Simulated Data of Valence XPS Polymers by MO Calculations Using the Model Molecules. I. Hydrocarbon-Polymers and Polymers containing O-, CO- and COO- Groups

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(Received August 13, 1997, accepted August 27, 1997)

The valence X-ray photoelectron spectra(XPS) of 33 polymers[hydrocarbons(11), O-groups(12), CO-groups(3), and COO-groups(7)] were analyzed by the semiempirical hydrogenic atoms in molecules, version 3 (HAM/3) and demon density-functional calculations using the model oligomers or monomers. Calculated AlKα valence photoelectron spectra were obtained using Gaussian lineshape functions of an approximate linewidth(0.10 I_k for the model molecules): $I_k = I'_k - WD$, as adopted in previous works. The vertical ionization potential(VIP) I'_k was calculated by restricted diffuse ionization (rDI) model. The theoretical spectra showed good agreement with the experimental spectra of the polymers between 0-40 eV.

Introduction

X-ray photoelectron spectroscopy [1-3] has become a powerful tool for providing precise information concerning the core-level binding energies and the valence electronic structure of polymers. The theoretical studies [4-22] on X-ray photoelectron(XPS) and ultra-violet photoelectron spectra of polymers showed that information on the polymer electronic structure can be obtained through MO calculations for simple model oligomers, or using a crystal model of one-dimensional periodicity.

Some XPS studies [8, 10, 11, 23] of simple model oligomers and saturated hydrocarbons demonstrated that information on the conformation and tacticity dependence can be obtained through spectral simulation by MO calculations. Recently, Delhalle et al.[24] found evidence of folded structure at the surface of polyethylene lamellae in the XPS valence band. In our previous papers[16-18, 20], we used syndiotactic model molecules for analysis of XPS of polymers, because we found that the tacticity had little effect on the calculated energy structure, in contradiction to the results of other workers[23, 24].

For better assignment [20-22] of the valence XPS of polymers involving carbon, nitrogen, oxygen and fluorine, we tested the perfomance of the semiempirical hydrogenic-atoms-in-molecule, version 3 (HAM/3) MO method [25-27] in that the results can be directly compared with experiment, because it uses the idea of "transition state" [28] rather than Koopmans' theorem to predict vertical ionization potentials(VIPs).

In recent studies of density functional theory(DFT) using the deMon DFT program[29] which uses the idea of transition state, we simulated the valence XPS of polymers involving C,N, O, F, S and Cl atoms and calculated core-electron binding energies(CEBEs) of the model molecules by considering an energy shift WD to account for solid-state effects[30-34].

We have already calculated the valence spectra of about seventy polymers by both HAM/3 and deMon programs using the model molecules and the present paper, thus, provides the thirty three results of all the polymers. Here, we used the same procedures of HAM/3 and DFT calculations to simulate the valence XPS of the polymers involving C and O atoms [$(CH_2\text{-}CXY)_n$ (X;Y)= {(H;H) (PE), (H;CH_3) (PP), (CH_3;CH_3) (PIB), (H;C_2H_5)(PB), (H;$CHCH_2$) (PBD), (H;C_6H_5) (PS), (CH_3;C_6H_5) (PαMS), (H;C_6H_4-CH_3) (P4MS)}, $(CH_2CHCHCH_2)_n$ PCBD), $(CH_2CHC(CH_3)CH_2)_n$ (PCI), $(C_6H_5C_6H_4C_6H_4C_6H_5)$ (PPHO), $((CH_2)_m\text{-}O)_n${(m)= (1)(PMG),(2)(PEG),(3)(PPG)}, $(CH_2CH(OCH_3))_n$ (PVME), $(CH_2CH(OC_2H_5))_n$ (PVEE), $(CH_2CH(OCH_2CH(CH_3)_2))_n$ (PVIBE), $(C_6H_3(CH_3)_2O)_n$ (PDMPO), $(C_6H_4OC_6H_4OC_6H_4(CO))_n$ (PEEK), $(CH_2CHOH)_n$ (PVA), $(CH_2CH(C_6H_4OH))_n$ (PHS), $(C_6H_{10}O_5)_n$ (CEL), $(C_{12}H_{22}O_5)_n$ (ECEL), $(CH_2CH(COCH_3))_n$ (PVMK),$(CH_2CH(COC_2H_5))_n$ (PVEK), $(CH_2C(CH_3)(COCH_3))_n$ (PMIPK), $(CH_2CH(OCOCH_3))_n$ (PVAC), $(CH_2CHCOOH)_n$ (PAA), $(CH_2C(CH_3)COOH)_n$ (PMAA), $(CH_2CH(COOCH_3))_n$ (PMA), $(CH_2C(CH_3)(COOCH_3))_n$ (PMMA), $(CH_2C(CH_3)(COOC_2H_5))_n$ (PEMA), and $((CH_2)_2OCOC6H_4COO)_n$(PET)]. The simulation of the valence spectra was performed on the model oligomers or monomers using standard convolution techniques by a Gaussian lineshape and using the Gelius model [35] for molecular photoionization cross-section. The linewidth of a peak of ionization energy Ik was taken to be 0.10 Ik (proportional to the ionization energy), as in previous studies [20-22].

Theoretical Background

For the comparison between calculations for single molecules of the oligomer or monomer model and experiments on a solid polymer, we must shift each computed VIPs (or CEBEs), I'_k by a quantity *WD* [36] as $I_k(E_F) = I'_k - WD$, to convert to ionization energy $I_k(E_F)$ relative to the Fermi level. This quantity *WD* denotes the sum of the work function of the sample and other energy effects, such as the polarization energy, the width of the interchain band formation and the peak broadening in the solid state [37-42].

Now, let us consider an electronic process of ionization or excitation for single molecules using Slater's transition-state(TS) method at fixed molecular geometry. We define

$$E(x) = E_0 + xE_1 + x^2 E_2 + x^3 E_3 + x^4 E_4 + \cdots , (1)$$

where $E(0)$ and $E(1)$ correspond to the initial and final states respectively and x is assumed to be a continuous variable. From Eq. 1, the endothermicity we seek is given by

$$\Delta E = E(1) - E(0) = E_1 + E_2 + E_3 + E_4 + \cdots , (2)$$

If we define the first derivative($F(x)=\partial(x)/\partial x$), in Slater's transision-state concept, ΔE is approximated by

$$F(1/2) = E_1 + E_2 + 3E_3/4 + E_4/2 + \cdots \quad ,(3)$$

with an error of

$$d_{TS} = F(1/2) - \Delta E = - E_3/4 - E_4/2 + \cdots \quad ,(4)$$

For ionization of an electron from molecular orbital(MO) ϕ_k, for example, we can apply the Janak theorem [43] and set $F(1/2)$ to $-\varepsilon_k$ at $x = 1/2$.

For the VIPs of the valence regions, we use the so-called diffuse ionization (DI) model which Asbrink et al. [25] proposed in the HAM/3 method. In the rDI model, half of an electron is removed evenly from the valence MOs and the negative of the resulting orbital energies correspond to calculated VIPs. This allows us to obtain all the valence VIPs in a single calculation. The C_2H_2 molecule, with five valence mos and ten valence electrons can be used as an example. For the rDI model, each valence MO of C_2H_2 has 0.95 α and 0.95 β electrons.

Practical Details of Calculation

1) MO calculations

The model oligomer or monomer molecules [$H\text{-}(CH_2\text{-}CXY)_k\text{-}H$ (k = 3, 2 or 1), respectively] were calculated by the MO calculations using HAM/3 or deMon density-functional program [29]. For the geometry of the molecules, we used the optimized cartesian coordinates from the semiempirical AM1 (version 6.0) method [44].

The deMon calculations were performed with the exchange-correlation potential labeled as B88/P86, made from Becke's 1988 exchange functional [45] and Perdew's 1986 correlation functional [46]. In the program, we used a non-random grid and a polarized valence double-zeta (DZVP) basis [29] of (621/41/1*) for C, and (41) for H to calculate VIPs of model molecule with auxiliary fitting functions labeled (4,4;4,4) for C, and O, (3,1;3,1) for H.

2) Spectral simulation

In order to simulate the valence XPS of polymers theoreti cally, we constructed from a superposition of peaks centered on the VIPs, I_k. As was done in previous works[19-22], each peak was represented by a Gaussian curve. The intensity was estimated from the relative photoionization cross section for Al Kα radiation using the Gelius intensity model [35]. For the relative atomic photoionization cross-section, we used the theoretical values from Yeh [47]. In the case of the linewidth(WH(k)), we used WH(k)= 0.10 Ik for the models, as adopted in previous works [20-22].

For thirty three polymers, we cited the experimental valence XPS by Beamson and Briggs [3].

Results and Discussion

As stated in previous works, VIPs predicted by Koopmans' theorem are often too high, by approximately 8% [48]. In contrast, the VIPs of small molecules calculated by the deMon density functional program have an absolute deviation of 0.4 eV from experiment [49] and the deviation of over 50 calculated CEBEs from observed values is within 0.29 eV [50, 51]. Based on such performance, we have some confidence in modeling polymers by applying the density functional method on the model monomer or oligomer. The agreement between simulated and experimental XPS of polymers gives us further assurance about our interpretation of the different regions of the spectra.

For thirty three polymers[$(CH_2\text{-}CXY)_n$ (X;Y)= {(H;H)(PE), (H;CH_3)(PP), (CH_3;CH_3)(PIB), (H;C_2H_5)(PB), (H;$CHCH_2$)(PBD), (H;C_6H_5)(PS), (CH_3;C_6H_5)(PαMS), (H;C_6H_4-CH_3)(P4MS)}, $(CH_2CHCHCH_2)_n$(PCBD), $(CH_2CHC(CH_3)CH_2)_n$(PCI), ($C_6H_5C_6H_4C_6H_4C_6H_5$)(PPHO), $((CH_2)_m\text{-}O)_n$ {(m)= (1)(PMG),(2)(PEG), (3)(PPG)}, $(CH_2CH(OCH_3))_n$ (PVME), $(CH_2CH(OC_2H_5))_n$ (PVEE), $(CH_2CH(OCH_2CH(CH_3)_2))_n$ (PVIBE), $(C_6H_3(CH_3)_2O)_n$(PDMPO), $(C_6H_4OC_6H_4OC_6H_4(CO))_n$ (PEEK), $(CH_2CHOH)_n$ (PVA), $(CH_2\text{-}CH(C_6H_4OH))_n$ (PHS), $(C_6H_{10}O_5)_n$ (CEL), $(C_{12}H_{22}O_5)_n$ (ECEL), $(CH_2CH(COCH_3))_n$ (PVMK), $(CH_2CH(COC_2H_5))_n$ (PVEK), $(CH_2\text{-}C(CH_3)(COCH_3))_n$ (PMIPK), $(CH_2CH(OCOCH_3))_n$ (PVAC), $(CH_2CHCOOH)_n$ (PAA), $(CH_2C(CH_3)COOH)_n$ (PMAA), $(CH_2CH(COOCH_3))_n$ (PMA), $(CH_2C(CH_3)(COOCH_3))_n$ (PMMA), $(CH_2C(CH_3)(COOC_2H_5))_n$ (PEMA), and $((CH_2)_2OCOC_6H_4COO)_n$ (PET)], simulated spectra showed good accordance with experimental ones. We, furthermore, provided photoionization cross section of the main atomic orbitals, and the orbital nature in the tables for each polymer. The simulated data were due to HAM/3 calculations, since we obtained similar results using a deMon program.

In the case of the simulated spectra using model monomer, dimer or trimer molecules, the spectra appeared to show good agreement with the experimental ones, when we used an approximate linewidth of 0.10 I_k. It is very interesting that we can observe the characteristic spectra which are due to the photoionization cross-section of any contributing atomic orbitals of the constituent elements of the functional groups. For these thirty three polymers, we have clarified the orbital nature of the finger-print spectra which were characterized from the constituent elements(C and O) in the range of 0-40 eV.

Conclusion

We have calculated the valence XPS of hydrocarbon-polymers, and polymers involving O-, CO-, and COO-groups by HAM/3 and deMon DFT calculations using the model monomers or oligomers. We emphasize that the calculated vips using rDI by HAM/3 and deMon programs showed better correspondence with experiment than were those predicted by Koopman's theorem.

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この論文は，高分子の価電子スペクトルが，モデルクラスターのHAM計算により，再現できる事を，多くの高分子に対して示した論文であり，非常に価値がある．通常このような論文のオリジナリティーはなかなか認めてもらえず，日の目を見ない事が多いが－－－従って中途半端なJournalではrejectされると思うが－－－最終的に最も引用されたり，または引用されなくとも，ハンドブック的に多くの研究者が参照する論文である．従って，ページ数は多いが，データまで含めて完全な形で，publishすることは大いに意義のある事である．印刷は，Atomic Data & Nucl. Data TablesやJ. Phys. Chem. Ref. Dataなどの雑誌のように印刷すれば（各物質ごとに1ページとする），多くの研究者が使いやすいものになると思う．

著者

コメント有り難うございました。河合先生のコメントどうりと思います。著者としては、シミュレートしたデータを皆様に使用して頂きたく投稿致しました。本文の中にも引用しましたように、代表的な高分子は、すでにいくつかのjournalに掲載されていますが、纏めた形で掲載させて頂くことに価値があると思われます。

石田雅也氏（住友化学）

２種類の計算方法（ＨＡＭ／３とｄｅＭｏｎ）を用いてＶＩＰを計算されておられますが、本文や表を見るだけでは、どのスペクトルがどちらの手法で求められたものなのかが不明です。この点がわかるように本文を修正し、表にもどの手法で求めた結果かを記述すべきと思います。

田中浩三氏（住友化学）

２種類の計算方法の結果について、これらの手法の使い分けかたやそれらの特徴について考察があると良いと思います。

簗嶋裕之氏（住友化学）

ｐ５最終行、”thirty three”は”thirty two”の間違いではないでしょうか。

著者

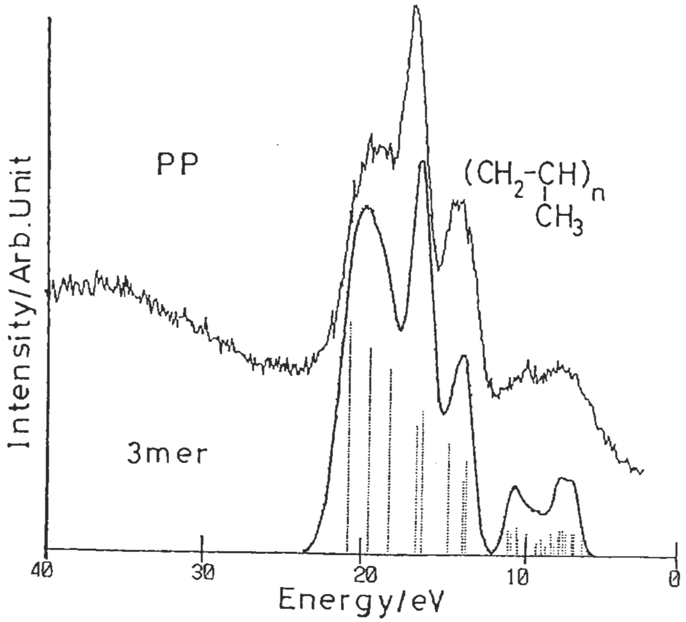
コメント有り難うございます。HAM/3でもdeMonでも全く同様の結果が得られます。今回の表と図の結果はHAM/3によるものを示しました。これについては本文のResults and Discussionの中に書きました。高分子化合物の数は３３に変更致しました。

P P Observed peaks, VIP, main AO PICS, orbital nature and functional group for valence XPS of PP. [(the gap between observed and calculated VIPs) = 5.5 eV]

peak(eV)	VIP(eV)	main AO PICS	orbital nature[b]	functional group
20.0	25.76;24.50	C2s	sσ (C2s-2s)-B	-C(main chain),-CH_3
(18-23)[a]	23.24		sσ (C2s-2s)-B	-CH_3,-C(main chain)
17.0	21.49;21.44;21.06	C2s	sσ (C2s-2s)-B	-CH_3,-C(main chain)
(15.5-18)[a]				
14.5	19.43;18.50;18.38	C2s	pσ (C2s-2p)-B	-C(main chain),-CH_3
(12-15.5)[a]				
7.5	12.91;12.76;12.49	C2p	pσ (C2p-2s)-B	-C(main chain),-CH_3
	12.38;12.14;11.94	C2p	pσ (C2p-2s)-B	-C(main chain),-CH_3
(4-12)[a]	many adjacent levels			
	15.67;15.46;15.14	C2p	pσ (C2p-2s)-B	-C(main chain),-CH_3
	13.3~14.5	C2p	pπ_p(C2p-2p)-B	-C(main chain),-CH_3
	11.0~11.6	C2p	pπ_p(C2p-2p)-B	-C(main chain),-CH_3

[a] shows the peak range.

[b] π_p indicates the pseudo π orbitals of the CH_2 groups. B and NB mean bonding and non-bonding, respectively. (C2s-2s),(C2s-2p) mean (C2s-C2s),(C2s-2p), respectively.

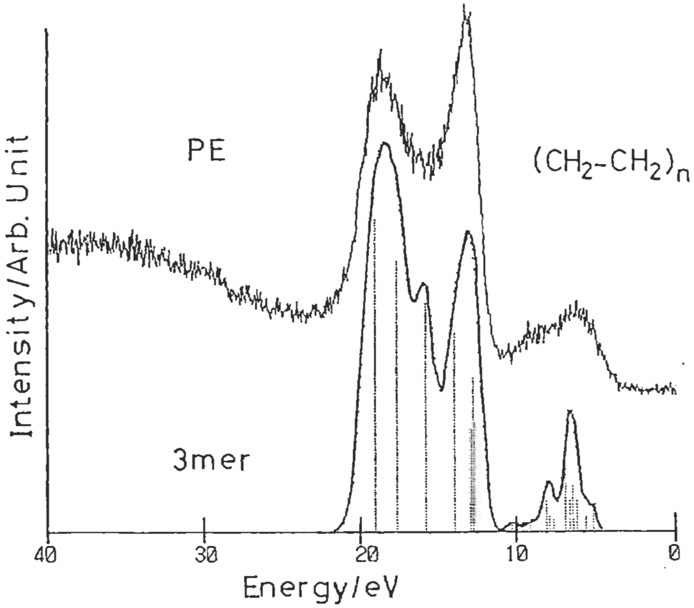


P E Observed peaks, VIP, main AO PICS and orbital nature for valence XPS of PE [(the gap between observed and calculated VIPs) = 5.5 eV]

peak(eV)	VIP(eV)	main AO PICS	orbital nature[b]
19.0	25.02	C2s	sσ (C2s-2s)-B
(16-22)[a]	23.62;21.84	C2s	sσ (C2s-2s)-B
13.5	19.97;18.99;18.78	C2s	pσ (C2s-2p)-B
(12-16)[a]			
6.5	12.86;12.63;12.47	C2p	pσ (C2p-2s)-B
(4-12)[a]	many adjacent levels		
	13.6~16.3	C2p	pσ (C2p-2s)-B
	11.1~12.3	C2p	pπ_p(C2p-2p)-B

[a] shows the peak range.

[b] π_p indicates the pseudo π orbitals of the CH_2 groups. B and NB mean bonding and non bonding, respectively. (C2s-2s),(C2s-2p) mean (C2s-C2s),(C2s-C2p), respectively.



P B Observed peaks, VIP, main AO PICS, orbital nature and functional group for valence XPS of PB. [(the gap between observed and calculated VIPs) = 6.0 eV]

peak(eV)	VIP(eV)	main AO PICS	orbital nature[b]	functional group
19.0 (18.5-23)[a]	26.18;25.08;24.30	C2s	sσ (C2s-2s)-B	-C(main chain), $-C_2H_5$
17.5 (16-18.5)[a]	23.04;22.79;21.83	C2s	sσ (C2s-2s)-B	$-C_2H_5$, -C(main chain)
15.0 (14-16)[a]	20.82;20.21;20.11	C2s	sσ (C2s-H1s)-B	-C(main chain), $-C_2H_5$
13.0 (11.5-14)[a]	19.12;18.92;18.64	C2s	pσ (C2s-2p)-B	-C(main chain), $-C_2H_5$
(4-11.5)[a]	below 16.00 eV many adjacent levels	C2p C2p	{pσ (C2p-2s)-B, pπ (C2p-2p)-B}	-C(main chain), $-C_2H_5$ -C(main chain), $-C_2H_5$

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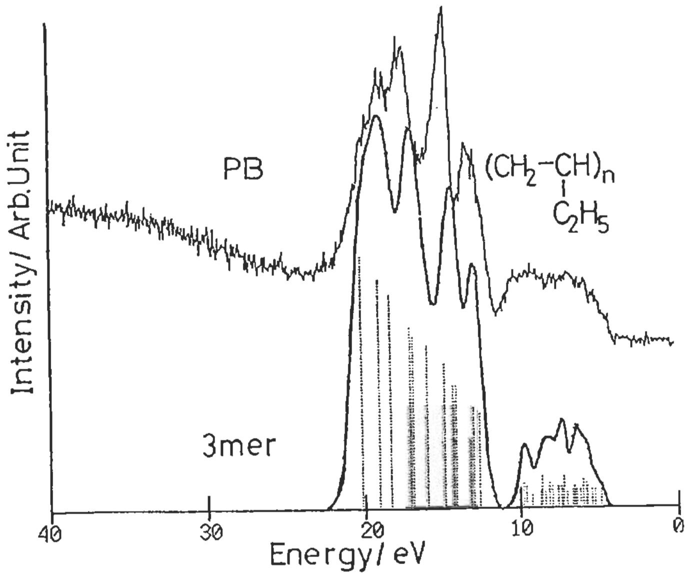
[a] shows the peak range.

[b] π_p indicates the pseudo π orbitals of the CH_2 groups. B ans NB mean bonding and non-bonding, respectively. (C2s-2s), (C2s-2p) mean (C2s-C2s), (C2s-C2p), respectively.



P I B Observed peaks, VIP, main AO PICS, orbital nature and functional group for valence XPS of PIB[(the gap between observed and calculated VIPs) = 5.5 eV]

peak(eV)	VIP(eV)	main AO PICS	orbital nature[b]	functional group
19.5 (19-22)[a]	26.42;25.36;24.34	C2s	sσ (C2s-2s)-B	-C(main chain), $-CH_3$
17.0 (14-19)[a]	{22.59;22.51;22.07; 21.92;21.69;21.35}	C2s	sσ (C2s-2s)-B	$-CH_3$, -C(main chain)
13.5 (11-14)[a]	18.61;18.27;17.96	C2s	pσ (C2s-2p)-B	-C(main chain), $-CH_3$
6.5 (3-11)[a]	13.10-11.93 below 16.07 eV many adjacent levels	C2p	pσ (C2p-2s)-B	-C(main chain), $-CH_3$
	11.81～10.67	C2p	$p\pi_p$(C2p-2p)-B	-C(main chain), $-CH_3$

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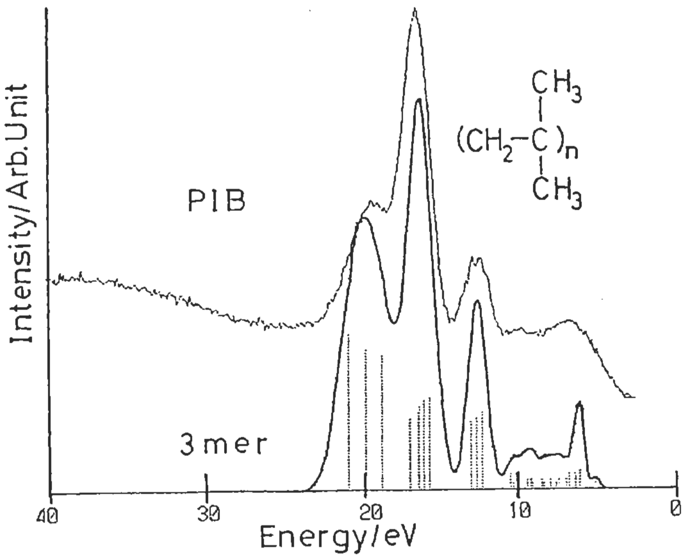
[a] shows the peak range.

[b] π_p indicates the pseudo π orbitals of the CH_2 groups. B and NB mean bonding and non-bonding, respectively. (C2s-2s), (C2s-2p) mean (C2s-C2s), (C2s-C2p), respectively.



P B D Observed peaks, VIP, main AO PICS, orbital nature and functional group for valence XPS of PBD. [(the gap between observed and calculated VIPs) = 5.0 eV]

peak(eV)	VIP(eV)	main AO PICS	orbital nature[b]	functional group
18.0 (16-24)[a]	25.92;24.78;23.95 22.53;22.23;21.45	C2s C2S	sσ (C2s-2s)-B sσ (C2s-2s)-B	-C(main chain), -C=C- -C=C-, -C(main chain)
14.0 (11-16)[a]	20.08;19.71;19.29 18.11;17.20;16.91	C2s C2s	sσ (C2s-C2s, H1s)-B pσ (C2s-2p)-B	-C(main chain), -C=C- -C(main chain), -C=C-
(3-11)[a]	below 15.98 eV many adjacent levels (11.13-15.98)	C2p C2p	pσ (C2p-H1s)-B pπ (C2p-2p)-B	-C(main chain), -C=C- -C(main chain)-C=C-
	9.37;9.22;9.04	C2p	pπ (C2p-2p)-B	-C=C-

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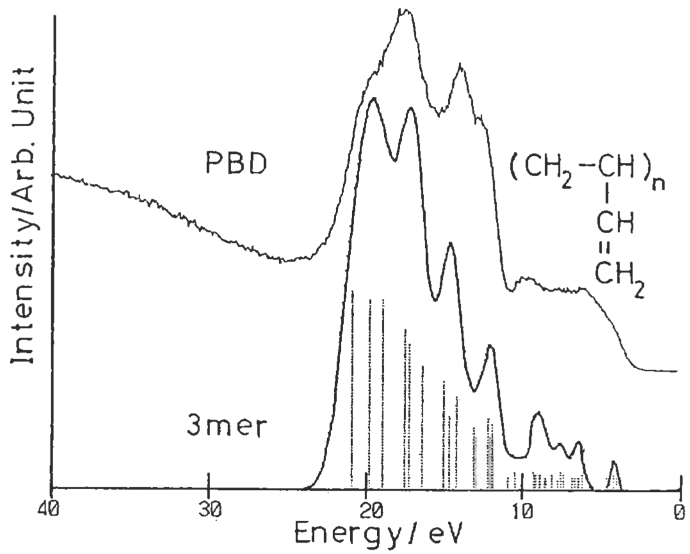
[a] shows the peak range.

[b] B and NB mean bonding and non-bonding, respectively. (C2s-2s), (C2s-2p) mean (C2s-C2s), (C2s-C2p), respectively.



P C B D Observed peaks, VIP, main AO PICS, orbital nature and functional group for valence XPS of PCBD. [(the gap between observed and calculated VIPs) = 5.0 eV]

peak(eV)	VIP(eV)	main AO PICS	orbital nature[b]	functional group
19.0 (16-22)[a]	[25.29;24.70;23.96; 22.93;21.87]	C2s	sσ (C2s-2s)-B	-C(main chain) -C=(main chain)
14.5 (13-16)[a]	20.77;19.65	C2s	sσ (C2s-2s)-B	-C=(main chain)
12.0 (11-13)[a]	[18.92;18.52;18.13; 17.64;17.45]	C2s	pσ (C2s-2p)-B	-C(main chain) -C=(main chain)
(5-11)[a]	below 15.13 eV many adjacent levels 11.27-15.13	C2p C2p	pσ (C2p-H1s)-B pπ (C2p-2p)-B	[-CH, -CH₂(main chain)] -C=(main chain)
4.0 (2.5-5)[a]	8.90;8.57;8.53	C2p	pπ (C2p-2p)-B	-C=(main chain)

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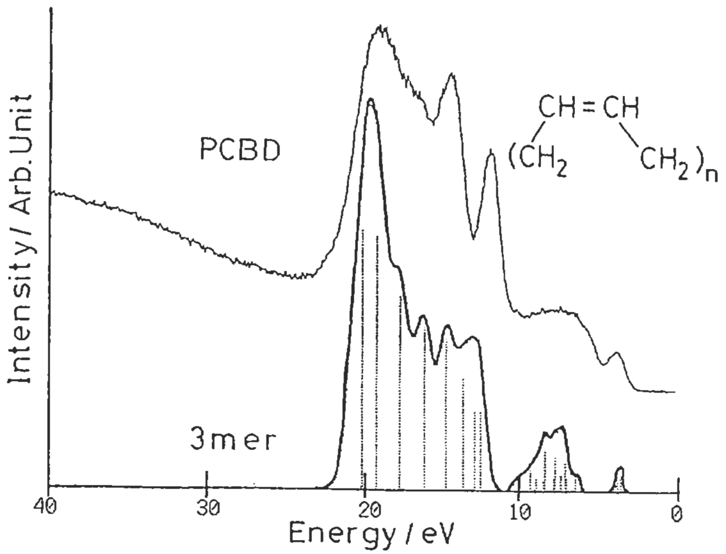
[a] shows the peak range.

[b] B and NB mean bonding and non-bonding, respectively. (C2s-2s), (C2s-2p) mean (C2s-C2s), (C2s-C2p), respectively.



P S Observed peaks, VIP, main AO PICS, orbital nature and functional group for valence XPS of PS. [(the gap between observed and calculated VIPs) = 5.0 eV]

peak(eV)	VIP(eV)	main AO PICS	orbital nature[b]	functional group
20.0	(26.81;26.44;26.30)	C2s	sσ (C2s-2s)-B	$-C_6H_5$,-C(main chain)
(19-23)[a]	(24.92;24.07)	C2s	sσ (C2s-2s)-B	-C(main chain),$-C_6H_5$
17.0	(23.18;22.55;22.48;	C2s	sσ (C2s-2s)-B	$-C_6H_5$
(15.5-19)[a]	22.42;22.04)			
	(21.89;21.31)	C2s	sσ (C2s-2s)-B	-C(main chain),$-C_6H_5$
13.5	(19.80;19.13;18.94;	C2s	sσ (C2s-2s)-B	-C(main chain),$-C_6H_5$
(12-15.5)[a]	18.27;18.15;18.12)	C2s	pσ (C2s-2p)-B	$-C_6H_5$
	(17.52;17.28;17.22)	C2s	pσ (C26-2p)-B	$-C_6H_5$,-C(main chain)
10.0	(15.42;15.27;	C2p	pσ (C2p-H1s)-B	-C(main chain),$-C_6H_5$
	15.11;14.81)	C2p	pσ (C2p-H1s)-B	$-C_6H_5$,-C(main chain)
(3.5-12)[a]	many adjacent levels			
	(16.09;15.96;15.77)	C2p	pσ (C2p-H1s)-B	$-C_6H_5$,-C(main chain)
	14.6~13.7	C2p	pσ (C2p-H1s)-B	$-C_6H_5$,-C(main chain)
	(13.4~8.9)	{C2p	pσ (C2p-H1s)-B	$-C_6H_6$,-C(main chain);
		C2p	$p\pi_p$(C2p-2p)-B	$-C_6H_5$,-C(main chain)}

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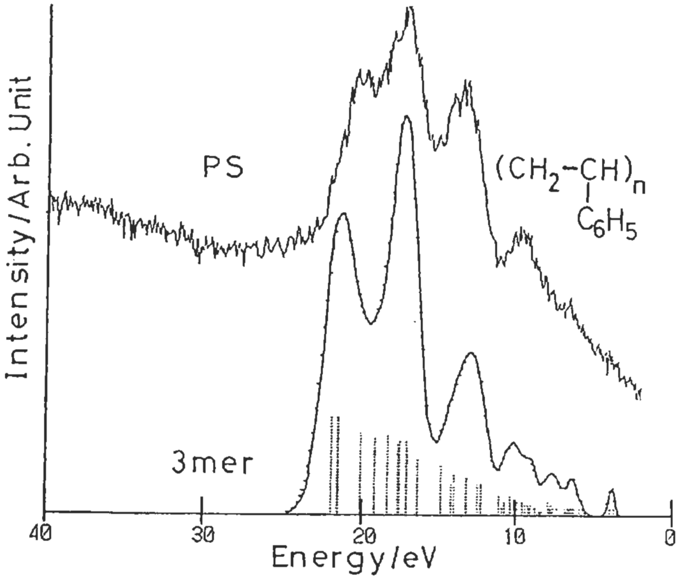
[a] shows the peak range.

[b] π_p indicates the pseudo π orbitals of the CH_2 groups. B and NB mean bonding and non bonding, respectively. (C2s-2s),(C2s-2p) mean (C2s-C2s),(C2s-2p), respectively.



P C I Observed peaks, VIP, main AO PICS, orbital nature and functional group for valence XPS of PCI. [(the gap between observed and calculated VIPs) = 5.0 eV]

peak(eV)	VIP(eV)	main AO PICS	orbital nature[b]	functional group
20.0 (19.5-23)[a]	25.90;25.34;24.81	C2s	sσ (C2s-2s)-B	-C-C=(main chain),$-CH_3$
18.0 (17-19.5)[a]	23.38;22.53;21.92	C2s	sσ (C2s-2s)-B	$-CH_3$,-C-C=(main chain)
16.5 (15.5-17)[a]	21.12;21.17;20.74	C2s	sσ (C2s-C2s,H1s)-B	$-CH_3$,$-CH_2-$
14.5 (13-15.5)[a]	19.93;19.23;18.89	C2s	pσ (C2s-2p)-B	-C-C=(main chain),$-CH_3$
12.0 (10.5-13)[a]	17.06;16.63;16.41	C2s	pσ (C2s-2p)-B	$-CH_3$,-C-C=(main chain)
(5-10.5)[a]	below 10.5 eV many adjacent levels (11.31-15.54)	C2p	{σ (C2p-C2s,H1s)-B, pπ (C2p-2p)-B}	{-C-C=(main chain), $-CH_3$,$-CH_2-$}
4.0 (2.5-5)[a]	8.77;8.57;8.49	C2p C2p	{pπ (C2p-2p)-B, $p\pi_p$(C2p-2p)-B}	{C=C(main chain), $-CH_3$,$-CH_2-$}

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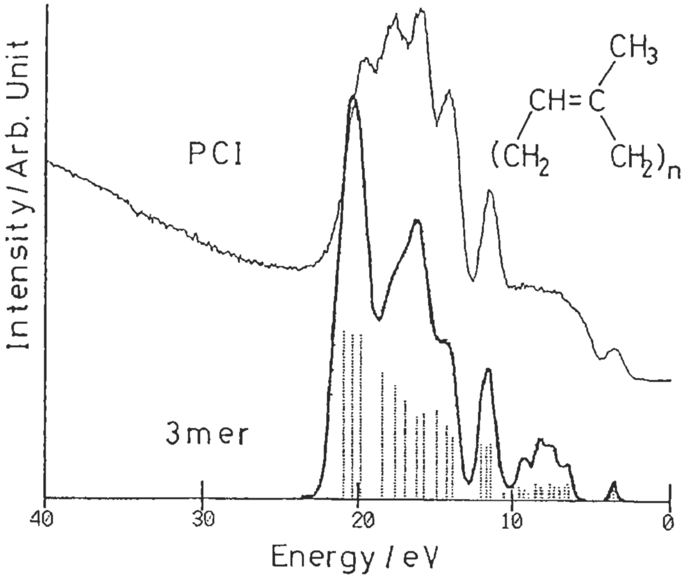
[a] shows the peak range.

[b] B and NB mean bonding and non-bonding, respectively. (C2s-2s),(C2s-2p) mean (C2s-C2s),(C2s-C2p), respectively.

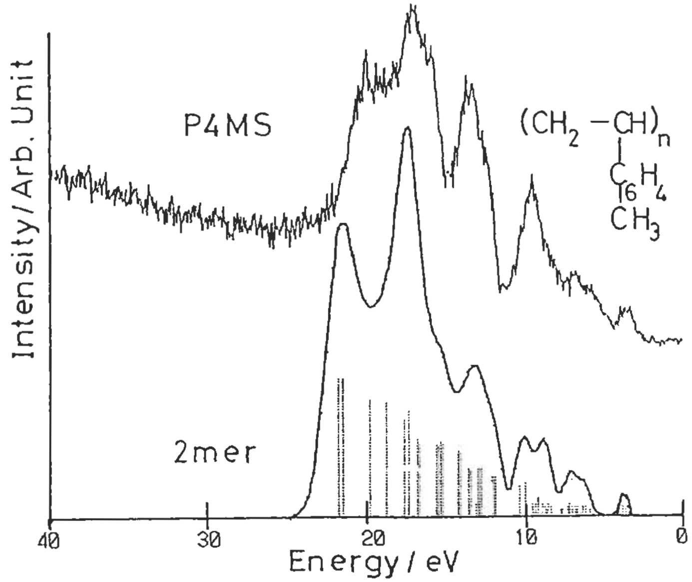


P4MS Observed peaks, VIP, main AO PICS, orbital nature and functional group for valence XPS of P4MS. [(the gap between observed and calculated VIPs) = 5.0 eV]

peak(eV)	VIP(eV)	main AO PICS	orbital nature[b]	functional group
20.0 (18-22)[a]	{26.68;26.44; 24.79;23.74}	C2s	sσ (C2s-2s)-B sσ (C2s-2s)-B	{-C(main chain), -C_6H_4,-CH_3}
17.0 (15.5-18)[a]	{22.67;22.40;22.35; 21.85;21.59;20.39}	C2s	sσ (C2s-2s)-B	-C_6H_4,-CH_3
14.5 (12-15.5)[a]	{19.25;18.65;18.11; 18.00;17.17;16.96}	C2s C2s	sσ (C2s-2s)-B pσ (C2s-2p)-B	-C(main chain),-C_6H_4,-CH_3 -C(main chain),-C_6H_4,-CH_3
9.5 (4-11)[a]	15.31;15.37;15.00 many adjacent levels (10.84-15.41)	C2p C2p C2p	pσ (C2p-H1s,C2s)-B {pσ (C2p-H1s,C2s)-B, pπ, pπ_p(C2p-2p)-B}	-C(main chain),-C_6H_4,-CH_3 {-C(main chain), -C_6H_4,-CH_3}
3.5 (2.5-4)	{9.01;8.90; 8.81;8.65}	C2p C2p	{pπ_p(C2p-2p)-B, pπ (C2p-2p)-B}	{-C(main chain),-CH_3 -C_6H_4}

[a] shows the peak range.

[b] π_p indicates the pseudo π orbitals of the CH_2 groups. B and NB mean bonding and non-bonding, respectively. (C2s-2s),(C2s-2p) mean (C2s-C2s),(C2s-C2p), respectively.

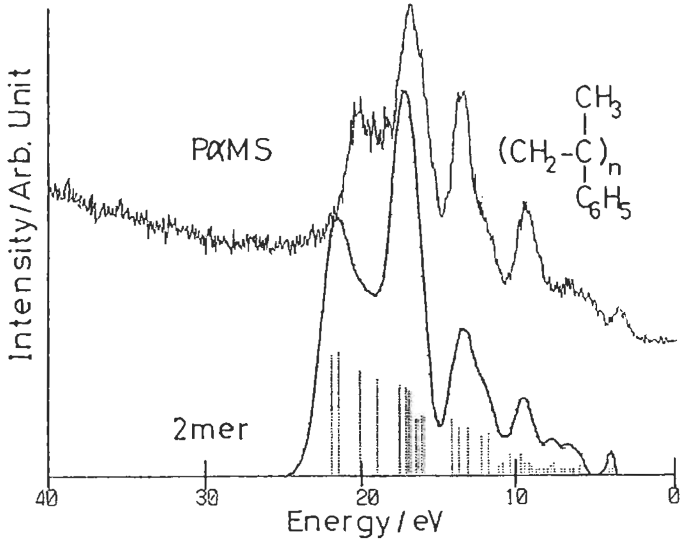


PαMS Observed peaks, VIP, main AO PICS, orbital nature and functional group for valence XPS of PαMS. [(the gap between observed and calculated VIPs) = 5.0 eV]

peak(eV)	VIP(eV)	main AO PICS	orbital nature[b]	functional group
20.0 (18-22)[a]	{26.90;26.46; 25.00;23.93}	C2s	sσ (C2s-2s)-B sσ (C2s-2s)-B	{-C(main chain), -C_6H_5,-CH_3}
17.0 (15.5-18)[a]	{22.58;22.50;22.10; 21.96;21.46;21.13}	C2s	sσ (C2s-2s)-B	-C_6H_5,-CH_3
14.5 (12-15.5)[a]	{19.12;18.74;18.13; 18.09;17.20;16.81}	C2s C2s	sσ (C2s-2s)-B pσ (C2s-2p)-B	-C(main chain),-C_6H_5,-CH_3 -C(main chain),-C_6H_5,-CH_3
9.5	{14.74;14.67; 14.43;14.20}	C2p C2p	pσ (C2p-H1s,C2s)-B	{-C(main chain), -C_6H_5,-CH_3}
(4-11)[a]	many adjacent levels (10.93-16.10)	C2p	{pσ (C2p-H1s,C2s)-B, pπ, pπ_p(C2p-2p)-B}	{-C(main chain), -C_6H_5,-CH_3}
3.5 (2.5-4)	{9.13;9.12; 9.02;8.94}	C2p C2p	{pπ_p(C2p-2p)-B, pπ (C2p-2p)-B}	{-C(main chain),-CH_3 -C_6H_5}

[a] shows the peak range.

[b] π_p indicates the pseudo π orbitals of the CH_2 groups. B and NB mean bonding and non bonding, respectively. (C2s-2s),(C2s-2p) mean (C2s-C2s),(C2s-C2p), respectively.



PMG Observed peaks, VIP, main AO PICS, orbital nature and functional group for valence XPS of PMG. [(the gap between observed and calculated VIPs) = 5.0 eV]

peak(eV)	VIP(eV)	main AO PICS	orbital nature[b]	functional group
26.0 (22-32)[a]	32.41;31.07;30.17	O2s	{sσ (O2s-C2s)-B, pσ (O2s-C2p)-B}	$-O-CH_2-$
18.0 (13-21)[a]	{22.06;21.53; 20.45;18.90}	C2s O2s(0.7),C2s(0.3)	{pσ (C2s-O2P)-B, sσ (C2s-O2s)-B}	$-CH_2-O-$
12.0 (10.5-13)[a]	{16.80;16.61;16.01; 15.47;15.27}	O2p(0.6),C2p(0.4)	{pσ (O,C2p-H1s)-B, pπ_p(C2p-2p)-B}	$-CH_2-O-$
9.5 (8-10.5)[a]	14.51;14.01;13.70	O2p(0.6),C2p(0.4)	{pσ (O,C2p-H1s)-B, pπ_p(C2p-2p)-B}	$-CH_2-O-$
6.0 (4-8)[a]	{11.70;10.98;10.74; 10.29;10.13}	O2p	pπ (lone pair)-NB	$-O-CH_2-$
	{13.10;12.52}	O2p(0.6),C2p(0.4)	pπ_p(O2p-C2p)-B	$-O-CH_2-$

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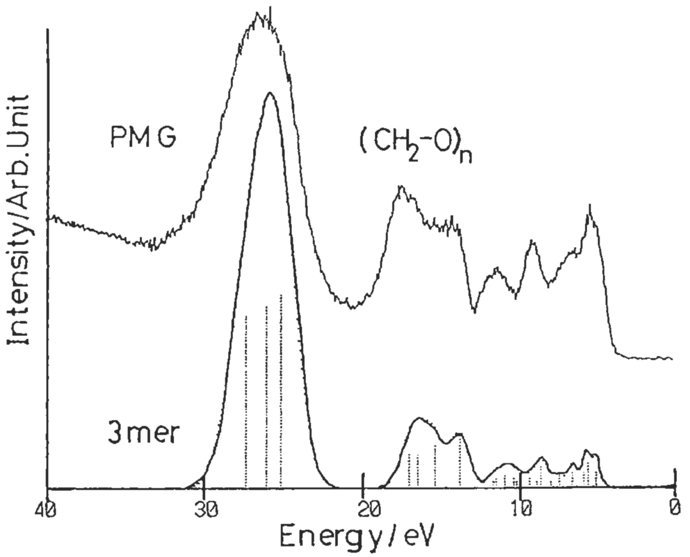
[a] shows the peak range.

[b] π_p indicates the pseudo π orbitals of the CH_2 groups. B and NB mean bonding and non-bonding, respectively. (C,O2s-2p) means (C2s-C2p) and (O2s-O2p), (C2p,O2p-C2p) denotes (C2p-C2p) and (O2p-C2p), and so on.



PPhO Observed peaks, VIP, main AO PICS, orbital nature and functional group for valence XPS of PPhO. [(the gap between observed and calculated VIPs) = 5.0 eV]

peak(eV)	VIP(eV)	main AO PICS	orbital nature[b]	functional group
20.0 (18-22)[a]	{27.12;26.58; 25.83;25.03}	C2s	sσ (C2s-2s)-B	$-C_6H_4,-C_6H_5$
17.0 (15.5-18)[a]	(23.57-20.23)	C2s	sσ (C2s-2s)-B	$-C_6H_4,-C_6H_5$
14.5 (11-15.5)[a]	(18.21-16.34)	C2s	{sσ (C2s-2s)-B, pσ (C2s-2p)-B}	$-C_6H_4,-C_6H_5$
9.0 (4-11)[a]	many adjacent levels (15.53-10.92)	C2p	{pσ (C2p-H1s,C2s)-B, pπ (C2p-2p)-B}	$\{-C_6H_4,-C_6H_5\}$
3.5 (2.5-4)	(9.01-8.65)	C2p	pπ (C2p-2p)-B	$-C_6H_4,-C_6H_5$

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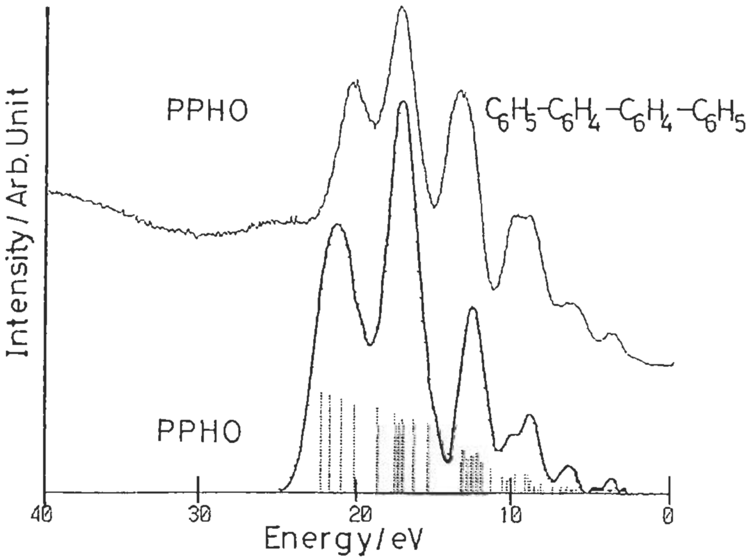
[a] shows the peak range.

[b] B and NB mean bonding and non-bonding, respectively. (C2s-2s),(C2s-2p) mean (C2s-C2s), (C2s-C2p), respectively.

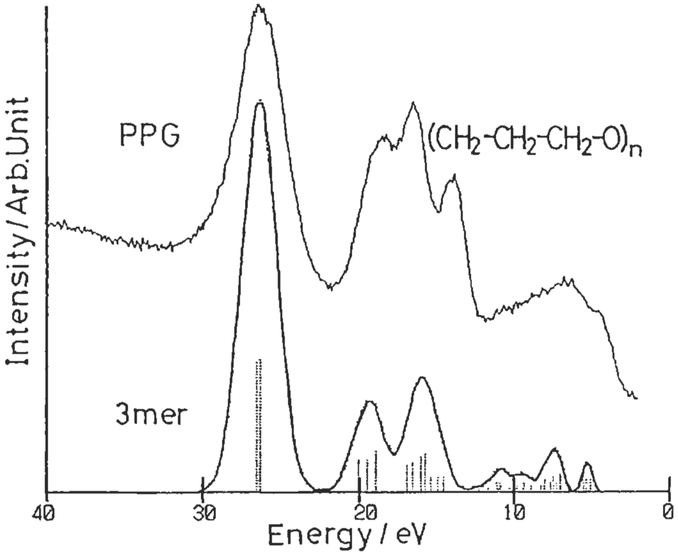


P P G Observed peaks, VIP, main AO PICS, orbital nature and functional group for valence XPS of PPG. [(the gap between observed and calculated VIPs) = 4.0 eV]

peak(eV)	VIP(eV)	main AO PICS	orbital nature[b]	functional group
26.5 (22-32)[a]	(30.60;30.40;30.29)	O2s(0.9), C2s	{sσ (O2s-C2s)-B, pσ (O2s-C2p)-B}	-O-C(main chain) -O-C(main chain)
18.5 (18-22)[a]	(24.01;23.50;22.94)	C2s(0.9), O2s	sσ (C2s-C, O2s)-B	-C-C-O(main chain)
17.0 (15-18)[a]	19.70-20.92	C2s(0.6), O2s	sσ (C2s-C, O2s)-B	-C-C-O(main chain)
14.5 (12-15)[a]	(18.55;18.88;19.31)	C2s	pσ (C2s-2p)-B	-C-C-(main chain)
7.0 (3-12)[a]	11.01-11.98 many adjacent levels	O2p(0.4), C2p, O2s	pπ_p(O, C2p-C2p)-B	-O-C-C(main chain)
	12.05-16.72	O2p(0.6), C2p	pπ_p(O, C2p-C2p)-B	-O-C-C(main chain)
5.0	9.50;9.31;9.10	O2p	pπ (lone pair)-NB	-O-

[a] shows the peak range.

[b] π_p indicates the pseudo π orbitals of the CH_2 groups. B and NB mean bonding and nonbonding, respectively. (O, C2p-2p) means (O2p-C2p) and (C2p-C2p). (C, O2p-C2p) denotes (C2p-C2p) and (O2p-C2p), and so on.

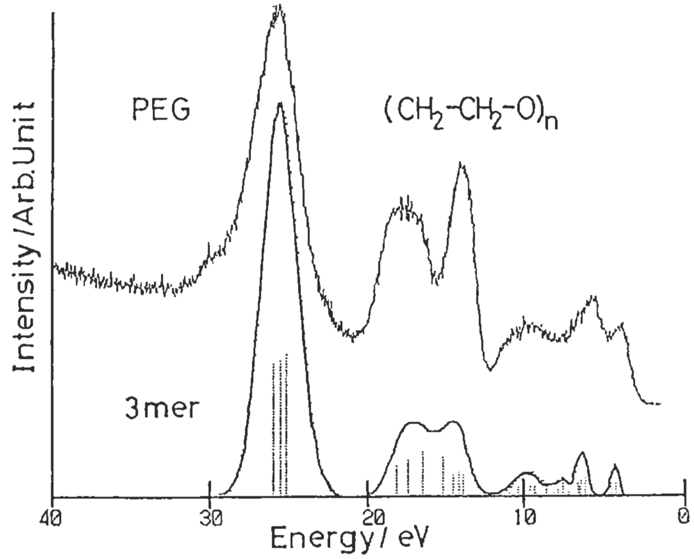


P E G Observed peaks, VIP, main AO PICS, orbital nature and functional group for valence XPS of PEG. [(the gap between observed and calculated VIPs) = 5.0 eV]

peak(eV)	VIP(eV)	main AO PICS	orbital nature[b]	functional group
26.0 (24-31)[a]	(31.05;30.64;30.19; 30.05)	O2s	sσ (O2s-C2s)-B, pσ (O2s-C2p)-B	-O-C(main chain) -O-C(main chain)
18.0 (16-20)[a]	(22.99;22.05;21.17)	C2s(0.7) O2s(0.2)	sσ (C2s-2s)-B sσ (C2s-O2s)-B	-C-(main chain) -C-O-(main chain)
14.0 (12-15.5)[a]	(19.57;19.11;18.81)	C2s(0.6), O2s, O2p	pσ (C2s-O2p)-B pσ (C2s-2p)-B	-C-O-(main chain) -C-(main chain)
(3-12)[a]	below 16.56 many adjacent levels	O2p, C2p, O2s, C2s	pσ (O, C2p-2p)-B pπ (C, O2p-C2p)-B	-C-O-(main chain) -C-O-(main chain)
6.0	(12.09;11.73;11.34; 11.29)	O2p	pπ (lone pair)-NB	-O-C-C-
4.0	(9.73;9.61;9.34;9.34)	O2p	pπ (lone pair)-NB	-O-C-C-

[a] shows the peak range.

[b] B and NB mean bonding and nonbonding, respectively. (O, C2p-2p) means (O2p-C2p) and (C -C2p). (C, O2p-C2p) denotes (C2p-C2p) and (O2p-C2p), and so on.



PVEE Observed peaks, VIP, main AO PICS, orbital nature and functional group for valence XPS of PVEE. [(the gap between observed and calculated VIPs) = 4.0 eV]

peak(eV)	VIP(eV)	main AO PICS	orbital nature[b]	functional group
26.0 (23-31)[a]	30.81;30.46;30.31	O2s(0.9), C2s	{sσ (O2s-C2s)-B, pσ (O2s-C2p)-B}	-O-C
18.5 (17-22)[a]	21.78-24.73	C2s(0.8), O2s	sσ (C2s-O, C2s)-B	-C-C-, -C-O-
14.5 (12-17)[a]	18.18-20.10	C2s(0.7), O2p, O2s	pσ (C2s-O, C2p)-B	-C-O-, -C-C-
(3-12)[a] 7-12	many adjacent levels 11.77-16.46	O2p, C2p, O2s, C2s	pπ_p(O, C2p-C2p)-B	-O-C-, -C-C-
6.5	11.27;10.80;10.66	O2p	pπ (lone pair)-NB	-O-C-C-
4.5	9.81;9.67;9.44	O2p	pπ (lone pair)-NB	-O-C-C-

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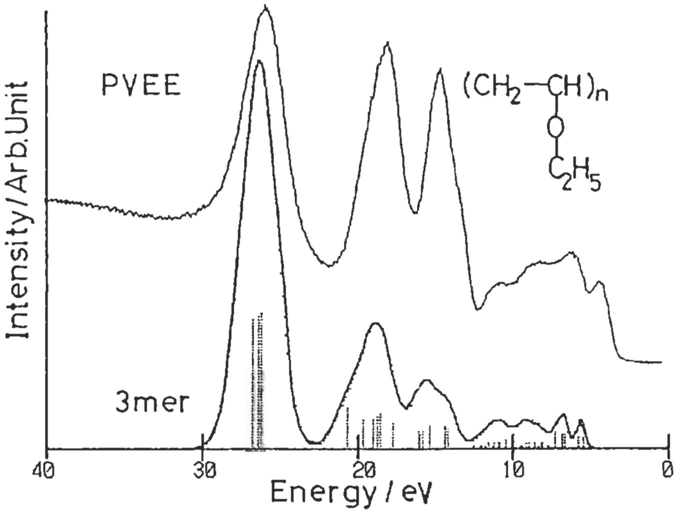
[a] shows the peak range.

[b] π_p indicates the pseudo π orbitals of the CH_2 groups. B and NB mean bonding and non-bonding, respectively. (O, C2p-2p) means (O2p-C2p) and (C2p-C2p). (C, O2p-C2p) denotes (C2p-C2p) and (O2p-C2p), and so on.



PVME Observed peaks, VIP, main AO PICS, orbital nature and functional group for valence XPS of PVME. [(the gap between observed and calculated VIPs) = 4.5 eV]

peak(eV)	VIP(eV)	main AO PICS	orbital nature[b]	functional group
26.5 (23-31)[a]	(30.86;30.52;30.38)	O2s(0.94;C2s(0.06)	sσ (O2s-C2s)-B	-O-C-, -O-CH_3
19.5 (18.5-22)[a]	(24.59:23.39)	C2s(0.8);O2s(0.2)	sσ (C2s-C2s, O2s)-B	-C-(main chain), -C-O
16.5 (15.5-18.5)[a]	(21.30;21.20;20.94) 22.00	C2s(0.5);O2s(0.5) C2s	sσ (C2s-O2s)-B pσ (C2s-O2p)-B	H_3C-O, -C-(main chain) -C-(main chain), H_3C-O
14.0 (12.5-15.5)[a]	(19.34;18.16;18.05)	C2s(0.7);O2s(0.3)	sσ (C2s-O2s)-B	-C-O-, -CH_3
10.5 (9-12)[a]	(14.77;14.61;14.32) many adjacent levels	O2p(0.5);C2p(0.5) O2p(0.5), C2p(0.5)	pσ (O, C2ps-C2p, 2s)-B pσ, pπ (C, O2p-2p)-B pσ (C2p-H1s)-B}	-O-CH_3, -O-C- -O-C-, -O-CH_3 -CH-, -CH_3
6.5 (5-9)[a]	(11.01;10.58;10.44)	O2p(0.5);C2p(0.5)	pπ (O2p, C2p-C2p)-B	-O-C-, -O-CH_3
4.5 (3.5-5)[a]	(9.78;9.62;9.38)	O2p(0.9);C2p(0.1)	pπ (lone-pair)-NB	-O-

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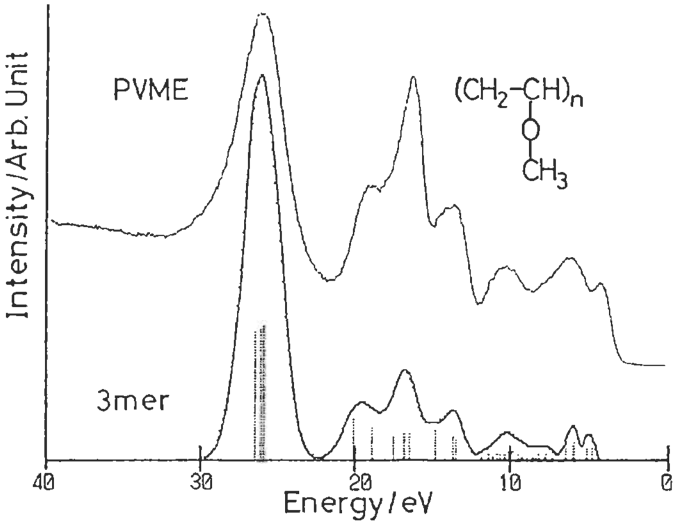
[a] shows the peak range.

[b] B and NB mean bonding and nonbonding, respectively. (C, O2s-2p) means (C2s-C2p) and (O2s-O2p), (C2p, O2p-C2p) denotes (C2p-C2p) and (O2p-C2p), and so on.

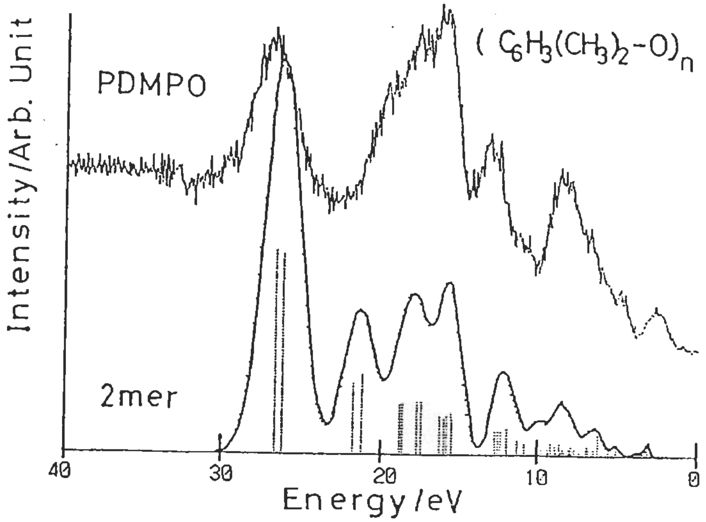


PDMPO Observed peaks, VIP, main AO PICS, orbital nature and the functional group for valence XPS of PDMPO.[(the gap between observed and calculated VIPs) = 5.0 eV]

peak(eV)	VIP(eV)	main AO PICS	orbital nature^{b}	functional group
27.0 (23-31)^{a}	31.54;31.11	O2s(0.9),C2s	{sσ (O2s-C2s)-B, pσ (O2s-C2p)-B}	-O-C=
16.5 (15-23)^{a}	20.37-21.20 26.68;26.14 22.41-23.74	C2s(0.9),O2s C2s(0.9),O2s C2s	sσ (C2s-C,O2s)-B sσ (C2s-C,O2s)-B sσ (C2s-C2s)-B	-C-C-O, -C=C-(benz) -C=C-(benz), -C-C-O -C-C-, -C=C-(benz)
13.0 (11-15)^{a}	15.89-17.72	C2s(0.7),O2p,C2p	pσ (C2s-O2p,C2p)-B	-C-C-O, -C=C-(benz)
8.5 (4-11)^{a}	13.28-13.90	C2p,O2p	pπ (C2p-C,O2p)-B	-C=C-(benz), C-O-
	many adjacent levels			
	14.16-15.15	O2p,C2p	pπ (O2p,C2p-C2p)-B	-O-C, -C=C-(benz)
	10.18-13.10	O2p,C2p	pπ (O,C2p-C2p)-B	-O-C-C, -C=C-(benz)
3.0 (2-4)^{a}	8.12-8.92	O2p,C2p	{pπ (lone-pair)-NB, pπ (C2p-C2p)-B}	-O- -C=C-(benz)

^{a} shows the peak range.

^{b} B and NB mean bonding and nonbonding, respectively. (C,O2s-2p) means (C2s-C2p) and (O2s-O2p), (C2p,O2p-C2p) denotes (C2p-C2p) and (O2p-C2p), and so on. (benz) means benzene nucleus.

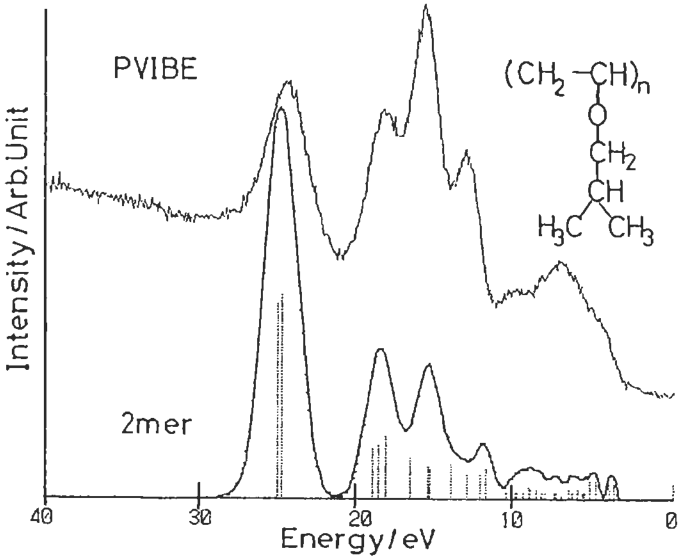


PViBE Observed peaks, VIP, main AO PICS, orbital nature and functional group for valence XPS of PViBE.[(the gap between observed and calculated VIPs) = 6.0 eV]

peak(eV)	VIP(eV)	main AO PICS	orbital nature^{b}	functional group
24.5 (21-29)^{a}	30.95;30.62	O2s(0.9),C2s	{sσ (O2s-C2s)-B, pσ (O2s-C2p)-B}	-O-C
18.0 (17-21)^{a}	(24.82;24.52;24.01)	C2s(0.9),O2s	sσ (C2s-C,O2s)-B	-C-C-, -C-O
15.5 (13.5-17)^{a}	21.20-22.45	C2s(0.9),O2s,O2p	{sσ (C2s-C,O2s)-B, pσ (C2s-C,O2p)-B}	-C-C-, -C-O
13.0 (11.5-13.5)^{a}	17.66-19.91	C2s(0.9),O2s,O2p	Pσ (C2s-O,C2p)-B	-C-C-, -C-O
7.0 (3-11.5)^{a}	13.16-13.33	O2p,C2p	pπ$_{p}$(O,C2p-C2p)-B	-O-C, -C-C
	many adjacent levels			
	13.88-16.36	O2p,C2p	pπ$_{p}$(C,O2p-C2p)-B	-O-C, -C-C
	11.40-12.03	O2p,C2p	pπ$_{p}$(C,O2p-C2p)-B	-O-C, -C-C
	11.10;10.76	O2p	pπ (lone pair)-NB	-O-C-C-
	9.99;9.72	O2p	pπ (lone pair)-NB	-O-C-C-

^{a} shows the peak range.

^{b} π_p indicates the pseudo π orbitals of the CH_2 groups. B and NB mean bonding and nonbonding, respectively. (O,C2p-2p) means (O2p-C2p) and (C2p-C2p). (C,O2p-C2p) denotes (C2p-C2p) and (O2p-C2p), and so on.

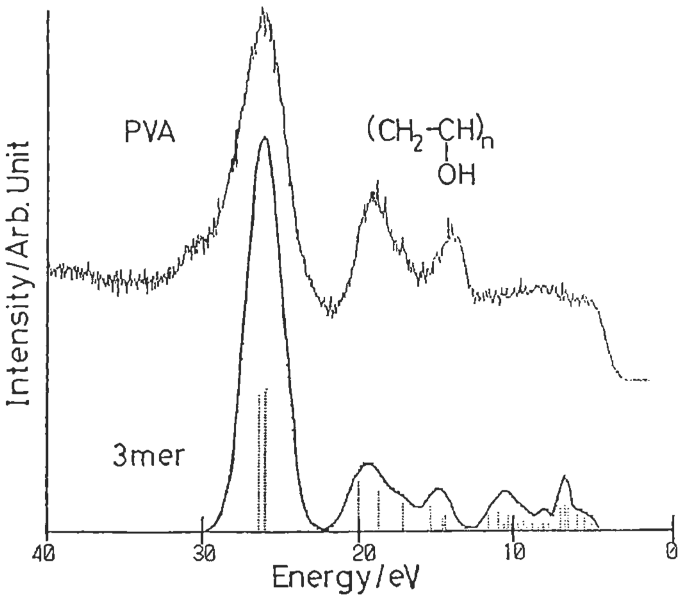


P V A Observed peaks, VIP, main AO PICS, orbital nature and functional group for valence XPS of PVA. [(the gap between observed and calculated VIPs) = 4.5 eV]

peak(eV)	VIP(eV)	main AO PICS	orbital nature[b]	functional group
26.0 (24-31)[a]	30.84;30.42;30.30	O2s	sσ (O2s-C2s)-B, pσ (O2s-C2p)-B	-O-C -O-C
20.0 (18-23)[a]	24.44;23.17	C2s(0.75),O2s(0.25)	sσ (C2s-2s)-B	-C(main chain),C-O-
14.0 (13-16)[a]	19.84;19.14;18.92 21.61	C2s(0.6),O2p,O2s	pσ (C2s-O2p)-B pσ (C2s-2p)-B	C-O-, -C(main chain) -C(main chain)
(5-13.5)[a]	below 16.21 many adjacent levels	O2p,O2s,C2p,C2s	pσ (O,C2p-2s)-B pπ (C2p,O2p-C2p)-B	C-O-, -C(main chain) -C(main chain),C-O-
	11.62;11.33;11.14	O2p	pπ (lone pair)-NB	C-O-
	10.55;10.10;9.62	O2p	pπ (lone pair)-NB	C-O-

[a] shows the peak range.

[b] B and NB mean bonding and nonbonding, respectively. (C,O2s-2p) means (C2s-C2p) and (O2s-O2p), (C2p,O2p-C2p) denotes (C2p-C2p) and (O2p-C2p), and so on.

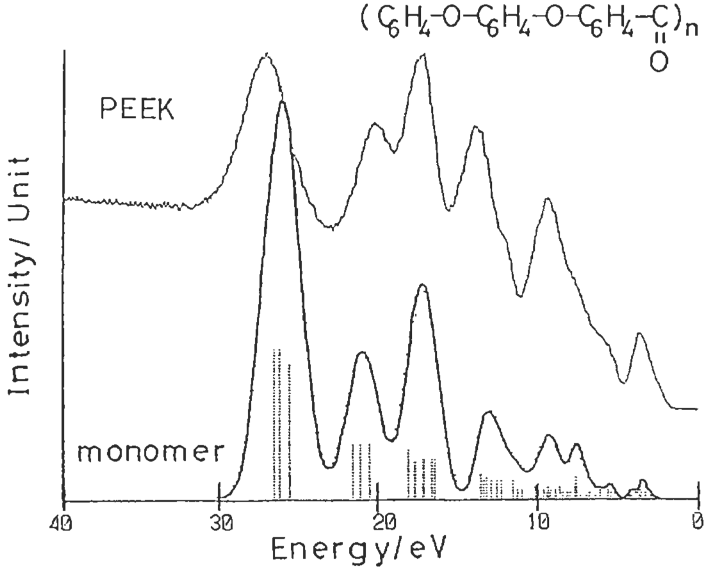


P E E K Observed peaks, VIP, main AO PICS, orbital nature and functional group for valence XPS of PEEK. [(the gap between observed and calculated VIPs) = 5.0 eV]

peak(eV)	VIP(eV)	main AO PICS	orbital nature[b]	functional group
27.0 (23-31)[a]	31.50;31.10;30.50	O2s(0.9),C2s	{sσ (O2s-C2s)-B, pσ (O2s-C2p)-B}	-O-C-, O=C
20.5 (19-23)[a]	26.50;26.01;25.48	C2s(0.8),O2s	sσ (C2s-C,O2s)-B	{-C=C-(benz), C-O-, C=O}
17.5 (16-19)[a]	21.43-23.13	C2s(0.9),O2s	sσ (C2s-C2s)-B	{-C=C-(benz), C-O-, C=O}
14.0 (11.5-16)[a]	17.29-18.65 16.01-16.62	C2s(0.6),O2p O2p,C2p,C2s	pσ, sσ (C2s-O2p,C2s)-B {pσ (C2s-O2p,C2s)-B, pπ (C2p-C,O2p)-B}	-C=C-(benz), -C-O- -C-O, -C=C-(benz)
9.5 (5-11.5)[a]	13.02-15.21 many adjacent levels	C2p,O2p,C2s	{pπ (C2p-C,O2p)-B, pσ (C2p-C2s)-B}	{ C-O-, C=O, -C=C-(benz)}
	10.52-12.70	O2p,C2p	pπ (O,C2p-C2p)-B	-O-C, -C=C-(benz), -C=O
3.5 (2-5)[a]	8.12-9.49	O2p,C2p	{pπ (lone-pair)-NB, pπ (C2p-C2p)-B}	-O-, =O -C=C-(benz)

[a] shows the peak range.

[b] B and NB mean bonding and nonbonding, respectively. (C,O2s-2p) means (C2s-C2p) and (O2 -O2p), (C2p,O2p-C2p) denotes (C2p-C2p) and (O2p-C2p), and so on. (benz) means benzene nucleus.



C E L Observed peaks, VIP, main AO PICS, orbital nature and functional group for valence XPS of CEL. [(the gap between observed and calculated VIPs) = 5.0 eV]

peak(eV)	VIP(eV)	main AO PICS	orbital nature[b]	functional group
26.0	30.52-32.39	O2s	sσ (O2s-C2s)-B	-O-C-
(22-32)[a]	29.85-30.31	O2s	sσ, pσ (O2s-C2s, C2p)-B	-O-C-
18.0	{24.71;24.15;	C2s(0.7), O2s	sσ (C2s-C2s, O2s)-B	C-C-, C-O-
(17-21)[a]	23.33;23.12}	C2s(0.9), O2s	sσ (C2s-C2s, O2s)-B	C-C-, C-O-
14.0	17.97-19.99	C2s(0.6), O2p	sσ, pσ (C2s-C2s, 2p, O2p)-B	C-C-, C-O-
(12-17)[a]	21.42;21.03;20.58	C2s(0.8), O2s	sσ (C2s-C, O2s)-B	C-C-, C-O-
7.0	10.75-12.98	O2p(0.6), C2p	pπ (O, C2p-O, C2p)-B	-O-C, -C-C
(3-12)[a]	many adjacent levels			
	13.17-16.82	O2p(0.5), C2p	pπ (C2p, O2p-C2p)-B	-O-C, -C-C
	9.20-10.13	O2p	pπ (lone-pair)-NB	-O-

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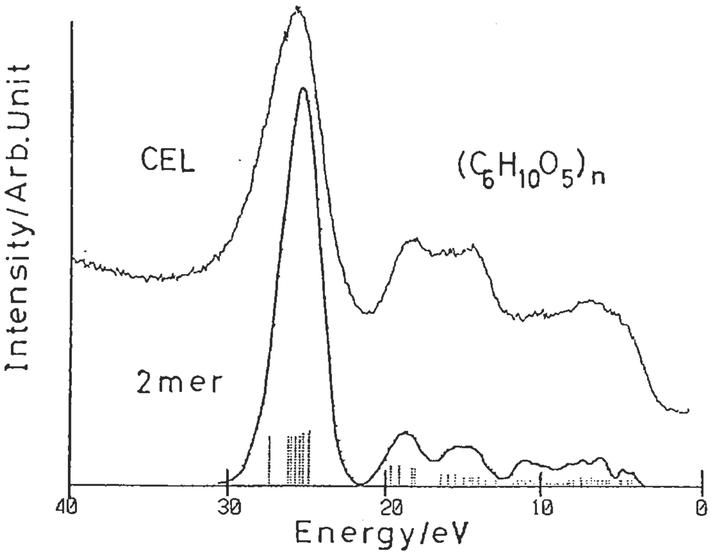
[a] shows the peak range.

[b] B and NB mean bonding and nonbonding, respectively. (C, O2s-2p) means (C2s-C2p) and (O2s-O2p), (C2p, O2p-C2p) denotes (C2p-C2p) and (O2p-C2p), and so on.



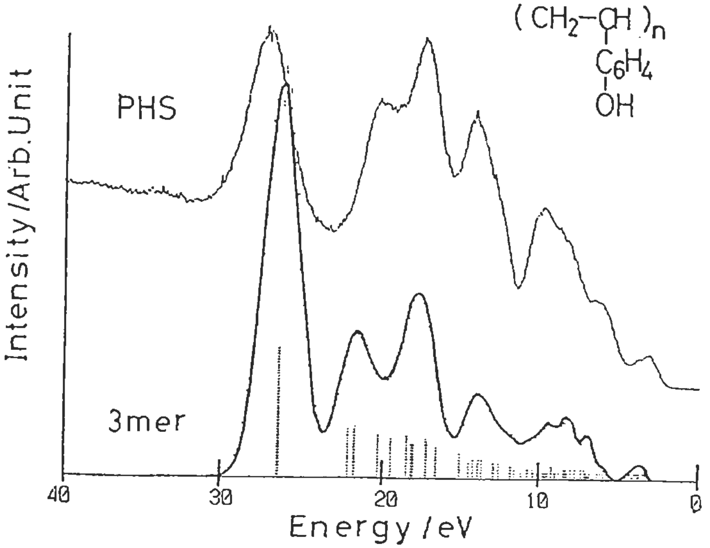
P H S Observed peaks, VIP, main AO PICS, orbital nature and functional group for valence XPS of PHS. [(the gap between observed and calculated VIPs) = 4.5 eV]

peak(eV)	VIP(eV)	main AO PICS	orbital nature[b]	functional group
27.5 (24-31)[a]	30.96;30.91;30.88	O2s	{sσ (O2s-C2s)-B, pσ (O2s-C2p)-B}	-O-C-
20.5 (19-24)[a]	24.74-26.68	C2s	sσ (C2s-C2s)-B	-C-C-, -C=C-(benz)
17.5 (16-19)[a]	21.09-23.87	C2s	sσ (C2s-C2s)-B	-C=C-(benz), -C-C-
14.5	18.22-19.58	C2s	sσ (C2s-C2s)-B	-C=C-(benz), -C-C-
(11.5-16)[a]	16.12-17.43	C2s(0.7), O2p	pσ, sσ (C2s-O2p, C2s)-B	-C-O, -C=C-(benz)
10.0	13.20-14.14	C2p, O2p	pπ (C2p-C, O2p)-B	-C=C-(benz), C-O-
(5-11.5)[a]	many adjacent levels			
	14.22-15.64	C2p, C2s	pπ, pσ (C2p-C2p, 2s)-B	-C=C-(benz), -C-C-
	10.44-12.94	O2p, C2p	pπ (O, C2p-C2p)-B	-O-C, -C=C-(benz), -C-C-
4.5 (2-5)[a]	8.19-9.07	O2p, C2p	{pπ (lone-pair)-NB, pπ (C2p-C2p)-B}	-O- -C=C-(benz)

---

[a] shows the peak range.

[b] B and NB mean bonding and nonbonding, respectively. (C, O2s-2p) means (C2s-C2p) and (O2s-O2p), (C2p, O2p-C2p) denotes (C2p-C2p) and (O2p-C2p), and so on. (benz) means benzene nucleus.



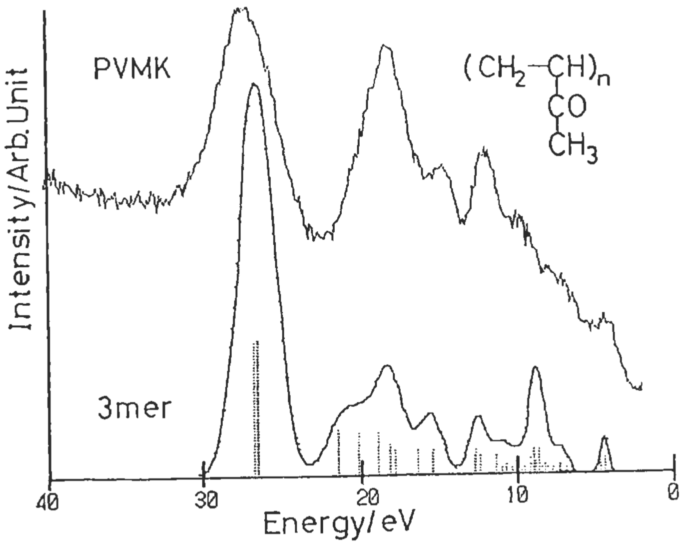
P V M K Observed peaks, VIP, main AO PICS, orbital nature and functional group for valence XPS of PVMK. [(the gap between observed and calculated VIPs) = 4.5 eV]

peak(eV)	VIP(eV)	main AO PICS	orbital nature[b]	functional group
27.0 (23-31)[a]	(31.26;31.06;30.97)	O2s(0.9);C2s(0.1)	sσ, pσ (O2s-C2s, C2p)-B	-C=O
18.0 (16-22)[a]	(23.36;22.64; 22.50;22.21)	C2s	sσ (C2s-C2s, O2s)-B	-CO-CH$_3$, -C-(main chain)
	(25.93:24.61)	C2s(0.2);O2s(0.2)	sσ (C2s-C2s, O2s)-B	-C-(main chain), -C=O
15.0 (13.5-16)[a]	(20.75;19.88;19.73)	C2s	sσ (C2s-2s, H1s)-B	-C-(main chain)
12.0 (11-13.5)[a]	(17.19;17.05;16.83)	C2s(0.8);O2s(0.2)	pσ (C, O2s-C, O2p)-B	-C-CO-, -CO-CH$_3$
	(15.81;15.44;15.15)	C2s	pσ (C2p-C2s, H1s)-B	-C-(main chain), CH$_3$
(3-11)	many adjacent levels			
	(14.8-13.8)	C2p	pσ (C2p-C2p, H1s)-B	-C-(main chain), CH$_3$
	(13.6-11.3)	C2p, O2p	{pσ (C, O2p-2p;C2p-h1s)-B pπ (C2p, O2p-C2p)-B]	-C-CO, -CO-CH$_3$
4.5 (3.5-5.5)[a]	(9.78;9.62;9.38)	O2p(0.9);C2p(0.1)	pπ (lone-pair)-NB	-C=O

---

[a] shows the peak range.

[b] B and NB mean bonding and nonbonding, respectively. (C, O2s-2p) means (C2s-C2p) and (O2s-O2p), (C2p, O2p-C2p) denotes (C2p-C2p) and (O2p-C2p), and so on.



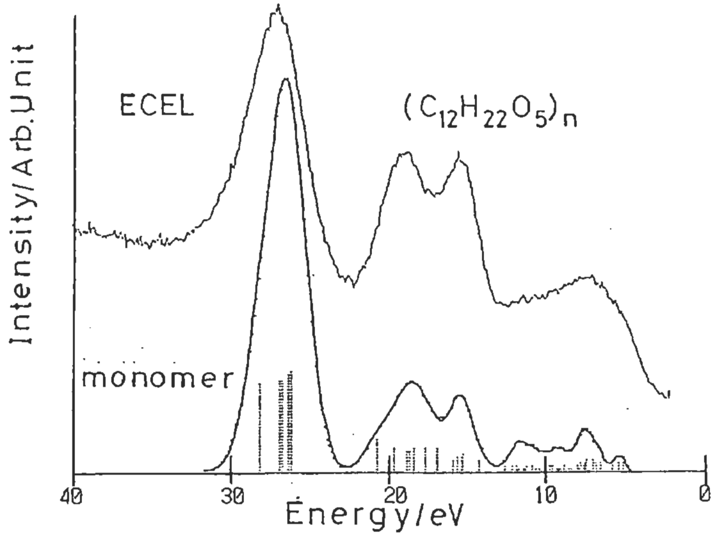
E C E L Observed peaks, VIP, main AO PICS, orbital nature and the functional group for valence XPS of ECEL. [(the gap between observed and calculated VIPs) = 4.0 eV]

peak(eV)	VIP(eV)	main AO PICS	orbital nature[b]	functional group
27.0 (23-33)[a]	30.10-32.13	O2s	{sσ (O2s-C2s)-B, pσ (O2s-C2p)-B}	-O-C-
19.0 (17.5-22)[a]	20.71-24.78	C2s(0.7), O2s	sσ (C2s-C2s, O2s)-B	C-C-, C-O-, -C$_2$H$_5$
16.0 (13-17.5)[a]	18.23-19.92	C2s(0.7), O2s, O2p	{pσ (C2s-C2p, O2p)-B, sσ (C2s-C2s)-B }	C-C-, C-O-, -C$_2$H$_5$
7.5 (3-13)[a]	10.60-11.77	O2p(0.6), C2p	pπ (O, C2p-O, C2p)-B	-O-C, -C-C, -C$_2$H$_5$
	many adjacent levels			
	11.94-16.59	O2p(0.5), C2p	pπ (C2p, O2p-C2p)-B	-O-C, -C-C, -C$_2$H$_5$
	9.26-9.86	O2p	pπ (lone-pair)-NB	-O-

---

[a] shows the peak range.

[b] B and NB mean bonding and nonbonding, respectively. (C, O2s-2p) means (C2s-C2p) and (O2-O2p), (C2p, O2p-C2p) denotes (C2p-C2p) and (O2p-C2p), and so on.



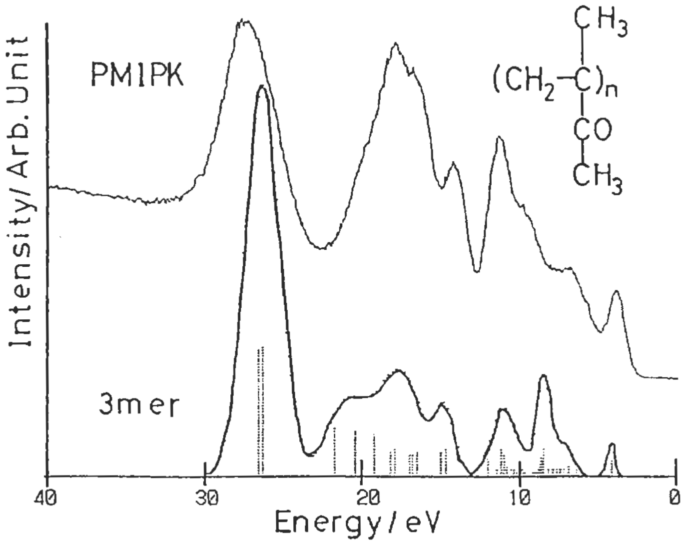
PMIPK Observed peaks, VIP, main AO PICS, orbital nature and functional group for valence XPS of PMIPK. [(the gap between observed and calculated VIPs) = 5.0 eV]

peak(eV)	VIP(eV)	main AO PICS	orbital nature[b]	functional group
28.0 (23-32)[a]	31.53;31.29;31.27	O2s(0.9), C2s, O2p	{sσ (O2s-C2s)-B, pσ (O2s-C2p)-B}	O=C
18.0 (15-23)[a]	23.17;22.97;22.91 24.26-26.67 21.58-22.05	C2s(0.8), O2s C2s(0.7), O2s C2s	sσ (C2s-C2s, O2s)-B sσ (C2s-C2s, O2s)-B sσ (C2s-2s)-B	-C-C-, -C=O -C-C-, -C=O -C-C-
14.5 (13-15)[a]	19.68-20.04	C2s	sσ (C2s-2s)-B	-C-C-
12.0 (5-13)[a]	15.54-17.03 many adjacent levels 11.30-15.34	C2s, O2s, O2p, C2p C2p, O2p	p, sσ (C2p, 2s-H1s, O2s)-B pπ $_p$, π (C2p-C, O2p)-B	$-CH_2$, -C=O -C-C-, -C=O
4.0 (3-5)[a]	9.46;9.18;9.17	O2p	pπ (lone pair)-NB	O=C-

---

[a] shows the peak range.

[b] π_p indicates the pseudo π orbitals of the CH_2 groups. B and NB mean bonding and non-bonding, respectively. (C, O2s-2p) means (C2s-C2p) and (O2s-O2p). (C2p, O2p-C2p) denotes (C2p-C2p) and (O2p-C2p), and so on.



PVEK Observed peaks, VIP, main AO PICS, orbital nature and functional group for valence XPS of PVEK. [(the gap between observed and calculated VIPs) = 5.0 eV]

peak(eV)	VIP(eV)	main AO PICS	orbital nature[b]	functional group
28.0 (23-32)[a]	31.37;31.18;31.11	O2s(0.9), C2s, O2p	{sσ (O2s-C2s)-B, pσ (O2s-C2p)-B}	O=C
19.5 (18-23)[a]	24.20-26.11 22.81-23.87	C2s(0.7), O2s C2s	sσ (C2s-C2s, O2s)-B sσ (C2s-2s)-B	-C-C-, -C=O -C-C-
16.5 (13.5-18)[a]	19.64-21.23	C2s	sσ (C2s-2s)-B	-C-C-
12.0 (9-13.5)[a]	15.57-17.18	{C2s, O2s, O2p, C2p; C2p}	{p, sσ (C2p, 2s-H1s, O2s)-B, pπ $_p$, σ (C2p-C2p, H1s)-B}	$-CH_2$, -C=O -C-C-, $-CH_2$
7.0 (5-9)[a]	12.92-13.35 many adjacent levels 13.53-15.17 11.42-12.77	O2p, C2p C2p, O2p, O2s, C2s C2p, O2p	pπ, π_p(O, C2p-C2p)-B pπ $_p$, π (C2p-C, O2p)-B pπ $_p$, π (C2p-C, O2p)-B	O=C-, -C-C- -C-C-, -C=O -C-C-, -C=O
4.0 (3-5)[a]	9.28;9.05;9.04	O2p	pπ (lone pair)-NB	O=C-

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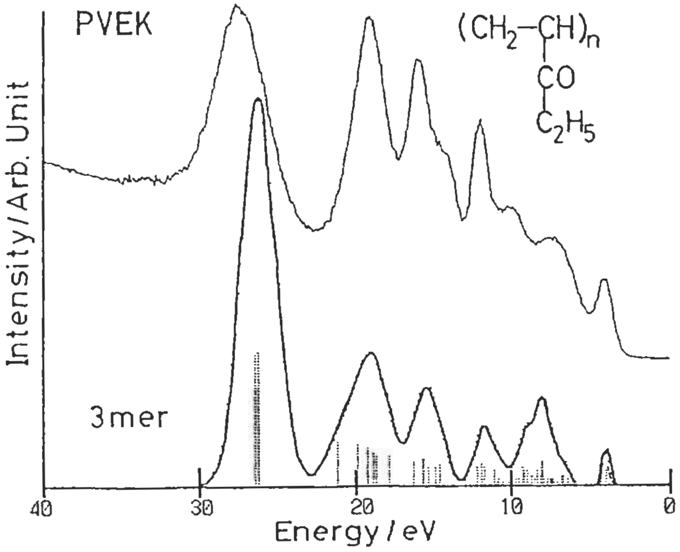
[a] shows the peak range.

[b] π_p indicates the pseudo π orbitals of the CH_2 groups. B and NB mean bonding and non-bonding, respectively. (C, O2s-2p) means (C2s-C2p) and (O2s-O2p). (C2p, O2p-C2p) denotes (C2p-C2p) and (O2p-C2p), and so on.

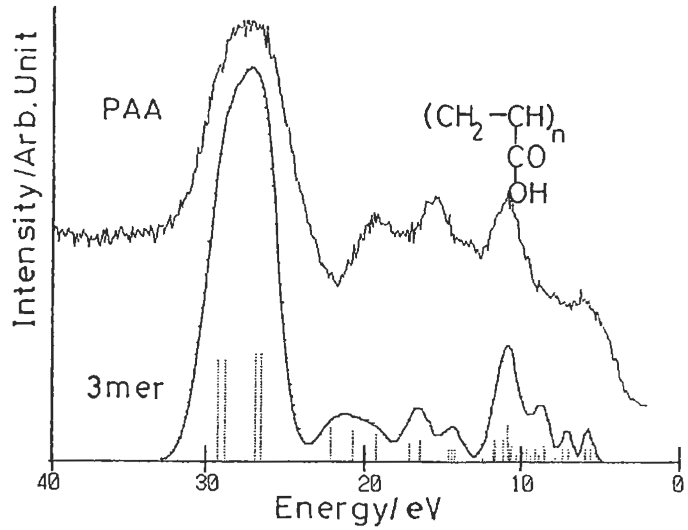


P A A Observed peaks, VIP, main AO PICS, orbital nature and functional group for valence XPS of PAA. [(the gap between observed and calculated VIPs) = 3.5 eV]

peak(eV)	VIP(eV)	main AO PICS	orbital nature[b]	functional group
26.5	32.70;32.30;32.24	O2s(0.9),C2s(0.1)	sσ (O2s-C2s)-B	-O-, O=C
(23-31)[a]	30.38;30.01;29.99	O2s	pσ (O2s-C2p)-B	O=C, -O-
19.5	25.56;24.18;22.73	C2s	sσ (C2s-2s)-B	-C-C-(main chain)
(17-22)[a]				
15.5	20.59;20.00;19.83	C2s(0.8),O2s,O2p	pσ (C2s-C,O2p)-B	-C-C-,-O-C=O
(12-17)[a]	18.13;17.96;17.71	C2s(0.7),O2p	pσ (C2s-C,O2p)-B	-C-C-,-O-C=O
11.0	(16.00-14.38)	O2s(0.7),O2p,C2s	pσ (O,C2p-2s)-B	O-, O=C
(10-12)[a]	many adjacent levels			
6.0	below 14.26 eV	O2p,O2s,C2p,C2s	{pσ (O,C2p-2s)-B,	-O-,O=,-C-
(3-10)[a]	many adjacent levels		pπ (C2p,O2p-C2p)-B}	
	10.91;10.62;10.61	O2p	pπ (lone pair)-NB	O=, -O-
	9.59;9.44;9.22	O2p	pπ (lone pair)-NB	O=, -O-

[a] shows the peak range.

[b] B and NB mean bonding and nonbonding, respectively. (C,O2s-2p) means (C2s-C2p) and (O2s-O2p). (C2p,O2p-C2p) denotes (C2p-C2p) and (O2p-C2p), and so on.

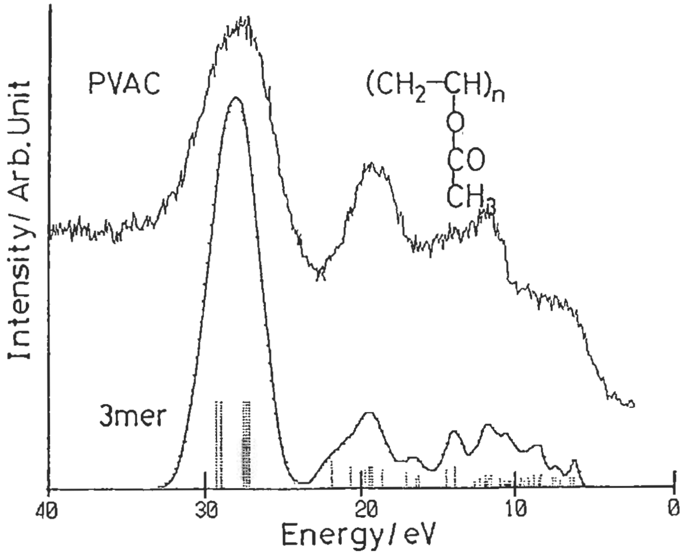


P V A c Observed peaks, VIP, main AO PICS, orbital nature and the functional group for valence XPS of PVAc. [(the gap between observed and calculated VIPs) = 3.0 eV]

peak(eV)	VIP(eV)	main AO PICS	orbital nature[b]	functional group
27.0	32.27;31.98;31.92	O2s(0.9),C2s(0.1)	sσ (O2s-C2s)-B	-O-
(23-32)[a]	30.51;30.31;30.11	O2s	pσ (O2s-C2p)-B	O=C-
19.0	22.68;22.38;22.24	C2s	sσ (C2s-2s)-B	-C-(main chain)
(16-22)[a]	24.78;23.58;21.55	C2s	sσ (C2s-2s)-B	-C-(main chain),-CH$_3$
	20.01;19.37;19.19	C2s(0.8),O2p(0.2)	pσ (C2s-O2p)-B	-C-O-C=O
12.0	(14.96-14.60)	O2s,O2p,C2s,C2p	pσ (O,C2p-2p)-B	-O-C-, O=C-
(10-15)[a]	17.40;16.91;16.84	O2s,O2p,C2s,C2p	pσ (O,C2p-2p)-B	-O-C-, O=C-
	(15.70-15.05)	O2p,C2p	pσ,pπ (C,O2p-2p)-B	{-C-C-(main chain), -C-O-, O=C-}
(3-8)[a]	below 14.01 eV many adjacent levels (14.01-11.39)	O2p,C2p	{pπ (O2p,C2p-C2p)-B: pσ (C2p-H1s)-B}	-O-,O=,-C- -CH$_3$
	10.67;10.44;10.16	O2p	pπ (lone pair)-NB	O=, -O-
	9.48;9.34;9.21	O2p	pπ (lone pair)-NB	O=, -O-

[a] shows the peak range.

[b] B and NB mean bonding and nonbonding, respectively. (C,O2s-2p) means (C2s-C2p) and (O2s-O2p). (C2p,O2p-C2p) denotes (C2p-C2p) and (O2p-C2p), and so on.



P M A Observed peaks, VIP, main AO PICS, orbital nature and functional group for valence XPS of PMA. [(the gap between observed and calculated VIPs) = 3.5 eV]

peak(eV)	VIP(eV)	main AO PICS	orbital nature[b]	functional group
27.5	32.30;31.97;31.96	O2s(0.9):C2s(0.1)	sσ (O2s-C2s)-B	-O-, O=C
(23-33)[a]	30.42;30.13;30.08	O2s(0.97);C2s(0.03)	pσ (O2s-C2p)-B	O=C, -O-
18.0	21.49;21.32;21.13	C2s(0.8);O2s(0.15)	sσ (C2s-C,O2s)-B	-O-C, -CH$_3$
(17-22)[a]	25.40;24.07;22.74	C2s	sσ (C2s-C2s)-B	-C-(main chain), -CH$_3$
	20.21;19.31;19.20	C2s	sσ (C2s-C2s)-B	-C-(main chain), -CH$_3$
15.0	17.25;17.01;16.92	C2s(0.7):O2s, O2p	pσ (C2s-C, O2p)-B	-C-(main chain), -O-CO-
(12.5-17)[a]	(16.16-15.16)	O2p(0.5);C2p(0.5)	pσ, pπ (O, C2p-2p)-B	-O-C=O-
11.0	(14.68-13.48)	O2s(0.5);O2p(0.3)	pσ (O, C2p-O2p, 2s)-B	-O-CO-, -C-(main chain)
(9.5-12.5)[a]	many adjacent levels			
	(13.16-11.84)	C2p(0.7), O2p(0.3)	pσ, pπ (O, C2p-2p)-B	-O-C=O
(4-9.5)[a]	11.74;11.48;11.34	O2p(0.7);C2p(0.3)	pπ (lone pair)-NB	O=C-, -O-
	10.56;10.31;10.28	O2p	pπ (lone pair)-NB	O=, -O-
	9.50;9.44;9.17	O2p	pπ (lone pair)-NB	O=, -O-

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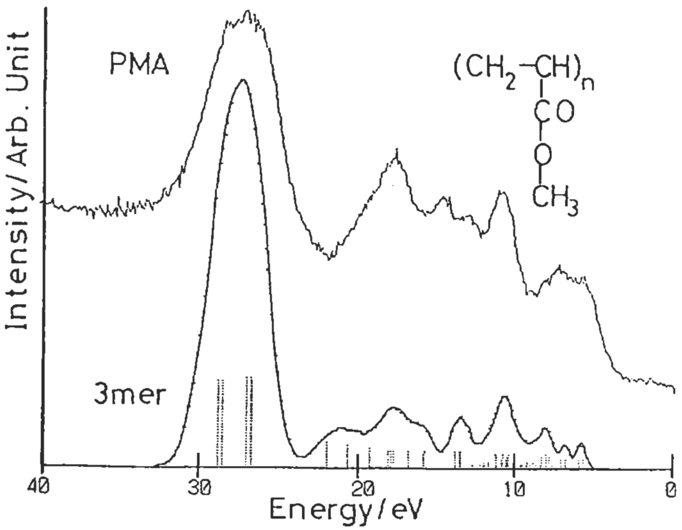
[a] shows the peak range.

[b] B and NB mean bonding and nonbonding, respectively. (C, O2s-2p) means (C2s-C2p) and (O2s-O2p), (C2p, O2p-C2p) denotes (C2p-C2p) and (O2p-C2p), and so on.



P M A A Observed peaks, VIP, main AO PICS, orbital nature and functional group for valence XPS of PMAA. [(the gap between observed and calculated VIPs) = 4.0 eV]

peak(eV)	VIP(eV)	main AO PICS	orbital nature[b]	functional group
27.0	32.95;32.59;32.52	O2s(0.9), C2s	{sσ (O2s-C2s)-B,	-O-C=O
(22-33)[a]	30.62;30.25;30.25	O2s	pσ (O2s-C2p)-B}	O=C-O-
19.0	26.36;25.10;23.94	C2s	sσ (C2s-2s)-B	-C-C-(main chain)
(18-22)[a]				
16.0	{21.64;21.34;21.13;	C2s	sσ (C2s-H1s)-B	-CH$_3$
(14-18)[a]	20.47;20.16;20.01}	C2s	pσ (C2s-O2p)-B	-C=O
11.0	14.55-16.01	O2p, O2s, C2p	pπ : pσ (O2p, 2s-C2p)-B	O=C-O-
(9-14)[a]	18.02;17.61;17.45	C2s(0.6), O2p	{pσ (C2s-2p)-B,	-C-C-(main chain)
			pπ (O2p-C2p)-B}	O=C-
6.0	11.52-14.27	O2p, C2p, O2s	pπ p, π (C2p-C, O2p)-B	{-C-C-(main chain),
(3-9)[a]	many adjacent levels			-O-C=O}
	10.57-11.09	O2p	pπ (lone pair)-NB	O=C-O-
	9.51-9.86	O2p	pπ (lone pair)-NB	O=C-O-

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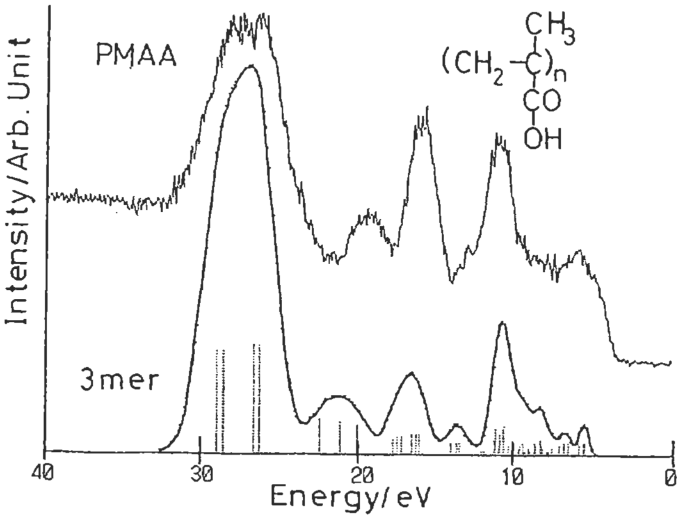
[a] shows the peak range.

[b] B and NB mean bonding and nonbonding, respectively. (O, C2p-2p) means (O2p-C2p) and (C2 -C2p), (C, O2p-C2p) denotes (C2p-C2p) and (O2p-C2p), and so on.

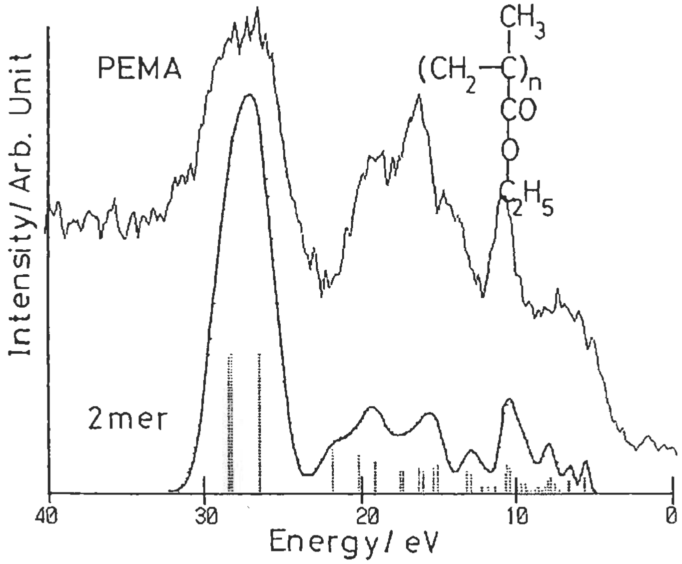


PEMA Observed peaks, VIP, main AO PICS, orbital nature and functional group for valence XPS of PEMA. [(the gap between observed and calculated VIPs) = 4.0 eV]

peak(eV)	VIP(eV)	main AO PICS	orbital nature[b]	functional group
28.0	{32.37;32.26;	O2s(0.9), C2s	sσ (O2s-C2s)-B,	-O-C=O
(22.5-32)[a]	30.48;30.39}	O2s	pσ (O2s-C2p)-B	O=C-O-C
19.0	23.00-25.77	C2s(0.9), O2s	sσ (C2s-C, O2s)-B	-C-C-, -C=O
(18-22.5)[a]				
17.0	19.10-21.51	C2s	sσ (C2s-C2s, H1s)-B	-C-C-, -CH$_3$
(15.5-18)[a]				
15.0	16.97;17.21	C2s, O2s, O2p, C2p	pσ (O2p-C2s;C2p-O2s)-B	-O-C-
(12-15.5)[a]	15.43-16.29	O2p, C2p	pπ, pπ$_p$(C2p-O2p, C2p)-B	-C=O, -C-C-
11.0	14.39-14.72	O2s, O2p, C2p	pπ, pσ (O, C2p, -C2p, O2s)-B	O=C-, C-C-
(9-12)[a]	many adjacent levels			
	13.13-13.92	O2p, C2p	pπ, pπ$_p$(C2p-O2p, C2p)-B	O=C-O-C, -C-C-
7.0	11.25-12.01	O2p, C2p	pπ, pπ$_p$(C2p-O2p, C2p)-B	O=C-O-C, -C-C-
(3-9)[a]	12.14-12.84	O2p, C2p	pπ, pπ$_p$(C2p-O2p, C2p)-B	O=C-O-C, -C-C-
5.0	10.67;10.62	O2p	pπ (lone pair)-NB	-O-C=O
4.0	9.69;9.65	O2p	pπ (lone pair)-NB	O=C-O-

[a] shows the peak range.

[b] B and NB mean bonding and nonbonding, respectively. (O, C2p-2p) means (O2p-C2p) and (C2p-C2p). (C, O2p-C2p) denotes (C2p-C2p) and (O2p-C2p), and so on.

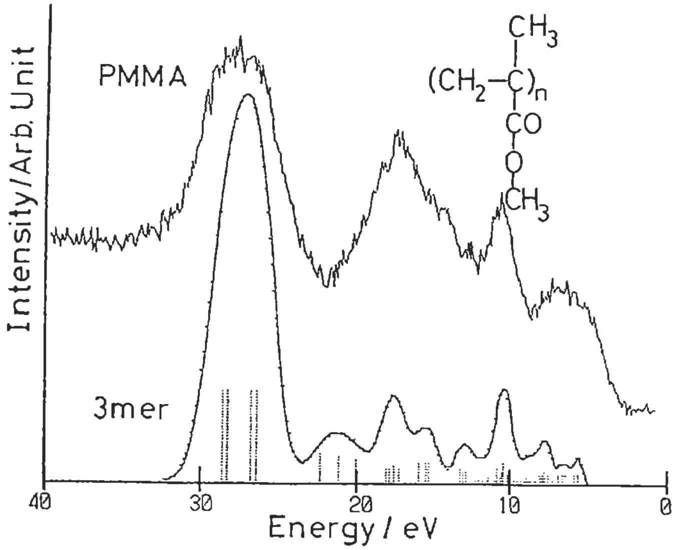


PMMA Observed peaks, VIP, main AO PICS, orbital nature and functional group for valence XPS of PMMA. [(the gap between observed and calculated VIPs) = 3.5 eV]

peak(eV)	VIP(eV)	main AO PICS	orbital nature[b]	functional group
27.0	32.63;32.32;32.25	O2s(0.9), C2s(0.1)	sσ (O2s-C2s)-B	-O-, O=C
(23-30)[a]	30.73;30.42;30.36	O2s	pσ (O2s-C2p)-B	O=C, -O-
17.0	{22.05;21.84;21.75;	C2s	pσ (C2s-O2p)-B	-O-CH$_3$
	21.60;21.46;21.18}			
(13-22)[a]	26.27;25.06;23.95	C2s	sσ (C2s-C2s)-B	-C-C-(main chain)
	19.90;19.40;19.28	C2s(0.9), O2s(0.1)	sσ (C2s-C, O2s)-B	-C-C-, -O-CH$_3$
10.0	(14.86-14.12)	O2s(0.5), O2p, C2s	pσ (O, C2p-O, C2s)-B	-O-CH$_3$
(9.5-12)[a]	many adjacent levels			
	(17.28-15.00)	O2p, C2p, O2s, C2s	pσ (O, C2p-2p)-B	-O-C-C-, O=C-C-
	(13.78-13.02)	O2p, C2p	pσ, pπ (C, O2p-2p)-B	-C-C-O-, O=C-C-
7.0	below 12.90 eV	O2p, C2p	pσ, pπ (C, O2p-2p)-B	-C-C-O-, O=C-C-
(3-9.5)[a]	many adjacent levels			
	10.91;10.62;10.41	O2p	pπ (lone-pair)-NB	O=C, -O-C
	9.88;9.68;9.57	O2p	pπ (lone-pair)-NB	O=C, -O-C

[a] shows the peak range.

[b] B and NB mean bonding and nonbonding, respectively. (C, O2s-2p) means (C2s-C2p) and (O2s-O2p). (C2p, O2p-C2p) denotes (C2p-C2p) and (O2p-C2p), and so on.



PET Observed peaks, VIP, main AO PICS, orbital nature and the functional group for valence XPS of PET. [(the gap between observed and calculated VIPs) = 4.0 eV]

peak(eV)	VIP(eV)	main AO PICS	orbital nature[b]	functional group
27.0 (23-32)[a]	32.28;32.04;31.95 29.44-30.37	O2s(0.9),C2s O2s	sσ (O2s-C2s)-B pσ (O2s-C2p)-B	-O-C-, O=C O=C, -O-C
18.5 (16-22)[a]	21.25-23.82 25.66-26.87	C2s C2s(0.8),O2s	sσ (C2s-C2s)-B sσ (C2s-C, O2s)-B	-C=C-(benz), -C-C- -C=C-(benz), O=C-O-
14.0 (12-16)[a]	17.12-19.96 15.60-16.84	C2s(0.5),O2p O2p,C2p,C2s	sσ, pσ (C2s-C2s, O2p)-B pπ, pσ (O, C2p-C2p, C2s)-B	-C=C-(benz), O=C-O- O=C-O, -C=C-(benz)
11.0 (6-12)[a]	14.09-14.86 many adjacent levels 11.66-13.79	O2p,C2p,O2s O2p,C2p	{pπ (O, C2p-C2p)-B, pσ (C2p-O2s)-B} pπ (O, C2p-C2p)-B	O=C-O, -C=C-(benz) O=C-O O=C-O, -C=C-(benz)
5.0 (3-6)[a]	9.12-10.65 7.44-7.88	O2p,C2p O2p,C2p	pπ (O, C2p-C2p, lone-pair)-B, NB pπ (O2p-C2p)-B	O=C-O, -C=C-(benz) O=C-O

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[a] shows the peak range.

[b] B and NB mean bonding and nonbonding, respectively. (C, O2s-2p) means (C2s-C2p) and (O2s-O2p). (C2p, O2p-C2p) denotes (C2p-C2p) and (O2p-C2p), and so on. (benz) means benzene nucleus.