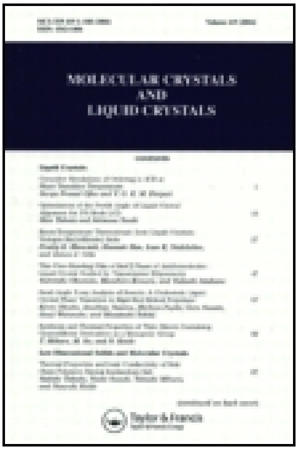

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Local Structure of Bromine and Iodine in Polyacetylene Studied by X-Ray Absorption Spectroscopy and Esr

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LOCAL STRUCTURE OF BROMINE AND IODINE IN POLYACETYLENE STUDIED BY X-RAY ABSORPTION SPECTROSCOPY AND ESR

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Abstract We report on a comparative study of the local structure of bromine and iodine in polyacetylene by X-ray absorption and ESR experiments. The results reveal a strong concentration dependence of the state of bromine in contrast to iodine. Polarization dependent X-ray absorption provides evidences for anisotropic configuration of dopants in stretch oriented samples.

INTRODUCTION

The motivation to study bromine doped $(CH)_x$ is in its unique concentration dependence of conductivity,[1-3] compared to the case of iodine. It has been proposed that the bromine doping in $(CH)_x$ proceeds in three successive stages.[3] That is, first, for low concentration, charge transfer doping is dominant, which is supposed to form Br_3^- ions and to increase the conductivity. For the second concentration range, substitution of bromine for hydrogen takes place, which causes a gradual reduction of conductivity. In the third stage, addition reaction of bromine to C=C double bond takes place, which reduces conjugation length and the conductivity finally drops to an insulating regime.

In order to obtain microscopic evidence for these processes, we first prepared three representative samples corresponding to each stage and studied them by standard EXAFS technique.[4] The analysis of the EXAFS data on the Br K edge showed that Br-C bond dominantly exists in Br-doped polyacetylene, nearly independent of Br concentration over its range from 5% to 60%, a result completely unexpected from the three stage model. This result indicates that substitution and/or addition reactions are taking place even at a concentration as low as 5%. However,the question remained whether substituted or added Br atoms are responsible to the observed Br-C bond.

In this paper, we first present the result of ESR measurement on the three samples and show the effect of substituted and added Br atoms separately. The rest of the paper is devoted to the result of polarized X-ray absorption spectroscopy on stretch oriented samples, which provides further information about the local structure and anisotropic bond formation of bromine and iodine in $(CH)_x$.

EXPERIMENTAL RESULTS AND DISCUSSION

ESR

Electron spin in polyacetylene is known to be in the form of a "neutral soliton",[5] which is distributed to about 15 CH units around a bond alternation kink in trans structure. Since it moves freely at room temperature, it gives us a narrow ESR signal. Now, what do we expect when bromine doping proceeds? First of all, charge transfer decreases the number of neutral solitons. Secondly, if substitution occurs we should expect a g-shift.[6] And thirdly if addition takes place, we can expect an increase in the linewidth at room-temperature as well as a decrease in its temperature dependence, caused primarily by the suppression of solition motion by short segmentation of the conjugation length. In $(CHI_y)_x$, ESR signal can be observed up to about y=0.10, and it disappears at higher concentration,[7] whereas in (CHBr$_y$)$_x$ we observe it up to much higher concentration.

Figure 1(a) shows an overall tendency for the linewidth to increase with halogen dopant concentration. This is consistent with strong spin-orbit coupling due to halogen atoms, which results in a decrease of the electronic relaxation time with a consequent increase in linewidth.[8] For the semi-insulating heavily doped sample (y=0.55), the linewidth is comparable to that of cis-rich sample and almost temperature independent. This implies a nearly perfect confinement of solition in a short conjugated segment comparable to the soliton width, caused by addition reaction. Another important result is the g-shift. The g-shift in halogen substituted aromatic radical is known to be roughly proportional to the spin density and the spin-orbit coupling constant of the halogen atom.[9] Therefore, a clear g-shift for (CHBr$_y$)$_x$ shown in Figure 1(b) gives a microscopic evidence for substituted Br atoms even for Br concentration less than 5%. On the other hand, the absense of g-shift in (CHI$_y$)$_x$

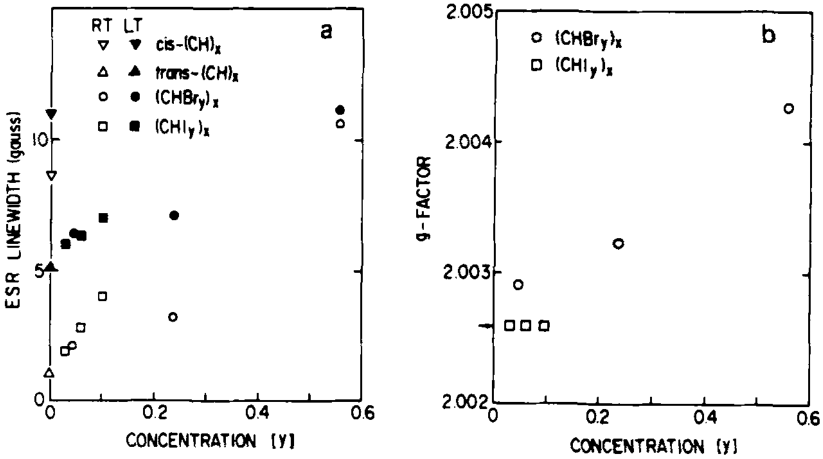


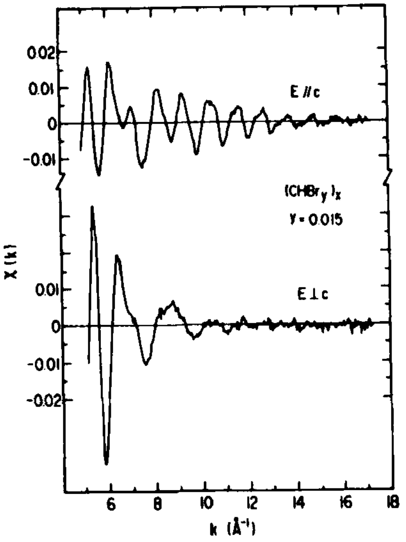
FIGURE 1 X-band ESR peak-to-peak linewidth (a), and g-factor (b) as a function of dopant concentration. Values for 300 K(RT) and 4 K(LT) are shown in (a). An arrow in (b) indicates a g-value of 2.0026 for undoped sample.

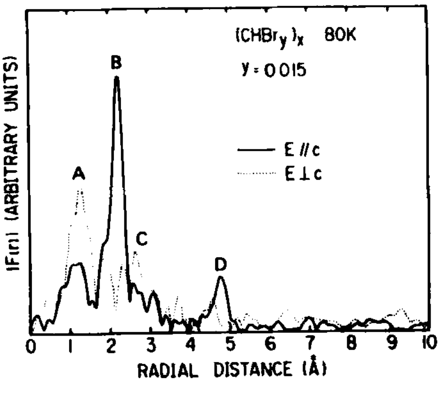
indicates that substitution of iodine is negligible, since its spin-orbit coupling constant is twice as large compared with bromine. Effect of added halogen to g-value should be small, since the spin density is negligibly small at aliphatic carbon.

Polarized EXAFS

Highly polarized X-ray of synchrotron radiation provides a powerful tool when combined with anisotropic low dimensional materials. 300% stretch oriented samples doped with bromine and iodine were prepared for polarized X-ray absorption spectroscopy. Experimental details are described elsewhere.[10]

In Figure 2 we campare the EXAFS oscillation of oriented $(CHBr_y)_x$ between two configurations; one with the polarization vector E of the X-ray parallel to the oriented polymer chain direction (E//c), and the other perpendicular to the polymer chain direction (E⊥c).[10] A large anisotropy in the oscillation amplitude reflects the difference in the backscattering amplitude between





Note that distances in the text are values after phase shift correction to those in Fig. 3.

FIGURE 2 (Left) Br K-edge EXAFS oscillations for $(CHBr_y)_x$ (y=0.015) as a function of k.

FIGURE 3 (Right) Fourier transform of χ(k) of Fig.2.

bromine and carbon. In E//c EXAFS, we see an extended oscillation characteristic to heavy bromine atoms, while in E⊥c EXAFS we see a rapid fall off due to scattering by light carbon atoms.

The result of Fourier transform is shown in Figure 3.[10] The predominant peak B at 2.55 Å corresponding to Br-Br distance is only observed in the E//c configuration, indicating a high degree of orientation of Br polyions. An interesting result is that a smaller peak D at 5.12 Å corresponding to nearly twice the nearest Br-Br distance is observed, which indicates the presence of linear Br_3^- or longer polybromine ions, aligned in this direction.

On the other hand, Br-C bond (peak A) at 2.0 Å shows lower anisotropy indicating a wide distribution of Br-C bond direction. More distant peaks C between 3.4 and 3.8 Å correspond to Br-C spacing between Br_3^- and $(CH)_x$ chain. It is very importment that these highly anisotropic spectra can be obtained in a very limited concentration region between y=0.014 and 0.036. At higher concentration the EXAFS anisotropy decreases gradually as doping

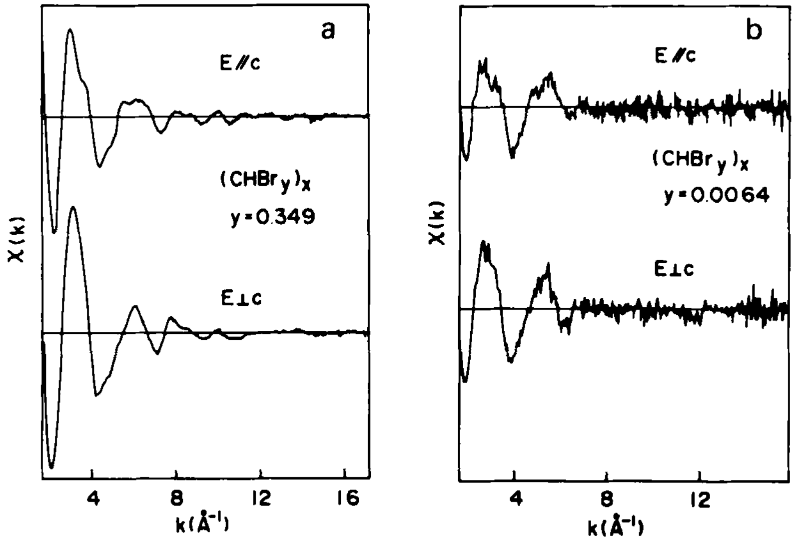


FIGURE 4 Br K-edge EXAFS oscillations for $(CHBr_y)_x$ plotted as a function of k. (a) y=0.349 (b) y=0.0064

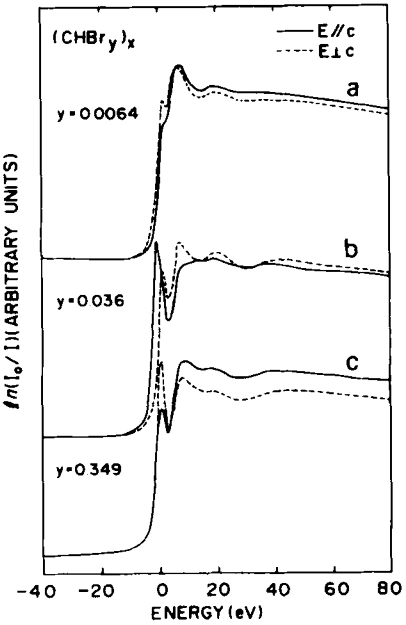
proceeds as shown in Figure 4(a), and we eventually have spectra similar to the unoriented films. What happens at lower concentration is more exciting. Figure 4(b) shows that we also lose the anisotropy at very low doping level. This result has a significant implication, since the conductivity increases rapidly at this concentration region. It appears that the conductivity increase is not directly related to the formation of Br_3^- ions. In other words, intra-chain conductivity may not be crucial for the drastic increase of conductivity at the low doping level.

The result of polarized EXAFS at I $L_{1,2,3}$ edge on oriented $(CHI_y)_x$ is almost independent of iodine concentration. A prominent peak around 3.1 Å corresponding to I-I bond shows a similar anisotropy due to oriented linear polyiodine ions. Except for a broad peak ranging from 3.5 to 4.5 Å, which corresponds to I-C spacing between dopant and $(CH)_x$ chain, no I-C bond is observed in the 1.6 to 2.0 Å range. Unobservably small number of I-C bond is consistent with our ESR data, but contradicts the ^{13}C NMR result.[11]

Polarized XANES

Finally we show another anisotropy in the X-ray absorption near edge structure (XANES), which reflect the anisotropy in the local electronic structure or chemical bond. Figure 5 shows polarization dependent XANES for oriented $(CHBr_y)_x$ samples. We first discuss the result for y=0.036, where Br_3^- gives a highly anisotropic EXAFS. The lowest energy peak seen most prominently in the E//c spectrum (Fig. 5b) is similar to the 1s-4pσ^* transition in Br_2 gas.[10] This peak arises from a transition of 1s to 4p antibonding LUMO of the linear Br_3^- molecule. This sharp peak shift to higher energy by 2 eV in the E⊥c spectrum. This new peak is assigned to a transition of 1s to 4p antibonding orbital of Br-C bond. Since the overall features of the E⊥c spectrum are similar to those of bromobenzene, Br-C bond due to substituted Br atoms seems dominant in this direction.[10] The presence of substituted Br in this concentration range is consistent with the ESR implication. For y=0.0064 (Fig. 5a) and y=0.349 (Fig. 5c), lowest energy peaks in the E//c and E⊥c spectra are all at the same energy as the latter one ascribed to Br-C bond. At high concentration (Fig. 5c), Br-C bond is extremely enhanced in the E⊥c spectrum.

A similar anisotropic spectra are observed in $(CHI_y)_x$. Figure 6 shows the near edge structure on I L_1 edge measured at 300 K. In the near edge structure in E//c spectrum, a sharp resonance (peak A) due to 2s-5p transition has been observed. The second-edge peak B of low intensity is interpreted as due to excitations into higher lying (6p,7p,..) valence states consistent with its dominance in the E⊥c spectrum, in which 5p orbitals are mostly occupied. The concentration dependence of polarized X-ray absorption spectra for $(CHI_y)_x$ is small.



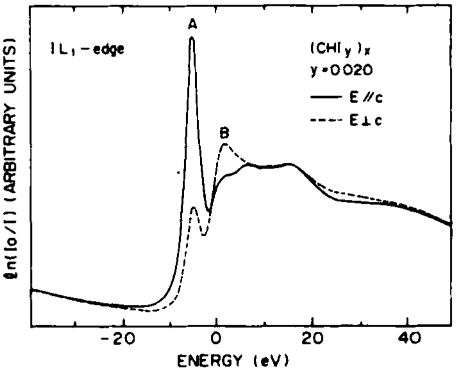


FIGURE 5 (Left) Br K near-edge spectra of $(CHBr_y)_x$.

FIGURE 6 (Right) I L_1 near-edge spectra of $(CHI_y)_x$.

CONCLUSION

We have shown that in $(CHBr_y)_x$, Br-C bond is observed in essentially the whole bromine concentration range, and that ESR is useful to see the effect of substituted and added bromine separately. Polarized EXAFS for $(CHBr_y)_x$ shows a strong concentration dependence. Highly anisotropic EXAFS oscillations in the concentration range from y=0.014 to 0.036 have revealed the presence of linear polybromine ions oriented along the polymer chain. Polarized EXAFS for $(CHI_y)_x$ shows a similar anisotropy due to oriented linear polyiodine anions, but no I-C bond has been observed. A large anisotropy is also observed in the near edge structure of oriented $(CHBr_y)_x$ and $(CHI_y)_x$, reflecting the anisotropy in the local electronic structure due to chemical bonds of dopant atoms.

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