

30 June 1999

OFFICE OF NAVAL RESEARCH
END-OF-THE-YEAR REPORT
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

GRANT: N00014-92-J-1369

PR No: 96PR02211-00

Title of GRANT:

“Mesomolecular Anilines:
New Horizons in Electrically Conducting Organic Materials”

Name of Principal Investigator:

Alan G. MacDiarmid

Name of Organization:

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Department of Chemistry

Address of Organization:

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Date Submitted:

30 June 1999
(01 June 98 to 31 May 99)

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PR Number: 96PR02211-00
 Grant Number: N00014-92-J-1369
 Grant Title: "Mesomolecular Anilines: New Horizons in Electrically Conducting Organic Materials"
 Principal Investigator: Alan G. MacDiarmid
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- a. Number of Papers submitted to refereed journals, but not published: 1
- b. Number of papers published in refereed journals: 7
- c. Number of books or chapters submitted, but not yet published: 1
- d. Number of books or chapters published: 0
- e. Number of printed technical reports/non-refereed papers: 13
- f. Number of patents filed: 0
- g. Number of patents granted: 2
- h. Number of invited presentations: 22
- i. Number of submitted presentations: 2
- j. Honors/Awards/Prizes for contract/grant employees (list attached)
- k. Total number of Full-time equivalent Graduate Students and Post-Doctoral associates supported during this period, under this R & T project number:
 - Graduate Students: 4
 - Post-Doctoral Associates: 1
 - Female Graduate Students: 2
 - Female Post-Doctoral Associates: 0
 - Minority* Graduate Students: 0
 - Minority* Post-Doctoral Associates: 0
 - Asian Graduate Students: 4
 - Asian Post-Doctoral Associates: 0
- l. Other funding (list attached)

* Minorities include Blacks, Aleuts, Native Americans, Hispanics, etc. NB: Asians are not considered an under-represented or minority group in science and engineering.

Part I

a. Papers submitted to refereed journals, but not yet published (at least 25% ONR supported)

June 1, 1998 – May 31, 1999

“Charge Transport of the Mesoscopic Metallic State in Partially Crystalline Polyanilines” submitted to Phys. Rev. B., J. Joo, S. M. Long, J. P. Pouget, E. J. Oh, A. G. MacDiarmid and A. J. Epstein.

b. Papers published in refereed journals (at least 25% ONR supported)

June 1, 1998 – May 31, 1999

“Charge Transport of the Mesoscopic Metallic State in Partially Crystalline Polyanilines,” J. Joo, S. M. Long, J. P. Pouget, E. J. Oh, A. G. MacDiarmid and A. J. Epstein, *Phys. Rev. B*, 57, 16, 1998, 9567.

“Preparation and Characterization of Electrostrictive Polyurethane Films with Polymer Electrodes,” J. Su, Q. M. Zhang, P.-C. Wang, A. G. MacDiarmid and K. J. Wynne, *Polymers for Adv. Technologies*, 9, 16, 1998, 317.

“Oligomers and Isomers: New Horizons in Poly-Anilines,” A. G. MacDiarmid, Y. Zhou and J. Feng, *Synthetic Metals*, 100, 1999, 131-140.

“Critical Dependency of the Conductivity of Polypyrrole and Polyaniline Films on the Hydrophobicity/Hydrophilicity of the Substrate Surface,” P-C. Wang, Z. Huang and A. G. MacDiarmid, *Synth. Met.*, 101, 1999, 852.

“AFM Studies of Composite 16-mer Polyaniline Langmuir-Blodgett (LB) Films,” A. Riul Jr., A. Dhanabalan, M.A. Cotta, P.S.P. Herrmann, L.H.C. Mattoso, A.G. MacDiarmid, O.N. Oliveria, Jr, *Synth. Met.*, 101, 1999, 830.

“EPR of Mesoscale Polyanilines,” K.R. Brenneeman, J. Feng, Y. Zhou, A.G. MacDiarmid, P.K. Kahol and A.J. Epstein, *Synth. Met.*, 101, 1999, 785.

“Sensors using Octaaniline for Volatile Organic Compounds,” J. Feng and A. G. MacDiarmid, *Synth. Met.*, 102, 1999, 1304.

c. Chapters in books submitted, but not yet published

“Doped Polymer Light-Emitting Devices and Sensors for Volatile Organic Compounds,” Eds. B. R. Hsieh, M. Galvin, Y. Wei, Amer. Chem. Soc. (1999) ‘Semiconductive Polymers’, A. G. MacDiarmid, F. Huang and J. Feng.

d. Books or chapters published (at least 25% ONR supported)

N o n e

e. Printed technical reports/non-refereed papers (at least 25% ONR supported)

“Application of Thin Films of Conjugated Oligomers and Polymers in Electronic Devices,” A. G. MacDiarmid, W. J. Zhang, J. Feng, F. Huang and B. R. Hsieh, *Proc. Int. Union Pure and App. Chem. (IUPAC), Gold Coast, Australia*, 1998, 302.

“Critical Dependency of the Conductivity of Polypyrrole and Polyaniline Films on the Hydrophobicity/Hydrophilicity of Substrate Surface,” A. G. MacDiarmid, P-C. Wang and Z. Huang, *Proc. Workshop on Processing Conducting Polymer Materials and Devices, Intell. Polym. Research Inst., Wollongong, Australia, 1998, 20.*

“Are Properties of Polyaniline Controlled by its Isomeric Composition?” A.G. MacDiarmid, *Proc. ACS, Div. of Polym. Mat.: Sc. and Eng.*, 80, 1999, 492.

“Isomers and Isomerization Processes in Poly-Anilines,” A. G. MacDiarmid, Y. Zhou, J. Feng, G. T. Furst and A. M. Shedlow, *Polym. Prepr.*, 40, 1, 1999, 246.

“The Effect of End Groups on the UV VIS Spectroscopic Properties of Oligoanilines,” J. Gao, W. J. Zhang, K. Li, C. Wang, Z. Wu, Y. Ji, Y. Zhou and A. G. MacDiarmid, *Polymer Prepr.*, 40, #1, 1999, 105.

“Polyaniline and Benzidine: An Oligoaniline Containing a Benzidine Unit,” J. Gao, W. J. Zhang, K. Li, C. Wang, Z. Wu, Y. Ji, Y. Zhou and A. G. MacDiarmid, *Polymer Prepr.*, 40, #1, 1999, 103.

“Polyaniline and Benzedine: An Oligoaniline Containing Benzedine Unit,” J. Gao, W. J. Zhang, Y. Yu, K. Li, C. Wang, Z. Wu, Y. Ji, Y. Zhou and A. G. MacDiarmid, *Polym. Prepr.*, 40, 1, 1999, 103.

“The Effect of End Groups on the UV/VIS Spectroscopic Properties of Oligoanilines,” J. Gao, W. J. Zhang, K. Li, C. Wang, Z. Wu, Y. Ji, Y. Zhou and A. G. MacDiarmid, *Polym. Prepr.*, 40, 1, 1999, 105.

“Modified Pseudo-High-Dilution Technique for Synthesizing Phenyl-Capped Oligoanilines,” J. Gao, W. J. Zhang, K. Li, C. Wang, Z. Wu, Y. Ji, Y. Zhou and A. G. MacDiarmid, *Polymer Prepr.*, 40, 1, 1999, 107.

“Electronic and Mechanical Properties of Single Wall Carbon Nanotubes – Polyaniline Composites,” *Abstr. MRS Mtg. Boston, Dec. 1998*, Z. Benes, J. E. Fischer, M. Ouyang and A. G. MacDiarmid.

“Effect of Chiral Dopant on Polyaniline-CSA Films,” abstr. submitted for March’99 *Bull. Amer. Phys. Soc.*, K. A. Bates, A. V. Sapirgin, W.-P. Lee, K. R. Breneman, D. Tigelaar, M. Platz, A. J. Epstein, M. Ouyang and A. G. MacDiarmid.

“Electroluminescence in σ -Conjugated Polymers: Polygermanes and Polyanilines,” ext. abstr. submitted to Int’l Conf. on Sci. & Tech. of Advanced Polym. (ICAP 99), Yamagata, Japan, July 26-30, 1999, A.G. MacDiarmid, F. Huang, I.D. Norris, D.H. Berry and S.M. Katz.

“Critical Dependency of the Conductivity of Polypyrrole and Polyaniline on the Hydrophobic / Hydrophilic of the Substrate Surface,” submitted to *Mat. Res. Soc. 1999 Fall Mtg.*, Boston, MA, Nov. 29-Dec. 3, 1999, P-C. Wang, Z. Huang and A.G. MacDiarmid.

f. Patents filed (at least 25% ONR supported)

N o n e

g. Patents granted (at least 25% ONR supported)

“Methods for Preparing Conductive Polyanilines.” Inventors: A.G. MacDiarmid, Y.N. Xia and J.M. Wiesinger. US Patent No. 5,773,568, Issued June 30, 1998.

“Conducting Substrate, Liquid Crystal Device Made Therefrom and Liquid Crystalline Composition in Contact Therewith.” Inventors: R. Shashidar, J.M. Clavert, R.J. Crawford, K.J. Wynne, T.G. Vargo, A.G. MacDiarmid and J.K. Avlyanov. US Patent No. 5,828,432, Issued October 27, 1998.

h. Invited Presentations

- May 29 - June 2 1998 ONR Polymer Program Review, Jacksonville, FL
“Oligomeric and Mesomolecular Anilines and Application in Sensors for Volatile Organic Compounds”
- June 14-16 1998 HIDE/DARPA Semi-Annual Review Meeting, Arlington, VA
“Active Camouflage Polymer Coatings”
- July 7- 11 1998 Intelligent Polymer Research Institute, Wollongong, Australia
“Dependency of Properties of Polyaniline and Polypyrrole on their Method of Preparation”
- July 11-13 1998 Int’l Union of Phys. & Appl. Chem., IUPAC, (Macro 98), Gold Coast, Australia
“Application of Thin Films of Conjugated Oligomers and Polymers in Electronic Devices”
- July 15-18 1998 Int’l Conf. on the Chemistry of Synthetic Metals (ICSM), Montpellier, France
“Role of Ionic Species in Determining Characteristics of Polymer LEDs”
- August 25-26 1998 Seminar, Allied Signal Corp., Morristown, NJ
“Application of Thin Films of Conjugated Oligomers and Polymers in Electronic Devices”
- September 28 1998 Seminar, Kyushu Institute of Technology, Japan
“ ‘Synthetic Metals’: A Novel Role for Organic Polymers”
- October 1-3 1998 Society Meeting of the Institute of Electronic, Information and Communication Engineering (IEICE) at Yamanashi University, Japan
“Doped Polymer Light-emitting Devices”
- October 12-14 1998 Taylor Lecturer in Materials Science, Penn State University, State College, PA
“ ‘Synthetic Metals’: A Novel Role for Organic Polymers”
Polyaniline: Synthetic Metal for the 21st Century?”
- October 19-25 1998 Int’l Symposium, Francqui Foundation, Brussels, Belgium
“Doped Polymer Light-Emitting Devices”
- October 28 1998 Seminar, Lehigh University, Bethlehem, PA
“ ‘Synthetic Metals’: A Novel Role for Organic Polymers”
- December 8 1998 ONR/Kent Displays Inc. “Kickoff” Meeting, Arlington, VA
- January 21-24 1999 Symposium on Polymeric Photovoltaics, Wollongong, Australia
“Micropatterning Polymer Circuits”
- January 25-26 1999 Int’l Advisory Bd. Mtg., Millenium Solar Project, Wollongong, Australia
“Micropatterning Polymer Circuits”

February 4-7 1999	DARPA/Santa Fe Science & Tech. Inc. "Kickoff" Mtg., Santa Fe, NM
March 1-2 1999	Int'l Seminar o Tech. Of Inherently Conducting Polymers, Clearwater Beach, FL "Polyanilines and Polypyrrole: Selected Applications"
March 2-3 1999	DARPA Principal Investigator Mtg., San Diego, CA
March 21-25 1999	ACS Nat'l Mtg., Anaheim, CA "Are Properties of Polyaniline Controlled by Its Isomeric Composition?" (Award) "Isomers and Isomerization Process in Poly-Anilines"
April 7-9 1999	Materials Research Society Spring Mtg., San Francisco, CA "Electroluminescence in <i>s</i> -Conjugated Systems"
May 5-6 1999	Society of Plastics Engineers Conf. (ANTEC 99), New York, NY "Electroluminescence in <i>s</i> -Conjugated Polymers"
May 7-13 1999	Synthetic Metals Quantum Workshop, Seoul, Korea "Electroluminescence in <i>s</i> -Conjugated Polymers"
May 23-25 1999	ONR Polymer Program Review, Jacksonville FL "Isomerism in Polyaniline: Key to Attining Its Predicted Conductivity of Cu, Ag?"

i. Submitted Presentations

March 22-23 1999	American Physical Society Mtg., Atlanta, GA "Organometallic LEDs derived from <i>s</i> @ <i>s</i> * Polymer Systems" "Polyaniline as a Light-Emitting Species in LEDs"
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j. Honors/Awards/Prizes for contract grant employees

- 1999 ACS Award in Chemistry of Materials
- Honorary Doctor of Humane Letters, University of Massachusetts Lowell, MA
- Honorary Doctor of Science, Victoria University of Wellington, New Zealand
- Regional Editor, *Synthetic Metals*.
- International Advisory Board, *Intelligent Polymer Research Institute*.
- International Advisory Board, *Millenium Solar Project*.
- Editorial Board, *New Polymeric Materials*.
- International Editorial Advisory Board, *Synthesis & Reactivity in Inorganic and Metal-Organic Chemistry*.

k. Full-time graduate and post-doctoral associates supported under this R & T project

Graduate Students

J. Feng
P-C. Wang
W. Wang
Y. Zhou

Post-Doctoral Associate

Dr. I. Norris

Part II

Principal Investigator: Alan G. MacDiarmid

Current Telephone Number: 215-898-8307

Cognizant ONR Program Officer: Kenneth J. Wynne

Long Term Research Objective

Polyaniline is probably the most technologically important conducting polymer (“synthetic metal”) presently in commercial production. It has been reported (*Kohlman, et. al., Phys. Rev. Lett., 78(20), 1997, 3915*) that its conductivity ($\sim 10^2$ S/cm) is far below its predicted intrinsic conductivity of $\sim 10^6$ S/cm, approximately equal to that of Cu or Ag. Our objective is to determine factors responsible for the non-attainment of its predicted intrinsic conductivity, to experimentally attain such conductivity and to controllably produce the polymer in a form having any desired preselected conductivity up to its maximum experimental value.

S & T Objective

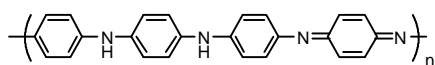
Determine the effect on the conductivity of polyaniline resulting from its isomeric composition, isomerism processes and phase separation within the polymer, method of processing and the nature of the substrate surface on which the polymer films are deposited.

Approach

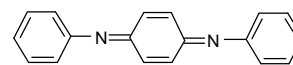
Our past and ongoing research supported primarily by this ONR Grant has determined for the first time that polyaniline consists of a very large number of different isomers which inhibit attainment of its high intrinsic conductivity (MacDiarmid et. al., *Synth. Met., 100, 1999, 131*) and that phase separation occurs as solutions of the polymer are evaporated. All of the above contribute to its smaller than expected conductivity. The conductivity of films has also been found to differ by $\sim 10^4$ depending on whether they are *in-situ* deposited on hydrophilic or hydrophobic substrates. The investigation has been facilitated in large part by synthesizing and studying mesomolecular anilines (oligomeric, short chain, low molecular weight forms of polyaniline).

S & T Completed

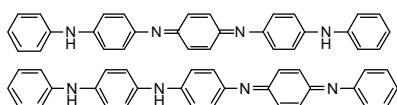
Polyaniline (Compound I)



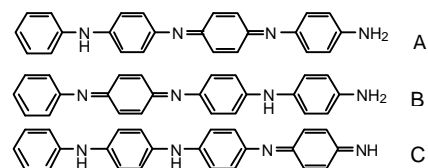
Phenyl/Phenyl End-Capped Dimer (Compound II)



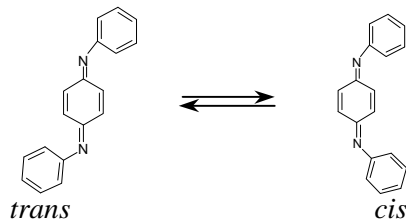
Phenyl/Phenyl End-Capped Tetramer (Compound III)



Phenyl/Amine End-Capped Tetramer (Compound IV)



- (i) Polyaniline and the dimer and the tetramers above have been synthesized and characterized.
- (ii) We have shown from ^1H and ^{13}C NMR studies that Compound II exists in two different isomeric forms and that the pure *trans* isomer converts to the *cis* isomer on dissolving in CDCl_3 at 25°C (activation energy ~ 20 kcal/mole)



- (iii) We have shown from ^1H and ^{13}C NMR studies and from vis/uv spectral studies at 25°C in d^6 -DMSO that Compound IV exists in positional isomeric forms (A) and (B) only, in rapid equilibrium. *Cis/trans* isomerism is also undoubtedly present.

It follows from the above data that *polyaniline (Compound I) also undoubtedly exists in an extremely large number of different isomeric forms, which would result in phase separation of the solid obtained from solution on evaporation of solvent. This would reduce inter-chain conductivity consistent with its lower than expected (intrinsic) conductivity. Indeed, we have identified two different isomeric forms of doped polyaniline. The unstable "blue" isomer converts to the stable "green" isomer in CHCl_3 solution during ~ 24 hours at room temperature.*

- (iv) We have shown from a series of SEM studies why a "memory effect" (Annual ONR Report, 1998) of polypyrrole for the hydrophilic substrate surface on which it is *in-situ* deposited persists even after film thickness studies show the original surface has been covered by the first-deposited polypyrrole. This is because the polypyrrole is deposited as spheres, leaving some of the original substrate surface exposed.
- (v) Continuing collaborative studies with Prof. Q. Zhang (Penn State Univ.) (Z-Y. Cheng et. al., *Proc. SPIE-The Int'l Soc. For Opt. Eng.*, May 1999) show that an *in-situ*-deposited polypyrrole electrode film on poly(vinylidene fluoride-trifluoroethylene) (PVDF-TrFE) copolymer results in a similar electrostrictive response to an electric field as a gold electrode but since it is more flexible than a gold electrode film it eliminates many problems associated with a gold electrode film.
- (vi) We have shown previously (MacDiarmid and Epstein, *Macromol. Chem. Macromol. Symp.*, **51,1**, 1991) that the method of processing polyaniline, mechanical orientation, degree of crystallinity, etc. can greatly affect its conductivity and mechanical properties. We have begun to process conducting polymers by a novel and little-known technique with the expectation of attaining enhanced conductivity and mechanical properties. During the past 10 years only four research groups worldwide have published on the electrospinning of ultra-thin polymer fibrils ($0.02 - 2 \mu\text{m}$) (R. Jaeger et. al., *Macromol. Symp.*, **127**, 1998, 141). Only one very brief preliminary reference has been made to the electrospinning of conducting polymer [polyaniline] fibrils. This non-mechanical

spinning process involves the spontaneous formation of a spray of solution of a polymer held at 20-30 Kvolt above a target plate at ground potential. Formation of the solvent species during the transport between the two electrodes results in the deposition of beautiful (dry) polymer fibrils on the target. As can be seen from the SEM (this report) of an 11 weight percent (camphorsulfonic acid-doped polyaniline/polyethylene oxide blend) our preliminary results have been highly successful. This is the first example of the application of electrospinning to a conducting polymer blend. We propose that the extremely rapid conversion of polymer solution to solid polymer may inhibit phase separation during solvent evaporation and give increased conductivity.

Impact/Navy Relevance

- The density of conducting polymers is approximately an order of magnitude less than that of copper metal. Considering the enormous weight of copper wiring in aircraft, a 10-fold reduction in weight of this vital component—a reduction which could be used for extra fuel, load etc. would be highly beneficial. Hence the importance of substantially increasing the conductivity of polyaniline.
- The problem of bulky repair/service manuals in cramped spaces, e.g. submarines, and their deterioration during use is an ever-present problem. A new phase of our work in collaboration with Dr. W. Doane, President, Kent Displays, Inc. (SBIR ONR Grant) utilizing our previous basic scientific findings during the past ~4 years supported completely by our ONR grant is underway. We will make use of our previous *in-situ* deposition of conducting polymers on hydrophilic vs. hydrophobic substrates as semitransparent electrodes in novel liquid crystal display devices. Particular effort is being directed at making “electronic books” consisting of only one polymer, flexible, transparent liquid crystal display page and a CD ROM in the cover containing the subject matter.
- The use of flexible conducting polymer films as a substitute for gold film electrodes in electroacoustic underwater communication devices is obviously of very considerable interest to the Navy. As shown in this report, conducting polymer films are equal to and even superior to gold film electrodes in certain respects.

Planned S & T Efforts

- *Isomerism in Poly-Anilines:* Conditions favoring the predominance of one given combination of positional and *cis/trans* isomers will be determined in order to produce polyaniline with higher conductivity.
- *Phase Separation in Poly-Anilines:* Conditions for avoiding phase separation during formation of the solid materials from solution will be studied by photoluminescence, electroluminescence, thermogravimetric analysis and differential scanning calorimetric techniques. A reduction in phase separation should result in higher conductivities. Extremely rapid “freezing” of the equilibrium present in solution so that it is retained in the solid state by the electrospinning method should be particularly useful.

- “*Electronic Books*”: Collaborative work with Dr. W. Doane (Kent Displays, Inc.) will be continued using previous information resulting from our ONR-supported studies on the effect of hydrophobicity/hydrophilicity of substrate surfaces on the conductivity of conducting polymers deposited on them.
- *Conducting Polymer Film Electrodes in Electrostrictive Systems*: Collaborative work will continue with Prof. Q. Zhang (Penn State Univ.) on optimizing conducting polymer film electrodes on electrostrictive materials in electroacoustic underwater communication devices.

Students Currently Working On The Project

Graduate Students

Pen-Cheng Wang

Wei Wang

Yao Zhou

Post-Doctoral Fellow

Dr. Ian Norris