

## VIII-N Studies of Electronic Structure of Organic Thin Films and Organic/Inorganic Interfaces by Electron Spectroscopies

Electronic structures of organic film surface and organic/inorganic interface are expected to play an important role in organic-device properties. We investigated surface structures and energy alignments to clarify their electronic structures using surface sensitive spectroscopy such as photoelectron spectroscopy combined with synchrotron radiation and metastable atom electron spectroscopy.

### VIII-N-1 Low Energy Electron Diffraction of the System In-[perylene-3,4,9,10-tetracarboxylic Dianhydride] on MoS<sub>2</sub>

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The system In-perylene-3,4,9,10-tetracarboxylic dianhydride ~PTCDA on MoS<sub>2</sub>, prepared by the sequential evaporation of PTCDA and In on a cleaved MoS<sub>2</sub> surface, was studied by low energy electron diffraction. The result indicates that reaction products form an ordered structure on the MoS<sub>2</sub> surface. From the analysis of the diffraction pattern, the presence of six symmetry-equivalent domains of an oblique unit cell of In-PTCDA species results with the dimensions of 9.5 Å, 16.3 Å, and an enclosed angle of 80.2°. In addition, splitting in two domains by a mirror plane exists with the rotation angle  $R5610.8^\circ$  with respect to each of the three equivalent surface crystal axes of the MoS<sub>2</sub> substrate. The new structure is explained by assuming that four In atoms are chemically bonded to the four carbonyl groups of the PTCDA molecules. Furthermore, it is concluded that the In<sub>4</sub>PTCDA species become tilted after a chemical reaction between the PTCDA molecules and the In atoms, which is in agreement with results previously obtained by angle-resolved ultraviolet photoemission experiments.

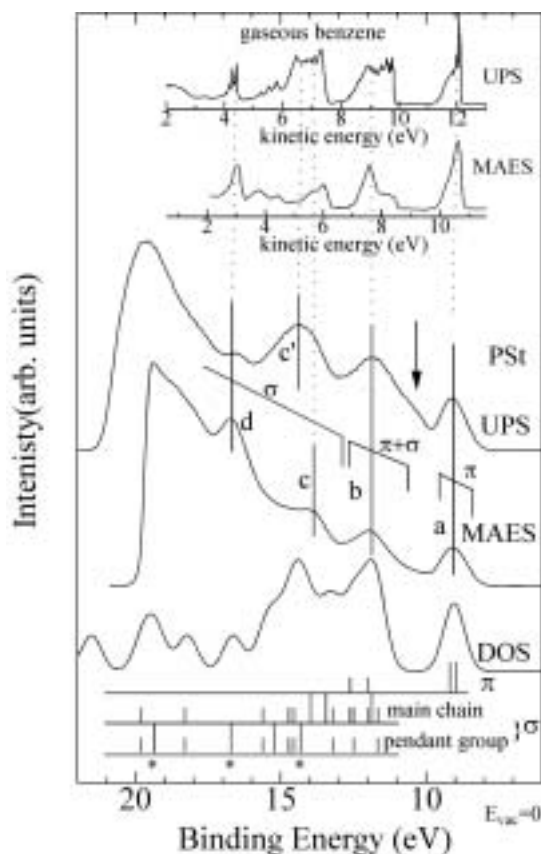
### VIII-N-2 Electronic Structure and Molecular Orientation at Thin Film Surfaces of Pendant-Group Polymers Studied by Outermost Surface Spectroscopy Using Metastable Atoms

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Metastable-atom electron spectroscopy (MAES) and ultraviolet photoelectron spectroscopy (UPS) were used to study the outermost surface of thin films of pendant group polymers: polystyrene (PSt), poly(2-vinylnaphthalene), and poly(9-vinylcarbazole). MAES is selectively sensitive to the outermost surface, and indicated that the surfaces of the polymer films were very clean,

even though they were prepared by spin-casting in a room atmosphere. In Figure 1 observed MAES and UPS of PSt are shown. By comparison with gas-phase spectra and molecular orbital calculations of model molecules with pendant groups, it was confirmed that the principal constituent at the outermost surface of these polymer films is the pendant groups. Furthermore, it was observed that the intensity for  $\sigma$ (C–H) states of the pendant group is stronger in MAES spectra than in UPS spectra, indicating many pendant groups are inclined at large tilt angles.



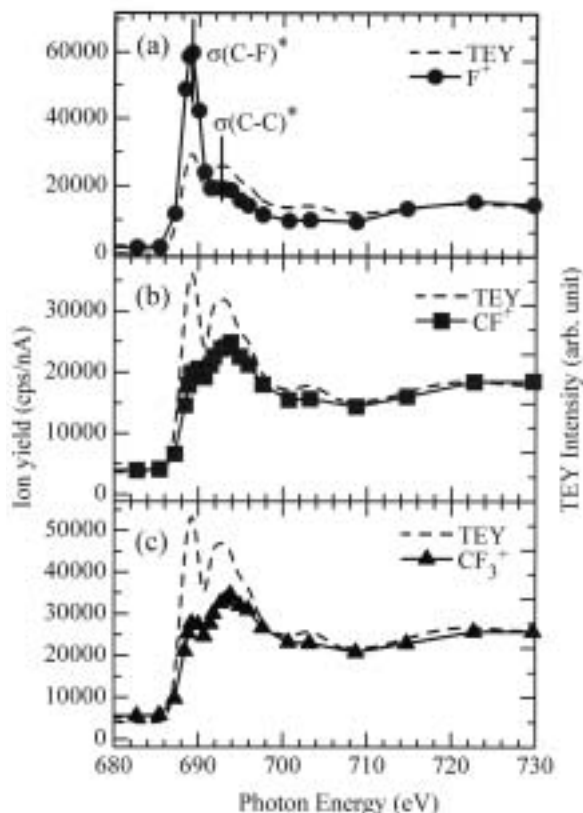
**Figure 1.** MAES and UPS of polystyrene (PSt) thin film. The vertical bars show the molecular orbital energies calculated by *ab initio* MO calculation (6-31G with diffuse function) for the model compound of PSt. The energy levels for the molecular orbital consisted of  $\pi$  orbital at pendant group and  $\sigma$  orbital at polymer chain are represented by the vertical bars marked by asterisk(\*). The density of states (DOS) was obtained by broadening with gaussian function (width = 0.8 eV). The calculated binding energy scale was contracted by 1.35 and shifted to fit with the experimental results. The inset shows the MAES and UPS of gaseous benzene.

### VIII-N-3 Photodegradation of Poly(tetrafluoroethylene) and Poly(vinylidene fluoride) Thin Films by Inner Shell Excitation

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Ion time-of-flight (TOF) mass spectra of poly(tetrafluoroethylene) (PTFE) and poly(vinylidene fluoride) (PVDF) thin films near fluorine and carbon *K*-edges were observed. For PTFE thin films peaks corresponding to  $F^+$ ,  $CF^+$ , and  $CF_3^+$  appeared, while for PVDF  $F^+$  and  $H^+$  were mainly observed. They indicate that for PTFE the polymer chain (C–C bonds) as well as C–F bonds are broken by irradiation of photons near fluorine and carbon *K*-edges, while for PVDF the bond scission occurs mainly at the C–F and C–H bond. Partial ion yields (PIY) of these ions for PTFE and PVDF thin films show strong photon energy dependencies near fluorine (Figure 1) and carbon *K*-edges. The excitation from fluorine  $1s$  to  $\sigma(C-F)^*$  is specially efficient for  $F^+$  ion production for both PTFE and PVDF.



**Figure 1.** PIY spectra of (a)  $F^+$ , (b)  $CF^+$  and (c)  $CF_3^+$  for PTFE thin film near the fluorine *K* absorption edge. TEY spectra (broken curve) are also shown for comparison. TEY spectra are renormalized at  $h\nu = 682.5$  eV and at  $h\nu = 730$  eV to fit PIY intensities.

### VIII-N-4 Intramolecular Energy-Band Dispersion in Oriented Thin Film of $n$ - $CF_3(CF_2)_{22}CF_3$ Observed by Angle-Resolved UV Photoemission and its Theoretical Simulation

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Poly(tetrafluoroethylene) (PTFE)  $(CF_2)_n$  is one of the most fundamental polymers, which is the perfluorinated analogue of polyethylene  $(CH_2)_n$  with a simple repeating  $CF_2$  unit. For such a one-dimensional polymer, we can expect the formation of one-dimensional intramolecular energy-band relation along the chain direction, and the energy-band structures of PTFE have been studied theoretically. Unfortunately, however, there was no experimental result to be compared with such calculated energy-band structure. In this work, we performed angle-resolved UV photoemission spectroscopy (ARUPS) with synchrotron radiation for the oriented thin films of perfluorotetracosane ( $n$ - $CF_3(CF_2)_{22}CF_3$ ; PFT), which is one of the oligomer of PTFE. The sample of PFT with their long chain axis being perpendicular to the surface was prepared by in-situ vacuum evaporation. The normal-emission spectra of the PFT film show incident photon energy dependence due to the intramolecular energy-band dispersion. We also performed the theoretical simulation of the spectra by using independent-atomic-center (IAC) approximation combined with *ab initio* MO calculations. The simulations successfully reproduced the  $h\nu$ -dependence of the observed ARUPS spectra. From the observed and simulated spectra, we deduced the value of inner potential  $V_0$ , which is the parameter defining the energy origin of the free-electron-like final state, and derived reliable energy-band dispersion relation.