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Probing Polymeric Interfaces with Synchrotron Techniques

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Synchrotron based Near Edge X-ray Absorption Fine Structure (NEXAFS) was utilized to probe the chemistry and structure of polymers in interfacial regions. With NEXAFS, the sample is exposed to tunable plane polarized, monochromatic X-ray radiation from a synchrotron light source. In these experiments, the incident radiation is scanned over the carbon K-edge region, an energy range from (280 to 330) eV. X-rays are preferentially absorbed by the sample when the incident radiation is the appropriate energy to allow the excitation of a core shell electron to an unoccupied molecular orbital. During electronic relaxation, Auger electrons and characteristic fluorescence photons are released. The electrons can only escape from the top surface of the sample (1 to 10) nm. NEXAFS has elemental sensitivity because the characteristic binding energies of the carbon, nitrogen, oxygen, and fluorine core electrons are well separated. In addition, due to the well-defined energy gap associated with a core shell / unoccupied orbital transition, NEXAFS is also sensitive to the bonding characteristics [1].

Because the incident synchrotron radiation is polarized, NEXAFS can also be utilized to probe molecular orientation. Figure 1a. shows a schematic of a poly(styrene) monomer. The $C1s \rightarrow \sigma^*_{C-C}$ transition is oriented with the polymer chain backbone. The $C1s \rightarrow \sigma^*_{C-H}$ transition is oriented perpendicular to the chain backbone. A pendant phenyl ring is normal to the chain backbone and contains a $C1s \rightarrow \pi^*_{C=C}$ transition that is perpendicular to the phenyl group and parallel to the chain backbone. Since the incident X-ray radiation is polarized, with the electric field vector perpendicular to the direction of the light propagation, measuring the NEXAFS spectra at different angles can be utilized to investigate the orientation of these absorption transitions.

Figure 1b. plots the $C1s \rightarrow \pi^*_{C=C}$ peak area for a series of poly(styrene)-like polymers as a function of the angle of incidence for the incoming radiation. Before integration, the spectra were pre and post-edge jump normalized. When the $\cos 2\theta$ is zero, the incident radiation is normal to the film surface. When $\cos 2\theta$ approaches 1, the incident radiation is in glancing mode relative to the film surface. Three polymers were investigated, poly(styrene), poly(4-methylstyrene), and poly(4-tertbutylstyrene). For each polymer, at the normal angle the $C1s \rightarrow \pi^*_{C=C}$ transition is stronger than in the glancing mode, indicating that nominally the phenyl groups are oriented perpendicular to the film surface. However, as the functional group of the ring becomes larger, the orientation is less pronounced (the decrease in peak area when moving from normal to glancing angles). Poly(styrene) has a stronger angular dependence than poly(4-methylstyrene). The least angular dependence is with poly(4-tertbutlystyrene), which has the bulkiest pendant group on the styrene ring. Steric effects from a bulky pendant group on the ring hinder surface orientation. The electron yield detector bias was set at 250 eV, so that only electrons with energy near the characteristic carbon Auger electrons are collected. These electrons escape from the top monolayer of the polymer surface, since the carbon Auger escape depth is approximately 10 Å. Therefore, the electron yield spectra in Figure 1b are extremely surface sensitive.

High energy X-ray Photoelectron Spectroscopy (XPS) is also being pursued as a mechanism to depth profile and investigate buried interfaces non-destructively with the synchrotron light source. One important advantage of high-energy synchrotron based XPS is the tunability of the incident X-ray radiation. If the incident X-ray energy is varied, then the kinetic energy of the ejected electron also changes. This allows improved depth profiling capability over typical laboratory based XPS. Figure 1c shows the "universal curve" describing the effective attenuation depth of an electron as a function of the kinetic energy of the electron [2]. Laboratory based XPS often operates near the minimum of the curve (circle near minimum) where the attenuation length of the electron is only a few monolayers. Operating near this minimum makes XPS extremely surface sensitive, where contamination layers can interfere with analysis. With synchrotron based XPS, the energy can be tuned up the universal curve (circle at higher kinetic energies) to escape depths near 10 monolayers. A larger portion of the signal will originate from below the contamination layer allowing studies of the desired underlying interfacial region and buried interfaces. In addition, the energy can be tuned up and down the universal curve allowing nondestructive depth profiling.

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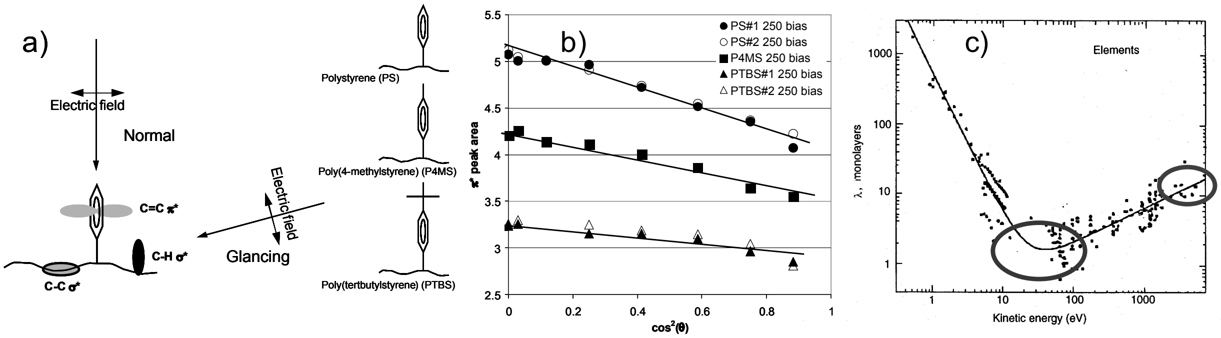

Fig. 1. a) A schematic of a polystyrene molecule and the various orbital transitions that can be probed with NEXAFS; b) Spectra as a function of angle for poly(styrene), poly(4-methylstyrene), and poly(4-tertbutylstyrene); c) The "universal curve" plotting the attenuation length of an electron as a function of the kinetic energy [2].