Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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To cite this article: M. A. Druy , M. F. Rubner , E. K. Sichel , S. K. Tripathy , T. Emma & P. Cukor (1984): Does Doping Method Influence the Electrical Properties of Polyacetylene?, Molecular Crystals and Liquid Crystals, 105:1, 109-122

To link to this article: http://dx.doi.org/10.1080/00268948408071646

Mol. Cryst. Liq. Cryst. 1984, Vol. 105, pp. 109-122
0026-8941/84/1054-0109/$18.50/0

DOES DOPING METHOD INFLUENCE THE ELECTRICAL PROPERTIES OF POLYACETYLENE?

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Abstract. The influence of doping method on the electrical properties of polyacetylene are considered. Cis-polyacetylene was doped chemically and electrochemically with the $(IrCl_6)^{2-}$ species. The conduction mechanism was found to be independent of doping method. Electrochemical doping, however, results in a more homogeneous distribution of dopant at the 15-200 angstrom level and a higher conducting material. Electrochemical doping also results in the incorporation of a non-hydrolyzed dopant species.

INTRODUCTION

When polyacetylene is exposed to suitable electron-donating or electron withdrawing species, the electrical conductivity of the polymer increases over twelve orders of magnitude.[1] Alternatively, the electrical conductivity may be increased by electrochemical oxidation or reduction.[2] Both of these methods of increasing the conductivity have been referred to as "doping" and it is common to refer to the chemical species involved as "dopants." In the case of chemical "doping," an electron transfer oocurs between the polymer and the "dopant" and the chemical species is incorporated into the polymer. An example of chemical doping is exposing polyacetylene to iodine, either in solution or to its vapor.[3] During electrochemical "doping," electrons are removed or added to the polyacetylene pi electron system via an external source of potential. Anions or cations from the supporting electrolyte are then incorporated into the polymer in order to maintain charge neutrality. The fundamental difference between the two methods of doping is that in the case of chemical doping, the species which is incorporated into the film is a result of the electron transfer between the polymer and the "dopant." While in electrochemical doping, the species which is incorporated into the film is a result of electrochemical oxidation or reduction. Thus, for electrochemical doping, the species would not have been incorporated into the polymer if no external battery was attached to the cell and the polyacetylene would not have become "doped." A well-known example of electrochemical doping is the use of polyacetylene as an anode in a cell which contains tetrabutylammonium perchlorate as the supporting electrolyte dissolved in methylene chloride.[4] In this case, as the polymer becomes oxidized, perchlorate anions are incorporated into the film.

One question that arises is whether dopant type or doping method influences the electrical properties of the doped polymer. Previously in our laboratory we have examined the temperature dependence of the resistivity, ρ, of polyacetylene doped with hexachloroiridate, iodine, and bromine.[5] We observed in the case of hexachloroiridate doping that $\rho=\rho_0 \exp(T_0/T)^{\frac{1}{2}}$ and in the case of bromine and iodine doping $\rho=\rho_0 \exp(T_0/T)^{\frac{1}{4}}$. This behavior was independent of the <u>cis-trans</u> content of the undoped polymer. In hexachloroiridate doping, this was attributed to a charging energy limited hopping process in which a charge carrier hops from one conducting cluster to another, creating a pair of negatively and positively charged clusters. Doping with iodine or bromine resulted in a conduction mechanism in which a charge carrier hops between dispersed atomic sites. We attributed these two different mechanisms of conduction to the nature of the dopant and its distribution. The diffusion rates of the dopant species in the polymer matrix are expected to be different and dependent on their relative sizes, and therefore one expects the dopant distribution to be affected. Recent results also indicate that the dielectric constant of doped polyacetylene is dopant species dependent.[6]

In order to determine whether doping method influenced the electrical properties of polyacetylene, we doped <u>cis</u>-polyacetylene both electrochemically and chemically with the hexachloroiridate species and investigated the temperature dependence of the resistivity and the distribution of the species (via transmission electron microscopy) in the polymer. In this paper we will summarize the results.

EXPERIMENTAL

Sample preparation: Polyacetylene was prepared in film form as described in our previous publications.[5] Polymerizations were carried out at -78°C, which results in the predominantly cis-isomer (80-95%) of polyacetylene. Details of the characterization, morphology, and microstructure of polyacetylene prepared using these procedures have been published in our earlier work.[3]

Chemical doping of polyacetylene was accomplished by immersing the polyacetylene film in a solution consisting of dihydrogenhexachloroiridate (IV), $H_2IrCl_6 \cdot 6H_2O$, dissolved in a 90/10 vol. % solution of nitromethane/acetic acid. The acetic acid was added to prevent impurities formed in the doping solution during standing from precipitating out of the solution and onto the polyacetylene film. All manipulations of the polymer and dopant were carried out using vacuum line techniques or in an inert atmosphere. A detailed description of the doping process can be found in a previous publication.[7]

Electrochemical oxidation (doping) of $(CH)_x$ pressed film was carried out under constant voltage (potentiostatic) conditions. All procedures, including washing the film after doping, were carried out in an inert atmosphere glove box. A two-compartment three-electrode cell was used. Oxidation of the $(CH)_x$ was performed at a voltage of +0.75 V vs. the Ag/Ag^+ electrode. The electrolytic solution was 0.01 M tetra-n-butylammonium hexachloroiridate (IV) in nitromethane. A detailed description of the doping procedure can be found in a previous publication.[7]

RESULTS AND DISCUSSION

Doping of Polyacetylene

A. Chemical Doping

In order to gain an understanding of the electrical properties of polyacetylene doped with the iridium salt, it is first necessary to determine the nature of the actual species incorporated in the polymer and the mechanism of its insertion. Elemental analysis revealed that the composition of the doped polymer varied; with the chlorine/iridium ratio ranging from the expected 6/1 ratio to as low as 4/1 (see Table 1). Since the iridium salt contains coordinated water, it is reasonable to assume that hydrolysis or aquation of the $(IrCl_6)^{2-}$ has taken place. MacDiarmid and Heeger[1] have reported on a number of dopants that contain hydrolyzable halogen and, depending on the handling and storage procedures, are incorporated in polyacetylene with or without coordinated H_2O.

TABLE 1 Elemental Analyses for $(CH)_x$ Doped With $(IrCl_6)^{2-}$

SAMPLE[b]	% C	% H	% Ir	% Cl	% O[a]	EMPIRICAL FORMULA
1	57.20	5.55	17.57	12.32	7.36	$CH_{1.0}(IrCl_{3.8}(OH)_2)_{0.19}\cdot(H_2O)_{.058}$
2	45.17	4.94	24.06	20.34	5.55	$CH_{1.14}(IrCl_{4.6}OH)_{.033}\cdot(H_2O)_{.059}$
3	51.52	4.95	21.01	16.34	6.1	$CH_{1.01}(IrCl_{4.2}(OH)_2)_{.025}\cdot(H_2O)_{.039}$
4	63.79	6.37	11.53	11.73	6.58	$CH_{1.05}(IrCl_{5.6}OH)_{.011}\cdot(H_2O)_{.066}$
5[c]	52.47	4.78	16.13	17.93	8.69	$CH(IrCl_6.6H_2O)_{0.019}$
6[d]	—	—	37.16	41.32	—	$IrCl_{6.02}$

a - OXYGEN DETERMINED BY DIFFERENCE

b - ANALYSIS BY SCHWARZKOPF MICROANALYTICAL LABORATORY, WOODSIDE, NY 11377

c - ELECTROCHEMICALLY DOPED $(CH)_x$

d - ANALYSIS OF AS RECEIVED DIHYDROGENHEXACHLOROIRIDATE

Spectrophotometric analysis of the doping solution containing $H_2IrCl_6\cdot 6H_2O$ (in nitromethane) revealed that the dopant was not hydrolytically stable on standing, and that the doping solution contains a mixture of hexachloroiridate and its hydrolysis products.[7] Both of these species are in turn incorporated in polyacetylene during the doping process, along with various amounts of coordinated water (vide elemental analysis). The various Cl/Ir ratios obtained for the doped films by elemental analysis, therefore, reflect the distribution of these hydrolysis products in the doping solution. It was also found that the rate of reaction of polyacetylene with the iridium salt and its hydrolysis products was the same under equivalent conditions. In other words, doping solutions that contained the chlorohydroxy species were equally effective as dopants for polyacetylene as solutions that only contained the hexachloro species.

There are two mechanisms that one must consider for spontaneous doping with $H_2IrCl_6\cdot 6H_2O$. The first involves the transfer of an electron from polyacetylene to $(IrCl_6)^{2-}$. In this case, the iridium (IV) species is reduced to an iridium (III) species which is incorporated into the polymer to maintain charge balance. Hexachloroiridate (IV) is well-known for its oxidizing ability[8] and therefore could be expected to enter into a formal oxidation-reduction mechanism. An alternative mechanism is referred to as "protonic acid" doping. In this mechanism, the polymer is oxidized by the H^+ ions and the iridium (IV) species is concommitantly introduced as an anion to maintain charge balance. The exact mechanism of protonic acid doping is believed to involve the addition of a proton to a carbon atom of the polymer chain which results in the formation of a C-H covalent bond.[9] The protonated carbon is sp^3 hybridized and the resultant positive charge is delocalized along the polymer chain. This mechanism, however, implies an interruption in the backbone conjugation for every charge carrier that is created and would ultimately limit the levels of conductivity that could be reached. Another interpretation of the protonic acid doping of polyacetylene using a species such as dihydrogen hexachloroiridate involves oxidation of this polymer by an active protonic species such as $(H^+)_2(IrCl_6)^{2-}$ as shown in Equation 1 for a doping level of 10 mole percent.

$$(CH)_x + 0.1x(H^+)_2(IrCl_6)^{2-} \longrightarrow \left[CH^{+0.2}(IrCl_6)^{2-}_{0.1}\right]_x + 0.2HB$$

Equation 1

As in the original mechanism of protonic acid doping, the hexachloroiridate species is introduced into polyacetylene as the unchanged iridium (IV) species. Oxidiation of the polymer backbone, however, is not accomplished by addition of a proton to the pi system but involves oxidation of the pi system by transfer of an electron to the active protonic species which, in turn, combines in its reduced form with a molecule B, presumably present in the solvent. Possible by-products (HB) of this reaction are H_2, HCl, and H_2O. The exact fate of the reduced protonic species, however, is still only speculative. The active protonic species plays a similar role as in the solution doping of polyacetylene with nitrosyl salts in which the nitrosyl cation oxidizes the polymer and is released into the solvent with the concommitant introduction of the anion into the oxidized polyacetylene.[10]

We believe that the dominant active dopant species, in this case, is a protonic acid such as

$(H_3O)^{2+}(IrCl_6)^{2-}\cdot 6H_2O$ or a hydrolyzed species thereof and that oxidation of polyacetylene occurs predominantly via the latter protonic acid mechanism.

This mechanism is supported by the following results. First, if the hexachloroiridate (IV) anion were the oxidizing species (mechanism 1), then other salts of $(IrCl_6)^{2-}$, such as the Na, K, Bu_4N salts, would also be effective as dopants for polyacetylene. However, solutions of these salts do not spontaneously dope polyacetylene. Thus, it is only the acid form of hexachloroiridate (IV) that will render polyacetylene conductive. Second, EPR spectra of polyacetylene doped with the iridium salt indicate the presence of the Ir (IV) species which is a d^5 octahedral complex with one unpaired electron.[7] This technique, however, is only sensitive to Ir (IV) and not to the Ir (III) species (which has no unpaired electrons) and therefore does not rule out the presence of the reduced hexachloroiridate (III) anion. The observation of Ir (IV) in the doped polymer does, however, support the protonic acid mechanism.

B. Electrochemical Doping

In comparison to the chemical method of doping polyacetylene with $H_2IrCl_6\cdot 6H_2O$, the hexachloroiridate anion can also be introduced in a much "cleaner" fashion using electrochemical techniques. As mentioned earlier, analysis of chemically doped $(CH)_x$ films revealed a varying Cl/Ir ratio. When polyacetylene is doped electrochemically with tetra-n-butyl ammonium hexachloroiridate (IV), the nature of the dopant is much less ambiguous. For example, as indicated in Table 1, the anion that is incorporated into polyacetylene films during electrochemical oxidation is the $(IrCl_6\cdot 6H_2O)^{2-}$ anion.

Although the chemical analysis of the electrolyte indicates the presence of lower chlorine-iridium ratio species such as $(IrCl_{6-y}(OH)_y)^{2-}$, there was no evidence for their presence in the visible absorption spectra of this material. Thus, their presence is only in minute quantities. Moreover, as evidenced by the chemical analysis of the electrochemically doped $(CH)_x$, they are not incorporated into the film during the doping process. Thus, one obtains the ideal Cl/Ir ratio of 6/1.

Another benefit from the electrochemical insertion of the $(IrCl_6)^{2-}$ species is that higher conductivities are obtained for given levels of doping. For example, at a dopant level of *ca.* 2 mole percent, the conductivity of chemically doped $(CH)_x$ was 1 $(ohm\text{-}cm)^{-1}$ while for the electrochemically doped $(CH)_x$, the conductivity was 100 $(ohm\text{-}cm)^{-1}$. The difference in conductivities is likely due to the different mechanisms of doping. In the chemical doping procedure the lower conductivities may be due to the introduction of some sp^3 hybridized carbons which is an inevitable consequence of using an electrophilic agent such as the acid form of the hexachloroiridate (IV). Thus, by using the electrochemical doping technique, one can insert the hexachloroiridate species and obtain higher conductivities than when the chemical doping method is used.

CONDUCTION MECHANISM

The temperature dependence of the resistivity for *cis*-polyacetylene doped with dihydrogen hexachloroiridate (chemically) and hexachloroiridate (electrochemically) is shown in Figures 1 and 2, respectively. The behavior of the resistivity is $\log \rho \; \alpha \; T^{-\frac{1}{2}}$ whether the polyacetylene is doped via a chemical or electrochemical method. Thus, the method of doping does not seem to be a factor governing the behavior of the resistivity in doped *cis*-polyacetylene. Previously we attributed the $T^{-\frac{1}{2}}$ behavior to a charging energy limited hopping process.[5] Since the temperature dependence of the resistivity of $(CH)_x$ doped with I_2 and Br_2 has a different functional form, our belief that the electrical properties of doped polyacetylene are sensitive to the type of dopant introduced into the polymer during oxidation is reinforced. In the past, we have examined the influence of doping speed on the electrical properties of polyacetylene doped with iodine from solution or by exposure to vapor and found no significant differences in the temperature dependence of the resistivity.[5] In this case, we have shown that the method of doping is also not an important factor in determining the ultimate electrical properties of polyacetylene. Thus, it is the dopant type, its resultant distribution, and the nature of its interaction with polyacetylene which determines the conduction mechanism in this polymer.

DISTRIBUTION OF DOPANT SPECIES

In an earlier publication we focused on the use of the hexachloroiridate species as a "staining" agent for

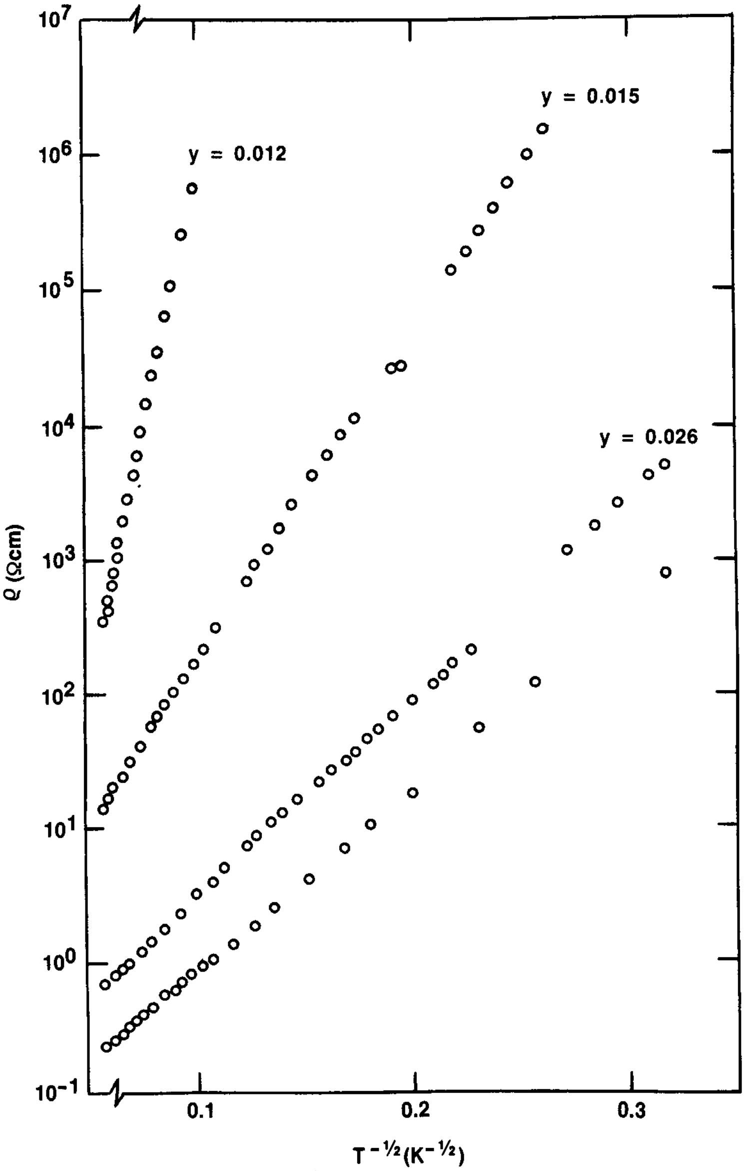

FIGURE 1 Log ρ vs. $T^{-\frac{1}{2}}$ for polyacetylene doped (chemically) with $H_2IrCl_6 \cdot 6H_2O$, y=mole fraction $(IrCl_6)^{2-}$.

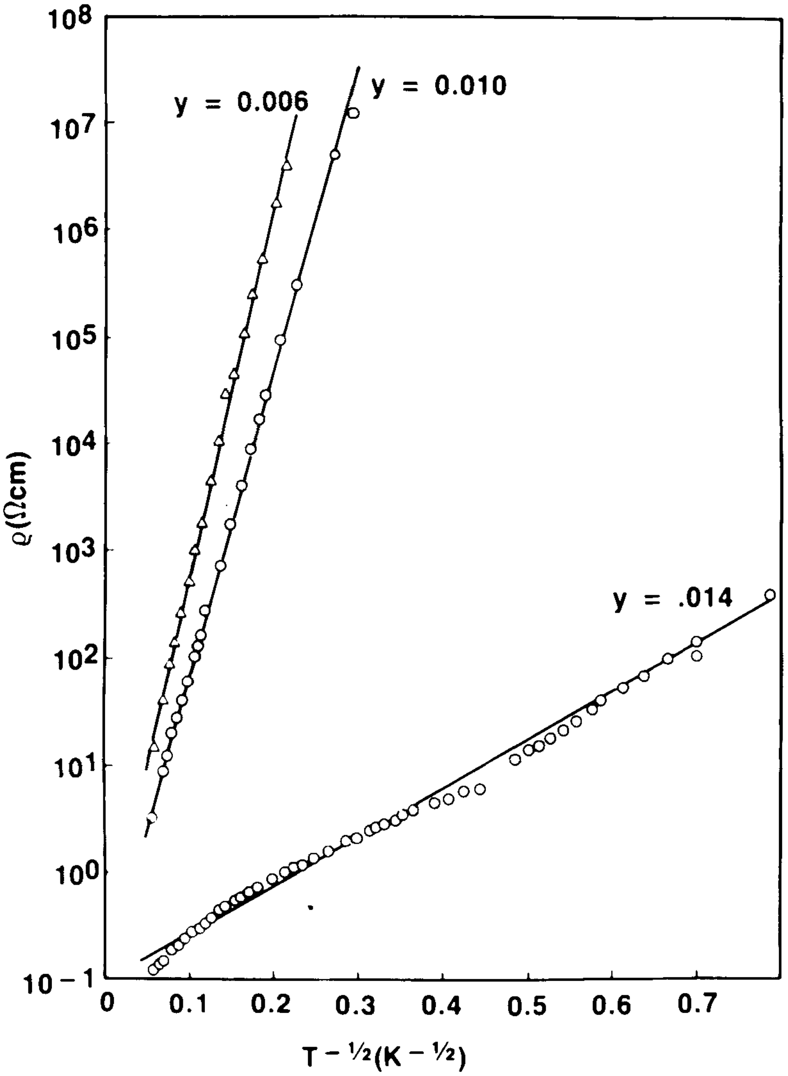

FIGURE 2 Log ρ vs. $T^{-\frac{1}{2}}$ for polyacetylene doped (electrochemically) with $(Bu_4N)_2IrCl_6 \cdot 6H_2O$, y=mole fraction $(IrCl_6)^{2-}$

elucidating the morphology of polyacetylene.[7] Since the hexachloroiridate species is large, its distribution in the polyacetylene matrix will be strongly diffusion controlled (during chemical doping). Transmission electron micrographs showed the dopant predominantly diffused into areas where a larger degree of disorder was expected to be present. This led to an inhomogeneous distribution of dopant on a few hundred angstrom scale.[7] Present also was an inhomogeneous distribution along the fibers. This "fine-scale" inhomogeniety is shown in Figure 3, a transmission electron micrograph of gel-like cis-polyacetylene doped with hexachloroiridate at a level beyond the semiconductor to metal transition.

In electrochemical doping, an extremely high electric field exists at the surface of the polyacetylene owing to the complex fibrillar morphology of polyacetylene.[11] The field is so large that ions (i.e. hexachloroiridate) will be forced into the fibrils during electrochemical oxidation. The transmission electron micrograph of gel-like cis-polyacetylene electrochemically doped with hexachloroiridate is shown in Figure 4. The sample was doped to a level beyond the semiconductor to metal transition and yet there appears to be almost no evidence for a "fine-scale" inhomogeniety. This is in contrast to what is observed for the chemical doping procedure. As stated above, however, the behavior of the temperature dependence of the resistivity was the same whether the polyacetylene was doped via chemical or electrochemical means. Due to the high electric field present during the electrochemical doping procedure, ions are at first uniformly drawn into the fibrils. As each ion makes its way into the fibril, a channel is created such that additional ions may diffuse into the fibril. Therefore, it is possible for ions to aggregate on a scale not resolvable in the transmission electron microscope. Even though the method of diffusion of the ions into the fibrils is different in the two methods of doping, it is the nature of the ion and not the method of doping which determines the conduction mechanism in $(IrCl_6)^{2-}$ doped polyacetylene. The use of electrochemical doping, however, does provide for a more homogeneous distribution of dopant at the 15-200 angstrom level and a higher conducting material is obtained. We also observed a semiconductor-metal transition at a lower dopant concentration for electrochemical doping than in chemical doping. This was also observed by Ikehata et al. by varying the doping rate of polyacetylene with AsF_5.[12]

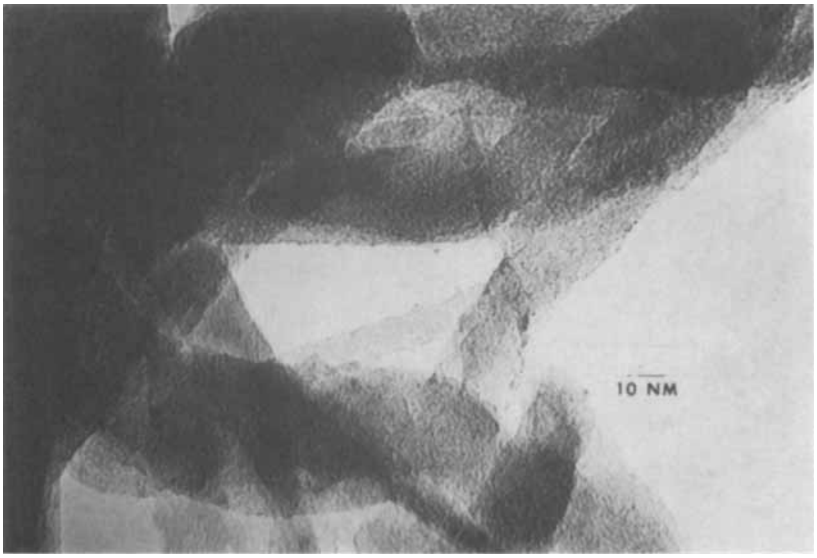

FIGURE 3 Transmission electron micrograph of heavily doped (chemically, with $H_2IrCl_6 \cdot 6H_2O$) _cis_-polyacetylene.

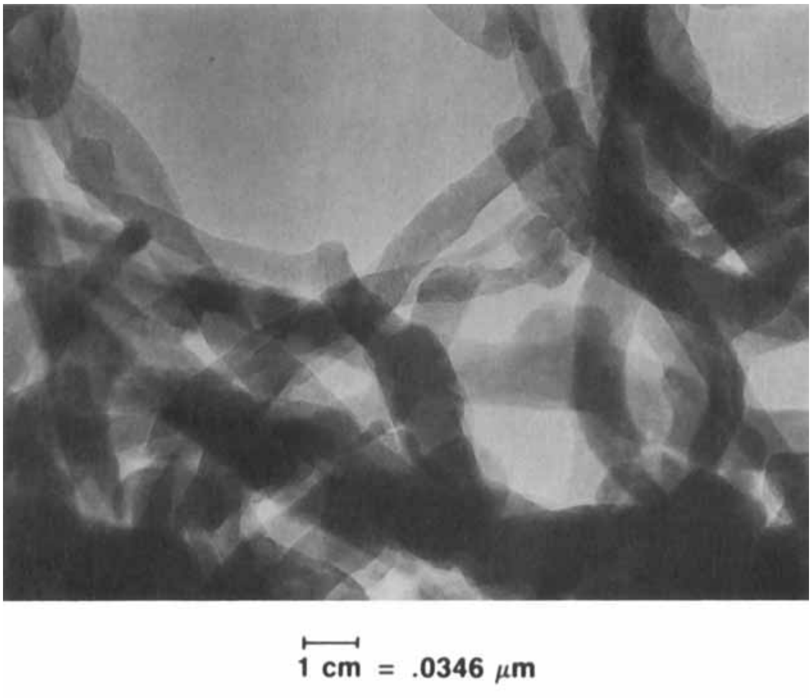

FIGURE 4 Transmission electron micrograph of heavily doped (electrochemically, with $(IrCl_6)^{2-}$) *cis*-polyacetylene.

Slower doping rates resulted in semiconductor-metal transitions at lower levels of doping. Due to the observation that electrochemical doping does provide for a more homogeneous distribution of dopant, it would not be unreasonable to postulate that a dopant does exist in which chemical doping would result in a charging energy limited hopping process and electrochemical doping would result in charge carriers hopping between dispersed atomic sites. This would, of course, imply that the size of this dopant not be so large as to force it to aggregate upon diffusion into the fibril. In other words, a smaller dopant than $(IrCl_6)^{2-}$ but larger than iodine might meet this requirement.

CONCLUSIONS

Comparison of the electrical properties of chemically doped polyacetylene and electrochemically doped polyacetylene in which the hexachloroiridate ion is incorporated into the fibrils indicates the behavior of the temperature dependence of the resistivity does not depend on the method of doping. In both cases the $\log \rho \propto T^{-\frac{1}{2}}$ behavior was observed. Transmission electron micrographs indicate, however, electrochemically doped polyacetylene exhibits far less fine scale inhomogeniety in dopant distribution.

The magnitude of the D.C. electrical conductivity during electrochemical doping is higher than the same level of doping obtained via chemical means. This is most probably due to chemical doping introducing some amount of sp^3 hybridized carbons and thus limiting electrical conduction and a more homogeneous distribution of dopant at the 15-200 angstrom level.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the technical support of Jacque Georger, Jr., Mark Knowles, Patricia Morris, and Kim Ostreicher.

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