

Soft X-Ray Characterization of Poly(imidazole) Thin Films

A. Marsh, D. Burnett, P. Rasmussen, J. Gland (U. Michigan), D. Fischer (NIST)

Abstract No. Mars1678

Beamline(s): U7A

Introduction: Polyvinazene, a new poly(imidazole) based on the monomer 2-vinyl-4,5-dicyanoimidazole, is a polymer which has high temperature stability and can be easily processed from solutions in concentrated aqueous ammonia into thin, yellow films. The pK_a of the imidazole hydrogen is about 5.5, and when removed, the anion is delocalized by the cyano groups. As a result, the ring is capable of binding low-valent metals with d electrons to back donate, so complexes of the polymer with Cu(I) could be created by coating the surface of the polymer film with the low-valent metal. Thin films of polyvinazene and polyvinazene-Cu(I) have been characterized using Near Edge X-ray Absorption Fine Structure (NEXAFS) at both the C-K-edge and N-K-edge.

Methods and Materials: Thin films of polyvinazene were made by casting several drops from a 1% (w/v) solution of the polymer in aqueous ammonia onto 1 cm² Si substrates. The molecular weight of the polyvinazene sample was about 200,000 g/mol. Cu(I) was dip-coated onto the surface of a polyvinazene film from a solution of tetrakisacetonitrile copper(I) hexafluoroborate in acetonitrile. NEXAFS spectra were recorded in the partial electron yield mode with charge compensation.

Results: Figure 2 shows the C-K-edge spectrum taken at normal incidence for a polyvinazene thin film. The following resonances resulting from transitions from the 1s orbital to unfilled molecular orbitals are present in the spectrum: 286.1 eV $1\pi^*$ and $C\equiv N \pi^*$, 288.3 eV C-H σ^* , 289.9 eV $2\pi^*$, 292.7 eV C-C, C-N σ^* , 300.4 eV C=C, C=N σ^* , and 310.2 eV $C\equiv C, C\equiv N \sigma^*$. Figure 3

shows the N-K-edge spectrum taken at normal incidence for a polyvinazene thin film. The following resonances resulting from transitions from the 1s orbital to unfilled molecular orbitals are present in the spectrum: 398.9 eV $1\pi^*$ and $C\equiv N \pi^*$, 400.8 eV N-H σ^* , 402.7 eV $2\pi^*$, 406.9 eV C-N σ^* , 413.9 eV C=N σ^* , and 422.7 eV $C\equiv N \sigma^*$. Comparison of spectra collected at normal and glancing incidence clearly indicates that the imidazole rings are oriented close to the surface plane. For the polyvinazene-Cu(I) film, spectra were collected at the "magic" angle of 55 degrees incidence so that resonances were independent of orbital orientation. For the polyvinazene-Cu(I) spectra, the same peaks are present, but some are shifted in energy and some have decreased in intensity. For the

N-K-edge spectra, shown in Figure 4, the

$1\pi^*$ peak shifts to lower energy, which indicates that the ring is binding to Cu(I) in a way that is changing the pi system, and the N-H σ^* peak decreases in intensity. In addition, the C-C, C-N σ^* , and C=C, C=N σ^* peaks also shift to lower energy, which indicates a change in bond lengths within the imidazole ring.

Conclusions: From the preliminary NEXAFS results, it can be concluded that Cu(I) replaces the H on the imidazole ring and is coordinated to a second ring through its pi system.

Acknowledgments: A. Marsh would like to acknowledge the NSF-IGERT Materials program at the University of Michigan for fellowship support.

References: P. Rasmussen, S. Reybuck, D. Johnson, R. Lawton, U.S. Patent 6096899, 2000.

J. Stöhr, *NEXAFS Spectroscopy*, New York: Springer, 1996.

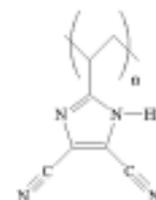


Figure 1. Repeat unit structure of polyvinazene.

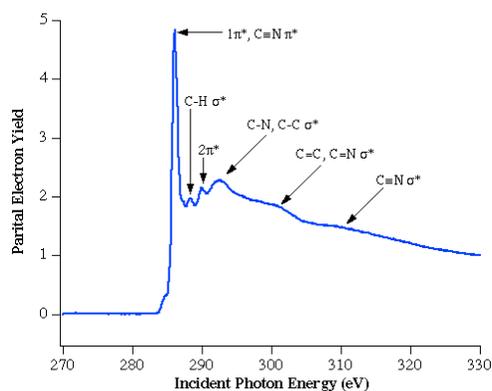


Figure 2. C-K-edge spectrum of a polyvinazene thin film.

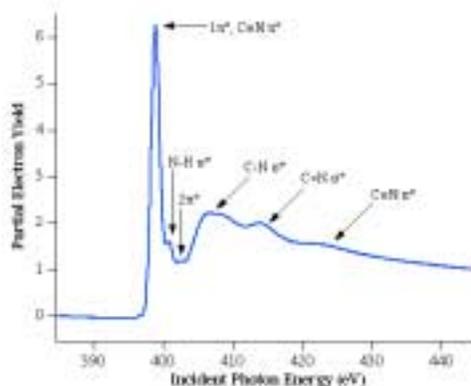


Figure 3. N-K-edge spectrum of a polyvinazene thin film.

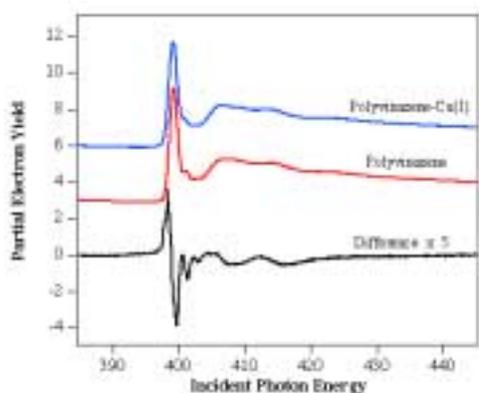


Figure 4. N-K-edge spectra for Cu(I) complexed to polyvinazene. The difference spectrum was found by subtracting the spectrum for polyvinazene-Cu(I) from the spectrum for polyvinazene.