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SEVENTH QUARTERLY R&D STATUS REPORT

Principal Investigator:
Alan G. MacDiarmid
Department of Chemistry
University of Pennsylvania

REPORTING PERIOD: 4/1/88 - 6/30/88

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SHORT TITLE OF WORK: **Conducting Electronic Polymers by
Non-Redox Processes**

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I. Research Groups*

1. University of Pennsylvania
 - (a) Department of Chemistry (A.G. MacDiarmid)
 - (b) Department of Materials Science (G.C. Farrington)
2. The Ohio State University
Department of Physics (A.J. Epstein)
3. Lockheed Advanced Aeronautics Corporation
Aeronautics Systems Group Research (T.S. Kuan)
4. Rensselaer Polytechnic Institute
Department of Chemistry (G.E. Wnek)
5. University of Rhode Island
Department of Chemistry (S.C. Yang)
6. Montclair State College
Department of Chemistry (B.D. Humphrey)

***Financial information for each group given in Section X.**

II. Description of Progress

1. University of Pennsylvania

a. Department of Chemistry (MacDiarmid)†

(i) Summary of Progress

N-Substituted Derivatives of Polyaniline*

10 me
10 gr
Fully N-methylated polyaniline was obtained analytically pure by the oxidative polymerization of $C_6H_5N(CH_3)(H)$ with $(NH_4)_2S_2O_8$ in 1.0M aqueous HCl. The resulting black-green polymer ($\sigma \sim 10^{-4}$ S/cm) was shown by IR studies to have a similar backbone structure to parent polyaniline, and upon heating, lost HCl and H_2O , yielding a black-brown solid, ($\sigma < 10^{-8}$ S/cm) containing $\sim 14\%$ oxidized groups. "Pseudo-protonic" acid doping of "emeraldine" base with neat $(CH_3)_2SO_4$ on the vacuum line yielded polymers whose extent of doping could be monitored continuously. The $\sim 50\%$ methylated "emeraldine" base ($\sigma \sim 10^{-2}$ S/cm) had a X_{Pauli} approximately half that of 50% proton doped "emeraldine" base, consistent with the symmetry-breaking effect of the methyl groups.

*Supported in part by URI and in part by NASA Grant No. NAG-10-0025.

The Oxidation State of "Emeraldine" Base*

The base form of polyaniline can be described by the general formula $[-(C_6H_4)-N(H)-(C_6H_4)-N(H)-]_y[-(C_6H_4)-N=(C_6H_4)=N-]_{1-y}$ where y can in principle range from y=1 (in the completely reduced form) to y=0 (in the completely oxidized form). In the true emeraldine oxidation state y=0.5.

6
"Emeraldine" base prepared in air has been found to have an oxidation state as defined above of (1-y) ~ 0.6 whereas when prepared under an inert atmosphere, (1-y) ~ 0.4 . The electronic spectrum of freshly prepared "emeraldine" base solutions in aqueous 80% acetic acid depends on the oxidation state: an absorption at $\lambda_{max} \sim 670$ nm (1.85 eV) is observed for the blue solutions of "emeraldine" base having (1-y) ~ 0.6 , whereas the same absorption is shifted to $\lambda_{max} \sim 760$ nm (1.63 eV) for the green solutions of

†In collaboration with Professor A.J. Epstein, Department of Physics, The Ohio State University.

→ (figure) ←

①

"emeraldine" base having (1-y) ~0.4. The blue solutions become green after ~0.5 hours. On standing, the absorption peaks of both solutions shift to an identical equilibrium value of $\lambda_{\max} \sim 787 \text{ nm}$ (1.58 eV). These observations can be used as a convenient color "spot-test" to gain information concerning the oxidation state of "emeraldine" base. The infrared spectra of the solid samples are consistent with the above (1-y) values.

*Supported in part by URI and in part by NSF Grant No. DMR-85-19059.

(ii) Major Equipment Purchased or Constructed

A 1760 series of Perkin-Elmer FTIR was purchased along with a 7700 Hewlett Packard computer and plotter. A substantial number of vacuum lines and specialty equipment using glassblowing techniques were built.

b. Department of Materials Science and Engineering
(Farrington)

Summary of Progress

Jonathan Foreman has studied the reductive electrochemistry of oriented ARA polyacetylene in tetrahydrofuran containing 1M LiClO₄ and, at least in preliminary experiments, found it to be electrochemically quite inactive. The orientation process may produce a material in which the rate of dopant diffusion is quite slow. The work is continuing with N- and ARA material.

Hong Yang has found, on the basis of direct diffusion measurements using EDAX, that Zn(II) ions appear to be quite mobile in linear PEO electrolytes. This result contrasts with earlier electrochemical data which indicated that the Zn(II) transport number in these materials is quite small. The result is quite interesting because of the potential usefulness of the Zn(II) electrolytes in solid state batteries.

Kimmy Wu has begun studying the oxidative electrochemistry of various new forms of polyacetylene in propylene carbonate containing 1M LiClO₄. Initial results show that N-polyacetylene behaves about the same as the previous Shirakawa material. Nor has any increase in the thermal or chemical stability for the N-material been found in TGA and DSC measurements.

2. The Ohio State University

Department of Physics (Epstein)†

(i) Summary of Progress

The conductivity and dielectric constant of the emeraldine polymer are studied at a frequency of 6.5×10^9 Hz as a function of temperature T and protonation levels spanning from insulating emeraldine base $\sigma_{DC}(295K) \sim 10^0 (\Omega \text{ cm})^{-1}$. Microwave conductivity is larger than dc by many orders of magnitude for base but approaches that of dc for more conducting emeraldine salts. For low protonated emeraldine polymers the dielectric constant is almost temperature independent and small. For higher protonation levels the dielectric constant is linear in T with deviations observed at maximum protonation level. The dielectric constant increases monotonically with protonation for intermediate and higher level protonated emeraldine salts. The temperature dependence of microwave conductivity differs from that of dc especially at lower temperatures. In general, the data supports the phase segregation of the polymer into "metallic islands" and insulating background with localization prevailing at low temperatures. In view of the presence of barriers within the "metallic islands" and increase of coherence length of the charge carriers with temperature, the phrase "textured metallic islands" is introduced to describe the delicate role of temperature on the interplay between localization and extended picture.

The temperature dependence of the x-band electron spin resonance for the emeraldine oxidation state of polyaniline has been investigated on different protonation levels ranging from unprotonated insulating emeraldine base to the metallic emeraldine hydrochloride. For all samples studied, the ESR spectra have been numerically analyzed and decomposed into two independent signals, one of them being Lorentzian in shape while the other one Gaussian. The ESR spectrum of emeraldine salt is very sensitive to water and oxygen. Exposure of the dry sample to moisture increases the linewidth by a factor of two in the first few seconds, followed by a slow decrease. Upon pumping the sample, the linewidth returns to its initial value. Exposure to oxygen is more striking. The linewidth is immediately increased by a factor of more than 100, while the signal amplitude is multiplied by about 2, without significant change in the line shape. This change is completely reversed upon placing the sample under vacuum.

†In collaboration with Professor A.G. MacDiarmid, Department of Chemistry, University of Pennsylvania.

The effects of physisorbed oxygen have been reported for polypyrrole and have been attributed to spin-flap scattering from the paramagnetic O_2 molecules. A similar origin is likely for polyaniline.

The intensity of the Gaussian components of the line is always less than the Lorentzian component. The small intensity of the Gaussian signal demonstrates the number of localized spins remains low for all samples. The variation with temperature of Lorentzian component indicates a contribution from both localized Curie-like spins and delocalized Pauli-like spins. The temperature dependence of the ESR peak-to-peak linewidth for Lorentzian signal shows that for $x=0.40$ and $x=0.50$ samples, the linewidth for x decreases with decreasing temperature and reaches a minimum at about 100K and 160K respectively, then increases with further decrease in temperature. The decrease of the linewidth with temperature for these highly protonated samples and subsequent rise at lower temperature may reflect a crossover from dominance of conduction electron-photon relaxation to interaction with localized spins at low temperatures. This is due to a competition between motional narrowing and broadening by fast relaxation as reported for polythiophene and polyacetylene.

The infrared spectra, photoinduced infrared spectra, and photoconductivity of polyaniline were measured. The oxidative doping of leucoemeraldine base yields changes in the infrared spectrum that are consistent with breaking the symmetry of the polymer and an overlap of the vibration modes with the continuum of states. Small photoinduced changes in the vibrational modes of emeraldine base also indicate this symmetry breaking and the creation of polarons. The absence of significant photoconductivity suggests that the photoexcited polarons have low mobility.

Upon protonation of EB to ES the exciting features show an increase in oscillator strength and the modes at 1501 and 1591 cm^{-1} show a red shift to 1486 and 1568 cm^{-1} . We note that no new modes appear upon doping, in contrast to polyacetylene and polythiophene, which show intense new features upon doping.

P-doping leucoemeraldine base with Cl_2 to form emeraldine hydrochloride results in significant changes in the infrared spectra. In particular, a new vibrational mode is seen at 1150 cm^{-1} ; and the modes at 1498 cm^{-1} and $\sim 1600\text{ cm}^{-1}$ change intensity, move or shift. Several of these same features are observed in EB, with subsequent changes upon doping EB to ES, as discussed in the previous paragraph. The 1591 cm^{-1} mode in EB is consistent with quinoids in this material. Because Raman data show strong peaks at 1188 cm^{-1} and

1623 cm^{-1} in LE, symmetry breaking by the introduction of charges or neutral imine groups to the original LE material can cause the 1188 cm^{-1} and 1623 cm^{-1} modes of LE to become IR active in EB. Doping to ES results in an overlap of the IR modes with the electronic continuum of the polaron band. The resulting IR absorption can be described in terms of a Fano effect causing shifts (i.e. dips preceded by peaks) and large enhancements of the IR modes.

The photoinduced signal is long-lived, having lifetimes greater than two hours at 80K, ~ 45 min at 200K, and ~ 6 min at 250K. These lifetimes agree with NMR measurements that predict ring rotations occurring with a free volume activation energy of 2000K.

Assuming the amplitude mode formalism is valid for EB, we calculate the polaron mass and the strength of the polaron pinning in EB. We take the two strongest features at 1144 and 1576 cm^{-1} to correspond to resonant Raman lines at 1188 and 1623 cm^{-1} . The calculation predicts a pinning parameter, α_p , of ~ 0.8 for EB. This value is substantially larger than the pinning parameters reported for polythiophene ($\alpha_p=0.31$) and for polyacetylene ($\alpha_p=0.06$), indicating large polaron pinning in EB.

The polaron mass, M_{pol} , was calculated based on the band effective mass for EB, m^* , and the ratio of the integrated intensities of the electronic and vibrational photoinduced absorptions (I_e/I_p). The band effective mass, determined from band structure calculations, was calculated to be $\sim 0.14m_e$ (electron mass) and the ratio $I_e/I_p \sim 560$. Thus, we calculate $M_{\text{pol}} \sim 56m_e$ as a lower limit for the polaron mass in EB. This large value for the polaron mass is consistent with low mobility of photoexcited polarons in EB.

We have undertaken extensive optical, photoinduced optical, magnetic, and transport studies of undoped and doped "new" $(\text{CH})_x$, $[\text{N}-(\text{CH})_x]$, and "ARA" $-(\text{CH})_x$. The optical absorption of a thin film of unoriented $\text{N}-(\text{CH})_x$ on polyethylene is very similar to that of conventional Shirakawa $(\text{CH})_x$, with an energy gap obtained by extrapolation of the absorption edge of 1.4eV. Photoinduced absorption spectroscopy of a thin unoriented sample of $\text{N}-(\text{CH})_x$ show the same features as those for $\text{S}-(\text{CH})_x$ including photoinduced solitons at $\sim 4000 \text{ cm}^{-1}$, photoinduced infrared modes at 1366 cm^{-1} and 1286 cm^{-1} as well as a broad pin mode at lower frequencies. These results establish that there is no essential difference in the electronic structure of $\text{N}-(\text{CH})_x$ and $\text{S}-(\text{CH})_x$ despite the differences in their preparation techniques and remarkable differences in their transport properties after doping.

The magnetic susceptibility of the iodine doped $N-(CH)_x$ was studied using the Faraday technique. The data, after subtraction for core diamagnetism, were decomposed as a sum of the Pauli-term ($\mu_B^2 N(E_F)$) and a Curie term. Undoped samples of $N-(CH)_x$ have a similar number of localized spins (neutral solitons) as $S-(CH)_x$ (200-500 ppm). For the $N-(CH)_x$ doped rapidly in iodine- CCl_4 solution, the decrease in the number of localized spins with doping is neither rapid nor monotonic, suggesting inhomogeneous doping under these conditions. The Pauli susceptibility for heavily doped $N-(CH)_x$ (0.05 (I_3)) is nearly the same as similarly doped $S-(CH)_x$. However, for lower doping levels there is a large Pauli susceptibility for the rapidly doped $N-(CH)_x$ as compared to the gas-phased doped $S-(CH)_x$, again supporting inhomogeneous doping via this route. The presence of a metallic density of states for highly doped $N-(CH)_x$ of high conductivity supports the idea that the conductivity in the very highly-conducting regime is not due to collective transport, but rather results from the high mobility of individual charge carriers because of the strong anisotropy of the electronic structure of the polymer system. The temperature dependent anisotropic conductivity of heavily doped "ARA"-(CH)_x differs markedly from that of $S-(CH)_x$. Room temperature conductivity reached as high as 2×10^4 S/cm with an anisotropy of a factor of 30. The temperature dependent data fit well the fluctuation-induced tunneling model of Sheng. Analysis of the T-dependent conductivity within the Sheng fluctuation-induced tunneling model suggests that for "ARA"-(CH)_x the distance between barriers decreases with aging, implying growth of new interruptions in the chains, whereas for $N-(CH)_x$ the islands seem to increase in size while the barriers themselves become larger, implying clustering in defects with time. Electric field dependence of current in the sample of highly conducting $N-(CH)_x$ measured at 4.2K is consistent with the Sheng fluctuation induced tunneling model, again pointing toward barrier limited conduction in these highly conducting forms of polyacetylene.

(ii) Major Equipment Purchased or Constructed

Miscellaneous items purchased this quarter include optical components, a removable hard disk, a low temperature thermometer, and a fuel cell for the glove box.

3. Lockheed Advanced Aeronautics Corporation

Aeronautics Systems Group Research (Kuan)

Summary of Progress

We received your request for quarterly reports covering the periods 1/1/88 through 3/31/88 and 4/1/88 through 6/30/88. Although we would like to contribute to these reports, we had no funding during those periods (see letter to Teh Kuan from Thomas Lynch, Lockheed Contract Coordinator). Because it is extremely important for us to avoid mixing contract funds, we were unable to work on the URI contract during those periods; therefore, we cannot legally state any progress for inclusion in the quarterly reports.

4. Rensselaer Polytechnic Institute

Department of Chemistry (Wnek)

Summary of Progress

We have developed an alternative approach to the synthesis of "segmented" polyacetylene (here referring to PA containing methylene defects). We employ classical Birch reduction chemistry, in which the substrate (PA here) is treated with potassium metal in liquid ammonia in the presence of t-butyl alcohol. N-type doping and protonation occur simultaneously. The flexible films have been characterized by FTIR spectroscopy. We find characteristic bands of trans-PA and polyethylene, including a doublet for the latter at 720-730 cm^{-1} . This splitting is indicative of sequences of at least 4-5- CH_2 - units in *crystalline* regions (liquid alkanes only show a single peak here). We are interested in this material because the allylic "ends" of the conjugated pi-systems represent moieties which can be derivatized. Experiments to demonstrate the viability of this idea are underway.

Polypyrrole/poly(styrene sulfonate) [PP/PPS] composites have been prepared by the method of Miller and coworkers. The ideas, as was demonstrated by Miller for small cations, is that the neutral polymer (undoped) looks like PSS and thus binds cations. However, upon oxidation (doping), cations are released as the sulfonates are called to be the counterions to p-type polypyrrole. We are interested in employing this approach for the reversible binding of cationic polypeptides (e.g., histone H3). Initial experiments show that in phosphate buffer, reduction of PP leads to dissolution of PPS. This may be due to a poor extent of molecular entanglement of our composite, or reactions between polypyrrole and phosphate during electrosynthesis. In any event,

release of sulfonate moieties cannot be tolerated. Two approaches we are investigating now are the use of different buffers (e.g., TRIS), and the synthesis of copolymers of pyrrole and pyrrole-N-(3-propyl) sulfonate. The latter compound was donated to us by Professor John Reynolds of the University of Texas at Arlington. The copolymer of course contains covalently bound sulfonate and hence it cannot be released upon eduction of the polypyrrole backbone. In all electrochemical polymerizations and subsequent redox cycles, the resistance of the polymers is being measured in-situ to determine the influence of buffering environment on electrical properties.

More has been learned about H3/PSS complexes in solution. Fluorescence experiments show that the 2:1 PSS/H3 complex can solubilize pyrene to a greater extent than either component alone. This suggests that a hydrophobic pocket is formed upon complexation. The meaning of this in the context of topology of the complex is under study.

5. University of Rhode Island

Department of Chemistry (Yang)

Summary of Progress

In our previous report (the sixth quarterly report) we mentioned that we discovered that the kinetics of the electrochemical doping process of polyaniline is strongly dependent on the substrate electrode for electrochemical polymerization.

We felt that we can learn how to make conducting polymers a better "switchable material" by understanding why the substrate has strong influence on the electrochromic color switching rate. We also suspected that the difference in the switching rate is a reflection of the surface morphology of polyaniline. So we decided to make a detailed investigation along this direction.

We proceed by measuring the rate of electrochemical doping induced color switching, and by examining the polymer morphology of very thin polyaniline films. We found that thin film polyaniline on platinum and gold substrate switches color faster (by about 70 times) than on tin oxide substrate. We also found that polymer morphology at the first 100 nm of the polymer is very different on these substrates. In these studies the kinetics was measured by a rapid scanning FTIR spectrometer with extended spectral range in near infrared and visible light regions, and the polymer morphology was studied with high resolution electron microscopy.

Our current understanding is that the activation energy for nucleation of polymer on the electrode surface sensitively influences the surface morphology. The difference in polymer morphology, in turn, influences the kinetics of the electrochemical doping process.

6. Montclair State College

Department of Chemistry (Humphrey)

Summary of Progress

During the period 4/1/88 - 6/30/88 spectroscopic studies of the conducting polymer/polysaccharide composite materials were carried out in order to further characterize the composite materials. Specifically, fourier transform infrared spectroscopy (FTIR) was performed in the surface analysis mode using a diffuse reflectance attachment. These studies further demonstrate the difference between previously synthesized surface modification materials in which conducting polymers were formed on the surface of a matrix, and the composite materials synthesized in which the matrix materials are porous and possess molecular sized cavities for the conducting polymer to form in.

The composite materials and surface modified materials were synthesized as described previously. All spectroscopic studies were performed using a Nicolet FTIR (model 20 DXC) and a Spectra Tech diffuse reflectance attachment. The most commonly studied materials were the polypyrrole/cellulose conducting composite and polypyrrole surface modified nomex felt.

In the case of the surface modified polypyrrole/nomex felt the diffuse reflectance FTIR exhibited a spectrum which matched that of the conducting polymer polypyrrole exclusively. In other words, no trace of the nonporous nomex felt matrix appeared in the spectrum. On the other hand, diffuse reflectance FTIR of the polypyrrole/cellulose composite materials exhibited only the matrix material spectrum. No feature of the conducting polymer spectrum was observed thereby demonstrating that little or none of the conducting polymer is localized at the surface of these composite materials. Parallel studies using polyaniline/polysaccharide composites yielded the same results. This evidence combines with UV-vis transmission studies (through the film, not just the surface), in which the presence of the conducting polymer overwhelms the spectral features of the matrix materials, to give a clearer picture of the properties and structure of these composites.

III. Working Relationships Involving University of Pennsylvania Personnel and Those of Subcontractors

The following interactions between personnel funded by the URI contract have taken place during this quarter:

1. May 20-22, 1988, Dr. A.G. MacDiarmid, Jim Masters, Sanjeev Manohar, Gabriel Asturias, Elliot Scherr and Dr. A.J. Epstein and Keith Cromack, John Ginder, Hamid Javadi, Fulin Zuo, Jingmin Leng, and Richard McCall met in Somerset, PA, for a joint group meeting of the Penn (Chemistry) and OSU (Physics) research groups.
2. June 7-8, 1988, Dr. A.G. MacDiarmid, Dave Swanson, Rakesh Kohli, Anjan Ray, Dave Kerschner, Gabriel Asturias, Nick Theophilou, Sanjeev Manohar, Jim Masters, Elliot Scherr and Dr. A.J. Epstein and Richard McCall, John Ginder, Fulin Zuo, Zhouhui Wang, Hamid Javadi, Rene Leversanne, Steve Treat and Keith Cromack met in Somerset, PA, for a joint group meeting of the Penn (Chemistry) and OSU (Physics) research groups.

IV. Miscellaneous Scientific Interactions of Key Personnel Associated with the Program involving (i) visits to their laboratories by persons concerned with conducting polymers, (ii) visits by them to other laboratories and (iii) lectures on their research at organized symposia.

1. April 6-8, 1988, Dr. Epstein visited DuPont de Nemours in Wilmington, Delaware to discuss joint conducting polymer processing research.
2. April 11, 1988, Dr. Alain Priou of ONERA, CERT, France visited Dr. MacDiarmid's laboratory. Title of the talk given, "Microwave Applications of Conducting Polymers."
3. April 11-12, 1988, Dr. Epstein attended the International Conference on the First Two Years of High-Temperature Superconductivity in Tuscaloosa, AL. Title of talk given, "Anomalous Magnetic Photoinduced and Structural Phenomena in High-T_c Materials."
4. April 13-14, 1988, Dr. MacDiarmid met with Dr. Epstein at the Ohio State University to discuss collaborative research.

5. April 13, 1988, Professor Eddy Chen of Shanghai University, China, visited Dr. Epstein's laboratory. Title of talk given, "In Situ ESR Experiments on Polyacetylene During Electrochemical Doping."
6. April 15, 1988, Dr. Eddy Chen of Shanghai University, China, visited Dr. MacDiarmid's laboratory.
7. April 18-19, 1988, Dr. Epstein attended the Swedish National Board for Technical Development Workshop on Conducting Polymers in Stockholm, Sweden. Title of talk given, "Unusual Magnetic Phenomena in Conducting Polymers: Solitons, Polarons, and Insulator-to-Metal Transitions."
8. April 20, 1988, Dr. Epstein visited the Department of Physics and Measurement Technology in Linköping University in Linköping, Sweden. Title of talks given, "Charge Conduction Mechanisms in Conducting Polymers" and "Magnetic Field and Photoinduced Defects in Ceramic Superconductors."
9. April 21, 1988, Dr. Epstein visited the Department of Physics and the Department of Chemistry at Chalmers Institute of Technology in Gothenberg, Sweden. Title of talk given, "Stable Defects in Ceramic Superconductors."
10. April 27-29, 1988, DARPA Polymer Program Review, Washington, DC, attended by Dr. A.G. MacDiarmid and Dr. A.J. Epstein. Title of the talk given, "Polymers by Non-Redox Processes: Synthesis, Physical Studies and Applications."
11. April 28, 1988, Dr. George Shier, Dow Chemical, Midland, MI, visited Dr. Epstein's laboratory. He discussed the role of new materials in industrial research.
12. April 28, 1988, Dr. G.E. Wnek gave an invited lecture at the University of Lowell, MA. Title of talk given, "Charge Carrier Chemistry in Electroactive Polymers."
13. May 4, 1988, Dr. Bill Farneth, DuPont de Nemours, Wilmington, Delaware visited Dr. Epstein's laboratory. He presented an informal discussion on the "Control of oxygen in high- T_c superconductors."
14. May 4, 1988, Dr. A.G. MacDiarmid attended "Frontiers In Materials Science Lecture Series on Electrical Properties and Applications of Materials," State University of New York, New Paltz, NY. Title of the talk given, "Conducting (Organic) Polymers: Basic Concepts and Potential Applications."

15. May 9-11, 1988, Dr. G.E. Wnek attended the Short Course on Conducting Polymers, Center for Materials Science, SUNY-New Paltz, NY. Title of invited lecture, "Electrically Conducting Polymers."

16. May 9-11, 1988, Dr. A.G. MacDiarmid attended a symposium on Electroactive Polymers: Materials, Properties, and Applications of Electrically Conductive, Ionically Conductive and Redox Polymer Systems, Westpoint, NY. Title of the talk given, "Inhibition of Corrosion of Steel by Electrically Conductive Polymers."

17. May 19, 1988, Dr. Gregory C. Farrington gave an invited lecture on "Polymer Electrolytes" at the Electrochemical Society Meeting in Atlanta, GA.

18. May 20, 1988, Dr. Susan P. Ermer, Lockheed Missiles and Space Company, Palo Alto, CA, visited Dr. Epstein's laboratory. She discussed current experiments and applications of conducting polymers for nonlinear optics.

19. May 23, 1988, Dr. Pentti Passiniemi and Dr. N. Yao of Neste Technology, Finland, visited Dr. MacDiarmid's laboratory. Title of the talk given, "Application Horizon of Conducting Polymers - Polythiophenes."

20. May 24, 1988, Professor Qian Renyuan, Academia Sinica, Beijing, China visited Dr. Epstein's laboratory. Title of talk given, "Conducting Polypyrrole."

21. June 2, 1988, Dr. Kiyotaka Ikawa and Dr. Youetsu Yoshihisa of Yuasa Battery Co., Tokyo, Japan, visited Dr. MacDiarmid's laboratory. Title of the talk given, "Ionically Conducting Organic Polymers with Lithium Battery."

22. June 6, 1988, Dr. Tian Tsong of the University of Minnesota, MI, met with Dr. Barbara Schneider and Dr. MacDiarmid at the University of Pennsylvania, Philadelphia, PA. Title of the talk given, "Interaction of Oscillating Electric Fields and Cell Membranes."

23. June 7-10, 1988, Professor Gerd Lehmann, Akademie der Wissenschaften der DDR, Dresden, East Germany visited Dr. Epstein's laboratory. Title of talk given, "Electronic Structure of Conjugated Polymers Between Polyacetylene and Graphite."

24. June 10, 1988, Dr. MacDiarmid visited Exxon Corporation, Florham Park, NJ, and conducted a one-day workshop for the Polymer Science Forum.

25. June 13-14, 1988, Dr. MacDiarmid visited Dr. Andrew Crilly of BBC, London at the University of Texas at Houston, TX and did a filming session on Conducting Polymers.
26. June 13-14, 1988, Dr. Epstein visited DuPont de Nemours in Wilmington, DE to discuss joint conducting polymer processing research.
27. June 16-17, 1988, Dr. Leonard J. Brillson, Xerox Webster Research Center, Webster, NY, visited Dr. Epstein's laboratory. Title of talk given, "Electronic and Atomic Properties of Metal-Semiconductor Interfaces."
28. June 17, 1988, Dr. Tatsuo Wada of Riken Institute of Physical and Chemical Research, Japan, visited Dr. MacDiarmid's laboratory. Title of the talk given, "Optical Non-Linear Responses of Organic Thin Films."
29. June 20-21, 1988, Mr. Andrew P. Monkman, Queen Mary College, London, England, visited Dr. Epstein's laboratory. Title of talk given, "ESR Studies of Polyaniline: A Probe to the Charge Transport Mechanism in Polyaniline."
30. June 20-24, 1988, Mr. Jan-Olov Nilsson and Ms. Kajsa Uvdal of Linköping University, Sweden, visited Dr. MacDiarmid's laboratory for discussing ongoing collaborative research. Title of Mr. Nilsson's talk, "Surface Physics and Chemistry of Some Organic Molecules Using Photoelectron Spectroscopy."
31. June 20-23, 1988, Ms. Marie-Louise Eidrup of Chalmers University of Technology, Sweden, visited Dr. MacDiarmid's laboratory for discussions involving collaborative research.
32. June 21, 1988, Dr. Maxime Nechtschein, Centre D'Etudes Nucleaires de Grenoble, Grenoble, France, visited Dr. Epstein's laboratory. Title of talk given, "Recent Results in Polyaniline Studies."
33. June 22-23, 1988, Dr. Hiroshi Koezuka of Mitsubishi Electric Corporation, Japan, visited Dr. MacDiarmid's laboratory.
34. June 22-24, 1988, Dr. Maxime Nechtschein of Grenoble, Cedex, France, visited Dr. MacDiarmid's laboratory. Title of the talk given, "Some Investigations on the Polyaniline Properties."
35. June 22-24, 1988, Mr. Andrew Monkman of Queen Mary College, London, visited Dr. MacDiarmid's laboratory. Title of the talk given, "Charge Transport Studies in Polyaniline."

36. June 23, 1988, Dr. Michio Yamaura of Teijin, Ltd., Japan, visited Dr. MacDiarmid's laboratory. Title of the talk given, "Structure and Properties of Biaxially Stretched Polypyrrole Films."

37. June 24, 1988, Dr. William Salaneck of Linköping University, Sweden, visited Dr. MacDiarmid's laboratory.

38. June 27 - July 2, 1988, Dr. A.G. MacDiarmid and his entire group from the University of Pennsylvania, Dr. A.J. Epstein and his entire group from the Ohio State University, Ms. Lynette Prezyna of Rensselaer Polytechnic Institute, and S.C. Yang, R.L. Clark, J.H. Hwang, Dina Zhang, R.J. Cushman of the University of Rhode Island attended the International Conference of Synthetic Metals in Santa Fe, New Mexico, sponsored by Los Alamos National Laboratory. The following talks and posters were presented. Underlined name is the name of the author who gave the talk or made the poster presentation.

- i "Polyanilines: Doping, Structure, and Derivatives," A. Ray, A.G. MacDiarmid and A.J. Epstein.
- ii "Highly-Conducting Polyacetylene," N. Theophilou, D.B. Swanson, A.G. MacDiarmid, F. Zuo, S.P. Treat, and A.J. Epstein.
- iii "¹⁵N NMR of Polyaniline," A.F. Richter, A. Ray, K.V. Ramanathan, S.K. Manohar, S.J. Opella, G.T. Furst, A.G. MacDiarmid and A.J. Epstein.
- iv. Poster, "Emeraldine Base: Protonated Deprotonation of Amine and Imine Sites," A. Ray, A.F. Richter, A.G. MacDiarmid, and A.J. Epstein.
- v. Poster, "Oxidation State of Polyanilines," G.E. Asturias, A.G. MacDiarmid, R.P. McCall and A.J. Epstein.
- vi. "Electronic Phenomena in Polyaniline," J.M. Ginder, A.J. Epstein and A.G. MacDiarmid.
- vii. "Photoexcitations in Emeraldine Base," M.G. Roe, J.M. Ginder, R.P. McCall, K.R. Cromack, A.J. Epstein, T.L. Gustafson, M. Angelopoulos and A.G. MacDiarmid.
- viii. "N-Substituted Derivatives of Polyaniline," S.K. Manohar, A.G. MacDiarmid, K. Cromack, J.M. Ginder and A.J. Epstein.

- ix. "Polarons and Excitons in Solutions of Emeraldine," E. Zuo, R.P. McCall, J.M. Ginder, M.G. Roe, A.J. Epstein, G.E. Asturias, S.P. Ermer, A. Ray and A.G. MacDiarmid.
- x. "Photoinduced Absorption Studies of La-Cu-O and Y-Ba-Cu-O Systems," J.M. Ginder, M.G. Roe, R.P. McCall, A.J. Epstein, E. Ehrenfreund, Y. Song, J.R. Gaines and S.I. Shah.
- xi. "Charge Conduction in Polyaniline," H.H.S. Javadi, F. Zuo, K. Cromack, A.J. Epstein, M. Angelopoulos and A.G. MacDiarmid.
- xii. Poster, "IR Absorption, Photoinduced IR Absorption, and Photoconductivity of Polyaniline," R.P. McCall, M.G. Roe, J.M. Ginder, T. Kusumoto, A.J. Epstein, G.E. Asturias, E. Scherr and A.G. MacDiarmid.
- xiii. Poster, "ESR of Protonated Emeraldine Base: Insulator-to-Metal Transition," H.H.S. Javadi, R. Laversanne, A.J. Epstein, R.K. Kohli, E.M.
- xiv. "Microwave Conductivity and Dielectric Constant of (TMTTF)₂X, X=SCN, ReO₄, SbF₆," R. Laversanne, H.H.S. Javadi, and A.J. Epstein.
- xv. "Kinetics of the Electrochromic Switching of Thin Film Polyaniline: Time Resolved Optical Spectra," D. Zhang and S. Yang.
- xvi. "Experimentally Determined pH-Potential Phase Diagram for Polyaniline," S.C. Yang, R.J. Cushman and D. Zhang.
- xvii. "Polyaniline: Polyelectrolyte Controlled Morphological Modifications," J.H. Hwang and S.C. Yang.
- xviii. "Spectro-Electrochemical Study of Chemically Modified Polyanilines,," R. Clark, B. Schmitz and S.C. Yang.

V. Publications

1. Papers Published

Acknowledging URI and Other Support

(i) Epstein and/or MacDiarmid (OSU and/or Penn)

"Photoexcitation of Polarons and Molecular Excitons in Emeraldine Base," Phys. Rev. Lett. **60**, 2789 (1988), M.G. Roe, J.M. Ginder, P.E. Wigen, A.J. Epstein, M. Angelopoulos and A.G. MacDiarmid. (Supported in part by URI and in part by NSF Grant No. DMR-85-19059).

"Protonation of Emeraldine: Formation of a Granular Polaronic Polymeric Metal," Mol. Cryst. Liq. Cryst., **160**, 165 (1988), A.J. Epstein and A.G. MacDiarmid. (Supported in part by URI and in part by NSF Grant No. DMR-85-19059).

"Frequency Dependent Conductivity of Emeraldine: Absence of Protonic Conductivity," Mol. Cryst. Liq. Cryst., **160**, 225 (1988), H.H.S. Javadi, F. Zuo, M. Angelopoulos, A.G. MacDiarmid and A.J. Epstein. (Supported in part by URI and in part by NSF Grant No. DMR-85-19059).

"Pseudo-Protonic Acid Doping of Polyaniline," Mol. Cryst. Liq. Cryst., **160**, 223 (1988), M. Angelopoulos, S.P. Ermer, S.K. Manohar, A.G. MacDiarmid and A.J. Epstein. (Supported in part by URI and in part by NSF Grant No. DMR-85-19059 and by NASA Grant No. NAG10-0025).

"Polyaniline: Solutions, Films and Oxidation State," Mol. Cryst. Liq. Cryst., **160**, 151 (1988), M. Angelopoulos, G.E. Asturias, S.P. Ermer, A. Ray, E.M. Scherr, A.G. MacDiarmid, M. Akhtar, Z. Kiss and A.J. Epstein. (Supported in part by URI and in part by NSF Grants No. DMR-85-19059 and DMR-86-15475 and in part by Chronar Corporation, Princeton, NJ.).

"Segmented Polyacetylene, (CHDy)_x: Electrochemical n-Doping Studies," Synth. Met., **24**, 283 (1988), M.X. Wan, G.A. Arbuckle, A.G. MacDiarmid and A.J. Epstein. (Supported in part by URI and in part by ONR Contract No. N00014-83-K-0209 and in part by NSF Grant No. DMR-86-15475).

"Polyaniline: A New Concept in Conducting Polymers," International Symposium on Development of Conducting Organic Polymers and Ultra-Thin Films and Their use in Electronics, Stockholm, Sweden, 6 (1988), A.G.

MacDiarmid. (Supported in part by URI and in part by ONR Contract No. N00014-83-K-0209 and by NSF Grants No. DMR-82-16718 and DMR-85-19059).

(ii) Wnek, MacDiarmid and Epstein (RPI/Penn/OSU)

"Electrochemistry of Ring Substituted Polyanilines: Effect of Substituents on Electronic Properties," Mol. Cryst. Liq. Cryst., **160**, 221 (1988), A. Ray, J.-C. Chiang, A.G. MacDiarmid, Y. Wei, W.W. Focke, G.E. Wnek and A.J. Epstein. (Supported in part by URI and in part by NSF Grant No. DMR-85-19059).

2. Papers Accepted/Submitted for Publication

(a) Acknowledging URI Support Only

(i) Yang (Rhode Island)

"Poly-(2-Methylaniline): The Effect of Chemical Modification on the Insulator/Conductor Transitions of Polyaniline," Synth. Met., in press (1988), R.L. Clark and S.C. Yang.

(b) Acknowledging URI and Other Support

(i) Epstein and/or MacDiarmid (OSU and/or Penn)

"Electronic Phenomena in Polyaniline," Synth. Met. in press (1988), J.M. Ginder, A.J. Epstein and A.G. MacDiarmid. (Supported in part by URI).

"The Oxidation State of 'Emeraldine' Base," Synth. Met., in press (1988), G.E. Asturias, R.P. McCall, A.G. MacDiarmid and A.J. Epstein. (Supported in part by URI and in part by NSF Grant No. DMR-85-19059).

"Highly-Conducting Polyacetylene," Synth. Met. in press (1988), N. Theophilou, D.B. Swanson, A.G. MacDiarmid, A. Chakraborty, H.H.S. Javadi, R.P. McCall, F. Zuo, S.P. Treat, and A.J. Epstein. (Supported in part by URI and in part by NSF Grant No. DMR-85-19059).

"Polyaniline: Protonation/Deprotonation of Amine and Imine Sites," Synth. Met., in press (1988), A. Ray, A.F. Richter, A.G. MacDiarmid and A.J. Epstein. (Supported in part by URI and in part by NSF Grant No. DMR-85-19059).

"N-Substituted Derivatives of Polyaniline," Synth. Met., in press (1988), S.K. Manohar, A.G. MacDiarmid, K. Cromack, J.M. Ginder and A.J. Epstein. (Supported in part by URI and in part by NASA Grant No. NAG10-0025).

"¹⁵N NMR of Polyaniline," Synth. Met., in press (1988), A.F. Richter, A. Ray, K.V. Ramanathan, S.K. Manohar, S.J. Opella, G.T. Furst, A.G. MacDiarmid and A.J. Epstein. (Supported in part by URI and in part by NSF Grant No. DMR-85-19059 and in part by NIH Grant No. GM-24266).

"Polyanilines: Doping, Structure, and Derivatives," Synth. Met., in press (1988), A. Ray, G.E. Asturias, D.L. Kershner, A.F. Richter, A.G. MacDiarmid and A.J. Epstein. (Supported in part by URI and in part by NSF Grant No. DMR-85-19059).

"Charge Conducting in Polyaniline," Synth. Met., in press (1988), H.H.S. Javadi, F. Zuo, K. Cromack, M. Angelopoulos, A.G. MacDiarmid and A.J. Epstein. (Supported in part by URI and in part by NSF Grant No. DMR-85-19059).

"ESR of Protonated 'Emeraldine': Insulator to Metal Transition," Synth. Met., in press (1988), H.H.S. Javadi, R. Laversanne, A.J. Epstein, R.K. Kohli, E.M. Scherr and A.G. MacDiarmid. (Supported in part by URI and in part by DOE Grant No. DE-FGO2-86ER 45271.A000).

"Photoexcitations in 'Emeraldine' Base," Synth. Met., in press (1988), M.G. Roe, J.M. Ginder, R.P. McCall, K.R. Cromack, A.J. Epstein, T.L. Gustafson, M. Angelopoulos and A.G. MacDiarmid. (Supported in part by URI and in part by NSF Grant No. DMR-85-19059).

"IR Absorption, Photoinduced IR Absorption and Photoconductivity of Polyaniline," Synth. Met., in press (1988), R.P. McCall, M.G. Roe, J.M. Ginder, T. Kusumoto, A.J. Epstein, G.E. Asturias, E.M. Scherr and A.G. MacDiarmid. (Supported in part by URI and in part by NSF Grant No. DMR-85-19059).

"Solution Studies of the Emeraldine Oxidation State of Polyaniline," Synth. Met., in press (1988), F. Zuo, R.P. McCall, J.M. Ginder, M.G. Roe, J.M. Leng, A.J. Epstein, G.E. Asturias, S.P. Ermer, A. Ray and A.G. MacDiarmid. (Supported in part by URI and in part by NSF Grant No. DMR-85-19059).

"Microwave Conductivity and Dielectric Constant of (TMTTF)₂X, X=SCN, ReO₄, SbF₆," Synth. Met., in press (1988), R. Laversanne, H.H.S. Javadi, and A.J. Epstein. (Supported in part by URI and in part by DOE Grant No. DE-FGO2-86ER 45271.A000 and in part by NSF Grant No. INT-8514202.)

"Photoinduced Absorption Studies of La-Cu-O and Y-Ba-Cu-O Systems," Synth. Met., in press (1988), J.M. Ginder, M.G. Roe, R.P. McCall, A.J. Epstein, E. Ehrenfreund, Y. Song, J.R. Gaines and S.I. Shah. (Supported in part by URI and in part by du Pont Corporation).

(ii) Farrington (Penn)

"Solid Polymer Electrolytes Containing Divalent Cations," 2nd Asian Conference on Solid State Ionics, Singapore, submitted (1988), R. Huq and G.C. Farrington. (Supported in part by URI and in part by NSF Grant No. DMR-85-19059).

(iii) Yang (Rhode Island)

"Experimentally Determined pH-Potential Phase Diagram for Polyaniline: Clues for Optically Distinguishable Sub-Phase in the Conductor Form," Synth. Met., in press (1988), S.C. Yang, R.J. Cushman and D. Zhang. (Supported in part by URI and in part by NSF under Grant No. CHE-82-16482).

"Polyaniline: Kinetics of Electrochemical Doping Studied by Time Resolved Absorption Spectroscopy," Synth. Met., in press (1988), D. Zhang, J.H. Hwang and S.C. Yang. (Supported in part by URI and in part by NSF under Grant No. CPE-82-16482).

"Morphological Modification of Polyaniline Using Polyelectrolyte Template Molecules," Synth. Met., in press (1988), J.H. Hwang and S.C. Yang. (Supported in part by URI and in part by an industrial grant).

VI. Patents

Patents resulting from URI support

The Ohio State University (Epstein)

A patent application for "Electromagnetic Radiation Absorbers and Modulators Comprising Polyaniline" was filed on May 13, 1988. The following have contributed towards this invention: A.J. Epstein, J.M. Ginder, M.G. Roe and H.H.S. Javadi.

VII. Changes in Personnel

1. University of Pennsylvania

a. Department of Chemistry (MacDiarmid)

Andrew Langman was hired from Manpower temporary service to put together a chemical inventory database, to assist with putting together quarterly reports, to handle computer graphics for reports and publications, and to lay out and do paste up for journal articles. He worked an average of thirty hours a week from June until August 1986, and is on call to come in as needed. He has worked intermittently from August 1986 to the present.

Dawn Zimmerman, Dr. MacDiarmid's secretary, began work on December 1, 1986. Ten percent of her time is charged to the URI grant.

Margaret Bristow began working on February 15, 1987 to assist with secretarial responsibilities. Thirty-four percent of her time is charged to the URI grant.

Jim Masters, who received his master's degree from the University of Oklahoma, joined Dr. MacDiarmid's research group effective May 1, 1988.

b. Department of Materials Science and Engineering (Farrington)

There were no changes in personnel during this quarter.

2. The Ohio State University

Department of Physics (Epstein)

Dr. Mitchell Gregg Roe resigned as a Postdoctoral Research Associate on May 31, 1988. He is currently a Principal Scientist in the Applied Optics Group at the Naval Research Laboratories in Washington, D.C.

Ms. Joanna Zinkon completed her appointment as an undergraduate secretarial aid on June 30, 1988.

Mr. Jingmin Leng began employment as a Research Aide on April 25, 1988.

Mr. Steve Treat completed his master's studies as a Graduate Research Associate on June 15, 1988 and is continuing his Ph.D. studies in another area of condensed matter physics.

3. Lockheed Advanced Aeronautics Corporation

Aeronautics Systems Group Research (Kuan)

There were no changes in personnel during this quarter.

4. Rensselaer Polytechnic Institute

Department of Chemistry (Wnek)

There were no changes in personnel during this quarter.

5. University of Rhode Island

Department of Chemistry (Yang)

Mr. Richard Cushman took a leave of absence from the graduate school to put time in the family business. No students are supported under this contract during this quarter.

6. Montclair State College

Department of Chemistry (Humphrey)

There were no changes in personnel during this quarter.

VIII. Contractual Administration

1. Prime Contract - University of Pennsylvania

Additional funding for \$1,008,000.00 was received by the University of Pennsylvania, Office of Research Administration, on June 28, 1988.

We had previously received \$500,000.00 on February 28, 1988. Therefore, the total for the second year funding will be \$1,508,000.00.

IX. Miscellaneous

Due to the fact that all funding for Year 2 (October 1, 1987 - September 30, 1988) was not received until June 28, 1988, considerable interruption of research was involved, particularly by Lockheed corporation, due to periods in which Lockheed had no funds. This involved a re-shuffling of research personnel. Although the receipt by the University of Pennsylvania of approximately 1/3 of the total second year budget on February 17, 1988 helped to alleviate this problem, stoppages of research still occurred due in part to the time lag involved between which the University of Pennsylvania received funding and the time by which the administration of the various organizations was able to use the new funding. For example, for Lockheed Corporation the amount of \$56,305 was not available until 6/28/88 (just two days before the end of the seventh quarter). Therefore, prior to and up to 6/28/88 their available balance was \$30,732 (funding added on 2/17/88 and continued up to 6/28/88) - \$97,152 (total spent and committed until 6/30/88) was (-66,420). Therefore, Lockheed did not practically have any funding available from URI until 6/28/88.

X. Fiscal Status
Expenditures and Commitments

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A. University of Pennsylvania: The following represents monies spent and/or committed to that portion of the program carried on at the University of Pennsylvania.

	1 1st Year Budgeted 9/15/86-9/30/87	2 2nd Year Budgeted 10/1/87-9/30/88	3 New Funding added on 2/17/88 & 6/28/88 = 577,611	4 Total Spent & Committed 9/15/86-6/30/88	5 Available Balance on 6/30/88	6 Budgeted Balance
U of P (Chem) (Dr. A.G. MacDiarmid)	727,044	577,611	187,466 + 390,145 = 577,611	804,806	499,849	499,849
U of P (MSE) (Dr. G.C. Farrington)	231,565	309,845	102,108 + 207,737 = 309,845	487,443	53,967	53,967

B. Subcontracts

	1st Year Budgeted 9/15/86-9/30/87	2nd Year Budgeted 10/1/87-9/30/88	New Funding added on 2/17/88 & 6/28/88 = 369,597	Total* Spent & Committed 9/15/86-6/30/88	Available Balance on 6/30/88 (1+3)-4	Budgeted Balance (1+2)-4
OSU (Dr. A.J. Epstein)	867,116	369,597	121,800 + 247,797 = 369,597	1,038,597	198,116	198,116
Lockheed (Dr. T. Kuan)	87,037	87,037	30,732 + 56,305 = 87,037	97,152	76,922	76,922
MM Inc. (Ms. M. Dolton)	37,143	30,246	11,985 + 18,261 = 30,246	49,127	18,262	18,262
Academic Subcontractors a. Dr. G.E. Wnek 1. MIT 2. RPI	36,996 36,006	0 69,940	0 31,862 + 38,078 = 69,940	36,796 59,054	200 46,892	200 46,892
b. Univ. Rhode Island (Dr. S. Yang)	31,862	31,862	31,862 = 31,862	39,339	24,385	24,385
c. Montclair State (Dr. B. Humphrey)	29,231	31,862	14,047 + 17,815 = 31,862	45,462	15,631	15,631

*The following represents monies paid on receipt of demand (i.e., bills) from participating subcontracts.