer introduces novel structural properties, such as a buried interface and increased chemical, mechanical, and thermal stability. Varying the structure of the thiol chains and the polymerization time can control the structure of the interface. Near Edge X-Ray Absorption Fine Structure (NEXAFS) experiments will provide detailed structural information necessary for understanding physical and chemical properties of polymerized monolayer assemblies. NEXAFS at the C-K-edge has been used to characterize the structure of a 15,9-polydiacetylene self-assembled monolayer.

Methods and Materials: 200 nm gold films were prepared, using a custom-built UHV system, by evaporating gold onto freshly cleaved mica then annealing for 2 hours. Monolayers were fabricated by immersing the substrates into a 1-mM solution of dinonacosyl-10,12-diyl-disulfide in chloroform for 48 hours. Strict light control was maintained during this step. The substrates were removed, rinsed with chloroform and deionized water, then dried under nitrogen. The 15,9-diacetylene monolayers were polymerized under nitrogen with a low-intensity UV lamp at a distance of 2 cm for times of 2 - 60 minutes. The 15 refers to the length of the chain above the polymer backbone, while the 9 refers to the chain length below the backbone. NEXAFS spectra were recorded in the partial electron yield mode with charge compensation.

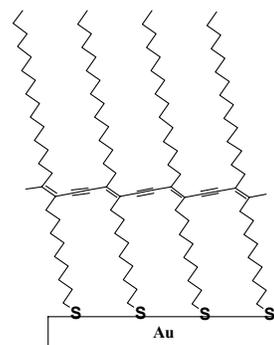


Figure 1. Structure of a polymerized self assembled monolayer.

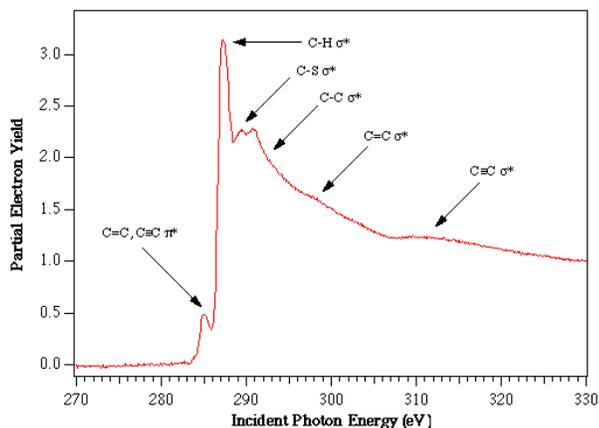


Figure 2. C-K-edge spectrum taken at normal incidence for a 15,9-polydiacetylene self-assembled monolayer.

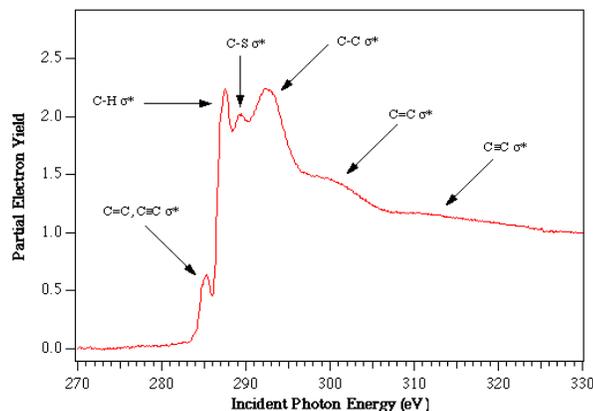


Figure 3. C-K-edge spectrum taken at glancing incidence for a 15,9-polydiacetylene self-assembled monolayer.

Results: Figure 2 shows the C-K-edge NEXAFS spectrum taken at normal incidence for a 15,9-polydiacetylene monolayer polymerized for 12 mins. The following peaks, due to transitions from C 1s orbitals to unfilled molecular orbitals, are present: 285.0 eV C=C, C≡C π^* , 287.2 eV C-H σ^* , 289.5 eV C-S σ^* , and 311.5 eV C≡C σ^* . The peak present at 290.7 eV is due to the overlap of the peak at 289.5 eV and the C continuum function. Figure 3 shows the C-K-edge NEXAFS spectrum taken at glancing incidence for the same 15,9-polydiacetylene monolayer. The following peaks are present: 285.4 eV C=C, C≡C π^* , 287.5 eV C-H σ^* , 289.4 eV C-S σ^* , 292.4 eV C-C σ^* , 300.2 eV C=C σ^* , and 311.4 eV C≡C σ^* .

Conclusions: Differences between the spectra at normal and glancing incidence clearly indicate that the polymer backbone lies parallel to the surface plane, while the alkyl chains are slightly tilted away from the surface normal.

Acknowledgments: The authors acknowledge financial support by the National Institutes of General Medical Sciences, National Institute of Health (grant no. GM 52555-01 A1).

References: M. Mowery, M. Cai, H. Menzel, C. Evans *J. Vac. Sci. Technol. A* **1999**, *17*, 2136-2141.

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