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OFFICE OF NAVAL RESEARCH

End-of-the-Year-Report

PUBLICATIONS/PATENTS/PRESENTATION/HONORS/STUDENTS REPORT

for

Grant No.: N00014-91-J-1303

R&T Code: 4132019---05

Conducting and Magnetic Polymers

Robert H. Grubbs and Dennis A. Dougherty

**Division of Chemistry and Chemical Engineering, 164-30
California Institute of Technology
Pasadena, CA 91125**

June 1, 1991

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OFFICE OF NAVAL RESEARCH
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT

R&T Number: 4132019---05

Contract/Grant Number: N00014-91-J-1303

Contract/Grant Title: Conducting and Magnetic Polymers

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- a. Number of papers submitted to refereed journals, but not published: 2
- b. Number of papers published in refereed journals (list attached)*: 4
- c. Number of Books or chapters submitted, but not yet published: 1
- d. Number of books or chapters published (list attached)*: 4
- e. Number of printed technical reports & non-refereed papers (list attached)*: _____
- f. Number of patents filed: 0
- g. Number of patents granted (list attached)*: 1
- h. Number of invited presentations at workshops or professional society meetings: 24
- i. Number of presentations at workshops or professional society meetings: _____
- j. Honors/Awards/Prizes for contract/grant employees (list attached)*: 6
(This might include Scientific Society Awards/Offices,
Promotions, Faculty Awards/Offices)
- k. Total number of Graduate Students and Post-Doctoral associates supported by at least 25% during this period under this R&T project number:
Graduate Students: 6
Post-Doctoral Associates: 2
including the number of,
Female Graduate Students: 1
Female Post-Doctoral Associates: 0
the number of
Minority* Graduate Students: 0
Minority* Post-Doctoral Associates: 0
and, the number of
Asian Graduate Students: 0
Asian Post-Doctoral Associates: 0
- l. Other funding (list agency, grant title, amount received this year, total amount, and period of performance)*

* Use the letter and an appropriate title as a heading for your list, e.g.:

b. Published Papers in Refereed Journals, or, d. Books and Chapters published

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

PART I.

(attached lists from summary page)

b. Papers published in refereed journals

RHG

"Electronic Properties of Junctions Between Silicon and Organic Conducting Polymers." M.J. Sailor, F.L. Klavetter, R.H. Grubbs, and N.S. Lewis, *Nature* 1990, 346, 155-157.

"Soluble, Chiral Polyacetylenes: Syntheses and Investigation of Their Solution Conformation." J.S. Moore, C.B. Gorman, R.H. Grubbs, *J. Am. Chem. Soc.* 1991, 113, 1704-1712.

"Substituted Polyacetylenes Through the Ring-Opening Metathesis Polymerization (ROMP) of Substituted Cyclooctatetraenes: A Route into Soluble Polyacetylene." C.B. Gorman, E.J. Ginsburg, M.J. Sailor, J.S. Moore, T.H. Jozefiak, N.S. Lewis, R.H. Grubbs, S.R. Marder, and J.W. Perry, *Synthetic Metals* 1991, 41-43, 1033-1038.

DAD

Novel Magnetic Properties of a Doped Organic Polymer. A Possible Prototype for a Polaronic Ferromagnet. D.A. Kaisaki, W. Chang, D.A. Dougherty, *J. Am. Chem. Soc.*, 1991, 113, 2764-2766.

d. Books or chapters published.

RHG

"Electrochemical Characterization of Soluble Polyacetylenes Derived from the Ring-Opening Metathesis Polymerization (ROMP) of Substituted Cyclooctatetraenes." R.H. Grubbs, N.S. Lewis, E.J. Ginsburg, C.B. Gorman, M.J. Sailor, and T.H. Jozefiak, *Soc. of Plastic Engineers*, submitted.

"Conjugated Polymers: The Interplay Between Synthesis, Structure, and Properties." C.B. Gorman and R.H. Grubbs, in *Conjugated Polymers: The Novel Science and Technology of Conducting and Nonlinear Optically Active Materials*, J.L. Brédas and R. Silbey, Eds., Kluwer Academic Publishers, in press (Oct, 1991).

"The Application of Ring-Opening Metathesis Polymerization to the Synthesis of Substitute Polyacetylenes." E.J. Ginsburg, C.B. Gorman, M.J. Sailor, N.S. Lewis, R.H. Grubbs, in *Olefin Metathesis and Polymerization Catalysts*, Y. Imamoglu, Ed., Kluwer Academic Publishers: the Netherlands, 537-541 (1990).

DAD

Approaches to Magnetic Organic Materials. D.A. Dougherty, R.H. Grubbs, D.A. Kaisaki, W. Chang, S.J. Jacobs, D.A. Shultz, K.K. Anderson, R.Jain, P.T. Ho, E.G. Stewart, in *Magnetic Molecular Materials*, D. Gatteschi et al. Eds., Kluwer Academic Publishers: The Netherlands, pp. 105-120 (1991).

g. Patents granted.

RHG/DAD

U.S. Patent Number: 5,026,783; issued June 25, 1991. High Energy Polymers Formed by Ring Opening Metathesis Polymerization.

j. Honors, Awards, Prizes

RHG

Bayer-Mobay Lecturer in Chemistry, Cornell University
The J. Clarence Karcher Lecture Series, The University of Oklahoma
The 3M Canada Lecturer in Materials Science, The University of British Columbia
Frontiers in Chemical Research, The Texas A & M University

DAD

ICI Pharmaceuticals Group 1991 Awards for Excellence in Chemistry

l. Other funding.

RHG

AFR, AFOSR-88-0094: Polymerization of Cyclohexadiene Derivatives: Avenues to Poly(paraphenylene) and Novel Materials.; \$100,300 (TDC); 9/1/91-8/31/92

CIT (Consortium): Synthesis of ROMP Catalysts \$48,000 (TDC) 7/1/91-6/30/92.

NSF, CHE-8922072: Mechanisms of Transition Metal-Catalyzed Reactions in Hydrocarbons; \$ 193,940 (TDC); 5/1/91-4/30/92.

ONR, N00014-88-K-0208: Conducting Polymers; \$132,912 (TDC); 1/1/91 - 12/31/91.

Dow Chemical Co.: Block Copolymer; \$150,000; 8/1/91 - 7/31/94.

DuPont : Functionalized Methathesis; \$150,000; 8/1/91 - 7/31/94.

DAD

NSF, CHE87-01008: Synthesis and Spectroscopy of New Biradicals and Related Structures; \$130,000 (TDIC); 4/1/91-3/31/92.

ONR, N00014-91-J-1344: Molecular Recognition and Biomimetic Catalysis Using Receptors Based on Bridged Anthracenes; \$107,000 (TDIC); 1/1/91-9/30/91.

NIH: Biomimetic Catalysis Through Molecular Recognition; \$142,315 (TDIC); 15% effort; 4/1/91-3/31/92.

Beckman Institute at Caltech: An Approach to Organic Spin Glasses; 11/1/90-10/31/91; \$42,500 (TDC).

PART II.a. Principle Investigators:

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Dennis A. Dougherty

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c. Cognizant ONR Scientific Officer:

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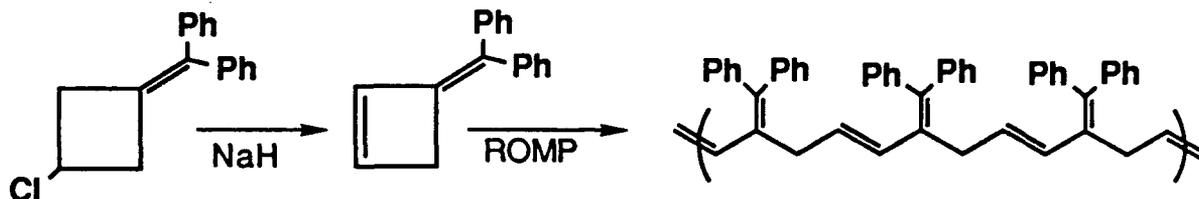
d. Brief description of project:

Unsaturated polymeric materials with interesting electronic, optical and magnetic properties are being prepared. The major route to these materials is through the Ring Opening Polymerization (ROMP) of highly unsaturated monomers. The ROMP of substituted cyclooctatetraene and methylenecyclobutenes has been the major route to such materials. Materials with tailored electronic and physical properties have resulted from these studies. A recent development has been the synthesis of a precursor polymer for a potential organic ferromagnetic.

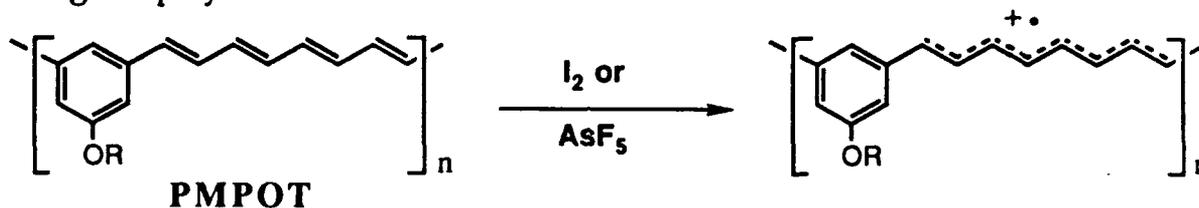
e. Significant results:

Progress has been made in a number of different areas of synthesis of conjugated polymers. Particular emphasis has been placed on determining the conformation of polyacetylenes in solution and the factors that control solubility and conjugation length. The most subtle probe used was a chiral side group that produces a chiral conjugated backbone. The cis to trans isomerization of soluble polyacetylenes has been investigated in detail and the activation energies for the process has been accurately determined. To force a cis double bond in the polymer, benzocyclooctatetraene has been prepared and polymerized. This material which is presently under study will simplify the analysis of cis polyacetylenes. Studies of the electrochemistry on the soluble polymers is well underway and the apparent band gap is being determined as a function of the steric and electronic effects of the substituents. Difunctional cyclooctatetraenes have been prepared and are being polymerized to determine the effect of substituent density on the properties of the resulting polyacetylenes. As part of the program in the synthesis of organic ferromagnetic materials, methylene cyclobutenes have been prepared and polymerized. Of particular importance to this and other polymerization

procedures, the monomer can be generated in the presence of the active catalyst. This observation eliminates the preparation and purification of reactive monomers.

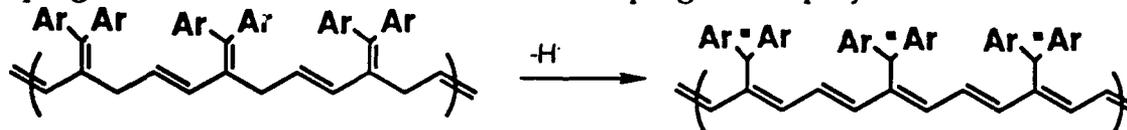


Also in connection with the pursuit of organic ferromagnetic materials, the first prototype of a "polaronic ferromagnet" has been prepared, and initial findings have appeared in print. The structure is based on poly(metaphenylene)octatetraene (PMPOT), which, on doping, produces room-temperature stable, paramagnetic centers that display ferromagnetic coupling along the polymer backbone.



f. Brief Summary:

During the next year the projects that have been initiated as described above on cis constrained polyacetylenes will be completed and a family of polyacetylenes that contain electron donating groups will be examined to determine electronic effects on band gaps in these materials. The studies of the methylene cyclobutene polymers will focus on the removal of a hydrogen atom from the backbone to introduce spin along the polymer chain. Functionalized aromatics are being introduced that will result in easier oxidation of the chain and will stabilize the resulting radicals. New derivatives of PMPOT are being prepared, with the aim of replacing the tetraene unit with structures that produce even more stable radicals on doping. This will allow electrochemical doping of the polymer.



g. Graduate Students:

Christopher Gorman
Michael Rock
Brenda Fiala