

From: MOLECULAR METALS  
Edited by William E. Hatfield  
(Plenum Publishing Corporation, 1979)

PROPERTIES OF DOPED POLYACETYLENE,  $(CH)_x$

R. L. Greene, T. C. Clarke, W. D. Gill, P. M. Grant,  
J. F. Kwak and G. B. Street

IBM Research Laboratory  
San Jose, California 95193, U.S.A.

Linear polyacetylene,  $(CH)_x$  is one of the simplest conjugated organic polymers, and it therefore has attracted the attention of polymer chemists and physicists for some time [1]. Each carbon atom is  $\sigma$  bonded to one hydrogen and two neighboring carbon atoms consistent with  $sp^2$  hybridization. The  $\pi$  electrons delocalize into the bands in which carrier transport can occur. In the absence of bond alternation and Coulomb correlation the trans form of  $(CH)_x$  would be a metal. In actuality the trans form of  $(CH)_x$  has bond alternation and is thus a semiconductor. In a recent series of studies Shirakawa and coworkers [2,3,4] have succeeded in synthesizing polycrystalline films of  $(CH)_x$  and have chemically doped these films with a variety of donors and acceptors to give n-type or p-type semiconductors. Transport and far IR transmission studies as a function of doping suggest that a semiconductor to metal transition occurs near 1 atomic % dopant concentration [3]. At the highest levels of acceptor doping, room temperature conductivities of an order a few hundred  $\text{ohm}^{-1}\text{cm}^{-1}$  were obtained; a remarkably large value considering that the  $(CH)_x$  films consist of tangled, randomly oriented fibrils (of average diameter  $200\text{\AA}$ ) with an overall film density only one-third the theoretical density determined from X-ray diffraction studies [5].

In this short paper we will review the work done on  $(CH)_x$  by our group at IBM Research San Jose. The details of most of this work were presented in March 1978 at the American Physical Society meeting in Washington, D.C., and are soon to be published in various journals. We will discuss band structure calculations [6], along with thermopower [7], electrical conductivity [7,8], Hall effect [8], optical absorption, reflectivity and photoconductivity experiments [9]. Most of the experiments have

been done on undoped  $(\text{CH})_x$  films and  $(\text{CH})_x$  films heavily doped ( $\sim 10\%$ ) with the acceptor  $\text{AsF}_5$ . We have also prepared high conductivity  $(\text{CH})_x$  films doped with transition metals [10] (Ag and Cu), thereby gaining new insight into the chemistry and physics of the doping process.

We begin with our band structure results, since an understanding of the energy bands is crucial to any interpretation of the physical properties. The one-electron bands of  $(\text{CH})_x$  in both the cis- and trans- conformations have been investigated by Grant and Batra [6]. Both one-dimensional (1D) and three-dimensional (3D) calculations have been done using the crystal structure suggested by Baughman, et al. [5].

The major results are the following:

- 1) Both cis and trans  $(\text{CH})_x$  have rather wide valence and conduction bands ( $\sim 5\text{eV}$ ) in the polymer chain direction. On the other hand, the interchain band dispersion is never larger than  $0.3\text{eV}$  which implies  $(\text{CH})_x$  is a 1D-like material. However, this interchain interaction appears to be enough to suppress the Peierls instability when the material is doped to metallic levels of conductivity.
- 2) There is a single particle band gap, of order  $1.0\text{eV}$ , in cis  $(\text{CH})_x$  for uniform carbon bond lengths. There is no band gap in trans  $(\text{CH})_x$  for uniform bond lengths (i.e., it is a metal). However, with bond alternation a gap appears reaching a maximum value of  $\sim 2.3\text{eV}$  for the extreme limit of pure single and double bonds.

The main conclusion of this work is that all the electronic properties of both pristine and doped  $(\text{CH})_x$  which have been observed to date can be interpreted within the framework of an itinerant one-electron band structure in which Coulomb interactions are negligible.

The optical experiments [9] give the most direct comparison with the band theory. Our absorption measurements on undoped  $(\text{CH})_x$  films show a steep absorption edge which can be interpreted (as in conventional inorganic semiconductors) to give a value for the band gap of  $E_g = 1.2 \pm 0.1\text{eV}$  for cis  $(\text{CH})_x$  and  $E_g = 0.97 \pm 0.1\text{eV}$  for trans  $(\text{CH})_x$ . These values agree remarkably well with the band calculations. In addition, we have recently observed the onset of photoconductivity at  $\sim 0.8\text{eV}$  in trans  $(\text{CH})_x$ , which agrees with earlier work on more poorly characterized material [11], and which confirms the interpretation of the absorption edge as being caused by the valence to conduction band transition. For both cis and trans  $(\text{CH})_x$  doped with  $10\%$   $\text{AsF}_5$  we observe an absorption in the near infrared which dominates the optical spectrum. We interpret this as caused by free carrier absorption since it is also

manifested as a plasma edge in our reflectivity data. A Drude analysis of the plasma edge gives  $\epsilon_{\infty}=2.0$ ,  $\hbar\omega_p=2.43\text{eV}$  and  $\tau=4.6\times 10^{-15}$  sec.

For 10%  $\text{AsF}_5$  doped films we find a room temperature dc electrical conductivity of order  $500 \Omega^{-1}\text{cm}^{-1}$  in agreement with the work of Chiang, et al. [3]. However, as the temperature is lowered to  $4.2^\circ\text{K}$  the conductivity ( $\sigma$ ) decreases by a factor of 5 for the Chiang, et al. [3] films and a factor of 1.5 for our films. This distinctly non-metallic behavior could be caused by 1) poor interfibril contact between metal fibers or 2) hopping via localized states in a semiconductor gap. To distinguish these possibilities we have performed a variety of different transport measurements. Perhaps the most useful, thus far, has been the thermoelectric power (S). The thermopower is a zero current measurement, so that breaks in a current path, unless accompanied by large breaks in the heat flow paths, do not produce sizable effects. Therefore, in most cases, the thermopower is a direct measurement of the intrinsic properties of a metal even when anisotropy and crystal imperfections result in non-metallic electrical conductivity behavior. We find, for 10%  $\text{AsF}_5$  doping in a cis-trans film, a small ( $\sim 10\mu\text{V}/^\circ\text{K}$ ), positive thermopower at  $300^\circ\text{K}$  with a linear slope vs. temperature, extrapolating to zero at  $0^\circ\text{K}$ . The sign is consistent with the acceptor doping, i.e., hole conduction, and the linear slope with zero intercept implies that the fibrils are metallic. Diffusion through localized states could give a linear thermopower but the magnitude and zero temperature intercept would be large [12]. In addition, we find that  $\sigma(T)$  from  $4.2^\circ\text{K}$  down to  $30\text{mK}$  is practically constant in value. This is most plausibly understood as due to tunnelling between metal particles (fibrils). Variable range hopping between localized states predicts an exponential increase in  $\sigma$  as T is lowered. The slope of the S vs. T allows us to estimate the valence bandwidth for cis  $(\text{CH})_x$  using a simple 1D tight binding model. With complete charge transfer to  $\text{AsF}_5$  (i.e., 0.1e per CH) we obtain a bandwidth of  $\sim 10\text{eV}$  in rough agreement with the better band calculation discussed above. Our experiments [10] on silver doping of  $(\text{CH})_x$  are strong evidence for complete charge transfer with  $\text{AsF}_5$  doping.

In an attempt to determine the number of free holes and their mobility Seeger and Gill [8] have measured the Hall effect on 10%  $\text{AsF}_5$  doped  $(\text{CH})_x$  films. They find a positive Hall coefficient, consistent with the thermopower, which changes very little in magnitude between  $300^\circ\text{K}$  and  $4.2^\circ\text{K}$  (consistent with metallic behavior). However, the magnitude of the Hall coefficient is anomalously low and cannot be interpreted in terms of a single band model unless one assumes a reduced value for the Hall mobility [i.e.,  $R_H=(1/nec)\mu_H/\mu_D$ ] relative to the conductivity mobility. Further work on this problem is in progress.

In summary then, we have briefly reviewed our theoretical and experimental work on heavily doped and undoped  $(CH)_x$ . Based on our results we have developed the following picture for this system. The undoped  $(CH)_x$  is a semiconductor with a medium band gap; the gap being caused by bond alternation in the trans case and by the chain symmetry in the cis case. Doping with strong oxidizing agents such as  $AsF_5$ , bromine, iodine, etc. leads to complete charge transfer with mobile delocalized holes in a wide valence band of the polymer and localized charge on the dopant. The mobile holes cause metallic behavior at all temperatures. In contrast to the interpretation of Chiang, et al. [3] we believe that doping does not create localized states in the band gap (such states may exist because of disorder). Rather, the acceptor level is at an energy which falls within the valence band. The hole is localized by Coulomb interaction with the charged acceptor sites at low dopant concentrations and delocalized because of self screening at higher concentrations. These initial studies and those of others suggest there is much interesting physics and chemistry to be done on  $(CH)_x$  and its modifications.

#### ACKNOWLEDGMENTS

We thank the ONR for partial support of this work. We also acknowledge the valuable discussions and experimental input of W. Bludau and K. Seeger during their visits to IBM San Jose and of our IBM colleagues I. Batra and T. Tani.

#### REFERENCES

1. For a summary and detailed references see A. A. Ovchinnikov, Soviet Physics Uspekhi 15, 575 (1973).
2. For example see To Ito, H. Shirakawa and S. Ikeda, J. Polym. Sci. Polym. Chem. Ed 13, 1943 (1975).
3. C. K. Chiang, et al., Phys. Rev. Lett. 39, 1098 (1977).
4. C. K. Chiang, et al., J. Am. Chem. Soc. 100, 1013 (1978).
5. R. H. Baughman, et al., to be published in J. Chem. Phys.
6. P. M. Grant, Bull. Am. Phys. Soc. 23, 305 (1978); P. M. Grant and I. P. Batra, submitted.
7. R. L. Greene, J. F. Kwak, T. C. Clarke and G. B. Street, Bull. Am. Phys. Soc. 23, 156 (1978) and 23, 305 (1978); also submitted to Solid State Comm.
8. K. Seeger, W. D. Gill, T. Clarke and G. B. Street, Bull. Am. Phys. Soc. 23, 305 (1978); also submitted to Solid State Comm.

9. W. Bludau, T. C. Clarke, P. M. Grant and G. B. Street, Bull. Am. Phys. Soc. 23, 304 (1978); to be published.
10. T. C. Clarke, R. H. Geiss, J. F. Kwak and G. B. Street, accepted by Chem. Comm.
11. A. Matsui and K. Nakamura, Japan J. Appl. Phys. 6, 148 (1967).
12. N. F. Mott and E. A. Davis, Electronic Processes in Non-Crystalline Materials (Oxford, 1971).