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Polyacetylene and Highly Conducting Charge Transfer Complexes

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X-ray diffraction, Raman spectroscopy, and x-ray photoemission measurements indicate that the metallic conductivity of iodine-doped polyacetylene results from the intercalation of iodine between close-packed planes of the parent phase to form a charge transfer complex. The polyacetylene chains donate charge to produce I_3^- and a second iodine species with lower charge density, most likely I_5^-. The structure of this charge transfer complex can be viewed as a perturbation of the structure of the parent polymer, which has been derived from x-ray diffraction analysis and lattice energy calculations.

1 INTRODUCTION

Shirakawa *et al.* and Chiang *et al.* have reported that the electrical conductivity of polyacetylene can be increased over eleven orders of magnitude by doping with electron acceptors such as iodine or AsF_5[1–6]. This increase in conductivity suggests the possibility that a semiconductor-metal transition occurs during doping.[2,5,7] The present work will utilize Raman scattering, x-ray diffraction, and photoemission techniques to characterize the structural origin of the enhanced conductivity for the polyacetylene-iodine system. It is of interest to determine the dopant species, location of the dopant, and the nature of the interaction between the dopant and the polyacetylene chains. Evaluation of the structure of the undoped polymer from x-ray diffraction and crystal packing analysis will provide a starting point for understanding structural aspects of the doped polymer.

II X-RAY DIFFRACTION AND CRYSTAL PACKING ANALYSES

Although polyacetylene, $(CH)_x$, is a well known polymer which has been investigated for several decades, the crystal structures of polyacetylene have not previously been determined. Since the structures of the doped polymers can be viewed as perturbations of the parent structures, knowledge of the latter structures is crucial for understanding the polyacetylene-iodine system.[7,8] Basic structural aspects of the cis polymer have been determined using both x-ray diffraction and crystal packing analyses.

Since only ten diffraction lines are observed for the available nonoriented samples, most of which are the supper-position of more than one *hkl*, only the basic packing mode can be deduced directly from the x-ray data. The observed diffraction spacings and packing calculations are consistent with the orthorhombic unit cell Pnma, where $a = 7.61$, $b = 4.47$ (chain axis), and $c = 4.39$ Å at 300°K.[8] With one CH per asymmetric unit, there are eight CH units per unit cell, corresponding to a calculated density of 1.16 gm/cm^3. This density is in good agreement with the bulk density derived from flotation measurements in a density gradient column, 1.165 gm/cm^3. In this space group with the above number of monomer units per unit cell, the polymer chain must be planar and contain both a center of symmetry and a mirror plane (normal to the chain direction).

The parameters to be determined from the intensity analysis are restricted to the setting angle of the polymer chains, ϕ, measured with respect to the (001) plane, and an isotropic temperature factor B. The C—C, C=C, and C—H bond lengths used in the diffraction intensity and crystal packing analysis are 1.46, 1.35, and 1.11 Å, respectively—wherein the C=C is parallel to the chain direction. The C=C—H bond angle is 120° and the C—C=C bond angle (127.3°) is chosen to be consistent with the determined chain-axis periodicity (4.47 Å). The intensity analysis provides $\phi = 59°$ and $B = 12$ Å^2

The basic structure determined by x-ray diffraction analysis is consistent with that obtained via lattice energy calculations. Packing calculations, which utilize the Williams IV potential,[9–11] predict that $a = 7.14$ Å, $c = 4.25$ Å, and $\phi = 51.7°$ at 0°K. Approximating the thermal expansion of polyacetylene by that of polyethylene, the discrepancy between the calculated and experimental unit cell parameters at 300°C is -2.6% for the *a*-axis and -1.4% for the *c*-axis. The slightly smaller predicted parameters are expected, since lattice expansion due to zero point vibrations are neglected in the calculations.

The crystal structure obtained for cis-polyacetylene is quite similar to that for the well known orthorhombic polyethylene. Despite the difference in backbone structure, the chain symmetries are both most likely $(m\bar{1})_t$.

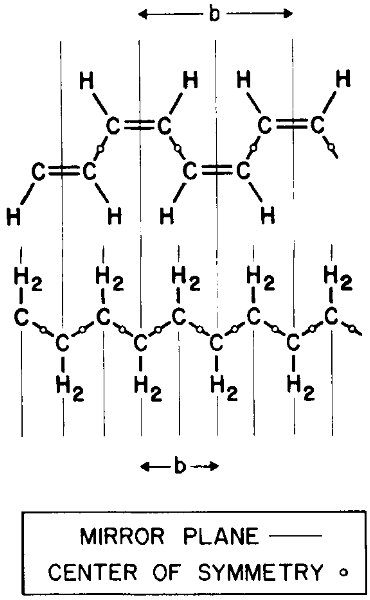

FIGURE 1 Comparison of the chain symmetries for orthorhombic cis-polyacetylene and polyethylene.

As illustrated in Figure 1, the mirror plane normal to the chain axis in cis-polyacetylene relates neighboring CH units in the chain direction, while this symmetry element in polyethylene takes a CH_2 unit into itself. As a consequence, the chain repeat length (unit cell dimension) in polyacetylene is approximately twice as long as in polyethylene and the unit cell in polyacetylene contains twice as many carbon atoms as in polyethylene. As shown in Figure 2, the chain-axis projection of the crystal structure of cis-polyacetylene is quite similar to that for orthorhombic polyethylene. Furthermore, the elastic constants, bulk Gruneisen coefficient (3.37), and lattice energy (−1.68 kcal/mole) derived from the crystal packing calculations are close to those previously obtained for polyethylene.[12,13]

III RAMAN SPECTROSCOPIC STUDIES

Raman and X-ray photoelectron spectroscopic studies on iodine-doped samples of cis-rich and trans-rich polyacetylene have shown the presence of iodine in two different forms, I_3^- and a less negatively charged species, probably I_5^-.[7] In all cases, a Raman line at 105–107 cm^{-1} and harmonics up to fourth order were observed. In addition, for heavily doped polymer

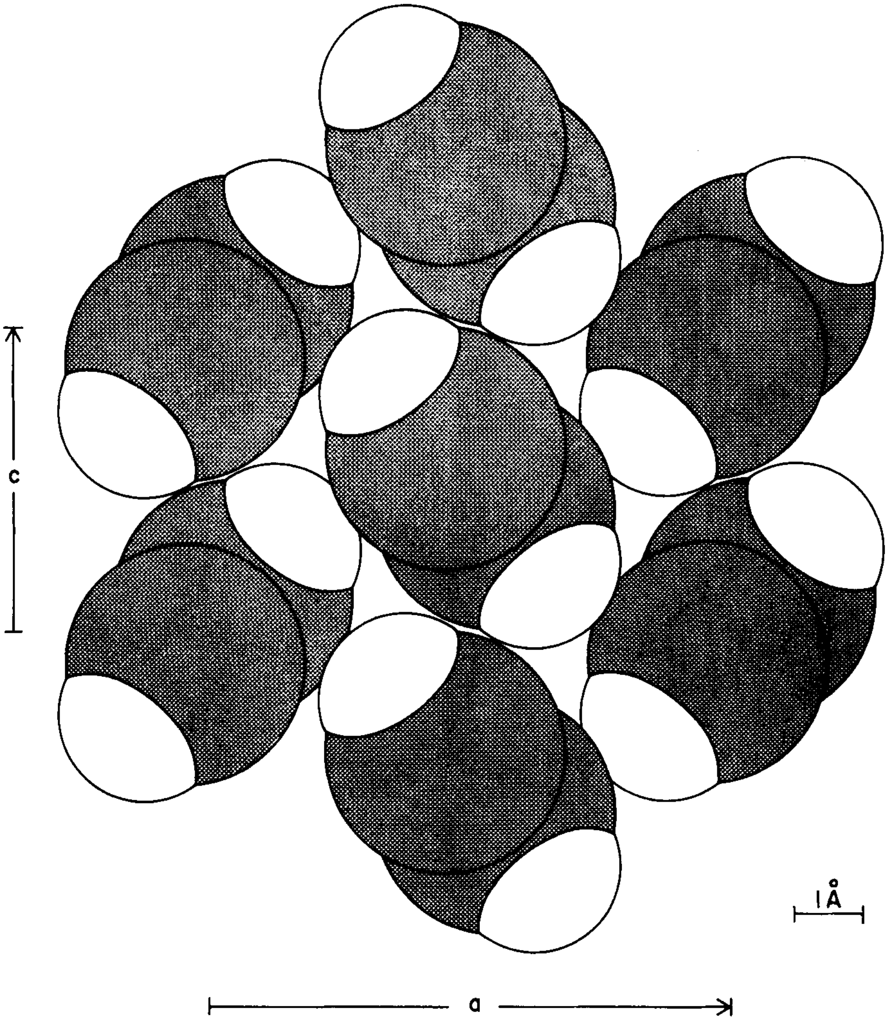

FIGURE 2 Chain-axis projection of the calculated structure of cis-polyacetylene. The atom dimensions correspond to van der Waals radii. White balls represent hydrogens and black balls represent carbons.

samples, $(\mathrm{CHI}_{0.16})_x$ and $(\mathrm{CHI}_{0.22})_x$, a second strong Raman line exists at about 160 cm^{-1} and a very weak line exists at 61 cm^{-1}.

The relative intensity of the bands at 105 cm^{-1} and 160 cm^{-1} is strongly dependent upon excitation wavelength.[7] A series of variously iodinated polyacetylene films also show dramatic differences in the relative intensity of these two lines for the same laser excitation wavelength, namely 5145 Å. The relative intensity ratio of the 160 cm^{-1} to the 105 cm^{-1} line at 5145 Å excitation varies from 0.14 to 1.33 for $(CHI_{0.07})_x$ and $(CHI_{0.25})_x$, respectively.

The band at 105–107 cm^{-1} can be assigned to the symmetric I-I stretching motion of I_3^-. This vibration has been observed in a number of systems, which are known to contain I_3^-. For example, this band occurs at 103 cm^{-1} and 105–108 cm^{-1} in cesium triiodide and in metal-phthalocyanine-iodine derivatives, $[CoPC]I_3$, respectively.[14,15] Of the several possible assignments for the 61 cm^{-1} band, we cannot favor any particular one based on the present evidence.

The high frequency band at 160 cm^{-1} (5145 Å laser excitation) is close to the asymmetric I_3^- stretching vibration previously observed at 143 cm^{-1} in other iodine complexes.[16] For comparison, the stretching vibration of I_2 occurs at 214 cm^{-1} in the gas phase and at 190 cm^{-1} in the solid phase.[17,18] It is tempting to assign the 160 cm^{-1} line to the asymmetric stretching vibration in I_3^-. However, the observed variation in relative line intensity as a function of excitation wavelength and iodine concentration differs from that expected if the higher frequency band is the asymmetric stretch of I_3^-. In our opinion, an alternative assignment for the high frequency Raman component is particularly attractive, that is, the existence of a second polyiodide species.

Nafie *et al.* concluded that for polyatomic molecules, the appearance of higher overtones is limited to only totally symmetric vibrations irrespective of the nature of the electronically excited state concerned.[18] Therefore, it was interesting to observe a very broad band at approximately 328 cm^{-1} (halfwidth ~54 cm^{-1}) for $(CHI_{0.25})_x$ and a much narrower band (half-width ~34 cm^{-1}) at approximately 316 cm^{-1} for $(CHI_{0.07})_x$. In both samples, bands of similar width exist at 212 ± 2 cm^{-1}.

The intensity of the 328 cm^{-1} band in $(CHI_{0.25})_x$ is twice the intensity of the 212 cm^{-1} band. In constrast, the ratio I(316 cm^{-1})/I(212 cm^{-1}) in $(CHI_{0.07})_x$ is 0.5. These observations suggest that the 328 cm^{-1} band in $(CHI_{0.25})_x$ may actually contain the third harmonic form 105 cm^{-1} and the second harmonic of the 160 cm^{-1} band. This evidence further supports that the 160 cm^{-1} band cannot be assigned to the asymmetric stretching of I_3^-, instead it may arise from a symmetric stretching motion of another polyiodide species.

IV X-RAY PHOTOELECTRON SPECTROSCOPY

The X-ray photoelectron spectra recorded using Alkα radiation at −35°C are consistent with the picture. The iodine $3d_{3/2}$ and $3d_{5/2}$ core level lines both show evidence of splitting for iodinated samples of either cis-rich or trans-rich polymer. This line splitting, which is not observed for compounds known to contain only I_3^-, suggests the presence of two types of iodines. The lower binding energy component (619.0 eV for $3d_{5/2}$) is assigned to I_3^-, while the higher binding energy component (620.6 eV for $3d_{5/2}$) can be associated with a less negatively charged iodine, such as in I_5^-. Valence band measurements on an iodinated cis-rich polymer film, $(CHI_{0.22})_x$, are consistent with a finite density of states at the Fermi level, as expected for a metal.[7]

V CONCLUSION

X-ray diffraction measurements on iodinated polyacetylene combined with the structural results on the parent polymer and the Raman and photoelectron studies, provide a model for the structure of iodinated polyacetylene. Similar interplanar spacings are observed for doped and undoped samples of either cis-rich or trans-rich polyacetylene. This suggests that the structure of the iodinated polymer can be viewed as a perturbation of the structure of the parent polymer. Most significantly, a new spacing (7.6–7.9 Å) is observed for the iodinated polymers at about twice the separation of close-packed planes of the parent polymers (3.7–3.8 Å). Since the van der Waals diameter of iodine (3.96 Å) is approximately equal to the separation of close-packed planes in the parent polymers, these results suggest that iodine intercalates between close-packed planes of polyacetylene. Consistent with the Raman and photoelectron results, the iodine is assumed to enter the polyacetylene crystals as I_3^- and as a second species in variable concentration with a lower charge per iodine, such as I_5^-. Assuming that linear arrays of I_3^- ions are incorporated into half of the chain sites (such as by intercalation between adjacent (100) planes of cis polyacetylene) a limiting iodine concentration of $(CHI_{0.33})_x$ is calculated for the fully intercalated complex. This result is in good agreement with the highest reported[8] concentration, $(CHI_{0.31})_x$. Since polyhalide species with a higher charge per iodine than I_3^- are not indicated, the predicted limiting iodine concentration places an upper limit of 0.11 electrons transferred per carbon atom in the polymer backbone. The packing calculations and x-ray diffraction analysis indicate that non-electronic properties related to intermolecular interactions for polyacetylene should be well approximated by those of polyethylene.

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