16:15:37 OCA PAD INITIATION - PROJECT HEADER INFORMATION 09/15/92 Active Cost share #: Rev #: 0 Project #: G-33-533 Center # : 10/11-6-P5105-0A0 Center shr #: OCA file #: Work type : INST Contract#: LTR DTD 910718 Document : GRANT Mod #: Prime #: Contract entity: GTRC Subprojects ? : N CFDA: PE #: Main project #: CHEMISTRY Unit code: 02.010.136 Project unit: Project director(s): COLLARD D M (404)894-4002 CHEMISTRY Sponsor/division names: CAMILLE&HENRY DREYFUS FND INC / NEW YORK, NY Sponsor/division codes: 500 / 157 950630 (reports) Award period: 920301 to 950630 (performance) Total to date Sponsor amount New this change 25,000.00 25,000.00 Contract value Funded 25,000.00 25,000.00 0.00 Cost sharing amount Does subcontracting plan apply ?: N Title: DREYFUS NEW FACULTY AWARD PROJECT ADMINISTRATION DATA 894-4820 OCA contact: Kathleen R. Ehlinger Sponsor technical contact Sponsor issuing office ROBERT L. LICHTER **ROBERT L. LICHTER** (212)753-1760 (212)753-1760 THE CAMILLE AND HENRY DREYFUS THE CAMILLE AND HENRY DREYFUS FOUNDATION, INC. FOUNDATION, INC. 445 PARK AVE. 445 PARK AVE. NEW YORK, NEW YORK 10022 NEW YORK, NEW YORK 10022 Security class (U,C,S,TS) : U ONR resident rep. is ACO (Y/N): Defense priority rating : N/A N/A supplemental sheet GIT Equipment title vests with: Sponsor Administrative comments -INITIATION OF PROJECT. MAYBE USED FOR ANYTHING "EXCEPT DEFRAYAL OF ACADEMIC -YEAR SALARY". BUDGET CHANGES DO NOT NEED SPONSOR APPROVAL.

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School of Chemistry and Biochemistry

**Georgia Institute of Technology** Atlanta. Georgia 30332-0400 404•894•4002 404•894•7452 Fax

Robert L. Lichter, Ph.D. Executive Director The Camille and Henry Dreyfus Foundation, Inc. 555 Madison Avenue New York, NY 10022

22 March, 1993

Dear Dr. Lichter,

Please find the attached progress report for award NF-91-61. The award has allowed for particular flexibility in financial planning which would not otherwise be possible. The award has attracted attention of the department and institute. Many collaborations and interesting possibilities have arisen in my first year at Georgia Tech. The report outlines a number of exciting teaching and research projects I am pursuing.

Yours sincerely,

David M. Collard Assistant Professor

# Progress Report: Award Number NF-91-61 March 1993

#### Research

As of Spring 1993, I have four graduate students working in my research laboratories Curtis Sayre (BS, Carnegie Melon), Mark Stoakes (BS, University of Iowa), Paul Henderson (BS, University of Florida) and Cameron Tyson (BS, Georgia Tech). Over the last year, four undergraduates have performed research for academic credit in the group: Myra Dawson, Manijeh Sadri, Vicky Camp and Allen Annis. Another student, Patrick Toy (Union College, Jackson, TN), visiting on an NSF-REU summer program, was particularly productive.

We have made some progress in the development of self-assembling monomers for the deposition of ordered electronically conductive polymers. This was the topic of two presentations in the last year (ACS Fall 1992 meeting, Washington DC: "Lamellar conducting polymers by electropolymerization of self-assembling monomers: potassium 3-(3-alkylpyrrol-1-yl)propane sulfonates" Collard, D. M.; Stoakes, M. S.; Fox, M. A., *Polymer Preprints (American Chemical Society Division of Polymer Chemistry)* **1992**, *33(2)*, 376. International Conference on Synthetic Metals, Gothenburg, Sweden: "Highly ordered conductive polymers by polymerization of self-assembling monomers" Collard, D. M.; Stoakes, M. S. *Synthetic Metals* **1993**, *55*, 1073). A complete paper with M. S. Stoakes as co-author is in preparation.

We have also prepared monolayers of alkylpyrroles and performed polymerizations in order to study the characteristics of individual polymer chains. This work, by Curtis Sayre, is the subject of a short paper which should be submitted soon.

A number of undergraduates have spent time preparing poly(alkylsulfonyl)benzenes. These were prepared as potential liquid crystalline materials. However, we have become intrigued by features of the <sup>1</sup>H NMR spectra of these compounds which we attribute to a restricted rotation and the formation of a particularly stable conformation. I hope to submit a full paper on this topic with four undergraduates as co-authors.

Other undergraduates have prepared 3-alkylthiophenes and 3-alkyl-2,2'-bithiophenes in order to prepare well-defined head-to-tail strictly alternating conductive copolymers.

In a collaboration with Professor Kenneth Hughes in this department we are beginning to investigate host-guest chemistry at solid-solution and solid-gas interfaces. This research is directed towards the development of an integrated optical sensor for aromatic hydrocarbons. This is supported in part by the Hazardous Substance Research

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Centers Program (South and Southwest) in collaboration with principle investigators at Georgia Tech Research Institute.

A number of collaborative studies are underway, and joint proposals have been submitted. These include interactions with Professors Bottomley, Tolbert, Gillis and Hughes in this department, Kahn at Clark-Atlanta University, and Hartman at Georgia Tech Research Institute.

Research seminars have been presented at: University of West Florida, Bob Jones University and Georgia Institute of Technology (Polymer Education and Research Center). Seminars will be presented soon at: James Madison University and University of Florida.

#### Teaching

My teaching schedule for the first three years of my academic appointment is:

Spring 1994: CHEM 3343, Polymer Organic Chemistry
Winter 1994: CHEM 3312, Organic Chemistry II
Fall 1993: CHEM 6321, Reactivity, Mechanism and Structure in Organic Chemistry I
Fall 1993: CHEM 4311, Organic Reactions I
Spring 1993: CHEM 3343, Polymer Organic Chemistry
Winter 1993: CHEM 3312, Organic Chemistry II, 174 students
Fall 1992: CHEM 6321, Reactivity, Mechanism and Structure in Organic Chemistry I, 28 students
Spring 1992: CHEM 3343, Polymer Organic Chemistry, 23 students
Winter 1992: CHEM 3313, Organic Chemistry III, 19 students
Fall 1991: CHEM 3313, Organic Chemistry III, 66 students

The first year was spent teaching sophomore level organic chemistry. The spring quarter class (Organic Chemistry of Polymers) is a new class for Georgia Tech, and one that I have spent considerable time developing. In the second year I taught the introductory graduate physical organic course (Chem 6321). For most of the students this course reintroduces the concepts of mechanistic organic chemistry. Chem 3312 is the large on-sequence section of organic chemistry at the sophomore level. Most of the students are chemical engineering majors. I will teach the polymer organic class again in Spring 1993. My third year responsibilities are the same as those in the second year, with the senior undergraduate organic class combined with the introductory graduate class. Course critiques have been very good.

In my second year I was awarded a *Lilly Foundation Teaching Fellowship*. This is to encourage innovative teaching. Through a seminar series offered by the Center for Enhancement of Teaching and Learning at Georgia Tech, and the Lilly Foundation conferences, I have been exposed to a number of issues concerning teaching and college scholarship. This has been a particularly

beneficial program. Funding associated with this program has allowed for further development of Chem 3343.

#### Other

Interactions with the faculty at Clark-Atlanta University on a collaborative research project has involved me with the concerns of minority student enrollment and retention. Georgia Tech attracts a large number of African American applicants for graduate study. Through mentoring and tutorials we are addressing a number of concerns these students have. The department has the stated goal of becoming the major producer of African American chemistry PhDs in the country.

In collaboration with another faculty member, I worked on a National Chemistry Week demonstration for presentation at SciTrek, a nationally acclaimed science museum in Atlanta.

#### **Funding Activities**

At present, we have a number of small funded projects. The Petroleum Research Fund and the Polymer Program Associates (a group of companies supporting polymer research at Georgia Tech) supports our work in conductive polymers. We are also working with the NASA-supported Center for High Performance Polymers and Ceramics at Clark Atlanta University on a collaborative project in conductive organics. A number of other research proposals have been submitted. Three teaching proposals have also been submitted.

The award of the Camille and Henry Dreyfus Foundation New Faculty Award has allowed for considerable flexibility in planning research and use of other (more restricted) funds. In the first year of this award, this funding was used for travel to Washington for presentation of a paper at the Fall 1992 ACS meeting.

Acquisition of multiyear funding remains the highest funding priority.

#### Current Support

Lilly Foundation, "Teaching Fellowship", Collard, \$7,500, 9/92-8/93.

Camille and Henry Dreyfus Foundation, "New Faculty Award", Collard, \$25,000, 9/91-8/96.

Petroleum Research Fund - American Chemical Society, "Control of Conducting Polymer Morphology by Self Assembly of Electroactive Monomers", Collard, \$21,000 (including \$3,000 undergraduate research supplement).

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- Georgia Tech PPA-PERC, "Control of Conductive Polymer Morphology by Molecular Self-Assembly", Collard, \$6,000,9/92-4/93.
- Hazardous Substance Research Center, "Development of an Integrated Optic Interferometer for in-situ Monitoring of Volatile Hydrocarbons", Walsh, Hartman, Ross, Hughes, Collard, \$105,914.
- NASA, "High Performance Polymers and Ceramics Center (HiPPAC)", Collard co-PI with 21 others.

#### **Proposals Submitted**

- NSF-Chemistry, "Self-assembly of amphiphic electrically conductive polymers" Collard, \$250,000, submitted 2/93, pending.
- NSF-NYI, "National Young Investigator", Collard, \$75,000, submitted 2/93, pending.
- NSF-ILI, "Polymer Chemistry in the Undergraduate Curriculum", Bottomley, Collard, Liotta, Tolbert, \$96,214, submitted 10/92, pending.
- Georgia Tech FRP, "Focused research program in the fabrication of molecular devices" Bottomley, Collard, Tolbert, Bidstrup, Martin, \$60,000, submitted 1/93, rejected
- NSF-Mat. Educ. Init., "Material Chemistry in the Undergraduate Curriculum" Collard, Bertrand, Hill, \$289,516, sumbitted 5/92, rejected.
- NSF-Chemistry, "Control of Conductive Polymer Morphology by Molecular Self-Assembly" Collard, \$245,000, submitted 5/92, rejected.
- NSF-ILI, "Polymer Chemistry in the Undergraduate Curriculum", Bottomley, Collard, Liotta, Tolbert, \$96,214, submitted 10/91, rejected.
- Proctor and Gamble Exporatory Research, "Polymerization of Self-Assembled Electroactive Monomers", Collard, \$149,979, submitted 3/92, rejected.
- NSF-NYI, "National Young Investigator", Collard, \$75,000, submitted 3/92, rejected.
- Oak Ridge Associated Universities, "ORAU Junior Faculty Enhancement Award, Collard, \$10,000, submitted 5/92, rejected.

Georgia Tech MARC, "Processable Conductive Polymers", Collard, \$25,000, submitted 5/92, rejected.

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- Georgia Tech MARC, "The Rational Design of Processable Electronically Conductive Polymers" Bottomley, Collard, Liotta, Tolbert, Turbini, \$115,000, submitted 5/92, rejected.
- Georgia Tech PERC, "Metal Surface Modification by Polymer Adsorption and in-situ Polymerization of Adsorbed Monomers", Collard, \$6,000, submitted 3/92, rejected.

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G-33-533 Dright Scat directly to Licht-r, copies Supplied OCA & COS. Agreement w/ Lichter to Submit Robert L. Lichter, Ph.D. reports every March from Director March from Nel #2 ÷-:)

23 March, 1994

Dear Dr. Lichter:

It was a pleasure to finally meet you, albeit briefly, at the Fox/Whitesell reception in San Diego. Please find the attached progress report for award NF-91-61. Things are progressing well at Georgia Tech, and new opportunities keep arising. The report outlines activities for the last year. I have also included an updated vita.

Yours sincerely,

David M. Collard Assistant Professor

Phone: (404) 894-4026 Fax: (404) 894-7452 david.collard@chemistry.gatech.edu

### **Progress Report: Award Number NF-91-61**

David M. Collard Georgia Institute of Technology, Atlanta, GA 30332-0400 March 1994

### Research

As of Spring 1994, I have three graduate students working in my research laboratories Curtis Sayre (BS, Carnegie Melon), Paul Henderson (BS, University of Florida), Cameron Tyson (BS, Georgia Tech). Another four students will begin research in Summer, 1994: Kikue Burnham (MS, Georgia Tech), Southeary Chau (BS, Emory University), Senji Inaoka (MS, Keio University, Japan), and Stacy Murphy (BS, Chicago State University). I have had continued success with undergraduate participation with my research efforts. Allen Annis, who worked on two projects (one paper accepted, one in preparation), has graduated and is now in the graduate program at Harvard. Manijeh Sadri and Thomas Wynn (co-authors on a manuscript in preparation) will graduate this spring and will pursue graduate studies (environmental engineering and chemistry, respectively). Ginger Barr, a Textiles Science and Engineering major, is working independently on a project under the direction of Curt Sayre, which should lead to a publication by the end of the summer.

Our work in the development of self-assembling monomers for the deposition of ordered electronically conductive polymers has developed further, with a full length paper accepted for publication in *Chemistry of Materials*. This has also been the topic of conference presentations. Curt Sayre has made significant progress towards self-assembled monolayers (SAMs) of heteroarene adsorbates. Polymerization on electrode modified with SAMs yields dense, highly conductive, strongly adhesive and robust films of  $\pi$ -conjugated polymers. An initial communication is in press (*J. Electroanal. Chem.*), and the work was the topic of a presentation at the Spring 1994 ACS meeting. A more

detailed description of the work will be submitted by Fall 1994, and we have been invited to present this work at the International Conference on Synthetic Metals, Seoul, Korea in the summer.

Our studies of the distorted geometry of poly(alkylsulfonyl)benzenes is coming to a conclusion. This project has been executed entirely by undergraduates (Toy, Sadri, Annis, Wynn), who will appear as co-authors on two manuscripts and a number of conference proceedings. An MS student will return to our initial interests in these molecules (liquid crystallinity) in the future.

Paul Henderson has continued the work of undergraduates in preparing 3alkylthiophenes, 3-alkyl-2,2'-bithiophenes and alkylated thiophene oligomers in order to prepare well-defined head-to-tail strictly alternating conductive copolymers.

Our collaboration with Professor Kenneth Hughes studying the host-guest chemistry at solid-solution and solid-gas interfaces has developed in the last year. Cam Tyson has adopted us as co-advisors, and has completed some nice synthetic work and selfassembly. This has taken both PIs into new areas.

Other collaborative programs are being initiated the Professors Liotta (polyester synthesis, stability and barrier properties), Tolbert and Bottomley (surface active conductive polymers).

### Teaching

Teaching responsibilities for the 1993-94 academic year were identical to those for the previous year. This allowed for further refinement of "Organic Chemistry of Polymers" (Chem 3343) and the introductory graduate physical organic chemistry course (Chem 6321). Winter quarter was spent teaching the large (195 students), on-sequence section of organic chemistry (Chem 3312). Course critiques have been very good.

During the last year I completed a *Lilly Foundation Teaching Fellowship* Funding associated with this program has allowed for further development of Chem 3343. Perhaps more valuable than the funding were the associated activities such as seminar series, in-class visitations, video-taping of lectures, and two Lilly Teaching Fellows Conferences.

We spent some time last year developing a procedure for an analytical chemistry laboratory experiment using gc-ms. This was in response to Allen Annis's dissatisfaction at the experiment used at present. He took a synthesis he was performing in the research lab and turned it into a nice demonstration of kinetics for a sequence of reactions. We have adopted this procedure in the undergraduate laboratories and a paper has been accepted for publication in *The Journal of Chemical Education*. Over the next year we will develop experiments utilizing thermal analysis equipment, to be purchased with an award from the NSF-ILI program. Our aim is for these experiments to be interdisciplinary to demonstrate principles from various undergraduate lecture courses.

We are in the initial stages of developing an outreach program as a community resource for the presentation of chemistry to the public. We have submitted a number of modest proposals (\$500 to \$7500) and preproposals to industry and the Polymer Division of the ACS.

At the end of the 1992-93 academic year I was awarded the Amoco-Foundation-Georgia Tech Junior Faculty Excellence in Teaching Award, and I recently received the Professor of the Month Award from Lambda Sigma, the National Sophomore Honors Society.

## **Funding Activities**

#### New Funded Proposals

- NSF-ILI, "Polymer Chemistry in the Undergraduate Curriculum", Bottomley, Collard, Liotta, Tolbert, \$96,214.
- Georgia Tech President's Office Interdisciplinary Seed Funding, "The Fabrication of Molecular Devices", Bottomley, Collard, Tolbert, Kohl, \$20,000, 7/93-6/94.
- Georgia Tech PERC, "Sequence Specific Copolymers and Regioregular Poly(3-Substituted Thiophene)s", Collard, \$6,750, 1/94-1/95.

### **Continuing Support**

Petroleum Research Fund Camille and Henry Dreyfus Foundation Hazardous Substance Research Center NASA-HiPPAC Lilly Foundation (expired June 1993)

#### **Progress Report: Award NF-91-61**

6-33-533

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David M. Collard Georgia Institute of Technology, Atlanta, GA 30332-0400 March 1995

### Research

As of Spring 1995, I have seven graduate students working in my research laboratories Curtis Sayre (BS, Carnegie Melon), Paul Henderson (BS, University of Florida), Cameron Tyson (BS, Georgia Tech). Kikue Burnham (MS, Georgia Tech), Southeary Chau (BS, Emory University), Seiji Inaoka (MS, Keio University, Japan), and Stacy Murphy (BS, Chicago State University). A stream of undergraduates have passed through the laboratory in the last couple of years. Current projects are briefly summarized.

Electronically Conductive Polymers. Our work on conductive polymers concentrates on the effects of surface structure on the deposition of high quality materials, formation of micron-scale patterns, and new monomers for the control of polymer microstructure. Curt Sayre has continued his work on self-assembled monolayers (SAMs) of heteroarene adsorbates. Polymerization on electrodes modified with SAMs yields dense, highly conductive, strongly adhesive and robust films of  $\pi$ -conjugated polymers. This work was presented at the Spring 1994 ACS meeting, as an initial communication (*J. Electroanal. Chem.*), a full paper (*Langmuir*), and invited presentations at the Southwest Regional ACS meeting (Fort Worth, TX, December 1994) and the International Conference on Synthetic Metals (Seoul, South Korea, July 1994). The *Langmuir* paper was reported in *Chemical and Engineering News* and *Inside R&D: The Weekly Report on Technical Innovation*. Micron-scale patterns have been formed and will be reported soon.

Seiji Inaoka has made good progress on the synthesis of amphiphilic monomers (sodium  $\omega$ -(3-thienyl)alkanesulphonates) with which we hope to address a number of

problems with other monomer-containing surfactants reported in *Chemistry of Materials* (1994).

Paul Henderson has completed a study of dialkyloligothiophenes which allow us to tailor the properties of polyalkylthiophenes through judicious choice of monomer structure. The study has been submitted to *Chemistry of Materials* as a full paper.

Two undergraduates (Ginger Barr and Daniel Connor) have worked on the use of surfactant electrolytes for the deposition of polypyrroles. This approach allows us to use aqueous solutions in place of organic solvents, and the electrolyte is incorporated into the polymer matrix to provide long range order and flexibility. Ginger Barr was the recipient of an ACS Polymer Division student summer scholarship to perform this research.

*Host-Guest Chemistry at Interfaces.* Cam Tyson and Stacy Murphy have prepared amphiphilic and water soluble calixarenes in order to prepare photonic sensors. A communication describing the host-guest chemistry of water soluble calixarenes is in preparation for submission. The amphiphilic calixarenes are being studied in Professor Hughes' group.

*Barrier Properties of PET.* We recently received funding from Hoechst Celanese Corporation for an investigation of the  $CO_2$  and  $O_2$  barrier properties of PET. With the aim of preparing a better soda bottle and a plastic beer bottle, we are performing synthetic work and collaborating with polymer processors at Case Western. This is a highly collaborative project which will require two Georgia Tech students to work at Hoechst Celanese for extended periods.

*Other Projects.* Kikue Burnham is performing synthetic work in the group on a series of cocaine antagonists. She is working in collaboration with Dr. Howard Deutsch of this department who has good contacts for animal testing. We are currently writing proposals to get this funded.

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Our bent benzene work will be over by the end of this year. We have an initial communication submitted, a full paper in preparation, and an MS thesis (Sotheary Chau) will be completed by the end of the year.

#### Teaching

Teaching responsibilities for the 1994-5 academic year were identical to those for the previous year: introductory graduate organic chemistry and sophomore organic chemistry. The department granted me a release from teaching in spring 1995.

New laboratory experiments have been developed in GC-MS and DSC in the analytical teaching laboratory (with an organic flavor). A proposal for a new FT NMR for the undergraduate teaching laboratory was submitted to NSF-ILI. This summer we will be presenting the polymer science portion of an "Advanced Materials" NSF faculty enhancement workshop, and a summer high school research experience program in polymer chemistry.

We received the ACS PolyEd Polymer Curriculum Award for the development of a k-12 polymer outreach program and the development of materials and methods for the portrayal of polymer chemistry in science museums. Undergraduates receive academic credit for participation in the program.

I was selected as one of the 1994 Research Corporation Cottrell Scholars, a program for young faculty entering the third year of a tenure track position promoting a balanced view of teaching and research in scholarship.

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#### Funding Activities (New Funded Proposals)

- Hoechst Celanese Corporation, "Improved properties of poly(ethylene terephthalate)", Collard, Liotta, \$225,000, 7/95-6/98.
- POLYED-ACS, "A precollege education program in polymers: The role of science museums and collaborations with colleges, schools and professional chemists", Collard, \$5,000 (including institutional match), 6/94-6/96.

Research Corporation, "Cottrell Scholarship", Collard, \$50,000, 7/94-6/96.

#### **Publications** (1994, published, in press, submitted)

- "Thiophene:3-Alkylthiophene Copolymers from Dialkyloligothiophenes", Henderson, P. T.; Collard, D. M. *Chemistry of Materials*, submitted.
- "Bent benzenes: <sup>1</sup>H NMR and crystal structure of 1,4-dibutyl-2,3,5,6-tetrakis-(propylsulphonyl)benzene" Collard, D. M.; Sadri, M. J.; Wynn, T. A.; VanDerveer, D. *Journal of Chemical Society, Chemical Communications*, submitted.
- "Spontaneously adsorbed monolayer-modified electrodes for deposition of polyheterocycles" Collard, C. N.; Sayre, C. N. Synthetic Metals, 1995, in press.
- "GC-MS experiments for instrumental analysis and organic chemistry Laboratories. The Kinetics and Mechanism of Bromination of Disubstituted Arenes" Annis, D. A.; Collard. D. M.; Bottomley, L. A. *Journal of Chemical Education*, **1995**, in press.
- "Spontaneously adsorbed monolayers of pyrrole-containing alkanethiols on gold" Sayre, C. N.; Collard, D. M. Langmuir, **1995**, 11, 302.
- "Self-assembled monolayers of 3-(ω-mercaptoalkyl)-pyrroles on gold" Collard, D. M.; Sayre C. N. Journal of Electroanalytical and Interfacial Chemistry, **1994**, 375, 367.
- "The electrochemical polymerization of self-assembled heteroarenes: Potassium 3-(3-Alkylpyrrol-1-yl)propane sulfonates" Collard, D. M.; Stoakes, M. S. *Chemistry of Materials*, **1994**, *6*, 850.
- "Self-assembled monolayer-modified substrates for electrochemical deposition of electronically conductive polymers" Collard, D. M.; Sayre, C. N. Polymer Preprints (American Chemical Society Division of Polymer Chemistry), **1994**, 35(1), 196.