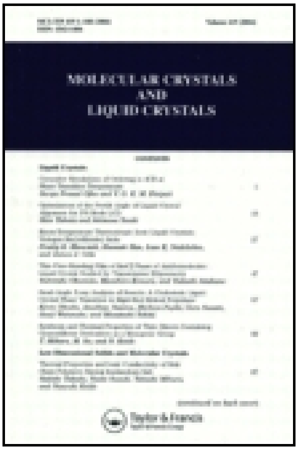

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Chemical Oxidation of Polyacetylene by Cupric Chloride

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CHEMICAL OXIDATION OF POLYACETYLENE BY CUPRIC CHLORIDE

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Abstract Polyacetylene, $(CH)_x$, has been oxidized (doped) by $CuCl_2$ to give highly conducting charge-transfer complexes. Conductivities of highly doped films range from 30 to 80 Scm^{-1} corresponding to y = 0.06 - 0.12. In lightly doped samples a rapid decrease in the activation energy of conduction is observed with increasing dopant concentration as well as the appearence of the typical dopant-associated IR-absorptions. Doping is believed to proceed via a partial reduction of $CuCl_2$ and the insertion of stabilizing anions such as $CuCl_3^-$.

INTRODUCTION

Recently it has been shown that metal halides, such as $FeCl_3$,[1] $InCl_3$[2] and several tetra-,[3] penta-[4] and hexahalides,[5] are capable of oxidizing $(CH)_x$ to give a variety of highly conducting organic metals whose physical and chemical properties vary depending on the inserted metal halide anion. Recently it was reported[6] that $CuCl_2$ acts as a poor doping agent towards $(CH)_x$. At a doping level of y = 0.04 the conductivity of the oxidized material was reported to be 1.8×10^{-3} Scm^{-1}. We now find that $(CH)_x$ can be chemically oxidized by $CuCl_2$ to give golden, flexible films with conductivities in the metallic regime.

EXPERIMENTAL

Cis-rich $(CH)_x$-films were synthesized according to the method developed by Ito et al.[7] at -78°C. Films of approximately 80% cis-contents were used in all experiments.

Oxidation of $(CH)_x$ was done by immersing films in saturated solutions of anhydrous $CuCl_2$ in dry nitromethane (predried with molecular sieves and $CaCl_2$ and distilled under argon, water content less than 10 ppm). For low doping levels dilute solutions were used. The doped films were washed with dry nitromethane 5-10 times and dried in dynamic vacuum over-night.

The DC electrical conductivity was measured using the standard four-probe technique. Graphite contact cement and Pt-wires were used to make electrical contacts. A Perkin-Elmer 682 IR-spectrophotometer, a Philips PW 1700 X-ray diffractometer and a Jeol JSM-35C scanning electron microscope equipped with a PGT System III energy dispersive X-ray unit were used for characterization of the oxidized films.

RESULTS AND DISCUSSION

The maximum conductivity we have obtained by doping $(CH)_x$ with $CuCl_2$ is 80 Scm^{-1} corresponding to a dopant concentration of $y = 0.12$ as indicated in Table I. At this high doping level the $(CH)_x$-film, which is brilliantly golden at intermediate doping levels ($y = 0.02 - 0.08$), is golden-blue which indicates that in spite of the high conductivity observed some chlorination of the polymer backbone has occured. This is supported by the observed increase in the Cl/Cu ratio which is 2.94 for $y \approx 0.036$ and 3.46 for $y = 0.12$. This "overdoping" has been observed for several $(CH)_x$-metal halide systems.

DOPANT CONCENTRATION* (y)	CONDUCTIVITY ($S\,cm^{-1}$)
0.0045	1×10^{-3}
0.008	1×10^{-2}
0.013	8×10^{-2}
0.036 [a)]	2.9
0.048	7.8
0.060	25
0.086	34
0.12 [b)]	80

* DOPANT CONCENTRATION DETERMINED FROM WEIGHT UPTAKE AS $CuCl_2$

a) ELEMENTAL ANALYSIS: Cl/Cu = 2.94
% C, H, Cu, Cl = 98.92 %

b) ELEMENTAL ANALYSIS: Cl/Cu = 3.46
% C, H ,Cu, Cl = 99.12 %

TABLE I Dopant concentration and conductivity of $CuCl_2$-doped $(CH)_x$.

Figure 1 shows the electrical conductivity of doped $(CH)_x$ as a function of dopant concentration. Figures 2 and 3 show the temperature dependence of the conductivity at different dopant concentrations and the activation energy of conduction as a function of dopant concentration, respectively. We notice a rapid decrease in the room temperature activation energy at low concentrations reaching 18 meV for $y = 0.1055$. Combined with magnetoresistance measurements performed on the same samples[8] we conclude that the conduction mechanism in lightly doped samples can be explained by the variable range hopping mechanism. In heavily doped samples the ordinary model for band conduction is qualitatively working.

Figure 5 shows middle infrared transmission through pristine

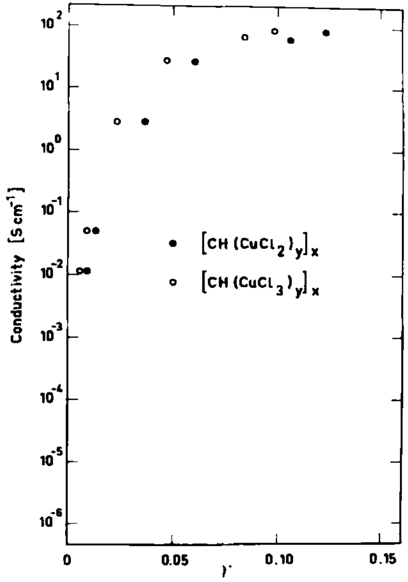

FIGURE 1 Electrical conductivity of $CuCl_2$-doped $(CH)_x$ vs. dopant concentration.

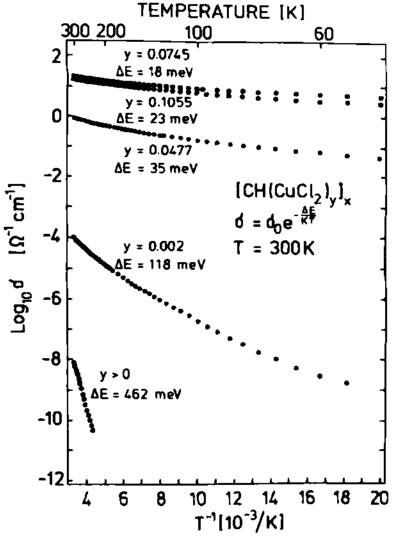

FIGURE 2 Electrical conductivity of $CuCl_2$-doped $(CH)_x$ vs. $10^3/T$ for different dopant levels.

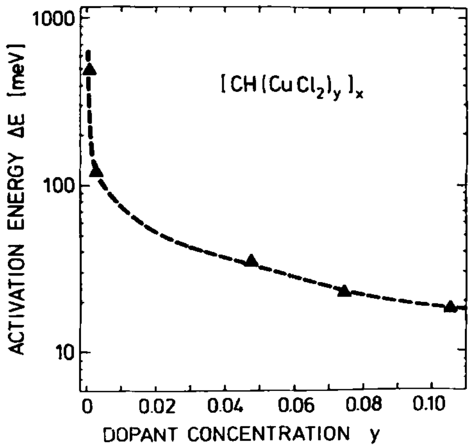

FIGURE 3 Activation energy of conduction as a function of dopant concentration.

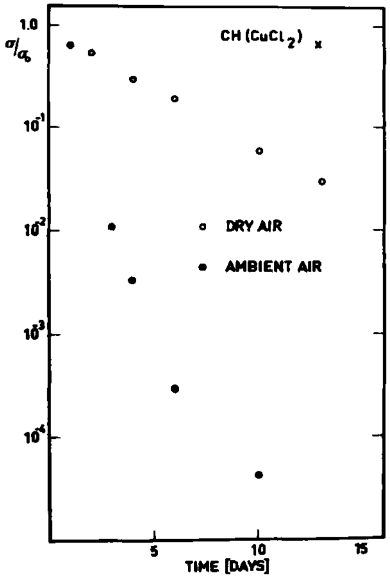

FIGURE 4 Relative conductivity of $CuCl_2$-doped $(CH)_x$ vs. time in ambient and dry air.

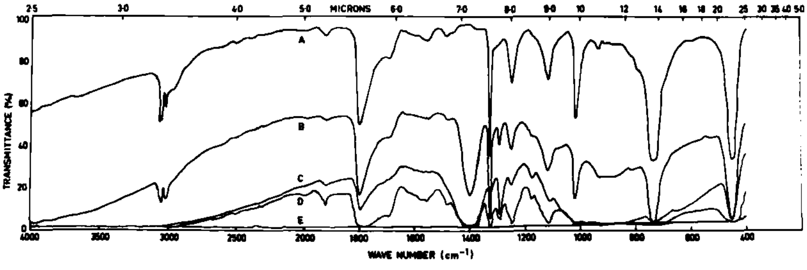

FIGURE 5 Middle infrared transmission of lightly $CuCl_2$-doped $(CH)_x$. Dopant concentration increases from A to E.

(A), lightly doped (B-D) and heavily doped (E) films. The doping effect of $CuCl_2$ is clearly demonstrated by the appearence of the typical dopant-associated absorptions at 1380 and 900 cm^{-1}.

Dopant profile analyses on several 120 μm thick films show that even at high doping levels the distribution of the dopant anion is inhomogeneous. This results in a higher dopant concentration on the film surfaces than in the bulk.

X-ray diffraction (XRD) analyses show new diffraction lines corresponding to CuCl in heavily doped films. This indicates that during the doping process a partial reduction of the oxidizing $CuCl_2$ takes place with the formation of an active dopant anion and the inactive species CuCl. Based on the XRD results and the observed Cl/Cu ratio (2.94) from elemental analyses of intermediately doped samples, we suggest that the doping proceeds via the following mechanism:

$$2CuCl_2 + e^- \longrightarrow CuCl_3^- + CuCl$$

The high Cl/Cu ratio of 3.46 in films of y = 0.12 should be regarded as signs of overdoping (chlorination) of $(CH)_x$ rather than indicating the formation of a divalent dopant anion such as $CuCl_4^{2-}$. Oxidation of $(CH)_x$ by a two-electron transfer has never been confirmed.[9]

The $CuCl_2$-doped films show poor stability in ambient air as indicated in Figure 4. The golden film turns dark blue in approximately two days with an accompaning decrease in conductivity of nearly two orders of magnitude. XRD analyses indicate that the copper species incorporated in the polymer react with moisture to form polynuclear complexes such as $Cu_7Cl_4(OH)_{10}\cdot H_2O$ irreversibely. The stability is significantly increased in dry air. The slow conductivity decrease is mainly due to the inherent instability of the polymer backbone towards attack by oxygen. In dry argon heavily doped films retain metallic conductivity for months. In dynamic vacuum at temperatures below 70-80 °C doped films show a reasonable stability typical of metal halide doped $(CH)_x$.[10] Chemical reactions between the dopant and the polymer becomes important at temperatures over 100 °C.

CONCLUSIONS

We have shown that polyacetylene, $(CH)_x$, can be chemically doped by the metal dihalide $CuCl_2$ to give films exhibiting metallic conductivity at doping levels higher than $y = 0.03$. The dopant distribution is inhomogeneous even at high dopant levels. The doping mechanism is suggested to proceed via a partial reduction of $CuCl_2$ to form the active dopant anion $CuCl_3^-$ and the nonactive species CuCl. $(CH)_x$ undergoes an irreversible chlorination when heavily doped. The doped films are extremely sensitive to moist air and water due to the reactivity of the incorporated copper species.

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