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ELECTRICAL CONDUCTIVITY OF HALOGEN-DOPED POLYACETYLENE.(U)
JUL 77 C K CHIANG, Y W PARK, A J HEEGER N00014-75-C-0962
UNCLASSIFIED LRSM-TR-77-3 NL

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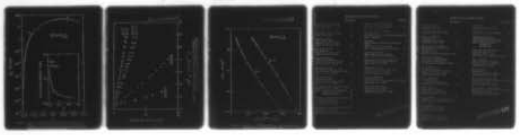

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REPORT DOCUMENTATION PAGE

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1. REPORT NUMBER: Technical Report No. 77-3

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle): Electrical Conductivity of Halogen-Doped Polyacetylene,

5. TYPE OF REPORT & PERIOD COVERED: Interim Technical Report,

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s): C. K. Chiang†, Y. W. Park†, A. J. Heeger†, H. Shirakawa, E. J. Louis and Alan G. MacDiarmid

8. CONTRACT OR GRANT NUMBER(s): N00014-75-C-0962

9. PERFORMING ORGANIZATION NAME AND ADDRESS: Departments of Chemistry and †Physics and the Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pa. 19104

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: NR-356-602

11. CONTROLLING OFFICE NAME AND ADDRESS: Department of The Navy, Office of Naval Research, Arlington, Virginia 22217

12. REPORT DATE: July 22, 1977 (22 Jul 77) — 15 p.

13. NUMBER OF PAGES: Thirteen

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office): Alan J. Heeger, Chwan K. Chiang, Y. W. Park,

15. SECURITY CLASS. (of this report): Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report): Hideki Shirakawa Edwin J. Louis

Distribution unlimited; approved for public release

DDC JUL 26 1977 C

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

LRSM-TR-77-3

18. SUPPLEMENTARY NOTES

Prepared for publication in Physical Review Letters

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Linear conjugated polymer, SP^2-hybridization, metallic behavior, polycrystalline films, semiconductors, trans-isomer, cis-isomer, infrared transmission, electrical conductivity, halogen doped $(CH)_x$, activation energy, Ziegler catalyst, X-ray diffraction, four-probe dc techniques, $(CHI_{0.23})_x$, silvery-films, $(CHBr_{0.05})_x$, poly-mono-bromo ethylene, insulator, $(CHI_y)_x$, $(CHBr_y)_x$, Hubbard band

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

When films of semiconducting polymer, trans-polyacetylene, $(CH)_x$, are exposed to chlorine, bromine or iodine vapor, uptake of halogen occurs; and the conductivity increases markedly, over seven orders of magnitude in the case of iodine. Although the randomness of the halogenated polyacetylene may be playing an important role, the behavior is like that of a series of semiconductors with activation energies which vary with halogen content. Transport and infrared studies of the most highly conducting composition $(CHI_{0.22})_x$ are suggestive of metallic behavior.

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OFFICE OF NAVAL RESEARCH

Contract N00014-75-C-0962

Task No. NR 356-602

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in the

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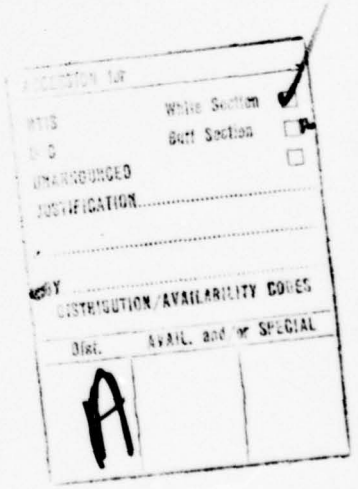

ELECTRICAL CONDUCTIVITY OF HALOGEN-DOPED POLYACETYLENE*

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ABSTRACT

When films of the semiconducting polymer, trans-polyacetylene, $(CH)_x$ are exposed to chlorine, bromine or iodine vapor, uptake of halogen occurs; and the conductivity increases markedly, over seven orders of magnitude in the case of iodine. Although the randomness of the halogenated polyacetylene may be playing an important role, the behavior is like that of a series of semiconductors with activation energies which vary with halogen content. Transport studies of the most highly conducting composition $(CHI_{0.20})_x$ are suggestive of metallic behavior.

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*Supported by the Office of Naval Research Contract No. N00014-75-C-0962.

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Polyacetylene is one of the simplest linear conjugated polymers with a single chain structure as shown in Figure 1. Each carbon is σ-bonded to one hydrogen and two neighboring carbon atoms consistent with sp^2 hybridization. The π-electrons are therefore available to delocalize into a band. In this idealized situation of a uniform chain (i.e., no bond alternation) the resulting half-filled conduction band would give rise to metallic behavior.

Studies[1] of π-π^* transitions in short chain polyenes (for example $(CH)_n$ where $n \leq 18$) have indicated that the frequencies do not fall as n^{-2} as expected for a free electron picture, but appear to saturate at $\Delta E^{\pi-\pi^*}_{(n\ \text{large})} \simeq 2.4$ eV. Bond alternation is present in the polymer and would be expected to lead to semiconducting behavior. However, Ovchinnikov[1] has estimated the bond alternation energy gap to be too small and attributed the observed value to Coulomb correlation effects; i.e. a Hubbard gap.

In a series of studies Shirakawa et al.[2-6] succeeded in synthesizing high quality polycrystalline films of $(CH)_x$, and developed techniques for controlling the cis-trans-content.[4,5] These materials are semiconductors;[6] the trans isomer, which is the thermodynamically stable form at room temperature, has a higher conductivity ($\sigma_{273\ K} = 4.4 \times 10^{-5}$ ohm^{-1} cm^{-1}) than the cis isomer ($\sigma_{273\ K} = 1.7 \times 10^{-9}$ ohm^{-1} cm^{-1}).[6]

Shirakawa and Ikeda[8] have noted that exposure to bromine vapor for short periods caused a dramatic decrease in infrared transmission (400 cm^{-1} to 4000 cm^{-1}) suggesting the presence of electronic absorption at very low frequencies. In this paper, we present an initial study[8] of the effect of halogen doping on the electrical properties of polyacetylene. We

find that the electrical conductivity of halogen doped $(CH)_x$ can be systematically increased by as much as seven orders of magnitude, and the associated thermal activation energy decreased from initial values of about 0.3 eV[6] to near zero ($\sim$ 0.01 eV).

Polyacetylene crystalline films were prepared with the techniques developed by Shirakawa et al.[2-6] in the presence of a Ziegler catalyst. X-ray diffraction and scanning electron micrograph studies show that films of any cis and trans composition are crystalline and consist of matted fibrils. The cis-trans content was controlled by thermal isomerization;[4,5] in this paper we focus on results obtained from the trans form. Details of preparation and characterization have been published elsewhere.[8] Samples used in the electrical conductivity study were cut from polymer films approximately 0.1 mm to 0.5 mm in thickness. Platinum wires and Electrodag were used to make electrical contacts to the films. All measurements of the conductivity used four-probe direct current techniques.

The conductivity was monitored during the room temperature reaction with halogens. The halogen vapor pressure was controlled by the temperature of the halogen bath (connected to the separate conductivity cell by a glass tube). The halogen content in the final product and at various stages in the reaction were determined from weight up-take and verified by chemical analysis.

Figure 2 shows the electrical conductivity of polyacetylene as a function of iodine concentration. The initial sample was trans rich with room temperature conductivity of 3.2×10^{-6} $(\Omega\text{-cm})^{-1}$. After the three hour reaction, the sample containing approximately one

iodine per five CH, $(CHI_{0.23})_x$, reached a conductivity of 38 $(\Omega\text{-cm})^{-1}$; an increase of seven orders of magnitude. The sample cell was subsequently pumped out and the sample kept in vacuum. During this period, the conductivity remained high; 20 $(\Omega\text{-cm})^{-1}$ after two days. Separate measurements of three samples of $(CHI_{0.23})_x$ gave an average conductivity of 30 $(\Omega\text{-cm})^{-1}$.

Similar results have been obtained for the other halogens, bromine and chlorine. For the case of bromine the conductivity of the polymer increases by about four orders of magnitude to give silvery films of $(CHBr_{0.05})_x$ having a conductivity of 0.5 $(\Omega\text{-cm})^{-1}$ at room temperature. The fully brominated compound, poly-monobromoethylene is an insulator. Qualitatively similar results are obtained with chlorine, but the increase in conductivity is smaller (about three orders of magnitude).

The conductivities of samples of polyacetylene doped with various concentrations of iodine and bromine were measured as a function of temperature. The results for several $(CHI_y)_x$ samples are shown in Figures 3 and 4. The temperature range covered by the measurements depended on the resistance of the sample; for the highest conductivity sample, data were obtained over the entire range from 300 K to 3 K.

In general, we find that plots of $\ell n\, \sigma$ vs. $1/T$ do not give straight line behavior as seen for a few selected iodine concentrations in Figure 3. Plotting the data as $\ell n\, \sigma$ vs. $T^{-\frac{1}{2}}$ (or $T^{-\frac{1}{4}}$) tends to give more nearly

straight line behavior as shown in Figure 4. Nevertheless, we use the initial slope of the 1/T plots to determine the thermal activation energy, E_o, which serves as a simple index of the conductivity behavior. The activation energy is shown on the inset to Figure 3 as a function of iodine concentration. Pure trans-polyacetylene has an activation energy of approximately 0.3 eV[6]. On doping with halogen, the activation energy drops rapidly reaching a value as low as 0.016 eV at about 23% iodine. Similar results are obtained for bromine doping $(CHBr_y)_x$. In the latter case, E_o(Br) goes through a minimum value less than 0.1 eV at about $y \simeq 0.05$ increasing at high bromine content with insulating behavior observed in the fully brominated compound.

Figure 4 shows the temperature dependence of samples of the high conductivity polymer $(CHI_{0.23})_x$ plotted as log σ vs. $T^{-\frac{1}{d+1}}$ for d = 1 (open circles) and d = 3 (closed circles). The curves tend to be straight over a substantial temperature interval suggesting that $\sigma = \sigma_o \exp[-(T_o/T)^{\frac{1}{d+1}}]$. However, more extensive experimental studies are required before a strong conclusion on the best value of n or even the validity of such an expression can be reached. Figures 3 and 4 do indicate that a simple semiconductor picture with a single activation energy is inadequate to describe the high conductivity regime.

Although the initial polyacetylene is crystalline, disorder may play an important role in the doped polymer. The results summarized in Figures 3 and 4 are typical of transport in disordered and amorphous

systems.[9] Variable range hopping between localized states[10,11] leads to temperature dependences of the form $\sigma \propto \exp[-(T_o/T)^{\frac{1}{d+1}}]$ where d is the dimensionality of the transport (e.g. d = 3 for three dimensional motion, etc.).

Studies of the temperature dependence of the conductivity of polycrystalline $(SN)_x$ and organic conductors such as TTF-TCNQ often show activated behavior even though the single crystal data indicate metallic behavior. The low apparent activation energy and high room temperature conductivity of doped polyacetylene suggest that this may be the case in this system as well. The value of $\sigma(300\ K) = 30\ (\Omega\text{-cm})^{-1}$ found for $(CHI_{0.23})_x$ is indeed comparable to or greater than typically found for $(SN)_x$ polycrystalline compactions[12] or films[13] (reported values range from 10 $(\Omega\text{-cm})^{-1}$ to 60 $(\Omega\text{-cm})^{-1}$ depending upon substrate conditions)[14] or polycrystalline compactions of TTF-TCNQ ($\sigma(300\ K) \simeq 15\ (\Omega\text{-cm})^{-1}$).[15] Moreover, the temperature behavior shown in Figures 3 and 4 is qualitatively similar to that found[16] in $(SN)_x$ films where the temperature dependence has been attributed to interparticle contact.

If indeed the doped polyacetylene is approaching metallic behavior, the relative importance of bond alternation and Coulomb correlation effects must be considered.[1] Doping with halogen acceptors might be expected to remove electrons from the otherwise filled lower Hubbard band thereby leading to a large reduction in activation energy and an approach to metallic behavior. Alternatively, the doping may tend to reduce the bond alternation toward a more uniform chain. Structural, magnetic and infrared studies relevant to these questions are underway.

In summary, we have shown that halogen doped polyacetylene forms a new class of conducting polymers in which the electrical conductivity can be systematically and continuously varied over a range of seven orders of magnitude. The associated thermal activation energy decreases with halogen doping. The properties of the high conductivity compositions are suggestive of metallic behavior in which the transport is limited by interparticle contact in the polycrystalline films.

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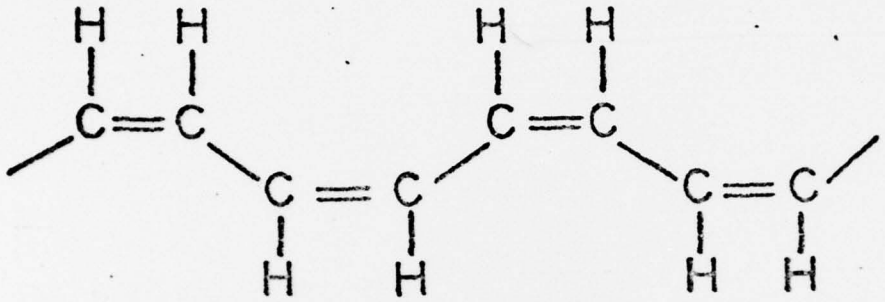
Figure Captions:

Figure 1: Polymer chain structure of polyacetylene; cis and trans forms are shown.

Figure 2: Electrical conductivity of iodine doped polyacetylene films, $(CHI_y)_x$, as a function of iodine concentration. The inset shows the activation energy as obtained from measurements of the temperature dependence (see text).

Figure 3: Normalized temperature dependence of the electrical conductivity of $(CHI_y)_x$ films for various concentrations of iodine (y = 0, 0.013, 0.037, 0.079, 0.19, and 0.23).

Figure 4: The log σ vs. $T^{-\frac{1}{d+1}}$ for $(CHI_{.23})_x$. The two curves correspond to d = 1 (• • •) and d = 3 (o o o).



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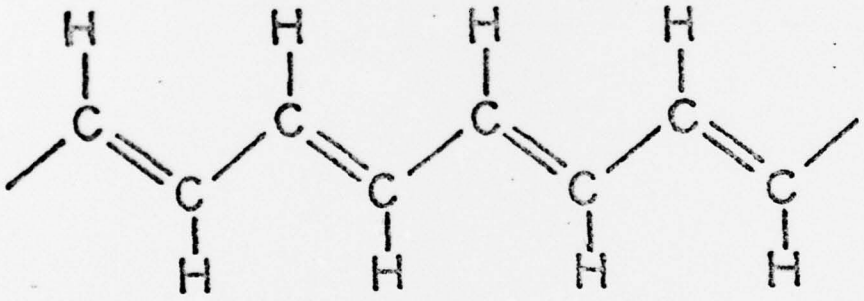

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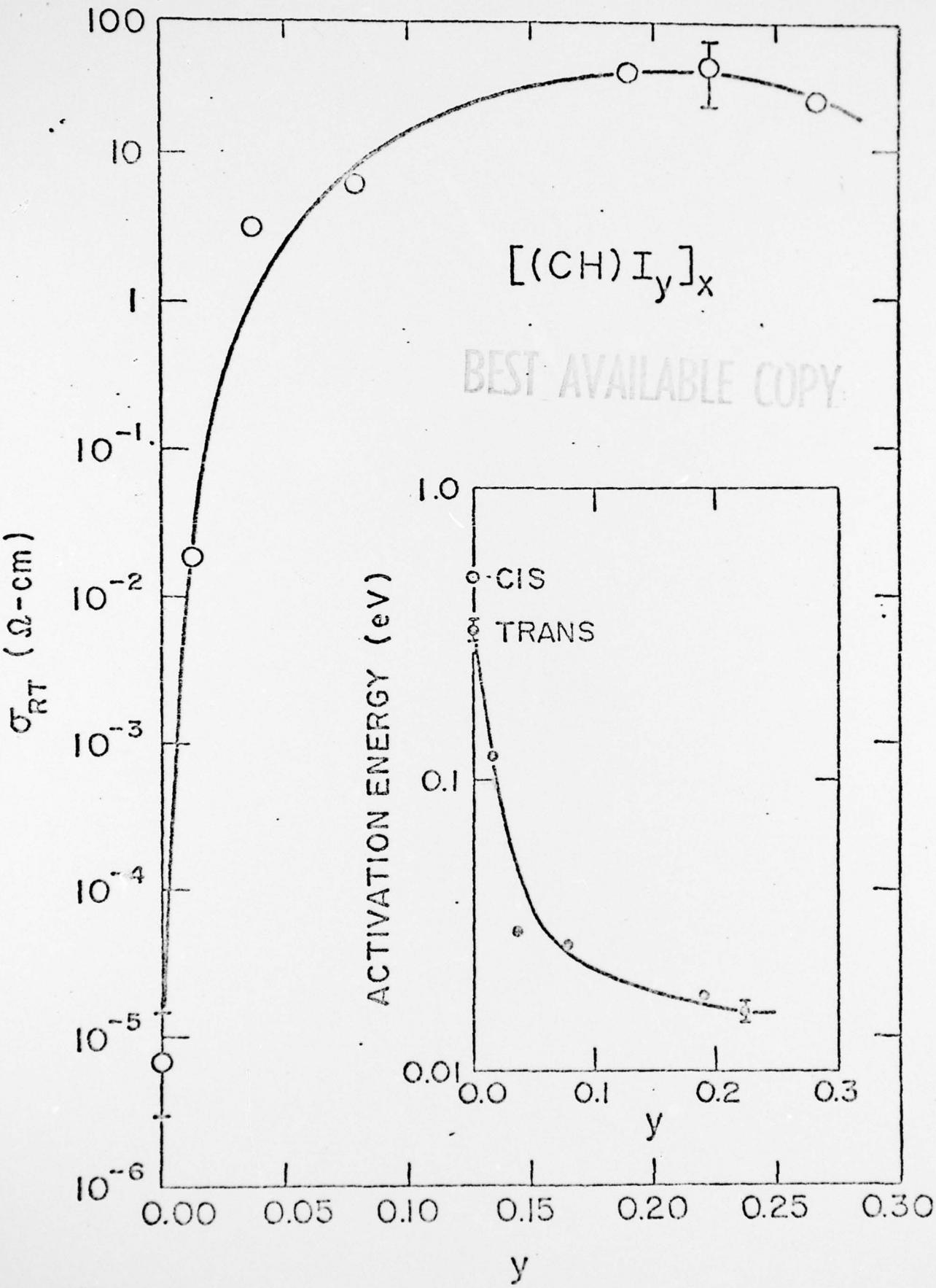

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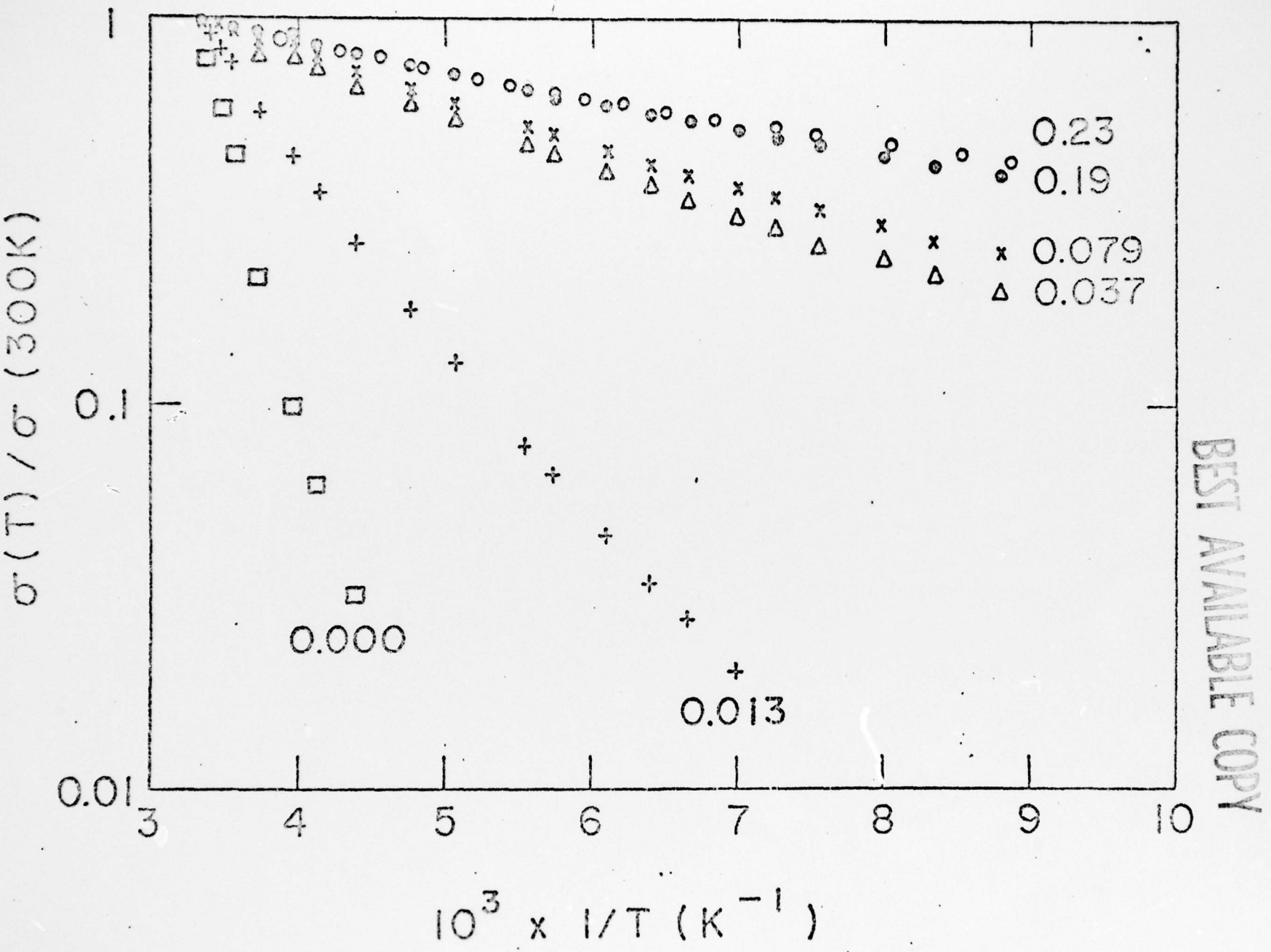

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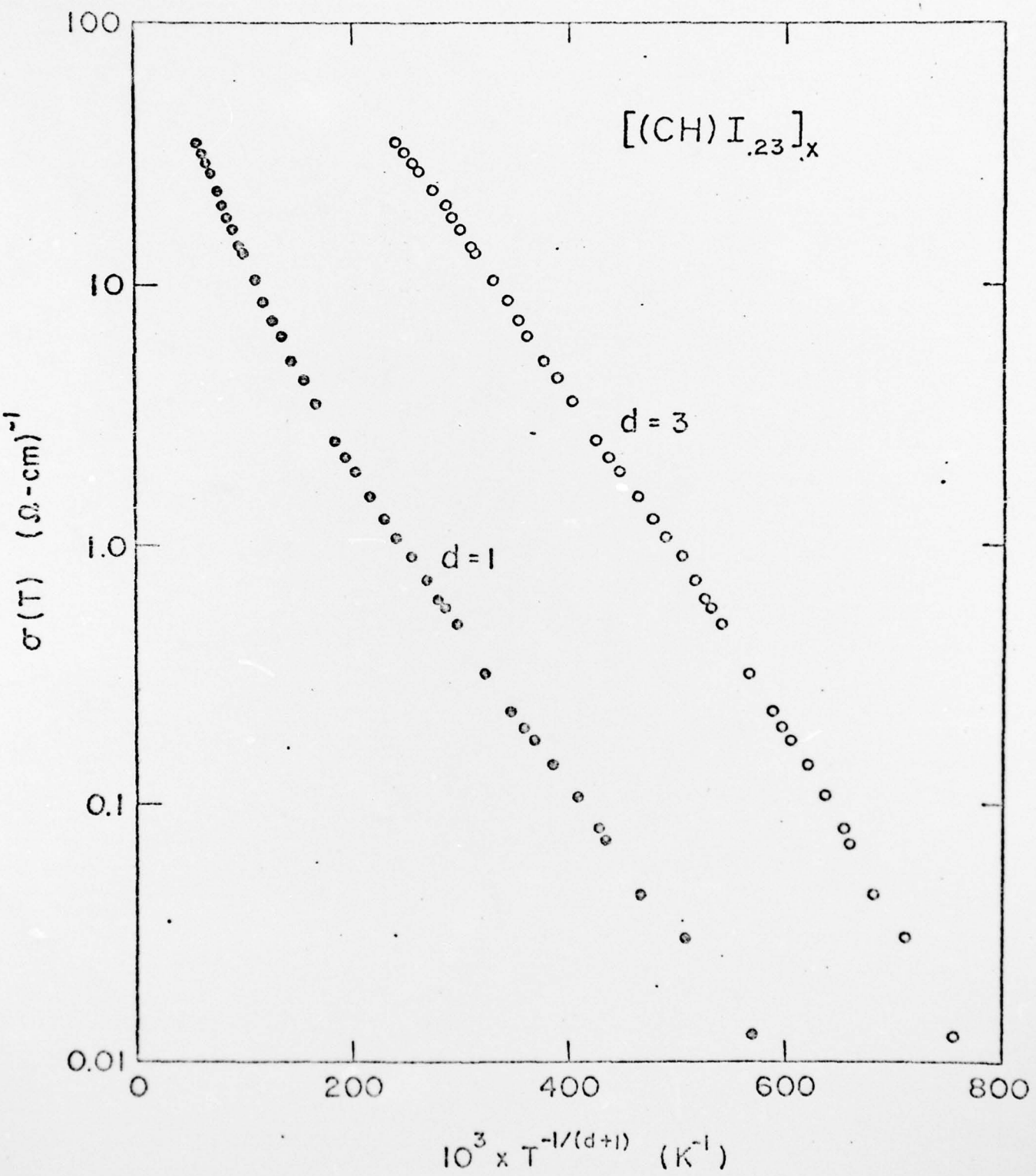

Figure 4: The log σ vs. $T^{-\frac{1}{d+1}}$ for $(CHI_{.23})_x$. The two curves correspond to d = 1 (• • •) and d = 3 (o o o).

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