

Electronic properties of polyacetylene doped with FeCl_3

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Trans and *cis* $(\text{CH})_x$ were chemically doped with FeCl_3 using nitromethane solutions as well as by using the vapor pressure of solid FeCl_3 . Electrical conductivities were measured vs temperature for all samples. Room temperature conductivities of approximately 100 mho/cm were achieved. Thermoelectric power was also measured as a function of temperature. The room temperature thermoelectric power starts at $+850 \mu\text{V/K}$ for the dilutely doped samples and decreases to $+12 \mu\text{V/K}$ for the more heavily doped samples which exhibit metallic thermoelectric power, proportional to the absolute temperature.

INTRODUCTION

The organic polymer polyacetylene, $(\text{CH})_x$, has been widely studied since 1974 when it was first synthesized in the form of large, continuous, shiny films.¹ Interest in this polymer intensified when it was discovered that its electrical properties could be controlled by several chemical techniques.² These various chemical doping procedures resulted in transforming this intrinsically semiconducting organic polymer into a modified polymer which exhibits electrical properties all the way from insulating to metallic.³

Interest in this polymer intensified even further after the soliton theory of Su, Schrieffer, and Heeger was offered to explain the electronic properties of polyacetylene.^{4,5} Several reviews have appeared in the literature and so we will only review the fundamental ideas.⁶ Briefly, the soliton in *trans* $(\text{CH})_x$ is a topological distortion or kink in the bond alternation pattern of the chain. According to the soliton theory, the effect of this distortion on the band structure is that a single localized state is created at midgap. The occupancy of this single localized state can be either zero, one, or two. This naturally occurring neutral soliton has a single unpaired electron in this state. Adding or subtracting electrons from the electronic structure of the neutral polymer either adds an electron to this state, giving an occupancy of two, or removes the one electron there, giving an occupancy of zero (negative or positive solitons, respectively). In the case of the neutral soliton, the unpaired electron gives the soliton a magnetic moment, or spin, of $1/2$. In either of the charged cases, the unpaired spin is either removed (positive soliton) or paired with another electron (negative soliton), which results in no magnetic moment, or spin zero. Thus, the soliton model predicts an anomalous charge-spin relation for the charge carriers in polyacetylene.

The existence of the midgap soliton state has considerable experimental support through optical absorption measurements.⁷ These measurements are consistent with theoretical calculations.^{8,9} The anomalous magnetic moment-charge relation cited has also been probed using electron spin resonance (ESR) techniques to follow the formation of neutral solitons during the *cis*-to-*trans* isomerization process.¹⁰ In addition, monitoring the spins via ESR while doping *trans* $(\text{CH})_x$ shows that the spin signal is reduced as the unpaired spin is removed, as described in the previous paragraph.

Thus, the electronic properties of *trans* $(\text{CH})_x$ are influenced by the magnetic state of the charge carriers in a rather novel way. It is then interesting to consider what interactions might exist among the spins. Nuclear magnetic resonance (NMR) techniques have been applied to both the proton and carbon-13 nuclei in *trans* $(\text{CH})_x$ and information on the spatial extent of the soliton, its mobility, and diffusion characteristics have been deduced.^{11,12} Work in this area is continuing. However, one tool which is commonly used in other areas of solid state physics but which has not yet been successfully applied to *trans* $(\text{CH})_x$ is to externally introduce a magnetic moment into the system. One area of continuing controversy in the general field of conducting polymers has to do with the nature of the doping process, the nature of the final active doping agent in the material, the location of the dopant ion, the effect of the dopant ion on the electrical transport and other properties, and the interactions, if any, between the dopant ion and the polymer chain itself. It is hoped that several magnetic species can be identified which will effectively dope polyacetylene. This has provided the motivation for this work. We regard FeCl_4^- (III) as a viable magnetic impurity candidate and the remainder of this paper is devoted to describing some of the chemical techniques used to dope $(\text{CH})_x$ with this ion and the resulting electronic properties of the doped polymer.

SAMPLE PREPARATION

All of the samples used in this work were synthesized at the Naval Ocean Systems Center using the conventional Shirakawa procedure.¹ The synthesis reaction was performed using purified reagents and under well controlled conditions at approximately -78°C . The procedure used has been found to yield high purity polyacetylene ($>99\%$ carbon and hydrogen by independent analysis). The isomeric content of the polymer produced is approximately 90% *cis* as determined by infrared spectroscopy. The samples were kept either in evacuated vessels or in a well maintained environmental chamber with a moisture content under 1 ppm and an oxygen content under 10 ppm. A certain fraction of each synthesis reaction was stored in vacuum in liquid nitrogen to maintain the sample purity and isomeric content. Great care has been taken in sample synthesis, handling, and storage to preserve the original quality of the samples.

The samples to be discussed at this time were doped using dilute FeCl₃ solutions in nitromethane. Anhydrous FeCl₃ (98%, packed under argon) was obtained from Alfa Products packed under argon. Before use, this material was further dried by heating in a vacuum oven, attached to the environmental chamber, under dynamic vacuum at approximately 150 °C for several hours. Thus treated, the dried FeCl₃ was transferred into the environmental chamber and stored in the protected environment until use. ESR spectra of (CH)_x samples doped with this material show only the Fe(III) and the intrinsic (CH)_x spin resonances.¹³ No evidence of chemical impurities containing spin is seen. Thus, it was not deemed necessary to purify the FeCl₃ reagent further. Spectrophotometric grade nitromethane (Gold Label, 96%) was obtained from Aldrich Chemical. This nitromethane was then distilled under 99.999% pure helium gas, the middle cut being collected and stored in the environmental chamber until use. The actual doping solutions were then prepared in the environmental chamber immediately before use. The appropriate amount of FeCl₃ was weighed using a Perkin-Elmer microbalance kept in the environmental chamber. Just enough solution was prepared for immediate use, generally no more than 50–100 ml at a time. A sample of (CH)_x was then weighed and placed in the doping solution for some period of time, discussed below. At the end of the prescribed period of time, the (CH)_x sample was removed from the doping solution and washed several times with the same nitromethane solution used to prepare the doping solution in order to remove any unreacted FeCl₃, all in the environmental chamber. Then the sample was enclosed in an evacuable vessel, removed from the environmental chamber, evacuated to high vacuum (< 10⁻⁶ Torr) for at least 1 h to remove any residual solvent, reintroduced into the environmental chamber, and weighed inside. The final weight after doping, washing, and drying was then compared to the original weight to allow an estimate of the doping level. Figure 1 illustrates the effect of performing this procedure on a set of (CH)_x samples using a 0.01 M FeCl₃ solution. From such studies, 18 h was chosen as the doping period. It is advanta-

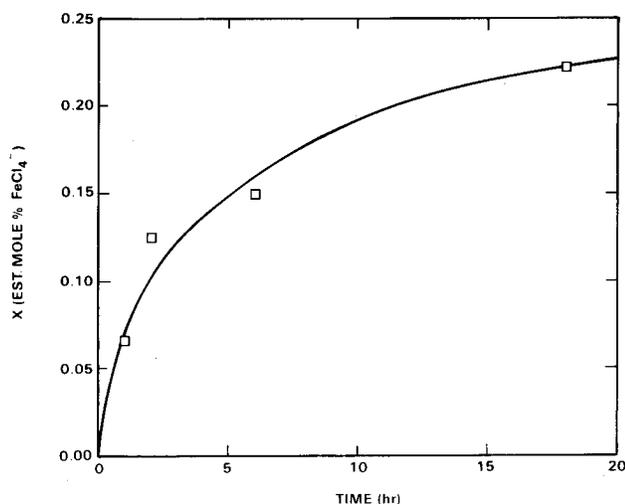


FIG. 1. Dopant level vs time for polyacetylene doped with FeCl₃ in nitromethane.

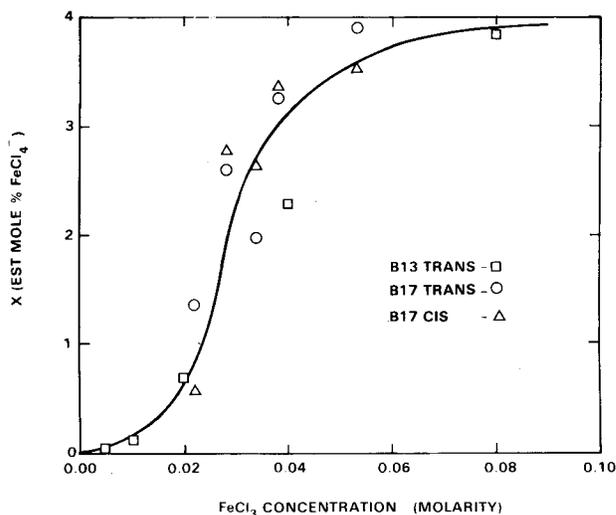


FIG. 2. Dopant level vs concentration of FeCl₃ in nitromethane.

geous to use the shortest time possible to minimize possible contamination and after 18 h most of the doping has taken place, as indicated in the figure. The estimated mol % dopant level was deduced from weight uptake measurements and the hypothetical half-reaction



The model reaction described by Eq. (1) is considered a working equation, and agrees with the most recently published work on this dopant.^{14,15} Mössbauer spectra taken on samples similarly treated have shown the presence of both Fe(III) and Fe(II).¹⁶ Quantitative analysis of the samples so treated shows a Cl/Fe ratio closest to three. The unreacted FeCl₃ is washed out after doping, yet the final samples show an ESR signal appropriate for FeCl₄⁻ (III). Thus, FeCl₃ acts as an acceptor or *p*-type dopant whereby the reaction described by Eq. (1) removes electrons from the band structure of the *trans* (CH)_x, presumably removing single electrons from the soliton states, leaving a *p*-type carrier of charge. The estimated mol % of FeCl₄⁻ indicated in Fig. 1 and throughout the paper is then computed using Eq. (1) as follows: the weight uptake after doping, washing, and drying gives the amount of FeCl₃ reacted. Assuming the equal proportionation of Eq. (1) is approximately correct, this number is then simply divided by two to give an estimate of FeCl₄⁻ present in the final sample—presumably the final active dopant expressed as a mol % (relative to the number of CH units).

The effect of varying the molarity of the doping solution is illustrated in Fig. 2. The doping was performed for 18 h in all cases. Different synthesis batches were used for this analysis—B13 and B17 refer to batches 13 and 17, respectively. Both *cis* and *trans* starting materials were used. The *cis* starting material was *cis*-rich (CH)_x, meaning it started generally in the range of 60%–90% *cis*. The *trans* (CH)_x was thermally isomerized before doping by placing the material in a vacuum oven, under dynamic vacuum, and heating to 150 °C for several minutes. This procedure has been found to yield undamaged (CH)_x in excess of 90% *trans* as indicated by infrared spectroscopy. As shown in the figure, one can control

the final dopant level via the concentration of the doping solution. This was the procedure adopted.

Selected samples which were doped according to the procedure described above were subjected to quantitative chemical analysis by an outside laboratory for iron and chlorine content.¹⁷ One representation of the results is illustrated with Fig. 3. The estimated wt% of iron, deduced from Eq. (1) and the measured weight uptake, is represented by the ordinate; the wt% of iron from the quantitative analysis of the samples is represented by the abscissa. Note that there is a linear relationship between these two measures of the iron content but the slope is greater than unity. The measured stoichiometry from the quantitative analysis gives a molar Cl/Fe ratio which varied from 3.04 to 3.44. The slope in Fig. 3, being greater than unity, along with the Cl/Fe ratio in excess of the ideal value of three, is consistent with the belief that some of the FeCl₂ reaction product is being washed out of the sample along with the excess unreacted FeCl₃. Recently, Pron *et al.* have reported evidence to support the hypothesis that FeCl₄⁻ is the only active dopant when (CH)_x is doped with FeCl₃.¹⁵ Moreover, their results indicate that the FeCl₂ produced by the reaction shown with Eq. (1) may react with residual moisture in the system to form hydrated species, FeCl₂ · nH₂O, which are insoluble in nitromethane and can never be completely washed out of the polymer.¹⁵ This is probably the source of residual FeCl₂ in the system. However, the neutral FeCl₂ should play no role in electronic conduction and, having no spin, should not influence the ESR studies on these materials.

In the doping of polyacetylene, slow doping has been shown to produce more uniformity in the dopant distribution.¹⁸ One way to dope (CH)_x slowly with FeCl₃ is by simply exposing the polymer to the vapor for a period of time. The melting temperature of FeCl₃ is 306 °C, so the vapor pressure of FeCl₃ over the solid at room temperature is probably less than 10⁻⁴ Torr. The idea of trying to dope the polymer in this manner was obtained from reports in the literature of

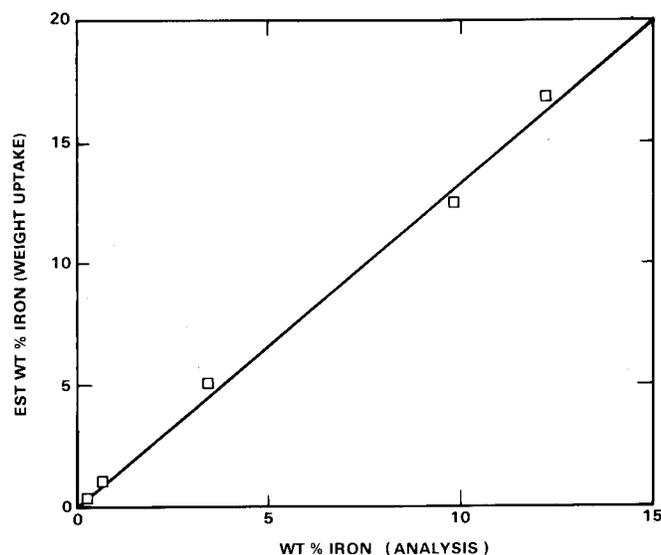


FIG. 3. Iron content of (CH)_x samples doped with FeCl₃ in nitromethane via weight uptake and quantitative chemical analysis.

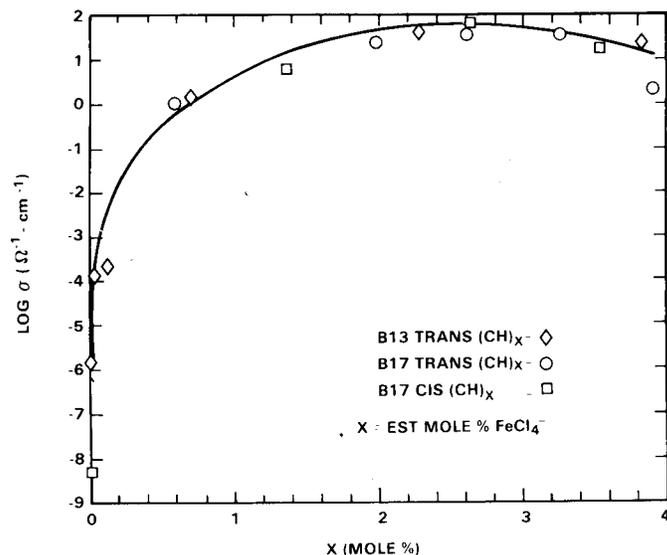


FIG. 4. dc conductivity vs dopant level for *cis* and *trans* (CH)_x doped with FeCl₃ in nitromethane solutions.

successful graphite intercalation using the vapor pressure of a solid below the melting temperature.¹⁹ The results obtained from this slow doping technique will be discussed in the next section.

In addition to the doping techniques already discussed, the FeCl₄⁻ ion can also be inserted into (CH)_x using electrochemical techniques. One can prepare an electrolytic solution of Li⁺/FeCl₄⁻/nitromethane following published procedures.²⁰ Then, using a specially fritted triple chamber electrochemical cell, we have doped (CH)_x with FeCl₄⁻ directly. This work will be reported elsewhere.

ELECTRONIC PROPERTIES

The effect on the electrical conductivity of treating (CH)_x with FeCl₃ in nitromethane as described in the previous section is illustrated with Fig. 4. The conductivity plotted on the ordinate is the dc conductivity at room temperature measured with the usual four probe technique. Four distinct electrical contacts were made with the sample using conducting graphite paint—Acheson Electrodag 110. The abscissa is the estimated mol % of FeCl₄⁻ as described above. The figure represents data taken on two different batches of *trans* (CH)_x and one batch of *cis* (CH)_x. Aside from the initial conductivities (before doping), which are about three orders of magnitude different for the two isomers, there was no significant difference in the final conductivities for the two isomers. Previous work has shown that doping *cis* (CH)_x results in the concurrent isomerization to the *trans* isomer.²¹ This is probably the reason that the final conductivities are independent of the isomeric content of the starting material. One interesting feature of the FeCl₃ doped (CH)_x is that there is a dopant level, approximately 3 mol %, where the conductivity peaks at about 100 mho/cm and then starts to decline. This is in marked contrast to the most effective dopants for this polymer such as AsF₅. The physical appearance of the polymer progresses from the silvery sheen of the pristine material, to a shiny golden color at approximately 1–2 mol %, then changes to a bluish black

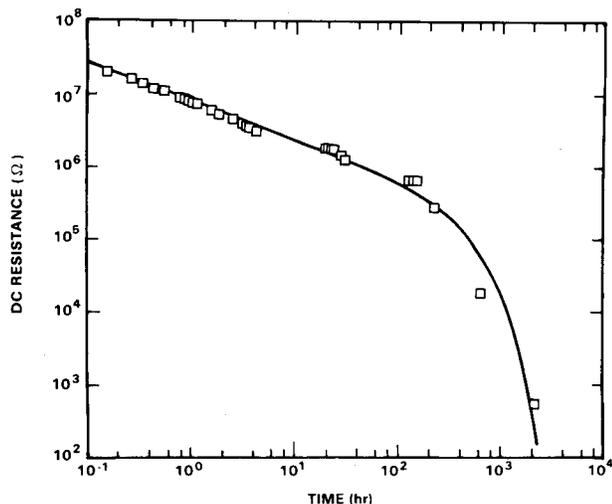


FIG. 5. dc resistance vs time for $(\text{CH})_x$ doped with FeCl_3 vapor at room temperature.

appearance just past the peak in conductivity, and finally becomes dark blue-black in color and less conducting at the highest dopant levels. The nature of the degradation at higher dopant levels has not been explored in this work.

In the last section, the slow doping by exposure to FeCl_3 vapors at room temperature was mentioned. The results obtained are illustrated by Fig. 5. The ordinate is the two-probe dc resistance of the sample. The abscissa represents the time measured in hours. This is slow doping, the total duration being approximately 3 months. After this period of time the conductivity had increased approximately five orders of magnitude to 1.2 mho/cm from a starting value of 9×10^{-6} mho/cm. From the weight uptake, the dopant level can be estimated using Eq. (1). The result was a FeCl_4^- level of 0.27 mol %. This is consistent with the conductivity vs dopant level shown in Fig. 4. Attempts to dope $(\text{CH})_x$ with FeCl_3 vapors at 100°C resulted in considerable sample degradation. Intermediate temperatures were not pursued for this study. However, it is likely that temperatures slightly above room temperature could be used to dope $(\text{CH})_x$ with FeCl_3 vapors more rapidly than the room temperature results presented here.

The temperature dependence of the resistance for a collection of samples is illustrated in Figs. 6(a) and 6(b), for FeCl_3 doped *cis* and *trans* $(\text{CH})_x$, respectively. These samples were doped with FeCl_3 in nitromethane solutions. The four-probe dc resistance is plotted vs the absolute temperature. The measurements were made in a Lake Shore Cryogenics closed cycle refrigerator system. The actual sample resistances are plotted. However, the sample geometries were all similar so this is proportional to the actual resistivities. Note that for both the *cis* and *trans* starting materials, the most conducting samples are not the most heavily doped. This is consistent with the data presented in Fig. 4. These results are in qualitative agreement with previously reported results on the conductivity of FeCl_3 doped $(\text{CH})_x$, even though the chemical techniques employed are somewhat different.²² The data is shown only up to 300 K, near room temperature. However, samples have been measured up to

about 380 K, and permanent sample degradation begins to occur near 350 K.

Conductivity in polymers such as $(\text{CH})_x$ is generally limited by carrier hopping from discrete conducting regions. These conducting regions may be individual fibers, bundles of fibers, regions of increased order and crystallinity, and perhaps regions where the dopant level is higher. Variable range hopping models of conductivity have been discussed in the literature.²³ The general form of the variable range hopping conductivity is usually expressed as

$$\sigma(T) = C(T)e^{-A/T^{(1+d)}}, \quad (2)$$

where $C(T)$ is usually a slowly varying function of temperature, A is a constant depending on the details of the mechanism, and the d in the exponent is the effective dimensionality of the hopping. The fit to this equation is better than a fit to a simple semiconductor activation conductivity. The best fit of these data to such a hopping conductivity yields a power of T of 0.40 ± 0.03 . This corresponds to an effective di-

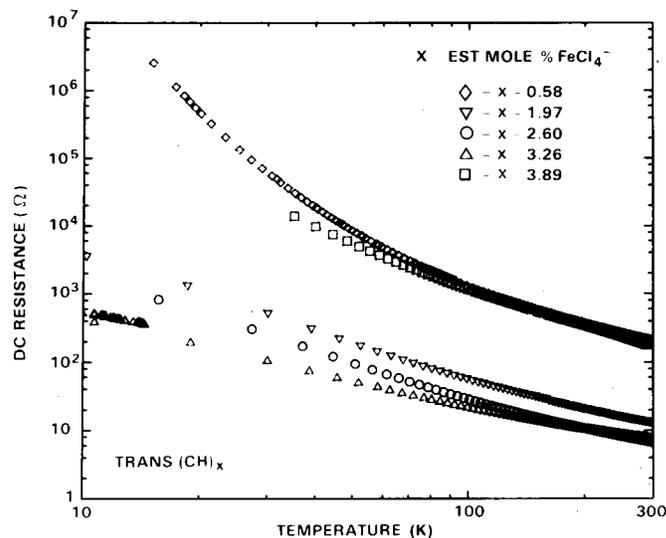
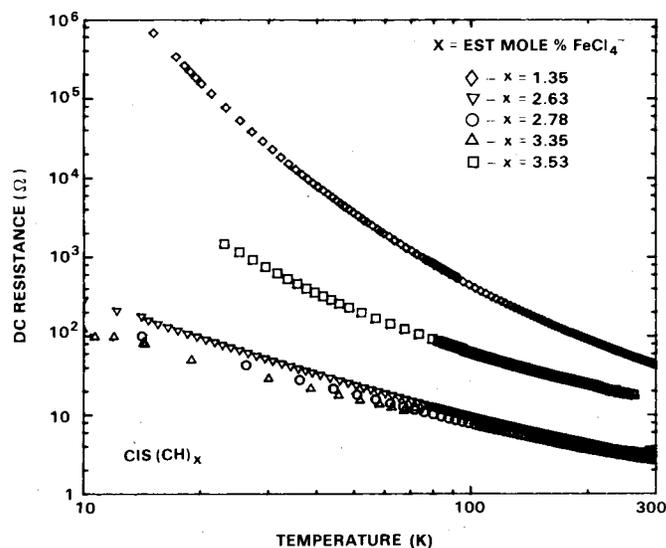


FIG. 6. (a) dc resistance vs absolute temperature for *cis* $(\text{CH})_x$ doped with FeCl_3 in nitromethane solution. (b) dc resistance vs absolute temperature for *trans* $(\text{CH})_x$ doped with FeCl_3 in nitromethane solution.

mensionality for hopping of 1.5. Representative samples of both *cis* and *trans* $(\text{CH})_x$ are illustrated in Fig. 7, where the dc resistance is plotted on a log scale vs the absolute temperature to the negative 0.40 power.

In addition to the electrical conductivity, another transport measurement which allows the effectiveness of a dopant to be evaluated is the thermoelectric power. To measure the thermoelectric power, the sample is suspended between, and thermally anchored to, two quartz blocks. The two quartz blocks are then alternately heated to produce a thermal gradient along the length of the sample. The voltage developed across the sample is then measured with a high impedance voltmeter. The temperature gradient between the blocks is measured with a thermocouple. The thermoelectric power is then given by the electric field produced in the sample divided by the thermal gradient. That is, $S = E/\nabla T = \Delta V/\Delta T$, where S is the thermoelectric power, also called the thermopower, E is the electric field in the sample developed as a result of the thermal gradient ∇T . The geometrical factors conveniently cancel so that the thermopower is actually given by just the ratio of the voltage developed across the sample ΔV divided by the temperature difference ΔT . The thermopower is a useful and interesting measurement to make because it is a zero-current transport measurement which is little affected by breaks in the conducting medium. In the simplest case, the thermopower simply measures the thermal diffusion of charge carriers along the fibers. In a disordered material like $(\text{CH})_x$, the sign of the thermopower gives the sign of the dominant charge carrier. The temperature dependence of the thermopower can distinguish between metallic and semiconducting behavior, being proportional to the absolute temperature and decreasing to zero as the temperature goes to zero for a metal, and diverging approximately as $1/T$ for a semiconductor.

The results of thermopower measurements on these FeCl_3 doped samples of $(\text{CH})_x$ are illustrated in Figs. 8 and 9. Figure 8 shows the thermopower vs absolute temperature

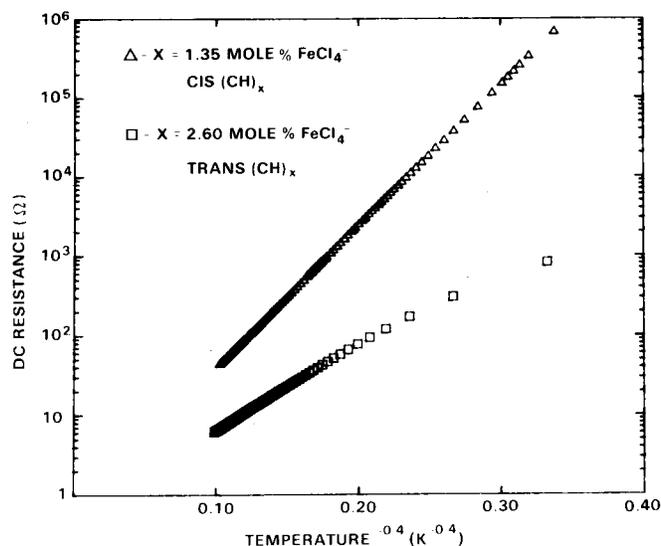


FIG. 7. $\text{Log}(R)$ vs $T^{-0.4}$ for *cis* and *trans* $(\text{CH})_x$ doped with FeCl_3 in nitromethane solutions.

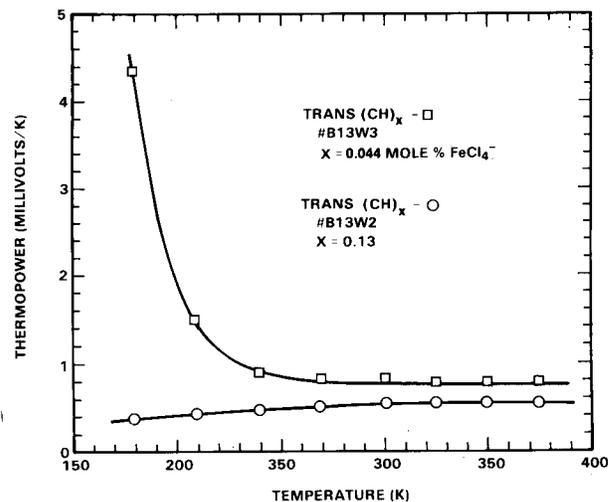


FIG. 8. Thermopower of $(\text{CH})_x$ dilutely doped with FeCl_3 in nitromethane solutions.

for two dilutely doped samples of *trans* $(\text{CH})_x$. It is known from prior work that pristine *trans* $(\text{CH})_x$ has the properties of a *p*-type semiconductor due to naturally occurring impurities.²⁴ The thermopower of such undoped materials is approximately $+850 \mu\text{V/K}$ and diverges at low temperatures as appropriate for a semiconductor. The most dilutely doped sample shown in Fig. 8 behaves similarly. The thermopower starts out about $+850 \mu\text{V/K}$ and begins to diverge between 200 and 250 K. The other dilutely doped sample shown in Fig. 8 starts with a reduced thermopower of approximately $550 \mu\text{V/K}$ and does not diverge on the scale shown. These samples become very resistive as they are cooled as shown in Fig. 6, and therefore become very difficult to measure. The $x = 0.13 \text{ mol } \% \text{ FeCl}_4^-$ sample shown in Fig. 8 would probably diverge at lower temperatures. The thermopower for heavier doped samples is illustrated in Fig. 9. The gradual change to thermopower characteristic of a metal is demonstrated with this figure. At a dopant level of approximately 3.84 mol % FeCl_4^- , the thermopower has decreased to a room temperature value of about $+12 \mu\text{V/K}$ and approaches zero as the temperature is decreased. These results are in qualitative agreement with previously reported results on samples with high dopant levels.²⁵ Thus, from the thermopower results, we can conclude that FeCl_3 doped *trans* $(\text{CH})_x$ has *p*-type semiconductor properties when dilutely doped and then becomes metallic at dopant levels of a few mol %. Furthermore, the charge carriers are always positive, indicating that FeCl_3 acts as an acceptor dopant which is at least qualitatively consistent with Eq. (1).

One interesting observation is that the heaviest doped samples showed the most metallic behavior by the thermopower, whereas conductivity measurements showed a peak in the conductivity at moderate dopant levels. As discussed earlier, the thermopower measurement is not very sensitive to breaks in the conduction path. However, such breaks in the highly conducting segments would adversely affect the electrical conductivity because many more hopping sites would be introduced. It is therefore probable that the degradation seen is accompanied by chain breakage along the

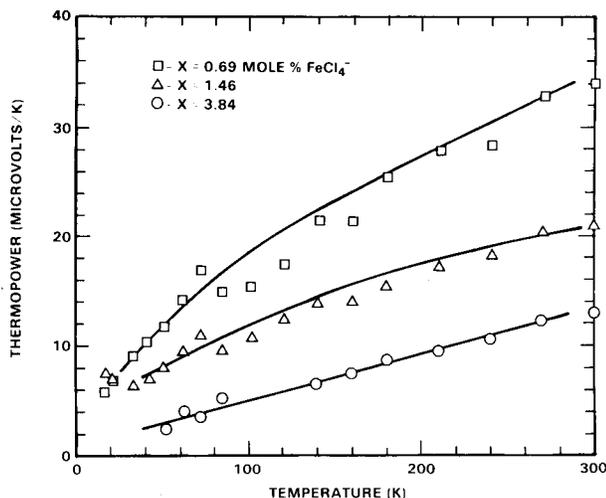


FIG. 9. Thermopower of (CH)_x heavily doped with FeCl₃ in nitromethane.

polymer backbone while at the same time increased doping enhances the conductivity of the remaining shorter segments.

CONCLUSION

We have shown that both *cis* and *trans* (CH)_x can be doped to high conductivity using FeCl₃ in nitromethane solution. (CH)_x can also be doped very slowly by exposing the polymer to the very low pressure vapors of FeCl₃ above the solid at room temperature. The resulting polymer exhibits a conductivity maximum at approximately 2.5–3.0 mol % FeCl₄⁻. Attempting to dope the polymer to higher levels results in a loss of conductivity. The conductivity of these samples exhibits a variable range hopping conductivity with an effective dimensionality of approximately 1.5. Thermoelectric power measurements on these samples show that the effective dopant, FeCl₃, acts as an acceptor dopant. The doped polymer exhibits *p*-type conductivity as evidenced by a positive thermoelectric power for all dopant levels. The room temperature thermoelectric power decreases from 850 μV/K for very dilutely doped samples to +12 μV/K for the more heavily doped samples which exhibit metallic thermoelectric power, proportional to the absolute temperature.

Thus, FeCl₃ is an effective dopant for (CH)_x and also contributes a local magnetic moment to the system due to the final FeCl₄⁻ (III) active specie. Magnetic measurements on these samples are in progress using the techniques of electron spin resonance and magnetic susceptibility.

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