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## POLARIZED EXAFS AND NEAR-EDGE SPECTRA OF HALOGEN-DOPED POLYACETYLENE

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## ABSTRACT

Polarized EXAFS and near-edge spectra were measured for  $(\text{CHBr}_y)_x$  and  $(\text{CHI}_y)_x$  on the Br K- and I L-edges over a wide range of dopant concentration. The analysis of EXAFS and near-edge spectra indicates that, in the lightly doped region ( $0.01 < y < 0.2$ ), polybromine ions highly oriented along the c-axis are formed while bromines also form covalent bonds with polyacetylene chain which increases in number on going to heavily doped region ( $y > 0.2$ ). Bromines are incorporated as isolated ions in the early stage of doping ( $y < 0.01$ ). In  $(\text{CHI}_y)_x$ , iodines form linear polyions which are chemically less reactive. The difference in the magnitude and dopant concentration dependence of electrical conductivity between bromine and iodine doping is ascribed to the degree of termination of conjugated chains by an addition reaction of halogens.

## INTRODUCTION

Polyacetylene,  $(\text{CH})_x$  is the simplest conjugated system which has been extensively studied because of its unique properties as a conducting polymer. The electrical conductivity of pristine  $(\text{CH})_x$  increases by many orders of magnitude upon doping with electron acceptors such as bromine or iodine [1]. Previous polarized EXAFS [2,3] and near-edge [2] spectra of bromine-doped trans-polyacetylene,  $t\text{-(CHBr}_y)_x$  have been interpreted as an evidence for polybromine ions highly oriented along the c-axis. Two structure models have been proposed based on the different interpretations of a short Br-C distance observed in the Fourier transform of EXAFS oscillations. Oyanagi et al. attributed this distance to the Br-C bonds originating from bromines which are covalently bonded with polyacetylene by a substitution or addition reaction [2] whereas Krone et al. interpreted this peak as the distance between the polybromine ions and polyacetylene chains [3] assuming that bromines exist only as polybromine ions. In this paper, the two structure models are examined on the basis of the dopant-concentration dependence of polarized EXAFS and near-edge spectra.

## EXPERIMENTAL

Trans-rich  $(\text{CH})_x$  films were prepared as previously described by Shirakawa et al. [4] and stretch-oriented by uniaxial drawing. Halogen doping was carried out by exposing trans- $(\text{CH})_x$  films to bromine or iodine vapor at room temperature. Halogen content was determined by a weight uptake immediately

after the doping. Polarized X-ray absorption experiments were performed with the EXAFS spectrometer at the Photon Factory [5]. Polarized Br K-EXAFS and near-edge spectra were measured for  $(\text{CHBr}_y)_x$  samples with  $y$  between 0.007 and 0.6 whereas I L-edge data were collected for  $(\text{CHI}_y)_x$  with  $y$  between 0.02 and 0.2. For the measurement of Br K-edge absorption spectra, a silicon (311) channel-cut monochromator was used while for I L-edge data, a silicon (111) double crystal monochromator was detuned by 90 % to remove the higher harmonics.

## RESULTS AND DISCUSSION

As previously reported [2], anisotropic Br K-EXAFS oscillations of  $(\text{CHBr}_y)_x$  with respect to the polarization direction shown in Fig. 1 indicate that polybromine ions are highly oriented along the c-axis. The results of Fourier transform of Br K-EXAFS oscillations times  $k^3$  for  $(\text{CHBr}_y)_x$  with  $y=0.02$ , 0.08, and 0.179 are shown in Fig. 2 with  $E$  parallel to the c-axis.

The most prominent peak observed at 2.2 Å is due to the first nearest Br-Br distance and the less intense peak located at 4.8 Å is due to the second nearest Br-Br distance. They are 2.55 Å and 5.12 Å, respectively, if the phase shift is corrected. Since these peaks appear only in the direction of c-axis and the second nearest peak should be observed when bromines form linear polyions with larger number of atoms than three, the results shown in Fig. 2 demonstrate that polybromine ions are highly oriented along the c-axis in  $\text{trans-(CHBr}_y)_x$  over a wide range of bromine concentration.

Although the overall features are similar for three samples, the magnitude of Br-Br peak decreases with increasing dopant concentration whereas the intensity of a short Br-C distance observed at 1.1 Å increases. This short Br-C distance is attributed to bromines covalently bonded to polyacetylene chain by either substitution or addition reaction [2,6].

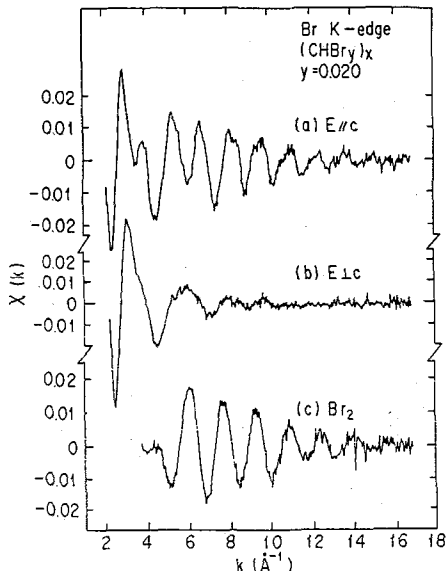


Fig. 1 Polarized Br K-EXAFS oscillations of  $(\text{CHBr}_y)_x$  with  $y=0.02$ .

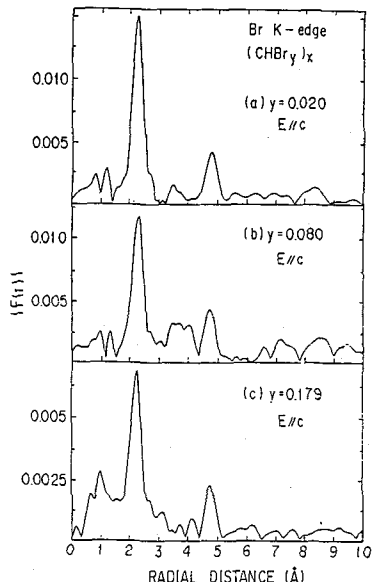


Fig. 2 Fourier transform of Br K-EXAFS for  $(\text{CHBr}_y)_x$  with parallel orientation.

The Fourier transform in Fig. 2 emphasizes Br-Br correlation suppressing Br-C contribution since the backscattering amplitude of Br extends to a large  $k$ -region whereas that of C damps rapidly with  $k$ . The contribution of Br-Br bond

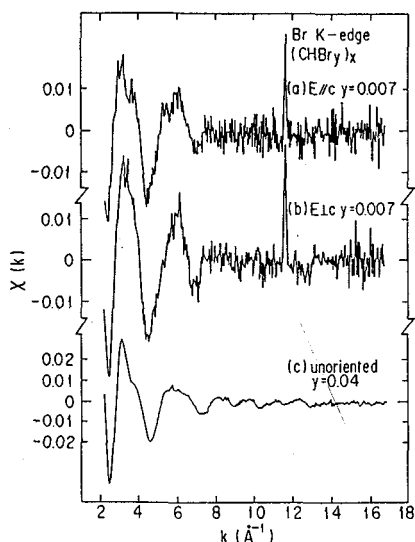


Fig. 3 Polarized Br K-EXAFS oscillations of  $(\text{CHBr}_y)_x$  with  $y=0.007$ .

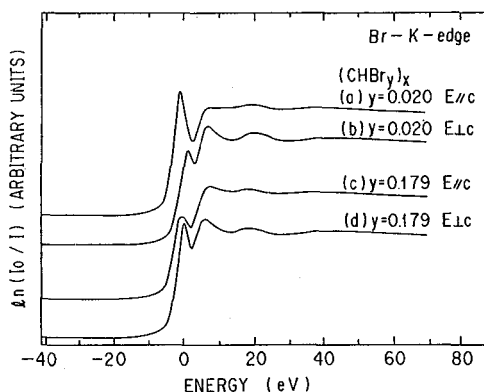


Fig. 4 Polarized Br K-XANES spectra of  $(\text{CHBr}_y)_x$ .

is estimated to be less than 30% for  $(\text{CHBr}_y)_x$  with  $y=0.02$  from the coordination number of bromine determined for the Br K-EXAFS with E parallel to the c-axis [2]. The ratio of bromines in the form of polybromine ion further decreases in the more heavily doped region. In Fig. 2, a short Br-C distance observed for  $(\text{CHBr}_y)_x$  with  $y=0.179$  is 1.92 Å after the phase shift correction, which is quite close to the Br-C covalent bondlength.

If there is only polybromine ions intercalated between polyacetylene chains as proposed by Krone et al. [3], the local structure of bromines is expected to be independent on the dopant concentration. Oyanagi et al. have attributed longer Br-C distance (3.4-3.8 Å) to the correlation between polybromine ion and the polyacetylene chain, which is roughly the sum of van der Waals radii of bromine and carbon [2].

Figure. 3 shows the EXAFS oscillations for lightly doped  $(\text{CHBr}_y)_x$ . On going to the lightly doped region, the Br-Br peak intensity decreases its intensity and for  $(\text{CHBr}_y)_x$  with  $y<0.01$ , only Br-C peak is observed, indicating that the ratio of Br-Br bond to the Br-C bond is small in this region. These results imply that bromines are doped as isolated ions in the early stage of doping.

Summarizing the EXAFS results for  $(\text{CHBr}_y)_x$ , bromines are doped as ions in the lightly doped region with  $y<0.01$  (Region I), which forms polybromine ions with further doping in the more heavily doped region for  $0.01<y<0.2$  (Region II). Throughout these two regions, a part of bromines are substituted with hydrogens whereas in the most heavily doped region for  $y>0.2$  (Region III), most of bromines form Br-C bonds by an addition reaction [2,6,7].

In Fig. 4, the near-edge spectra of  $(\text{CHBr}_y)_x$  are shown with E parallel and perpendicular to the c-axis. A sharp peak observed 9-10 eV below the threshold in all spectra is due to the transition from Br 1s state to the unfilled 4p bound states. In Region II, this peak decreases its intensity and broadens for  $(\text{CHBr}_y)_x$  with E parallel to the c axis as shown in Fig. 4 (c). These result indicate that there is two species of bromine, i.e. Br-Br bond and Br-C bond. The broadening of this peak results from the increased higher energy component which is clearly observed with E perpendicular to the c-axis as shown in Fig. 4 (b). The increased intensity of higher energy peak in Fig. 4 (d) for  $(\text{CHBr}_y)_x$  with E perpendicular to the c-axis indicates that the ratio of Br-C bond increases on going to heavily doped region, which is consistent with the EXAFS results and two-species model [2].

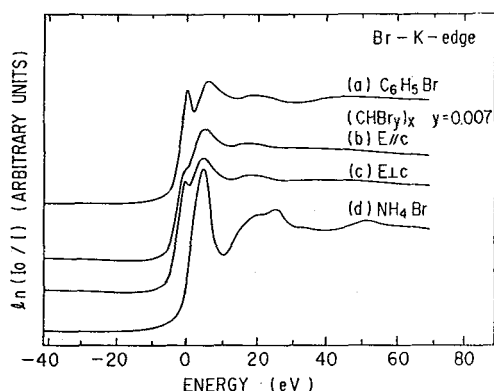


Fig. 5 Polarized Br K-XANES spectra of  $(\text{CHBr}_y)_x$ .

The near-edge spectra of  $(\text{CHBr}_y)_x$  in Region I is characterized by a small anisotropy with respect to polarization as indicated in Fig. 5. The near-edge structures within 40 eV above the threshold observed in  $(\text{CHBr}_y)_x$  are similar to those of bromobenzene, which suggests that most of bromines form Br-C bonds in Region I. In this region, the dip between the sharp spike and the threshold diminishes as indicated in Fig. 5 (b) and (c). These results are consistent with the assumption that bromines are incorporated as isolated ions in the early stage of doping since the threshold of the sharp resonance peak observed for bromine ions is located between the 4p peak and continuum threshold of  $(\text{CHBr}_y)_x$  as indicated in Fig. 6 (d).

The Fourier transform of polarized I L-EXAFS shows that iodines are separated with each other by 2.88 Å, which is the intermediate value between  $\text{I}_2^-$  (2.76 Å) and  $\text{I}_3^-$  (2.92 Å). The radial distribution around iodine is characterized by a long I-C distance (4.06-4.68 Å) which might be the distance between the polyiodine ion and polyacetylene. Since the contribution of I-C bond is estimated to be very small, most of iodines form linear polyions which are oriented along the c-axis with a less degree of orientation than that of  $(\text{CHBr}_y)_x$ , partly due to the incommensurate geometry of polyiodine ions with respect to polymer backbone. The Fourier transform results for  $(\text{CHI}_y)_x$  are not sensitive to the dopant concentration, indicating that most of iodines are intercalated with a linear chain structure.

These results are consistent with the fact that electrical conductivity of  $(\text{CHI}_y)_x$  is always greater than that of  $(\text{CHBr}_y)_x$  in magnitude for the same amount of dopant and gradually increases with further doping in the heavily doped region.

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