Theoretical X-ray Photoelectron and Auger Electron Spectra of Polymers by Density Functional Theory Approaches Using Model Molecules

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We propose a new approach for analysis of Auger electron spectra (AES) of polymers by density functional theory (DFT) calculations with the Slater's transition state concept. Simulated AES and X-ray photoelectron spectra (XPS) of three polymers (PE, PcBD, and PS) by our DFT calculations using model dimers are in good accordance with the experimental ones. The combined analysis of AES and XPS can help us to clarify the electronic structure of polymers from the theoretical viewpoint.

1. Introduction

Polymer films elaborated on several substrates modify their surface properties and lead to new materials with useful applications in widely demanding fields of electronics, catalysis, biotechnology, and space. Although until around 1990 year one was unable to obtain the reasonable Auger electron spectra (AES) of insulating polymer films due to the surface damage using a few k eV electron source of the normal Auger instrument, Beamson and Briggs [1] observed AES of polymers using the X-ray photoelectron spectrometer which can avoid the damage problems of polymer films considerably well. They used the ESCA300 spectrometer with Al Ká 1486.7 eV radiation and very thin polymer films, which may be formed by spin casting from dilute solution [ca 0.05-0.10 % (w/w) with a ca .100-Hz rotation speed]. The AES were recorded as the condition, photon energy = 150 eV, slit width = 1.9 mm, X-ray source power = 2.8 kW as details in ref. [1].

Recently, we proposed a new approach for analysis of AES of polymers by density functional theory (DFT) calculations with Slater's transition state concept, and showed that the simulated X-ray photoelectron spectra (XPS) and AES of four polymers by DFT calculations are in good accordance with the experimental ones [2]. The experimental Auger electron and X-ray photoelectron spectra of polymers are directly linked to the theoretical results of the electronic states as obtained by DFT or molecular orbital (MO) calculations using model molecules, since polymers consist of the repetition units.

In the study, we perform the theoretical analysis of X-ray photoelectron spectra (XPS) and Auger electron spectra (AES) for three polymers [$(CH_2CH_2)_n$ poly(ethylene) (PE), $(CH_2CH=CHCH_2)_n$ poly(cis-butadiene) (PcBD), $(CH_2CH(C_6H_5))_n$ poly(styrene) (PS)]. The theoretical valence XPS and AES of the polymers were computed by DFT calculations using model dimmers, as was done in the previous works [2]. In order to simulate the spectra, we used the standard convolution by Gaussian line shape.

2. Theoretical Details

In order to explain solid-state effect, a quantity *WD* is defined in our early works [3]. This quantity *WD* denotes the sum of the work function of the sample (*W*) and other energy effects (*Delta*), such as the polarization energy, the width of the intermolecular band formation, and the peak broadening in the solid-state, and so on. For the comparison between the calculated CEBEs for single molecules of

model molecules and experimental ones of the polymer, we must shift each computed CEBE (or VIP) I'_k by a quantity WD as $I_k(I_{FL}) = I'_k - WD$, to convert to one $I_k(I_{FL})$ relative to the Fermi level.

2.1. CEBEs, VIPs, and AEEs

In the generalized transition state (GTS) method [4], the vertical ionization potential of core or valence region is approximated by

$$I_j = E(1) - E(0) \approx \{F(0) + 3F(2/3)\}/4, \quad (1)$$

where $F(\lambda) = E(\lambda)/\lambda$, and the λ $(0 \le \lambda \le 1)$ is assumed to be a continuous variable and represents the fraction number of electron removed from the Kohn-Sham molecular orbital (KS MO) ϕ_j, with $E(0)$ and $E(1)$ denoting the total energies of the neutral molecule and cation molecule, respectively. According to Janak theorem, $F(\lambda)$ becomes the negative KS orbital energy, $\mathring{a}_i(\lambda)$. For the CEBE calculation, the GTS method can be applied by the 'unrestricted' fashion (uGTS method) as stated in previous works [2,3]. For the VIPs calculation, the restricted generalized diffuse ionization (rGDI) model is introduced as indicated in previous works [2,3]. In the rGDI model, the 2/3 electron is removed evenly from all $\acute{a}$ and $\hat{a}$ valence MOs as each approximated $F(2/3)$ for each valence MO, and the VIPs obtained using Eq. (1).

In recent our work [2], we showed that the calculation of Auger electron energy may be expressed in terms of the single hole ionization energy for an electron in the core orbital, I_c, and the sum of two single ionization energies and correction terms. We can then give the Auger electron energy in following way,

$$E_{cjk} \approx I_c - I_j - I_k^* - WDC, \quad (2)$$

where I_c and I_j denote the CEBE and VIP obtained by Eq. (1). The WDC is the work function, other energy effect, and the correction terms. For the calculation of VIP' I_k^*, the restricted diffuse ionization (rDI) model is used in the $N-1$ electron system. Therefore, one and half of the electrons are removed evenly from the all valence KS MOs in the neutral molecule.

The negative of the resulting orbital energies correspond to calculated VIP's, I_k^*.

2.2. Intensity of Valence XPS and AES

The intensity of valence XPS was estimated from the relative photoionization cross-section for Al $K\alpha$ radiation using the following Gelius intensity model [5],

$$M_j^{XPS} = N \sum_{A,\mu} |C_{A\mu j}|^2 \, \sigma_{A\mu}^{AO}, \quad (3)$$

where the l refers to the atomic subshell on the central atom A, and $|C_{Alj}|^2$ and $\acute{o}_{Al}^{AO}$ represent the electron density populations and the photoionization cross section of the atomic orbitals, ϕ_{Al}, respectively. For the relative atomic photoionization cross-section, we used the theoretical values from Yeh [6].

For the relative Auger transition intensity, the one-center intensity model proposed by Ramarker and co-workers was used [7]. The relative Auger intensities are given as

$$M_{cjk}^{AES} = N' \sum_{\mu,\nu} |C_{\mu j}|^2 |C_{\nu k}|^2 \, P_{c\mu\nu}. \quad (4)$$

Here $|C_{ij}|^2$ and $|C_{lk}|^2$ represent the electron density populations of the atomic orbitals, ϕ_l and ϕ_l, respectively, on the central atom A associated with the molecular orbitals, ϕ_j and ϕ_k. N' and P_{cli} denote a statistical factor and the appropriate weighted subshell Auger transition probabilities, respectively. For the subshell Auger transition probabilities, we used the theoretical values from M. H. Chen and co-workers [8].

3. Results and Discussion

3.1. Valence XPS of PE, PcBD, and PS Polymers

The valence XPS of PE, PcBD, and PS polymers are shown in Figs. 1a)-c), respectively. For PE in Fig. 1a), the peaks at around 19.0 eV and 14.0 eV are due to sσ(C2s-C2s) and pσ(C2s-C2p) bonding of main chain, respectively. On the other hand, for PcBD in Fig. 1b), the peak at around 20.0 eV is due to sσ(C2s-C2s) bonding of [C=C-] and [C-C-] functional groups, and the peak at

around 14.0 eV is due to $s\sigma(C2s\text{-}C2s)$ and $p\sigma(C2s\text{-}C2p)$ bonding of [C-C-] functional groups. One of the reasons why the peaks around 14 eV is weak in the theoretical spectra of PE and PcBD is considered as the underestimation of the $s\sigma$ and $p\sigma$ bonding populations by the use of dimer model.

In the case of PS, each peak in the calculated spectra is good accordance with the experimental one. The peaks at around 21.0 and 17.5 eV are due to $s\sigma(C2s\text{-}C2s)$ bonding of [C-C-] main chain and [C=C-] pendant. The $p\sigma$ bonding contributes to the peaks from around 13.0 eV, while the peaks below 9.0 eV are due to $p\delta(C2p\text{-}C2p)$ bonding.
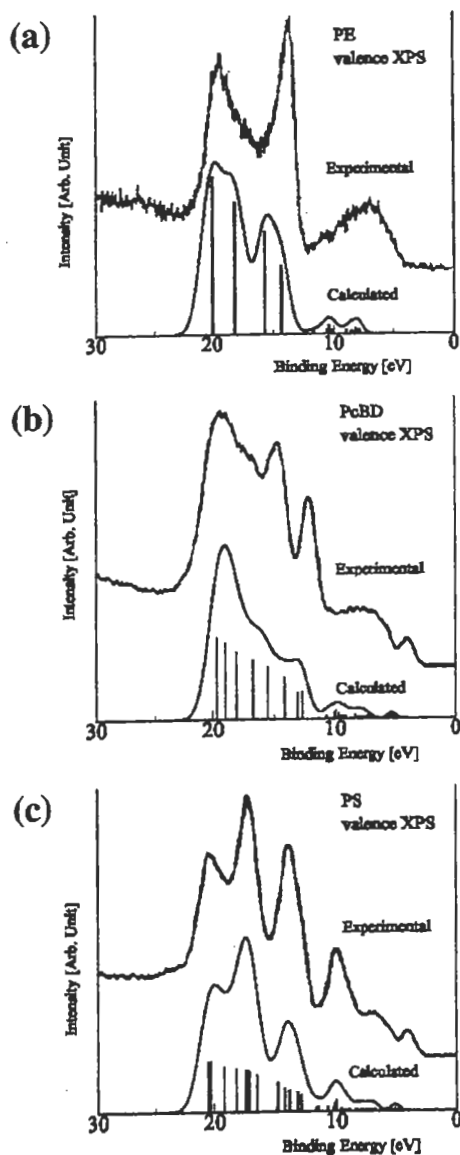

Fig. 1 Simulated valence X-ray photoelectron spectra of three polymers with the experimental spectra, (a) PE; (b) PcBD; (c) PS.

3.2. AES of PE, PcBD, and PS polymers

In this section, we demonstrate the analysis of AES of three polymers from the theoretical viewpoints. The electronic state for AES of polymers can be clarified by our DFT calculations.

Figs. 2-4 show the AES of PE, PcBD, and PS polymers. In simulated spectra of the figures, we showed total carbon KVV AES with solid lines and the individual KL_1L_1, $KL_1L_{2,3}$, and $KL_{2,3}L_{2,3}$ transition spectra with dashed lines, respectively. In the experimental AES, we can see a characteristic difference in the energy range of 270–250 eV. The spectra of PE and PcBD have double broad peaks, while the spectrum of PS has the single broader peak. In the case of PE and PcBD, the peaks are due to the superposition of $KL_1L_{2,3}$ and $KL_{2,3}L_{2,3}$ transitions. Especially, the peak of $KL_1L_{2,3}$ transitions shows intense shoulder at around 260 eV, arising from the transitions between $s\sigma$- and $p\sigma$- or $p\delta$-electron orbitals of main chain. On the other hand, we cannot see the shoulder in the PS, since the pendants make relatively large contributions to these ranges.

In Figs. 3b) and 4b), we also show each contribution of transition for functional groups ([CH=CH-], [CH₂CH₂-] for PcBD, and [CH₂CH-], [C₆H₅-] for PS). In [CH=CH-] group of PcBD, we can see the characteristic peak depending on the $KL_{2,3}L_{2,3}$ transitions between $p\delta$ electron orbitals. In the case of PS, the transitions for the main chain are due to totally average contributions, while those of the pendant are reflected by each transition between $s\sigma$ and $p\delta$ electron orbitals.
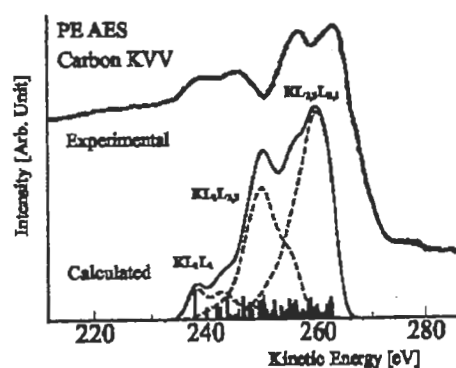

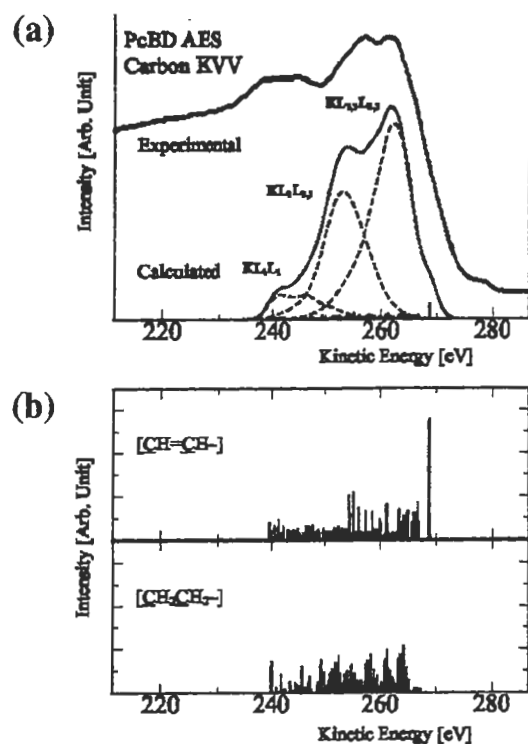**Fig. 2** Simulated KVV Auger electron spectra of PE with the experimental spectra.

Fig. 3 (a) Simulated KVV Auger electron spectra of PcBD with the experimental spectra; (b) each contribution of functional group
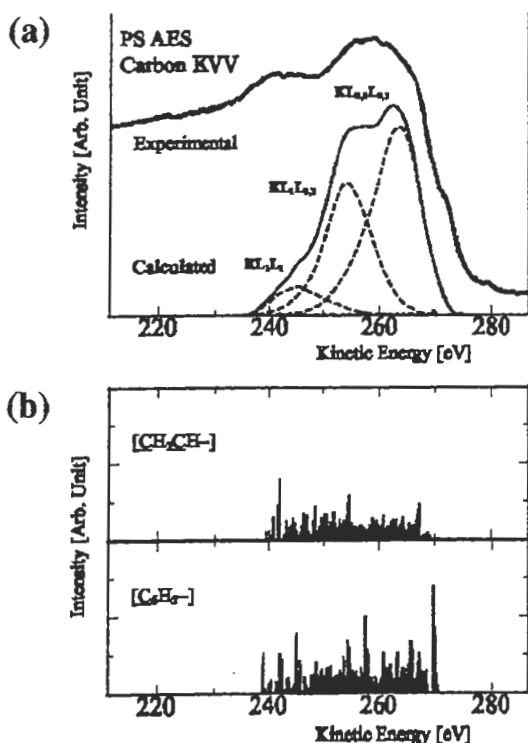

Fig. 4 (a) Simulated KVV Auger electron spectra of PS with the experimental spectra; (b) each contribution of functional group

4. Conclusion

We have simulated the Auger electron and valence X-ray photoelectron spectra of three polymers (PE, PcBD, and PS) by density functional theory (DFT) calculations using model dimers. The theoretical spectra showed fairly good accordance with the experimental ones. Our theoretical approach to XPS and AES is a useful method to clarify the electronic structure for polymers.

Acknowledgments

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