Simulation of XPS of Poly(vinyl alcohol), Poly(acrylic acid), Poly(vinyl acetate), and Poly(methyl methacrylate) Polymers by an *Ab Initio* MO Method Using the Model Molecules

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ABSTRACT: The X-ray photoelectron spectra (XPS) of polymers $[(\text{CH}_2-\text{CHR})_n]$ ($\text{R}=\text{OH}$, COOH , and OCOCH_3) and $(\text{CH}_2-\text{C}(\text{CH}_3)\text{COOCH}_3)_n$ were simulated by an *ab initio* MO method using model molecules of $[\text{H}-(\text{CH}_2-\text{CHR})_3-\text{H}]$ ($\text{R}=\text{OH}$, COOH , and OCOCH_3) and $\text{H}-(\text{CH}_2-\text{C}(\text{CH}_3)\text{COOCH}_3)_2-\text{H}$, respectively. The calculated Al-K_α photoelectron spectra were obtained using Gaussian functions of a fixed linewidth of 2.1 and 1.3 eV for core O_{1s} and C_{1s} energy levels, respectively, and given using Gaussian functions of a fixed approximate linewidth ($0.15E_k$) for valence energy levels. $E_k = E'_k - (E_{\text{DKT}} + WD)$, where E'_k is the eigenvalue of each MO and $(E_{\text{DKT}} + WD)$ is an approximate shift in the energy scale to account for sum of the difference due to the Koopmans' theorem and work function and other energy effects. We assumed that the sum corresponds to the shift we must apply before we can compare the calculated spectrum for the single model molecule with the observed spectrum for the solid. The theoretical spectra without considering the contraction factor in the energy scale showed fairly good agreement with the spectra of polymers as observed, although the shift values were used as 10, 26.5, and 21.5 eV for valence, core O_{1s} and C_{1s} core energy levels of the four polymers, respectively.

KEY WORDS XPS / *Ab initio* MO / Spectral Simulation / Orbital Nature
/ Polymer / Poly(vinyl alcohol) / Poly(acrylic acid) / Poly(vinyl acetate) /
Poly(methyl methacrylate) /

The X-ray photoelectron spectroscopy (XPS) technique^{1,2} from monochromatized X-ray radiation provided precise information on core level binding energies and linewidths, and recorded the distribution of the valence electronic levels which constitute a unique fingerprint of a compound. On the other hand, there have been many theoretical studies of the electronic structures of polymers by the *ab initio* and semi-empirical molecular orbital (MO) calculations. In these calculations, XPS core and ultraviolet-ray photoelectron spectroscopy (UPS) and XPS valence level studies^{3–20} of simple model oligomers of polymers showed from both theoretical and experimental viewpoints that information on the polymer molecular structure can be obtained through

spectral analysis using MO calculations.

To analyze photoelectron spectra of polymers, we need to estimate the wavefunction of the cationic state corresponding to each MO losing an electron after X-ray irradiation. Some studies^{3,4} have shown that the core binding energies of poly(methyl methacrylate) (PMMA) using the monomer model molecules (methyl methacrylate and the substitution compounds) are in good accordance with the theoretical values as calculated by the delta self-consistent-field, ΔSCF , method. However, we can simulate the XPS with Koopmans' theorem and the usual MO calculations of the ground state using *ab initio* and semi-empirical MO methods. In previous papers,^{15–17} we used the shifts of about 10 eV in the energy

axis due to Koopmans' theorem to analyze the XPS of polymers using MO calculations by HONDO and PM3 programs.^{21,22}

The analysis of XPS of polymers by MO calculations as many workers reported, using Koopmans' theorem, had to be contracted and shifted in the energy scale for a good fit with the observed spectra. As is often the case in the framework of the MO techniques, the calculations of ground states yield very wide valence electronic structures and the contractions of the energy scale became necessary to obtain the best fit. The contraction factors, then, vary the system under studies. For example, the values of 0.77 and 0.82 for valence effective Hamiltonian (VEH)^{23,24} and STO-3G basis¹⁰ *ab initio* investigations, respectively, have been used in all the comparison which have been made between the calculated and experimental valence spectra. Thus, in other previous works,¹⁸⁻²⁰ we have performed better assignment of the valence XPS of polymers involving carbon, nitrogen, oxygen, and fluorine by the semi-empirical MO hydrogenic atoms in molecule (HAM)/3 method²⁵⁻³⁰ using the model oligomers. The MO method doesn't need the contraction because it uses the idea of "transition state"³¹ to predict vertical ionization potentials (VIPs) for photoelectron spectra.²⁶

For the simulation of the valence XPS using MO methods, the linewidth of the peak shape represented by a Gaussian or a Gaussian-Lorentzian function was generally used as instrument resolution values (*e.g.*, 0.5, 0.7 eV, and so on). In a previous work,¹⁸ we proposed the Gaussian functions of a fixed approximate linewidth ($0.10I_k$; I_k is evaluated from the vertical ionization potentials using the HAM/3 method), which corresponds to the experimental result that the inner valence spectra are broader. Here, we used the Gaussian functions of an approximate linewidth ($0.15E_k$), to obtain the good simulation of the valence XPS with the Koopmans' theorem and without the contraction factor due to the normal MO

calculation of the ground state using an *ab initio* MO method.

The present paper offered the theoretical simulation for the photoelectron spectra of the polymers (poly(vinyl alcohol) (PVA), poly(acrylic acid) (PAA), poly(vinyl acetate) (PVAC), and poly(methyl methacrylate) (PMMA)) by the *ab initio* RHF-SCF MO method using the model molecules. We have used the syndiotactic model molecules in the previous works¹⁵⁻¹⁷ for the model molecules. The HONDO7²¹ program was used in the present calculations. The simulation of the valence XPS was obtained by taking the eigenvalues for each MO from the MO calculation and using the Gelius model³² for molecular photoionization cross-section (PICS). The theoretical spectra for both core and valence energy levels are constructed from a superposition of the peaks centered at the calculated eigenvalues. A fairly good fit between the theoretical and the observed spectra enables us to determine which region of each spectrum of the polymers is due to the PICS for any atomic orbitals of the constituent elements of the functional groups.

THEORETICAL

The model molecules $[H-(CH_2-CHR)_3-H]$ ($R=OH$, $COOH$, and $OCOCH_3$) and $H-(CH_2-C(CH_3)COOCH_3)_2-H$ were calculated by the *ab initio* RHF-SCF MO method, using the HONDO7 program.²¹ For C and O atoms, we used the (4s2p) basis sets and for H atoms we used the (2s) basis set reported by Huzinaga *et al.*³³ and Dunning *et al.*³⁴ For the geometry of the model molecules, we used the optimized structures from the semi-empirical AM1 (version 6.0) method.²²

The electronic states of the polymers by the MO calculations using the dimer or the trimer model molecules will enhance the effects of the edges of the main chain. Then, we intended to omit the contribution of the edge segments of the main chain, in order to simulate the XPS.

For analysis of core C_{1s} spectra of the four polymers, we omitted the contribution of both edge segments of the main chain.

In the case of the valence spectra, we, however, added the contribution of the edge segments to the simulation, since the MO eigenvalues of the edge segments were very close to those of internal segments of the main chain. In a previous study,¹⁸ we tested by comparing the valence XPS of six polymers $[(CH_2-CHR)_n]$ ($R=H, CH_3, OH,$ and F), $(CH_2-CH_2-NH)_n$ and $(CH_2-CH_2-O)_n$ with HAM/3 results on the model n -mer molecules ($n=2$ to 5). The results suggested that the trimer model is quite adequate in simulating valence XPS of solid molecules.

Because calculations for single molecules based on the dimer or trimer model are compared to experiments on solid, we must shift each computed eigenvalue E'_k by a sum quantity $(E_{DKT} + WD)$ as $E_k(E_F) = E'_k - (E_{DKT} + WD)$. The quantity, E_{DKT} , is the difference due to the Koopmans' theorem, and the other quantity WD ³⁵ denotes a sum of the sample work function, WF (sample), and other energy effects, such as polarization energy, the width of interchain band formation and the peak broadening in the solid state.^{8,9,36-39} In this work, we chose the fixed approximate values of the sum $(E_{DKT} + WD)$ as 10 eV for valence spectra, and 26.5 and 21.0 eV for O_{1s} and C_{1s} spectra, respectively, to provide the good agreement on the location of the main features of the simulated spectrum.

Valence XPS of Polymers

Gelius-Siegbahn³² proposed a model to explain the intensities of the photoelectron lines of molecules. In the LCAO-MO approximation, the PICS of molecular orbitals is related to the cross section for the ionization of the atomic orbitals and the atomic populations in the molecular orbitals,

$$\sigma_j^{MO} = \sum_{A,\lambda} P_{A\lambda j} \sigma_{A\lambda}^{AO} \quad (1)$$

Table I. Relative photoionization cross-section (PICS) of each atomic orbital for H, C, and O atoms (relative to C_{2s})

Atomic orbital		Al- K_α (Nefedov <i>et al.</i>) ⁴⁰
H	1s	0.0093
C	2s	1.0000
	2p	0.0324
O	2s	2.9480
	2p	0.2029

where the coefficient $P_{A\lambda j}$ is the gross atomic population on atom A from AO in MO j , and $\sigma_{A\lambda}^{AO}$ is the relative PICS of AO $A\lambda$. In order to obtain theoretical spectral patterns of the polymers in the range of 0–40 eV, we substituted the calculated MO results and the *ab initio* relative PICS for Al- K_α (1486.6 eV) radiation of Nefedov *et al.*⁴⁰ based on the Hartree-Fock-Slater methods in eq. 1. For the population, we substituted the total value of the double ζ basis set. The atomic PICS as described by Nefedov was obtained under the assumption that the electrostatic atomic field was spherically symmetrical. In this study, we used the relative PICS values for each AO in Table I.

For the simulation of the theoretical valence XPS of the polymers, we constructed from a superposition of peaks centered on the shifted eigenvalues, E_k . The peak shape is represented by a Gaussian function;

$$f(x) = A(k) \exp\{-B(k)(x - E_k)^2\}, \quad (2)$$

where the intensity, $A(k)$, is estimated from the relative PICS for Al- K_α radiation. For $B(k)$, we use the linewidth $WH(k) = 2(\ln 2/B(k))^{1/2}$. The linewidth is introduced for two reasons: (a) we are approximating the density of states by discrete MO levels, and (b) each state has a natural linewidth due to instrumental resolution, electronic relaxation processes, vibrational broadening and so on. By trial and error, we found that simulated spectra have a reasonable appearance when we choose a simple form for the linewidth as $WH(k) = 0.15$

E_k for trimer or dimer molecule.

Core XPS of Polymers

In order to simulate the core XPS of the polymers, we also used the peak shape of eq 2. In the equation, the intensity, $A(k)$, is estimated as an arbitrary unit. For the line width, $WH(K)$, we found the fixed approximate values as 2.1 and 1.3 eV for O_{1s} and C_{1s} , respectively, by trial and error.

EXPERIMENTAL

The experimental photoelectron spectra of the polymers were obtained on a Perkin-Elmer model PHI 5400 MC ESCA spectrometer, using monochromatized $Al-K_\alpha$ radiation. The spectrometer was operated at 600 W, 15 kV, and 40 mA. The photon energy is 1486.6 eV. A pass energy of 35.75 eV was employed for high-resolution scans in the valence band analysis (50 eV of range). The angle between the X-ray source and the analyzer is fixed at 45° . The spot size in the measurement was 3×1 mm.

The use of dispersion compensation yielded the instrumental resolution of 0.5 eV with full width at half-maximum on the Ag_{3d} line of silver. Multiple scan averaging on a multi-channel analyzer helped to guarantee accurate data for the valence band region, although a very low photoelectron emission cross section was observed in this range. The unresolved ESCA signals were deconvoluted and the signal intensities (peak areas) were determined using nonlinear least-squares fitting software, which allowed signals to vary between Gaussian and Lorentzian line shapes.

We used the commercially-available poly-(vinyl alcohol) (PVA) (Wako Pure Chemical Industries, Ltd; M_w 88000), poly(acrylic acid) (PAA) (Scientific Polymer Products, Inc.; M_w 4000000), poly(vinyl acetate) (PVAC) (Aldrich Chemical Co., Inc.; M_w 194800), and poly-(methyl methacrylate) (PMMA) (Aldrich Chemical Co., Inc.; M_w 93300). Samples were

prepared by cast-coating each polymer solution on an aluminium plate, while water and chloroform were used for the PVA and (PAA, PVAC, PMMA) polymers, respectively. A low energy electron flood gun was used to avoid the charging effect on the surface of the sample. The C_{1s} line position of CH_2 groups on the polymer films were used as calibration references of 285.0 eV for these polymers.

RESULTS AND DISCUSSION

The present study was made to simulate the core and valence XPS of polymers using the *ab initio* MO method. We ascertained that all of the occupied MO energy levels of the model molecules as calculated by the MO method, correspond to the core and valence XPS of the polymers, although there was relatively large energy level differences between the theoretical and the observed values. The agreement between the simulated and the observed spectra gives us further assurance about our interpretation of the different regions of the spectra.

Valence XPS of PVA, PAA, PVAC, and PMMA Polymers

In Figures 1a), b) and 2a), b), the simulated spectra of PVA, PAA, PVAC, and PMMA using the trimer or dimer models are compared with the observed XPS. As mentioned earlier, the simulation used Gaussian lineshape function for each MO with the linewidth of 0.15 E_k and $E_k = E'_k - (E_{DKT} + WD)$. The shift values, $(E_{DKT} + WD)$, were estimated as 10 eV for all these polymers. For PVA polymer, Boulanger *et al.*¹⁰ used the empirical contracted and shifted values in the energy scale; $E'_k = 0.82E_k - 2.90$, to obtain the best fit between theoretical and the experimental peak position. They needed to give the shifted value of about 10 eV by an STO-3G basis *ab initio* calculations, to simulate without the contraction value, 0.82. In the study, the linewidth of the peak shape represented by Lorentzian-Gaussian function was used as a fixed value of

Figure 1. a) Valence XPS of PVA with the simulated spectrum and with the spectral pattern of the trimer model molecule as calculated using HONDO program. b) Valence XPS of PAA with the simulated spectrum and with the spectral pattern of the trimer model molecule using HONDO program.

1.5 eV.

Our simulated spectra with the spectral patterns using the model molecules are in fairly good accordance with the observed spectra of the polymers, although a slightly wide valence electronic structures in the energy axis of the simulated spectra are due to the Koopmans' theorem using normal MO calculations of the ground state: It can also be seen that there are small differences between observed and simulated peaks in Figure 1a), b) and 2a), b). For PMMA (Figure 2b)), the simulated peaks in the range of 19–23 eV correspond to the shoulder of observed peak between 19 and 22 eV. We can see the shoulder in the valence spectra of PMMA in Beamson *et al.*² (Their

Figure 2. a) Valence XPS of PVAC with the simulated spectrum and with the spectral pattern of the trimer model molecule as calculated using HONDO program. b) Valence XPS of PMMA with the simulated spectrum and with the spectral pattern of the dimer model molecule using HONDO program.

spectra were obtained in the better resolution than our result obtained in Figure 2b).)

Tables II and III show the observed peaks, the Koopmans' value, the main AO for the PICS, the orbital nature and the functional group for PVA and PAA using the model trimer molecules (similar tables for PVAC and PMMA is omitted, as shown in a previous paper.¹⁷ In Figures 1a), b) and 2a), b), the intense spectra of PVA, PAA, PVAC, and PMMA around 26–28 eV are determined by the O_{2s} main contributions, respectively. It is interesting that the intense spectra, characteristic of O_{2s} contributions, correspond to the splitting theoretical values of $\sigma(O_{2s}-C_{2s})$ -bonding and $\rho(O_{2s}-C_{2p})$ -bonding orbitals

Table II. Observed peaks, Koopmans' values, main atomic orbital photoionization cross section (AO PICS), orbital nature and functional group for valence band spectra of PVA

Peak/eV	Koopmans' value/eV	Main AO PICS	Orbital nature ^b	Functional group
26.0 (24–31) ^a	37.76; 37.56; 37.50	O _{2s}	$s\sigma(\text{O}_{2s}-\text{C}_{2s})-\text{B}$ $p\sigma(\text{O}_{2s}-\text{C}_{2p})-\text{B}$	–O–C –O–C
20.0 (18–23) ^a	29.45; 28.30; 26.48	C _{2s}	$s\sigma(\text{C}_{2s}-\text{C}, \text{O}_{2s})-\text{B}$	–C(main chain), C–O–
14.0 (13–16) ^a	24.10; 22.55; 22.47	C _{2s} (0.8), O _{2s} , O _{2p}	$p\sigma(\text{C}_{2s}-\text{C}, \text{O}_{2p})-\text{B}$	C–O–, C(main chain)
(5–13.5) ^a (3–9) ^a	below 19.10 eV many adjacent levels 13.73; 12.90; 12.58 12.43; 12.20; 11.19	O _{2p} , O _{2s} , C _{2p} , C _{2s} O _{2p} O _{2p}	$p\sigma(\text{O}, \text{C}_{2p}-2s)-\text{B}$ $p\pi(\text{C}_{2p}, \text{O}_{2p}-\text{C}_{2p})-\text{B}$ $p\pi(\text{lone pair})-\text{NB}$ $p\pi(\text{lone pair})-\text{NB}$	C–O–, –C(main chain) –C(main chain), C–O– C–O– C–O–

^a Shows the peak range. ^b B and NB mean bonding and nonbonding, respectively. (C, O_{2s–2p}) means (C_{2s}–C_{2p}) and (O_{2s}–O_{2p}), (C_{2p}, O_{2p}–C_{2p}) denotes (C_{2p}–C_{2p}) and (O_{2p}–C_{2p}), and so on.

Table III. Observed peaks, Koopmans' values, main atomic orbital photoionization cross section (AO PICS), orbital nature and functional group for valence band spectra of PAA

Peak/eV	Koopmans' value/eV	Main AO PICS	Orbital nature ^b	Functional group
26.5 (23–31) ^a	41.08; 40.90; 40.75 37.62; 37.51; 37.32	O _{2s} (0.9), C _{2s} (0.1) O _{2s}	$s\sigma(\text{O}_{2s}-\text{C}_{2s})-\text{B}$ $p\sigma(\text{O}_{2s}-\text{C}_{2p})-\text{B}$	–O–, O=C O=C, –O–
19.5 (17–22) ^a	31.55; 30.25; 28.57	C _{2s}	$s\sigma(\text{C}_{2s}-2s)-\text{B}$	–C–C–(main chain)
15.5 (12–17) ^a	25.76; 25.00; 24.65 22.88; 22.26; 22.01	C _{2s} (0.8), O _{2s} , O _{2p} C _{2s} (0.7), O _{2p} , O _{2s}	$p\sigma(\text{C}_{2s}-2p)-\text{B}$ $p\sigma(\text{C}_{2s}-\text{O}_{2p})-\text{B}$ $p\sigma(\text{C}_{2s}-2p)-\text{B}$ $p\sigma(\text{C}_{2s}-\text{O}_{2p})-\text{B}$	–C–C–(main chain) –O–C=O –C–C–(main chain) –O–C=O
12.0 (9–12) ^a	19.33; 19.22; 19.09 18.83	O _{2s} (0.7), O _{2p} , C _{2s} O _{2s} (0.6), C _{2s} , O _{2p}	$p\sigma(\text{O}_{2p}-2s)-\text{B}$ $p\sigma(\text{O}, \text{C}_{2p}-2s)-\text{B}$	–O–, O=C O=C, –O–
6.0 (3–9) ^a	below 18.66 eV many adjacent levels 13.18; 13.09; 12.78 12.70; 12.52; 12.26	O _{2p} , O _{2s} , C _{2p} , C _{2s} O _{2p} O _{2p}	$p\sigma(\text{O}, \text{C}_{2p}-2s)-\text{B}$ $p\pi(\text{C}_{2p}, \text{O}_{2p}-\text{C}_{2p})-\text{B}$ $p\pi(\text{lone pair})-\text{NB}$ $p\pi(\text{lone pair})-\text{NB}$	–O–, O=, –C– O=, –O– O=, –O–

^a Shows the peak range. ^b B and NB mean bonding and nonbonding, respectively. (C, O_{2s–2p}) means (C_{2s}–C_{2p}) and (O_{2s}–O_{2p}), (C_{2p}, O_{2p}–C_{2p}) denotes (C_{2p}–C_{2p}) and (O_{2p}–C_{2p}), and so on.

except PVA.

Although we have examined the simulation of four polymers using the trimer or dimer model molecules, we think the results suggest that the observed spectra can be simulated by considering the model molecules using Gaussian functions of an approximate linewidth.

The reason is as follows: The approximate linewidth which we used here corresponds to the experimental result that the linewidth of spectra in the inner valence energy levels is broader than in the outer energy levels. As mentioned in a previous paper,¹⁷ the spectral linewidths below about 13 eV are determined

by the splittings of many adjacent MO levels. By contrast, the linewidths in the range of 13–30 eV are governed by the relaxation of the inner valence 2s electron states for the MO energy levels.

Let us discuss the meaning of the Gaussian functions of an approximate linewidth (cE_k : we used $c=0.15$ for this study) which we have used. For the obtained XPS of any substances, we can see that the spectra of the inner binding energy levels (2s-, 3s-, and 4s-orbital levels) in the same shell (L-, M-, and N-shell) except K-shell become broader than those of outer binding energy levels (np- or nd-orbital levels). In this study, the linewidth (2–4 eV) of 2s spectra for the polymers was broader than that

of 2p-spectra (we can assume the lifetime longer than an instrumental resolution of 0.5 eV). Then, let us consider why the inner valence spectra is broader than the outer, from the lifetime of the hole of each level based on the uncertainty principle.

The hole of the 2s-orbital levels of polymers involving second row atoms by the X-ray radiation will be filled by electrons from the outer many adjacent occupied p-orbital levels through ultraviolet-ray emission process and the hole of 2p-orbital levels is far from being filled by electrons, since there are no occupied levels above the 2p-levels. Thus, the lifetime of the 2s-hole will be shorter than that of 2p-hole.

Figure 3. a) Core O_{1s} and C_{1s} XPS of PVA with the simulated spectra of the trimer model molecule using HONDO. b) Core O_{1s} and C_{1s} XPS of PAA with the simulated spectra of the trimer model molecule using HONDO.

Figure 4. a) Core O_{1s} and C_{1s} XPS of PVAC with the simulated spectra of the trimer model molecule using HONDO. b) Core O_{1s} and C_{1s} XPS of PMMA with the simulated spectra of the dimer model molecule using HONDO.

In the case of the core 1s-levels, the hole cannot be filled by 2s electrons according to the selection rule of $\Delta L = \pm 1$, and the hole can relax in two different ways, by Auger process and by the X-ray emission. Thus, the lifetime of the hole may be longer than that of 2s-levels. Therefore, a good fit between our simulation and the observed spectra of polymers seem to confirm that our general interpretation discussed above is reasonable.

Another reason of the broadening of the inner-valence bands in polymers is partly due to the same reason as for gas-phase single molecules: the breakdown of the one-particle picture accompanying shake-up phenomena. The foot and the wing of the broader peak of the inner valence ionization results from the transition which was considered as mixing between single ionization and simultaneous

ionization-excitation (shake-up) configurations.⁴¹⁻⁴⁵

Core XPS of PVA, PAA, PVAC, and PMMA Polymers

The simulated core O_{1s} and C_{1s} spectra, as calculated by the MO method using the model molecules, correspond to the XPS core energy level spectra of the polymers (as shown in Figures 3a)—4b)), although there were large differences in energy levels due to the Koopmans' theorem and work function and other energy effects. For this simulation, we used fixed energy shifts and fixed linewidths for each MO level of the calculated O_{1s} and C_{1s} , since we considered the polymers which consist of three common atoms C, H, and O.

In the case of analysis of C_{1s} spectra, we omitted the contribution of both edge segments

Table IV. Observed O_{1s} and C_{1s} binding energies of four polymers, Koopmans' energies of the model molecules, and the relative intensity, shifted value and the half width of each MO levels for the simulated spectra using model molecule

Polymer	Atom	Functional group	Binding energy	Koopmans' theorem	Relative intensity	Shifted value	Linewidth (halfwidth)
			eV	eV		eV	eV
PVA	O_{1s}	OH	532.2	559.1; 558.9; 558.9	1.0	26.5	2.1(1.5) ^a
	C_{1s}	CH ₂	285.0	305.9; 305.9	1.0	21.0	1.3(1.3) ^a
		CH(OH)	286.5	307.2; 307.2	1.0	21.0	1.3(1.4) ^a
PAA	O_{1s}	C=O	532.7	559.9; 559.8; 559.5	1.0	26.5	2.1(1.8) ^a
	C_{1s}	OH	534.0	561.0; 560.8; 560.7	1.0	26.5	2.1(2.0) ^a
		CH ₂	284.8	306.6; 306.5	1.5	21.0	1.3(1.4) ^a
		CH	285.6	307.1; 307.0	1.5	21.0	1.3(1.7) ^a
		C=O	289.1	311.1; 311.0; 310.7	1.0	21.0	1.3(1.5) ^a
PVAC	O_{1s}	C=O	532.5	559.6; 559.6; 559.5	1.0	26.5	2.1(1.8) ^a
	C_{1s}	-O-	533.7	560.5; 560.4; 560.4	1.0	26.5	2.1(1.8) ^a
		CH ₂	285.0	305.9; 305.8	1.5	21.0	1.3(1.7) ^a
		CH ₃ (-O-)	285.7	306.5; 306.4; 306.4	1.0	21.0	1.3(1.9) ^a
		CH	286.7	307.8; 307.8	1.5	21.0	1.3(1.9) ^a
		C=O	289.2	310.8; 310.7; 310.7	1.0	21.0	1.3(1.8) ^a
PMMA	O_{1s}	C=O	532.0	559.6; 559.0	1.0	26.5	2.1(1.7) ^a
	C_{1s}	-O-	533.6	560.5; 560.3	1.0	26.5	2.1(1.8) ^a
		CH ₃	284.6	305.9; 305.8	1.0	21.0	1.3(1.3) ^a
		CH ₂	285.2	306.6	2.0	21.0	1.3(1.2) ^a
		>C<	285.8	307.1	2.0	21.0	1.3(1.3) ^a
		CH ₃ (-O-)	286.8	307.6; 307.5	1.0	21.0	1.3(1.6) ^a
		C=O	289.0	310.6; 310.3	1.0	21.0	1.3(1.4) ^a

^a The value of parenthesis was obtained from the lineshape analysis of observed O_{1s} and C_{1s} spectra.

of the main chain. The C_{1s} relative intensity of each functional group for the model molecules was considered as the number of the carbon for the functional group in the monomer unit of the polymers in the Table 4. By trial and error, we found the energy shifted values as 26.5 and 21.0 eV for the O_{1s} and C_{1s} spectra, respectively. These values correspond to the differences of 30.0 and 23.7 eV for the O_{1s} and C_{1s} , respectively, between the Koopmans' values of methyl methacrylate and the observed results of PMMA as we calculated from the references.^{3,4}

The linewidth of each MO levels for the O_{1s} and C_{1s} was evaluated as 2.1 and 1.3 eV, respectively. The estimated values agreed well with the values obtained from the lineshape analysis of the observed O_{1s} and C_{1s} spectra (as shown in Table IV).¹⁷ This indicates that we can obtain good assignments with the Koopmans' theorem due to the usual MO calculations of the ground state for N electrons using the *ab initio* HONDO program.

CONCLUSION

We have analyzed the core and valence XPS of PVA, PAA, PVAC, and PMMA polymers by an *ab initio* MO method using model molecules of $[H-(CH_2-CHR)_3-H]$ ($R=OH$, $COOH$, and $OCOCH_3$) and $H-(CH_2-C(CH_3)-COOCH_3)_2-H$, respectively. The theoretical $Al-K_\alpha$ photoelectron spectra were simulated using Gaussian functions of fixed linewidths of 2.1 and 1.3 eV for core O_{1s} and C_{1s} energy levels, respectively, and given using Gaussian functions of a fixed approximate line width, $0.15 E_k$, for valence energy levels. $E_k = E'_k - (E_{DKT} + WD)$, where E'_k is the eigenvalue of each MO due to the usual MO calculations and $(E_{DKT} + WD)$ is an approximate shift to account for sum of the difference due to the Koopmans' value and work function and other energy effects. The valence approximate linewidth ($0.15 E_k$), implying that the spectra of the inner valence levels are broader was

shown to depend on the hole lifetime in the 2s-dominant MO levels filled by the outer 2p-dominant electrons through the ultraviolet ray emission process.

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