

Simulated Data of Valence XPS of Polymers by MO Calculations Using the Model Molecules. II. Cl-, COO-, F-, N-, S-, and Si-Containing Polymers

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The valence X-ray photoelectron spectra (XPS) of 30 polymers [three Cl-, five COO-, four F-, ten N-, two S-, and six Si- containing groups] 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 AlK α 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

In the previous works [1-6], we performed better assignment of valence X-ray photoelectron spectra (XPS) of polymers by semiempirical Hydrogenic Atoms in Molecules, version 3 (HAM/3) MO [7-9] and deMon density-functional theory (DFT) [10] calculations using the model molecules. The reason relies on both HAM/3 and deMon programs in that the results can be directly compared with experiment, because it uses the idea of "transition state" [11] rather than Koopmans' theorem to predict vertical ionization potentials (VIPs).

In recent study [12], we simulated the valence XPS of thirty-three polymers involving O-, CO-

and COO-groups with HAM/3 program using the model molecules, by considering an energy shift WD to account for solid-state effects [2-6,13-16]. Here, we used the same procedures of HAM/3 and deMon DFT calculations to simulate the valence XPS of Cl-, F-, N-, S-, Si-, and COO-containing polymers [(CH₂-CXY)_n (X;Y) = {(H;Cl) (PVC), (Cl;Cl) (PVDC), (H;C₆H₄Cl) (P4CS), (H;F) (PVF), (F,F) (PVDF), (H;OCOCF₃) (PVTFA), (H;CN) (PAN), (H;CONH₂) (PAM), (CH₃; CONH₂) (PMAM), (H;C₃NH₄) (P4VP), (H;C₄H₆NO) (PNVP)}, (CH₂(CH₂)₃-CH₂COO)_n (PCL), (CH₂(CH₃)-COO)_n (PL), (CH₂-COO)_n (PG), (CH₂-CH(C₆H₅)-CH(COO)CH(CO))_n (PSCMA), (C₂H₄-C(CH₃)₂-C₆H₄-OCOO)_n (PBAC), (CF₂-CF₂)_n (PTFE), (CH₂-CH₂-NH)_n

(PEI), $((\text{CH}_2)_5\text{-CO-NH})_n$ (N6), $(\text{C}(\text{C}_2\text{H}_5))_n$ (PEOx), $(\text{CO-NHC}_6\text{H}_4\text{-CH}_2\text{-C}_2\text{H}_4\text{-NH-CO-NH-(CH}_2)_3\text{-NH})_n$ (PUa), $(\text{CO-NHC}_6\text{H}_4\text{-CH}_2\text{-C}_6\text{H}_4\text{-NH-COO(CH}_2)_4\text{-O})_n$ (PU), $(\text{CH}_2\text{-CH}_2\text{S})_n$ (PETHS), $(\text{C}_6\text{H}_4\text{S})_n$ (PPS), $(\text{Si}(\text{CH}_3)_2)_n$ (PDMS), $(\text{Si}(\text{C}_6\text{H}_{13})_2)_n$ (PDHS), $(\text{Si}(\text{CH}_3)\text{C}_6\text{H}_5)_n$ (PMPS), $(\text{Si}(\text{CH}_3)(\text{C}_6\text{H}_5)\text{-CH}_2)_n$ (PMPSM), $(\text{Si}(\text{CH}_3)_2\text{-O})_n$ (PDMSO), $(\text{Si}(\text{C-H}_3)(\text{C}_6\text{H}_5)\text{-O})_n$ (PMPSO)]. 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 [17] for molecular photoionization crosssection. The linewidth of a peak of ionization energy I_k was taken to be $0.10 I_k$ (proportional to the ionization energy), as in previous studies.

Computational Approach

As indicated in previous works [1-6,12], we used the relation between calculations for molecules of the oligomer or monomer model and experiments on a solid polymer; $I_k(E_F) = I_k - WD$, where I_k is the ionization energy relative to the Fermi level. I_k and WD denote computed VIPs and the sum of the work function of the sample and other energy effects, respectively.

For ionization of an electron from molecular orbital(MO) ϕ_k , for example, we can apply the Janak theorem [18] and set $F(1/2)$ to $-\epsilon_k$ at $x = 1/2$: we defined $E(x) = \sum x^k E_k$, where $E(0)$ and $E(1)$ correspond to the initial and final states, respectively, and x is assumed to be a continuous variables. We also defined the first derivative $F(x) = \partial E(x) / \partial x$. In the case of the VIPs of the valence regions, we use the restricted diffuse ionization (rDI) approximation which As-brink et al. [7] proposed in the HAM/3 method. In the rDI model,

one can spread the partial electron removal over the whole set of valence molecular orbitals(MOs), hence allowing the determination of all VIPs in one single run. Thus, only two SCF calculations are needed to calculate the whole valence XPS spectrum within the DFT/rDI approximation, whatever the size of the system.

The model oligomer or monomer molecules $[\text{H}-(\text{CH}_2\text{-CXY})_k\text{-H}]$ ($k = 3, 2$ or 1) without and with Cl-, S- and Si-atoms were calculated by the MO calculations using HAM/3 and deMon DFT programs, respectively. For the geometry of the molecules, we used the optimized cartesian coordinates from the semiempirical AM1 (version 6.0) method [19]. The deMon calculations were performed with the exchange-correlation potential labeled as B88/P86, made from Becke's 1988 exchange functional [20] and Perdew's 1986 correlation functional [21]. In the program, we used a nonrandom grid and a polarized valence double-zeta (DZVP) basis [10] of (621/41/1*) for C and O, (41) for H and (6321/521/1*) for Cl, S and Si 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 and (5,4;5,4) for Cl, S and Si.

In the calculation of core-electron binding energies (CEBEs) between 100.0 and 600.0 eV, we needed the accurate numbers of five figures, while the valence XPS in the range of 0-50 eV were able to be simulated considerably well with the three significant figures. The valence spectra can, thus, be analyzed with a polarized valence double-zeta (DZVP) basis set and without a larger consistent-correlation polarized valence triple-zeta (cc-pVTZ) basis. In order to simulate the valence XPS of polymers theoretically, we constructed from a superposition of peaks centered on the VIPs, I_k . As was done in previous works

[1-6,12] each peak was represented by a Gaussian curve. The intensity was estimated from the relative photoionization cross section for Al K α radiation using the Gelius intensity model. For the relative atomic photoionization crosssection, we used the theoretical values from Yeh [22]. In the case of the line-width ($WH(k)$), we used $WH(k) = 0.10I_k$ for the models, as adopted in previous works. For polymers except for Si-containing groups, we cited the experimental valence XPS by Beamson and Briggs [23]. In the case of Si-containing polymers, we referred to experimental results by us [5].

Results and Discussion

A feature of the present study is the use of the rDI model using deMon program for the simulation of valence spectra of Cl-, S- and Si-containing polymers, since we were only able to calculate the valence XPS of polymers involving C, N, O and F atoms with the HAM/3 program. In previous work [25], we simulated thirty three polymers [hydrocarbons(11), O-groups(12), CO-groups(3), and COO-groups(7)] by HAM/3 calculations using model oligomers or monomers. The simulated spectra showed good accordance with experimental ones. Here we calculated valence XPS of COO-, N- and F-containing polymers using HAM/3 program, and simulated the valence spectra of Cl-, S- and Si-containing polymers using deMon DFT program.

(a) Cl-containing polymers

For PVC, PVDC, and P4CS, the intense peaks (at around 6 or 5 eV) are due to 3p lone-pair orbitals of the pendant Cl of the polymers. Broader spectra between 15 and 22 eV are determined by the Cl 3s main contributions, respec-

tively. We showed the orbital characters of PVC, PVDC, and P4CS in tables. The WD was underestimated as 4.0 and 3.0 eV for models of PVC and (PVDC, P4CS) polymers, respectively.

(b) COO-containing polymers

The theoretical spectra of PCL, PL, PG, PSCMA, and PBAC polymers with the spectral patterns show good accordance with the experimental valence binding energy spectra. The intense spectra, which are due to O 2s-dominant contribution at around 28 eV, correspond to the theoretical values of s- σ (O 2s-C 2s)-bonding and p- σ (O 2s-C 2p)-bonding orbitals. In the assignment of these polymers, the s- σ and p- σ orbitals depend on the two components, -O- and >C=O.

(c) F-containing polymers

For PVF, PVDF, PTFE, and PVTFA polymers, the intense spectra in the range of 30-40 eV, characteristic of F 2s contributions, correspond to the VIP of s- σ (F 2s-C 2s)- and p- σ (F 2s-C 2p)-bonding orbitals. For PVTFA, the shoulder peak between 25 and 30 eV is due to the s- σ (O2s-C2s) and p- σ (O2s-C2p)-bondings of the side chain -O- and O=C groups. In these figures, the peaks at around 20 eV correspond to the VIP of s- σ (C 2s-C 2s)-bonding orbitals which result from the main chain -C-C- groups.

(d) N-containing polymers

Theoretical spectra of PEI, PAN, PAM, PMAM, N6, P4VP, PNVP, PEOx, PUa, and PU polymers appear to show good agreement with the observed ones. For P4VP, intense spectra in the range of 20-25 eV are determined by N 2s main contributions, while large peaks between 20 and 30 eV for N6, PEOx, PUa, and PU are due to both N 2s and O 2s main contributions,

respectively. In these spectra, the double peaks between 12 and 20 eV result mainly from p- σ (C 2s-N 2p) and s- σ (C 2s-C 2s) bonding orbitals. The peaks (at around 5 eV) are due to lone-pair orbitals of main chain N and/or O for these polymers.

(e) S-containing polymers

For PETHS and PPS, the theoretical spectra also appear to show a considerably good agreement with the experimental ones. We showed the orbital characters in the tables.

(f) Si-containing polymers

In figures of PDMS, PDHS, and PMPS, there exist the characteristic spectra, in the range of 12-22 eV, due to the difference between the pendant groups (-CH₃, -C₆H₁₃ and -C₆H₅). Simulated spectrum of PMPSM show good accordance with the observed ones. The intense peak at around 17 eV is due to s- σ (C 2s-C 2s) and s- σ (C 2s-Si 3s) bonds of the pendant phenyl group and main chain -Si-C, respectively. The peaks (around 21.0 and 14.0 eV) at both sides of the intense signal result from s- σ (C 2s-C 2s) and p- σ (C 2s-C 2p) bonding orbitals of the pendant phenyl, respectively. The spectrum at around 10.5 eV relies on the p- σ (Si 3s-C 2p) bonds of the main chain. For PDMSO and PMPSO, the intense peak (at around 26 eV) is due to s,p- σ (O 2s-Si 3s, 3p) bonds of the main chain, respectively.

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 polymers, we have clarified the orbital nature of the finger-print spectra which were characterized from the constituent elements (C, Cl, F, N, O, S and Si) in the range of 0-40 eV.

Conclusion

We have calculated the valence XPS of Cl-, COO-, F-, N-, S-, and Si-containing polymers 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 Koopmans' theorem.

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査読者コメント

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JSA Vol.3, No.3(I)の論文の続編で、今回はCl, Siなどを含むポリマーの価電子帯XPSスペクトルの計算と実験の比較に関する論文である。

(I)はヘテロな原子が入らず、CHOのみの分子だったので、計算結果は実験と非常に良い一致を見せていたが、今回はCHO以外の原子が入ったためか(I)の論文に比べて、計算は実験とあまりよく一致しているとは言えない。しかしながら、高分子のピークの帰属は十分できる程度にはよく合っているので、出版の価値は高い。

(I)の論文と比較して、今回のポリマーはどこが計算が難しかったか、あるいは、基底関数の任意性や、適切さ等に関する考察がほしい。というのは今回の一致の悪さの原因は、基底関数が原因ではないかと考えるからである。基底を変えた場合に、スペクトルがどの程度変化するかは、次回の論文に期待するとして、(6321/521/1*)等の基底依存性に関する簡単な記述もあった方がよい。

著者

コメント有り難うございます。

基底関数の依存性に関しましては既に調べました。以下の記述に関しましては、Computational Approachの箇所に加えさせていただきます。

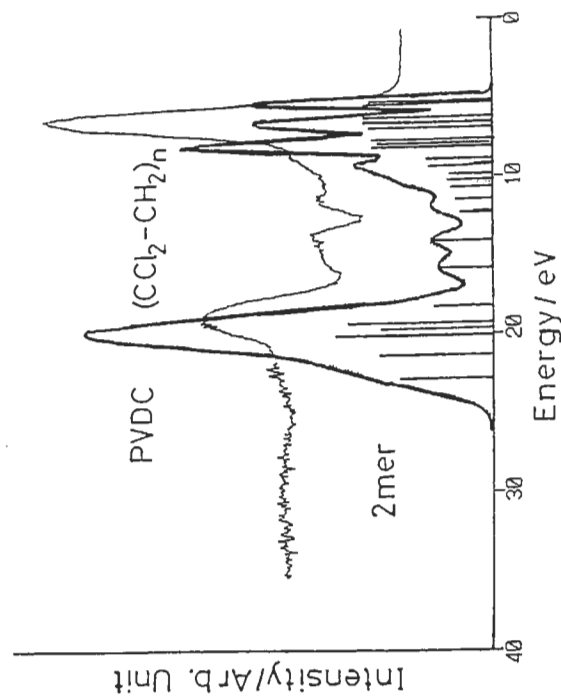
価電子帯(0-50 eV)のスペクトル計算では、有効数字は3桁で充分と考えられます。著者らが計算した結果では基底関数 cc-pVTZ(consistent-correlation polarized valence triple-zeta)では、有効数字5桁まで信頼できる結果が得られます。

これに対しDZVP(polarized valence double-zeta)では有効数字3桁の結果が得られます。従って価電子帯に関しては小さい基底関数DZVPで十分な結果が得られます。今回のPVC, PVDC, PETHSのシミュレーション結果は、cc-pVTZによる著者らのJ. Phys. Chem. Vol. 100, 19455-19460 (1996)の結果と同等です。

PVDC Observed peaks, VIP, main AO PICS, orbital nature and the functional group for valence XPS of PVDC. [(the shift between observed and calculated VIPs) = 3.0 eV]

peak(eV)	VIP(eV)	main AO PICS	orbital nature*	functional group
21.5 (20-23)*	25.90:24.34	C13s(0.7), C2s	σ (C13s-C2s)-B	Cl-C-
18.5 (16-20)*	(23.17:22.66; 23.31:21.33)	C13s(0.8), C2s	$\sigma, p\sigma$ (C13s-C2s, C2p)-B	Cl-C-
14.5 (12-16)*	18.92:17.22	C13s(0.6), C2p, C13p	$\sigma, p\sigma$ (C2s-C13s, 3p, C2s)-B	-C-Cl, -C-C-
10.5 (9-12)	12.18-15.54	C13p(0.8), C13s, C2p	$p\pi$ (C2p, C13p-C2p)-B	-C-Cl, -C-C-
7.0 (5-9)*	8.53-11.38	C13p	$p\pi$ (lone-pair)-NB	-Cl
		many adjacent levels		

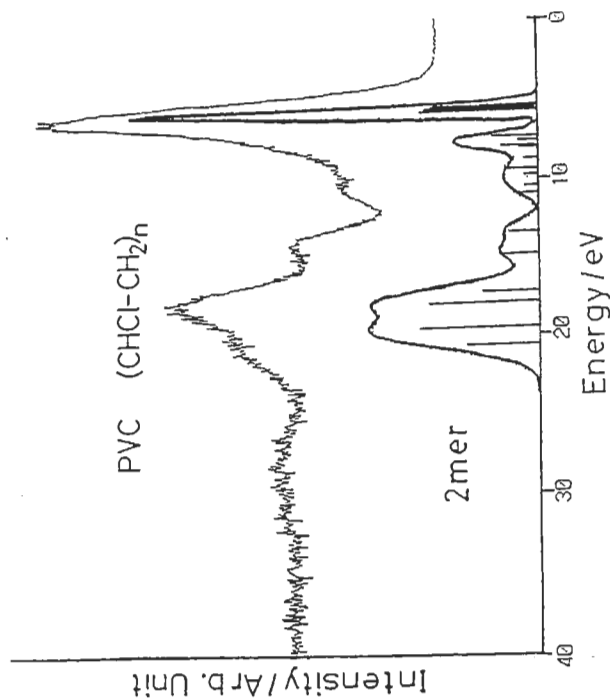
* shows the peak range.
 B and NB mean bonding and nonbonding, respectively. (C13s-C2s, 2p) means (C13s-C2s) and (C13s-C2p). (C2p-C2p, 2s, C13p) denotes (C2p-C2p), (C2p-C2s) and (C2p-C13p), and so on.



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

peak(eV)	VIP(eV)	main AO PICS	orbital nature*	functional group	
20.5 (20-23)*	24.71:23.56	C13s(0.7), C2s(0.3)	σ (C13s-C2s)-B	Cl-C-	
18.0 (16-20)*	22.05:21.24	C13s(0.8), C2s(0.2)	$\sigma, p\sigma$ (C13s-C2s, 2p)-B	Cl-C-	
14.5 (12-16)*	18.99:17.63	C2s(0.6), C13s, C13p	$\sigma, p\sigma$ (C2s-C2s, 2p, C13s)-B	C-C-, -C-Cl	
10.0 (9-12)*	(15.28:14.74; 14.32:13.65)	C13p(0.7), C13s, C2p	$p\pi$ (C2p-C2p, C13p)-B	C-C-, -C-Cl	
6.5 (4-9)*	9.76-10.02	C13p	$p\pi$ (lone-pair)-NB	-Cl	
		many adjacent levels			
		11.65-12.99	C13p(0.9), C2p	$p\pi$ (C13p, C2p-C2p)-B	Cl-C-, -C-C-

* shows the peak range.
 B and NB mean bonding and nonbonding, respectively. (C13s-C2s, 2p) means (C13s-C2s) and (C13s-C2p). (C2p-C2p, 2s, C13p) denotes (C2p-C2p), (C2p-C2s) and (C2p-C13p), and so on.

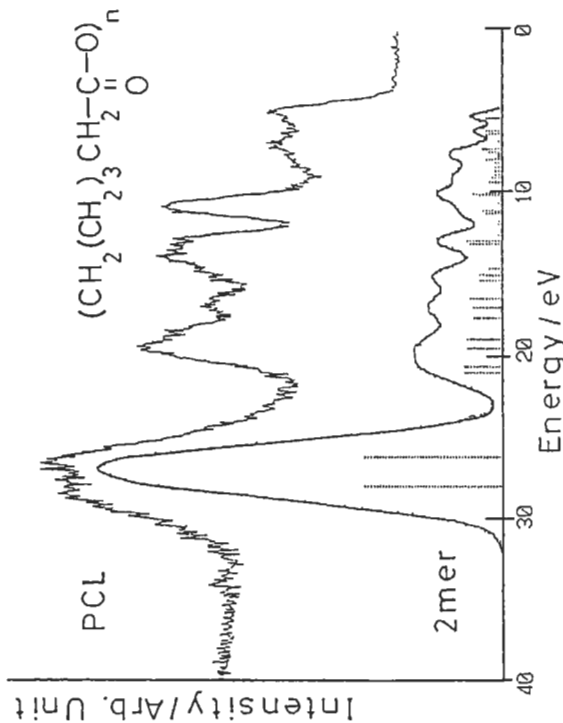


P. C. L. Observed peaks, VIP, main AO PICS, orbital nature and functional group for valence XPS of PCL. [(the gap between observed and calculated VIPs) = 4.0 eV]

peak (eV)	VIP (eV)	main AO PICS	orbital nature ^a	functional group
27.5 (22-32)*	32.07; 31.91 30.17; 30.08	O2s(0.9), C2s O2s	sσ (O2s-C2s)-B, pσ (O2s-C2p)-B	-O-C=O O=C-O-
19.0 (17.5-21)*	22.98-24.95	C2s	sσ (C2s-C2s)-B	-C-C-
17.0 (16-17.5)*	20.49-21.64	C2s(0.9), O2s, O2p	sσ (C2s-C, O2s)-B	-C-C-, -C-O
14.0 (12-16)*	18.58-19.34 17.14; 16.92	C2s, O2s, O2p O2p, C2s, O2s, C2p	sσ (C2s-C, O2s)-B p, sσ (C2s-O2p, 2sC2s)-B	-C-C-, -C-O -O-C=O, -C-C-
11.0 (9-12)*	14.11-15.29 15.80-16.62	O2p, C2p, C2s O2p, C2p	pπ s, pπ σ (O, C2p-C2p, 2s)-B pπ s (C, O2p-C2p)-B	O=C=O, -C-C- -C-C-, -C-O-
(4-9)*	12.16-13.50	O2p, C2p	pπ, pπ s (C, O2p-C2p)-B	O=C=O-, -C-C-
7.0 5.0	10.93-11.98 9.38-10.42	O2p, C2p O2p	pπ, pπ s (C, O2p-C2p)-B pπ (lone pair)-NB	-C-C-, O=C-O- O-, -O-

* 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.

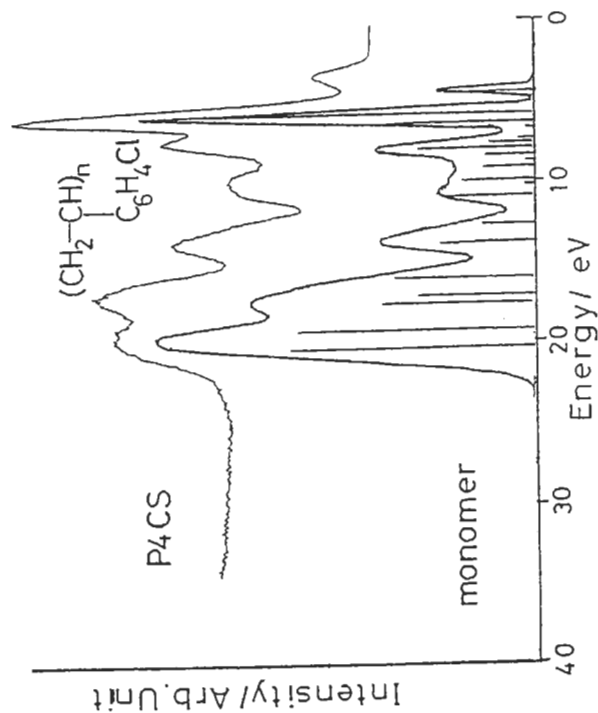


P4CS Observed peaks, VIP, main AO PICS, orbital nature and the functional group for valence XPS of P4CS. [(the shift between observed and calculated VIPs) = 3.0 eV]

peak (eV)	VIP (eV)	main AO PICS	orbital nature ^a	functional group
19.0 (18-22)*	24.83; 23.58	C13s(0.7), C2s(0.3)	sσ (C13s-C2s)-B	Cl-C-
16.5 (14-18)*	22.0; 21.4; 20.3	C2s(0.7), C13s(0.3)	sσ (C2s-C13s)-B	C-Cl
13.0 (11-14)*	18.1; 18.0; 17.0	C2s(0.8), C13s	sσ, pσ (C2s-C13s, 3p, C2s)-B	-C-Cl, -C-C-
10.0 (8-11)*	13.25-15.14	Cl3p(0.8), C13s, C2S	pπ (C2p, Cl3p-C2p)-B	Cl-C, -C-C-
7.0 (6-8)*	11.48-12.92	Cl3p(0.9), C13s, C2S	pπ (Cl3p, C2p-C2p)-B	Cl-C, -C-C-
5.0 (4-6)*	9.92-10.83	Cl3p	pπ (lone pair)-NB	-Cl
3.0 (2-4)*	8.47; 9.13	Cl3p, C2p	pπ (lone pair)-NB, pπ (C2p-C2p)	-Cl, -C-C-

* shows the peak range.

^b B and NB mean bonding and nonbonding, respectively. (Cl3s-C2s, 2p) means (Cl3s-C2s) and (C13s-C2p). (C2p-C2p, 2s, Cl3p) denotes (C2p-C2p), (C2p-C2s) and (C2p-Cl3p), and so on.

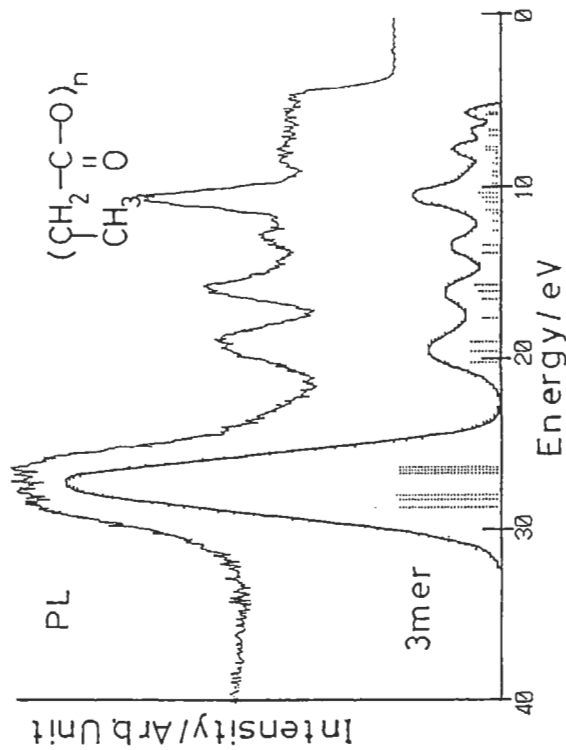


P L Observed peaks, VIP, main A0 PICS, orbital nature and functional group for valence XPS of PL. [(the gap between observed and calculated VIPs) = 4.0 eV]

peak(eV)	VIP(eV)	main A0 PICS	orbital nature ^b	functional group
27.0 (22-32)*	32.73;32.27;31.95 30.70;30.47;30.32	O2s(0.9), C2s O2s	sσ (O2s-C2s)-B, pσ (O2s-C2p)-B	-O-C=O O=C-O-
19.0 (17-21)*	24.10;23.47;22.93	C2s(0.9), O2s	sσ (C2s-C, O2s)-B	-C-C-O-
16.0 (14-17)*	19.67-21.57	C2s(0.9), O2s, O2p	sσ (C2s-C, O2s)-B	-C-C-, -C-O
13.0 (12-14)*	17.84;17.97;17.30 15.49-16.48	C2s, O2s, O2p, C2p O2p, C2p	p, sσ (C2s-C2s, O, C2p)-B pπ s, pπ (C, O2p-C2p)-B	-C-C-, -C-O -C-O-, -C-C-, -C=O
10.5 (9-12)*	13.73-15.32	O2p, C2p	pπ, pπ s (O, C2p-C2p)-B	O=C-, -C-O-, -C-C-
(4-9)*	11.61-13.36 many adjacent levels 10.96;10.71;10.61 9.84;9.70;9.59	O2p, C2p O2p O2p	pπ s, pπ (C, O2p-C2p)-B pπ (lone pair)-NB pπ (lone pair)-NB	-C-O-, -C-C-, -C=O =O, -O- O=

* 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.

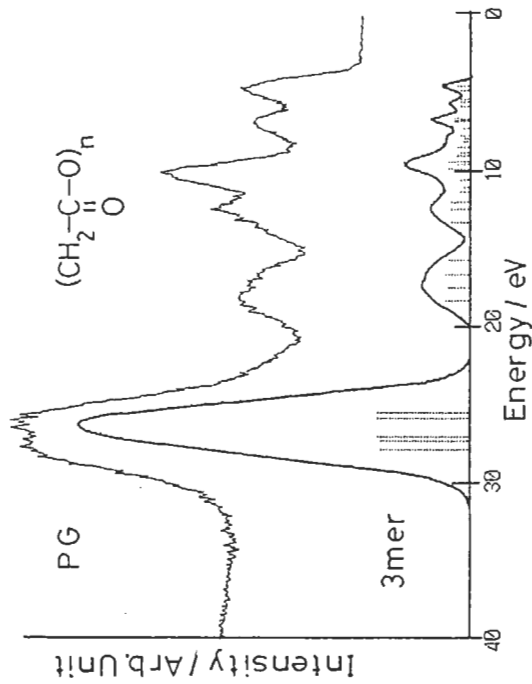


P G Observed peaks, VIP, main A0 PICS, orbital nature and functional group for valence XPS of PG. [(the gap between observed and calculated VIPs) = 5.0 eV]

peak(eV)	VIP(eV)	main A0 PICS	orbital nature ^b	functional group
27.0 (21-32)*	32.84;32.32;32.05 30.84;30.51;30.44	O2s(0.9), C2s O2s	sσ (O2s-C2s)-B, pσ (O2s-C2p)-B	-O-C=O O=C-O-
18.0 (15-21)*	20.68-23.29	C2s(0.7), O2p, O2s	s, pσ (C2s-C, O2s, 2p)-B	-C-C-O-
13.0 (11.5-15)*	18.32;17.50;17.09 15.56-16.38	C2s(0.7), O2s, O2p O2p, C2s, C2p	p, sσ (C2s-O2p, 2s)-B pπ s, pσ (O2p-C2p, 2s)-B	-C-O-, -C=O -O-C-C-
10.5 (8.5-11.5)*	13.57-15.09 many adjacent levels 12.37-13.15	O2p, C2p O2p, C2p	pπ s, pπ (C, O2p-C2p)-B pπ s, pπ (C, O2p-C2p)-B	-C-O-, -C-C-, -C=O -C-O-, -C-C-, -C=O
7.0 (6-8.5)*	11.87;11.84;11.71	O2p	pπ (lone pair)-NB	-O-, =O
5.0 (4-6)*	11.01;10.73;10.56 9.93;9.71;9.66	O2p O2p	pπ (lone pair)-NB pπ (lone pair)-NB	=O, -O- O=

* 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.

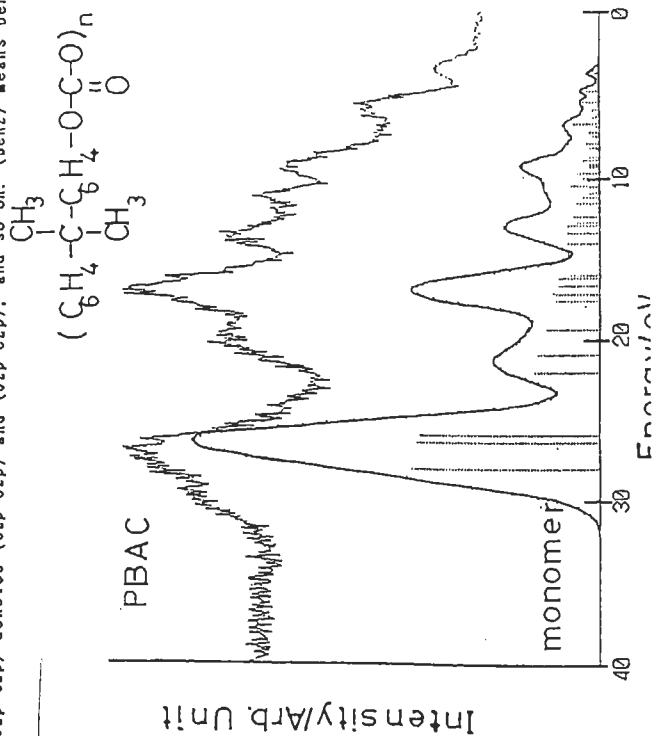


P B A C Observed peaks, VIP, main AO PICS, orbital nature and functional group for valence XPS of PBAC. [(the gap between observed and calculated VIPs) = 5.0 eV]

peak(eV)	VIP(eV)	main AO PICS	orbital nature ^b	functional group
27.0 (23-32)*	32.98;31.30;30.81	O2s	s σ, p σ (O2s-C2s, 2p)-B.	-O-C-, O=C
20.0 (19-23)*	27.00;25.89;24.28	C2s	s σ (C2s-C2s)-B	(-C=C-(benz), -C-C-C-)
17.0 (15-19)*	20.97-22.61	C2s	s σ (C2s-C2s)-B	(-C=C-(benz), -C-C-C-)
14.0 (12.5-15)*	17.40-19.07	C2s(0.7), O2p	s σ, p σ (C2s-C2s, O2p)-B	(-C=C-(benz), -C-O-, -C=O)
11.5 (11-12.5)*	15.44-16.55	O2p, C2p, C2s	p π, p σ (O, C2p-C2p, 2s)-B	C=O, -C=C-(benz)
10.0 (7-11)*	13.94-14.78	O2p, C2p, C2s	p π, p σ (O, C2p-C2p, 2s)-B	C=O, -C=C-(benz)
			many adjacent levels	
			O2p, C2p	0=C, -C=C-(benz)
6.0	11.72-12.44	C2p, O2p	p π (C2p-C, O2p)-B	-C=C-(benz), C=O
4.0	8.69-10.04	C2p, O2p	p π (C2p-C2p, lone-pair)-B, NB	-C=C-(benz), -O-
(2-7)*	10.89-11.37	C2p	p π (C2p-C2p)-B)	-C=C-(benz)

* 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.

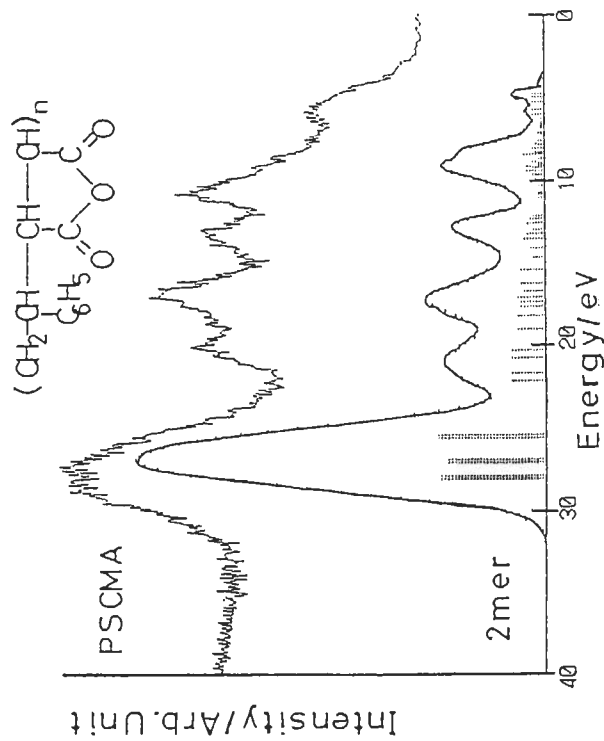


P S C M A Observed peaks, VIP, main AO PICS, orbital nature and functional group for valence XPS of PSCMA. [(the gap between observed and calculated VIPs) = 5.0 eV]

peak(eV)	VIP(eV)	main AO PICS	orbital nature ^b	functional group
28.0 (23-32)*	31.86-33.07	O2s(0.9), C2s	s σ, p σ (O2s-C2s, 2p)-B	-O-C-, O=C
	30.53;30.37	O2s	p σ, s σ (O2s-C2p, 2s)-B	O=C, -O-C
20.0 (19-22)*	25.28-27.16	C2s	s σ (C2s-C2s)-B	(-C=C-(benz), -C-C(main chain))
17.0 (15-19)*	20.41-24.07	C2s	s σ (C2s-C2s)-B	(-C=C-(benz), -C-C(main chain))
13.5 (12-15)*	17.20-19.74	C2s(0.6), O2s, O2p	p σ, s σ (C2s-O2p, O, C2s)-B	(-C=C-(benz), -C-O-, -C-C(main chain), C=O)
11.0 (7-12)*	13.44-15.16	O2p, O2s, C2s, C2p	(p π (O, C2p-C2p)-B, p σ (C2p-C, O2s)-B)	(O=C, -C=C-(benz) -C-C, -C-O-)
	15.41-16.14	O2p, C2s, C2p	p π, p σ (O, C2p-C2p, 2s)-B	-C=C-(benz), O=C, -O-C
	11.30-13.36	O2p, C2p	p π (O, C2p-C2p)-B	O=C, -C=C-(benz)
6.0 (2-7)*	9.84-11.05	O2p	(p π (O2p-C2p, lone pair)-B, NB	O=C, -O-
	9.01-9.37	C2p	p π (C2p-C2p)-B)	-C=C-(benz)

* 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.

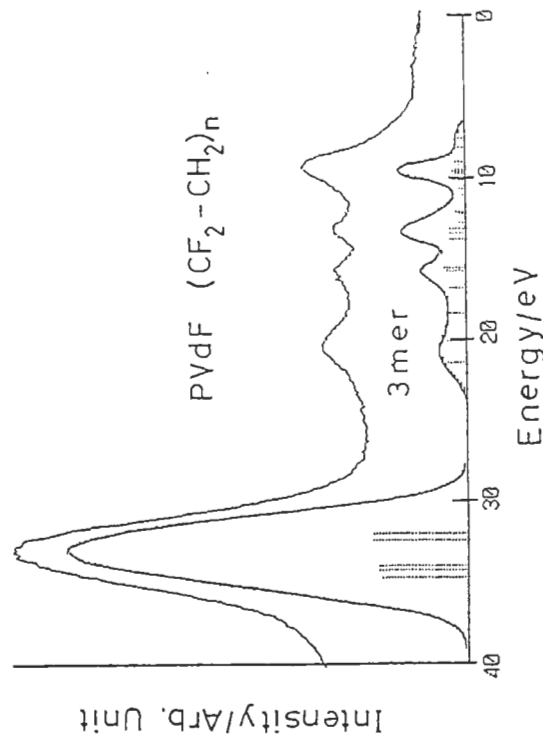


P V d F Observed peaks, VIP, main A0 PICS, orbital nature and functional group for valence XPS of PVdF. [(the gap between observed and calculated VIPs) = 4.0 eV]

peak (eV)	VIP (eV)	main A0 PICS	orbital nature ^b	functional group
33.0 (28-40)*	38.66;38.25;37.97 36.34;36.00;35.94	F2s F2s	sσ (F2s-C2s)-B, pσ (F2s-C2p)-B	F-C F-C
20.5 (18-24)*	25.48;24.10;22.43	C2s(0.8), F2s(0.2)	sσ (C2s-C,F2s)-B -C(main chain), C-F	
16.0 (14.5-18)*	20.85;19.79;19.60	C2s(0.4), F2s, F2p	{pσ (C2s-F,C2p)-B, sσ (C2s-F2s)-B}	C-F, -C(main chain) C-F
13.0 (11.5-14.5)*	17.87;17.85;17.48; 17.25;17.22; (16.10-16.86)	F2p, C2p, F2s F2p, C2p, F2s, C2s	{pσ (C2p-F2s)-B, pπ _s (F2p, C2p-C2p)-B}	C-F, -C(main chain)
9.5 (5-11.5)*	(13.05-13.99) below 15.09 eV	F2p many adjacent levels	pπ (lone pair)-NB pσ (C2p-C2s)-B	F-C
	15.09;14.77;14.22 12.15;11.61;10.97	F2p F2p, C2p	pπ _s (F2p, C2p-C2p)-B pπ (lone pair)-NB	C-F F-C

* shows the peak range.

^b π_s indicates the pseudo π orbitals of the C-F, B and NB mean bonding and nonbonding, respectively. (C, F2s-2p) means (C2s-C2p) and (F2s-F2p). (C2p, F2p-C2p) denotes (C2p-C2p) and (F2p-C2p), and so on.

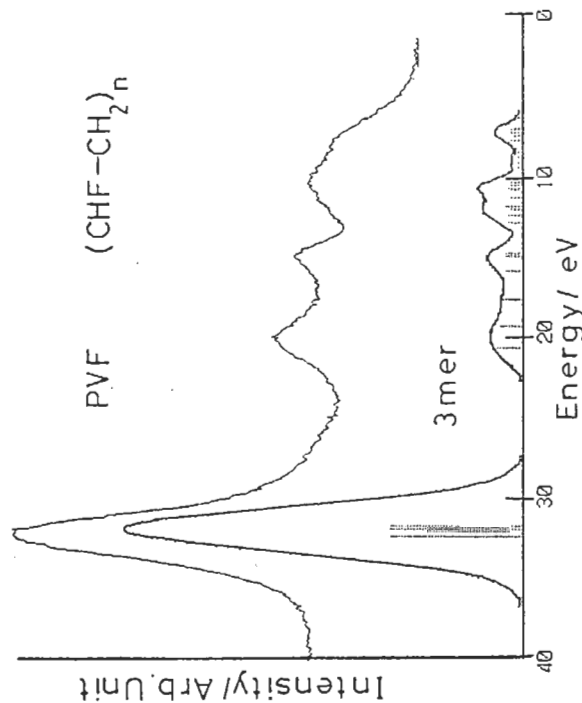


P V F Observed peaks, VIP, main A0 PICS, orbital nature and functional group for valence XPS of PVF. [(the gap between observed and calculated VIPs) = 4.5 eV]

peak (eV)	VIP (eV)	main A0 PICS	orbital nature ^b	functional group
32.5 (29-36)*	36.88;36.45;36.19	F2s	sσ (F2s-C2s)-B, pσ (F2s-C2p)-B	F-C F-C
19.0 (18-23)*	25.14;23.75;22.07	C2s(0.7), F2s(0.3)	sσ (C2s-2s)-B -C(main chain), C-F	
15.5 (13.5-17.5)*	20.35;19.43;19.23	C2s(0.5), F2p, F2s	pσ (C2s-F2p)-B pσ (C2s-2p)-B	C-F, -C(main chain) -C(main chain)
11.0 (4-13)*	below 17.26 eV 12.27;11.98;11.78 11.57;11.45;10.85	F2p, C2p, F2s, C2s F2p F2p	pσ (F, C2p-2s)-B pπ _s (C2p, F2p-C2p)-B pπ (lone pair)-NB pπ (lone pair)-NB	C-F, -C(main chain) -C(main chain), C-F C-F

* shows the peak range.

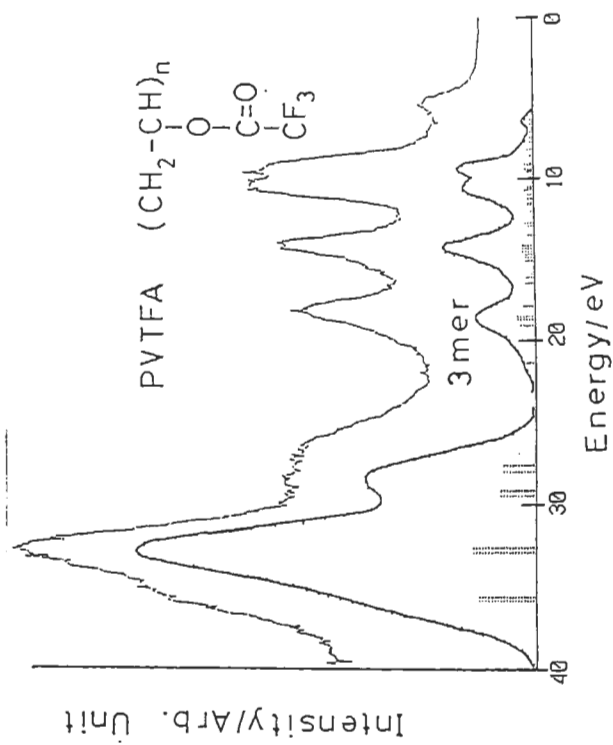
^b π_s indicates the pseudo π orbitals of the C-F, B and NB mean bonding and nonbonding, respectively. (C, F2s-2p) means (C2s-C2p) and (F2s-F2p). (C2p, F2p-C2p) denotes (C2p-C2p) and (F2p-C2p), and so on.



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

peak(eV)	VIP(eV)	main AO PICS	orbital nature ^b	functional group
33.0 (30-40)*	39.87:39.84:39.62 36.88:36.84:36.67; 36.63:36.60:36.57)	F2s F2s	sσ (F2s-C2s)-B, pσ (F2s-C2p)-B	F3C- F3C-
28.0 (22-30)*	33.44:33.10:33.08 31.93:31.58:31.49	O2s O2s	sσ (O2s-C2s)-B pσ (O2s-C2p)-B	-O-C, C=O C=O, -O-C
18.0 (16.5-22)*	25.29:23.98:23.04; 22.67:22.45:21.85)	C2s(0.7), O2s, F2p F2s(0.4), C2s, F2p	s, pσ (C2s-O2s, F2p)-B s, pσ (C2s-F2s, Fp)-B	-C-C-C, O-C-C-F C-F
14.0 (12-16.5)*	18.14-18.52 18.72-20.48 16.78-17.56	F2s(0.5), F2p C2s, F2p, O2p O2p, C2s	pσ (F2s-C2p)-B pσ (C2s-F, O2p)-B pσ (C2s-O2p)-B	F-C C-F, C-O, C=O C-O, C=O
10.0 (7-12)*	13.13-14.80 many adjacent levels 15.00-16.18 12.02-13.03	F2p(0.8), O2p, C2p O2p, O2s, C2s O2p, C2p	pπ _s (F, O2p-C2p)-B, pπ, pσ (O2p-C2p, 2s)-B pπ _s , π (O2p-C2p)-B	O-C-C-F -O-C, O=C -O-C, C=O
5.5 (4-7)*	11.79:11.48:11.04 10.63:10.36:10.34	O2p O2p	pπ (lone pair)-NB pπ (lone pair)-NB	-O-C, C=O C=O, -O-C

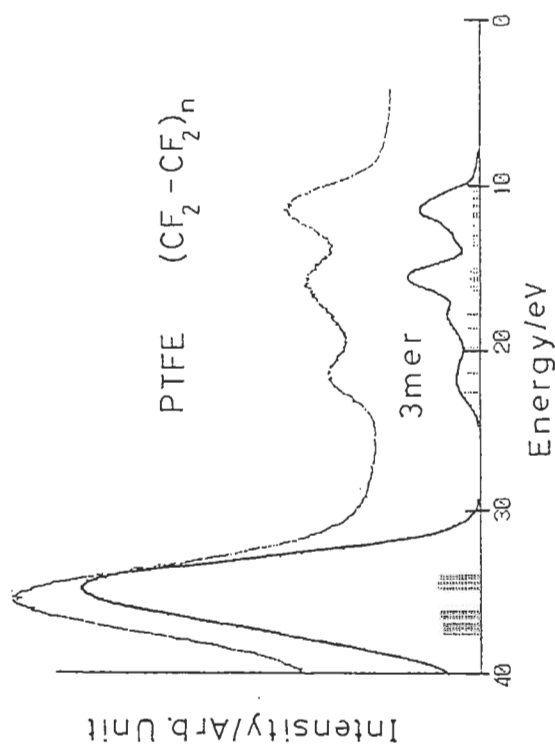
* shows the peak range.
^b π_s indicates the pseudo π orbitals of the C-F, B and NB mean bonding and nonbonding, respectively. (C, F2s-2p) means (C2s-C2p) and (F2s-F2p). (C2p, F2p-C2p) denotes (C2p-C2p) and (F2p-C2p), and so on.



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

peak(eV)	VIP(eV)	main AO PICS	orbital nature ^b	functional group
35.5 (28-40)*	41.63-38.78 38.65-37.93	F2s F2s	sσ (F2s-C2s)-B, pσ (F2s-C2p)-B	F-C F-C
21.5 (20-25)*	26.71:25.56:24.13 C2s(0.7), F2s(0.3)	C2s(0.7), F2s(0.3)	sσ (C2s-C, F2s)-B	-C(main chain), C-F
16.0 (14-20)*	20.43-19.03	F2s, F2p, C2s	[pσ (F2p-C2s)-B, pσ (C2p-F2s)-B]	F-C
22.79:21.93:21.82		F2s, F2p, C2s	[pσ (F2p-C2s)-B, pσ (C2p-F2s)-B]	F-C
11.5 (8-14)*	below 17.66 eV many adjacent levels	F2p	[pπ (lone pair)-NB, pπ _s (F2p-C2p)-B]	F-C

* shows the peak range.
^b π_s indicates the pseudo π orbitals of the C-F, B and NB mean bonding and nonbonding, respectively. (C, F2s-2p) means (C2s-C2p) and (F2s-F2p). (C2p, F2p-C2p) denotes (C2p-C2p) and (F2p-C2p), and so on.

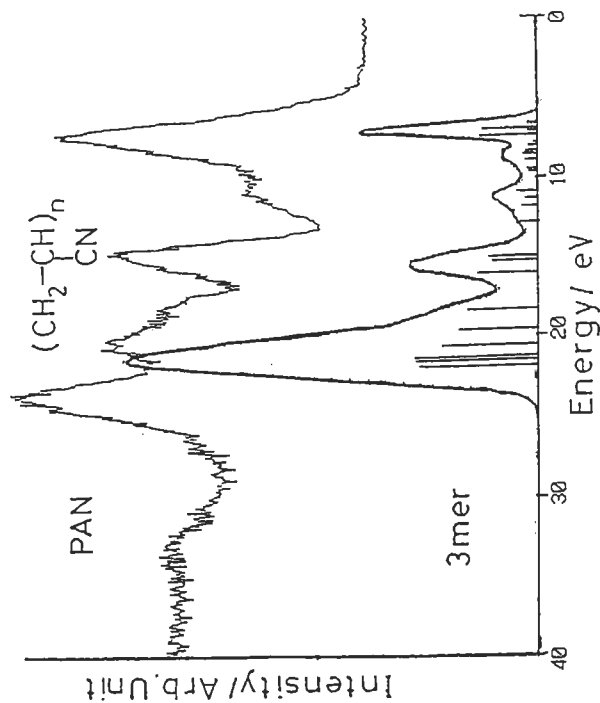


PAN Observed peaks, VIP, main A0 PICS, orbital nature and functional group for valence XPS of PAN. [(the shift between observed and calculated VIPs) = 4.0 eV]

peak(eV)	VIP(eV)	main A0 PICS	orbital nature ^a	functional group
25.4 (22.1-28.0)*	25.8:25.4:25.3	N2s(0.6), C2s(0.4)	sσ (N2s-C2s)-B	N≡C-
20.5 (17.0-22.1)*	24.5:23.5:22.2	C2s(0.7), N2s(0.3)	sσ, pσ (C2s-N2s, C2p)-B	-C-C, -C≡N
14.3 (13.0-17.0)*	19.9:19.2:18.9	C2s(0.9), N2s	pσ (C2s-C2p)-B	-C-C
7.0 (4.3-13.0)*	11.3:11.0:10.9 11.82-16.76 10.48-11.09	N2s(0.8), N2p C2p N2p(0.8), C2p	pσ (N2p-N2s)-B pπ (C2p-C2p)-B pπ (N2p-C2p)-B	N≡C- -C-C N≡C-

* shows the peak range.

^a B means bonding. (C2s-N2s, C2p) means (C2s-N2s) and (C2s-C2p).

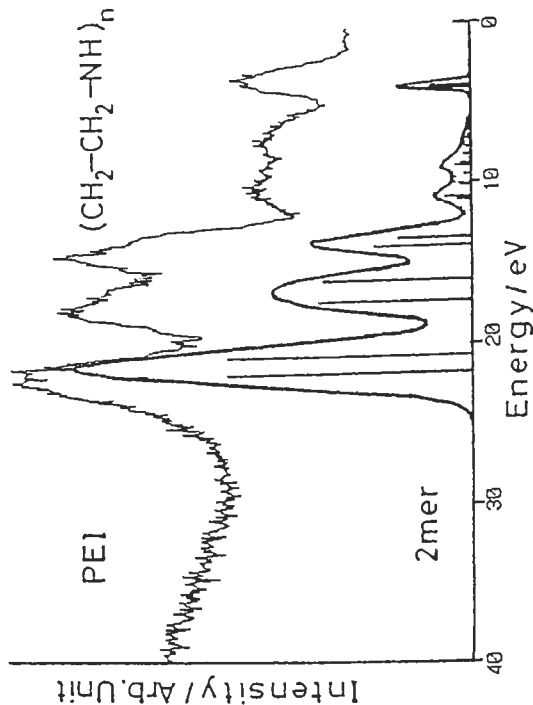


PEI Observed peaks, VIP, main A0 PICS, orbital nature and functional group for valence XPS of PEI. [(the gap between observed and calculated VIPs) = 5.0 eV]

peak(eV)	VIP(eV)	main A0 PICS	orbital nature ^a	functional group
22.5 (20-26)*	(28.33:27.81:26.94; 26.81)	N2s(0.8), C2s(0.2)	sσ (N2s-C2s)-B, pσ (N2s-C2p)-B	-N-C(main chain) -N-C(main chain)
18.0 (16-20)*	(22.78:21.60:20.54)	C2s(0.7) N2s(0.2), N2p(0.1)	sσ (C2s-2s)-B sσ (C2s-N2s)-B	-C-(main chain) -N-C(main chain)
15.0 (13-16)*	(19.72:19.27:18.94)	C2s(0.7), N2p, C2p	pσ (C2s-N2p)-B pσ (C2s-2p)-B	-C-N-(main chain) -C-(main chain)
(5.5-12)*	below 16.22 many adjacent levels	N2p, C2p N2p, C2p	pσ (N, C2p-C2p)-B pπ (C, N2p-C2p)-B	-C-C-N-(main chain) -C-C-N-(main chain)
4.0 (2-5.5)*	(8.35:8.34:8.13)	N2p	pπ (lone pair)-NB	C-N-

* shows the peak range.

^a B and NB mean bonding and nonbonding, respectively. (C, N2s-2p) means (C2s-C2p) and (N2s-N2p). (C2p, N2p-C2p) denotes (C2p-C2p) and (N2p-C2p), and so on.

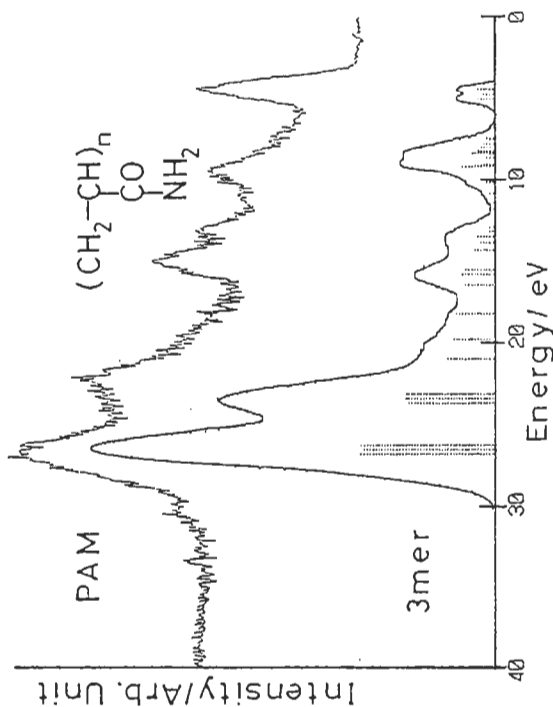


P A M Observed peaks, VIP, main A0 PICS, orbital nature and functional group for valence XPS of PAM. [(the gap between observed and calculated VIPs) = 4.0 eV]

Peak(eV)	VIP(eV)	main A0 PICS	orbital nature ^b	functional group
27.0 (25-32)*	30.77:30.45:30.22	O2s(0.8);N,C2s(0.1)	sσ (O2s-C2s)-B	O=C-, -C-NH ₂
22.5 (17-25)*	27.67:27.38:27.12 25.00:23.78:22.20	N2s(0.6);O2s(0.4) C2s	sσ (N,O2s-C2s)-B sσ (C2s-C2s)-B	H ₂ N-C-, O=C- -C-(main chain)
15.5 (12-17)*	(20.47:19.83: 19.56) 18.36:17.88:17.50 17.20:17.17:16.99	C2s C2s C2s C2s(0.5);N2p(0.5)	{sσ (C2s-H1s)-B; pσ (C2s-C,N2p)-B} pσ (N,C2p-C2s)-B pσ (N,C2p-C2s)-B	{-C-(main chain), -C-NH ₂ -C-NH ₂ H ₂ N-C-
9.0 (6-12)*	(13.18-13.01) many adjacent levels (15.36-13.96) (12.62-10.93)	{O2s(0.5);C2p(0.3); O2p(0.2)} C2p C2p(0.1);O2p(0.3)	pσ (O,C2p-O2p,2s)-B O2p(0.2) pσ, pπ (C2p-C,N,O2p)-B pσ, pπ (O,C2p-2p)-B	O=C-C-, -C-(main chain) O=C-, H ₂ N-C-, -C-C- -C=O
4.5 (3-6)*	(9.39:9.10:9.06; 8.78:8.49:8.42)	O2p;N2p O2p;N2p	pπ (lone pair)-NB pπ (lone pair)-NB	-C=O, -NH ₂ -C=O, -NH ₂

* 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.

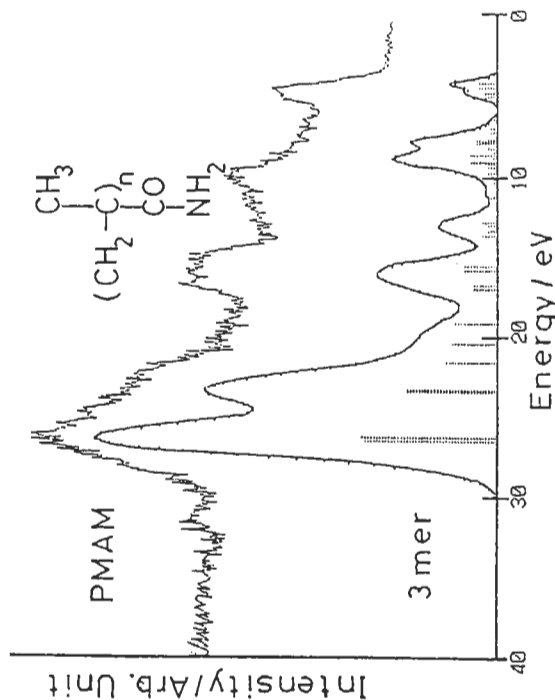


P M A M Observed peaks, VIP, main A0 PICS, orbital nature and functional group for valence XPS of PMAM. [(the gap between observed and calculated VIPs) = 4.5 eV]

Peak(eV)	VIP(eV)	main A0 PICS	orbital nature ^b	functional group
27.0 (20-30)*	31.01:30.81:30.74 27.96:27.82:27.75 26.08:24.88:23.64	O2s(0.8);N,C2s(0.1) N2s(0.6);O2s(0.4) C2s	sσ (O2s-C2s)-B sσ (N,O2s-C2s)-B sσ (C2s-C2s)-B	O=C-, -C-NH ₂ H ₂ N-C-, O=C- -C-(main chain)
15.0 (14-18)*	(21.55:21.40:21.20; 20.36:20.29:20.08)	C2s C2s(0.8);O2s(0.2)	sσ (C2s-H1s)-B; s,pσ (C2s-O2s,N2p)-B	-C-(main chain) -C=O, -C-NH ₂
10.5 (7-14)*	(13.60-13.19) many adjacent levels (18.01-13.67) (13.10-10.97)	O2s(0.5);C2s,2p;O2p N2p;C2p C2p(0.7);O2p(0.3)	pσ (O,C2p-O2p,2s)-B pσ, pπ (C2p-C,N,O2p)-B pσ, pπ (O,C2p-2p)-B	O=C-, -C-CB ₃ O=C-, H ₂ N-C-, -C-C- -C=O
5.5 (4-7)*	(9.57:9.41:9.32; 8.97:8.77:8.72)	O2p;N2p O2p;N2p	pπ (lone pair)-NB pπ (lone pair)-NB	-C=O, -NH ₂ -C=O, -NH ₂

* shows the peak range.

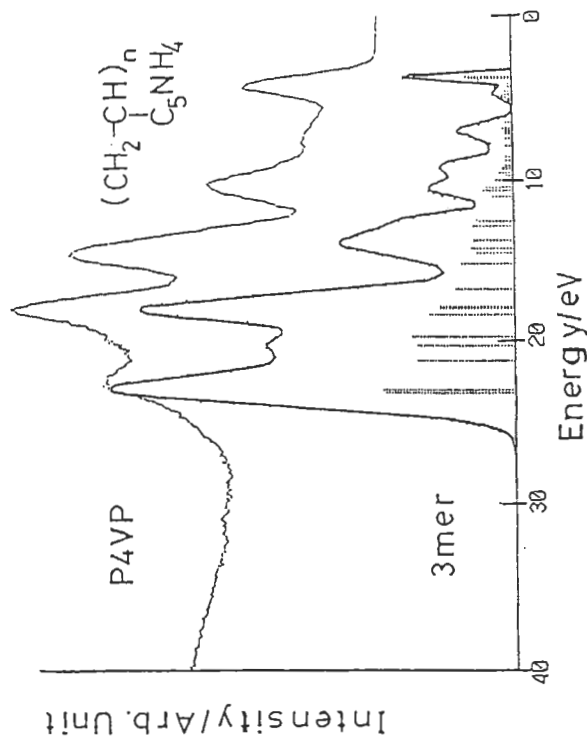
^b B and NB mean bonding and nonbonding, respectively. (C,O2s-2p) means (C2s-C2p) and (O2s-O2p). (C2p,O2p-C2p) denotes (C2p-C2p) and (O2p-C2p), and so on.



P 4 V P Observed peaks, VIP, main A0 PICS, orbital nature and functional group for valence XPS of P4VP. [(the gap between observed and calculated VIPs) = 5.0 eV]

peak (eV)	VIP (eV)	main A0 PICS	orbital nature ^b	functional group
22.5 (21-26)*	28.06:27.94:27.86	N2s(0.6), C2s(0.4)	$s\sigma$ (N2s-C2s)-B,	-C-N=C-(pyridine)
18.0 (16-21)*	21.70-22.95 23.28-26.13	C2s(0.8), N2s C2s(0.6), N2s(0.2)	$s\sigma$ (C2s-2s)-B $s\sigma$ (C2s-N2s)-B	-C-C-(pyridine) [-C-(main chain); =C-N=C-(pyridine)]
15.0 (12-16)*	18.82:18.72:18.69 19.29-20.16 17.50-17.84	C2s(0.6), N2p C2s C2s(0.6), N2s, C2p	$p\sigma$ (C2s-N, C2p)-B $s\sigma$ (C2s-C2s)-B $s\sigma, p\sigma$ (C2s, 2p-N2s)-B	-C-C-N=C-(pyridine) -C-(main chain) =C-N=C-(pyridine)
10.5 (6-12)*	15.44-16.03 many adjacent levels 13.54-15.36 11.41-12.91	C2s, N2s, C2p C2p, N2p N2p, C2p	$p\sigma$ (C2p-C2s, N2s)-B $p\pi, p\pi$ (C, N2p-C2p)-B $p\pi, p\pi$ (N, C2p-C2p)-B	[=C-N=C-(pyridine), -C-(main chain)] =C-N=C-, -C- =C-N=C-, -C-
4.5 (3-6)*	8.90:8.77:8.70 9.11-9.92	N2p, C2p C2p, N2p	$p\pi$ (N, C2p-C2p)-B $p\pi$ (C, N2p-C2p)-B	=C-N=C-(pyridine) =C-N=C-(pyridine)

* shows the peak range.
^b B and NB mean bonding and nonbonding, respectively. (C, N2s-2p) means (C2s-C2p) and (N2s-N2p). (C2p, N2p-C2p) denotes (C2p-C2p) and (N2p-C2p), and so on.

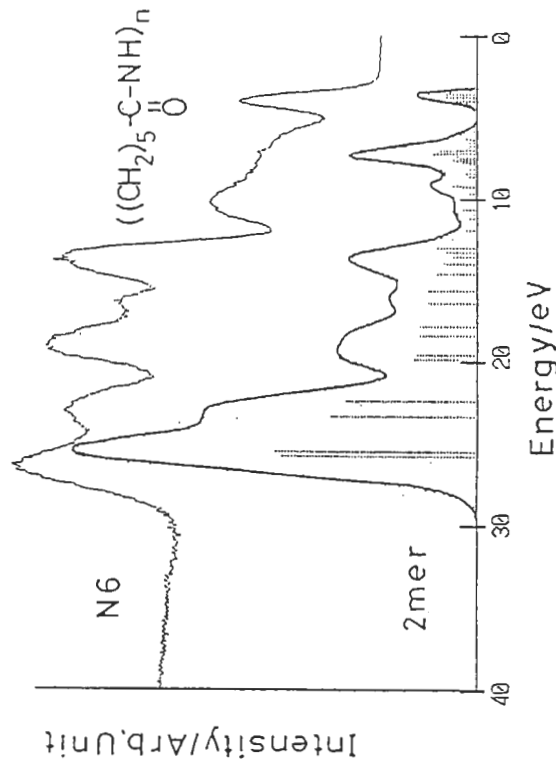


N 6 Observed peaks, VIP, main A0 PICS, orbital nature and functional group for valence XPS of N6. [(the gap between observed and calculated VIPs) = 5.0 eV]

peak (eV)	VIP (eV)	main A0 PICS	orbital nature ^b	functional group
26.5 (24.5-30)*	30.66:30.37	O2s(0.7), N2s, C2s	$[s\sigma$ (O2s-C2s)-B, $p\sigma$ (O2s-C2p)-B]	-C=O
23.0 (21-24.5)*	28.24:27.32	N2s(0.6), O2s(0.4)	$p\sigma$ (N, O2s-C2p)-B	-N-C, O=C
19.0 (16-21)*	22.79-24.79 21.41:20.67	C2s C2s	$s\sigma$ (C2s-2s)-B $s\sigma$ (C2s-2s)-B	-C-C- -C-
14.0 (12-16)*	18.06-19.59	C2s(0.7), N2p, O2s	$p\sigma$ (C2s-N2p)-B	-C-N
10.5 (5-12)*	10.87-16.96 many adjacent levels	O2p, N2p, C2p	$[p\pi$ (O, N, C2p-C2p)-B, $p\sigma$ (C2p-N2s)-B]	C=O, -C-N -CH2
3.5 (3-5)*	9.07:8.91:8.74:8.60	O2p, N2p	$p\pi$ (lone pair)-NB	O=C, C-N

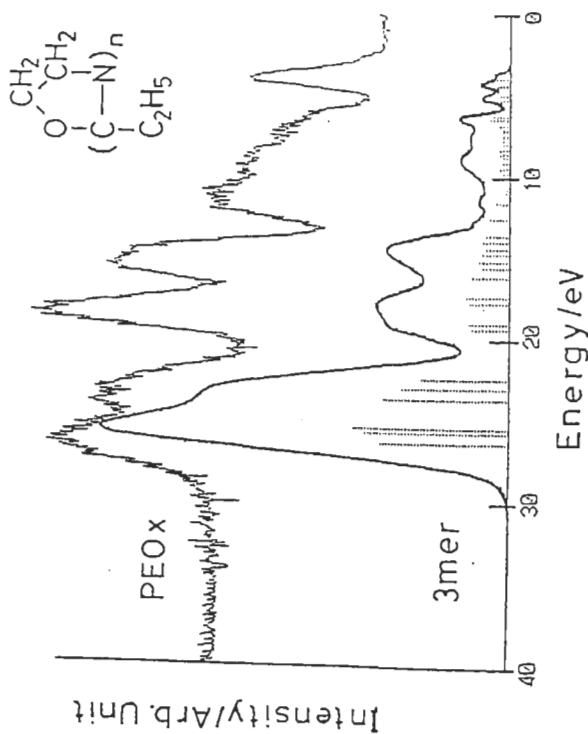
* shows the peak range.

^b B and NB mean bonding and nonbonding, respectively. (C, N2s-2p) means (C2s-C2p) and (N2s-N2p). (C2p, N2p-C2p) denotes (C2p-C2p) and (N2p-C2p), and so on.



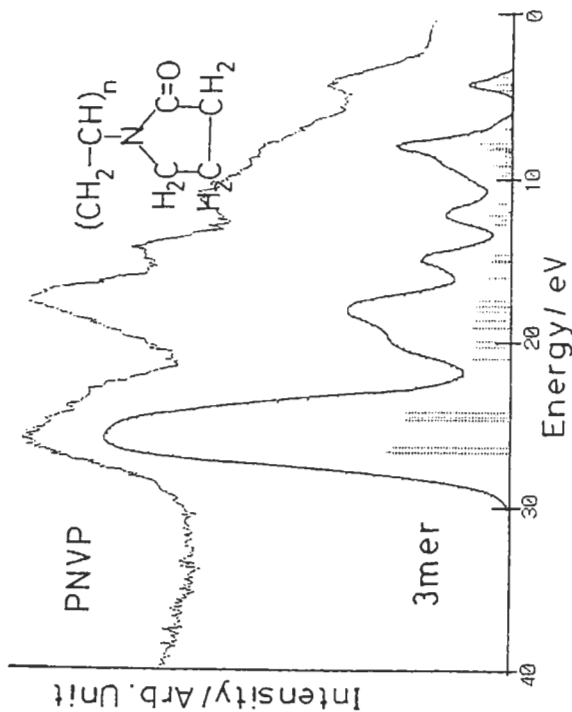
PEOX Observed peaks, VIP, main AO PICS, orbital nature and functional group for valence XPS of PEOx. [(the gap between observed and calculated VIPs) = 5.0 eV]

peak(eV)	VIP(eV)	main AO PICS	orbital nature ^b	functional group
26.5 (25-30)*	31.17:30.59:30.28	O2s(0.8), N2s, C2s	sσ (O, N2s-C2s)-B	C-O-C, C-N-C
23.5 (21-25)*	28.55:27.93:27.31	(N2s(0.5), O2s(0.4), C2s(0.1))	sσ (N, O2s-C2s)-B, pσ (N, O2s-C2p)-B	C-O-C, C-N-C C-O-C, C-N-C
18.5 (17-21)*	[24.34:24.19:23.90; 22.68:22.64:22.31]	C2s C2s(0.7), O2s, N2s	sσ (C2s-2s)-B sσ (C2s-O, N2s)-B	-C-C- C-O-C, C-N-C
15.5 (14-17)*	18.65-21.14	(C2s(0.5), O2s, N2p, C2p)	{pσ (C2s-N2p)-B, pσ (C, O2s-C2p)-B}	-C-N-C- -C-C, C-O-C
(6-14)*	11.29-17.61	O2p, N2p, C2p	pσ (O, N, C2p-C2p)-B pπ s (O, C, N2p-C2p)-B	C-O-C, C-N-C C-O-C, C-N-C
4.0 (2.5-5)*	10.27:9.99 8.63-9.44	O2p, N2p N2p, O2p	pπ (lone pair)-NB pπ (lone pair)-NB	-O-, -N- -N-, -O-
* shows the peak range. * π s indicates the pseudo π orbitals of the C-O, C-N and C-C bonds, B and NB mean bonding and nonbonding, respectively. (C, N2s-2p) means (C2s-C2p) and (N2s-N2p), (C2p, N2p-C2p) denotes (C2p-C2p) and (N2p-C2p), and so on.				



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

peak(eV)	VIP(eV)	main AO PICS	orbital nature ^b	functional group
26.0 (21.5-30)*	31.18:31.09:30.62 29.16:28.96:28.69	O2s(0.6):N, C2s(0.2) O2s(0.6):N2s(0.3)	sσ (O, N2s-C2s)-B pσ (O, N2s-C2p)-B	O=C, -N-C- O=C, -N-C-
17.5 (16-21.5)*	(22.48:22.28; 22.12:21.88) 25.47:24.73:24.36 23.59:23.05	C2s(0.8):O2s(0.2) C2s C2s(0.8):N2s(0.2)	sσ (C2s-C, O2s)-B sσ (C2s-C2s)-B sσ (C2s-C, N2s)-B	-C-C-O-, -C-N- -C-(main chain), -C- -C-(main chain), -CH3
14.5 (13-16)*	(19.56-19.09) 20.54	C2s C2s	sσ, pσ (C2s-C2s, N2p)-B sσ, pσ (C2s-C2s, N2p)-B	-C-C-, -C-N- -C-C-, -C-N-
11.0 (6-13)*	(17.30:16.99; 16.75:16.74) (16.56-11.12)	O2p(0.7):C2s(0.2) C2p, O2p, N2p	pσ (C2p-C2s)-B pσ, pπ (C, O, N2p-2p)-B	-C-N-, -C-C- -C-C-, -C-O-, -C-N-
4.0 (2-6)*	9.15:8.06:8.63 8.77:8.68:8.36	O2p(0.5):N2p(0.3) O2p(0.7):N2p(0.2)	pπ (lone pair)-NB pπ (lone pair)-NB	O=C-, -N- O=C-, -N-
* shows the peak range. * 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.				

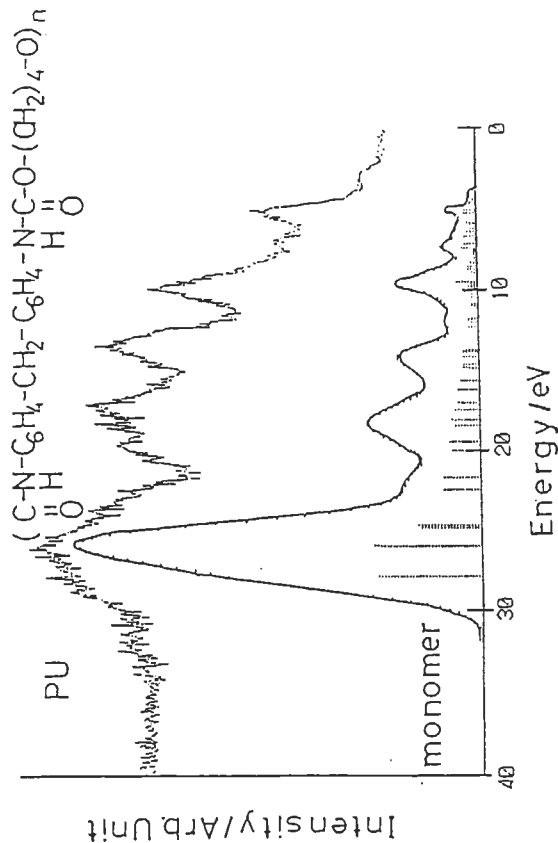


P U Observed peaks, VIP, main AO PICS, orbital nature and functional group for valence XPS of PU. [(the gap between observed and calculated VIPs) = 4.0 eV]

peak(eV)	VIP(eV)	main AO PICS	orbital nature ^b	functional group
26.0 (21-32) ^a	31.87;31.82;29.93; 29.86;29.83; 28.70;28.58; 26.38;25.60	02s(0.8), C2s, N2s 02s N2s(0.6), 02s, C2s C2s(0.7), N2s, 02s	σ (0, N2s-C2s)-B, ρ (02s-C2p)-B ρ (N, 02s-C2p)-B σ (C2s-C, N2s)-B	-O-C, O=C, -N-C O=C, -O-C -N-C, O=C, -O-C -C-, C=C-, -C-N-
17.5 (15-21) ^a	22.41;22.39;22.05 23.93;23.42 19.54-21.36	C2s C2s C2s(0.8)	σ (C2s-C2s)-B σ (C2s-2s)-B ρ (C2s-0, N2p)-B	-C-, C=C- -C-, C=C- -C-, -C-N-, -C-O
13.5 (12-15) ^a	18.04;17.81 18.51-18.78 17.57;17.70	C2s(0.5), N2p, 02p C2s(0.4), 02s, N2p C2s(0.5), N2p, C2p	ρ (C2s-N, 02p)-B ρ (C2s-N, C2p)-B ρ (C2s-N, C2p)-B	-C-, -C-N-, C=O -C-, -C-N-, C=O -C-, -C-N-
10.0 (7-11) ^a	13.53;13.48 many adjacent levels 13.62-16.53 12.29-13.22	02s(0.6), 02p, C2p many adjacent levels 02p, N2p, C2p 02p, N2p, C2p	ρ (02p-02s, C2p)-B many adjacent levels ρ (0, N, C2p-C2p)-B ρ (C2s-N, C2p)-B	O=C -C-, -C-, N-C=O, C=O -C=C-, C=O, N-C=O
5.5 (2.5-7) ^a	9.20-11.35 many adjacent levels 11.41-11.97 8.10-8.90	02p, N2p C2p 02p, N2p, C2p	ρ (lone pair)-NB ρ (C2p-C2p)-B ρ (lone pair)-NB	C-N- -C=C- O-, -O-, -N-, -C-

^a shows the peak range.

^b B and NB mean bonding and nonbonding, respectively. (C, N2s-2p) means (C2s-C2p) and (N2s-N2p). (C2p, N2p-C2p) denotes (C2p-C2p) and (N2p-C2p), and so on.

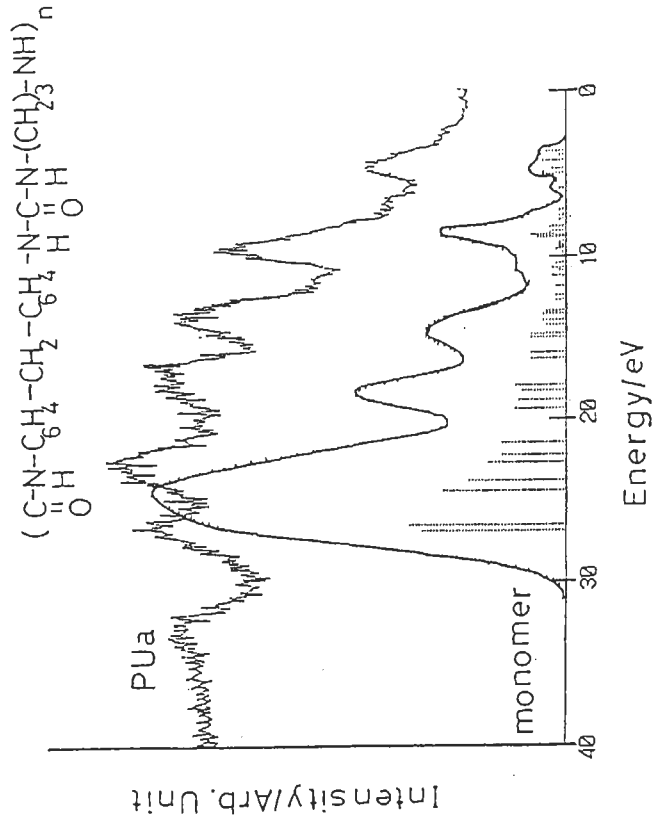


P U a Observed peaks, VIP, main AO PICS, orbital nature and functional group for valence XPS of PUA. [(the gap between observed and calculated VIPs) = 4.0 eV]

peak(eV)	VIP(eV)	main AO PICS	orbital nature ^b	functional group
27.0 (25-30) ^a	30.81;30.52	02s(0.7), N2s, C2s	ρ (0, N2s-C2s)-B, ρ (02s-C2p)-B	O=C, -N-C
24.0 (21-25) ^a	26.61-28.39 26.15;25.39	N2s(0.6), 02s, C2s C2s(0.8), N2s	ρ (N, 02s-C2p)-B σ (C2s-C, N2s)-B	-N-C, O=C -C-, C=C-, -C-N-
17.5 (16-21) ^a	23.30;22.74;22.18; 22.15;21.82	C2s C2s	σ (C2s-C2s)-B σ (C2s-C2s)-B	-C-, C=C- -C-, C=C-
14.0 (12-15) ^a	18.88;18.71;18.65 20.22;19.78 17.37-18.15	C2s(0.5), 02s, N2p C2s(0.6), N2p, 02s C2s(0.5), N2p, C2p	ρ (C2s-02s, N2p)-B ρ (C2s-N, C2p)-B ρ (C2s-N, C2p)-B	-C-N-, C=O -C-, -C-N-, C=O -C-, -C-N-
10.0 (8-12) ^a	12.10-12.79 many adjacent levels 13.06-16.69	02s(0.6), 02p, C2p many adjacent levels N2p, C2p	ρ (02p-02s, C2p)-B many adjacent levels ρ (N, C2p-C2p)-B, ρ (C2p-C2p)-B	O=C, -C=C- -N-C-, -C=C- -C=C-
5.5 (2.5-7) ^a	7.84-8.92 9.77-11.70	02p, N2p C2p, N2p, 02p	ρ (lone pair)-NB ρ (C2p-C2p)-B, ρ (lone pair)-NB	O=C, -N-C- -C=C- O-, -N-

^a shows the peak range.

^b B and NB mean bonding and nonbonding, respectively. (C, N2s-2p) means (C2s-C2p) and (N2s-N2p). (C2p, N2p-C2p) denotes (C2p-C2p) and (N2p-C2p), and so on.

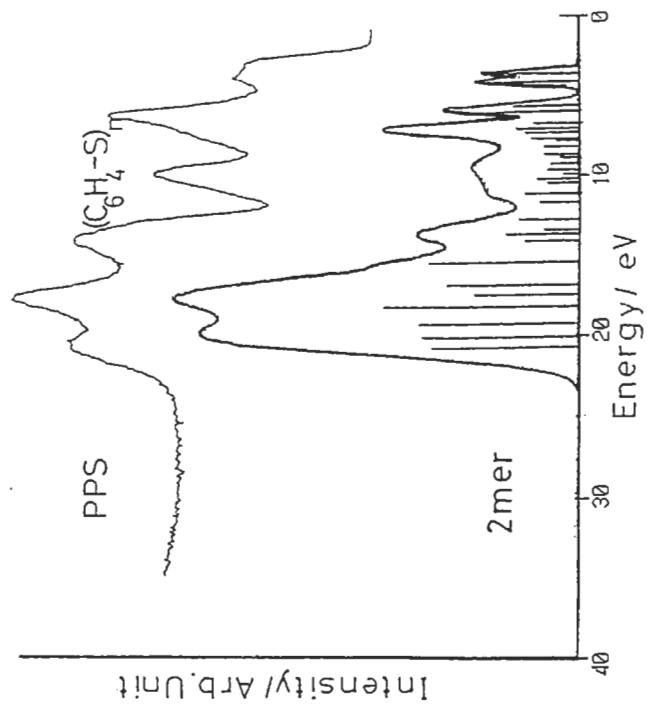


PPS Observed peaks, VIP, main AO PICS, orbital nature and the functional group for valence XPS of PPS. [(the shift between observed and calculated VIPs) = 3.5 eV]

peak (eV)	VIP (eV)	main AO PICS	orbital nature*	functional group
20.7 (19.6-23)*	24.4:23.7:22.9	C2s(0.5), S3s(0.5)	σ (C2s-C2s, S3s)-B	-C=C-C, =C-S
17.5 (15.8-19.6)*	21.81 19.06-21.09	S3s(0.6), C2s(0.4) C2s(0.6), S3s(0.4)	σ (S3s, C2s-C2s)-B σ , σ (C2s-C2p, S3s)-B	-S-C=, -C=C- -C=C-C, =C-S
13.8 (11.5-14.4)*	16.40-17.76	C2s(0.7), S3s, S3p	$p\sigma$ (C2s-C2p, S3p)-B	-C=C-, =C-S
10.1 (8.6-11.5)*	11.80-15.26	S3p(0.7), C2s	$p\sigma$ (S3p-C2s, C2p)-B	-S-C=
6.3 (4.6-8.6)*	10.34-11.36	S3p(0.8), S3s	$p\pi$ (S3p-C2p)-B	-S-C=
4.0 (2.0-4.6)*	7.62:7.12 8.82:8.28	S3p C2p	$p\pi$ (lone-pair)-NB $p\pi$ (C2p-C2p)-B	-S-

* shows the peak range.

* B and NB mean bonding and nonbonding, respectively. (S3p-C2s, C2p) means (S3p-C2s) and (S3p-C2p). (S3s, C2s-C2s) denotes (S3s-C2s) and (C2s-C2s), and so on.

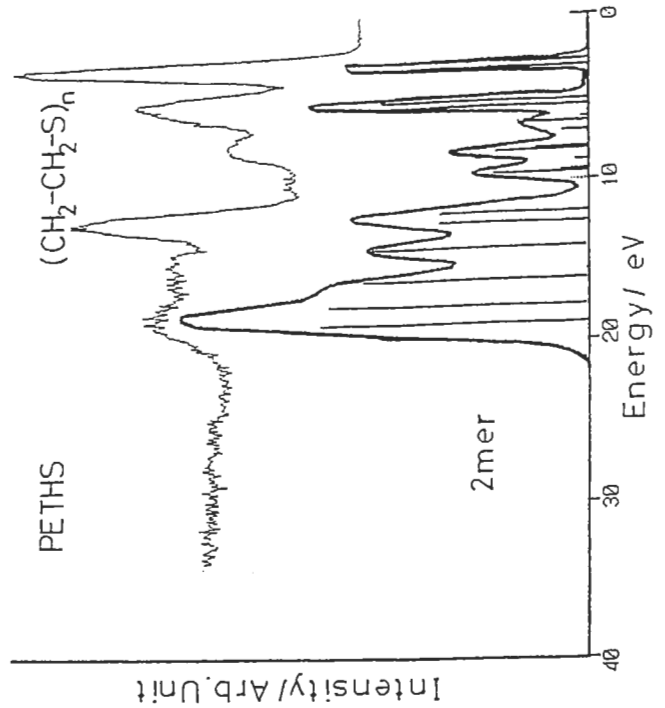


PETHS Observed peaks, VIP, main AO PICS, orbital nature and functional group for valence XPS of PETHS. [(the shift between observed and calculated VIPs) = 5.0 eV]

peak (eV)	VIP (eV)	main AO PICS	orbital nature*	functional group
18.7:15.8 (14.4-22.4)*	{24.84:23.24; 20.95}	S3s(0.7), C2s(0.2)	σ (S3s-C2s)-B	-S-C-
12.7 (10-14.4)*	18.78:17.51	S3s(0.8), C2s(0.3)	σ , $p\sigma$ (S3s, C2s-C2s, S3p)-B	S-C-, -C-C
8.1 (6.9-10)*	13.19-15.34	S3p(0.7), S3s(0.2)	$p\pi$, σ (S3p, S3s-C2p)-B	-S-C
5.5 (4.3-6.9)*	10.27-12.29	S3p(0.8), S3s	$p\pi$ (S3p-C2p)-B	-S-
3.9 (2-4.3)*	9.76-10.02	S3p	$p\pi$ (lone-pair)-NB	-S-

* shows the peak range.

* B and NB mean bonding and nonbonding, respectively. (S3p, S3s-C2p) means (S3p-C2p) and (S3p-C2p). (S3s, C2s-C2s, S3p) denotes (S3s-C2s) and (C2s-S3p), and so on.

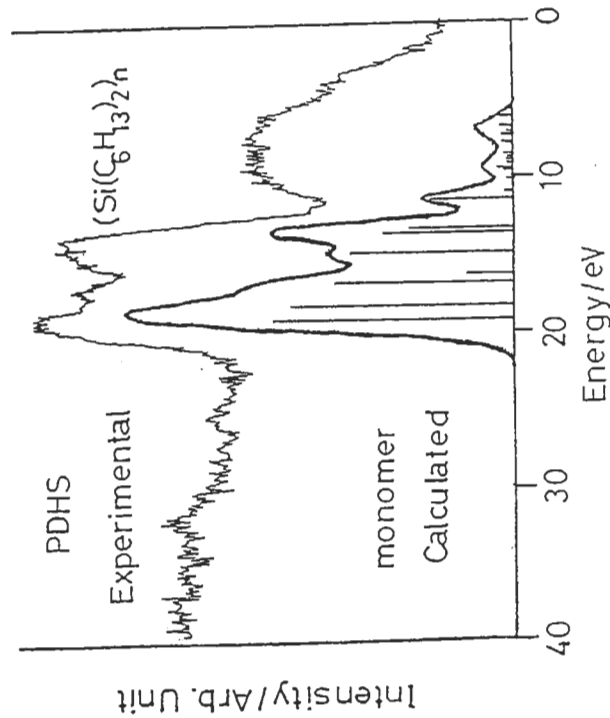


PDMS Observed peaks, VIP, main A0 PICS, orbital nature and functional group for valence XPS of PDMS. [(the shift between observed and calculated VIPs) = 3.0 eV]

peak(eV)	VIP(eV)	main A0 PICS	orbital nature*	functional group
19.5 (18.0-22.0)*	22.34:21.38	C2s	$s\sigma$ (C2s-C2s)-B	-C-C
17.0 (16.0-18.0)*	19.96:19.33	Si3s(0.5), C2s(0.5)	$s\sigma$ (Si3s-C2s)-B	Si-C
14.0 (11.5-16.0)*	18.0:16.7:16.4	C2s(0.9), Si3s, C2p	$p\sigma$ (C2s-C2p)-B	-C-C
10.5 (9.5-11.0)*	14.58 14.11:13.30	Si3s(0.9), C2p, Si3p C2p, Si3s, Si3p	$p\sigma$ (Si3s-C2p)-B $p\sigma$ (C2p-Si3s, 3p)	Si-C -C-Si
8.0 (6.0-9.5)*	11.60-12.74	C2p, Si3p, C2s	$p\sigma$ (C2p-Si3p, C2s)-B	-C-Si, -C-C
4.5 (2.0-6.0)*	9.99-10.99 many adjacent levels 9.9:8:9.3	C2p(0.6), Si3p Si3p(0.8), C2p	$p\pi$ (C2p-Si3p)-B $p\pi$ (Si3p-C2p)-B	-C-C, -C-Si Si-C

* shows the peak range.

* B means bonding. (C2p-Si3s, 3p) means (C2p-Si3s) and (C2p-Si3p).

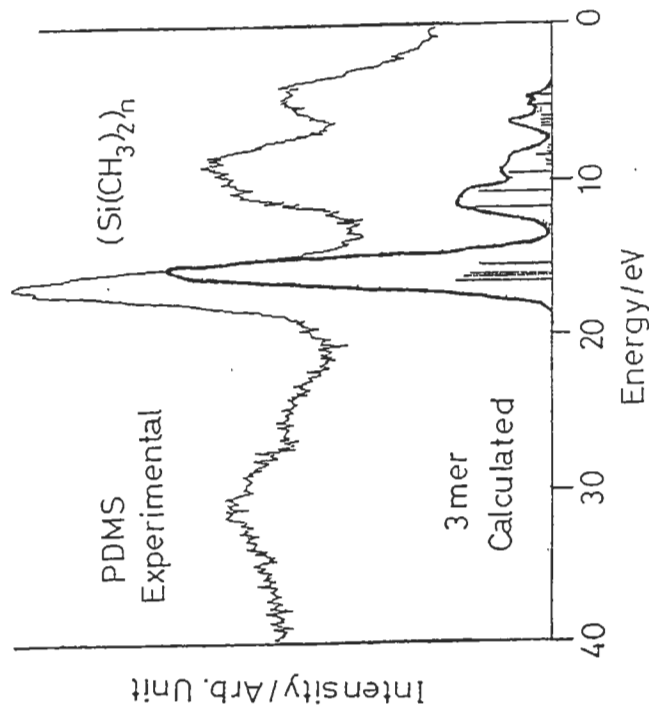


PDMS Observed peaks, VIP, main A0 PICS, orbital nature and functional group for valence XPS of PDMS. [(the shift between observed and calculated VIPs) = 3.5 eV]

peak(eV)	VIP(eV)	main A0 PICS	orbital nature*	functional group
17.0 (13.5-21.0)*	{20.7;19.8;19.6; 19.0;18.9;18.9}	C2s(0.7), Si3s(0.3) C2s	$s\sigma$ (C2s-Si3s)-B $s\sigma$ (C2s)	Si-C -CH ₃
10.5 (10.0-12.5)*	15.3;14.2;13.0	Si3s(0.9), C2s, Si3p	$p\sigma$ (Si3s-Si3p)-B	Si-Si
9.0 (6.5-10.0)*	11.86-12.63 many adjacent levels 11.43-11.79	C2p, Si3s, Si3p C2p, Si3p	$p\sigma$ (C2p-Si3s, Si3p)-B $p\sigma$ (C2p-Si3p)-B	-C-Si -C-Si
4.5 (1.5-6.5)*	9.47-10.14 8.7;8.1	Si3p(0.7), C2s, C2p Si3p(0.7), Si3s	$p\sigma$ (Si3p-C2s, C2p)-B $p\sigma$ (Si3p-Si3s)-B	Si-C Si-

* shows the peak range.

* B means bonding. (Si3s-C2s, C2p) means (Si3s-C2s) and (Si3s-C2p).

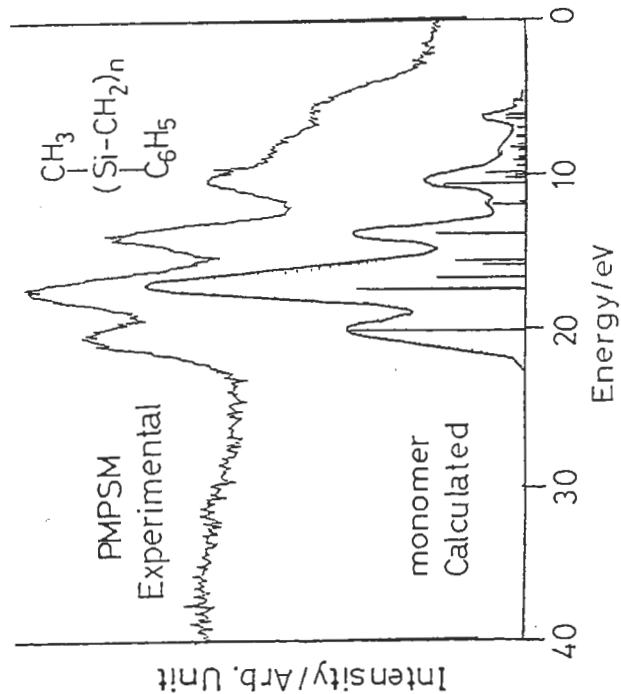


PMPSM Observed peaks, VIP, main AO PICS, orbital nature and functional group for valence XPS of PMPSM. [(the shift between observed and calculated VIPs) = 3.5 eV]

peak(eV)	VIP(eV)	main AO PICS	orbital nature*	functional group
21.0 (19.5-23.5)*	23.51	C2s	$s\sigma$ (C2s-C2s)-B	-C-C(phenyl)
17.0 (15.0-19.0)*	18.94-20.97	C2s(0.9), Si3s	$s\sigma$ (C2s-C2s, Si3s)-B	-C-C(phenyl), -C-Si
14.0 (12.0-15.0)*	17.19; 17.16	C2s(0.9), C2p	$p\sigma$ (C2s-C2p)-B	-C-C(phenyl)
10.5 (9.0-12.0)*	15.2; 13.9; 13.2 15.10; 13.35	Si3s, C2s, C2p C2p	$p\sigma$ (C2p-Si3s, C2s)-B $p\pi$ (C2p-C2p)-B	-C-Si, -C(phenyl) -C-C(phenyl)
8.5 (7.0-9.0)*	11.72-12.80	C2p, Si3p	$p\pi$ (C2p-C2p, Si3p)-B	-C-C(phenyl), C-Si
6.0 (3.0-7.0)*	10.17-11.57 many adjacent levels	C2p(0.6), Si3p	$p\pi$ (C2p-C2p, Si3p)-B	-C-C(phenyl), Si-C
	8.52-9.65	Si3p(0.7), C2p	$p\pi$ (Si3p, C2p-C2p)-B	Si-C, C-C(phenyl)

* shows the peak range.

* B means bonding. (C2p-Si3s, C2s) means (C2p-Si3s) and (C2p-C2s).

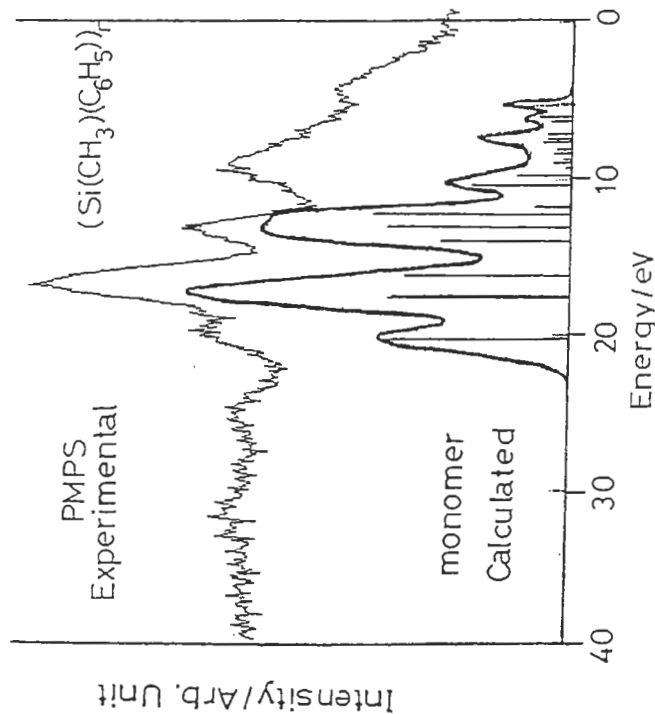


PMPS Observed peaks, VIP, main AO PICS, orbital nature and functional group for valence XPS of PMPS. [(the shift between observed and calculated VIPs) = 3.5 eV]

peak(eV)	VIP(eV)	main AO PICS	orbital nature*	functional group
19.5 (18.5-22.0)*	23.71	C2s	$s\sigma$ (C2s-C2s)-B	-C-C(phenyl)
17.0 (14.5-18.5)*	{21.09; 19.65; 20.98}	C2s(0.8), Si3s(0.2) C2s	$s\sigma$ (C2s-Si3s)-B $s\sigma$ (C2s)	Si-C -C-C(phenyl), -CH ₃
13.0 (12.0-14.5)*	16.6; 15.7; 15.3 17.45; 17.46	Si3s(0.9), C2s, Si3p C2s(0.8), Si3s, Si3p	$p\sigma$ (Si3s-Si3p)-B $p\sigma$ (C2s-C2p)-B	Si-Si -C-C(phenyl)
9.5 (8.0-11.5)*	13.9; 13.5; 13.2 many adjacent levels 11.56-12.77	Si3s, C2s, C2p, Si3p C2p, Si3p, Si3s	$p\sigma$ (C2p-Si3s, C2s)-B $p\pi$ (C2p-C2p, Si3p)-B	-C-C(phenyl), -C-Si -C-C(phenyl)
7.0 (6.0-8.0)*	10.63-11.13	Si3p(0.9), C2p	$p\pi$ (Si3p-Si3p)-B	Si-Si
4.5 (1.5-6.0)*	8.63-9.88	Si3p(0.7), C2p	$p\pi$ (Si3p-C2p)-B	-C-C(phenyl), Si-C

* shows the peak range.

* B means bonding. (C2p-Si3s, C2s) means (C2p-Si3s) and (C2p-C2s).

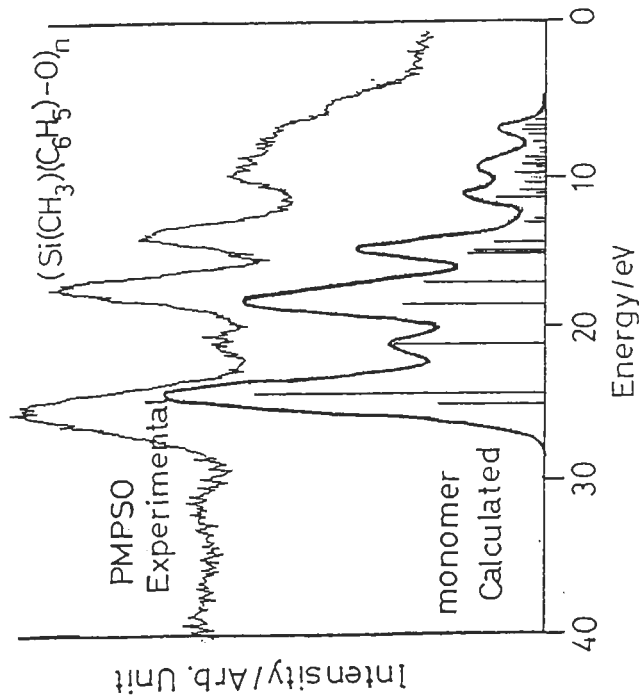


PMP2O Observed peaks, VIP, main A0 PICS, orbital nature and the functional group for valence XPS of PMP2O. [(shift between observed and calculated VIPs) = 3.0 eV]

peak (eV)	VIP (eV)	main A0 PICS	orbital nature*	functional group
26.0 (23-30)*	27.47:26.83	02s	$s\sigma, p\sigma$ (02s-Si3s, Si3p)-B	-O-Si
21.0 (20-22)*	26.83	C2s	$s\sigma$ (C2s-C2s)-B	-C-C(phenyl)
17.0 (15.5-20)*	21.03:20.95 19.52	C2s C2s(0.8), Si3s	$s\sigma$ (C2s-C2s)-B $s\sigma$ (C2s-Si3s)-B	-C-C(phenyl) C(methyl)-Si
14.0 (11.5-15.5)*	17.5:17.4:16.9 15.48:15.27	C2s(0.6)Si3s, 02p Si3s, Si3p, C2s, C2p	$p\sigma$ (C2s, Si3s-C2p)-B $p\sigma$ (C2p-Si3s, C2s)-B	-C-C(phenyl)-Si -C-C(phenyl)-Si
9.5 (6-11)*	13.6:13.5:13.4 many adjacent levels 10.56-12.84	C2s, Si3s, Si3p, 02p 02p, Si3p, Si3s, C2p	$p\sigma$ (C2p-C2s, Si3s, p)-B $p\pi$ (C2p-C2p, Si3p)-B	-C-C(phenyl)-Si -C-C(phenyl)-Si
5.0 (3-6)*	9.6:9.4:9.1 10.1:8.8:8.7	02p, Si3p C2p, Si3p	$p\pi$ (lone-pair)-NB $p\pi$ (C2p-C2p, Si3p)-B	-O- -C-C(phenyl)-Si

* peak range.

* B and NB, bonding and nonbonding, respectively. (C2p-C2p, Si3p) means (C2p-C2s) and (C2p-Si3p), and so on.



PDMSO Observed peaks, VIP, main A0 PICS, orbital nature and the functional group for valence XPS of PDMSO. [(the shift between observed and calculated VIPs) = 3.0 eV]

peak (eV)	VIP (eV)	main A0 PICS	orbital nature*	functional group
26.0 (23-28)*	27.55:26.93	02s	$s\sigma, p\sigma$ (02s-Si3s, Si3p)-B	-O-Si
17.0 (16-19)*	20.04:19.69 19.26:18.99	C2s(0.7), Si3s(0.2), Si3p C2s(0.9), Si3p(0.1)	$s\sigma$ (C2s-Si3s)-B $p\sigma$ (C2s-Si3p)-B	C-Si C-Si
13.0 (10-14)	16.76:15.26	Si3s(0.6), 02p(0.3)	$p\sigma$ (Si3s-02p)-B	Si-O
8.5 (6-10)*	13.30 many adjacent levels 11.63-12.78 10.22-11.20	Si3s(0.6)02s, Si3p, 02p Si3p, 02p, 02s, C2p 02p(0.6), Si3p(0.3)	$p\sigma$ (Si3s-02p; 02s-Si3p)-B $p\pi$ (Si3p-O, C2p)-B $p\pi$ (Si3p-02p)-B	Si-O, C-Si Si-O
5.0 (4-6)*	9.04-9.44	02p(0.7), Si3p(0.2)	$p\pi$ (Si3p-02p)-B; $p\pi$ (lone-pair)-NB	Si-O, -O-

* shows the peak range.

* B and NB mean bonding and nonbonding, respectively. (Si3p-C2s, 02s) means (Si3p-C2s) and (Si3p-C2s), and so on.

