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X-Ray Photoelectron Spectroscopic Study of Highly Conductive Bromine-doped Polyacetylene

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The bromine-doped polyacetylenes were studied by X-ray photoelectron spectroscopy. The IR, Raman, and mass spectra were also measured. We find that below the doping content at which the electrical conductivity shows the maximum, bromine content is higher in the surface region than in the bulk. The C 1s peak of X-ray photoelectron spectrum is composed of at least two components with the splitting of about 1.7 eV. The relative intensities of two components change with bromine content. The higher-binding-energy component of C 1s peak is attributed to positively charged carbon atoms in the metallic domains where dopant is highly concentrated, and the lower-binding-energy component to carbon atoms in the undoped low-conductive domains. The amount of charge transfer in the metallic domain is estimated to be about $0.3|e|$ per carbon atom. A possible reaction mechanism of bromine with polyacetylene is discussed.

Recently polyacetylene, $(CH)_x$, has attracted great interests because it exhibits metallic conductivity when treated with various dopants.[1–4] Its electrical conductivity at room temperature varies over twelve orders of magnitude by doping with suitable electron acceptors such as halogens and AsF_5. Although the properties of these doped polyacetylenes have been investigated by many groups, more information concerning their structures and electronic states is needed in order to understand the electrical behaviors of these systems. It is important to determine the chemical state of dopant in the polymer and the nature of interaction between dopants and polymer chains. Previously we reported the results of X-ray photoelectron spectroscopic (XPS) studies of the iodine-doped polyacetylene.[5] The bromine-doped polyacetylene shows an electrical behavior similar to that of the iodine-doped polyacetylene when doping content is low. However, much heavier doping is possible in the case of bromine as compared with iodine.[3] Here we report the results of XPS studies on the bromine-doped polyacetylene.

Experimental

A polyacetylene film was prepared by the method described previously.[6] All samples used in the present experiment were obtained from the same batch of polyacetylene. Polymerization was performed at −78 °C to give *cis*-polyacetylene. A *trans*-polyacetylene film was obtained by heating a *cis*-polyacetylene film at 200 °C for 1 h. Film thickness was approximately 0.1 mm.

Bromine treatment was carried out at room temperature by direct contact of a polyacetylene film with Br_2 vapor. The extent of doping was controlled by measuring the electrical conductivity of a reference film contained in the same vessel by means of the standard four-probe method. The bromine content of a doped sample was determined by elemental analysis.

Prior to XPS studies, a sample film was cut off to several parts to measure Raman, IR, and mass spectra.

X-Ray photoelectron spectra were taken with a McPherson ESCA 36 electron spectrometer employing Mg $K\alpha$ (1253.6 eV) radiation. Special care was taken to prevent samples from exposing to the air prior to XPS measurements. After XPS measurements, sample films were used for elemental analysis and for measurements of Raman and IR spectra. The binding energies of observed photoelectron peaks were calibrated by use of Au $4f_{7/2}$ peak (83.8 eV) of a very thin gold film deposited onto the sample surface.

Raman spectra were taken with a Spex 1401 double monochromator equipped with a Spectra Physics 166-01 Kr ion laser, a JEOL JLG-4A Ar ion laser, and an NEC He-Cd laser. The laser lines between 647.1 nm and 325.0 nm were used to obtain Raman spectrum. The IR spectra were measured by ATR method by use of a HITACHI EPI-G3 double beam grating IR spectrometer.

Mass spectra were obtained on a JMS-D300 mass spectrometer (JEOL) using a direct insertion probe. Polyacetylene samples were directly inserted into the ion source and the mass spectra were measured at room temperature.

Results

The electrical conductivity of bromine-doped *trans*-polyacetylene, $(CHBr_n)_x$ is shown in Fig. 1 as a function of the bromine content, n, which was determined by elemental analysis. The general feature of conductivity change is almost same as those previously reported by other authors,[3] except for small differences as regards the bromine content and the conductivity value at the maximum. It should be noted that a bromine-doped polyacetylene film exhibits conductivity as high as $10^{-2}\,\Omega^{-1}\,cm^{-1}$ even at a high doping level of $n=0.63$. The conductivity abruptly decreased when bromine content was further increased. The variation of conductivity with bromine content was found to be almost same in the case of *cis*-polyacetylene, but the conductivity at the maximum point was a little higher as compared with *trans*-polyacetylene.

As shown in Fig. 2, the Br 3d peak in the XPS spectrum of a bromine-doped polyacetylene film decreased its intensity as we repeated XPS measurements on the same sample, indicating that doped bromine was

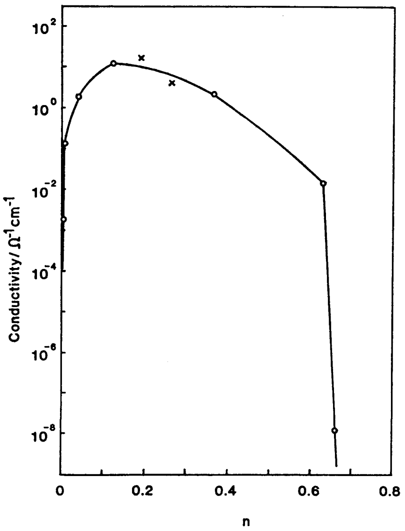

Fig. 1. The electrical conductivity of bromine-doped polyacetylene, $(CHBr_n)_x$, as a function of n determined by elemental analysis.
(○): Trans, (×): cis.

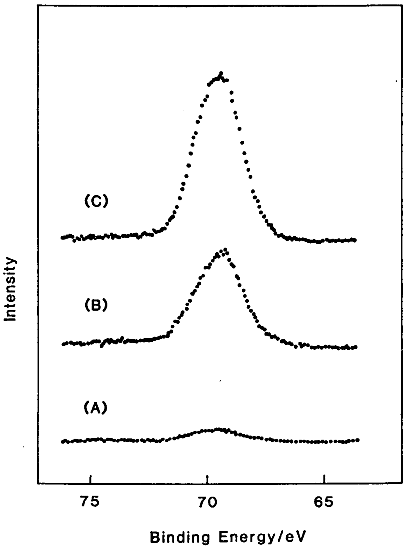

Fig. 3. The Br 3d peaks of *trans*-$(CHBr_n)_x$ obtained by the initial measurement.
(A): n=0.008, (B): n=0.127, (C): n=0.661.

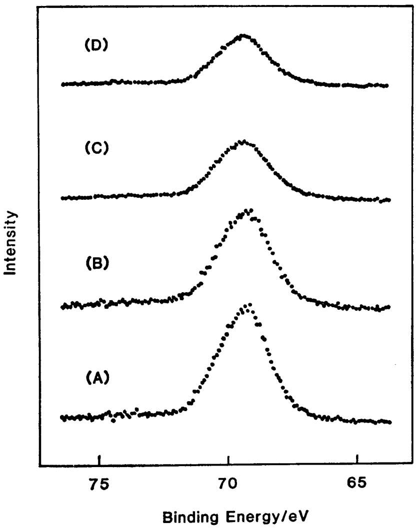

Fig. 2. The time dependent Br 3d spectra of *trans*-$(CHBr_{0.127})_x$.
(A): 5 h, (B): 7 h, (C): 10 h, and (D): 20 h in a vacuum of the spectrometer.

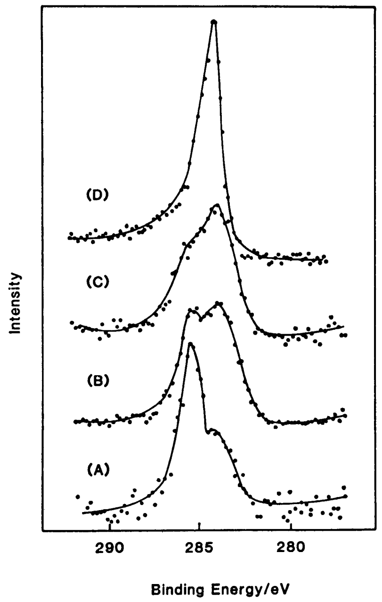

Fig. 4. The C 1s peaks of *trans*-$(CHBr_n)_x$ obtained by the initial measurement.
(A): n=0.696, (B): n=0.368, (C): n=0.127, (D): n=0.008.

gradually lost from the film during XPS measurements. We observed a similar phenomenon in the case of iodine-doped polyacetylene.[5] But there is a slight difference between two cases. In the case of bromine-doped polyacetylene, Br 3d peak does not appreciably change its shape accompanying the decrease of its intensity whereas I 3d peak of iodine-doped polyacetylene was found to change its shape.[5]

Figure 3 shows the Br 3d peaks of several films of different bromine content. The spectra shown here are those obtained by the initial measurement on each sample. The binding energy of Br 3d peak did not vary with bromine content. The peak width (FWHM) was about 2.3 eV in the cases of bromine-doped polyacetylene films of $n>0.04$, it being a little larger at lower bromine content. In the cases of bromine-doped *cis*-polyacetylene films, the Br 3d peak width was about 2.6 eV.

In contrast to Br 3d peak, the shape of C 1s peak of bromine-doped polyacetylene markedly varies with bromine content as shown in Fig. 4. The observed peak shape suggests that the peak is composed of two components separated by 1.7—2.0 eV, and the intensity of the higher-binding-energy component increases while that of the lower-binding-energy component decreases on increasing bromine content. Figure 5 shows the change of the C 1s peak shape of a doped film upon the reduction of bromine content caused by keeping the film in a vacuum. Note that the peak shape varies with bromine content, but the total intensity remains nearly constant.

We estimated the atomic ratio of bromine to carbon, n_{XPS}, from the ratio of the integrated intensities of Br3d and C1s peaks, with the reference to the relative intensities of the corresponding peaks in the XPS spectrum of tetrabromobenzene. The results are given in Table 1, where the value in the column expressed as "initial" is the Br/C atomic ratio which was determined from the data of the first XPS measurement of the sample concerned, and the value in the column expressed as "final" is the one which was determined from the data of the last measurement of the same sample usually after repetition of XPS measurements for 15—20 h. The XPS atomic ratio n_{XPS} is larger than the atomic ratio n from elemental analysis in the cases of $n \leq 0.127$, but they almost agree with each other in the cases of $n > 0.127$. This shows that doped bromine is more concentrated in the surface region than in the bulk at lower bromine content, but is distributed more homogeneously in heavily doped films.

Figure 6 shows the change of n_{XPS} with the time for which the sample has been kept in a vacuum. The

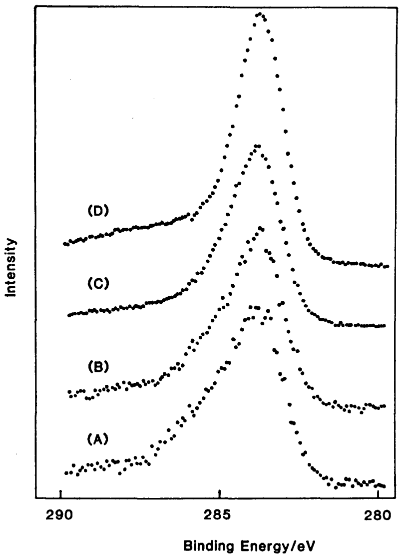

Fig. 5. The change of the C 1s peak shape of *trans*-$(CHBr_{0.042})_x$ upon the reduction of bromine content caused by keeping the sample in a vacuum.
(A): 2 h, (B): 5 h, (C): 11 h, (D): the C 1s peak shape of *trans*-$(CH)_x$.

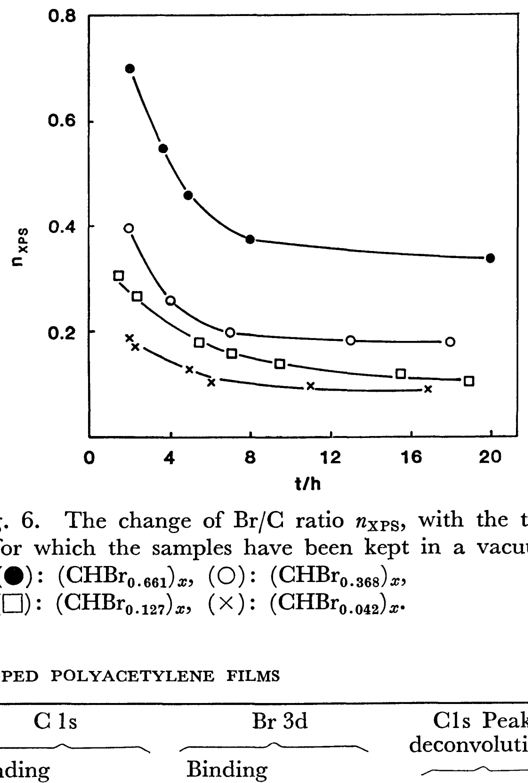

Fig. 6. The change of Br/C ratio n_{XPS}, with the time for which the samples have been kept in a vacuum.
(●): $(CHBr_{0.661})_x$, (○): $(CHBr_{0.368})_x$,
(□): $(CHBr_{0.127})_x$, (×): $(CHBr_{0.042})_x$.

TABLE 1. XPS RESULTS OF BROMINE-DOPED POLYACETYLENE FILMS

Sample	Electrical conductivity	Br/C Atomic ratio				C 1s		Br 3d		C1s Peak deconvolution	
	σ	n[a]		n_{XPS}[b]		Binding energy	FWHM	Binding energy	FWHM	C_1/C[c]	ΔE[d]
	Ω^{-1} cm^{-1}	Initial	Final	Initial	Final	eV	eV	eV	eV		eV
trans-$(CHBr_n)_x$	$<10^{-8}$	0.697	0.665	0.76	0.20	285.5 283.8		69.3	2.3	0.74	1.7
	1.2×10^{-8}	0.661	0.647	0.70	0.34				2.3	0.75	1.6
	1.8×10^{-2}	0.633	0.576	0.63	0.19				2.2	0.69	1.7
	3.5×10^{0}	0.368	0.262	0.39	0.18				2.2	0.43	1.7
	1.3×10^{1}	0.127	0.112	0.31	0.12				2.2	0.33	1.8
	3.0×10^{0}	0.042	0.035	0.19	0.09	285.1 283.6		69.3	2.2	0.28	1.5
	1.5×10^{-1}	0.008	0.002	0.03	0.02				2.6		
	2.9×10^{-3}	0.000_4	0.000_3	0.00_9	0.00_2				2.6		
cis-$(CHBr_n)_x$	2.0×10^{1}	0.194	0.188	0.27	0.14	285.7 283.7		69.5	2.6	0.39	2.0
	5.6×10^{0}	0.264	0.246	0.39	0.16	285.6 283.8		69.3	2.6	0.53	1.8
trans-$(CH)_x$						283.8	1.8				

a) Br/C atomic ratio determined by elemental analysis (initial; the value before XPS measurement, final; the value after XPS measurement). b) Br/C atomic ratio determined by XPS measurements at initial and final measurements. c) Relative area ratio of the higher-binding-energy component of C 1s peak to total C 1s peak. d) Splitting of two components of the spectra.

n_{XPS} value rapidly decreases first, but its decrease is leveled off after about 8 h.

Since the C1s peak of a bromine-doped film seems to be composed of two components, we decomposed the observed peak into two component peaks using the C1s peak shape of an undoped polyacetylene film as the standard. The procedures used here are almost the same as those described in our previous paper.7) Let us denote the carbon atom which is responsible for the higher-binding-energy C1s component, as C_1. We estimated the ratio of C_1 atoms to the total carbon atoms. The C_1/C atomic ratio thus obtained is always close to the Br/C atomic ratio n_{XPS}. Thus we can consider that the atomic ratio of C_1 to Br is always about 1:1.

The Raman spectra of undoped and lightly doped ($n<0.05$) polyacetylene films were previously investigated by several groups.8–10) It was reported that, according to the observed Raman spectra, doped bromine must be exclusively in the form of Br_3^-. We obtained the same conclusion for lightly doped films. The Raman spectra of heavily doped films were found to be similar to those of lightly doped films showing that doped bromine is primarily in the form of Br_3^- ion, but the possibility of the presence of other bromine species could not be excluded from the observed data. In fact, the band attributable to C–Br stretching vibration was found in the IR spectra of heavily doped films. After XPS measurements, the Raman lines at 158 and 316 cm^{-1}, which are due to the symmetric stretching mode of Br_3^- and its overtone, respectively, appreciably reduced their intensities, indicating the decrease of Br_3^- during the XPS measurements. As we have already mentioned, bromine content decreases when a doped film is kept in a vacuum. It was confirmed by mass spectroscopy that the chemical species which come out from a doped film are mostly HBr in the case of a lightly doped film, and HBr and Br_2 in the case of a heavily doped film. Therefore, we have to consider that the decrease of Br_3^- is accompanied by the formation of C–Br bond. However, it was hard to confirm whether the intensity of C–Br stretching band in IR spectrum increased after XPS measurement or not.

Discussion

According to the conductivity change with bromine content, we can classify the bromine doping of polyacetylene into the following three stages: The stage A ($n\leq 0.127$) where conductivity steeply increases with increasing bromine content, the stage B ($0.127<n\leq 0.63$) where conductivity gradually decreases and the stage C ($n>0.63$) where an abrupt decrease of conductivity takes place on further increase of bromine content.

In the case of films of the stage A, the atomic ratio of hydrogen to carbon was found to be 1:1 by elemental analysis. From this fact we can conclude that doped bromine exists primarily as Br_3^- without forming C–Br bond by the substitution of hydrogen of polyacetylene chain with bromine. However, HBr is evolved as a doped film is kept in a vacuum. Possibly this is because Br_3^- can be lost from a film only by performing a reaction with polymer chain to form C–Br bonds with an evolution of HBr.

In the XPS spectrum of a lightly doped film, the C1s peak is asymmetric with a shoulder in the higher-binding-energy side of the main peak. This shoulder is likely to be due to the higher-binding-energy component which clearly appears as a peak in the spectrum of a heavily doped film. One possible interpretation for this higher-binding-energy component could be to attribute it to the carbon atom forming C–Br bond. But this is rather unlikely to be the case since its intensity decreases in parallel to the decrease of bromine content when the film is kept in a vacuum. It should be also noted that the energy separation 1.7 eV from the main peak is too large in comparison with the chemical shift of C1s between C–Br and C–H carbons: the shift is expected to be about 1 eV or less. Thus we consider that the higher-binding-energy C1s component is associated with positively charged carbon atoms which are closely interacting with Br_3^- ions.

Recently Fincher *et al.*11) proposed, from the investigations of the optical absorption spectra and Raman spectra of doped polyacetylene films, that, in a lightly doped polyacetylene film, the dopant is not uniformly distributed, but forms domains of high dopant concentration, where polyacetylene chain becomes metallic having a uniform C–C bond length, and the remaining regions are in the undoped low-conductive state. This inhomogeneous domain model seems to be consistent with our XPS data. We will attribute the higher-binding-energy C1s component to the carbon atoms in the metallic domain and the other component to the carbon atoms in the low-conductive domain. In the metallic domain, carbon atoms must be positively charged as a result of charge transfer to bromine to form Br_3^-. The positive charge per carbon atom (C_1) of the metallic domain can be estimated from the observed splitting of the two components of C1s peak. Since C1s level is known to be shifted by about 5.6 eV per unit charge,12) the splitting observed for the doped film of $n=0.127$ corresponds to about $+0.3|e|$. The C_1/Br atomic ratio determined from XPS data provides another independent way to estimate the positive charge per carbon atom since one electron per three bromine atoms should be transferred from polyacetylene chains in the metallic domain, in other words, from C_1 atoms. As shown in Table 2, the values obtained by this way are also about $+0.3|e|$ in agreement with the values from the chemical shift.

It was reported by Salaneck *et al.* that a shoulder appeared on the higher-binding-energy side of C1s peak of polyacetylene upon doping with $AsF_5$13) or with iodine.14) They attributed this shoulder to the plasmon loss associated with charge carriers along polyacetylene chain. However we believe that the shoulder observed in these cases is of the origin similar to the higher-binding-energy C1s component of bromine doped polyacetylene.

Doped bromine must exist mainly in the form of Br_3^- also in the stages B and C, but the substitution

Table 2. Comparison of the charge per C atom estimated from the intensity ratio of higher-binding energy C1s component (C_1) and Br 3d peak and from the splitting of C1s peak of lightly doped polyacetylene

	Estimated from C_1/Br_3 atomic ratio		Estimated from C1s splitting	
	C_1/Br_3^-	Charge per C atom	ΔE/eV	Charge per C atom
trans-$(CHBr_{0.127})_x$	3.2	0.31	1.7	0.30
trans-$(CHBr_{0.042})_x$	4.5	0.22	1.5	0.26
cis-$(CHBr_{0.194})_x$	4.4	0.23	2.0	0.36

or addition reaction of bromine with polyacetylene chain is likely to take place more in these stages. In fact, H/C atomic ratio was found to be 0.95 by elemental analysis in the case of a heavily doped polyacetylene film.

When a film of the stage B is kept in a vacuum, Br3d peak and the higher-binding-energy C1s component decrease their intensities, by evolving HBr from the film. This HBr evolution was markedly enhanced as the film was heated to 150 °C.[15] Probably HBr is formed by the reaction of Br_3^- with polyacetylene chain as in the case of a film of the stage A.

In the stage C, all experimental evidences do suggest that the addition reaction of bromine to C=C double bond significantly takes place in the doping process. The abrupt drop of conductivity in the stage C is likely to be due to the breakdown of π-electron conjugated system of a polyacetylene chain. Thus there must be a considerable amount of carbon atoms having C–Br bond. However even in this case, the higher-binding-energy C1s component which is stronger than the lower-binding-energy one, can not be attributed to the carbon atoms with C–Br bond since its intensity rapidly decreases just by keeping the film in a vacuum at room temperature, by evolving Br_2 and HBr. Seemingly the higher-binding-energy C1s component which appears in the XPS spectra of films of the stage C, is again due to the carbon atoms positively charged by the electron transfer to bromine and in close interaction with Br_3^- ions thus formed, as we have postulated for the stages A and B. Probably the C1s peak due to the carbon atoms with C–Br bond and the one due to the carbon atoms in the undoped regions emerge into the lower-binding-energy C1s component because their energy difference is small, possibly less than 0.5 eV.

Summary and Conclusion

Summarizing all the experimental results obtained in the present study, we postulate the following picture for the bromine doping of polyacetylene. In the first doping stage ($n \leq 0.127$), the doping proceeds inhomogeneously by forming domains in which doped bromine, in the form of Br_3^-, is highly concentrated and polyacetylene chains are in metallic state as the result of charge transfer to bromine by the amount of about 0.3 electron per carbon atom. The conductivity steeply increases on increasing average bromine content because of the increase of the volume fraction of metallic domain.

In the second stage ($0.127 < n \leq 0.63$), the substitution reaction takes place beside the above mentioned doping mechanism, so that the rate of the conductivity-increase with bromine content is leveled down. In the third stage ($n > 0.63$), the addition reaction of bromine to C=C double bond of polyacetylene chain significantly takes place, which results in a marked reduction of the length of π-conjugated system, thus causes an abrupt decrease of conductivity.

The computer used was HITAC-M200H at the Computer Center, the University of Tokyo.

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