Characterization of Polymer Conformations using EELS

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The development of modern electron energy-loss spectroscopy (EELS) techniques coupled with the new design of TEM allow one to probe both local elemental information and structural properties of polymeric materials.[1] The specific features in low-loss and K-shell core-loss spectra of light elements (e.g., C, N, and O) have been utilized to characterize the chemical compositions and bonding states of polymers.[2] The spectroscopic signals collected from the spatially resolved EELS can be also used to generate a spectrum image in a TEM/STEM, which enables the direct visualization of nanoscale morphologies of polymer systems possessing more than one phase.[3] *Ab initio* density functional theory (DFT) is often used to simulate and understand EELS spectra of solid state materials in both low-loss and the fine structure of core level excitations (i.e., ELNES).[4-5] In combination with DFT calculations, the detailed information about the conformational dependence of EELS spectra for polymers can be obtained when experiments are conducted on a TEM/STEM with a monochromator.

We have performed EELS on a 200 kV Zeiss Libra 200 TEM/STEM equipped with a monochromator to investigate molecular conformations in different types of polymers. Both low-loss and carbon K-edge EELS spectra have been acquired with the highest energy resolution of 0.15 eV. The polymers being studied include: (1) simple long chain hydrocarbon and fluorocarbon polymers: polyethylene and polytetrafluoroethylene (PTFE); (2) perfluorosulfonic acid ionomers which have a PTFE backbone and sulfonated perfluoroether side chains: Nafion and Aquivion (a short-side-chain version of Nafion); (3) a hydrocarbon based polymer containing phenyl groups on the backbone: polystyrene; and (4) polymers consisting of aromatic and sulfur units on backbones: polysulfide, polysulfone and poly(ether sulfone).

Results of using this approach to characterize chain conformations of PTFE are shown in Figs. 1 and 2. The experimental spectra show several unique features in the low-loss region and the onset of the carbon K edge for PTFE. DFT methods are employed to calculate the low-loss and core-loss spectra of PTFE with the consideration of effects of phase transitions, chain orientation, and polarization. The shape and width of the characteristic peaks in the experimental spectra are well reproduced in the DFT calculations. By comparing the spectra from experiments and theory, we have demonstrated an application of combining high resolution EELS and DFT calculations to discriminate changes of chain conformation and orientation for PTFE in different phases.

References:

Figure 1. Simulated valence EELS spectra for PTFE of different conformations (planar, H136, H157 and defected) are compared with experimental results. Peaks due to interband transitions (a and b) in the experimental spectrum are predicted in the simulated spectra for PTFE in disordered phase (a' and b').

Figure 2. Simulated fine structures of carbon k-edge spectra for PTFE in different conformations are compared with the experimental spectrum. All spectroscopic features observed in the experimental ELNES are well reproduced in the simulation for PTFE with helical reversal defects.