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Homogeneous doping and semiconductor-to-"metal" transition in polyacetylene

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The conductivity of iodine-doped *cis*- and *trans*-polyacetylenes was measured as a function of dopant concentration per C—H unit, y, from parts-per-million to the metallic regime. The sharp semiconductor-to-"metal" (S-M) transitions span over only 2 orders of magnitude of y and the $\log\sigma$-vs-$\log y$ relationships for the two isomers are identical over a large portion of the transitional region. The change in thermoelectric power S occurs even more abruptly over only twofold increase in dopant concentration. The midpoints of the transition for σ vs y and S vs y are nearly the same at $y \sim 7\times10^{-4}$. The number of Curie spins decreases rapidly during the transition; the EPR linewidth and line shape of *cis*-polyacetylene were not affected by doping. These behaviors are suggested as indicative of uniform doping. Polyacetylenes, both *cis* and *trans*, doped with AsF_5 by a "slow" method yielded inhomogeneous materials devoid of a distinct S-M transition. Using an improved "cyclic" doping procedure, we obtained homogeneously doped *trans*-$[CH(AsF_5)_y]_x$ which exhibits σ-vs-y and σ-vs-S dependence nearly the same as iodine-doped polymers. The results are interpreted in terms of a phase transition. In lightly doped materials the charged soliton and polaron defects are pinned by the potential of one dopant ion, and these materials are said to be in a glassy state. Conversion to a liquid state takes place when the average separation of uniformly distributed dopant ions is less than the defect domain widths so that a defect interacts with two or more dopant ions. Conduction is probably via electron hopping between the charged soliton and polaron states in the transitional regime. This solition melting transition occurs at about 100-fold lower in dopant concentration than that for the onset of Pauli susceptibility. We were unable to achieve uniform doping of *cis*-polyacetylene with AsF_5.

I. INTRODUCTION

Polyacetylene was first synthesized by Natta, Mazzanti, and Corradini in 1958.[1] Extensive current interest in this material was initiated by the demonstration[2,3] of more than 12 orders of magnitude increase in the conductivity σ and the formation of a metallic state by doping. Novel physics has emerged[4–6] to interpret the properties of polyacetylenes. The topological solition had been invoked to analyze the magnetic resonance,[7–10] magnetic susceptibility,[11–13] infrared,[14–16] and photoconductivity and luminescence[17,18] data for undoped polyacetylenes. A mechanism of conduction involving hopping between neutral and charged solitons (ISH model) had been proposed[19,20] for lightly doped polyacetylenes. The power-law dependence of dc conductivity on tempeature,[21] the $\omega^{0.6}$ and strong temperature dependence of ac conductivity,[22] the effect of pressure on dc conductivity,[23] and the temperature-independent thermoelectric power coefficient, (TEP) S,[23–27] had been cited as evidences in support of the ISH model. Charged solitons have been proposed to be the major carriers.

However, the elegant and coherent soliton-doping hypothesis is cloudy in the transitional region between undoped semiconductor and heavily doped metallic regimes. This uncertainty may be traced to the question of homogeneity of doping and lacking of extensive data for intermediately doped materials. Based on limited data of conductivity and its "activation" energy, and infrared transmission at relatively high dopant concentrations,[2,3] polyacetylene is said to undergo a semiconductor-to-"metal" transition[25] at $y \sim 1-3\times10^{-2}$ (we place metal in quotations to emphasize that the doped polymers merely have high conductivities but are not metals in the classical sense, and y is the number of dopants per C-H unit). Heeger and MacDiarmid[28] suggested that at low concentration the p-type dopants act as acceptors to create localized positive carriers in the gap. When the concentration is increased to a critical level, then the screening from carriers will destroy the bound states giving rise to the semiconductor-"metal" transition. This will occur when the screening length becomes less than the radius of the most tightly bound Bohr orbit of the positive carrier and acceptor in the bulk dielectric medium. The critical carrier concentration is said to be of the order $n_c \sim [(4a_H)^{-1}(m^*/m_e\epsilon)]^3$ where a_H is the Bohr radius, $m^*/m_e \sim 1$, and $\epsilon \sim 10$ for the dielectric constant. It was estimated that $n_c \sim 10^{20}-10^{21}$ cm^{-3} which corresponds to a few percent assuming one carrier per dopant. More recently results obtained by slow doping with fixed amounts of AsF_5 (Ref. 29) indicate a smaller value for n_c.

In contrast to the conductivity data, Pauli susceptibility was observed[13,25] only when y exceeds 6—10%. This implies that the high conductivity of intermediately doped polyacetylenes is not due to free carriers. Theoretical analysis[30] showed that the band gap of polyacetylene is not closed except for very high dopant levels. When *cis*-polyacetylene was lightly doped with AsF_5, the Pauli susceptibility was found to increase linearly with dopant concentration.[31,32] The authors proposed that the doping is nonuniform, that the properties of doped polyacetylenes are dominated by the formation of metallic islands separated by undoped polymer, and that the semiconductor-"metal" transition would be a percolation transition. Moses *et al.*[29] argued that doping of *cis*-polyacetylene is necessarily inhomogeneous because of the associated *cis-trans* isomerization; "only in *trans*-polyacetylene, where the ground state is truly degenerate, is it possible for the doping to proceed uniformly through the formation of low-energy solitons via zero-energy midgap state. Doping of *cis*-polyacetylene would require generation of higher-energy polarons." However, Tomkiewicz *et al.*[32] did observe Pauli susceptibility in *trans*-polyacetylene doped with 0.5 mol % of AsF_5.

It goes without saying that the transport properties of doped polyacetylene cannot be understood unless extensive and careful measurements are made in the transitional doping regime. We have made such determinations, and found nearly the same σ vs y and S vs y dependencies in the intermediate doping levels for both *cis*- and *trans*-polyacetylene doped with iodine and *trans*-polyacetylene doped with AsF_5. These transitions are very abrupt and y_c appears to lie at a much lower concentration than previously reported. These materials also have very similar variations of unpaired spin concentration with y. Since these properties would be different if each polymer has nonuniform and dissimilar distribution of dopant ions, the results imply that homogeneous dopings have been achieved in these systems. In contrast and based on those criteria proposed in this paper, AsF_5 doping of *cis*-polyacetylene is inhomogeneous. These results also suggest that there may be a relationship between the number of dopant ions per effective conjugated polyacetylene chain. The similarities found for the iodine-doped *cis* and *trans* isomers raise doubts concerning the relevance of the mobility of solitons to the transport properties in the transitional regime.

II. EXPERIMENTAL TECHNIQUES

The polyacetylene films used in this work were prepared by polymerization initiated by Ziegler-Natta catalyst.[33–36] The polymer obtained at 195 K is rich in *cis* content ($>88\%$). Strips of freshly synthesized *cis*-polyacetylene were thermally isomerized to the *trans* polymer under an optimum condition of 453 K for 15 min.

A. "Slow" doping

The doping chamber is a glass cylindrical vessel ~ 50 ml in volume and furnished with a stopcock. At the center of the chamber is a four-probe glass insert with appropriate electrical leads. A strip of polyacetylene is mounted on the four-probe glass with Electrodag; additional specimens are placed in this vessel for other measurements.[36]

After the apparatus is thoroughly evacuated and the dopant reached thermal equilibrium with the bath in which it is immersed, the dopant is admitted into the doping chamber through a vacuum manifold. The vapor pressure of the dopant is kept at or below 0.1 Torr for overnight doping of polyacetylene to the "metallic" state. Doping for shorter periods of time gave samples having desired lower doping levels and conductivities.

B. "Cylic" doping

This is the method we feel capable of giving uniform doping with AsF_5. The dopant reservoir is one liter in volume with a finger immersed in a pentane slush bath (143 K) at which temperature the vapor pressure of AsF_5 is less than 0.1 Torr. There is a section of the manifold isolatable by four stopcocks with a volume of $\sim$ 8—10 ml which serves to meter the dopant. After the doping chamber is thoroughly evacuated, the metering section is opened to the AsF_5 reservoir, the stopcock between them is closed, and the stopcock separating the metering section and the doping vessel is opened. This exposes the polyacetylene to AsF_5 at a pressure of about 0.01 Torr. After 15 sec of exposure the system is evacuated. This procedure is repeated until the desired conductivity is reached. For instance, to obtain $[CH(AsF_5)_{0.0001}]_x$ the "cyclic" procedure is repeated about 50 times

C. Assay

For iodine doping, $^{125}I_2$ was used for $y<10^{-3}$, and the polymer radioassayed with a Beckman Gamma 4000 or Packard Gamma Counter. For dopant concentration of $y>10^{-4}$, the level of doping was determined by weight gain. The concentration of AsF_5 was determined by trace elemental analysis for As by Gailbrath Laboratories for $y<10^{-3}$, the precision is $\pm 10\%$ at the lowest doping level by assay of large specimens. Higher levels were determined by weight gain.

D. EPR

EPR spectra were recorded with a Varian Associates X-band spectrometer. The concentration of unpaired spins was obtained by double integration of the spectra and compared with a standard tetramethylpiperidinoxyl solution.

E. Thermopower

Thermoelectric power coefficient was measured by mounting a freshly synthesized rectangular polyacetylene film specimen (from 0.5×0.2 cm^2 to 1.0×0.5 cm^2) between two copper blocks using pressure contracts. The apparatus was enclosed in a nitrogen-filled glove bag. One of the copper blocks was heated to give a temperature difference of 2°—5° measured with a copper-Constantan differential thermocouple, a Keithley 610C electrometer and Keithley 147 nanovolt null detector. The limiting impedance of the measuring system is 10^{11} Ω. For each sample the voltage was measured as a function of internal resistance for 10^1—10^{11} Ω. The value of S was calculated from the voltage value at the midpoint of the V vs R curve. At this point the internal and sample resistances are matched.

F. Electron microscopy

Ultrathin films of polyacetylene of about 100 nm in thickness were polymerized directly onto gold grids[37] for transmission electron-microscopy investigations. Doping of these films was done as described above. A Japan Electric Optic Laboratory 100CX STEM instrument was used for this study.

III. RESULTS

A. Conductivity of iodine-doped polyacetylenes

In the early study of iodine doped *trans*-polyacetylene by Chiang *et al.*,[38] the concentration dependence of conductivity was measured down to $y=0.017$. The data was plotted as $\log_{10}\sigma$ vs y. Extrapolation of this data to the conductivity of undoped polymer led the authors to conclude that the semiconductor-to-"metal" (*S-M*) transition occurs at dopant concentration of a few percent. In contrast, Mihaly *et al.*[39] found for iodine doped *cis*-polyacetylene a linear $\log_{10}\sigma$ vs $\log_{10}y$ from $y\sim5\times10^{-4}$ to 0.2, without any indications of a *S-M* transition. The first study did not extend to low dopant concentration and the latter investigation seems to have been made on inhomogeneously doped specimens. We have carried out extensive conductivity measurements on polyacetylenes doped from very low (ppm) concentrations to the "metallic" regime.

The results on *trans*-$[\mathrm{CHI}_y]_x$ are shown in Fig.1; also included are other literature data.[38,40,41] Between $y=1.2\times10^{-6}$ and 10^{-4}, the values of σ_{RT} remained constant and are not significantly different from that of undoped *trans*-polyacetylene. There is a gradual increase of conductivity when y exceeds 10^{-4}. The $\log_{10}\sigma_{\mathrm{RT}}$ vs $\log_{10}y$ relationship becomes linear between $10^{-3}\lesssim y\lesssim10^{-2}$ for a 10^4 increase in σ_{RT}. Above $y=10^{-2}$, σ_{RT} continues to increase steadily but more gradually until the saturation value is reached.

The undoped *cis*-polyacetylene has σ_{RT} about 10^{-4} lower than the *trans* polymer. It remained constant until $y\sim10^{-5}$, above which level σ_{RT} increases rapidly (Fig. 2). The saturation doped *cis*-$[\mathrm{CHI}_y]_x$ has σ_{RT} higher than the *trans* isomer.

The conductivity of polyacetylene at a given dopant concentration is sensitive to the rate of doping. In general, rapid doping yields polymer with higher conductivity than slowly doped materials of the same dopant concentration below the transitional region and the converse was found above the transition. However, we have not made a systematic investigation of this behavior, i.e., σ vs y as a function of the dopant pressure and doping time.

Mossbauer,[42,43] Raman,[44] and photoelectron[45,46] spectroscopic data showed iodine dopant to be present mainly as I_3^- ions but also in the form of I_5^- ions at a very high level of doping. We recast and combine the results of Figs. 1 and 2 into Fig. 3 in the form of $\log_{10}\sigma$ vs $\log_{10}y$ (I_3^-) for two purposes: one is better comparison with data of AsF_5-doped polyacetylene; the other is to show how remarkably the same are the conductivities of *cis*- and *trans*-polyacetylenes in the dopant concentration ranges of $1.8\times10^{-4}\leq y(\mathrm{I}_3^-)\leq10^{-2}$. This agreement implies the same increase in carrier mobilities with doping for the two

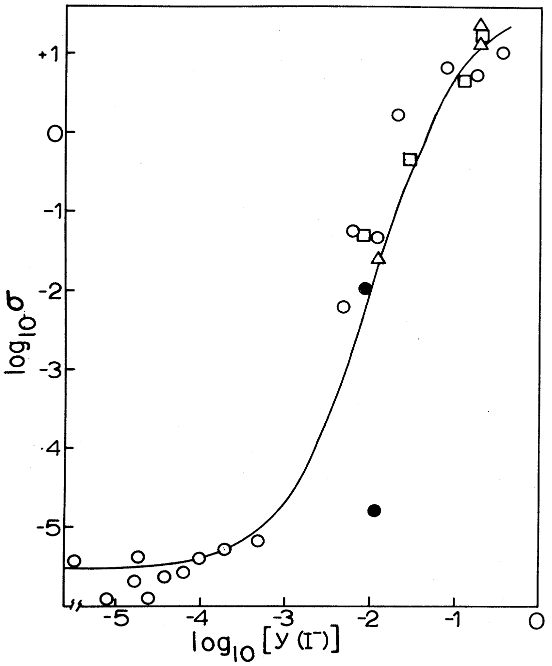


FIG. 1. Variation of conductivity with y for *trans*-$[\mathrm{CHI}_y]_x$: (○) this work; (□) Epstein *et al.* (Ref. 40); (●) Sichel *et al.* (Ref. 41); (△) Chiang *et al.* (Ref. 38).

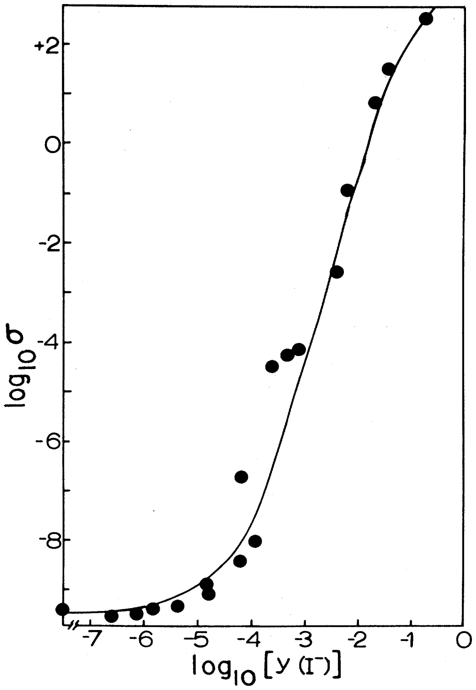


FIG. 2. Variation of conductivity with y for *cis*-$[\mathrm{CHI}_y]_x$.

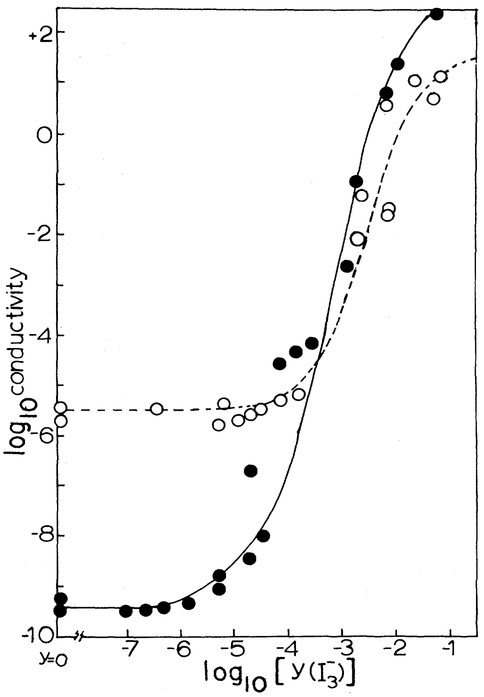


FIG. 3. Replot of the data in Figs. 1 and 2 in the form of σ_{RT} vs y (I_3^-): ○, *trans* polymer; ● *cis* polymer.

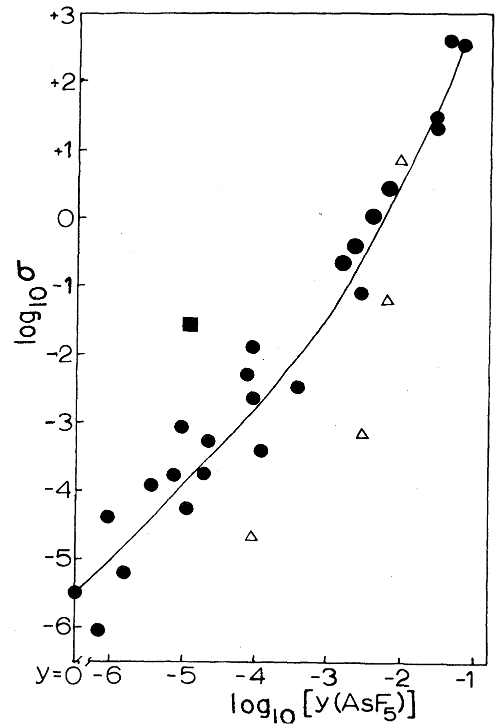


FIG. 4. Variation of conductivity with y for *trans*-$[CH(AsF_5)_y]_x$: (●) doped with "slow" procedure; (■) doped rapidly; (△) data of Park *et al.* (Ref. 25).

isomers. The midpoint of the *S*-*M* transition appears to occur at $y(I_3^-) \sim 10^{-3}$. Recently at the Les Arcs meeting, Schneider, Wortmann, and Kaindl reported that some small amount of I^- ion may be present in $[CHI_{<0.014}]_x$ samples.

B. "Slow" AsF_5-doped polyacetylenes

In cognizance of the possibility of inhomogeneous doping with AsF_5, various laboratories had developed "slow" doping procedures similar to that described in Sec. II A. We have measured the conductivity of *cis*- and *trans*-polyacetylene doped with AsF_5 by the slow method. The results for the *trans* isomer are given in Fig. 4. Below $y < 10^{-4}$ we found $\sigma \alpha y^{1.25}$; above $y > 10^{-3}$ the conductivity increases more rapidly with dopant approximately to the 1.9th power. There is no clear *S*-*M* transition. The results for *cis*-$[CH(AsF_5)_y]_x$ are even more surprising (Fig. 5). The $\log_{10}\sigma$ vs $\log_{10}y$ plot is nearly linear for $10^{-6} \leq y \leq 0.14$ with a slope of about 2.3. These results may be interpreted as the formation of metallic domains by the slow AsF_5 doping procedure even at the lowest dopant concentration. Increasing doping produces more and larger metallic islands. The absence of a percolation threshold suggests that conduction between the domains is possible even at low dopant concentrations, for instance if the metallic domains were preferentially formed near the surface of the polyacetylene fibrils.

C. "Cyclic" AsF_5-doped polyacetylenes

Because doping at ambient temperature by <0.1 Torr of AsF_5 resulted in apparently heterogeneous materials,

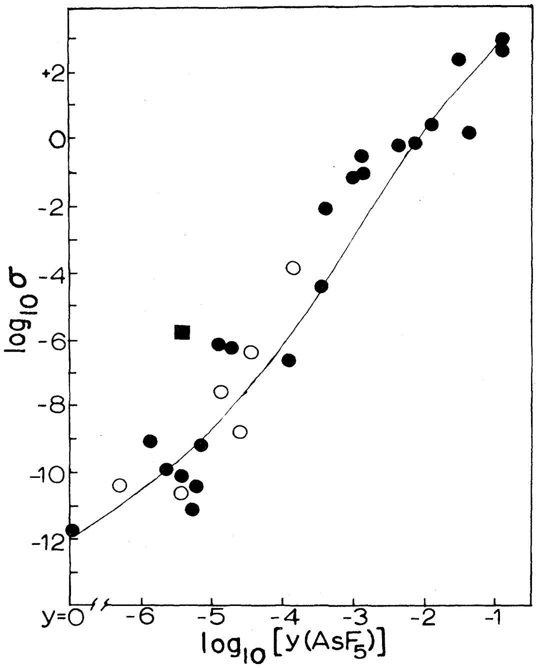


FIG. 5. Variation of conductivity with y for *cis*-$[CHI(AsF_5)_y]_x$ doped with various methods: (●) "slow" procedure; (■) rapid doping; (○) "cyclic" method.

we have carried out doping with the polymer specimen kept at lower temperatures down to 195 K. However, no significant differences in doped conductivities were observed for polyacetylene kept at different temperatures during doping.

MacDiarmid pointed out to us that one of the side products of AsF_5 doping is AsF_3 which is a gaseous substance but not a dopant for polyacetylene:

$$2[CH]_x + 3y AsF_5 \rightarrow 2[CH(AsF_6)_y]_x + y AsF_3 \ . \quad (1)$$

It is possible that AsF_3 may act as a barrier against the infusion of AsF_5. Consequently, a "cyclic" procedure[47] described in the experimental section was used to remove by evacuation AsF_3 or other unknown side products which may impede the diffusion of AsF_5 into the polymer fibril.

The results of σ_{RT} vs y for "cyclic" doped *trans*-$[CH(AsF_5)_y]_x$ are shown in Fig. 6. For comparison, the results for *trans*-$[CH(I_3)_y]_x$ are given as the dashed curve. The two sets of data are in agreement within experimental error and sample to sample variation. We might add that these sigmoidal curves are very similar to the $\log_{10}\sigma$ vs $\log_{10}y$ for polyacetylenes electrochemically doped with ClO_4^- under conditions where equilibrium is known to have been reached.[48] When this "cyclic" method was applied to dope *cis*-polyacetylene, the $\log_{10}\sigma$ vs $\log_{10}y$ dependence is not noticeably different from that shown in Fig. 5.

D. Thermoelectric power.

Park *et al.*[24] first reported the thermopower for undoped *trans*-polyacetylene to be 900±50 $\mu V K^{-1}$. We have made measurements on numerous samples of many different polymer synthesis and found S to have higher values of 1450±150 $\mu V K^{-1}$. A possible cause for the difference is the method of determination or the impedance of the apparatus which is higher in ours. Another source of the discrepancy may be the lower concentration of intrinsic carriers present in our undoped polymers. Very low levels of iodine doping cause a gradual decrease of S (Fig. 7). Precipitous decrease of S occurs between 4.5×10^{-4} and 10^{-3} for $y(I_3^-)$. The former results imply only slight increases of the number of carriers at low dopant concentration. In this region AsF_5 and I_2 dopings differ somewhat. The value of S is 1050±50 $\mu V K^{-1}$ for AsF_5-doped *trans*-polyacetylene at $y = 4 \times 10^{-6}$. In other words, at ppm AsF_5 doping, the thermopower is close to the values found by Park *et al.*[24] for the undoped polymer. Figure 7 showed that S is relatively constant at ~ 900 $\mu V K^{-1}$ for $10^{-5} < y < 3 \times 10^{-4}$. As in the iodine case, thermopower drops very sharply between y of 4.4×10^{-4} and 9×10^{-4}. Very heavily iodine-doped polymer has slightly larger S values than heavily AsF_5-doped *trans*-polyacetylene. These results showed the S-M transition for the intrinsic transport property of polyacetylene fibrils is very abrupt spanning only about twofold changes in dopant concentration. The transitions are comparably sharp for iodine- and AsF_5-doped *trans*-polyacetylenes with nearly the same midpoints for the transitions.

E. Electron microscopy

We have developed the method of direct polymerization onto gold electron microscopy (EM) grids.[37] The resulting polyacetylene films are less than 100 nm thick and contain only microfibrils and fibrils of about 3 and 20 nm in average diameter, respectively.[49,50] This afforded specimens with nascent morphology, not perturbed or modified by

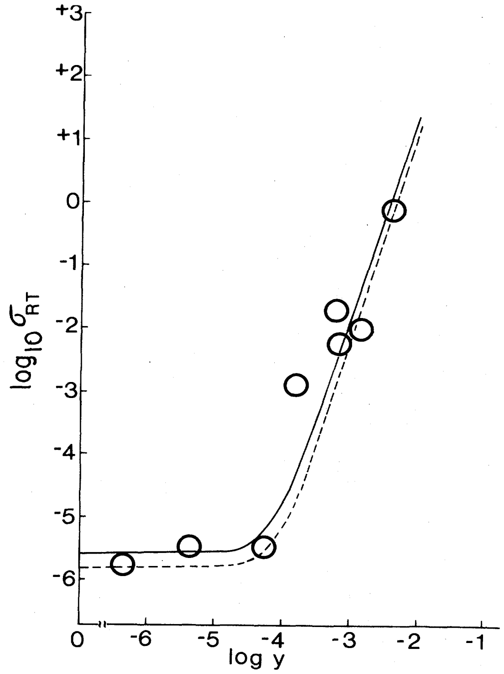


FIG. 6. Variation of conductivity with y for *trans*-$[CH(AsF_5)_y]_x$ doped with the "cyclic" procedure. Broken curve is that of *trans*-$[CH(I_3)_y]_x$.

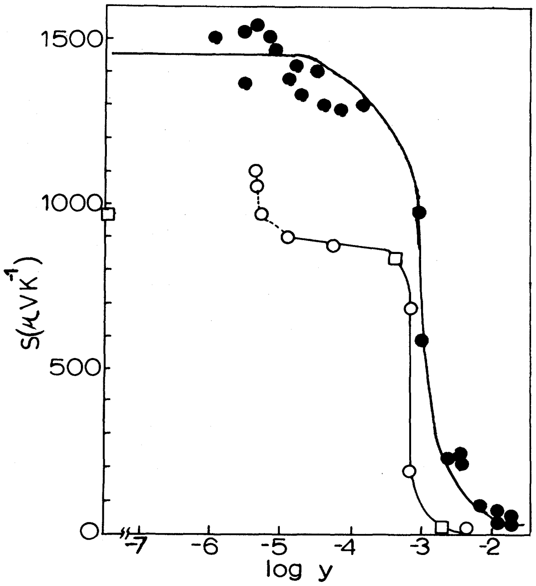


FIG. 7. Variation of S vs $\log_{10}y$. (○) *trans*-$[CH(AsF_5)_y]_x$: (●) *trans*-$[CH(I_3)_y]_x$. (□) *trans*-$[CH(AsF_5)_y]_x$ from Ref. 21.

handling or exposure to environment. We have doped such ultrathin film and obtained direct transmission EM.

For *cis*-polyacetylene doped with iodine to intermediate level, Fig. 8(a) showed fusion of the large diameter fibrils. This is especially noticeable where the density of fibrils is high. The small-diameter microfibrils showed local and irregular swelling along its length. When polyacetylene is doped to maximum level, Fig. 8(b) showed greatly swollen and fused fibrils. All the microfibrils had disappeared unless the smallest entity in this figure represents the swollen microfibrils. This is improbable because it would represent more than a tenfold increase in diameter. More likely, mi-

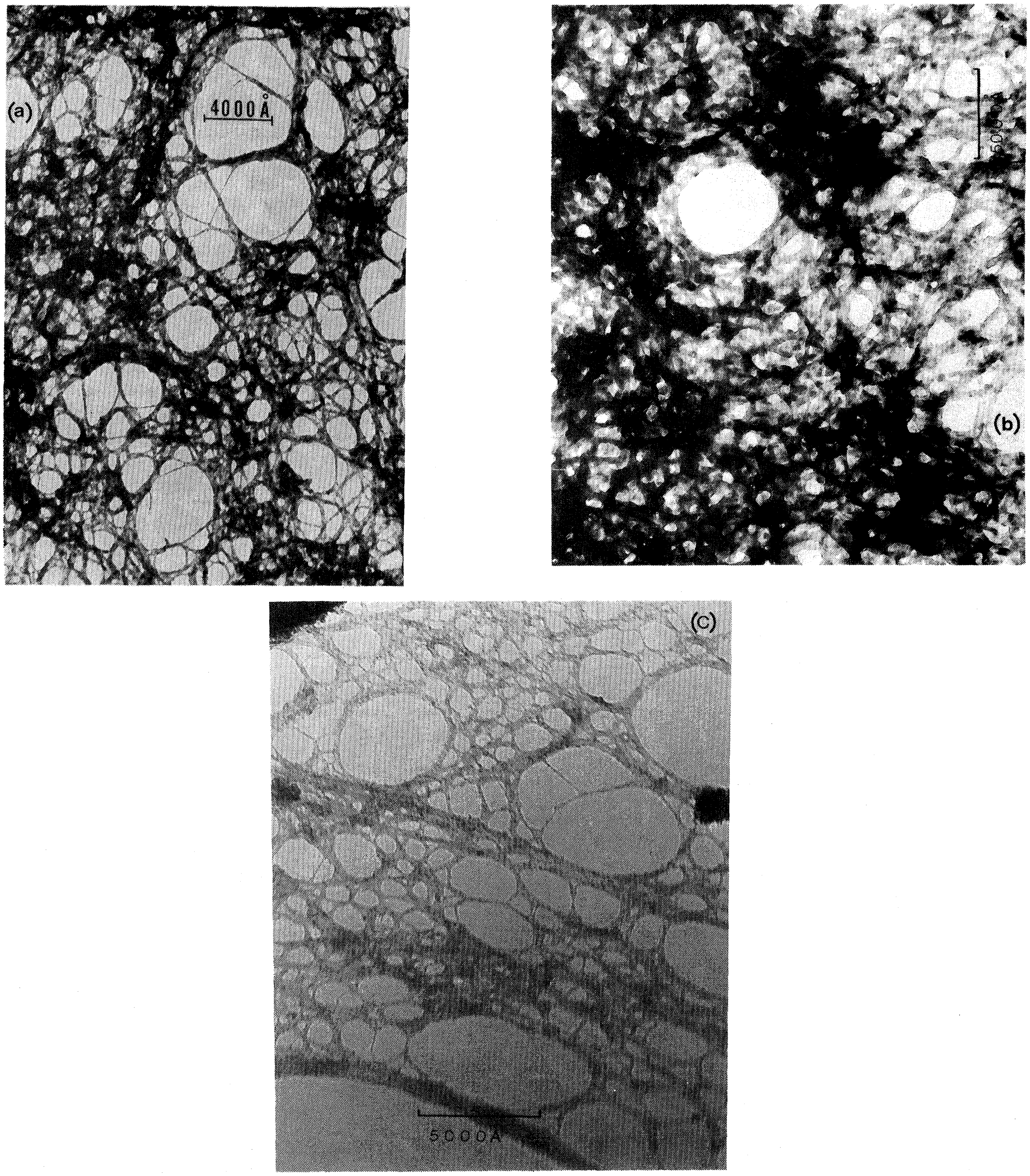


FIG. 8. Electron micrographs of *cis*-polyacetylene doped with iodine: (a) doped to intermediate level observed at 298 K; (b) doped to maximum level observed at 123 K; (c) doped very slowly with iodine and then kept at 195 K for 8 d, observed at 298 K.

crofibrils have fused with others upon doping. In both Figs. 8(a) and 8(b) there were very dark regions which may be due to high concentrations of dopant. Figure 8(c) is particularly interesting. The ultrathin polyacetylene was doped more slowly than the specimens shown in Figs. 8(a) and 8(b). Except for a few dark spots which may be due to catalyst residue, the remainder of the micrographs showed very uniform doping. Where fibrils are aggregated, they appeared to be fused together. However, the microfibrils remained; some of them have uniform appearance throughout their lengths while others do not.

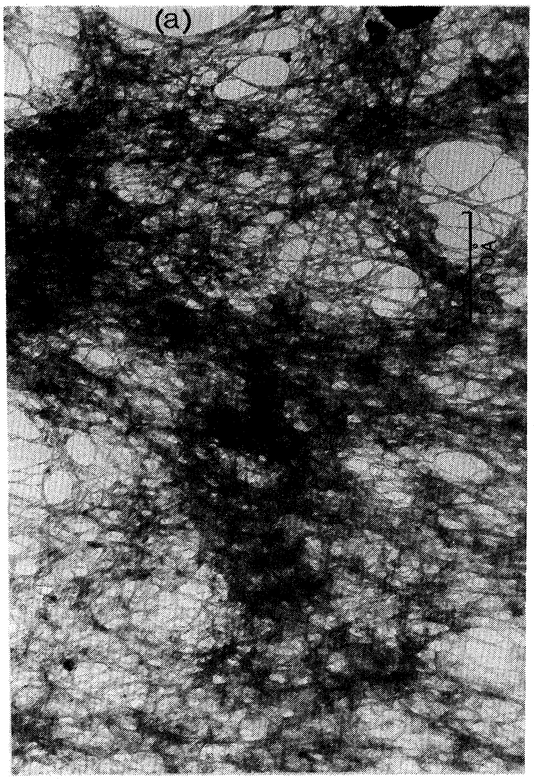
The results of the effect of iodine doping on the morphology of ultrathin film of *trans*-polyacetylene (Fig. 9) are essentially similar to those described above for the *cis* polymer.

Figure 10 showed the morphology of AsF_5-doped *cis*-polyacetylene. At intermediate levels of doping there was swelling and fusion of fibrils and the doping appeared to be nonuniform [Fig. 10(a)]. At heavy levels of AsF_5 doping [Fig. 10(b)] the polymer fibrils appeared to be fused into a more or less continuous mass. The dark spots found here and there are probably metallic domains. Except for a few microfibrils and fibrils, the remainder of the specimen no longer has a discernible fibrillar morphology. Epstein *et al.*[51] had also observed swollen polyacetylene fibrils upon doping, the degree of swelling was said to be greater for AsF_5 than iodine doping.

F. EPR

Neither the EPR intensity nor the linewidth of *trans*-polyacetylene is affected by light iodine doping up to $y(I_3^-) \sim 3\times10^{-4}$. The signal is symmetric and its linewidth is independent of microwave power. This is in contrast to undoped *trans*-polyacetylene whose EPR linewidth of the neutral defect increases with increasing microwave power.[10] The EPR intensity begins to decrease rapidly for $y(I_3^-) > 3\times10^{-4}$ and none was observable for $y(I_3^-) > 7\times10^{-3}$. Whereas the sample-to-sample variability of unpaired spin concentration for undoped *trans*-polyacetylene is a factor of 3, iodine-doped polymers appear to have spin concentrations which have smaller variability of $\sim \pm 30\%$.

Iodine-doped *cis*-polyacetylene has EPR intensity about an order of magnitude less than that in the *trans*-polyacetylene. The sample-to-sample variability of unpaired spin concentration is about a factor of 3 at all levels of doping. Thus, unlike the case of *trans*-polyacetylene, iodine doping did not eliminate the scattering of EPR measurements in *cis*-polyacetylene. Explanations for these different behaviors had been given previously.[10] The EPR intensity starts to decrease at about $y = 3\times10^{-4}$ but because of the initial low number of unpaired spin and its broad linewidth the decrease can neither be followed with accuracy nor to a high level of doping (Fig. 11). The EPR signal disappears at $y(I_3^-) > 3\times10^{-4}$. This change can be better observed by following the EPR amplitude with time of doping a sample directly in the EPR cavity (Fig. 12). The amplitude was constant but decreases rapidly after 2 min of doping. It is estimated that under these particular conditions, the poly-



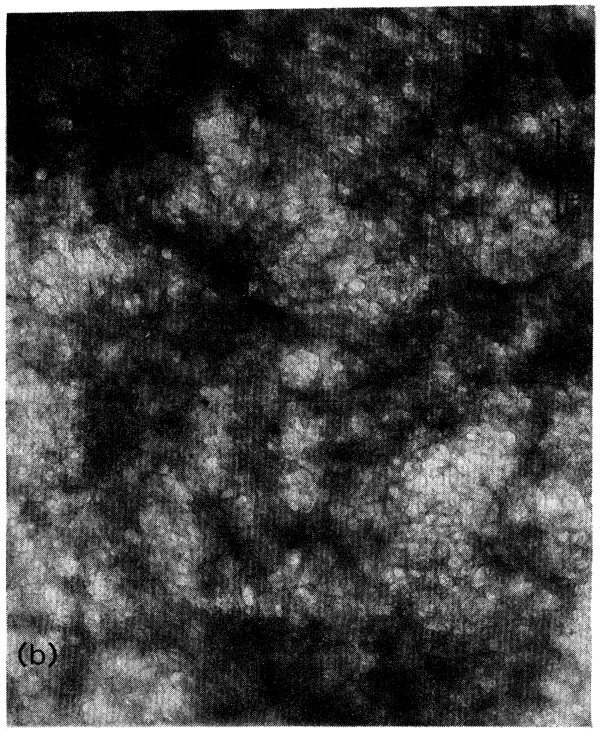


FIG. 9. Electron micrographs of *trans*-polyacetylene doped with iodine: (a) lightly doped for 5 sec at 296 K; (b) heavily doped.

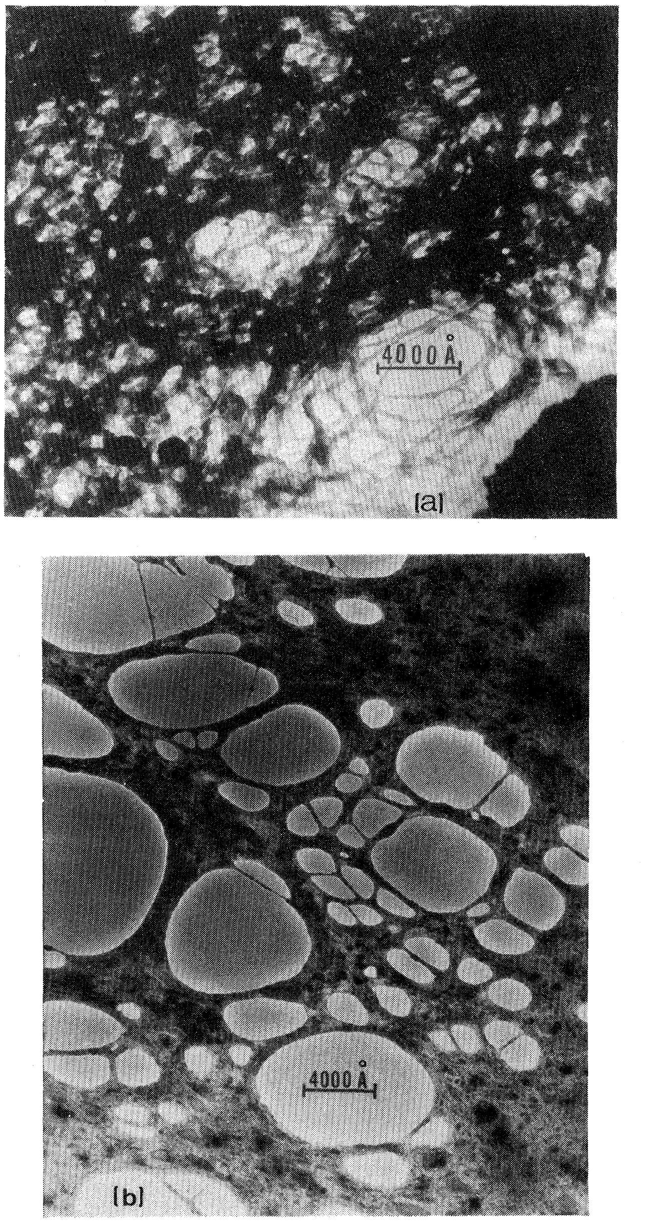


FIG. 10. Electron micrographs of *cis*-polyacetylene doped with AsF_5: (a) intermediate doping level; (b) heavily doped.

mer was doped to $y(I_3^-) \sim 3 \times 10^{-4}$.

All the EPR spectra of *cis*-$[CHI_y]_x$ have a Lorentzian line shape. Furthermore, the linewidth is constant at 6—7 G for all levels of doping. This shows that no extensive *cis-trans* isomerization occurred at $y(I_3^-) = 7 \times 10^{-3}$. Otherwise the spectra would show a narrow component (*vide infra*). In other words, doping probably causes local isomerization of a segment of the chain, the length of the isomerized segment is not sufficiently long to cause motional narrowing of the EPR linewidth of the $S = \frac{1}{2}$ soliton. Therefore, introduction of a dopant does not seem to result in the isomerization of the entire chain.

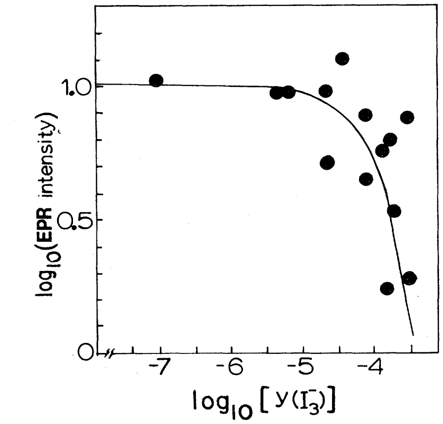


FIG. 11. Variation of EPR intensity vs doping for *cis*-$[CH(I_3)_y]_x$.

The variation of unpaired spin concentration with AsF_5 doping of *trans*-polyacetylene is shown in Fig. 13. For samples of *trans*-$[CH(AsF_5)_y]_x$ for $0 < y < 5 \times 10^{-3}$, the EPR intensity obeys Curie law dependence increasing by a factor of 2 when temperature is lowered from 298 to 133 K. Therefore, there is no Pauli susceptibility. Also included are the data of Ikehata *et al.*[52] The spin concentration remained relatively constant up to $y \sim 10^{-3}$, though there is much more scattering than those of iodine doping. The EPR intensity decreases rapidly for $y > 10^{-3}$.

In the case of *cis*-polyacetylene, doping with AsF_5 even using the "cyclic" procedure, one often observes four general types of EPR line shapes depending upon the dopant concentration. The spectra in Fig. 14 are representative of (a) undoped *cis*-$[CH]_x$; (b) $y \simeq 0.005$ which contains both a broad and narrow component; (c) samples doped in the range $0.008 < y < 0.02$ which is like the diffusive neutral defects in *trans*-polyacetylene; and (d) heavily doped "me-

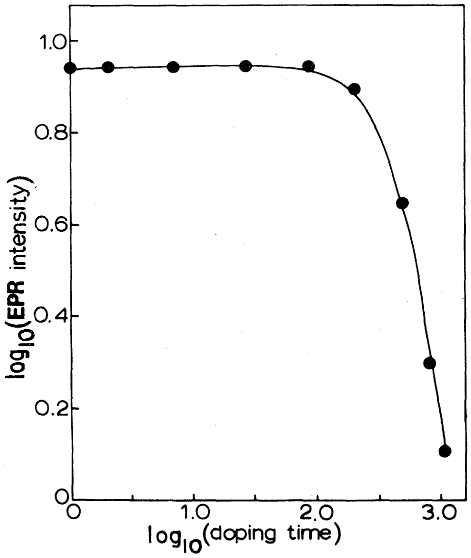


FIG. 12. Variation of EPR intensity with time doping (in min) of *cis*-polyacetylene with iodine.

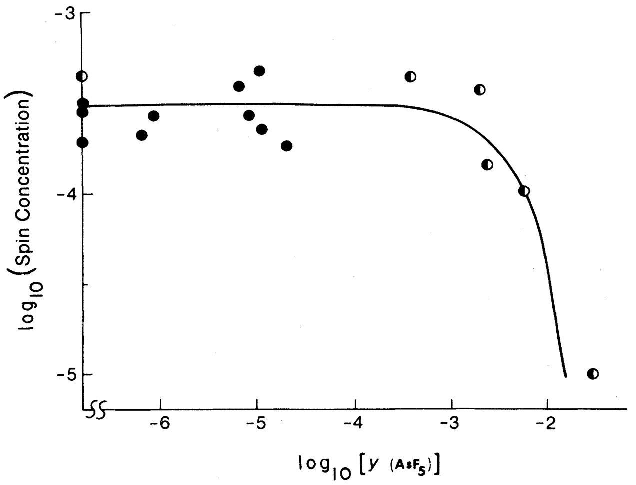


FIG. 13. Variation of EPR intensity vs doping with AsF_5 of *trans*-polyacetylene: (●) this work; (○) data of Ikehata *et al.* (Ref. 52).

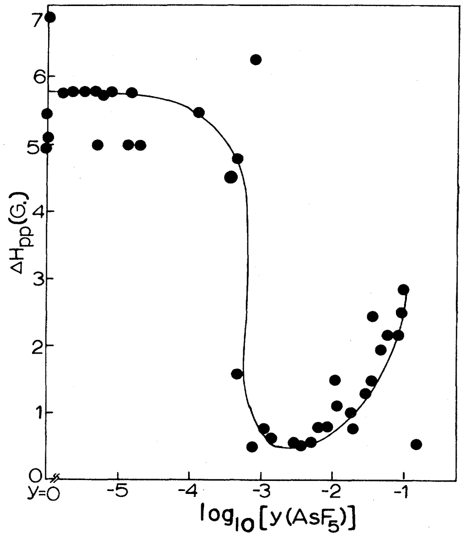


FIG. 15. Variation of EPR linewidth of *cis*-$[CH(AsF_5)_y]_x$ with doping level.

tallic" material displaying Dysonian line shape. Francois *et al.*[53] reported similar results for sodium doping of *cis*-polyacetylene. Figure 15 shows the linewidth change with AsF_5 doping of *cis*-polyacetylene. ΔH_{pp} is $\sim$ 6 G for $y < 10^{-4}$ but narrowed dramatically to $\sim$0.5 G at $y \sim 10^{-3}$. It is in this transitional region where EPR shows both the broad and narrow components. The linewidth increases with further doping due to development of a Dysonian line shape (Fig. 16). These results can be interpreted to mean that a small fraction of the polyacetylene chains were extensively or completely isomerized by AsF_5 doping at $y = 10^{-3}$ even though there may be only about 15% *trans* structure in *cis*-$[CH(AsF_5)_{0.03}]_x$ overall as indicated by ^{13}C NMR results. The failure to observe the broad EPR of the unpaired spins in the *cis* structure at a much higher doping level is due to the following. Isomerization creates more neutral defects in the *trans* segments, and the neutral solitons in the *trans* chains have EPR linewidths less than a tenth of that in the *cis* chains. Taken together, the latter signal became too weak to be discerned from the baseline as the in-

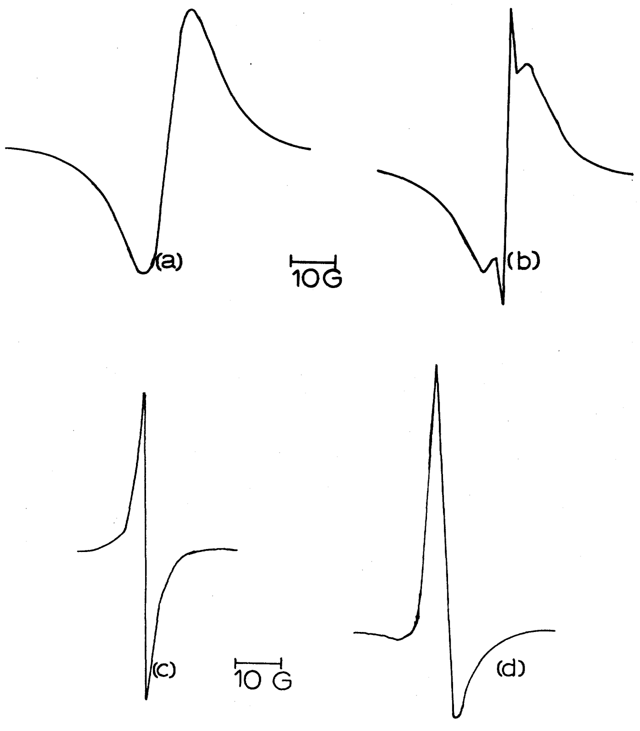


FIG. 14. EPR spectra of *cis*-$[CH(AsF_5)_y]_x$ at room temperature: (a) $y=0$; (b) $y=5\times10^{-4}$; (c) $8\times10^{-3}\le y\le0.02$; (d) $y\sim0.08$.

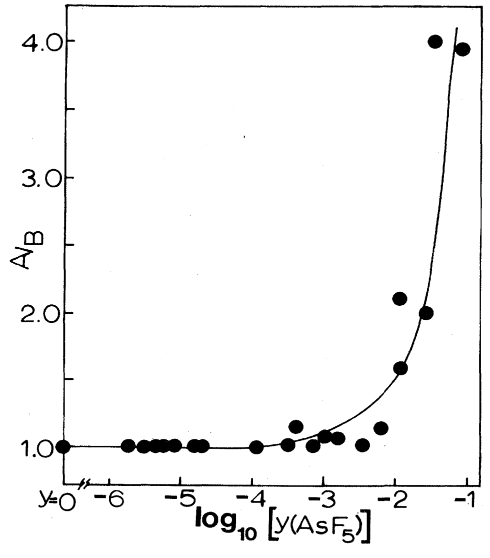


FIG. 16. EPR asymmetry of *cis*-$[CH(AsF_5)_y]_x$ with doping level.

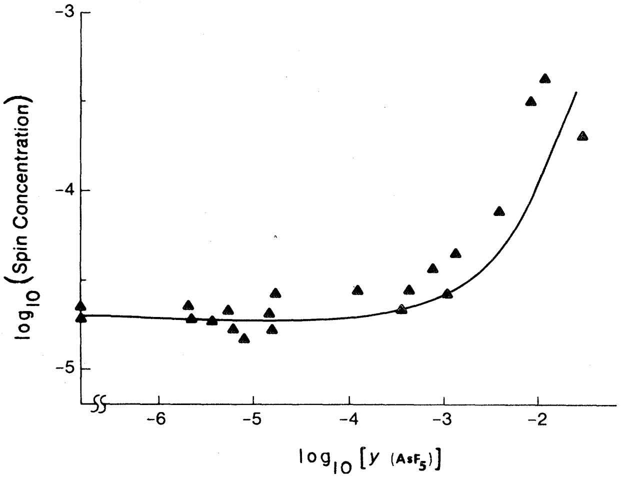


FIG. 17. Variation of unpaired spin per C—H unit vs doping with AsF_5 for *cis*-polyacetylene.

strument gain is reduced to record the growth of the narrow component.

The variation of spin concentration with doping for *cis*-$[CH(AsF_5)_y]_x$ is shown in Fig. 17. The temperature dependence of EPR intensity was measured for $0<y<10^{-2}$. It increases by about 1.3-fold when the temperature was lowered from 298 to 133 K. Consequently, there may be some contribution of Pauli susceptibility. The EPR intensity increases for $y>10-3$ and reaches a concentration comparable to that of undoped *trans*-polyacetylene at $y \sim 10^{-2}$. A few representative EPR saturation curves for *cis*-$[CH(AsF_5)_y]_x$ are shown in Fig. 18; the EPR cannot be saturated for $y>0.018$. Table I gives the relaxation results for those samples which could be saturated. The linewidths are quite close to those found for the solitons in *trans*-polyacetylene. The signals probably arise from defects in the *trans* regions of the *cis* polymer. The values of T_1 are much smaller compared to those of *trans*-$[CH(AsF_5)_y]_x$ at a similar doping level.[10]

IV. DISCUSSION OF RESULTS

A. Doping uniformity

The crystalline fibrillar morphology of polyacetylene renders the material inherently susceptible to nonuniform doping. Uniform dopant distribution can result if either the rate of dopant diffusion is faster than its fixation by charge transfer or there is a redistribution by migration of the charge on the polymer chain and of the dopant ion. Both these possibilities are likely for iodine. The linear I_3^- ions are cylindrical in shape which can probably move from one intercalated position to another. Iodine is not a strong electron acceptor and iodine doping of poly(methylacetylene)[54] and poly(ferrocenylene-phenylene-vinylene-phenylene)[55] are reversible processes, i.e., the dopant can be quantitatively removed from the polymers. The trigonal bipyrimidal AsF_5 is approximately spherical in shape with a large diameter[41]; it is also a very strong electron acceptor. Consequently, uniform doping is generally more difficult to achieve with this dopant.

TABLE I. EPR relaxation data for *cis*-$[CH(AsF_5)_y]_x$.

y	ΔH_{pp}^0 (G)	T_1 (sec)	T_2 (sec)
0	~ 7	5.6×10^{-6}	9.3×10^{-9}
2×10^{-3}	~ 0.5	7.7×10^{-8}	1.3×10^{-8}
5×10^{-3}	~ 0.8	7.9×10^{-8}	8.2×10^{-8}
8×10^{-3}	~ 0.8	3.0×10^{-8}	8.2×10^{-8}

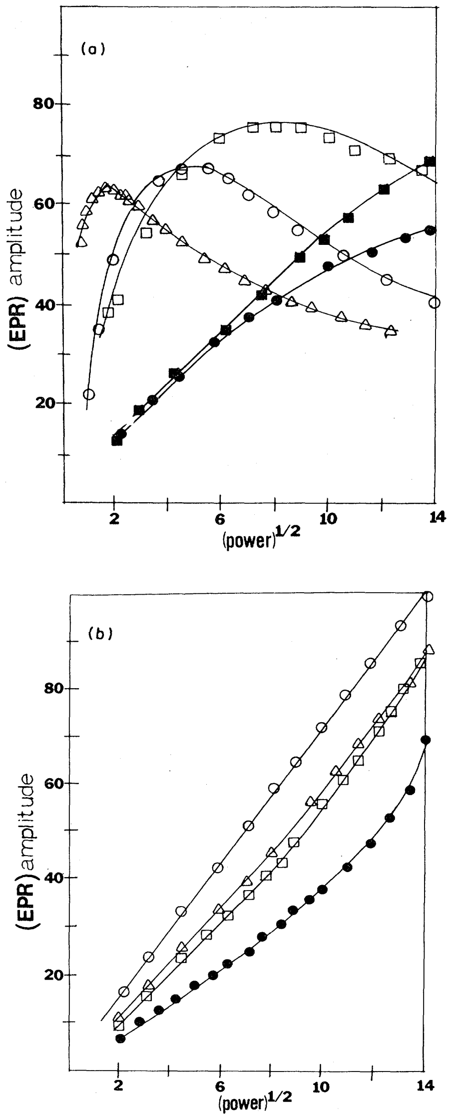


FIG. 18. EPR saturation curves at room temperatuare for *cis*-$[CH(AsF_5)_y]_x$ for y values: (a) (△) 0; (○) 5×10^{-3}; (□) 8×10^{-3}; (●) 1.8×10^{-2}; (■) 3.3×10^{-2}; (b) (○) 4.8×10^{-2}; (△) 6.5×10^{-12}; (□) 7.9×10^{-2}; (●) 9.4×10^{-2}.

Doping of polyacetylene does not form definite stoichiometric complexes as, for instance, in the case of alkali-metal intercalation compounds of graphite. Consequently, homogeneous or uniform doping of polyacetylene does not have a precise chemical meaning; they refer rather to the statistical spatial distribution of the dopant ions.

As such a sample may appear to be homogeneous by one measurement but not by another. Therefore, a doped polyacetylene specimen can only be said to be relatively more or less uniform than another which may depend on the subjective view of the investigator. This is not to deny the need to set forth some criteria.

An *a priori* hypothesis is that the charged carriers in lightly doped polyacetylenes have low mobility. In the soliton and polaron concepts, they are strongly pinned. The material may be considered to be in a glassy state. i.e., soliton glass or polaron glass. The very large increase in carrier mobility reflected in the abrupt change in thermopower may be viewed as a melting of the glassy state or unpinning of the charged species. A phase transition can be said to take place. Herein lies the basis for our proposed criteria for doping uniformity. In the pretransitional region, the transport properties should either remain constant or change gradually depending upon the number of intrinsic carriers as compared to injected carriers. During the phase transitions the transport properties should change as sharply as possible with the smallest increments in doping levels. Such changes should be relatively independent of the particular dopant as long as the same doping mechanism applies and the amount of charge transferred per dopant is comparable. A corollary is that if the changes in properties in the transitional regime are grossly different for two dopants, then either one or both doped polyacetylenes are nonuniform.

Certain EPR characteristics seem to be associated with heterogeneity in doping, such as the appearance of a new component in the spectra, large increase of EPR intensity, and the emergence of a Dysonian line shape, all at relatively low doping level of less than a percent. In addition, the observation of Dysonian EPR of very large A/B ratio is indicative of presence of metallic domains. Large A/B asymmetry corresponds of $T_D/T_2 \gg 1$, where T_D is the time it takes the electron to diffuse through the skin depth δ and $T_D = (3\delta^2/2V\Lambda)$ with V being the velocity of the electron and Λ its mean free path. Since δ is small for metals and if the entire specimen is uniformly metallic, then EPR cannot be observed because the microwave radiation is unable to penetrate the material.

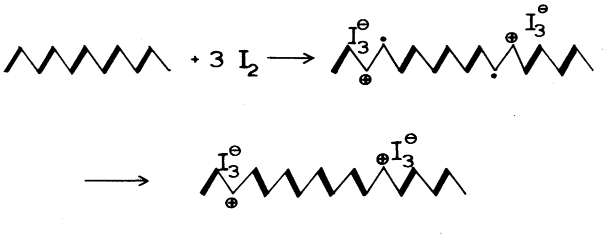
According to the above criteria, we believe that both *cis*- and *trans*-polyacetylenes can be doped uniformly by iodine. The σ vs y curves for the two systems in the transitional regime are nearly superimposable (Fig. 3). The unpaired spin concentrations remain constant at very low doping level, begin to decrease at $y(I_3^-) \sim (1-3) \times 10^{-4}$, and become too small to measure at 10 times these dopant concentrations. There was never in the case of *cis*-$[\mathrm{CHI}_y]_x$ a narrow linewidth component in the EPR spectra of these polymers. It is generally recognized that the conductivity of doped polyacetylenes can be limited by interfibril resistance. So, as one might expect, the S vs y change is more abrupt than the σ vs y dependence. For *trans*-$[\mathrm{CHI}_y]_x$, most of the decrease in S with doping occurs within about a factor of 2 increase in y. Similar measurements on *cis*-$[\mathrm{CH}]_x$ are underway.

According to chemical consideration, AsF_5 is an extremely strong Lewis acid and oxidizing agent. It probably reacts with polyacetylene much more readily than iodine. Thus Figs. 4 and 5 showed that even “slow” AsF_5 doping of polyacetylene can result in heterogeneous materials as judged by the lack of sharp transitions. In Fig. 4 the data of Park *et al.*[25] showed a sharp σ vs y transition suggesting uniform doping was achieved. On the other hand, the rapid increase of EPR intensity and emergence of Dysonian line shape reported by Goldberg *et al.*[7] suggests that their doping was nonuniform. It is possible that these workers may have used dissimilar doping procedures and that some kind of cryogenic pumping was used by the former.

In the present work, *trans*-$[\mathrm{CH}]_x$ cyclic doped with AsF_5 appears to be an uniform material according to the above. Furthermore the close agreement between this and *trans*-$[\mathrm{CHI}_y]_x$ in their σ vs y curves (Fig. 6) supports the criterion of dopant independence. However, there are also some differences between these two systems. *Trans*-$[\mathrm{CH(AsF_5)}_y]_x$ exhibited a sharp drop of S at ppm doping, whereas it did not occur for iodine doped polymer. A possible explanation may be the initial AsF_5 doping occurs in the fibril surface.

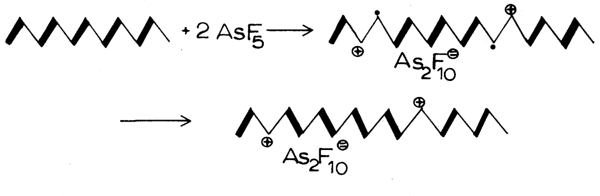
In the above three systems, *cis*-$[\mathrm{CHI}_y]_x$, *trans*-$[\mathrm{CHI}_y]_x$, and *trans*-$[\mathrm{CH(AsF_5)}_y]_x$, which have been considered by us to be uniformly doped materials, the EPR intensities dropped sharply as $y > \sim 10^{-3}$. There are two possible explanations. The first is that the phase transition switches on various relaxation processes such as via modulation of hyperfine interaction or of quadrupole interaction, Heisenberg exchange, or spin-orbit coupling. The other is the annihilation of the neutral defects. The latter is found to be true by magnetic susceptibility measurements. The number of Curie spins in *trans*-$[\mathrm{CHAsF_5}]_x$ (Ref. 11) and in $[\mathrm{CHI}_y]_x$ (Ref. 13) has been shown to decrease greatly in the transitional doping region. It seems that soliton annihilation can take place when the soliton glass is transformed to a soliton liquid state.

The fact that the number of Curie spins is unchanged with doping in the pretransitional regime is interesting. A possible interpretation is that chemical doping creates a pair of polarons which rapidly evolves into a pair of charged solitons:



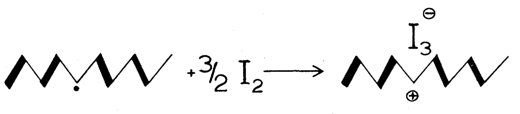
(2)

or



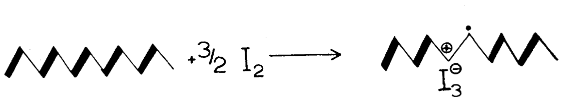
(3)

An alternative explanation may be that there are random conversions of neutral defects into charged defects:



(4)

and also single polaron dopings



(5)

resulting in no net change in Curie spin concentration in this lightly doped regime.

Cis-$[CH(AsF_5)_y]_x$ is heterogeneous material even when doping is performed according to the "cyclic" method. The evidences are rather conclusive. There is no discernible transition in the σ vs y dependence (Fig. 5). Doping develops a narrow component in the EPR spectra (Fig. 15), increases the number of Curie spins (Fig. 17), which assumes Dysonian line shape (Fig. 14) of large A/B ratio (Fig. 16). Furthermore, the Curie susceptibility is small compared to the Pauli susceptibility,[32] which increases with doping from $y=3\times10^{-3}$ to 4×10^{-2}. All these observations are contrary to the criteria proposed above for uniform doping. Figure 10(a) showed distinct dark doped regions and light fibrils which may contain little or no dopant. For heavily doped samples, Fig. 10(b) showed the presence of dark spots which may be heavily doped metallic domains dispersed in poorly defined remnants of fibrils which may be lightly doped.

The difficulty of uniform doping of *cis*-$[CH]_x$ with AsF_5 may be attributed to the initial reaction converting the fibril surface to doped *trans* structure. This transformation may hinder the diffusion of AsF_5 into the interior of the fibrils or it may inhibit the *cis-trans* isomerization of neighboring molecules. Also because of the large diameter of the spherically shaped AsF_5, it can cause large expansion of the interchain separation resulting in preferential doping of the neighboring sites along the same chain or adjacent chains.

B. Intrinsic carriers and intersoliton hopping conduction

A novel mechanism of conduction for undoped and lightly doped polyacetylene has been put forth by Kivelson.[19,20] This model assumes the presence of pinned charged solitons S^+ and neutral solitons S^0 (with impurity ions close by). When S^+ and S^0 are found within hopping distance, an electron from S^0 hops to S^+; the initial and final states have nearly the same energy. The process is very weakly temperature dependent according to some power law. The model predicts a temperature independent TEP:

$$S=\pm(k_B/|e|)[(x+2)/2+\ln(y^0/y^+)]\ , \tag{6}$$

where $x\approx13$ is the exponent of the power-law relationship of σ vs y, y^0 is the concentration of neutral soliton, and y^+ is that of the charged solition. The dc conductivity is given by

$$\sigma_{dc}=\frac{Ae^2\gamma(T)}{k_BT}\left[\frac{\xi}{R_0^2}\right]y^0\frac{y^0y^+}{(y^0+y^+)^2}\exp\left[\frac{-2BR_0}{\xi}\right]\ , \tag{7}$$

where $A=0.45$, $\gamma(T)\simeq500[T/(300\ \mathrm{K})]^{x+1}$ eV, R_0 depends on the separation of impurity ions, $\xi=4.4$ Å, and $B=1.39$. The model requires the presence of intrinsic charged carriers in undoped *trans*-polyacetylene. Based on the σ_{dc} data[20] and Eq. (7), TEP data[23] and Eq. (6), y^+ was estimated to be about 3×10^{-5} and 4×10^{-4}, respectively. The $\sigma_{ac}(\omega)$ data[22] led to $y^+\sim2.4\times10^{-4}$. Similar estimates were obtained from depletion measurements on heterojunctions.[56] The EPR data showed the concentration of neutral soliton to be $y^0\sim(3-5)\times10^{-4}$.

The intrinsic levels of y^+ and y^0 are expected from the structure of *trans*-polyacetylene and the catalysis of the polymerization. We have pointed out[10,57] that there is on the average one S^0 for every two *trans*-$[CH]_x$ chains. Two S^0 on the same chain would lead to relaxation by multiphonon or nonradiative processes and effective annihilation. We have used radioquenching techniques to determine the number average molecular weight of polyacetylene and the effect of polymerization conditions on it.[58,59] The typical polyacetylene film made by the standard procedure[33] has ~850 C-H units; thus y^0 should be $\sim6\times10^{-4}$ in agreement with general observations. Therefore, y^0 would be dependent on the polymer molecular weight and any interruption of conjugation in a chain such as chain branching, crosslinking and other defects.

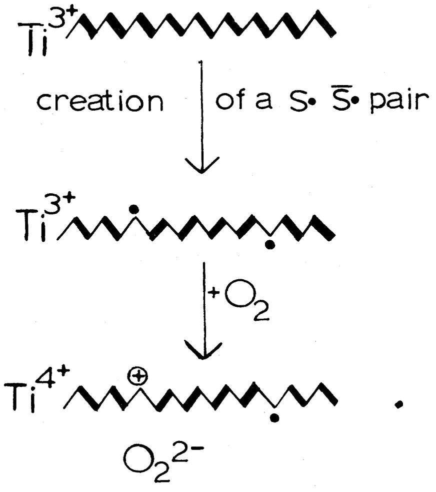
To account for the intrinsic charged solitons, we note the mechanism of polymerization. The catalyst is a trivalent ethyl titanium species[60] and propagation proceeds via insertion of the monomer via *cis* opening of the triple bond[61]:

$$Ti^{3+}Et+n\,CH{\equiv}CH\rightarrow Ti^{3+}{-}(CH{=}CH)_n{-}Et\ , \tag{8}$$

where Et is an ethyl radical. On the average there occur 3–5 chain transfer events per active Ti^{3+} site with triethylaluminum:

$$Ti^{3+}{-}(CH{=}CH)_n{-}Et+AlEt_3 \rightarrow Ti^{3+}Et+Et_2Al{-}(CH{=}CH)_n{-}Et\ . \tag{9}$$

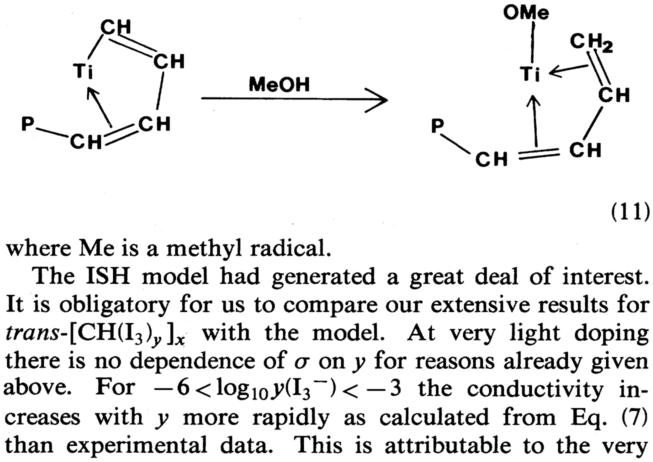
If a soliton-antisoliton pair is formed on a chain bound to a Ti^{3+} ion, one neutral soliton can be converted to a positive soliton by the following processes:



(10)

This two-electron redox process is thermodynamically far more favorable[62–64] than one-electron oxidation of a neutral soliton by oxygen. According to this proposal and taking into account chain transfer events (*vide supra*), there should be about $(3\times850)^{-1}=2.4\times10^{-4}$ to $(5\times850)^{-1}=4\times10^{-4}$ of y^+ in undoped polyacetylene. This is in agreement with the various estimates for y^+ given above.

The bonding between polyacetylene and the titanium is apparently quite strong. We have analyzed many samples of polyacetylene for Ti and found it to be about $(0.2\pm0.015)\%$ regardless of whether the polymers were washed thoroughly with pentane, or overnight with methanol or *n*-butanol. Based on the value of $\overline{M}_n$, this analysis corresponds to about one-fifth of the polyacetylene molecules bound to a Ti in agreement with the chain transfer results. We found that titanium content can be lowered only by washing with HCl—MeOH. Unfortunately, HCl can act as dopant for polyactetylene. The unusual stability of the titanium bond to the polymer may be attributed to $p\pi$-$d\pi$ interaction. The structures before and after methanol wash may be represented as follows:



(11)

where Me is a methyl radical.

The ISH model had generated a great deal of interest. It is obligatory for us to compare our extensive results for *trans*-$[\mathrm{CH(I_3)}_y]_x$ with the model. At very light doping there is no dependence of σ on y for reasons already given above. For $-6<\log_{10}y(\mathrm{I_3}^-)<-3$ the conductivity increases with y more rapidly as calculated from Eq. (7) than experimental data. This is attributable to the very strong exponential dependence on R_0 in the model. It may be possible to treat the separation of intrinsic carriers as an adjustable parameter to obtain better fit. The ISH model failed completely for $y>10^{-3}$ because of the rapid decrease of the neutral soliton concentrations as shown in Figs. 11 and 13 and Ref. 10. At these doping levels the conductivity calculated from Eq. (7) falls rapidly with increasing y.

The ISH model also encounters difficulties in interpreting the thermopower data. According to Eq. (6) small changes in S require very large changes in y^0/y^+. Since we expect the model to be applicable only to lightly doped polyacetylene (i.e., for dopant concentration less than the *S-M* transition), a very large increase in y^+ is required for appreciable decrease in S because y^0 is nearly constant according to EPR. Let us also consider the thermopower of undoped *trans*-polyacetylene. The values of S of ~900 and $1450\ \mu\mathrm{V\,K}^{-1}$ obtained by Park *et al.*[25] and us, respectively, would imply 500-fold difference in y^+. The lower y^+ or higher S may be suggested as due to unintentional compensation. However, the fact the S is not affected noticeably by iodine doping to $y(I_3^-)\sim10^{-5}$ seems to rule out the compensation argument. Chaiken and Beni[65] had derived expressions for S for correlated hopping regime for attractive and repulsive interactions. No agreement was obtained between their equations and our experimental results.

The conductivity of undoped *cis*-polyacetylene is 4—5 orders of magnitude lower than that of the *trans* isomer, and the EPR spin concentration is about 10 times smaller by comparison. Doping commences to affect conductivity at $y\sim10^{-6}$, suggesting that any intrinsic carrier concentration would be of that order. This low concentration may be attributed to the low mobility of the neutral defects in the *cis* polymer as judged by its broad temperature-independent EPR linewidth[2] and the lack of effect of dopant on EPR T_1 below $y=10^{-3}$ concentration.[10] Consequently, reaction (10) has low probability. Together with the low number of neutral defects, the low intrinsic carrier concentration may be rationalized. Above $y>10^{-6}$, σ_{RT} increases with doping as a result of carrier injection.

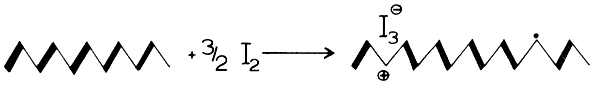
C. Semiconductor-to-“metal” transition

According to conductivity measurements, the transition region covers 10^2 change in dopant concentration for *trans*-polyacetylene; it is $\sim10^4$ change in y for the *cis* isomer. In the overlapping region of transition for the two polymers, there is almost 10^4 increase in conductivity for a tenfold change in y (between 3×10^{-4} and 3×10^{-3}). In comparison, TEP data showed an even more abrupt decrease of S, and most of the decrease in S occurs within a factor of change in y. Moses *et al.*[29] had reported TEP results which are in agreement with ours, though they did not have data within the sharp transition region nor at very low dopant concentration. With our results, the *S-M* transition is clearly delineated. If one takes TEP to be a true measure of the intrinsic transport properties of the polyacetylene fibrils, then they become “metallic” at $y\sim10^{-3}$.

The most remarkable aspect of our present results is the fact the $\log_{10}\sigma_{\mathrm{RT}}$ vs $\log_{10}y$ curves in the transitional region of $y\geq2\times10^{-4}$ are the same for iodine-doped *cis*- and *trans*-polyacetylene and $\mathrm{AsF_5}$-doped *trans* polymer. There was no EPR linewidth change in *cis*-$[\mathrm{CHI}_y]_x$ up to $y(\mathrm{I_3}^-)=7\times10^{-3}$ when the signal intensity vanished. Also the electron diffraction patterns for *cis*-$[\mathrm{CHI}_y]_x$ with $y(\mathrm{I_3}^-)$ between 3×10^{-3} contain mainly the reflections of the *cis* structure with new reflections of doped structures and a faint (002) reflection for the *trans* isomer.[50] In other words, there is very little *trans* structure in the transitional region of doped *cis*-polyacetylene. It is not known what the length of the *cis* backbone isomerized to the *trans* structure by each dopant is, but it seems reasonable to suppose a minimum length corresponding to the domain width of the excitation. This is about $\xi_0=14a$ for a neutral soliton,[8] $1.6\xi_0$ for a free charged solition,[66] $1.4\xi_0$ for a pinned charged charged soliton,[66] and $1.24\xi_0$ for a polaron.[67]

In the oversimplified version, soliton wave functions are localized on individual chains. We have shown[68] that there is both interchain and intrachain diffusion of neutral solitons though the former is about 3×10^5 greater. Soliton glass transition should occur when the excitation domains overlap and the average separation R between the dopant ions is of the order of domain widths. If we assume that the distribution of dopant ions is uniform in the samples described above, then the increase of conductivity begins at $y\approx10^{-4}$ or $R\approx28$ Å. The midpoint of transition is at $y=7\times10^{-4}$ or $R=18.5$ Å, and the fibrils became "metallic" according to TEP at $y=10^{-3}$ or $R=165$ Å. These are compared with the domain widths of 24 Å for a pinned charged soliton and 21 Å for a polaron. Consequently, in the transitional region the excitation came under the influence of more than one dopant ion. The excitation is converted from a glassy state in which the Coulombic interaction is between the charged defect and one dopant ion, to a liquid state in which the interaction is with two or more dopant ions.

Of all the doping processes, Eq. (4) is the most favorable because the neutral and pinned charged solitons have nearly the same energy within 10%.[66] The direct introduction of a charged soliton requires about $2(2\Delta_0)/\pi\approx0.9$ eV for the formation of a kink-antikink pair:



(12)

where $\Delta_0\sim0.7$ eV is the order parameter. The energy of a polaron is $2(\sqrt{2}\Delta_0)/\pi\approx0.6$ eV.[67,69] Therefore, a polaron is the lowest energy state available to a single electron. At low levels of doping a polaron introduces two defect levels and bonding and antibonding states situated 0.3 eV above the valence band and below the conduction band.

In the presence of both charged soliton and polaron states, a probable mechanism of conduction is electron hopping between them; the initial and final states for such processes have nearly the same energies. According to this interpretation *cis*-polyacetylene doped to the same y as *trans*-polyacetylene would have the same conductivity as long as doping induces the isomerization of a segment of the *cis* backbone to the *trans* structure equal to or greater than the excitation domain widths. This is true even though the specimens may still have largely the *cis* structure at the doping levels for soliton glass transition.

At high levels of doping adjacent polarons interact to form charged solitons carrying no spin as represented in Eqs. (2) and (3), which causes the observed disappearance of the EPR signal. With the increasing number of charged solitons, a band of charged solitons may emerge. Epstein *et al.*[70] found for $[\mathrm{CH(I_3)}_y]_x$ with y from 0.017 to 0.048 the temperature-dependent conductivity to be consistent with a mechanism of variable range hopping between states in the charged soliton band.

Mele and Rice[30] made a theoretical study of the electronic structure of doped finite-model polymers as a function of dopant concentration. They found that the midgap "band" simply grows with increasing dopant concentration always accommodating the excess dopant-induced charge with an equal number of empty states from the conduction band. This persists to $y=0.14$. By introducing multidimensional fluctuation in dopant ions and Coulombic effect, the *S-M* transition was found to occur over the range of y between 5% and 10%. Much has been said about the turning on of Pauli susceptibility in doped polyacetylenes. There may be a real transition to a nearly degenerate Fermi gas and change of the temperature and frequency dependencies of conductivity. However, this Pauli transition must be considered to be different from the soliton melting transition discussed above for sudden changes in σ and S at very low doping levels.

V. CONCLUSIONS

This work demonstrated that uniform doping can be achieved for *cis*- and *trans*-polyacetylene with iodine and the latter polymer with $\mathrm{AsF_5}$ doping. Several reasonable criteria may be adopted for uniformity of doping. There should be little changes in EPR intensity, conductivity, and thermopower for lighty doped polyacetylene and there should not be two EPR components in homogeneously doped *cis*-polyacetylene. The semiconductor-to-"metal" transition is a very abrupt one with nearly all the changes in S occurring within about a twofold increase in dopant concentration. The change is also quite sharp for conductivity though it occurs over about 100-fold increase in dopant concentrations because of interchain and interfibril contributions. Nevertheless, the midpoint of transition occurs at nearly the same dopant concentration for both σ and S. The number of Curie spins also decreases greatly. The results are interpreted as the occurrence of a phase transition whereby charged defects pinned by the potential of an dopant ion in a glassy state are converted to a soliton liquid in which the charged defects interact with two or more dopant ions. The transition occurs when the average separation of the uniformly distributed dopant ion is comparable to the defect domain widths. According to this interpretation, largely *cis*-polyacetylenes have the same conductivities as *trans*-polyacetylenes doped to same levels in the transitional regime.

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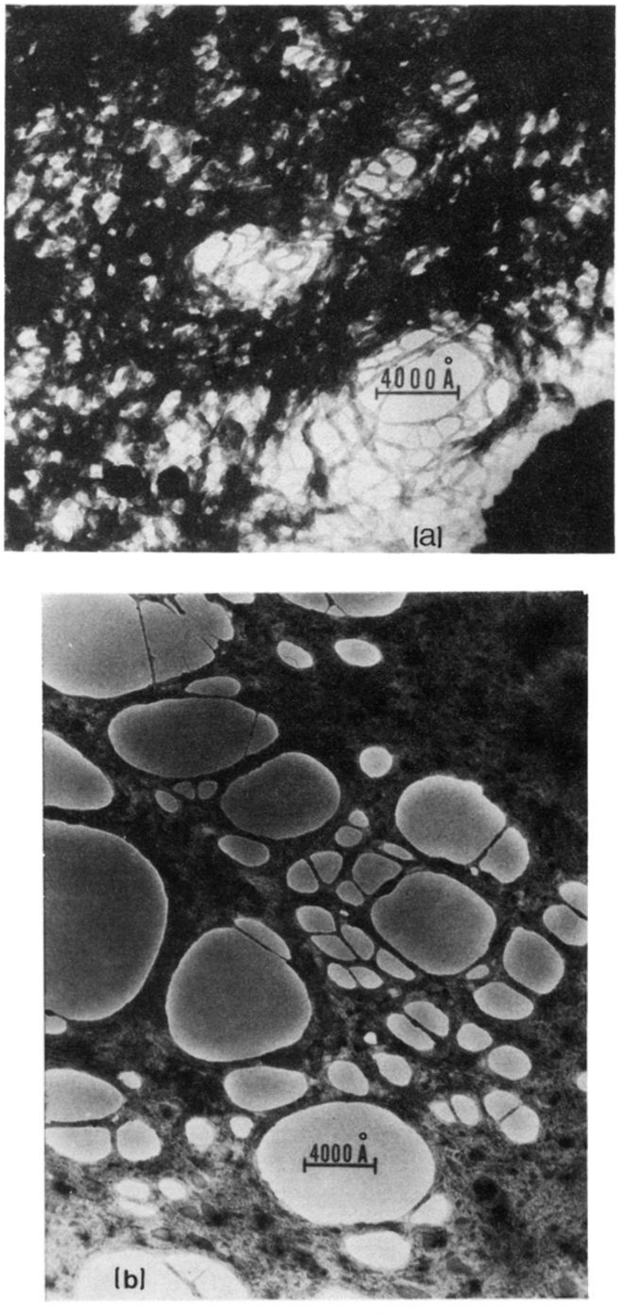

FIG. 10. Electron micrographs of *cis*-polyacetylene doped with AsF_5: (a) intermediate doping level; (b) heavily doped.

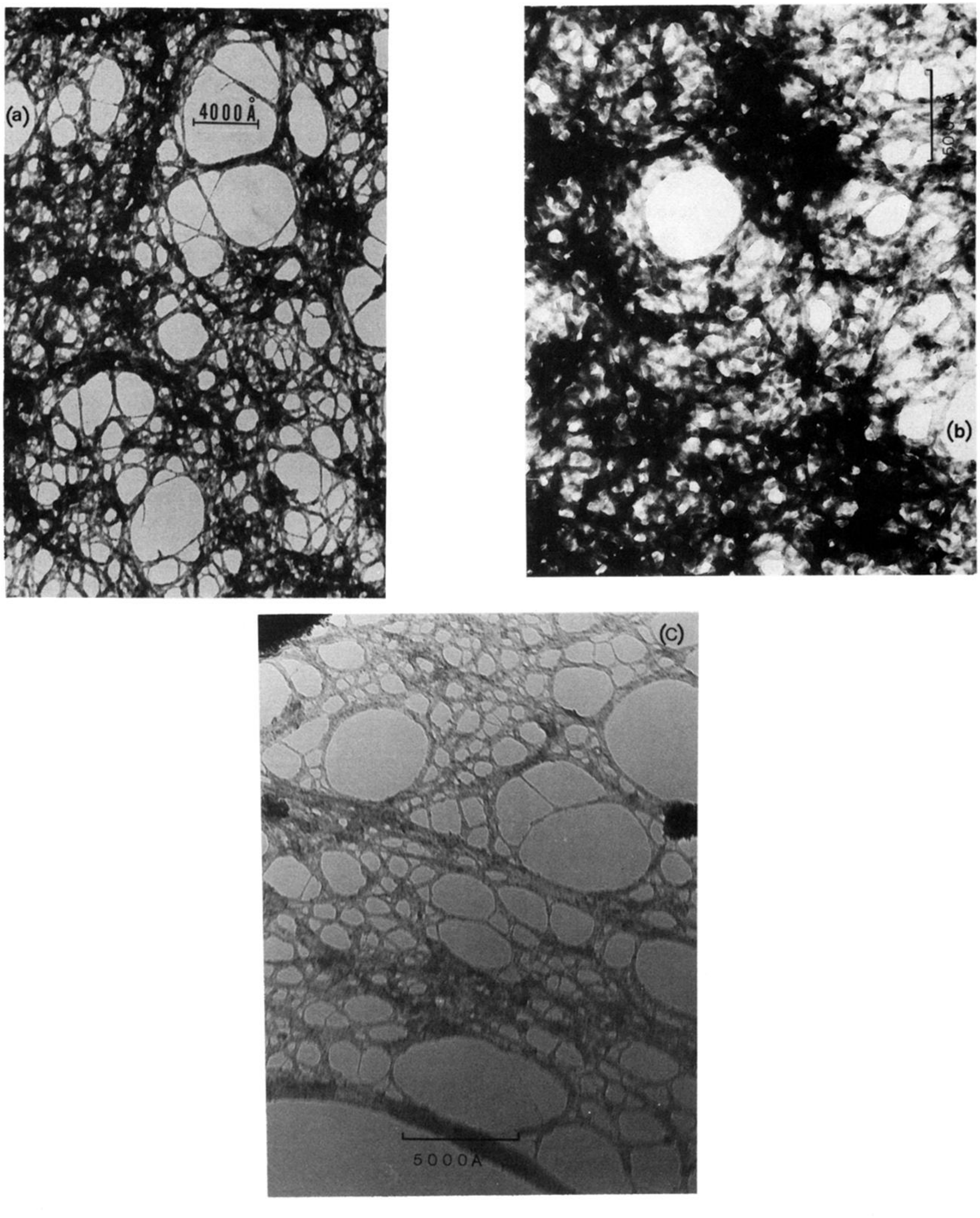

FIG. 8. Electron micrographs of *cis*-polyacetylene doped with iodine: (a) doped to intermediate level observed at 298 K; (b) doped to maximum level observed at 123 K; (c) doped very slowly with iodine and then kept at 195 K for 8 d, observed at 298 K.

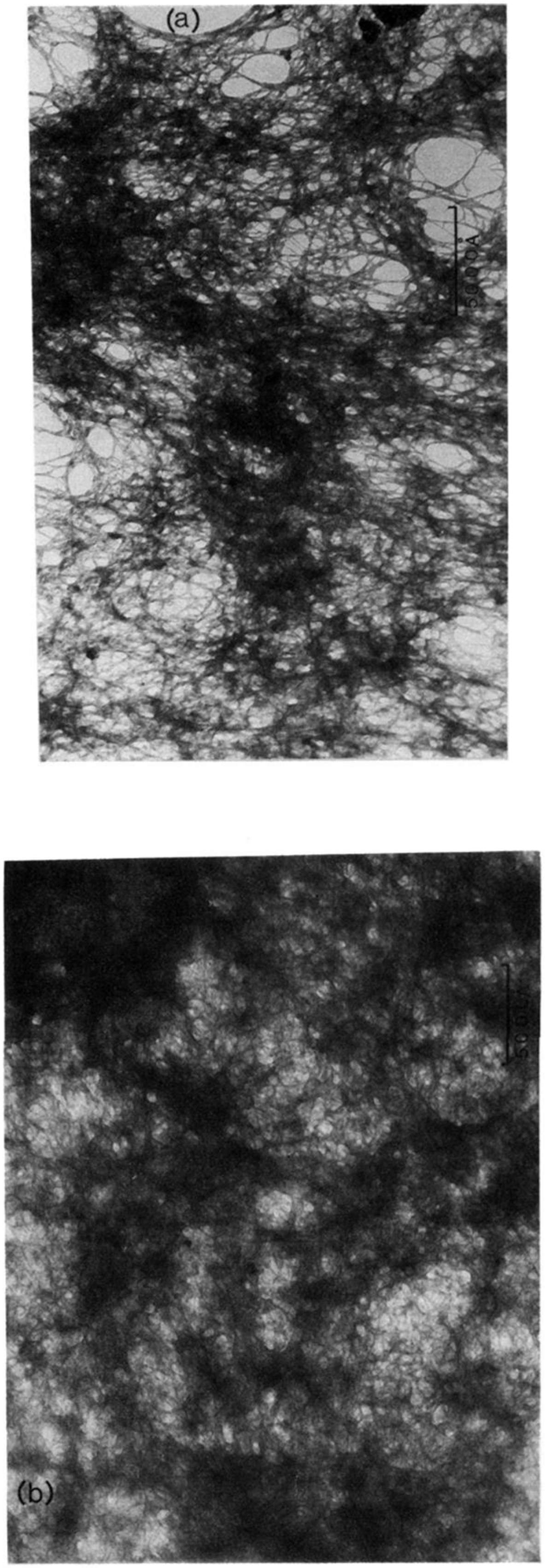

FIG. 9. Electron micrographs of *trans*-polyacetylene doped with iodine: (a) lightly doped for 5 sec at 296 K; (b) heavily doped.