Photoelectron Spectra of Polypyrrole: The Effect of the Ambient Atmosphere to the Spectra

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(Received April 3, 1990)

Ultraviolet and X-ray photoelectron spectra of carefully prepared undoped as well as doped polypyrrole have been measured. Reliable UPS of undoped polypyrrole must be the first one in spite of its popularity, because of its instability in the air. Our UPS were compared with those of presumably polymerized pyrrole by X-ray irradiation and other reported results. We examined the validity of these spectra and we found the deformation of the UPS caused by air exposure of the undoped film. A comparison of our UPS with theoretical calculation gave 1.40 Å as an estimated bond distance between α,α' carbon atoms. Both Cls and Nls XPS were asymmetric and consisted of a few peak components, which was not dependent on doping. Their peak envelopes varied with its historical back ground. While the Cls peak envelopes were not deformed so seriously by air exposure, the Nls envelopes were affected by slight air exposure as were observed in the UPS.

There have been a controversy on the results and their interpretation of X-ray photoelectron spectra (XPS) of polypyrrole. Salaneck and his co-workers[1] measured the XPS of doped and undoped polypyrrole. They reported that the peak shapes of Cls and Nls spectra of both doped and undoped species were essentially symmetric, but the spectra of doped polypyrrole were skewed by the excitation of Fermi surface electrons. Pfluger and Street[2] also obtained asymmetric peak shapes of doped polypyrrole, but they attributed the origin of asymmetry in the Cls spectrum to the chemical shift of carbon atoms induced by a nitrogen atom, and that of Nls to the difference of distance between the nitrogen atoms and the counter anions in the polymer. As have been repeatedly reported,[3,4] the undoped polypyrrole film is unstable in the ambient atmosphere. In order to overcome this nature, Skotheim's group prepared polypyrrole in an ultra-high vacuum chamber with an aid of solid electrolyte and measured its XPS without exposing the specimen to the air.[5] They observed an asymmetric Nls spectrum in an as-grown film, and reported that the spectrum changed in accordance with varying the cell bias. However, they could not go into details of the Cls spectra, since there were two types of carbons in the specimen, namely polypyrrole and poly(oxyethylene), base film of the specimen. Instead of polypyrrole, polythiophene or poly(3-methylthiophene) which is more stable in the air has been measured to settle the argument.[6,7] XPS of polycarbazole which has a pyrrole unit in its molecular structure has been also reported to clarify the existence of chemical shift caused by the nitrogen atom.[8] In spite of these efforts, it seems that the argument is not settled yet. Settlement requires to measure the XPS of polypyrrole itself in a carefully controlled condition.

The situation of ultraviolet photoelectron spectra (UPS) of polypyrrole is more or less the same. There has been no reported reliable spectrum of undoped polypyrrole as far as the authors have known. Salaneck et al.[1] measured a X-ray irradiated pyrrole film and claimed that they obtained the spectrum of "polypyrrole." Their result was questioned by Pfluger et al.,[9] because the spectrum of X-ray irradiated pyrrole showed no prominent low-energy peak (shoulder) due to the bonding π-orbital which was observed by them in the spectra of anion and oxygen (air) doped polypyrrole and was predicted by a CNDO/S3 calculation.[10] Recently Tourillon and Jugnet[7] reported UPS and XPS of poly(five-membered heterocycle)s including polypyrrole and polythiophene. They did not show the spectrum of undoped polypyrrole. They only mentioned that they have found the π-band extension (the same as the low energy shoulder due to the bonding π-orbital) in the spectrum of undoped polypyrrole just below the Fermi level, as was observed in the spectra of polythiophene[7,11,12] and poly(3-methylthiophene).[6] They also mentioned that the spectrum of air exposed polypyrrole differed from that of a non air exposed film.

The color of carefully prepared undoped polypyrrole is yellow or dark yellowish green, but it turns into black when the film is exposed to air only 1 minute or less. This must be the reason of the controversy and the lack of reliable UPS data. In this paper we report the photoelectron spectra of undoped and doped polypyrrole with various doping levels prepared carefully in a dry box attached to a photoelectron spectrometer. We also discuss how the ambient atmosphere changes the spectra.

Experimental

Synthesis and treatments of polypyrrole were carried out in an argon filled dry box which was connected directly to an ultra-high vacuum photoelectron spectrometer. Pyrrole supplied by Tokyo Kasei Kogyo Co. Ltd. was dehydrated with CaH_2 and deoxygenated by repeated freeze-thaw cycles under 1.0×10^{-4} Torr or less vacuum combined with vacuum

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distillation before use (1 Torr=133.322 Pa). Supporting electrolyte was $(C_4H_9)_4NBF_4$ (Tokyo Kasei Kogyo Co., Ltd.) and it was recrystallized from ethanol three times and then vacuum dried. Acetonitrile was used for synthesizing solvent. The solvent was dehydrated with P_2O_5 and distilled then deoxygenated by the same method used for pyrrole. Electropolymerization was performed in a single compartment cell with three electrodes. Polypyrrole films were deposited onto a platinum working electrode with a platinum counter electrode and a platinum reference electrode. An Ag/AgCl reference electrode was used to examine the potential difference with the platinum reference electrode, and it was found to be negligible small. A Hokuto Denko Ltd. potentiostat/galvanostat, HA-301, was used to oxidize pyrrole monomers. The solutions used for the preparation of the films contained 0.05 M pyrrole and 0.15 M electrolyte. Potentiostatic electrolysis of 1.2 V to the Pt reference electrode was carried out at room temperature for 10 min. The current varied but remained mainly around 0.3 $\mathrm{mA\,cm^{-2}}$. Estimated thickness of the films were several tens nanometer or less. Undoping process was performed by applying negative potential of 0.2—2 V to the reference electrode and by controlling undoping time. Doping levels of the polymers were determined by the intensity of the fluorine 1s spectrum.

Photoelectron spectra were recorded by the Kratos XSAM-800 ultrahigh vacuum spectrometer equipped with Mg and Al X-ray guns, a DC discharge helium lamp and a fast insertion lock system. Pt4f lines from the substrate were used for energy calibration of the XPS in the course of measurements. The Fermi level of the spectrometer for the UPS measurement was determined using the Fermi edge of a gold evaporated film. Binding energies in the following text are referred to the Fermi level of each specimen. Base pressure of the spectrometer was 3×10^{-10} Torr. The pressure during the XPS measurements was less than 1×10^{-9} Torr, and 4×10^{-9} torr or less during the UPS measurements. The prepared film with the Pt substrate was introduced into the spectrometer through the air lock system. An analyzing chamber of the spectrometer was evacuated down to 5×10^{-9} Torr within 30 min after an introduction of the specimen into the chamber. Surface cleaning procedures of the specimens such as Ar ion bombardment or heating were not performed, since such treatments might damage the specimen.

Results and Discussion

Valence Band Spectra. Figure 1A is a He II spectrum of undoped polypyrrole. To have a clear onset position of the spectrum, an expanded He I spectrum of undoped polypyrrole is also shown in the inserted figure. The spectrum begins at 0.3 eV below the Fermi level. Assuming that undoped polypyrrole is an intrinsic semiconductor, an estimated band gap of undoped polypyrrole is 0.6 eV. This value is consistent with the value obtained by the optical measurements.[3,13,14] We do not go into details whether this band gap is due to bipolaron bands or intrinsic ones. First distinct structure is a shoulder at around 2.5 eV below E_f, which corresponds with the bonding π-orbital observed in doped polypyrrole[9] and in both doped and undoped poly(3-methylthiophene),[6,7] and calculated by a CNDO/S3 method.[10] There is a peak at 4.2 eV below E_f. This is due to the π-orbitals which are not affected upon polymerization of pyrrole rings. Theoretical calculations also give density of valence states (DOVS) at this energy region.[10,15] There is a broad band at 9 eV accompanied by a

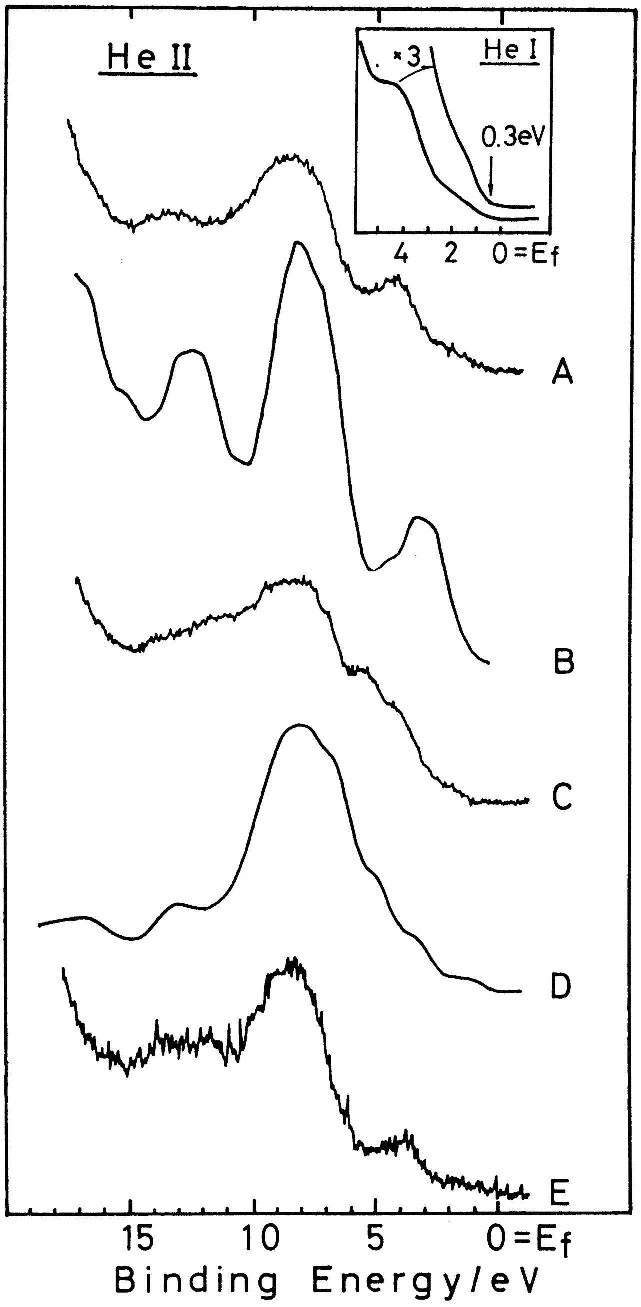

Fig. 1. He II spectra of undoped polypyrrole; (A) the present result of undoped species and the inserted figure is He I spectrum to show the onset of the spectrum clearly, (B) Salaneck's result (Ref. 1) on X-ray irradiated pyrrole, (C) our result of polypyrrole undoped then exposed to air for 5 min, (D) Pflug-er's result (Ref. 9) on undoped then oxygen exposed polypyrrole, (E) our result of doped then air exposed polypyrrole.

shoulder located at 7.5 eV. This structure is due to a mixture of σ- and π-orbitals. There is a faint structure at around 13 eV below E_f, which is derived from σ-orbitals of pyrrole. This structure was also observed in the spectrum of condensed pyrrole,[1] that is, this band is not affected upon polymerization.

Figure 1B is the spectrum of X-ray irradiated pyrrole reported by Salaneck et al.[1] A comparison of the spectra reveals following differences between them; (a) the shift of each peak, (b) the appearance of the structure near the Fermi level and (c) sharpness of the peaks. The spectrum obtained by Salaneck's group seems to shift toward lower binding energy than ours. The shift may be caused by the difference in either energy calibration or work functions. They attributed the reason of the lack of the low binding energy shoulder to its small photoelectron cross section. However, the shoulder is observed as is seen in Fig. 1A and that is also reported in the doped polypyrrole.[9] Therefore their spectrum is dubious to claim to be that of polypyrrole. Sharpness of their spectra also reflects its monomeric (molecular) nature rather than polymeric one. Apart from the absolute binding energy of each peak, a relative relation of each peak of both spectra A and B is in good agreement.

Ford et al.[10] pointed out that an α,α' carbons bond length between the pyrrole rings influenced the shape of the band located between 5 and 10 eV. They concluded that the bond length was 1.49 Å through a comparison of their calculated DOVS results with the spectrum (Fig. 1B) obtained by Salaneck et al.[1] However, Salaneck's result is not sufficient to compare, as described above. Therefore, their conclusion is worth to reconsider. A comparison of the Fig. 10 of Ref. 10 and our results reveals that the estimated bond length is not so long as 1.49 Å. The bond length is rather shorter than that value. Our spectrum seems to be well reproduced by using 1.40 Å as the α,α' bond distance. This value is slightly smaller than 1.45 Å which is a proposed distance for pyrrole oligomers.[15,16] As Ford et al. did not show the calculation on the polymer of the 1.45 Å bond length, we are not able to be decisive on the value of 1.40 Å. However a much stronger interaction can be expected between the pyrrole rings in the polymer than those in the oligomer. The stronger interaction means the shorter bond distance. Therefore, our conclusion is plausible even if it is not exact.

Our spectrum (panel A) differs very much from doped or oxygen-exposed undoped polypyrrole (Fig. 1D) reported by Pfluger's group.[9] In order to have better understanding we measured 5 minutes air-exposed undoped polypyrrole (Fig. 1C). The spectrum is quite different from the spectrum A or B. It shows a large band at 8 eV and low binding energy side shoulders located at about 1.9, 3.6, and 5.3 eV. The spectrum is identical to the spectrum of oxygen-exposed polypyrrole reported by Pfluger's group,[9] if a small shift of the spectrum is considered. This shift is acceptable, since the spectrum C begins at 0.3 eV below the Fermi level while the spectrum D begins just at the Fermi level. Thus the electronic structure of undoped polypyrrole is easily changed by the slight exposure of air as is observed in its color change.[13] This relates to the easily oxidized nature of undoped polypyrrole.

The UPS of doped polypyrrole does not suffer deformation by the air exposure, as is shown in Fig. 1E. The spectrum is the same as that of doped one (Fig. 2D). That is, the electronic structure of doped polymer is not influenced by the air exposure. The deformation of the spectrum, which means the change of the electronic structure, takes place only in the undoped species. Furthermore, the effect induced by the air exposure on the neutral polymer is different from the one caused by the doping anions.

Figure 2 shows He I and He II spectra of polypyrrole undoped by applying −0.2 V (A) and −2 V (B) to the reference electrode and 25% doped (C) and as-prepared doped polypyrrole (D). The spectra of both undoped

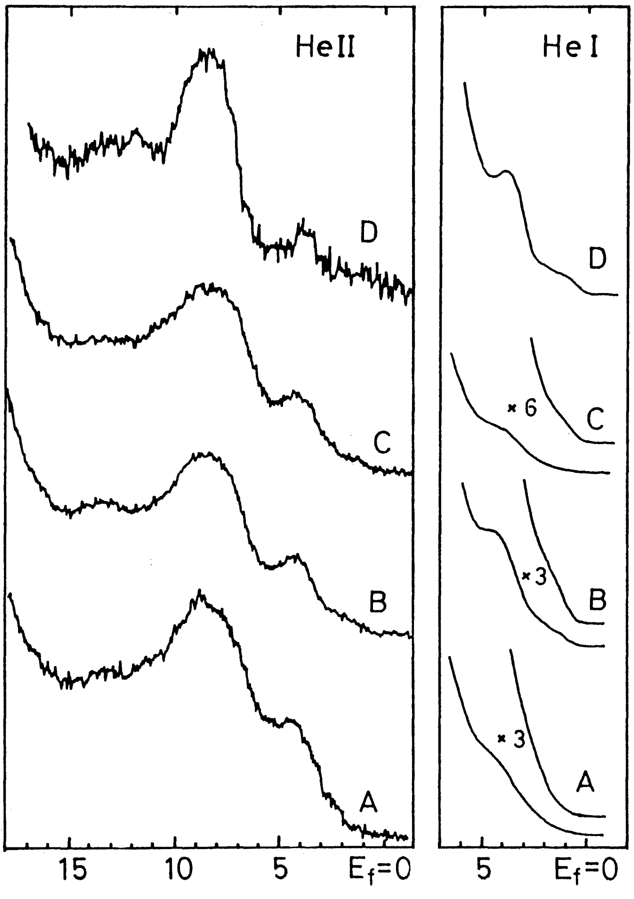

Fig. 2. He I and He II spectra of polypyrrole; (A) undoped by applying −0.2 V to the reference electrode, (B) undoped by applying −2 V to the reference electrode, (C) 25% doped by applying −0.2 V to the reference electrode, (D) doped (as-prepared).

species begin at 0.3 eV below the Fermi level, while those of doped ones move toward the Fermi level. The spectrum of 25% doped polypyrrole begins at 0.1_5 eV below the Fermi level, and that of as-prepared one begins just at the Fermi level. This movement of the onset of the spectrum indicates that the band gap decreases with increase of dopant concentration. This phenomenon must be closely related to an exponential increase of its electric conductivity upon doping.[4]

In He I and He II spectra paneled A the existence of the new band near the Fermi level is difficult to point out, because the spectra grow their intensity slowly. However, in other spectra, particularly in the He I spectra, the new band is observed as a distinct shoulder at around 1.5 eV below the Fermi level. Though the first peaks (or shoulders) of these spectra are difficult to point out the exact positions, the second peaks, particularly panels B and D clearly show their peak positions at 4.2 eV and 3.9 eV, respectively. This energy difference is the same as that of their spectral onsets. The spectra A and B should be the same from a view point of specimen as undoped ones, but there is a slight difference between them. The peak located at 4.2 eV is clearly observed in the spectrum B, while the structure in the spectrum A is not so distinct but is vaguely observed. The treatment of the film may be crucial.

In the spectrum D the band located at around 9 eV is intenser than the other spectra. The reason of this enhancement is superposition of the F2p levels, since the F2p levels of tetrafluoroborate anions locate at this energy region.[1]

Threshold energy, E_{th}, of undoped polypyrrole is ranging between 4.0 and 4.2 eV, which is in good agreement with the calculated ionization potential.[15] This small threshold energy relates closely to its easily oxidized nature. E_{th} of doped polypyrrole is found to be 4.7 eV. This difference in the E_{th}'s is understood as follows; the electrons of undoped polypyrrole are ejected easier than those of doped one, since the electron density of the former is higher than the latter.

Nitrogen 1s and Carbon 1s Spectra. Figure 3 shows nitrogen 1s spectra of polypyrrole with different histories. Left side figure is their full spectra, and right side figure indicates their main peak region with peak fitting results. Panel A is the spectrum of polypyrrole undoped with −2 V reducing potential vs. the reference electrode. Panel B is of −0.2 V applied undoped one. Panel C is of undoped one but exposed to air for 5 min before the measurement. Panel D is of 25% doped one. Panel E is of as-prepared one, namely doped polypyrrole. Panel F is the same as E but was exposed to air after the preparation. All the spectral shapes of the main peaks are asymmetric. Even undoped polypyrrole gives an asymmetric peak. This finding is to the contrary of Salaneck's deduction that undoped polypyrrole gives symmetric spectral envelope.[1] All spectra can be deconvoluted into four peak components. The strongest component locates at between 399.6 and 400.0 eV, which is due to neutral nitrogen 1s core level.

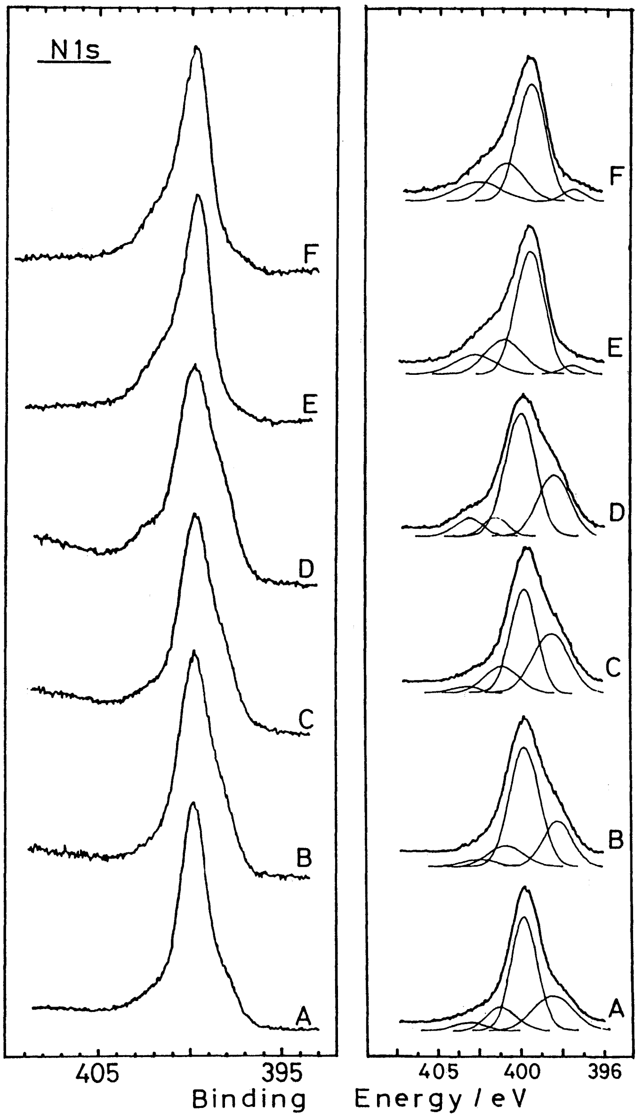

Fig. 3. Full N1s X-ray photoelectron spectra of polypyrrole at the left, and main peak regions together with results of peak fitting at the right; (A) undoped by applying −2 V to the reference electrode, (B) undoped by applying −0.2 V to the reference electrode, (C) the same as (A) but exposed to the air for 5 min before the measurement, (D) 25% doped by applying −0.2 V to the reference electrode, (E) doped (as-prepared), (F) doped then exposed to air.

Two types of undoped polypyrrole films give slightly different results. The main peaks of both spectra locate at 399.8 eV, but their FWHM's differ by 0.2 eV. The second largest peak component of both spectra also locates at almost the same position of 398.3—5 eV, but their intensities and FWHM's are different as are shown in Table 1. This peak is due to

Table 1. The Results of Peak Fitting of N1s and C1s Spectra

	N1s			C1s		
	Peak position	Intensity	FWHM	Peak position	Intensity	FWHM
	eV	%	eV	eV	%	eV
Undoped with −2V applied	398.5	26	2.3	284.2	48	1.9
	399.8	84	1.5	285.0	59	1.6
	401.0	18	1.7	286.1	29	2.0
	402.5	6	1.7	288.1	6	1.6
Undoped with −0.2V applied	398.3	33	1.7	284.5	54	2.0
	399.8	87	1.7	285.3	55	1.7
	400.8	15	2.0	286.6	23	2.0
	402.0	5	1.8	288.3	10	1.7
−2V Undoped then exposed to air	398.5	44	2.1	284.2	47	1.9
	399.8	76	1.5	285.0	61	1.6
	400.9	20	2.0	286.1	31	2.1
	402.6	5	1.4	288.4	4	1.9
25% Doped (−0.2V applied)	398.4	46	1.9	284.8	48	2.2
	400.0	91	1.8	285.4	56	1.7
	401.2	14	1.5	286.9	26	2.2
	402.5	14	1.6	288.9	4	1.4
As-prepared	397.6	7	1.2	284.1	45	2.0
	399.6	89	1.7	285.0	59	1.7
	400.9	25	2.1	286.2	31	2.1
	402.2	14	2.3	288.0	7	2.2
As-prepared then exposed to air	397.6	9	1.3	284.2	39	2.2
	399.6	85	1.7	285.0	60	1.8
	400.8	28	2.0	286.2	29	2.1
	402.2	14	2.6	288.0	8	2.4

those nitrogen atoms which get about the 1/4 charge, when an empirical relation of 5.8 eV shift per unit charge[17] is adopted. Probably the different applying reducing potentials make various environment of the nitrogen atoms, and hence the amounts of charges they get may be different. This relates to the slight difference observed in the UPS. This lower binding energy component is also observed in air exposed (panel C) and partially doped (panel D) polypyrrole with stronger intensity. This enhancement is not caused by the doping process, since the spectra of doped polypyrrole (the spectra E and F) do not show such a large low binding energy peak component. The appearance of this low binding energy component suggests an electron-rich surrounding near the nitrogen atoms in undoped polypyrrole. A possible reasoning is dehydrogenation from some nitrogen atoms.[18]

Doped polypyrrole showed skewed spectrum toward high binding energy as reported earlier.[1,2] Our peak fitting gives two high binding energy components at 400.9 and 402.2 eV and a small low binding energy component at 397.6 eV. It is consistent with Pfluger and Street's results on the peak positions of the high binding energy components, but it differs in the FWHM's and the area. They attributed the origin of these components to the difference in the distance between nitrogen atoms and the anions, i.e., 1 : 2 : 2 for the ratio of the counterions' least affected nitrogen neighbors, next nearest nitrogen neighbors and nearest nitrogen neighbors. A widening trend in the FWHM's of these respective nitrogen atoms was an additional evidence to their conclusion. However, our results question on their conclusion in terms of both the ratio and the FWHM's. These components are observed even in undoped polypyrrole although they are small. That is, the counterions are not responsible for the formation of the asymmetry of doped polypyrrole. Further the FWHM's of peak components do not show widening trend as they have claimed. These components grow its intensity in accordance with the dopant concentration (including the air exposed one), as the electric conductivity increases.[4] These facts support Doniach-Sunjic type Fermi surface electron excitation as the origin of the high binding energy peak components (peak asymmetry). The existence of the low binding energy component indicates occurrence of dehydrogenation even in the doped state though it is small.

Skotheim et al. reported that the spectrum of the as-prepared (doped) film consisted of a few peaks rather than of one asymmetric peak. They also reported an asymmetric peak envelope for undoped one.[5] Their results are to the contrary of our results. The reason is not clear. However, as their solid electrolyte cell is a complicated one from a view point of photoelectron measurement, their description on the doped and/or undoped film may be erratic.

When undoped polypyrrole is exposed to air, the intensity of the 399.8 eV peak decreases and that of the 398.5 and 401.0 eV peaks increase. Enhancement of the 398.5 eV is very strong. Easily oxidized nitrogen atoms in the neutral polymer may have a crucial key.[18] The air exposure of the doped polymer also shows the same tendency, but the amount of change is small. Doped polypyrrole is strong enough to resist the effect of the air exposure.

Carbon 1s XPS results are shown in Fig. 4. Explanations of panels A—F of each spectrum are the same as in Fig. 3. All spectra are asymmetric as are observed in the N1s spectra. The main peak region can be deconvoluted into four components. There are two intense peaks at 284.2 and 285.0 eV in both undoped and doped polypyrrole. (In the spectra of B and D they locate at slightly higher binding energies.) Observation of two intense components even in the undoped specimen indicates that they are not caused by doping of polypyrrole but they are characteristic to polypyrrole itself. They must correspond to two chemical states of carbon atoms, namely α- and β-carbons.[2] The energy separation of these two components corresponds to the chemical shift induced by nitrogen atoms.[19]

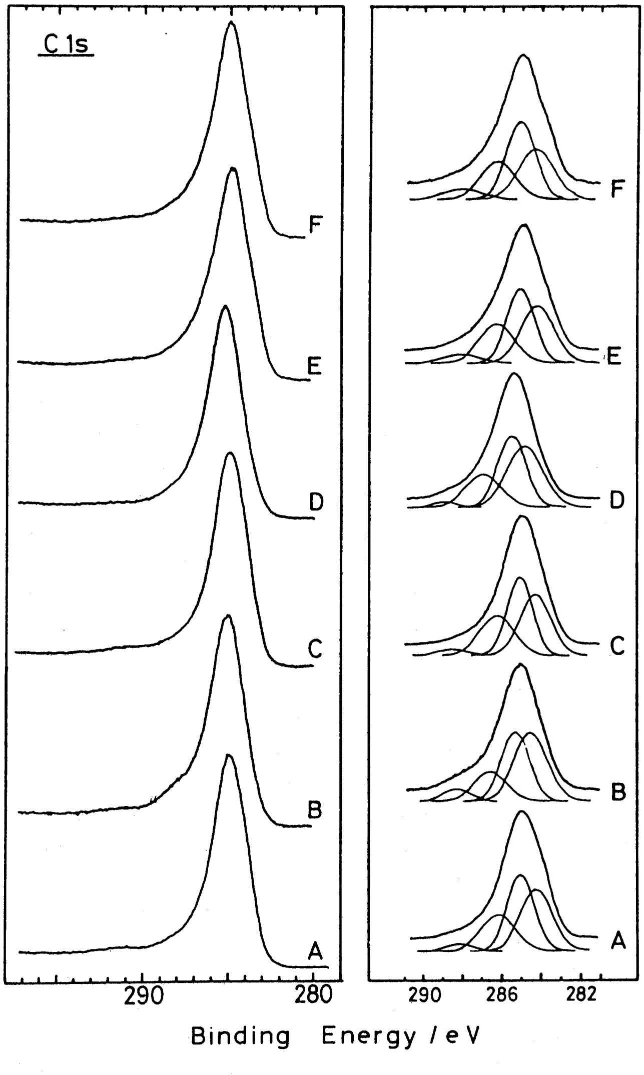

Fig. 4. Full C1s X-ray photoelectron spectra of polypyrrole at the left, and main peak regions together with results of peak fitting at the right; the explanation of each panel is the same as in Fig. 3.

There is another intense (about a half intensity of above two components) peak at 286.1—2 eV in all spectra. (Again a slight shift is observed in the spectra of B and D). The intensity of this peak is slightly stronger when the polymer is doped. The existence of this component is the main reason of the peak asymmetry. On the other hand, the C1s spectra of poly(3-methylpyrrole) or poly(3-methylthiophene) are symmetric.[7] Substitution at the 3-position prevents the hetero-bonding. Therefore, this peak component is probably due to the hetero-bonding. However, there still remains ambiguities on this explanation: (A) Even the hetero-bonding is the bonding between carbon atoms. The bonding between ordinary carbon atoms does not produce such a large chemical shift as are observed in the figure. (B) There should be hetero-bonding even in the 3-position substituted polymers, such as bond termination. Therefore, spectra reported in Ref. 7 might be recorded with poorer resolution. (C) Overall C 1s FWHM's of doped and undoped polypyrrole are 2.60 and 2.41 eV, respectively. FWHM's of conducting (doped) polymers are usually wider than that of less conducting (undoped) ones.[20] Therefore, Doniach-Sunjic type asymmetry proposed by Salaneck's group[1] as was observed in the conductive graphite compounds or the excitation of valence band electrons (shake-up)[6] could be still the reason of this peak.

The highest peak component observed at between 288.0 and 288.9 eV in every spectrum must be the satellite peak, since the energy separation between this peak and the other two main peak components is about 3 eV, which is the π-π^* transition energy obtained by optical measurement.[13]

Air exposure of the undoped film causes a slight intensity increase of the 286.1 eV peak. The ambient air may work as the dopant. The other peaks are not affected by the air exposure. When the polymer is doped, no serious change is observed upon the air exposure. This suggests that the once oxidized (doped) film is stable enough to resist further oxidation or deformation.

Summary

Photoelectron spectra of carefully synthesized poly-

pyrrole depend upon its handling and history. Slight exposure of the undoped polymer to the ambient atmosphere causes drastic change in the UPS. While the UPS of both doped and undoped polypyrrole are essentially the same, those of the air-exposed and non-air-exposed undoped polymers are completely different. The doped polymer is resistible from oxidation or deformation caused by the air exposure. Both N1s and C1s XPS give asymmetric peak envelopes. The N1s peak shapes of undoped polymers depend on the applied reduction potential, and the air exposure causes a large spectral change. The dopant or the air exposure induces no drastic change in the C1s spectra.

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