

Effect of dopant-molecule size on the electrical conductivity of polyacetylene

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We have measured the temperature dependence of the conductivity of *cis*-polyacetylene doped with iodine and with $\text{H}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$. The iodine dopant was introduced from the vapor phase under various vapor pressures and also from solution. The IrCl_6 was introduced from solution. We find $\log \rho \propto T^{-1/4}$ for $(\text{CH})\text{I}_y$ and $\log \rho \propto T^{-1/2}$ for $(\text{CH})_x$ doped with IrCl_6 . We attribute the difference to separate transport mechanisms. We suggest that the size and shape of the dopant molecule is the controlling variable rather than the doping conditions.

The mechanism of electrical conduction in doped polyacetylene has remained controversial. It has been proposed that there are at least three dopant regimes: (1) at the very lowest dopant levels, below 0.003 mole fraction, phonon-assisted hopping between soliton bound states in *trans*-polyacetylene has been proposed¹; (2) at higher dopant levels, still below the metal-to-insulator transition, thermally activated behavior has been observed with a variety of explanations offered²⁻⁴; (3) above a critical dopant concentration, metallic conductivity has been proposed.⁴ Experiments²⁻⁴ on doped polyacetylene in regimes (2) and (3) have been performed on *cis* starting material. We have used *cis* material in this work.

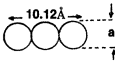
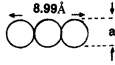
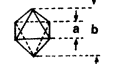
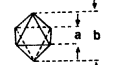

This paper concentrates on regime (2) in which two different behaviors have been reported and the difference has been attributed to differences in doping homogeneity.^{2,3} In the case of AsF_5 dopant there is evidence from the temperature and electric field dependence of the conductivity that the dopant molecules cluster together, forming conducting islands of heavily doped $(\text{CH})_x$.² The $\log \rho \propto T^{-1/2}$ behavior is attributed to charging-energy-limited tunneling in which charge carriers tunnel between conducting islands, as described in the model of Sheng.⁵ The applicability of this model to polyacetylene has been criticized on the basis of optical⁶ and magnetic-susceptibility⁷ data for doped polyacetylene. Electrical conductivity and magnetic susceptibility may be sensitive to different types of doping inhomogeneities. It has been shown that doping technique influences the magnetic susceptibility.^{8,9} In this work we study the temperature dependence of the resistivity.

In the case of iodine dopant, $\log \rho \propto T^{-1/4}$ behavior is reported,³ although earlier studies¹⁰ could not distinguish between $T^{-1/4}$ and $T^{-1/2}$. When $\log \rho \propto T^{-1/4}$ behavior is found in disordered semiconductors, it is attributed to variable range hopping of carriers among atomic sites in three dimensions¹¹; the $\log \rho \propto T^{-1/4}$ behavior of doped polyacetylene is explained by a similar mechanism.

The novel feature of our work is the suggestion that the transport mechanism does not depend on the doping conditions but rather on the size and shape of the dopant molecule. We have investigated a large spherical dopant molecule (IrCl_6) and a small one (I) which forms linear chains of three atoms. Some preliminary work on Br and FeCl_3 dopants is also mentioned. We compare and contrast our results with previously published data for I (linear chain) and AsF_5 (large spherical molecule) dopants. Table I shows the dimensions and structure of the dopant molecules.^{12,13}

Polyacetylene was prepared according to the method of Wnek *et al.*¹⁴ The resultant gel was pressed into films. X-ray diffraction and scanning electron micrograph studies show that the as-prepared films are polycrystalline with a fibrillar morphology, fiber diameters are 200–300 Å.¹⁵ All measurements

Table I. Dopant molecules: sizes and shapes.

DOPANT	STRUCTURE	DIMENSIONS
I I_3^-	LINEAR CHAIN 	$a = 3.37 \text{ \AA}$
Br Br_3^-	LINEAR CHAIN 	$a = 3.00 \text{ \AA}$
IrCl_6^{2-}	OCTAHEDRON 	$a = 6.08 \text{ \AA}$ $b = 8.6 \text{ \AA}$
AsF_6^{-1}	OCTAHEDRON 	$a = 4.41 \text{ \AA}$ $b = 6.24 \text{ \AA}$
FeCl_4^{2-}	TETRAHEDRON 	$a = 7.05 \text{ \AA}$

were carried out on 80–95% *cis* materials as evidenced by their infrared spectra (determined by the method of Ito *et al.*¹⁶).

If doping conditions determine the dopant homogeneity, which in turn controls the electrical properties of polyacetylene, it should be possible to vary the electrical properties by using different doping techniques. With that aim, dopants were introduced into the $(\text{CH})_x$ films under four experimental conditions:

Method (1). The polymer was placed in a vacuum desiccator containing solid iodine. The desiccator was evacuated and then sealed. The extent of doping was determined by the exposure time.

Methods (2) and (3). The polymer film was placed in a flask connected to another flask containing iodine. The entire system was evacuated (with the iodine at liquid-nitrogen temperatures) and sealed. The flask containing the iodine was then allowed to rise to the desired doping temperature, 0 °C for method (2) and 25 °C for method (3), and maintained at that temperature for the duration of the doping procedure.

Method (4). The polymer film was exposed to a solution containing the dopant dissolved in dry nitromethane (0.002 mole/100 ml). The excess dopant was washed off the film with pure nitromethane and the film was placed in dynamic vacuum for one hour to remove residual solvent. The following materials were used as solution dopants: dihydrogen hexachloroiridate ($\text{H}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$), iodine, bromine, and ferric chloride.

In all of the above methods, doped samples were placed in dynamic vacuum for 1–24 h until a constant weight was obtained. The concentration of the dopant was determined by weight uptake and occasionally by element analysis. It should be noted that, although the composition of polyacetylene doped with the iridium salt is given as $\text{CH}(\text{IrCl}_6)_y$, elemental analysis revealed that the true composition is $\text{CH}(\text{IrCl}_{5.5})_y(\text{H}_2\text{O})_x$. The significance of this result, along with other chemistry-related data for $\text{CH}(\text{IrCl}_6)_y$, will be presented in a future paper.

We have found that the electrical resistivity of iodine-doped polyacetylene follows a $\log \rho \propto T^{-1/4}$ behavior over a range of dopant levels ($0.006 \leq y \leq 0.03$) and independent of doping techniques. Our results indicate that our doping techniques, whether slow or rapid doping, do *not* control the temperature dependence of the resistivity. Therefore, if the homogeneity of dopant determines the electrical properties, it depends on something other than the doping technique.

Figure 1 shows the mole uptake of iodine versus time for the various techniques. Figure 2 shows the $\log \rho \propto T^{-1/4}$ temperature dependence of the resistivity of several $(\text{CH})_x$ samples doped by the different techniques. Graphical presentations of data are sometimes insufficient to determine the power-law

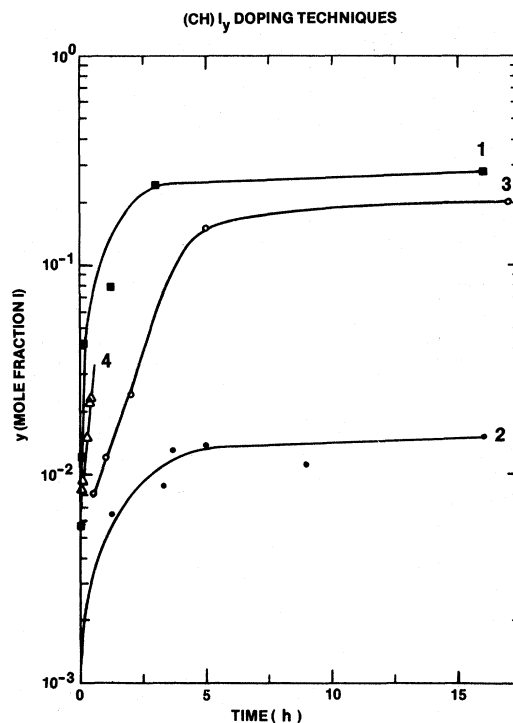


FIG. 1. Mole uptake of iodine as a function of time for different doping methods: (1) rapid doping in a saturated iodine vapor at room temperature; (2) slow doping in a 0 °C slush bath; (3) slow doping at room temperature; (4) doping from solution.

dependence of $\log \rho$ on T . Therefore we have done a computer-assisted fit to a function of the form $\log \rho \propto T^{-N}$ for 18 $(\text{CH})_x$ samples. The results are shown in Table II. The results confirm that $N = \frac{1}{4}$ gives a good fit to the data, with the possible exception of method (2). The samples doped by technique (2) may have been contaminated with oxygen because of the length of time required for doping.

We turn now to $\text{CH}(\text{IrCl}_6)_y$. The temperature dependence of the resistivity is in marked contrast to the iodine dopant. A $\log \rho \propto T^{-1/2}$ behavior was observed, as shown in Fig. 3, for $y \geq 0.012$. A computer-assisted fit for the data shown in Fig. 3 found $N = 0.49 \pm 0.01$. It is notable that our results for the IrCl_6 dopant are identical to results reported for vapor phase doped AsF_5 in *cis*- $(\text{CH})_x$.²

Finally, we mention some preliminary experiments on the temperature dependence of the resistivity of polyacetylene solution doped with FeCl_3 and Br. For two samples with FeCl_3 dopant we found $N = 0.44 \pm 0.014$, and four samples doped with bromine we found $n = 0.255 \pm 0.004$. Bromine, like iodine, is a small molecule which occurs as a linear chain of three atoms: Br_3^- , just as I_3^- . The behavior of the FeCl_3 dopant is more difficult to interpret. FeCl_4^{2-} ,

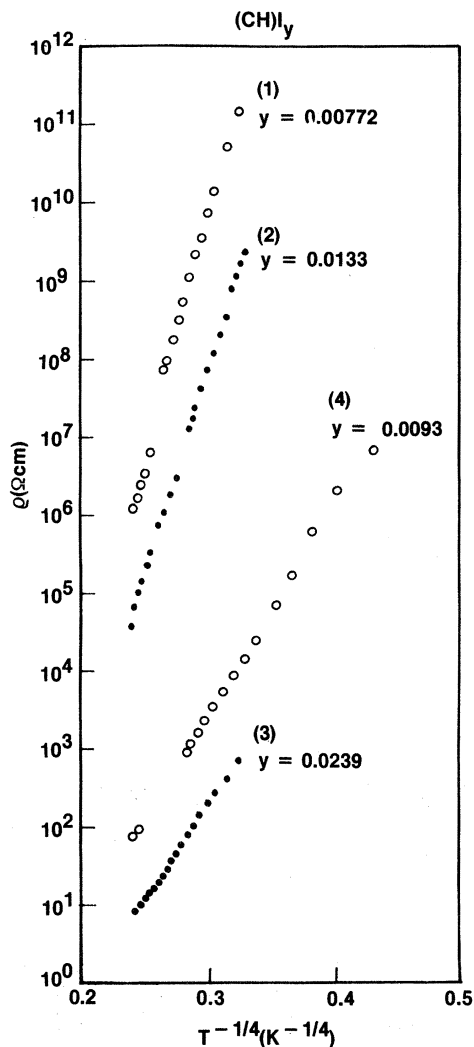


FIG. 2. $\log \rho$ vs $T^{-1/4}$ for $(\text{CH})\text{I}_y$ doped by different methods: (1), (2), (3), (4).

the reported¹⁷ dopant species, might occur as a planar or a tetrahedral structure; therefore its effective size and shape are uncertain. In Table I we have assumed a tetrahedral structure. The $\log \rho \propto T^{-0.44}$ behavior can be modeled by two conduction mechanisms in parallel: variable range hopping and charging energy

TABLE II. Properties of $(\text{CH})\text{I}_y$. Values of N for $(\text{CH})\text{I}_y$ where $\log \rho \propto T^{-N}$.

No. of samples tested	Doping technique	N
9	1	0.28 ± 0.03
3	2	0.36 ± 0.06
2	3	0.26 ± 0.02
4	4	0.23 ± 0.05

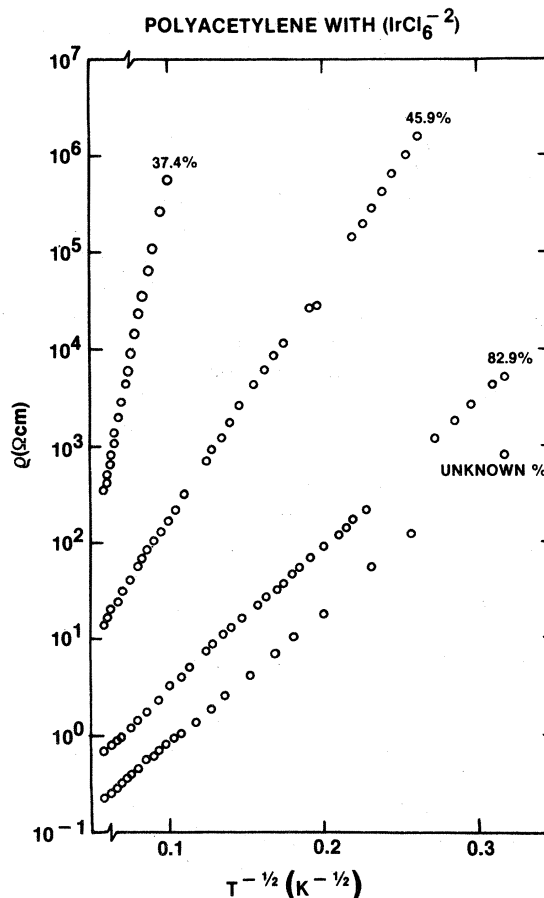


FIG. 3. $\log \rho$ vs $T^{-1/2}$ for polyacetylene doped with IrCl_6 from solution. Weight percent dopant 37.4%, 45.9%, 82.9%, and unknown amount in one sample.

limited tunneling. The dominant conduction mechanism is charging energy limited tunneling.

In conclusion, we have shown that $(\text{CH})_x$ with I and IrCl_6 have different electrical properties, and we attribute the difference to the size and shape of the dopant molecule. Our results suggest that different conduction mechanisms exist in iodine-doped and IrCl_6 -doped *cis*-polyacetylene. We tentatively identify them as variable range hopping and charging energy limited tunneling, respectively. We propose that doping *cis*- $(\text{CH})_x$ with large spherical molecules (AsF_5 , IrCl_6) results in conducting islands among which the charge carriers move. It is possible that the first large dopant molecules to strike the $(\text{CH})_x$ surface open channels and that it is energetically favorable for the next molecules to follow already established pathways to the dopant sites, thus causing inhomogeneous doping. There may be a lower doping limit before dopant aggregation occurs.

In the case of the small dopant atoms forming a linear chain, e.g., I_3^- , we have shown that the doping conditions investigated do not influence the function-

al dependence of the resistivity on temperature. We find $\log \rho \propto T^{-1/4}$. The linear-chain dopants may cause less disturbance in the polymer chains than the large spherical molecular dopants. In particular, it may be possible for the dopant to infiltrate the polymer as an intercalant.¹⁸

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