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Chemistry and Physics of Polyacetylene, $(CH)_x$: The Prototype Conducting Polymer

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A method has been devised for synthesizing polyacetylene, $(CH)_x$, of variable density ranging from ~0.03 to ~0.4 g/cc. The resulting polymer shows potential for microwave absorption. Polyacetylene can be chemically doped with resulting control of electrical conductivity over a range of 12 orders of magnitude. It has also been discovered that $(CH)_x$ can be reversibly p- and n- doped electrochemically, suggesting the possible use of conducting polymers in novel rechargeable batteries. Polyacetylene undergoes a semiconductor to metal transition upon p- and n-chemical or electrochemical doping. Magnetic, optical, I/R and phototransport changes associated with this transition show that soliton doping and soliton excitations play a dominant role in determining the electronic properties of the polymer.

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"Chemistry and Physics of Polyacetylene, $(CH)_x$: The Prototype Conducting Polymer"

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CONTENTS

1. SUMMARY OF WORK PERFORMED

Polyacetylene, $(CH)_x$, is the simplest conjugated organic polymer and is therefore of special fundamental interest. The electrons from the unsaturated π-system are delocalized along the polymer chains. However, because of the combined effects of bond alteration and Coulomb correlation, there is an energy gap in the excitation spectrum leading to semiconducting behavior. As a result of the large overall bandwidth (8-10eV) and unsaturated π-system, $(CH)_x$ is fundamentally different from either the traditional organic semiconductors made up of weakly interacting molecules (e.g., anthracene, etc.) or from other saturated polymers with monomeric units of the form $\left(\overset{R}{\underset{}{-C-}}\overset{R}{\underset{}{-}} \right)$ where there are no π-electrons (e.g., polyethylene, etc.). Polyacetylene is therefore electronically more nearly analogous to the traditional inorganic semiconductors; and indeed our studies have shown that $(CH)_x$ can be doped with a variety of donor or acceptor species. The principal findings are summarized below together with the corresponding paper numbers as given in Section 2.

Work at the University of Pennsylvania has focused in three general areas:

1. Fundamental studies of the electrochemistry of $(CH)_x$. This has resulted in the discovery of reversible electrochemical p- and n-doping of $(CH)_x$ (#2). This opens an enormous new area of potential dopants for study. The reversible electrochemical doping of $(CH)_x$ to metallic levels has resulted in the development of light-weight rechargeable batteries (#6, #9, #15).
2. Synthetic work resulting in the development of new forms of polyacetylene; for example, the variable density $(CH)_x$ synthesized using a gel as an intermediate step. The density of the resulting polymer can be varied from that of a foam-like material (density ~0.03 gm/cm^3) to that of the as-formed films (~0.4 gm/cm^3). The foam-like material has been

shown to be an efficient microwave absorber (after suitable doping) and may find application as a radar absorbing material (#1).

3. *Fundamental studies* of the doping and transport mechanisms in this new class of conducting polymer (#8, #10). In particular, experimental studies have confirmed the soliton doping mechanism (#8). These results opened a whole new area of soliton physics for study and they have introduced entirely new concepts into the chemistry of these polymers (#18). Selected specific accomplishments are listed below:
   A. Demonstration of chemical doping of an organic polymer, $(CH)_x$, with resulting control of electrical conductivity over a range of twelve orders of magnitude (#18).
   B. Demonstration of a semiconductor to metal transition in this organic polymer (#18).
   C. Demonstration of donor and acceptor doping with resulting n-type or p-type material (#4, #5).
   D. Demonstration and development of electrochemical doping techniques leading to high energy density and high current density batteries and to a variety of other possible applications (#2, #9, #14, #16, #17).
   E. Demonstration of photon induced electron-hole production and separation in a p-n heterojunction diode; photovoltaic phenomena and photoconductivity in $(CH)_x$ (#7, #11).
   F. Development of a theoretical basis for understanding the doping mechanism; solitons in polyacetylene (#8, #18).
   G. Demonstration from experimental studies of magnetic, optical, ir, and phototransport in $(CH)_x$ that soliton doping and soliton excitations play a dominant role in determining the electronic properties (#3, #4, #7, #11, #15).

H. Demonstration (via a sub-contract to the U. of Massachusetts) through in situ ESR measurements that the paramagnetism in trans-$(CH)_x$ arises from defects induced during isomerizaton. There are no free spins in cis-$(CH)_x$. This result is of fundamental importance to the development of the soliton concepts as applied to $(CH)_x$. Scanning electron microscopy studies show that the nascent morphology of $(CH)_x$ films is clearly fibrillar (#15).

I. Development (via a sub-contract to the U. of Massachusetts) of alternative synthetic procedures leading to low density foam-like material. The resulting "foam" has been shown to be an effective microwave absorber (#1).

2. PUBLICATIONS AND PATENTS PENDING

A. Publications

1. "Microwave Properties of Low-Density Polyacetylene", A. Feldblum, Y. W. Park, A. J. Heeger, A. G. MacDiarmid, G. Wnek, F. Karasz, and J. C. W. Chien, J. Poly Sci: Polym. Phys. Ed., 19, 173 (1981). (Supported by DARPA/ONR).
2. "Organic Batteries: Reversible n- and p-Type Electrochemical Doping of Polyacetylene, $(CH)_x$", D. MacInnes, Jr., M. A. Druy, P. J. Nigrey, D. P. Nairns, A. G. MacDiarmid, and A. J. Heeger, J.C.S. Chem. Comm., 317 (1981). (Supported by DARPA/ONR, N.S.F. and N.S.F.-M.R.L. grants).
3. "Infrared-active Vibrational Modes of Charged Solitons in $(CH)_x$ and $(CD)_x$", S. Etemad, A. Pron, A. J. Heeger, A. G. MacDiarmid, E. J. Mele, and M. J. Rice, Phys. Rev. B, 23, 5137 (1981). (Supported by DARPA/ONR).
4. "Experimental Studies of Sodium-Doped Polyacetylene: Optical and ESR Results for Metallic $(CHNa_y)_x$ ", T.-C. Chung, A. Feldblum, A. G. MacDiarmid, and A. J. Heeger, J. Chem. Phys. 74, 5504 (1981). (Supported by DARPA/ONR).
5. "Electrical Conductivity of Heavily Doped Polyacetylene at Ultralow Temperatures", C. M. Gould, D. M. Gates, H. M. Bozler, A. J. Heeger, A. G. MacDiarmid, and M. A. Druy, Phys. Rev. B, 23, 6820 (1981). (Supported by DARPA/ONR and N.S.F. Grant No. D.M.R. 79-00830).
6. "Lightweight Rechargeable Storage Batteries Using Polyacetylene, $(CH)_x$ as the Cathode-Active Material", P. J. Nigrey, D. MacInnes, Jr., D. P. Nairns, A. G. MacDiarmid, and A. J. Heeger, J. Electrochem. Soc., 128, 1651 (1981). (Supported by DARPA/ONR).

7. "Photoconductivity in Polyacetylene", S. Etemad, T. Mitani, M. Ozaki, T.-C. Chung, A. J. Heeger, and A. G. MacDiarmid, Solid State Commun., 40, 75 (1981). (Supported by DARPA/ONR).
8. "Inter-Soliton Electron Hopping Transport in Trans-$(CH)_x$", D. Moses, J. Chen, A. Denenstein, M. Kaveh, T.-C. Chung, A. J. Heeger, and A. G. MacDiarmid, Solid State Commun., 40, 1007 (1981). (Supported by DARPA/ONR).
9. "Utilization of Polyacetylene, $(CH)_x$, in the Fabrication of Rechargeable Batteries", P. J. Nigrey, D. MacInnes, Jr., D. P. Nairns, A. G. MacDiarmid, and A. J. Heeger, Conductive Polymers, Ed., Raymond B. Seymour (Plenum Publishing Corp.), p. 227, (1981). (Supported by DARPA/ONR).
10. "Recent Advances in the Chemistry and Physics of Polyacetylene: Solitons as a Means of Stabilizing Carbonium Ions and Carbanions in Doped $(CH)_x$", A. G. MacDiarmid and A. J. Heeger, Proceedings of the Molecular Electronic Devices Workshop, Ed., F. L. Carter, Washington, D.C., p. 259, 1981. (Supported by DARPA/ONR and N.S.F.-M.R.L. Grant No. DMR-79-23647).
11. Photoexcitations in Polyacetylene", L. Lauchlan, S. Etemad, T.-C. Chung, A. J. Heeger, and A. G. MacDiarmid, Phys. Rev. B, 24, 3701 (1981). (Supported by DARPA/ONR and Army Research Office DAA G29-81-K-0058).
12. "Transport, Magnetic and Structural Studies of Polyacetylene", A. J. Heeger and A. G. MacDiarmid, Mol. Crys. Liq. Cryst., 77, 1 (1981). (Supported by DARPA/ONR, N.S.F. Grant No. DMR-80-09822 and N.S.F.-M.R.L. Grant No. DMR-79-23647).
13. "Electrochemistry of Polyacetylene, $(CH)_x$: Lightweight Rechargeable Batteries using $(CH)_x$ as the Cathode-Active Material," A. G. MacDiarmid,

P. J. Nigrey, D. F. MacInnes, Jr., D. P. Nairns and A. J. Heeger, Org. Coat. Plast. Chem., 44, 372 (1981). (Supported by DARPA/ONR).

14. "Electrochemical Isomerization of Cis-$(CH)_x$ to Trans-$(CH)_x$", T.-C. Chung, A. Feldblum, A. G. MacDiarmid, and A. J. Heeger, J. Polym. Sc. Polym. Lett. Ed., 20, 427 (1982). (Supported by DARPA/ONR and N.S.F.).
15. "Electron Paramagnetic Resonance Saturation Characteristics of Pristine and Doped Polyacetylenes", J. C. W. Chien, G. E. Wnek, F. E. Karasz, J. M. Warakomski, L. C. Dickinson, A. J. Heeger, and A. G. MacDiarmid, Macromolecules, 15, 614 (1982). (Supported by DARPA/ONR).
16. "Lightweight Rechargeable Storage Batteries Using Polyacetylene, $(CH)_x$, As the Cathode-Active Material", reply to Dr. Sigmund Schuldiner's criticism, P. J. Nigrey, D. MacInnes, Jr., D. P. Nairns, A. G. MacDiarmid, and A. J. Heeger, J. Electrochem. Soc., 129, 1271 (1982). (Supported by DARPA/ONR).
17. "Opto-Electrochemical Spectroscopy of trans-$(CH)_x$", A. Feldblum, J. H. Kaufman, S. Etemad, A. J. Heeger, T.-C. Chung, and A. G. MacDiarmid, Phys. Rev. B, 26, 1982. (Supported by DARPA/ONR and by DOE Grant No. DE-AC02-81-ER-10832).
18. "Polyacetylene, $(CH)_x$: The Prototype Conducting Polymer", S. Etemad, A. J. Heeger, and A. G. MacDiarmid, Annual Review of Phys. Chem., 33, 443 (1982). (Supported by DARPA/ONR, N.S.F., N.S.F.-M.R.L. and DOE).
19. "Effect of Non-uniform Doping on Electrical Transport in Trans-$(CH)_x$: Studies of the Semiconductor-Metal Transition", D. Moses, A. Denestein, J. Chen, A. J. Heeger, P. McAndrew, T. Woerner, A. G. MacDiarmid and Y.W. Park, Phys. Rev. B, 25, 12, (1982), (Supported by DARPA/ONR, and the Korean Science and Engineering Foundation).
20. "Chemical and Electrochemical Isomerization of Polyacetylene: In Situ Optical Studies", A. Feldblum, A. J. Heeger, T. C. Chung and A. G.

MacDiarmid, J. Chem. Phys., 77, 5114, (1982), (Supported by DARPA/ONR).

21. "Electrochemistry of $(CH)_x$: Lightweight Rechargeable Batteries Using $(CH)_x$ as the Cathode- and Anode-Active Materials", P. J. Nigrey, A. G. MacDiarmid, and A. J. Heeger, Mol. Cryst. Liq. Cryst. 83, 309, (1982), (Supported by DARPA/ONR, N.S.F. and DOE).
22. "Pressure Dependence of the Photoabsorption of Polyacetylene", D. Moses, A. Feldblum, E. Ehrenfreund, A. J. Heeger, T. C. Chung and A. G. MacDiarmid, Phys. Rev. B, 26, 3361 (1982). (Supported by DARPA/ONR and N.S.F.-M.R.L. Grant No. DMR-79-23647).
23. "The Aqueous and Non-Aqueous Electrochemistry of Polyacetylene: Application in High Power Density Rechargeable Batteries", A. G. MacDiarmid, M. Aldissi, R. B. Kaner, M. Maxfield and R. J. Mammone, Org. Coat. Appl. Polymer Sci. Proc, 48, 531, (1983). (Supported by DARPA/ONR and DOE Grant No. DE-AC02-81-ER10832).
24. "The Electrochemistry of Polyacetylene: Application in High Power Density Rechargeable Batteries", A. G. MacDiarmid, M. Aldissi, R. B. Kaner, M. Maxfield and R. J. Mammone, Electrochem. Soc. Extended Abstracts, 83-1, 842, (1983). (Supported by DARPA/ONR, and DOE Grant No. DE-AC02-81-ER10832).
25. "The Aqueous and Non-Aqueous Electrochemistry of Polyacetylene: Application in High Power Density Rechargeable Batteries", A. G. MacDiarmid, R. B. Kaner, R. J. Mammone and A. J. Heeger, J. de Physique, 44, 543 (1983), (Supported by DARPA/ONR and DOE Grant No. DE-AC02-81-ER10832).

B. PATENTS PENDING

1. Serial No. 34052, Filed November 3, 1981, A. G. MacDiarmid, A. J. Heeger and P. J. Nigrey, "Reversible Electrochemical Doping of Conjugated Polymers."

3. PERSONNEL WHO RECEIVED FULL OR PARTIAL SUPPORT ON ONR CONTRACT #N00014-81-K-0648

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