Analysis of Valence XPS of Polymers by MO Methods using the Model Molecules

Kazunaka Endo

Tsukuba Research Laboratory, Mitsubishi Paper Mills Ltd.
46 Wadai Tsukuba-City, Ibaraki 300-42, *Japan*

For better assignment of the valence XPS of 66 polymers, we used the semiempirical HAM/3 MO and ab initio deMon density functional methods in that the results can be directly compared with experiment, because it uses the idea of "transition state" rather than Koopmans' theorem to predict vertical ionization potentials (VIPs). We introduce the analysis of valence XPS of representative polymers [$(CH_2-CHR)_n$ ($R = H$, CH_3, OH, $COOH$, F, Cl), $(CH_2-CR_2)_n$ ($R = F$, Cl), $(CH_2-CH_2-O)_n$, $(CH_2-CH_2-NH)_n$] by the MO methods using the model oligomers. The calculated Al K α photoelectron spectra were obtained using Gaussian lineshape functions of an approximate linewidth (0.10 I_k); $I_k = I'_k - WD$, where I'_k is the vertical ionization potential (VIP) of each MO and WD is a shift to account for sample work function, polarization energy and other effects. To explain the broader linewidth for the inner valence spectra, we propose that the lifetime of the $2s$ hole states are shorter because the holes can be filled by $2p$ electrons in ultra-violet emission or radiationless transition. The theoretical spectra showed good agreement with the observed spectra of polymers between 0-40 eV.

TEL 0298-64-3530 *FAX* 0298-64-4319