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X-RAY PHOTOELECTRON SPECTROSCOPIC STUDY OF HIGHLY CONDUCTIVE IODINE-DOPED POLYACETYLENE

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The X-ray photoelectron spectra of iodine-doped polyacetylene $(CHI_x)_n$ films are studied. By comparing with the results of Raman spectroscopy, it is concluded that iodine is more concentrated in the surface region than in the bulk when the amount of the doped iodine is small (i.e., $x<0.05$). It is probable that in a heavily iodine-doped film, iodine is distributed more homogeneously throughout the film, and that a considerable amount of iodine in the surface region can be easily liberated when the film is kept in vacuum. The mole ratio of I_5^-/I_3^- is higher in the surface region than in the bulk.

Recently, polyacetylene-halogen complexes were found to show metal-like high electrical conductivities, and have been recognized as a new type of organic conductors.[1∿3] Although the properties of these complexes have been investigated by several groups, more information concerning the structures and electronic states of these systems are required to assist in the understanding of their electrical behavior. In this paper, we will report the results of our X-ray photoelectron spectroscopic (XPS) studies on the iodine-doped polyacetylene films.

Samples used in this study were cut from films approximately 0.1 mm in thickness prepared as described previously.[4] X-ray photoelectron spectra were taken with a McPherson ESCA 36 Electron Spectrometer using Mg Kα (1253.6 eV) as the stimulating radiation. Special care was taken to prevent the samples from exposing to the air prior to the XPS measurements. As a consequence, we were able to obtain the XPS spectra which showed practically no O 1s peak. The binding energies of observed photoelectron peaks were calibrated by use of the Au $4f_{7/2}$ peak (83.8 eV) of a very thin gold film deposited onto the sample surface. Prior to XPS studies, a part of each sample film was cut off for the measurement of the Raman spectrum. The Raman spectra were also examined on the samples which had been used for XPS measurements.

It is known that iodine is gradually removed from an iodine-doped polyacetylene film when it is kept in vacuum.[3] In effect, the intensity and shape of I 3d peaks varied with time as the XPS measurements were repeated on the same sample. The I 3d peaks obtained by the initial measurement are shown in Fig.1 for three of the heavily iodine-doped films. The observed peak shapes indicate that there are at least two iodine species, which is consistent with the previous XPS results.[5] Both the I $3d_{3/2}$ peak and I $3d_{5/2}$ peak can be considered to be composed of two components with their energy separation of about 1.5 eV. It has been concluded from the Raman spectra that the iodine species present in the doped films are I_3^- and I_5^-.[5] Through the comparison of the spectral patterns in the XPS and Raman spectra[6], we attribute the higher binding-energy component to I_5^- and the lower binding-energy one to I_3^-. The relative intensities of these two components varied from sample to sample even if their total iodine contents were almost the same. This is also consistent with the results of Raman spectroscopy.[6] We determined the ratio of iodine atoms which exist as I_5^- and those which exist as I_3^- by the analysis of the profiles of I 3d peaks. The atomic ratio of iodine to carbon was also determined from the intensity ratio of I $3d_{5/2}$ and C 1s peaks. The change of the iodine content with time for which the sample was kept in the XPS spectrometer, is shown in Fig.2 for the case of a heavily iodine-doped

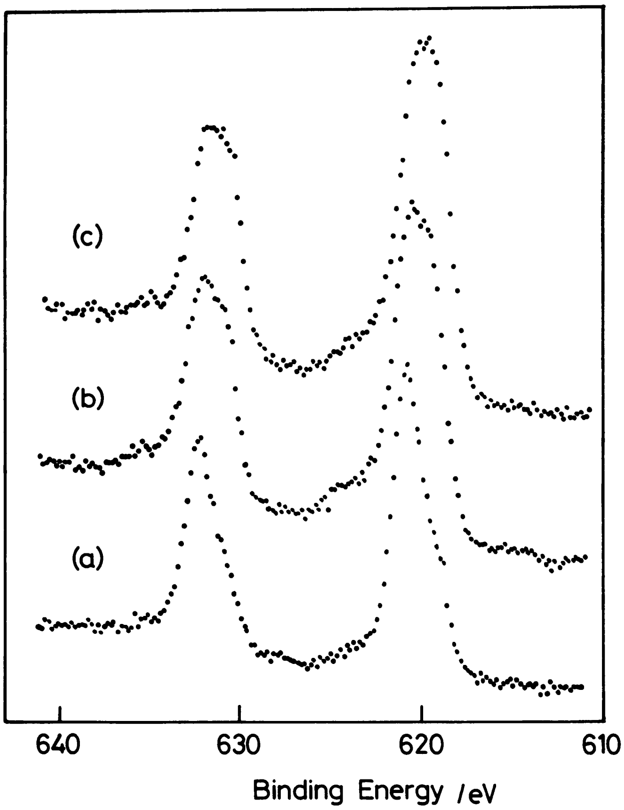

Fig.1 I 3d peaks in the initial XPS spectra of (a) *trans*-$(CHI_{0.226})_n$, (b) *trans*-$(CHI_{0.2060})_n$ and (c) *cis*-$(CHI_{0.2206})_n$

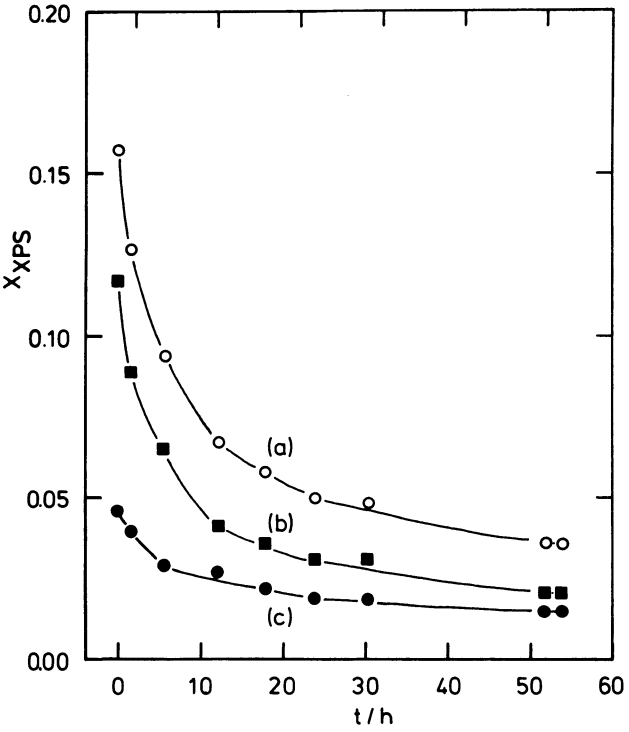

Fig.2 Decrease of iodine/carbon atomic ratio with time measured by XPS on *trans*-$(CHI_{0.226})_n$.
(a) overall iodine, (b) iodine in the form of I_5^- and (c) iodine in the form of I_3^-

Table 1. XPS and Raman results of iodine-doped polyacetylene films

Sample	x^{*1}	x_{XPS}^{*2}	I_5^-/I_3^- mole ratio			C 1s	
			XPS*3	Raman(6471Å)*4 (a)	(b)	Binding Energy/eV	fwhm/eV
cis-$(CHI_x)_n$	0.2206	0.15_5	0.28	0.09	0.16	283.7	2.2
	0.1014	0.08_3	0.34	0.09	0.21	283.7	1.9
	0.0456	0.06_0	0.37	0.06	0.13	283.8	1.8
	0.0297	0.05_7	0.36	0.09	0.12	283.8	1.7
	0.0178	0.02_3	0.53	-	-	283.8	1.6
	0.0098	0.02_3	0.50	-	-	283.8	1.6
trans-$(CHI_x)_n$	0.2060	0.14_3	0.68				2.1
	0.0385	0.05_6	0.72				1.8
	0.0175	0.02_9	0.61				1.6

*1 x is the I/C atomic ratio determined from the weight change in doping process.

*2 The iodine/carbon atomic ratio determined from the relative intensities of the I $3d_{5/2}$ and C 1s peaks with reference to the intensity data of the XPS spectrum of iodanil. Maximum error is estimated to be about 10 %.

*3 The mole ratio of I_5^- and I_3^- have been determined by the peak shape analysis of the I $3d_{5/2}$ peak using the corresponding peak of $(PhCONH_2)_2H^+I_3^-$ as reference.

*4 a) after XPS measurement and b) before XPS measurement.

trans-rich polyacetylene film $(CHI_{0.226})_n$.[7] The total iodine content decreased very rapidly and leveled off after the first several hours. The amount of I_5^- decreased more rapidly than that of I_3^-. This behavior is consistent with the Raman results.[6] We noted that, even in the initial XPS measurement, the I/C atomic ratio determined from the observed spectrum was significantly smaller than the value determined from the weight change in the process of iodine doping. This could mean that a considerable amount of iodine had been already liberated from the film, at least, from the surface region. On the other hand, when the amount of the initially doped iodine is samll, the iodine decreasing rate was quite small, and, at the same time, the I/C ratio determined from the XPS spectrum was found to be larger than the value determined by the weight change in the doping process.

Keeping in mind the phenomena mentioned above, we compared the XPS spectra of various iodine-doped films. In each case we took up the spectrum obtained immediately after the sample was put into the spectrometer. The binding energy and width (full-width at a half-maximum height, fwhm) of C 1s peak and the I/C atomic ratio determined from the spectrum of each film are given in Table 1. In this table we express an iodine-doped *cis*-rich polyacetylene film as *cis*-$(CHI_x)_n$.[7] As shown there, the C 1s binding energy does not appreciably vary with the iodine content, although there seems to be a tendency to decrease slightly with an increase of the latter. The width of C 1s peak increases rapidly from 1.6 eV to 1.8 eV in the early stage of doping ($x<0.05$). On further increasing the iodine content, the increment of the width becomes gradual (up to 2.2 eV). In the case of $x<0.05$, the atomic ratio by XPS, x_{XPS}, is larger than x, but the former becomes appreciably smaller than the latter when $x>0.05$.

The results described above seem to indicate that, at a lower iodine content ($x<0.05$), iodine is more concentrated in the surface region than in the bulk of a polyacetylene film, and is in a rather strongly bound state, but, in a heavily doped film, it is probable that iodine is distributed more homogeneously throughout the film and that a considerable amount of iodine in the surface region is in a loosely bound state so as to be easily liberated.

It has been reported that the electrical conductivity of a polyacetylene film increases steeply on increasing the amount of the doped iodine in the region of $x<0.05$, and its increase levels off in the region of $x>0.05$.[3] This seems to be in close correlation with the states of the doped iodine revealed by the present XPS studies.

We estimated the mole ratio of I_5^- and I_3^- from the analysis of I 3d peak profile. The results are given in Table 1. The mole ratio can be obtained also from the intensities of the Raman spectrum lines characteristic of I_5^- and I_3^-, respectively, In table 1, we give the values determined from the Raman spectra before and after the XPS measurements. For each sample, there is a significant discrepancey between the value by XPS and that by Raman spectrum. It should be noted that the mole ratio from Raman spectrum gives the composition in the bulk whereas the one by XPS mainly reflects the composition in the surface region. Thus the data given in Table 1 indicate that the mole ratio of I_5^-/I_3^- is appreciably higher in the surface region than in the bulk.

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7) Although *cis-trans* isomerization may proceed to some extent on iodine doping, especially in the case of a heavy doping, we will use the expression, *trans*-rich and *cis*-rich, according to the configuration of the film before the doping.

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