研究論文

Analysis of Microcapsule Resin Using the X-ray Photoelectron Spectral Method

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X-ray photoelectron spectroscopy have been used to analyze the microcapsule material which consists of polyurea, poly-urethane, gelatin and melamine. We determined which material was involved in the microcapsule, melamine or non-melamine(gelatin, polyurea and polyurethane) from the core N 1s spec-tral analysis. The linewidth of the N 1s spectra of melamine-resin, 2.5 eV, is larger than that of non-melamine materials(polyurea(2.1 eV) and gelatin(1.9 eV)). This depends on the nitrogen functional groups: The melamine involves two functional groups, amino and triazine-ring nitrogens. while polyurea and gelatin have amino groups. The N 1s spectra of melamine-resin and polyurea were simulated by an ab initio MO calculations using the melamine and 1,3 dimethyl urea molecules. respectively. On the other hand. we produced the two kinds of capsule-resin in formation of shell material around oil drops in water. The shell material is synthesized from the reactions between polyvalent phenyl-isocyanate and (polyhydric alcohol. or polyvalent amine). The difference of the material between polyurethane and polyurea was determined by the valence X-ray photoelectron spectra.

1. Introduction

In previous papers[1-5], we showed better assignments of the valence X-ray photoelectron spectra(XPS) of polymers involving carbon, nitrogen, oxygen, fluorine. sulfur and chlorine by the semiempirical HAM/3 and ab initio deMon density-functional calculations[6-9] using the model molecules. An aim of the present study is to analyze the material of the microcapsule from the valence XPS.

A microcapsule is used as a microscopic container which involves the dyes in recording materials such as carbonless duplicating and heat-sensitive papers. The microcapsule is made of gelatin. melamine-resin. polyurea and polyurethane. We need a lot of time to analyze the capsule material chemically, since we must eliminate other substances involved in the capsule. For the melamine- and urea-resin, we have to examine each monomer after the resin was hydrolyzed by phosphoric aqueous solution[10]. In the case of polyurea and polyurethane. the material must be identified from the proton nmr of the sample in polar organic solvents(dimethyl sulfoxide (DMSO), dimethyl acetoamide(DMA) and so on)[11]. In the present study. an aim is to analyze the capsule material using an X-ray photoelectron spectroscopy (XPS) method without the complicated chemical treatment.

As we know. there is no study on the analysis of the microcapsule material using the XPS method. We. here. noticed the X-ray photoelectron N 1s spectra of the constituent element for the capsule. to determine which material is involved in the capsule: melamine or non-melamine(gelatin. polyurea and so on). The difference between the melamine and non-melamine was discussed with the linewidth of the N1s spectra for the capsule.

Furthermore. we produced the two kinds of microcapsules(polyurea or polyurethane) in formation of shell material around oil drops in water. We could determine whether the capsule material is polyurea- or polyurethane-resin from the valence X-ray photoelectron spectra.

2. Experiment

The X-ray photoelectron spectra were obtained on a PHI 5400 MC spectrometer. using monochromatized Al K alpha radiation. The spectrometer was operated at 400 W. 15 kV. and 26.7 mA. The

photon energy was 1486.6 eV. A pass energy of 35.75 eV was employed for high-resolution scans in the N 1s spectra region of 390-410 eV and in valence band analysis in the range of 0-50 eV. The angle between the X-ray source and the analyzer was fixed at 45°. The spot size in the measurement was 3 x 1 mm^2.

The use of dispersion compensation yielded an instrumental resolution of 0.5 eV with the full width at half-maximum(FWHM) on the Ag 3d line of silver. Multiple-scan averaging on a multi-channel analyser was used for the valence-band region due to a very low emission cross section. The reproducibility of the binding energy(BE) for N 1s spectra is within ± 0.1 eV.

We used commercially-available gelatin(IK-158; Nitta Gelatin LTD), melamine, urea and formalin. For gelatin, the sample is formed by cast-coating solution on aluminium plate. Two kinds of samples except gelatin were prepared by coating the microcapsule suspension on aluminium plate and produced by fixing the resin powder with a copper-metal-tape involving an acrylic-typed adhesive(3M copper tape). The microcapsule is generally produced in formation of shell material around oil drops in water. In this case, the oil drops is stably formed by addition of a surface active agent, the carboxylic sodium salt. We washed it out using a centrifuge, to purify the surface of the microcapsule. In the case of the capsule samples, we detected Na 1s spectra of the salts on the XPS measurements. We were able to neglect the effect in the present study.

For polyurethane and polyurea, the materials were shown in Table 1. The microcapsule of polyurethane was made of polyvalent phenyl-isocyanate and polyhydric alcohol, while the polyurea consisted of polyvalent phenyl-isocyanate and polyvalent amine. The microcapsules were also produced in formation of shell material around oil drops in water.

A low-energy electron flood gun was used in order to avoid any charging effect on the surface of the sample. We used the Au4f core level of the gold decoration films(or disc) as a calibration reference. The C1s line positions of the maximum peak due to phenyl groups on the capsule-resin could be fixed at 284.6 eV for the polyurea or polyurethane material which we produced.

For unavailable polymers, polyurethane [(CO-NH-C$_6$H$_4$CH$_2$-C$_6$H$_4$-NH-CO-O-(CH$_2$)$_4$-)$_n$] and polyurea [(CO-NH-C$_6$H$_4$CH$_2$-C$_6$H$_4$-NH-CO-NH-(CH$_2$)$_3$-NH)$_n$] as references, we cited the valence XPS by Beamson and Briggs[12].

3. Molecular Orbital Calculations

We peformed an ab initio molecular orbital(MO) calculation using the model molecules of the microcapsule materials, to compare the XPS N 1s binding energies with the theoretical ore MO eigenvalues due to the Koopmans' theorem. We used melamine and 1,3-dimethyl urea instead of the melamine-resin and polyurea, respectively. The model molecules were calculated by the ab initio restricted Hartree-Fock SCF MO method, using the HONDO7 program[13]. For C, O, and N atoms, we used the (4s2p) basis sets and for H atoms we used the (2s) basis set reported by Huzinaga et al. [14] and Dunning et al.[15]. For the geometry of the model molecules, we used the optimized values from the semi-empirical AM1(version 6.0) MO method[16].

For polyurethane and polyurea as references, we calculated monomer molecules [H-(CO-NH-C$_6$H$_4$CH$_2$-C$_6$H$_4$-NH-CO-O-(CH$_2$)$_4$-O)-H and H-(CO-NH-C$_6$H$_4$CH$_2$-C$_6$H$_4$-NH-CO-NH-(CH$_2$)$_3$-NH)-H by the semiempirical HAM/3 program(the new version extended by Chong)[17]For the geometry of the molecules, we used the optimized structures from the semiempirical AM1 method[16].

In the HAM/3 program, three sets of relative atomic photoionization cross-section had been stored as permanent data:(a) Gelius empirical parameters for MgK alpha(1253.6 eV) radiation, (b) theoretical values from Nefedov et al[18] for MgK alpha radiation, and (c) theoretical values from Nefedov et al. for Al K alpha(1486.6 eV) radiation. All three sets were used to compute the relative photoionization cross-section for the occupied MOs, which were tabulated in the computer output. In this paper, we report the results from set (c) only,
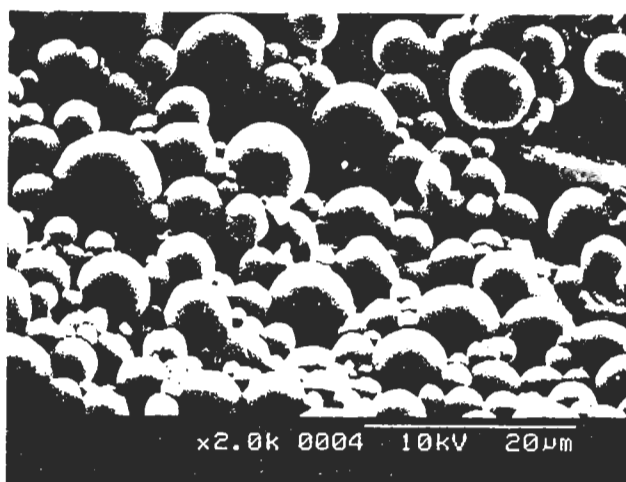
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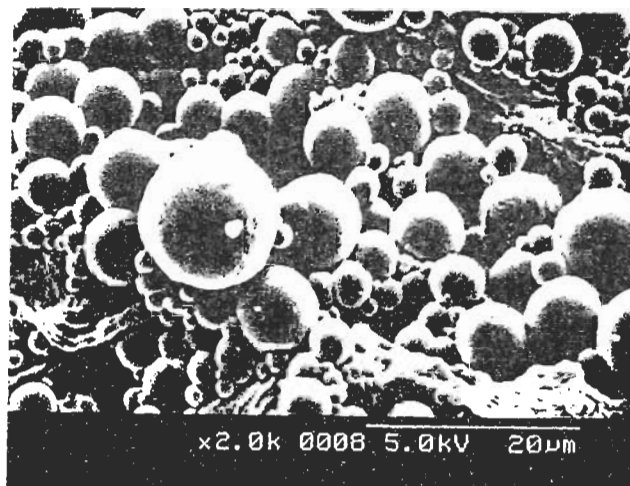
b)

Fig. 1 Photographs of microcapsules using a Scanning Electron Microscope. (a) melamine-resin shell, (b) polyurea shell.

because Al K alpha radiation was used in the present experiments.

In order to simulate the valence XPS of the polymers theoretically, we constructed from a superposition of peaks centered on the vertical ionization potentials, Ik. As was done in previous works[1-5]. each peak was represented by a Gaussian curve. In the case of the linewidth(WH(k)), we used $WH(k) = 0.10$ Ik for the models, as adopted in previous works[1-5].

4. Results and Discussion

It is interesting that we see the size of capsules from the photographs of microcapsules. The photographs of an scanning electron microscope(SEM) (Fig. 1 (a) and (b)) showed microcapsules in the size range of a few to ten μm. We thought the material of the capsule shell can be analyzed with the core XPS N 1s spectra. since the analytical depth of the XPS is considered to be less than 5 nm and the thickness of the capsule shell approximates 10 to 100 nm.
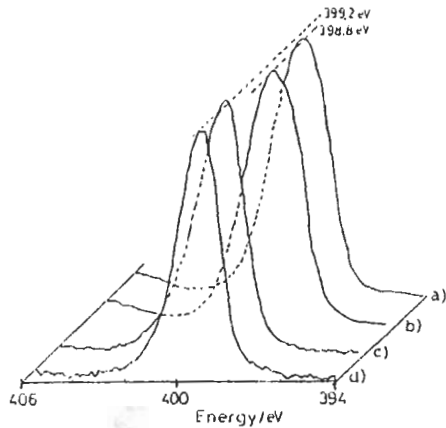
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Fig. 2　XPS N1s spectra of microcapsule material. (a) melamine resin(powder), (b) melamine-resin(capsule),(c) polyurea(capsule), (d) gelatin (film)
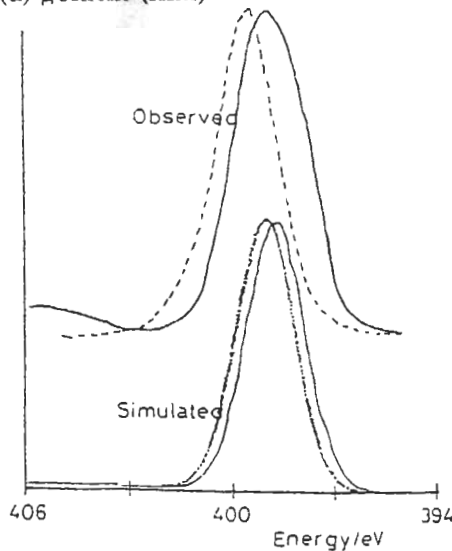

Fig. 3. Simulated N1s spectra of melamine-resin (solid line) and polyurea (dotted line) by an ab initio MO calculations using the model molecules (lower) and the observed spectra(upper).

Table I. Microcapsule materials as produced in formation of shell

material around oil drops in water.

polyvalent phenyl-isocyanate	polyhydric alcohol, or polyvalent amine
	╱ R
(a) OCN-φ-CH₂-φ-NCO (P-MDI)(0.7)	H₃C-CH₂-C—R (0.2)
(P-MDI)-N=C=N-(PMDI)(0.3)	╲ CH₂—R
(b) OCN-φ-CH₂-φ-NCO (P-MDI)(0.7)	H₂N-CH₂-CH₂-NH-CH₂-CH₂-NH₂
(P-MDI)-N=C=N-(PMDI)(0.3)	(0.2)

Where φ = C₆H₄ and R = -CH₂-O-(CH₂-CH(CH₃)-O)ₙ-H

XPS method is to study the bond-nature of

the functional groups of the material elements. Let us consider the constituent groups of the capsule materials. For gelatin and polyurea, the nitrogen is a common -NH-bond: peptide(-NH-CO-) and urea(-NH-CO-NH-) bonds. respectively. In the case of melamine resin. the material involves the two different bonding nitrogens. The one is -NH-CO- bonds and the other the double -C=N- bonds of 1.3.5-triazine ring. Then. we may be able to observe the single and double peaks of the XPS N 1s spectra for (gelatin and polyurea) and melamine-resin. respectively.

Fig. 2 showed the single peaks of observed N 1s spectra for melamine-resin(powder and capsule), polyurea(capsule) and gelatin. We can see the differences of the BE and the FWHM of the spectra between melemine-resin and non-melamine(polyurea and gelatin) in Table 2. This is due to the functional groups involved nitrogen.

For polyurea and melamine-resin. the simulated core N 1s spectra. as calculated by the MO method using the model molecules. seem to correspond to the XPS N 1s spectra of the capsule materials(as shown in Fig. 3). although there were large differences in energy levels due to the Koopmans' theorem and work function and other energy effects[19]. For this simulation. we used fixed energy shifts and fixed linewidths for calculated N 1s spectra. By trial and error, we found the energy shifted values as 25.0 for N 1s
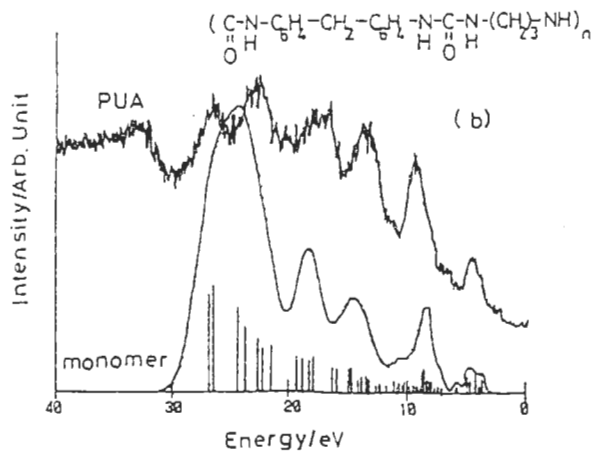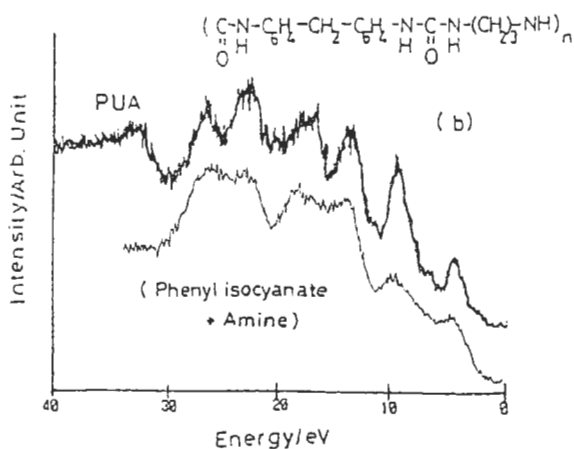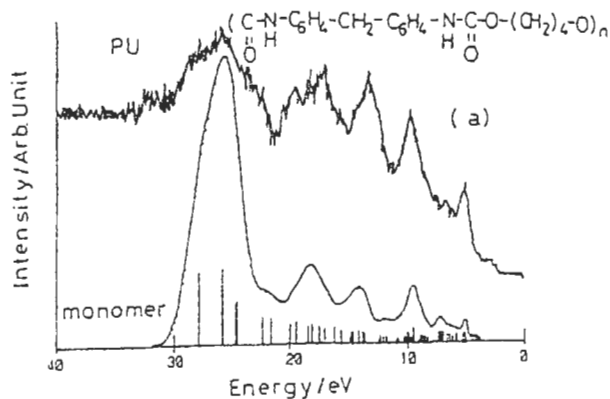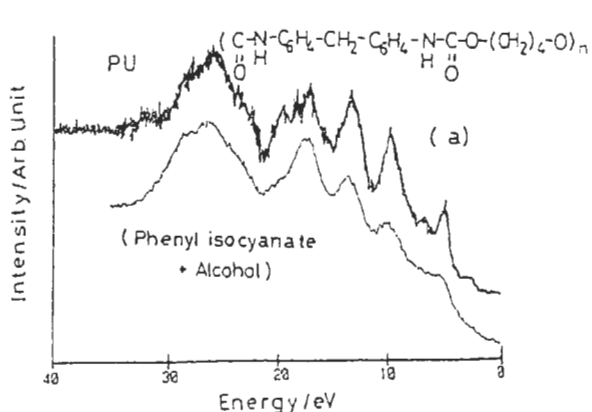
Fig. 4 Valence XPS for two kinds of microcapsule-resin with the spectra of polyurethane and polyurea as observed by Beamson and Briggs[12]. (a) a cited spectrum of polyurethane(upper) and observed one of capsule-resin which consisted of polyvalent phenyl-isocianate and polyhydric alcohol. (b) a cited spectrum of polyurea (upper) and observed one of capsule-resin which was made of polyvalent phenyl-isocyanate and polyvalent amine(lower).

Fig. 5. (a)Valence XPS of polyurethane as obtained by Beamson amd Briggs with the simulated spectrum of the monomer model using HAM/3. (b)Valence XPS of polyurea as obtained by Beamson and Briggs with the simulated spectrum of the monomer model using HAM/3.

spectra. The linewidth of each MO level for the N 1s was evaluated 0.6 eV. The estimated BE and FWHM differences between melamine and 1,3-dimethyl urea agrees considerably well with the observed N 1s energy difference between melamine-resin and polyurea(as shown in Fig.3 and Table 3). This indicates that we can obtain good assignments with the Koopmans' theorem due to the normal MO calculations of the ground state for N electrons using the ab initio HONDO program.

In the case of the microcapsules as produced in formation of shell material around oil drops in water, we tried to observe valence XPS for two kinds of the produced resin, in order to determine which resin is made of, polyurethane or polyurea. The valence band spectrum of the capsule-resin which was produced from the reaction between polyvalent phenyl-isocyanate and polyhydric alcohol corresponds well to the spectra of the polyurethane which we cited (Fig. 4 (a)). It can be seen, in Fig. 4 (b), that the spectrum of the capsule-resin which consisted of polyvalent phenyl-isocyanate and polyvalent amine is also in agreement with the valence spectra of the polyurea as a reference.

Furthermore, we performed the MO calculations with the HAM/3 program using the monomer model for the cited polyurethane and polyurea[12], to examine

Table 2. Observed binding energy (BE) and full width of

half maximum (FWHM) of XPS N 1s spectra of

materials for capsule shell

material	BE (eV)	FWHM (eV)
melamine-resin(powder)	398.8	2.5
melamine-resin(capsule)	398.8	2.5
polyurea(capsule)	399.3	2.1
gelatin(film)	399.2	1.9

Table 3. Simulated BE and FWHM of XPS N1s Spectra of melamine-

resin and polyurea using model molecules.

material	Koopmans' value* (eV)	calculated BE (eV)	FWHM (eV)	observed BE (eV)	FWHM (eV)
melamine-resin		398.8	2.1	398.8	2.5
-NH	424.0(399.0)				
-N=C-	423.6(398.6)				
polyurea	424.1(399.1)	399.1	2.0	399.3	2.1

*Values in parenthesis were shifted as 25.0 eV from the Koopmans'

theorem.

Table 4. 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	O2s(0.7),N2s,C2s	[sσ (O,N2s-C2s)-B, pσ (O2s-C2p)-B]	O=C,-N-C
24.0 (21-25)[a]	26.61-28.39 26.15;25.39	N2s(0.6),O2s,C2s C2s(0.8),N2s	pσ (N,O2s-C2p)-B sσ (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	sσ (C2s-C2s)-B sσ (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),O2s,N2p C2s(0.6),N2p,O2s C2s(0.5),N2p,C2p	sσ,pσ (C2s-O2s,N2p)-B pσ (C2s-N,C2p)-B pσ (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	O2s(0.6),O2p,C2p N2p,C2p	pσ (O2p-O2s,C2p)-B [pσ (N,C2p-C2p)-B, pπ (C2p-C2p)-B]	O=C,-C=C- -N-C-,-C=C- -C=C-
5.5 (2.5-7)[a]	7.64-8.92 9.77-11.70	O2p,N2p C2p,N2p,O2p	pπ (lone pair)-NB [pπ (C2p-C2p)-B, pπ (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.

the electronic states of the polymers. In Fig. 5 a),b), the simulated spectra of polyurethane(PU) and polyurea(PUA) with the spectral patterns are compared with the experimental XPS as obtained by Beamson and Briggs[12]. As mentioned earlier[1-3], the simulation used a Gaussian lineshape function for each MO with a model linewidth of 0.10 Ik and Ik = Ik' - WD. The simulated spectra using the monomer model are in good accordance with the experimental spectra of the polymers. The shift due to the WD effects was estimated as 4.0 eV for PU and PUA, respectively.

In the figure, large peaks between 20 and 30 eV correspond to both N2s and O2s main contributions. The double peaks in the range of 12-20 eV result mainly from p sigma(C2s-N2p) and s sigma(C2s-C2s) bonding orbitals. We showed the orbital characters of PUA in Table 4 (The similar table for PU is omitted).

5. Conclusion

We have analyzed the microcapsule material which consists of polyurea, polyurethane, gelatin and melamine with X-ray photoelectron spectral method.

(1) We determined which material was involved in the microcapsule, melamine or non-melamine(gelatin, polyurea and polyurethane) from the core N 1s spectral analysis.

(a)The linewidth of the N 1s spectra of melamine-resin, 2.5 eV, is larger than that of non-melamine materials(polyurea(2.1 eV) and gelatin(1.9 eV)). his depends on the nitrogen functional groups: The melamine involves two functional groups, amino and triazine-ring nitrogens, while polyurea and gelatin have amino groups.

(b)The N 1s spectra of melamine-resin and polyurea were simulated by an ab initio MO calculations using the melamine and 1,3 dimethyl urea molecules, respectively.

(2) We produced the two kinds of microcapsules(polyurea or polyurethane) in formation of shell material around oil drops in water. The difference of the material between polyurea and polyurethane was determined by the valence X-ray photoelectron spectra. We simulated the experimental results. as observed by Beamson and Briggs. with the semiempirical HAM/3 MO calculations using the model monomers.

6. References

1) Endo K., Kaneda Y., Aida M., Chong D. P., J. Phys. Chem. Solids 56.1131(1995).

2) Aida M., Kaneda Y., Kobayashi N., Endo K., Chong D. P., Bull. Chem. Soc. Jpn. 67,2972(1994).

3) Endo K., Inoue C., Kaneda Y., Aida M., Kobayashi N., Chong. D. P., Bull. Chem. Soc. Jpn. 68,528(1955).

4) Endo K., Kaneda Y., Okada H., Chong D. P., Duffy P., to be published.

5) Endo K., Aida M., Chong D. P., to be published.

6) Asbrink L., Fridh C., Lindholm E., Chem. Phys. Lett. (1977)52.63: Quantum Chemistry Program Exchange 12.398(1980).

7) Asbrink L., Fridh C., Lindholm E., Chem. Phys. Lett. 52.69(1977).

8) Lindholm E., Asbrink L., In Molecular Orbitals and their Energies. Studied by the Semiempirical HAM Method. Springer-Verlag, Berlin(1985).

9) St-Amant., Salahub D. R., Chem. Phys. lett. 169.387(1990); St-Amant A., Ph. D. Thesis. University of Montreal(1991).

10) "Bunseki Kagakubinran" edited by The Japan Society for Analytical Chemistry(1981) Marusen LTD.

11) M. Sumi, Y. Chokki, Y. Nakai, M. Nakabayashi and T. Kanzawa, Macromol. Chem. 78,146(1964).

12) Beamson G., Briggs D., "High resolution XPS of Organic Polymers. The Scienta ESCA 3000 Database." Wiley, Chichester(1992).

13) Dupuis M. S., Watts J. D., Villar H. G., Hurst G. J. B., HONDO. version 7;Scientific and engineering Computations Dept. 48B. IBM Corp; New York. 12401:1978.

14) Huzinaga S., Andzelm J., Klobukowski M., Radzio-Andzelm. E., Sakaki Y., Takewaki H., "Gaussian Basis Sets for Molecular Calculations." Elsevier, Amsterdam, 1984.

15) Dunning T. H. Jr., Hay P. J., In "Methods of Electronic Structure Theory,"

Schaefer H. F., III. Ed., Plenum, New York, N. Y. 1977.

16) Stewart J. J. P., J. Comp. Chem. 10,289(1988).

17) Chong D. P., Can. J. Chem. 63,2007(1985).

18) Nefedov V. I., Sergushin N. P., Band I. M., Trzhaskovskaya, M., J. Electron Spectrosc. Relat. Phenom. 2,383(1973).

19) Inoue C., Kaneda Y., Aida M., Endo K., Polymer J. 27, 300(1995).