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22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL
Kenneth J. Wynne	(805) 893-3184	

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

R&T Number: 4132012
Contract/Grant Number: N00014-91-J-1235
Contract/Grant Title: Program for Research in Conducting Polymers
Principal Investigators:

Alan J. Heeger, Dept. of Physics and Materials Dept., Univ. of Calif., Santa Barbara
Paul Smith, Materials Dept., University of California, Santa Barbara
Fred Wudl, Dept. of Physics and Dept. of Chemistry, Univ. of Calif., Santa Barbara
Mailing Address:
Institute for Polymers and Organic Solids
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University of California, Santa Barbara
Santa Barbara, CA 93106-5090
Phone Number: (805) 893-3184 FAX Number: (805) 893-4755

a. Number of papers submitted to refereed journals, but not published: 8
b. Number of papers published in refereed journals (list attached): 11
c. Number of books or chapters submitted, but not yet published: 0
d. Number of books or chapters published (list attached): 0
e. Number of printed technical reports and non-refereed papers (list attached): 7
f. Number of patents filed: 1
g. Number of patents granted (list attached): 0
h. Number of invited presentations at workshops or professional society meetings: 24
i. Number of presentations at workshops or professional society meetings: 24
j. Honors, Awards, Prizes for contract/grant employees: 0
(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 the period under this R&T project number:

Graduate Students: 4
Post-Doctoral Associates: 5

including the number of,
Female graduate students: 0
Female Post-doctoral Associates: 0

the number of
Minority Graduate Students: 0
Minority Post-Doctoral Associates: 0

and, the number of
Asian Graduate Students: 2
Asian Post-Doctoral Associates: 3

l. Other funding - list agency, grant title, amount received this year, total amount, and period of performance (see attached list)

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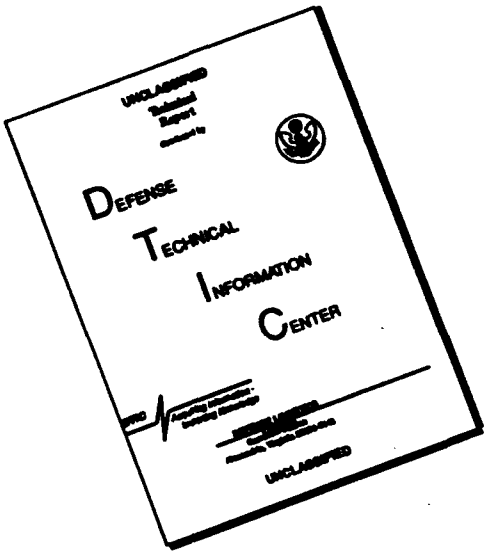

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Final Technical Report

N00014-83-K-0450

Program for Research on Conducting Polymers

Institute for Polymers and Organic Solids
University of California, Santa Barbara
Santa Barbara, CA 93106

Principal Investigators:

Professor Alan J. Heeger
Department of Physics and Materials Department (joint)

Professor Paul Smith
Materials Department and Department of Chemical Engineering (joint)

Professor Fred Wudl
Department of Physics and Department of Chemistry (joint)

I. Summary of Research Results:

This broad based interdisciplinary program, involved synthesis and characterization of new conducting polymers, processing of these conducting polymers into highly oriented fibers and films, and measurement of the electrical and optical properties of the materials.

Substantial progress was made during the course of N00014-83-K-0450. This progress is documented in the forty-seven (47) publications which resulted from the research and twelve (12) in the ONR Technical Reports which were prepared for distribution. At the beginning of those period of ONR sponsored research, conducting polymers were available in mg quantities, they were unstable and they were intractable. Today, large quantities are available (in some cases in commercial scale), and there are specific systems which are both stable and processible. Moreover, it is now clear (largely as a result of the effort at UCSB) that the desired combination of properties is available:

Electrical and Optical Properties of Metals & Semiconductors

AND

Mechanical Properties and Processing Advantages of Polymers.

II. Technical Reports Submitted from N00014-83-K-0450

The technical reports are listed below; copies are attached for detailed information.

End of Year Report - May 1, 1983-April 30, 1984

Semi-Annual Report - November 1, 1985

Semi-Annual Report - November 1, 1986

End of Year Report - October 1, 1987

End of Year Report - October 1, 1987-September 30, 1988

End of Year Report - July 15, 1988

End of Year Report - June 1, 1989

End of Year Report - June 1, 1989-May 31, 1990

End of Year Report - May 1990-May 1991

III. Publications

The following publications credited ONR N00014-83-K-0450 for support:

1. Charge Storage in Doped Poly(thiophene) (Polymer Journal)
2. Fundamental Electrochemical Studies of Polyacetylene
3. First-Order Transition to a Metallic State in Polyacetylene: A Strong Coupling Polaronic Metal (Phys. Rev. Lett.)
4. Semiconducting Polymers: Fast Response Non-Linear Optical Materials (Synthetic Metals).
5. X-Ray Scattering from Polythiophene: Crystallinity and Crystallographic Structure (Macromolecules).
6. Charge Storage in Conducting Polymers: Solitons, Polarons and Bipolarons (Polymer Journal).
7. Alkali Vapor Phase Doping of Polyacetylene (Solid State Commun.).)
8. Infrared Activity of Photoexcitations in Polythiophene (Solid State Commun.).)
9. Nonlinear Excitations and Nonlinear Phenomena in Conductive Polymers (A. C. S. Symposium Series 1987)
10. Chromism of Soluble Polythienylenes (Polymer Science Part B: Polymer Phys. 25).
11. Electrochromic Switching of the Optical Properties of Polyisothianaphthene (J. Electrochem. Soc.)
12. Polarons and Bipolarons on a Conducting Polymer In Solution (Macrolmol..)
13. Semiconducting Polymers: Fast Response Non-Linear Optical Materials (Synthetic Metals).
14. Soluble Conducting Polymers: The Poly(3-Alkylthienylenes).
15. X-Ray Scattering from Sodium-Doped Polyacetylene: Incommensurate-Commensurate and Order-Disorder Transformations (Phys. Rev. Lett.)
16. X-Ray Scattering from Oriented Durham Polyacetylene: Structural Relaxation and the Nature of the Interchain Phase Order of the Bond Alternation Pattern (Macromol.).
17. Polarons and Bipolarons on a Conducting Polymer in Solution (Macromol.)
18. Optical Properties of Conducting Polymers (Chem. Rev. 88).
19. In-Situ Electron Spin Resonance Experiments on Polyacetylene During Electrochemical Doping (Synthetic Metals).
20. Intrinsic Conductivity of Conducting Polymers (Synthetic Metals).
21. Photoinduced Absorption and Resonant Raman Scattering of Polythiophene (Synthetic Metals).

22. Direct Evidence of the Importance of Electron-Phonon Coupling in La2CuO4: Photoinduced IR Active Vibrational Modes (Phys. Rev. B).
23. Infrared Photoexcitation and Doping Studies of Poly(3-methylthienylene) (Phys. Rev. B).
24. Localized Phonons Associated with Solitons in Polyacetylene: Coupling to the Non-Uniform Mode (Phys. Rev. B).
25. Bipolarons in Poly(3-methylthiophene): Spectroscopic, Magnetic and Electrochemical Measurements (Phys. Rev. B).
26. Electrically Conducting Polymers (Encyclopedia of Materials Science and Engineering).
27. Photoinduced Self-Localized Structural Distortions in $YBA_2Cu_3O_{7-\delta}$ Phys. Rev. B
28. Photoinduced Localized Charged Excitations in Polyaniline (Synthetic Metals).
29. Transient Photoconductivity in Oriented Trans-Polyacetylene Prepared by the Naarmann-Theophilou Method (Phys. Rev. B).
30. Solitons in Conducting Polymers (Reviews of Modern Physics 60).
31. Electrically Conductive Polyacetylene Fibers Through In Situ Polymerization in Carrier Gels (Polymer Commun.).
32. Long Lifetime Charged Photoexcitations in Polydiacetylenes: Strongly Localized Bipolarons (Solid State Physics).
33. X-Ray Scattering from Crystalline Polyaniline (Polymer Commun.).
34. Photogenerated Carriers in La_2CuO_4, $YBa_2Cu_3O_{7-\delta}$ and $Tl_2Ba_2Ca_{(1-x)}Gd_xCu_2O_8$: Polarizability-Induced Pairing of Polarons (Synthetic Metals).
35. Spectroscopic Studies of Polyaniline in Solution and in Spin-Cast Films (Synthetic Metals).
36. Electroabsorption of Polyacetylene (Phys. Rev. B).
37. Infrared Active Vibrational Modes of Heavily Doped "Metallic" Polyacetylene (Phys. Rev. B).
38. Photoinduced Self-Localized Polarons in $Tl_2Ba_2Ca_{(1-x)}Gd_xCu_2O_8$: A Proposal for Van Der Waals Pairing (Solid State Commun.).
38. Electroabsorption of Polyacetylene (Phys. Rev. B).
40. Infrared Active Vibrational Modes of Heavily Doped "Metallic" Polyacetylene (Phys. Rev. B).
41. Transient Photoinduced Conductivity in Semiconducting Single Crystals of $YBa_2Cu_3O_{6.3}$: Search for Photoinduced Metallic State and for Photoinduced Superconductivity (Solid State Commun.).
42. Photoexcited Polarons in High Temperature Superconducting Oxides: Structural Distortion and Low Frequency Polarizability (Reviews of Solid Sate Science).
43. High Performance Fibers of Conducting Polymers (Mol. Crystals and Liquid Crystals).
44. Pyroelectric and Piezoelectric Effects in Single Crystals of $YBa_2Cu_3O_{7-\delta}$. (Solid State Commun.).
45. Substitution Effects on Bipolarons in Alkoxy Derivatives of Poly(1-4-phenylene-vinylene) (Phys. Rev. B).
46. Poly(ketene) (PKT) (Journal of the American Chemical Society)
47. Synthesis and Characterization of Two Regiochemically Defined Poly(dialkylbithiophenes): A Comparative Study (Macrol.).

Part I

b. Papers published in Refereed Journals

d. Books (and sections thereof) Published

e. Printed Technical Reports Published and Non-Refereed Papers

g. Patents Granted

j. Honors/Awards/ Prizes

l. Other funding

b. Papers published in refereed journals:

Poly(ketene), K. C. Khemani and F. Wudl, Amer. J. Chem. Soc., 111, 9124 (1989).

Photogenerated Carriers in La_2CuO_4, $YBa_2Cu_3O_{7-\delta}$ and $Tl_2Ba_2Ca_{(1-x)}Gd_xCu_2O_8$: Polarizability-Induced Pairing of Polarons, C. M. Foster, A. J. Heeger, Y. H. Kim and G. Stucky, Synth. Metals 33, 171 (1989).

Spectroscopic Studies of Polyaniline in Solution and in Spin-Cast Films, Y. Cao, P. Smith and A. J. Heeger, Synth. Metals 32, 263 (1989).

Electroabsorption of Polyacetylene, S. D. Phillips, R. Worland, G. Yu, T. Hagler, R. Freedman, Y. Cao, V. Yoon, J. Chiang, W. C. Walker and A. J. Heeger, Phys. Rev. B 40 (14), 9751 (1989).

Transient Photoinduced Conductivity in Semiconducting Single Crystals of $YBa_2Cu_3O_{6.3}$: Search for Photoinduced Metallic State and for Photoinduced Superconductivity, G. Yu, A. J. Heeger, G. Stucky, N. Herron and E. M. McCarron, Solid State Commun. 72 4, 345 (1989).

Synthesis and Characterization of Two Regiochemically Defined Poly(dialkylbithiophenes): A Comparative Study, R. M. Souto Maior, K. Hinkelmann, H. Eckert and F. Wudl, Macromol. 23 1268 (1990).

Photoexcited Polarons in High Temperature Superconducting Oxides: Structural Distortion and Low Frequency Polarizability, C. M. Foster, Structural and Low Frequency Polarizability, C. M. Foster, A. J. Heeger, Y. H. Kim and G. Stucky and N. Herron, Reviews of Solid State Science 4 (2&3), 601 (1990).

High Performance Fibers of Conducting Polymers, A. Andreatta, S. Tokito, P. Smith and A. J. Heeger, Mol. Cryst. Liq. Cryst. 189, 169 (1990).

Pyroelectric & Piezoelectric Effects in Single Crystals of $YBa_2Cu_3O_{7-\delta}$, D. Mihailovic and A. J. Heeger, Solid State Commun. 75 (4), 319 (1990).

Mechanical and Electrical Properties of Poly(2,5-Thienylene Vinylene) Fibers, Shizuo Tokito, Paul Smith and Alan J. Heeger, Synth. Metals 36, 183 (1990).

Substitution Effects on Bipolarons in Alkoxy Derivates of Poly(1-4-phenylene-vinylene), K. F. Voss, C. M. Foster, L. Smilowitz, D. Mihailovic, S. Askari, G. Srdanov, Z. Ni, S. Shi, A. J. Heeger and F. Wudl, Phys. Rev. B 43 (6) (1991).

e. Printed technical reports and non-refereed papers:

"Conducting Polymers: The Route from Fundamental Science to Technology," Alan J. Heeger, Science and Applications of Conducting Polymers, edited by W. R. Salaneck, D. T. Clark and E. J. Samuelsen (Proceedings of the Sixth Europhysics Industrial Workshop, Lofthus, Norway, May 1990).

"Polyaniline Processed from Sulfuric Acid and in Solution in Sulfuric Acid: Electrical, Optical, and Magnetic Properties, Y. Cao, P. Smith and A. J. Heeger, Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics, and Molecular Electronics, edited by J. L. Brédas and R. R. Chance (NATO ASI Series).

"Synthesis and Characterization of a Water Soluble Polyparaphenylene Vinylene Derivative", S. Shi and F. Wudl, Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics and Molecular Electronics, edited by J. L. Brédas and R. R. Chance (NATO ASI Series).

Recent Progress in Conducting Polymers: Opportunities for Science and Opportunities for Technology, International Conference on Science and Technology of Synthetic Metals (ICSM '90), September 1990, Tübingen, Germany.

Mechanical and Electrical Properties of Highly Oriented Polyacetylene Films, International Conference on Science and Technology of Synthetic Metals (ICSM '90), September 1990, Tübingen, Germany.

The Cation Radical Salts of the Oxygen-Substituted Donor, BEDO-TTF, H. Yamochi, T. Nakamura and G. Saito, Internationa Confernce on Science and Technology of Synthetic Metals (ICSM '90), September 1990, Tübingen, Germany.

Polymers and an Unusual Molecular Crystal with Nonlinear Optical Properties, F. Wudl, P. M. Allemand, G. Srdanov, Z. Ni and D. McBranch, ACS Symposium Series No. 455, Materials for Nonlinear Optics: Chemical Perspectives, edited by Seth R. Marder, John E. Sohn and Galen D. Stucky.

CURRENT AND PENDING SUPPORT

Principal Investigator	Source of Support	Project Title	Award Amount	Period Covered by Award	% Effort Committed	Location Research	Co-PI
Current Support	AFOSR	"Oriented Electro/Optical Polymers Through In-Situ Chemistry During Gel Processing: A Research Opportunity"	$115,000[a]	9/15/90-9/14/91	10	UCSB	P. Smith F. Wudl
A.J. Heeger							
	AFOSR	Mesoepitaxy: A "Universal" Route to Oriented Materials"	$ 96,389[b]	6/15/90 6/14/91	5	UCSB	P. Smith
	NSF	"Conducting Polymers as Macromolecular Systems: Comprehensive Studies in Solution, In the Melt, and in the Solid State"	$ 78,000	5/1/91 4/30/92	5	UCSB	
	NSF-MRG	"Oriented Conducting Polymers: Solution Processing and Characterization" Renewal pending: $650,000/year over 7 P.I.s	$ 90,000[c]	3/1/90-2/28/91	10	UCSB	P. Pincus P. Smith F.Wudl D. Pearson
	Showa Denko	"Cooperative Program in Polymers and Organic Solids"	$ 50,000[d]	10/1/89-9/30/90	5	UCSB	F. Wudl
	EPRI	"Toward Improvements in the Current Carrying Capability of Conducting Polymers"	$112,384	1/1/91-5/15/92	5	UCSB	
	NSF	"Program of Cooperative Research on Conjugated Polymers With Prof. J.-L. Brédas (Chemistry, University of Mons, Belgium)"	$ 1,500[e]	11/1/90-10/31/91	1	UCSB	Wudl
	NSF	"Acquisition of a Sub-Picosecond Electro-Optic Sampling Facility"	$304,240	1 Year funding	5	UCSB	
	NSF	"Time-Resolved Optical Wavequide Experiments with Conjugated Polymers: Direct Measurement of the Magnitude and Sign of $\chi^{(3)}(\omega_1; \omega_1, \omega_2, -\omega_2)$"	$ 68,000	11/1/90-10/31/91	5	UCSB	

1. Other Funding

CURRENT AND PENDING SUPPORT

Principal Investigator	Source of Support	Project Title	Award Amount	Period Covered by Award	% Effort Committed	Location Research	Co-PI
Current Support (cont.)							
A.J. Heeger							
	NSF (SGER)	"Photogenerated Polarons in High-T_c Superconducting Oxides: Infrared Excitation Spectroscopy and Transient Photoinduced Conductivity in Semiconducting $YBa_2Cu_3O_{7-\partial}$	$ 49,000	2/15/91-1/31/92	1	UCSB	
	ONR	"Program for Research in Conducting Polymers"	$ 90,000[f]	10/1/90-9/30/91	10	UCSB	F. Wudl P. Smith
	INCOR	"Search for Photoinduced Metallic State and for Photoinduced Superconductivity: Transient Photoinduced Conductivity in Semiconducting Single Crystals of $YBA_2Cu_3O_{6.3}$"	$ 16,000	8/1/90-6/30/91	1	UCSB	
Pending Support							
	NSF	"Transport and Optical/IR Properties of Oriented Conducting Polymers Exhibiting High Conductivity and Excellent Mechanical Properties"	$91,428	First Year Funding Funding requested for three years	5	UCSB	
	NSF	"High Performance Oriented Conducting Polymers: High Conductivity in Combination with Excellent Mechanical Properties	$ 97,841	First Year Funding Funding requested for three years	5	UCSB	

a. Total award for this period is $345,000, shared by Heeger, Wudl and Smith. This is the final year.
b. Total award for this period is $175,002, shared by Heeger and Smith. This project will be funded for two more years beyond the current period at the same level.
c. The total NSF MRG award is for $441,000 for this third and final year. Renewal pending for $650,000/year, shared with F. Wudl, P. Smith, P. Pincus, D. Pearson, G. Fredrickson, and H.-W. Schmidt
d. The total award for this period is $102,305, shared by Wudl and Heeger.
e. Total award is $9,250 for three years, shared by Wudl and Heeger.
f. Total award for this period is $265,000, shared by Heeger, Wudl and Smith. This project will be funded for two more years beyond the current period, at the same level.

CURRENT AND PENDING SUPPORT

Principal Investigator	Source of Support	Project Title	Award Amount	Period Covered by Award	% of Effort Committed	Location Research	Co-PI
Current Support Paul Smith	AFOSR	"Oriented Electro/Optical Polymers Through In-Situ Chemistry During Gel Processing: A Research Opportunity"	$115,000[a]	09/15/90-09/14/91	10	UCSB	A.J. Heeger F. Wudl
	NSF-MRG	"Oriented Conducting Polymers: Solution Processing and Characterization"	$ 90,000[b]	03/15/90-03/14/91 FINAL YEAR	10	UCSB	P. Pincus D. Pearson F. Wudl A.J. Heeger
	AFOSR	Mesoepitaxy: A "Universal" Route to Oriented Materials"	$ 96,389[c]	6/15/90 6/14/91	5	UCSB	A.J. Heeger
	ONR	"Program for Research on Conductive Polymers"	$ 70,000[d]	10/01/89-09/30/90	5	UCSB	F. Wudl A.J. Heeger
	DSM	Research Gift	$ 50,000	1988-present			
Pending Support	*None*						

a. Total award for this period is $345,000, shared by Heeger, Wudl and Smith. This is the final year.
b. The total NSF MRG award is for $441,000, shared by Smith, Heeger, Pearson, Pincus & Wudl; this is the final year.
c. Total award for this period is $175,002, shared by Heeger and Smith. This project will be funded for two more years beyond the current period at the same level.
d. The total award for this period is $265,000, shared by Smith, Wudl and Heeger; final year: applying for renewal.

CURRENT AND PENDING SUPPORT

Principal Investigator	Source of Support	Project Title	Award Amount	Period Covered by Award	% of Effort Committed to Project	Location Research	Co-PI
Current Support Fred Wudl	NSF	"Oriented Conducting Polymers: Solution Processing and Characterization"	$ 35,000[a]	3/15/90-3/14/91 Renewal pending	3	UCSB	P. Pincus P. Smith A.J. Heeger D. Pearson
	Showa Denko	"Cooperative Program in Polymers and Organic Solids"	$ 52,300[b]	10/1/90-9/30/91	5	UCSB	A.J. Heeger
	AFOSR	"Oriented/Optical Polymers Through In Situ Chemistry During Gel Processing..."	$115,000[c]	9/15/90-9/14/91	2	UCSB	P. Smith A. J. Heeger
	NSF	"Synthesis of New Organic Materials: Ferromagnetic Organic Metals, Cyanovinyl Acceptors and Oxydonors"	$96,000[d]	4/1/91 3/31/92	15	UCSB	
	NSF	"High Strength Materials, Polymers for Nonlinear Optics and New Electrically Conducting Polymers"	$ 87,200	8/1/90-7/31/91	15	UCSB	
	NSF	"Molecular Atoms (Heterospherophanes)"	$157,000	9/1/89 8/31/91	10	UCSB	P. Pincus
	NSF	"Program of Cooperative Research on Conjugated Polymers With Prof. J.-L. Brédas (Chemistry, University of Mons, Belgium)"	$ 1,500[e]	11/1/90-10/31/91	1	UCSB	Heeger
	ONR	"Program for Research in Conducting Polymers"	$90,000[f]	10/1/90-9/30/91	5	UCSB	A. J. Heeger P. Smith

1. Other Funding

CURRENT AND PENDING SUPPORT (CONTINUED)

Principal Investigator	Source of Support	Project Title	Award Amount	Period Covered by Award	% of Effort Committed to Project	Location Research	Co-PI
Fred Wudl Page 2							
Proposals Pending	DOE	"High Temperature Organic Superconductors"	$ 90,000	First Year Funding Funding requested for Three years	5	UCSB	
	DOE	"Polyketenes and Polymers from Polyketal and Polyacetal Precursors"	$ 74,203	First Year Funding Funding requested for Three years	5	UCSB	
	NSF	SGER: "Functionalized Fullerenes: Unprecedented Materials Based on The New Carbon Allotrope"	$ 50,000	One Year Funding	1	UCSB	

a. The Total MRG renewal pending is $650,000, shared by Wudl, Heeger, Smith, Pincus, Pearson, Fredrickson, and Schmidt. Renewal is for three years..
b. Total award for this period is $104,658, shared by Wudl and Heeger.
c. Total award for this period is 345,000, shared by Wudl, Heeger and Smith. This is the final year.
d. This project will be funded for one year beyond the current period, at the same level.
e. The total award is $9250, for three years, shared by Wudl and Heeger.
f. Total award for this period is $265,000, shared by Wudl, Heeger and Smith. This project will be funded for two years beyond the current period, at the same level.

5/91

1. Other Funding

Part II

a. Principal Investigators

Alan J. Heeger
Paul Smith
Fred Wudl

b. Current Telephone Numbers

Alan J. Heeger	(805) 893-3184;	FAX: (805) 961-4755
Paul Smith	(805) 893-8104;	FAX: (805) 961-4755
Fred Wudl	(805) 893-3755;	FAX: (805) 961-4755

c. Dr. Kenneth J. Wynne (ONR-Chemistry)

d. Brief (100-200 words) description of project

This is an interdisciplinary project focused on the fundamental chemistry, physics and materials science of conducting polymers in the context of novel electronic phenomena associated with this emerging class of materials. The research draws upon and utilizes a broad base: synthesis and characterization of new conducting polymers, processing directed toward the achievement of chain oriented and chain extended materials with a goal of achieving the intrinsic electronic and optical properties, and physical measurements directed at characterizing these electronic and optical properties and of identifying the basic physical mechanisms involved in these phenomena.

e. Significant Results During Past Year

We reported visible light emission from Schottky diodes made from semiconducting polymers. Our results demonstrated that light emitting diodes can be fabricated by casting the polymer film from solution with no subsequent processing or heat treatment required. Electrical characterization reveals diode behavior with rectification ratios of 100,000. Electroluminescence quantum efficiencies (photons out per electrons in) of 1% have been achieved. The discovery of conducting polymer LEDs expands the possible applications for conducting polymers into the area of active light sources. Controlling the energy gap of the polymer, either through the judicious choice of the conjugated backbone structure or through side-chain functionalization, should make possible a variety of colors. Moreover, because of the processing advantages of of semiconductors cast from solution, large active areas can be envisioned.

f. Brief (100-200 words) summary of plans for next years work

Our recent success with light emitting diodes fabricated from semiconducting polymers has opened an entirely new direction for our research --- with many new questions. Specific areas of importance for next year's research include optimization of luminescence efficiency (how to minimize non-radiative recombination), the achievement of stable conjugated polymers which emit blue light, and the achievement of highly oriented thin films which emit polarized luminescence (the latter can then be used to fabricate LEDs emitting *polarized* light).
In the area of electrical properties, we have made significant progress in improving the quality of the materials (through orientation by means of polymer processing). To proceed to take advantage of this important progress, we initiated the re-construction of our transport laboratory to extend our measurement capabilities. The experimental capabilities within our electrical transport laboratory now include the following:

(i) Electrical conductivity as a function of temperature from 1K to 300°C. Measurements above room temperature are intended primarily for evaluation of thermal stability.
(ii) High pressure capability (up to 20kbar).
(iii) Magneto-resistance (as a function of temperature and pressure) in magnetic fields up to 60 kgauss.
(iv) Hall effect (vs temperature and vs pressure)
(v) Thermopower (vs temperature) as a function of magnetic field and as a function of pressure
(vi) AC complex conductivity over the extended frequency range from dc to 1 GHz.

The purpose of the focus on the addition of the high pressure capability is to increase the interchain electronic transfer interaction. As a result of our work in the past few years, we know that interchain delocalization to form anisotropic three-dimensional metals is of major importance. "Three-dimensionality" is essential for the achievement of high conductivities (for otherwise the mean free paths are limited by the tendency of the electronic states in quasi-one-dimensional systems to be localized by disorder).

g. List of names of graduate students and post-doctorals currently working on project

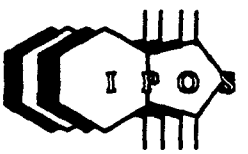
Graduate students: D. Braun, Kwanghee Lee

Postdoctoral Researchers: D. Moses, K. J. Ihn, Y. Cao, C. Zhang

Part III. Research Highlight

Viewgraphs and explanatory text on following pages:

Part III. Research Highlight

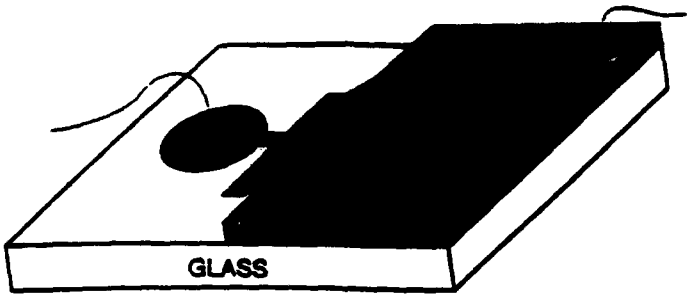


Visible Light Emission from Semiconducting Polymer Diodes

- We have reported visible light emission from Schottky diodes made from semiconducting polymers.
- Our results demonstrated that light emitting diodes can be fabricated by casting the polymer film from solution with no subsequent processing or heat treatment required.
- Electrical characterization reveals diode behavior with rectification ratios of 100,000.
- Electroluminescence quantum efficiencies (photons out per electrons in) of 1% have been achieved; the light emitted from these devices is bright and easily seen in a fully lighted room.
- Turn-on below 5 Volts; compatible with digital electronics.

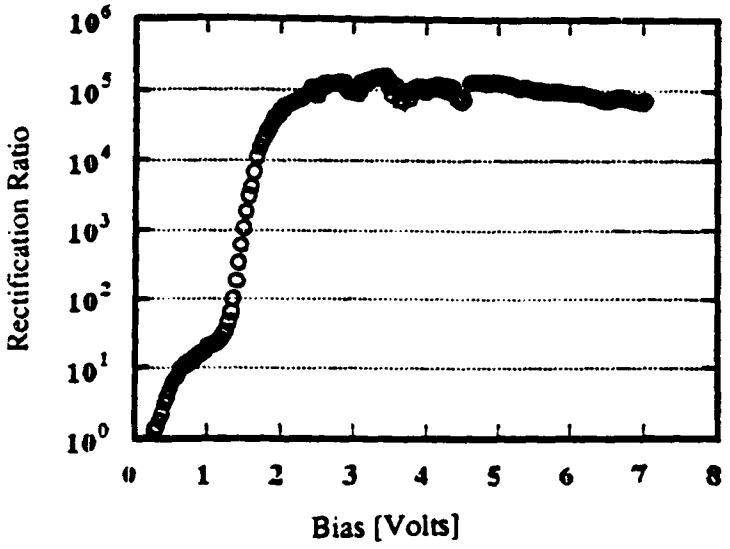
Principal Investigators:
Prof. Alan J. Heeger
Prof. Paul Smith
Prof. Fred Wudl

Structure of Polymer LED Device

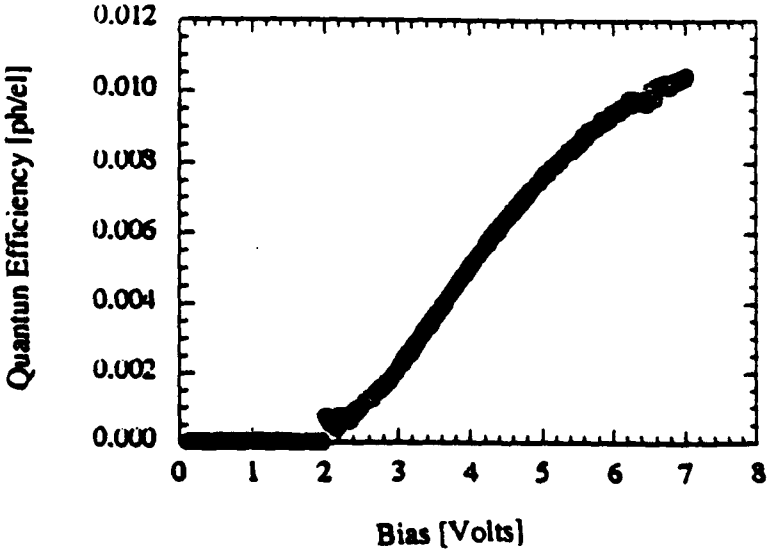


Light Out

Polymer LED Rectification Ratio vs Bias Voltage



Polymer LED Quantum Efficiency vs Bias Voltage



Part III. Research Highlight:

- The discovery of conducting polymer LEDs expands the possible applications for conducting polymers into the area of active light sources.

- Controlling the energy gap of the polymer, either through the judicious choice of the conjugated backbone structure or through side-chain functionalization, should make possible a variety of colors.

- Because of the processing advantages of of semiconductors cast from solution, large active areas can be envisioned.

- LEDs fabricated from conducting polymers offer a number of potential advantages to future technology.

Part III. Research Highlight

Paragraph of explanatory text

The light emitting diodes, LEDs, consist of a rectifying Indium contact on the front surface of a semiconducting polymer (MEH-PPV) film which is deposited by spin-casting onto a glass substrate, partially coated with a layer of indium/tin-oxide (ITO), the "ohmic" contact. The MEH-PPV films are prepared by spin-casting from tetrahydrofuran (THF) solution containing 1% MEH-PPV by weight. The resulting MEH-PPV films have uniform surfaces with thicknesses near 1200Å. Rectifying metal contacts are deposited on top of the polymer films by vacuum evaporation. The fabrication steps are shown schematically in the Figure.

Using these remarkably simple structure, diodes with rectification ratios of 10^5 have been achieved. Using low work function metals (such as Calcium) as the rectifying contact, LEDs with quantum efficiency (photons out to electrons in) of 1% have been achieved.

OFFICE OF NAVAL RESEARCH

END-OF-YEAR REPORT
June 1, 1989 - May 31, 1990

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS

Contract No. N0O014-83-K-0450

Principal Investigators:
Alan J. Heeger
Fred Wudl
Paul Smith
Institute for Polymers and Organic Solids
University of California, Santa Barbara
Santa Barbara, CA 93106

Submitted May, 1990

Part I

a. **Papers Submitted** to Refereed Journals (and not yet published)

Highly conductive and Stiff Fibers of Poly(2,5-dimethoxy-p-phenylenevinylene) Prepared from Soluble Precursor Polymer, S. Tokito, P. Smith and A. J. Heeger (submitted to Polymer).

The Synthesis and Characterization of Dimethyl Diacetoxy Pseudocene and Related Compounds, R. H. Jacobson and F. Wudl (submitted to Journal of Organic Chemistry).

b. Papers Published in Refereed Journals

Mechanical and Electrical Properties of poly(2,4-thienylenevimylene) fibers, S. Tokito, P. Smith and A.J. Heeger, Synth. Met. 36, 185 (1990).

Photoinduced Localized Charged Excitations in Polyaniline, Y. H. Kim, C. Foster, J. Chiang and A. J. Heeger, Synth. Metals 26, 49 (1988).

Spectroscopic Studies of Polyaniline in Solution and in Spin-Cast Films, Y. Cao, P. Smith and A. J. Heeger, Synth. Metals 32, 262 (1989).

Photogenerated Carriers in $La_2Cu_3O_4$, $YBa_2Cu_3O_{7-\delta}$ and $Tl_2Ba_2Ca_{(1-x)}Gd_xCu_xO_8$: Polarizability-Induced Pairing of Polarons, C. M. Foster, A. J. Heeger, Y. H. Kim and G. Stucky, Synth. Metals 33, 171 (1989).

Infrared-Active Vibrational Modes of Heavily Doped "Metallic" Polyacetylene, Y. H. Kim and A. J. Heeger, Phy. Rev. B 40 (12), 8393 (1989).

Photoinduced Self-Localized Polarons in $Tl_2Ba_2Ca_{(1-x)}Gd_xCu_2O_8$: A Proposal for Van Der Waals Pairing, C. M. Foster, A. J. Heeger and G. Stucky, Solid State Commun. 71 (11), 945 (1989).

X-Ray Scattering from Crystalline Polyaniline, Y. B. Moon, Y. Cao, P. Smith and A. J. Heeger, Polymer Commun. 30 196 (1989).

c. Books (and Sections thereof) Submitted for Publication

None

d. Books (and Sections thereof) Published

Fibers of Conducting Polymers: High Electrical Conductivity Combined with Attractive Mechanical Properties, Mat. Res. Symp. Proc. Vol. 173 (Materials Research Society, 1990) p. 269.

e. Technical Reports Published
None

f. Patents Filed
None

g. Patents Granted
None

h. Invited Presentations at Topical or Society Conferences

A. J. Heeger - June, 1989 - Invited Lecture
"Lower Dimensional Systems and Molecular Devices", Poros Island, Greece

A. J. Heeger -June, 1989 - Invited Lecture
SAMPE Conference "Electronic Materials and Processes", Los Angeles

A. J. Heeger - July, 1989 - Invited Lecture
International Conference: Materials and Mechanisms of Superconductivity High-Temperature Superconductors (M^2S-HTSC Conference), Stanford University, Palo Alto, CA

A. J. Heeger -September, 1989 - Invited Lecture
NATO Advanced Workshop on "Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics, and Molecular Electronics", Mons, Belgium

A. J. Heeger -September, 1989 - Invited Lecture
"Charge Transfer in Polymeric Systems" (Faraday Discussion), Oxford, England

A. J. Heeger - September, 1989 - Invited Lecture
AFOSR Review, Long Beach, California

A. J. Heeger - October, 1989 - Invited Lecture
Almaden Symposium
IV International Conference on Unconvential Photoactive Solids (UPS)
San Jose, California

A. J. Heeger -October, 1989
ONR Chemistry Division Polymer Program Discussion
Naval Research Laboratory, Washington, D.C.

A. J. Heeger - October, 1989
3rd Symposium on Electroresponsive Molecular and Polymeric Systems
Brookhaven National Laboratory, Upton, Long Island, New York

A. J. Heeger - November 27-December 2, 1989 - Invited Lecture
MRS Symposium "Electrical Optical and Magnetic Properties...", Boston

A. J. Heeger - December, 1989 - Invited Lecture
"Conducting Polymers: Recent Progress and Future Prospects", Maui

A. J. Heeger -December, 1989 - Invited Lecture
"Nonlinear Optical Effects on Conjugated Polymers", Honolulu, Hawaii

A. J. Heeger - February, 1990
Dupont Central Research Division - Seminar, Wilmington, Delaware

A. J. Heeger - February, 1990
Princeton University - Solid State Seminar, New Jersey

A. J. Heeger - March, 1990
NSF Workshop on Group Grants, Washington, D.C.

March, 1990
A. J. Heeger, F. Wudl, D. Pearson, P. Smith, H. Schdmit, P. Pincus -
APS Short Course "Conducting Polymers: Electronic and Optical Properties"
American Physical Society, Anaheim, California

A. J. Heeger - March, 1990
Lecture Trip
March 26 - Iowa State University - Seminar
March 27 - Center for Computational Sciences, Univ. of Kentucky - Seminar

A. J. Heeger - April, 1990 - Invited Lecture
MACHTEC 90, Dresden, East Germany

A. J. Heeger - April, 1990 - Invited Lecture
Rolduc Polymer Meeting, Netherlands

A. J. Heeger - May, 1990
UCLA, Chemical Physics - Invited Seminar

A. J. Heeger - May, 1990 - Invited Lecture
European Physical Society Workshop on the Science and Applications of Conducting Polymers, Lufthus, Norway

F. Wudl - June, 1989 - Invited Lecture
American Chemical Soc. regional meeting
Materials Chemistry Symposium, Reno, Nevada

F. Wudl - August 1989 - Invited Lecture
12th Int'l Congress of Heterocyclic Chemistry, Jerusalem, Israel

F. Wudl - August 27-31, 1989 - Invited Lecture
1st ISSP International Symposium on the Physics & Chemistry of Organic Superconductors, Japan

F. Wudl - September 1989
NATO meeting, Mons, Belgium

F. Wudl - November, 1989 - Invited Lecture
Materials Research Society meeting, Boston

F. Wudl - November 1989 - Invited Seminar, UC Berkeley

F. Wudl - March, 1990 - Invited Lecture
"Frontiers in Chemistry" series - "Novel Conductors"
Case Western Reserve University, Cleveland, Ohio

F. Wudl - April, 1990 - Invited Lecture
American Chemical Society meeting, Boston, MA

F. Wudl - May 2, 1990 - Invited Seminar
3M Company, St. Paul, Minnesota

F. Wudl - May 3, 1990 - Invited Seminar
University of Wisconsin at Madison

F. Wudl - May, 1990
First New Industrial Chemistry and Engineering Conference
"Future Directions in Polymer Science & Technology"
Keystone, Colorado

F. Wudl - May, 1990
International Conference on Organic Superconductors, Stanford University, Stanford, California

P. Smith - Award Lecture
Invited Lecture
Royal Dutch Chemical Society
Maastricht, Holland

P. Smith - October 28, 1989, Invited Lecture
Outstanding Achievement Award of the Fiber Society of America
Chapel Hill, NC

P. Smith - April, 1990 - Invited Lecture
Rolduc Polymer Meeting, Netherlands

P. Smith - May, 1990 - Invited Lecture
European Physical Society Workshop on the Science and Applications of Conducting Polymers, Lufthus, Norway

P. Smith - October-November 1989
Lecture Series, Japan

P. Smith - October 1989 - Invited Lecture
Polymer Society of Japan, Kyoto, Japan

D. McBranch - June, 1989 - Invited Lecture
NATO Advanced Study Institute, Mons, Belgium

C. Foster - July, 1989 - Invited Lecture
M^2S-HTSC Conference, Stanford University, Stanford, Calif.

C. Foster - September, 1989 - Invited Lecture
U.S.-Japan Conference on "Atomic Processes Induced by Electronic Excitation in Non-Metallic Solids", Japan

i. Contributed Presentations at Topical or Scientific Conferences

March 1990 - Contributed papers
American Physical Society meeting Anaheim, California

A. J. Heeger	"
Y. Cao	"
D. Moses	"
D. McBranch	"
G. Yu	"
C. M. Foster	"
D. Mihailovic	"

j. Honors/Awards/Prizes

A. J. Heeger - John Scott Award (Medal and Premium) for 1989

F. Wudl - Elected Fellow of the American Association for the Advancement of Science

P. Smith - Gold Medal of the Royal Dutch Chemical Society

P. Smith - Outstanding Achievement Award of the Fiber Society of America

k. Number of Graduate Students Receiving at least 25% Support on ONR grant or contract

Total: 2 Minorities: 0 Asian: 0

l. Number of Postdoctorals Receiving at least 25% Support on ONR grant or contract

Total 4 Minorities 3 Asian: 3

m. Other Funding - A. J. Heeger, Fred Wudl and Paul Smith (see attached)

CURRENT SUPPORT - A. J. HEEGER

Principal Investigator	Source of Support	Project Title	Award Amount	Period Covered by Award	% of Effort Committed to Effort	Location Research	Co-PI
Current Support	AFOSR	"Oriented Electro/Optical Polymers Through In-Situ Chemistry During Gel Processing: A Research Opportunity"	$110,000[a]	9/15/89-9/14/90	10	UCSB	P. Smith F. Wudl
A.J. Heeger	NSF-MRG	"Oriented Conducting Polymers: Solution Processing and Characterization"	$ 90,000[b]	3/1/89-2/28/90	10	UCSB	P. Pincus P. Smith F.Wudl D. Pearson
	ONR	"Nonlinear Optical Properties of Semi-conducting Polymers"	$101,477	6/1/89-5/30/90	5	UCSB	D. Moses
	ONR	"Program for Research on Conductive Polymers"	$ 80,000[c]	10/1/89-9/30/90	5	UCSB	F. Wudl P. Smith
	Showa Denko	"Cooperative Program in Polymers and Organic Solids"	$ 50,000[d]	10/1/89-9/30/90	5	UCSB	F. Wudl
	EPRI	"Toward Improvements in the Current Carrying Capability of Conducting Polymers"	$ 75,541	5/15/89-12/31/89	5	UCSB	
	NSF	"Program of Cooperative Research on Conjugated Polymers With Prof. J.-L. Brédas (Chemistry, University of Mons, Belgium)"	$ 1,500[e]	11/1/89-10/31/90	1	UCSB	Wudl

CURRENT SUPPORT - FRED WUDL

rincipal vestigator	Source of Support	Project Title	Award Amount	Period Covered by Award	% of Effort Committed to Project	Location Research	Co-PI
urrent upport red Wudl	NSF	"Oriented Conducting Polymers: Solution Processing and Characterization"	$ 35,000[a]	3/15/89-3/14/90	3	UCSB	P. Pincus P. Smith A.J. Heeger D. Pearson
	Showa Denko	"Cooperative Program in Polymers and Organic Solids"	$ 42,000[b]	10/1/89-9/30/90	5	UCSB	A.J. Heeger
	AFOSR	"Oriented/Optical Polymers Through In Situ Chemistry During Gel Processing..."	$ 50,000[c]	9/15/89-9/14/90	2	UCSB	P. Smith A. J. Heeger
	ONR	"Program for Research in Conducting Polymers"	$ 60,000[d]	10/1/89-9/30/90	5	UCSB	A. J. Heeger P. Smith
	NSF	"Synthesis of New Organic Materials: Ferromagnetic Organic Metals, Cyanovinyl Acceptors and Oxydonors"	$93,000[e]	4/1/89-3/31/90	15	UCSB	
	NSF	"High Strength Materials, Polymers for Nonlinear Optics and New Electrically Conducting Polymers"	$ 89,000	8/1/89-7/31/90	15	UCSB	
	NSF	"Molecular Atoms (Heterospherophanes)"	$157,000	9/1/89 8/31/91	10	UCSB	P. Pincus
	NSF	"Program of Cooperative Research on Conjugated Polymers With Prof. J.-L. Brédas (Chemistry, University of Mons, Belgium)"	$ 1,500[f]	11/1/89-10/31/90	1	UCSB	Wudl

CURRENT SUPPORT - PAUL SMITH

Principal Investigator	Source of Support	Project Title	Award Amount	Period Covered by Award	% of Effort Committed to Effort	Location Research	Co-PI
Current Support Paul Smith	ARO	"Tractable High Performance Polymers"	$ 25,000[a]	03/01/89-02/28/90	10	UCSB	A.J. Heeger D. Pearson H. Schmidt
	AFOSR	"Oriented Electro/Optical Polymers Through In-Situ Chemistry During Gel Processing: A Research Opportunity"	$100,000[b]	09/15/88-09/14/89	10	UCSB	A.J. Heeger F. Wudl
	NSF-MRG	"Oriented Conducting Polymers: Solution Processing and Characterization"	$ 90,000[c]	03/15/88-08/31/89	10	UCSB	P. Pincus D. Pearson F. Wudl A.J. Heeger
	ONR	"Program for Research on Conductive Polymers"	$ 70,000[d]	10/01/88-09/30/89	5	UCSB	F. Wudl A.J. Heeger
	DSM	Research Gift	$100,000	1988-present			
	DuPont	Research Gift	$ 60,000	1987-present			

Part II

a. Principal Investigators

Alan J. Heeger
Fred Wudl
Paul Smith

b.

Alan J. Heeger	(805) 961-3184
Fred Wudl	(805) 961-3755
Paul Smith	(805) 961-8104

c. Dr. Kenneth Wynne (ONR - Chemistry)

d. Brief (100-200 words) Description of Project

This is an interdisciplinary project focused on the fundamental chemistry, physics and materials science of conducting polymers in the context of the novel electronic phenomena associated with this emerging class of materials. The full range of research is involved: synthesis and characterization of new conducting polymers, processing directed toward the achievement of chain oriented and chain extended materials with a goal c· striving for intrinsic electronic and optical properties, and physical measurements directed at characterizing these electronic and optical properties and of identifiying the basic physical mechanism involved in these phenomena.

e. Significant Results During Last Year

Through studies of the electrical and mechanical properties of fibers of poly(thienylenevinylene) and poly (dimethdxyphenylenevinylene) we discovered that the electrical and mechanical properties improve together and in a correlated manner as the degree of chain extension and chain alignment are improved through tensile drawing. The result is conducting polymers with a remarkable combination of properties: high electrical conductivity, high strength and high modulus --- a combination that was thought by many to be impossible. The basic theoretical origin of this combination of properties has been identified in terms of coherent secondary bonds (interchain coupling) in chain extended and chain aligned systems. The conclusion is that this correlation between electrical and mechanical properties is intrinsic and can be expected to be a general feature of the class of conducting polymer materials.

f. Brief (100-200 words) Summary of Plans for Next Year's Work

Recent progress in our laboratories with blends of conducting polymers and traditional polymers has opened the way to a broad based study of such systems. In addition to the obvious advantages of such blends (one can design materials to have unique combination of properties associated with the two constituents), there are two specific advantages of blending conducting polymers:

(1) The use of blends cuts down on the volume fraction of the expebsive component; i.e. the conductive polymer. Thus for applications, blending offers the promise of major cost advantages.

(2) The use of blends "self-encapsulates" the conducting polymer. Since environmental stability remains a serious issue, this self-encapsulation can be an important feature.

During the next year we will use the soluble conducting polymers (soluble PPV derivatives, soluble P3AT's, soluble polyaniline, etc) and precursor polymers of conducting polymers to develop and process such blends.

g. List of Names of Graduate Students and Postdoctorals Currently Working on Project

Braun, David
Foster, Christopher
Karl Voss
Moses, Daniel (Associate Research Physicist)
Zhang, Chi
Liou, Kwangkyoung
Fite, Christian
Tokito, Shizuo

OFFICE OF NAVAL RESEARCH

END-OF-THE-YEAR REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/STUDENTS REPORT

for
Contract No. N00014-83-K-0450
(due date - June 1, 1989)

R&T Code 4132012

Title of Contract: Program for Research on Conducting Polymers

Principal Investigators:
Alan J. Heeger (Dept. of Physics and Materials Dept., UCSB)
Paul Smith (Materials Dept., UCSB)
Fred Wudl (Dept. of Physics and Dept. of Chemistry, UCSB)

Institute for Polymers and Organic Solids
University of California, Santa Barbara
Santa Barbara, CA 93106

Part I

a. Papers Submitted to Refereed Journals (and not yet published)

Y.H. Kim and A.J. Heeger, Infrared Active Vibrational Modes of Heavily Dopod Polyacetylene: Is "Metallic " Polyacetylene a Metal?, Physical Review B.

C.M. Foster, A.J. Heeger, G. Stucky and N. Herron, Photoinduced Polarons in $Tl_2Ba_2Ca_{(1-x)}Gd_xCu_2O_8$: A Proposal for Van der Waals Pairing, Solid State Communications

R.M. Souto-Maior, K. Hinkelmann, H. Eckert, and F. Wudl, Synthesis and Characterization of Two Regiochemically Defined Poly(alkylthiophenes): A Compative Study, Macromolecules; other support NSF

b. Papers published in Refereed Journals

M.J. Winokur, Y.B. Moon, A.J. Heeger, J. Barker and D.C. Bott, The Relationship Between Charge Transfer and Structure in Alkali Doped Polyacetylene, Solid State Commun. 68,1055 (1988)

Y.H. Kim, C.M. Foster, A.J. Heeger, S. Cox and G. Stucky, Photoinduced self-localized distortions in $YBa_2Cu_3O_{7-\delta}$, Phys. Rev. B38, 6478 (1988)

N. Basescu, J. Chiang, S. Rughooputh, T. Kubo, C. Fiter and A.J. Heeger, Implications of the New High Conductivity Polyacetylene, Synth. Met. 28, D43 (1989)

Y.H. Kim, D. Spiegel, S. Hotta and A.J. Heeger, Photoexcitation and Doping Studies of poly(3-hexylthienylene), Phys. Rev. B38, 5490 (1988)

R. Worland, S.D. Phillips, W. C. Walker, and A.J. Heeger, Electroabsorption and Nonlinear Optical Constants of Trans-Polyacetylene and Poly(3-hexylthiophene),Synth. Met. 28, D663

Y. H. Kim, M. Nowak, Z.G. Soos and A.J.Heeger, Strongly Localized Photogenerated Bipolarons in Polydiacetylenes,Synth. Met.28, D621 (1989)

R.M. Souto-Maior and F. Wudl, Regiochemically Defined Alkyl Substituted Polythiophenes, Synth. Met. 28, C281(1989)

B. C. Hess, J. Shinar, Q.-X. Ni, . Vardeny, and F. Wudl, Photoluminescence and Optically Detected Magnetic Resonanc in Polythiophene and Poly(3-alkylthiophenes): Substitution, Disorder and Ageing Effects, Synth. Met. 28, C365, (1989)

S. H. Askari, S. Rughooputh and F. Wudl, Soluble Subetituted-PPV Conducting Polymers: Spectroscopic Studies, Synth. Met. 28, E129 (1989); other support - NSF

Y.H. Kim, S.D. Phillips, M.J. Nowak, D. Spiegel, C.M. Foster, G. Yu, J. Chiang, and A.J. Heeger, Localization of Charged Excitations in Polyaniline, Synth. Met. 28, E291 (1989)

A.O. Patil, S. Rughooputh and F. Wudl, Poly(p-phenylene-vinylene): Incipient Doping in Conducting Polymers, Synth. Met. 28, E115 (1989); other support - NSF

Y.H. Kim, C. Foster, J. Chiang, and A.J. Heeger, Localized Charged Excitations in Polyaniline: Infrared Photoexcitation and Protonation Studies, Synth. Met. 28, E285 (1989)

M.J. Winokur, D. Spiegel, Y. Kim, S. Hotta and A.J. Heeger, Structural and Absorption Studies of the Thermochromic Transition in Poly(3-hexylthiophene), Synth. Met. 28, C419 (1989)

Y. H. Kim, C.M. Foster and A.J. Heeger, Polarons in High T_c Superconductors: IRAV Modes and Electronic Transitions to GFap States as in Conducting Polymers, Synth. Met. 28, F603 (1989)

Y.H. Kim, C. Foster, J. Chiang and A.J. Heeger, Photoinduced Localized Charged Excitations in Polyaniline, Synth. Met. 26, 49 (1988)

c. Books (and sections thereof) submitted for Publication

None

d. Books (and sections thereof) Published

Y.H. Kim, C.M. Foster, A.J. Heeger, S. Cox, L. Acedo, and G. Stucky in "Chemistry of High-Temperature Superconductors II", Ed. by David L. Nelson and Thomas F. George, ACS Symposium Series #377 (Amer. Chem. Soc., Washington, D.C. 1988)

e. Technical Reports Published (including ONR Technical Reports) and Papers Published in Non-Refereed Journals

In Situ Electron Spin Resonance Experiments on Polyacetylene During Electrochemical Doping, Chen et al (2C-21)

Intrinsic Conductivity of Conducting Polymers, Heeger et al, (2C-22)

Photoinduced Absorption and Resonant Raman Scattering of Polythiophene, Vardeny, et al (2C-23)

Direct Evidence of the Importance of Electron-phonon Coupling in La_2CuO_4: Photoinduced ir-active vibrational modes, Kim et al, (2C-24)

Infrared Photoexcitation and Doping Studies of Poly(3-methylthienylene), Kim etal (2C-25)

Localized Phonons Associated with Solitons in Polyacetylene: Coupling to the nonuniform mode, Schaffer et al. (2C-26)

Bipolarons in poly(3-methylthiophene): Spectroscopic, Magnetic, and eletrochemical measurements, Colaneri et al. (2C-27)

Electrically Conducting Polymers, Heeger et al.(2C-28)

Photoinduced Self-Localized Structural Distortions in $YBa_2Cu_3O_{7-\delta}$, Kim et al. (2C-29-1988)

Photoinduced Localized Charged Excitations in Polyaniline, Kim et al. (2C-30-1988)

Transient Photoconductivity in Oriented Trans-Polyacetylene Prepared by the Naarmann-Theophilou Method, Phillips et al. (2C-31-1988)

Solitons in Conducting Polymers, Heeger et al. (2C-32-1988)

Electrically Conductive Polyacetylene Fibers through In situ Polymerization in Carrier Gels, Chiang et al. (2C-33-1988).

Long-lifetime Charged Photoexcitations in Polydiacetylenes: Strongly Localized Bipolarons, Kim et al. (2C-34-1988)

f. Patents Filed

None

g. Patents Granted

None -

Pending: "Conductive Articles of Intractable Polymers and Methods of Making the Same"; Inventors: P. Smith, A.J. Heeger, F. Wudl and J. Chiang

h. Invited Presentations at Topical or Scientific Society Conferences

P. Smith, ICSM '88, Santa Fe, NM (June 1988)
P. Smith, Organized ACS Symposium on Processing of Conducting Polymers, ACS Meeting, Dallas (April, 1989)
P. Smith, NATO ASI on "Soft Condensed Matter", Gielo, Norway (April, 1989)

F. Wudl, Symposium on Processing of Conducting Polymers, ACS Meeting, Dallas (1989).
F. Wudl, Symposium on Conducting Polymers, ACS Meeting, Los Angeles (October 1988)
A.J. Heeger, Symposium on the Chemistry of High T_c Superconductivity, ACS Meeting, Los Angeles (October 1988)
A.J. Heeger, Symposium on Molecular Electronics, APS Meeting, St. Louis (March, 1989)

i. Contributed Presentations at Topical or Scientific/Technical Society Conferences

Y. Moon, Y. Cao, P. Smith, and A.J. Heeger, APS Meeting, St. Louis (March 1989)

C. Fite, Y. Cao, and A.J. Heeger, APS Meeting, St. Louis (March 1989)

Y.H. Kim, Z.G. Soos and A.J. Heeger, APS Meeting, St. Louis (March 1989)

Y.H. Kim and A.J. Heeger, APS Meeting, St. Louis (March 1989)

R. Souto-Maior and F. Wudl, ACS Meeting, Los Angeles (Sept. 1988)

j. Honors/Awards/ Prizes

A. J. Heeger, John Scott Award for 1989 (shared with Prof. A. G. MacDiarmid), $10,000 plus John Scott medal, awarded by John Scott Award Advisory Committee (via Board of Directors of City Trusts, Philadelphia)

k. Number of Graduate Students Receiving Full or Partial Support on this ONR Contract

Fourteen (14)

l. Number of Postdoctoral Fellows Receiving Full or Partial Support on this ONR Contract

Nine (9)

Part II

a. Principal Investigators

Alan J. Heeger
Paul Smith
Fred Wudl

b. Dr. Kenneth Wynne (ONR- Chemistry)

c. Current Telephone Number

Alan J. Heeger (805) 961-3184; FAX: (805) 961-4755
Paul Smith (805) 961-8104
Fred Wudl (805) 961-3755

d. Brief (100-200 words) description of project

This broad based program on conducting polymers is an interdisciplinary effort with roots in chemistry, physics and polymer science, and it involves a back-and-forth interplay between the various components. Within the Institute for Polymers and Organic Solids at UCSB, we have assembled a high quality group of graduate research students, postdoctoral researchers , technicians, Visiting scientists and faculty working in close collaboration across these three sub-areas. The addition of the Polymer Processing effort (Prof. Paul Smith and his group) represents a major dvelopment. To our knowledge, we are the only academic research effort in the world which spans the full range required for continued progress in the area of conducting polymers: Synthesis --- Polymer Processing --- Physical Measurements. We have assembled the general facilities, specialized equipment, and personnel needed to carry out the research program. We are confident that this research program will continue to lead to significant progress in the emerging field of conducting polymers.

e. Significant Results During Past Year

a. High molecular weight organic solvent soluble precursor polymers of PPV (and derivatives) were prepared.
b. We developed the technique of electroabsorption for conjugated polymers and successfully applied it to polyacetylene and polythiophene.
c. Photoinduced self-localization (polaron formation) was established for the high temperature superconducting materials with results in direct analogy with those seen in conducting polymers. The results provide insight into the mechanism for high temperature superconductivity, and they provide optimism for achieving the same phenomena in conjugated polymers.

f. Brief (100-200 words) summary of plans for next years work

We have shifted our emphasis to semiconducting polymers that are stable and that can be processed into films and fibers from solution . During the next year we will focus on these materials and on composites and blends of these materials with other polymers. In particular, we will extend our earlier work on the use of gel fibers and apply it to a variety of conducting polymers in order to obtain the desired combination of properties: stability, excellent mechanical properties and high conductivity. The gel state itself will be brought into a principal focus; doped conducting gels are a novel state of matter with interest for their own properties as well as for intermediates for processing into oriented films and fibers. Specific efforts along these lines will utilize the poly(3-alkythiophenes, poly(thienylenevinylene), dimethoxy-PPV, and dihexyloxy-PPV (note that PPV = polyphenylenevinylene). These materials will also be at the focus of our electroabsorption measurements.

g. List of names of graduate students and post-doctorals currently working on project

Graduate students

P. Allemand
C.M. Foster
T. Suzuki

Postdoctoral Researchers

D. Moses
S. Tokito

Part III. Research Highlight

a. Introductory viewgraph: Following page

Electronic/Optical Polymers: Commodities with Routine Properties or High Performance Materials (or both ?)

Two important classes of heavily doped polymers:

Commodities with Routine Properties

"Dirty" conductors with electrical conductivities of the order of 10 S/cm or less: Such systems can be achieved with relative ease; all that is required is a moderately high density of carriers. Carrier delocalization is neither required nor implied by such values.

High Performance Materials

True metals in which the carrier mean free path is at least a few lattice constants: polymers in which σ > several hundred S/cm.

In such systems, the molecular weight is sufficiently high, interchain order is sufficiently good, and the defect density is sufficiently low that delocalization occurs leading to "free" metallic carriers with mean free paths much greater than a carbon-carbon repeat unit.

Part III. Research Highlight

b. Figure: Following page

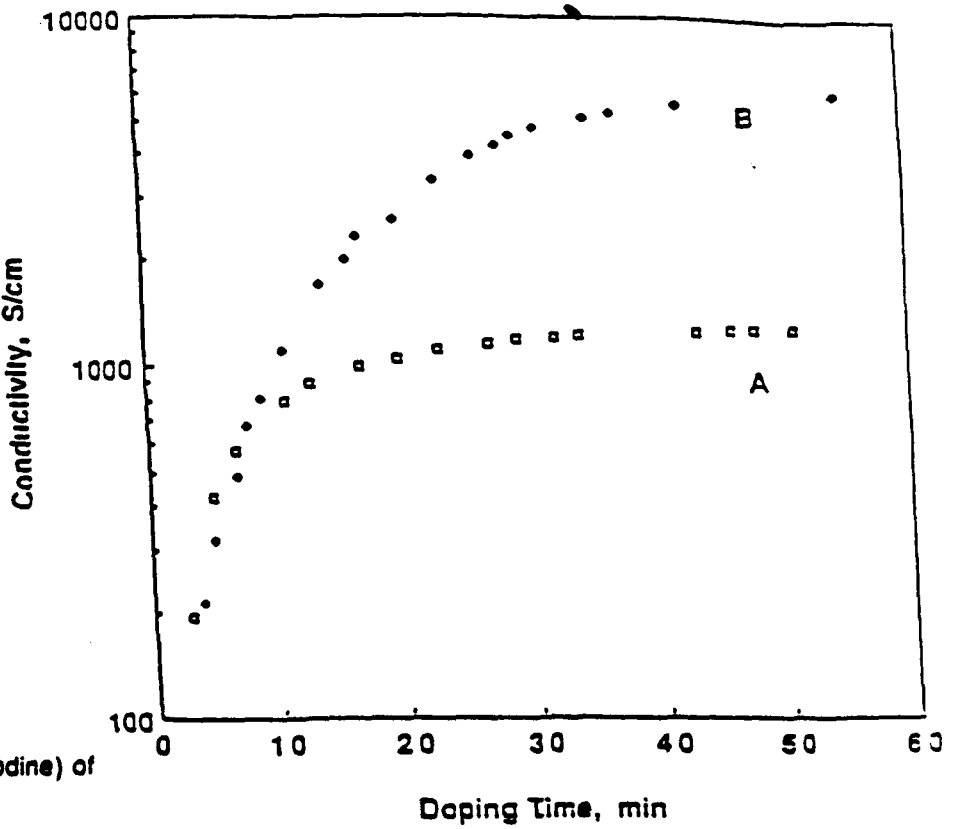
Electrical Conductivity:

Can we have high σ and high strength/modulus?

Existence Proof: Polyacetylene

	Oriented Polyethylene	Polyacetylene
Tensile Strength	10 times steel (wt. basis)	5 times steel (comparable with Kevlar)
	Copper	**Polyacetylene**
Conductivity	6×10^5 S/cm	$> 1 \times 10^5$ S/cm

Polyacetylene/polyethylene composite fibers (80%/20%)



Electrical conductivity vs doping time (iodine) of
A. as-polymerized
B. 2.2X drawn PAc/PE monofilaments (80%/20%)

Part III. Research Highlight

c. Concluding viewgraph: Following page

Conducting Polymer Blends and Composites Offer Promise Over Full Range of Properties from Commodity Materials with Routine Properties to High Performance Materials

Part III. Research Highlight

d. Paragraph of explanatory text

Electronic/Optical Polymers: Commodities with Routine Properties or High Performance Materials (or both ?)

There are two important classes of heavily doped polymers:

(1) Commodities with Routine Properties: "Dirty" conductors with electrical conductivities of the order of 10 S/cm or less. Such systems can be achieved with relative ease; all that is required is a moderately high density of carriers. Carrier delocalization is neither required nor implied by such values.

(2) High Performance Materials: True metals in which the carrier mean free path is at least a few lattice constants: polymers in which $\sigma >$ several hundred S/cm. In such systems, the molecular weight is sufficiently high, interchain order is sufficiently good, and the defect density is sufficiently low that delocalization occurs leading to "free" metallic carriers with mean free paths much greater than a carbon-carbon repeat unit.

The available data imply that the full range of properties will be available with conducting polymers and withblends/composites of conducting polymers with other polymer systems.

mailed 2/9/89

OFFICE OF NAVAL RESEARCH

END-OF-YEAR REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS

October 1, 1987-September 30, 1988
for
Contract No. NOOO14-83-K-0450

Principal Investigators:
Alan J. Heeger
Fred Wudl
Paul Smith
Institute for Polymers and Organic Solids
University of California, Santa Barbara
Santa Barbara, CA 93106

Part 1

a. Papers Submitted to Refereed Journals (and not yet published)

The Relationship Between Charge Transfer and Structure in Alkali Doped Polyacetylene, M. J. Winokur, Y. B. Moon, A. J. Heeger, J. Barker and D. C. Bott, Phys. Rev. B Rapid Commun. (in press)

X-Ray Scattering from Crystalline Polyaniline, Y. B. Moon, Y. Cao, P. Smith and A. J. Heeger, submitted to Polymer Commun.

Implications of the New High Conductivity Polyacetylene, N. Basescu, J. Chiang, S. Rughooputh, T. Kube, C. Fite and A. J. Heeger, Syn. Mtls. (in press).

Regiochemically Defined Alkyl Substituted Polythiophenes, R. Souto-Maior and F. Wudl, Syn. Mtls. (in press).

Electroabsorption and Nonlinear Optical Constants of Trans-polyacetylene and Poly(3-hexylthiophene), R. Worland, S. D. Phillips, W. C. Walker and A. J. Heeger, Syn. Mtls. (in press).

Polarons in High T_c Superconductors: IRAV Modes and Electronic Transitions to Gap States as in Conducting Polymers, Y. H. Kim, C. M. Foster and A. J. Heeger, Syn. Mtls. (in press).

Strongly localized Photogenerated Bipolarons in Polydiacetylenes, Y. H. Kim, M. Nowak, Z. G. Soos and A. J. Heeger, Syn. Mtls. (in press).

Localization of Charged Excitations in Polyaniline, Y. H. Kim, S. D. Phillips, M. J. Nowak, D. Spiegel, C. M. Foster, G. Yu, J. C. Chiang and A. J. Heeger, Syn. Mtls (in press).

Soluble Substituted-PPV Conducting Polymers: Spectroscopic Studies, S. H. Askari, S. D. Rughooputh and F. Wudl, Syn. Mtls. (in press).

b. Papers Published in Refereed Journals

In- Situ Electron Spin Resonance Resonance Experiments on Polyacetylene During Electrochemical Doping, Syn. Mtls. 24, 311 (1988).

Polarons and Bipolarons on a Conducting Polymer in Solution, M. J. Nowak, S.D.D. Rughooputh, S. Hotta and A. J. Heeger, Macromol. 20, 965 (1987).

Localized Phonons Associated with Solitons in Polyacetylene: Coupling to the Nonuniform Mode, H. E. Shaffer, R. H. Friend and A. J. Heeger, Phys. Rev. B 36, 7537 (1987).

Poly(p-phenyleneamineimine): Synthesis and Comparison to Polyaniline, F. Wudl, R. O. Angus, F. L. Lu, P. M. Allemand, D. J. Vachon, M. Nowak, Z.X. Liu and A. J. Heeger, J. Amer. Chem. Soc. 109, 3677 (1987).

Conformational Defects in Durham Polyacetylene: Photo-induced IR Absorption, R. H. Friend, H. E. Schaffer, A. J. Heeger and D. C. Bott, Phys. C: Solid State Phys. 20, 6013 (1987).

Direct Evidence of the Importance of Electron-phonon Coupling in La_2CuO_4: Photoinduced ir-active Vibrational Modes, Y. H. Kim, A. J. Heeger, L. Acedo, G. Stucky and F. Wudl, Phys. Rev. B 36, 7252 (1987).

Bipolarons in poly(3-methylthiophene): Spectroscopic, Magnetic and Electrochemical Measurements, N. Colaneri, M. Nowak, D. Spiegel, S. Hotta and A. J. Heeger, Phys. Rev. B 26, 7964 (1987).

Photoinduced Absorption and Resonant Raman Scattering of Polythiophene, Syn. Mtls. 18, 183 (1987).

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Photoinduced Self-Localized Structural Distortions in $YBa_2Cu_3O_{7-\delta}$, Y. H. Kim, C. M. Foster and A. J. Heeger, Phys. Rev. B 38 (10), 6478 (1988).

Photoinduced Localized Charged Excitations in Polyaniline, Y. H. Kim, C. Foster, J. Chiang and A. J. Heeger, Syn. Mtls. 26, 49 (1988).

Mechanism for Photogeneration of Metastable Charged Solitons in Polyacetylene, N. F. Colaneri, R. H. Friend, H. E. Schaffer and A. J. Heeger, Phys. Rev. B 38 (6), 3960 (1988).

Solitons in Conducting Polymers, A. J. Heeger, S. Kivelson, J. R. Schrieffer, W.-P. Su, Reviews of Modern Physics 60 (30), 781 (1988).

Electrically Conductive Polyacetylene Fibres Through In Situ Polymerization in Carrier Gels, Jin C. Chiang, Paul Smith, Alan J. Heeger and Fred Wudl, Polymer Commun. 29, 161 (1988).

Long-Lifetime Charged Photo-excitations in Polydiacetylenes: Strongly Localized Bipolarons, Y. H. Kim, M. Nowak, Z. G. Soos and A. J. Heeger, J. Phys. C: Solid State Phys. 21, L503 (1988).

Optical Properties of Conducting Polymers, A. O. Patil, A. J. Heeger and F. Wudl, Chem. Rev. 88, 183 (1988).

Intrinsic Conductivity of Conducting Polymers, S. Kivelson and A. J. Heeger, Syn. Mtls. 22, 371 (1988).

c. Books (and sections thereof) Submitted for Publication

None

d. Books (and sections thereof) Published

None

e. Technical Reports Published and Papers Published in Non-refereed Journals

None

f. Patents Filed

"Conductive Articles of Intractable Polymers and Methods of Making the Same", Inventors: P.Smith, A.J. Heeger, F. Wudl, and J. Chiang (Filed October 5, 1987)

g. Patents Granted

None

h. Invited Presentations at Topical or Scientific/Technical Society Conferences

A. J. Heeger (Invited talks specifically focused on research carried out during this ONR Contact)

Nobel Symposium on "Physics of Low-Dimensional Systems, Graftavallen, Sweden, June 1988

STU Workshop on Conducting Polymers, Stockholm, Sweden, April, 1988

Optical Society of America, Topical Meeting on Nonlinear Optical Properties of Materials, Rensselaer Polytechnic Institute, Troy, New York, August 1988

F. Wudl (Invited talks specifically focused on research carried out during this ONR Contract

International Conference on Synthetic Metals (ICSM '88), Santa Fe, New Mexico, June 1988

Peter A. Leermaker's Symposium: Conductors and Superconductors, Wesleyen University, May 5, 1988

Gordon Conference (Polymers), New Hampshire, June 1988

IUCCP Symposium, Texas A & M, March 1988

American Chemical Society Meeting, Los Angeles, September 1988

N. Basescu
International Conference on Synthetic Metals (ICSM '88), Santa Fe, New Mexico, June 1988

P. Smith
International Conference on Synthetic Metals (ICSM '88), Santa Fe, New Mexico, June 1988

Y. H. Kim
Internaticnal Symposium on Conducting Polymers, Brookhaven National Laboratory, October 1987

i. Contributed Presentations at Topical or Scientific/Technical Society Conferences

A. American Physical Society Meeting, New Orleans, March 21-25, 1988

Localized Charged Excitations in Polydiacetylenes, Y.H. Kim, Z. Soos, H.E. Schaffer and A.J. Heeger

Photoinduced and Doping Induced Infrared Absorption in Poly(phenylenevinylene) C.M. Foster, Y.H. Kim, A.O. Patil, and A.J. Heeger

Infrared Photoinduced Absorption Studies of Polyaniline, Y.H. Kim, C. Foster, J.C. Chiang and A.J. Heeger

Electroabsorption in Conjugated Polymers, R. Worland, S. Philips and A.J. Heeger

Photoexcitation Studies of Y-Ba-Cu-O Compounds, Y.H. Kim, C. Foster and A. J. Heeger

Polyacetylene Composite Fobers Made by Gel Processing J. Chiang, N. Basescu, P. Smith, A.J. Heeger, and F. Wudl

B. International Conference on Synthetic Metals (ICSM '88), Santa Fe, NM, June 26-July 1, 1988

Implications of the New High Conductivity Polyacetylene, N. Basescu, J. Chiang, S. Rughooputh, T. Kub, C. Fite and A.J. Heeger

Regiochemically Defined Alkyl Substituted Polythiophenes, R. Souto-Maior and F. Wudl

Electroabsorption and Nonlinear Optical Constants of Trans-polyacetylene and poly(3-hexylthophene), R. Worland, S.D. Phillips, W. C. Walker, and A.J. Heeger

Photoinduced Localized Charged Excitations in Polyaniline, Y.H. Kim, J. Chiang, and A.J. Heeger

Polarons in High T_c Superconductors: IRAV Modes aand Electronic Transitions to Gap States as in Conducting Polymers, Y.H. Kim, C.M. Foster and A.J. Heeger

Strongly Localized Photogenerated Bipolarons in Polydiacetylenes, Y. H. Kim, M. Nowak, Z.G. Soos and A.J. Heeger,

Localization of Charged Excitations in Polyaniline, Y.H. Kim, S.D. Phillips, M.J. Nowak, D. Spiegel, C.M. Foster, G. Yu, J.C. Chiang, and A.J. Heeger

Soluble Substituted-PPV Conducting Polymers: Spectroscopic Studies, S. H. Askari, S.D. Rughooputh and F. Wudl

j. Honors/Awards/Prizes

NONE

k. Number of Graduate Students Receiving Full or Partial Support on ONR Contract

Ten (10)

l. Number of Postdoctoral Fellows Receiving Full or Partial Support on ONR Contract

Six (6)

PART II

a. Principal Investigators
Professor Alan J. Heeger, Professor Fred Wudl, and Professor Paul Smith

b. Cognizent ONR Scientific Officer
Dr. K. Wynne/ Dr. J. Milliken

c. Current Telephone Number
(805) 961-3184

d.Brief (100-200) description of project
This broad based Program on Conducting Polymers is an interdisciplinary effort with roots in chemistry, physics and polymer science, and it involves a back-and-forth interplay between the various components. Within the Institute for Polymers and Organic Solids at UCSB we have assembled a large and highquality group of graduate research students, post-doctoral researchers, technicians and Visiting Scientists working in close collaboration across these three sub-areas. The addition of the Polymer Processing effort to this program represents a major departure and a major development. To our knowledge, we are the only academic research effort in the world which spans the full range required for continued progress in the area of conducting polymers: --- SYNTHESIS --- POLYMER PROCESSING --- PHYSICAL MEASUREMENTS. We have assembled the broad base of facilities, equipment, and personnel needed to carry out such a program. We are confident that this research program will continue to lead to significant progress in the important emerging field of conducting polymers.

e. Significant Results During the Last Year
ELECTRICALLY CONDUCTIVE POLYACETYLENE FIBERS THROUGH IN-SITU POLYMERIZATION IN CARRIER GELS

We discovered a novel route for fabricating continuous fibers and films of polyacetylene. Although initially applied to polyacetylene, the methods are general, and can be used to process other so-called "intractable (conductive) polymers in pre-shaped carrier gels. Specifically, the technique involves in-situ polymerization in gel fibers containing 2% ultra-high molecular weight polyethylene. The composite polyacetylene/polyethylene fibers produced comprised up to 82% of polyacetylene; they exhibited electrical conductivities of 1,200 S/cm and 6000 S/cm. respectively for the as-polymerized and 2.2X drawn monofilaments.

f. Brief (100-200 words) summary of plans for next years work
Emphasis will be on the synthesis, characterization, processing and physical properties of polymers from the class of which poly(phenylenevinylene) is the prototype. This includes di-alkoxy

substituted (on the benzene ring) PPV derivatives, which are both more stable and have a smaller energy gap than the parent material. In addition we will work on th eanalogous family based on poly(thienylenevinylene). Initial goals will be to synthesize selected materials in sufficient quantity to allow a full range of characterization, rheological studies, and processing. Our plan is to continue to push toward high quality, chain-oriented materials in order to attempt to explore intrinsic properties.

g. List of names of graduate students and post-doctorals currently (i.e. June, 1988) working on project.

Graduate Students

C. Foster
Y. Moon
R. Souto-Maior
D. Spiegel
G. Yu

Post-doctoral Researchers

D. Moses
Y. Cao
S. Askari
Y.Kim
A. O. Patil
A. N. Patil

h. Technical Reports submitted to ONR during the year

1. Optical Properties of Conducting Polymers, A. O. Patil, A.J. Heeger and F. Wudl

2. Polarons and Bipolarons on a Conducting Polymer in Solution

Reports on the rest of the publications are in preparation.

OFFICE OF NAVAL RESEARCH

END-OF-THE-YEAR REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS

REPORT

(July 15, 1988)

for

Contract # N00014-83-K-0450

"Program for Research on Conducting Polymers"

Principal Investigators:
Professor Alan J. Heeger
Professor Fred Wudl
Professor Paul Smith

Institute for Polymers and Organic Solids
University of California, Santa Barbara
Santa Barbara, CA 93106

PART 1

a. Papers Submitted Refereed Journals (and not yet published)

Implications of the New High Conductivity Polyacetylene, N. Basescu, J. Chiang, S. Rughooputh, T. Kube, C. Fite and A.J. Heeger (Synth. Met., in press)

Regiochemically Defined Alkyl Substituted Polythiophenes, R. Souto-Maior and F. Wudl, (Synth. Met., in press)

The Relationship between Charge Transfer and Structure in Alkali Doped Polyacetylene, M.J. Winokur, Y.B. Moon, A. J. Heeger, J. Barker and D.C. Bott (Phys. Rev B, in press)

Electroabsorption and Nonlinear Optical Constants of Trans-polyacetylene and poly(3-hexylthophene), R. Worland, S.D. Phillips, W. C. Walker, and A.J. Heeger (Synth. Met., in press)

Mechanism for photogeneration of metastable charged solitons in polyacetylene, N.F. Colaneri, R.H. Friend, H.E. Schaffer, and A.J. Heeger Phys. Rev.B (in press)

Photoexcitation and Doping Studies of Poly(3-hexylthienylene), Y.H. Kim, D. Spiegel, S. Hotta, and A.J. Heeger, *Phys. Rev. B (in press)*

Photoinduced Localized Charged Excitations in Polyaniline, Y.H. Kim, J. Chiang, and A.J. Heeger (Synth. Met., in press)

Photoinduced Self-Localized Structural Distortions in $YBa_2Cu_3O_{7-\delta}$, Y.H. Kim, C.M. Foster, A.J. Heeger, S. Cox, and G. Stucky (Phys. Rev. B, in press)

Polarons in High T_c Superconductors: IRAV Modes aand Electronic Transitions to Gap States as in Conducting Polymers, Y.H. Kim, C.M. Foster and A.J. Heeger (Synth. Met., in press)

Strongly Localized Photogenerated Bipolarons in Polydiacetylenes, Y. H. Kim, M. Nowak, Z.G. Soos and A.J. Heeger, (Synth. Met., in press)

Localization of Charged Excitations in Polyaniline, Y.H. Kim, S.D. Phillips, M.J. Nowak, D. Spiegel, C.M. Foster, G. Yu, J.C. Chiang, and A.J. Heeger, (Synth. Met., in press)

Soluble Substituted-PPV Conducting Polymers: Spectroscopic Studies, S. H. Askari, S.D. Rughooputh and F. Wudl, (Synth. Met., in press)

b. Papers Published in Refereed Journals

Electrically Conductive Polyacetylene Fibers through In-Situ Polymerization in Carrier Gels, J.C. Chiang, P. Smith, A.J. Heeger, and F.Wudl, Polymer Communications (August, 1988)

In-Situ Electron Spin Resonance Experiments on Polyacetylene During Electrochemical Doping, Synth. Met. 24, 311, (1988)

Optical Properties of Conducting Polymers, A. O. Patil, A.J. Heeger and F. Wudl, Chem. Rev. 88, 183 (1988)

Polarons and Bipolarons on a Conducting Polymer in Solution, M.J. Nowak, S.D.D. Rughooputh, S.Hotta and A.J. Heeger, Macromolecules 20, 965 (1987)

Intrinsic Conductivity of Conducting Polymers, S. Kivelson and A.J. Heeger. Synth. Met. 22, 371, (1988)

X-Ray Scattering from Oriented Durham Polyacetylene: Structural Changes after Electrochemical Doping, Y.B. Moon, M. Winokur, A.J. Heeger, J. Barker, and A.J. Heeger, Macromolecules 20, 2457(1987)

Localized Phonons Associated with Solitons in Polyacetylene: Coupling to the Nonuniform Mode, H.E. Schaffer, R.H. Friend and A.J. Heeger, Phys. Rev.B36, 7537 (1987)

Poly(p-phenyleneamineimine): Synthesis and Comparison to Polyaniline, F. Wudl, R.O. Angus, F.L. Lu, P.M. Allemand, D.J. Vachon, M. Nowak, Z.X. Liu and A.J. Heeger, J. Am. Chem. Soc. 109, 3677 (1987)

Conformational Defects in Durham Polyacetylene: Photo-induced IR Absorption, R.H. Friend, H.E. Schaffer, A.J. Heeger and D.C. Bott, J. Phys. C: Solid State Phys, 20, 6013 (1987)

Direct Evidence of the Importance of Electron-phonon Coupling in La_2CuO_4: Photoinduced ir-active Vibrational Modes, Y.H. Kim, A.J. Heeger, L. Acedo, G. Stucky, and F. Wudl, Phys. Rev.B36, 7252 (1987)

Bipolarons in poly(3-methylthiophene): Spectroscopic, Magnetic and Electrochemical Measurements, N. Colaneri, M. Nowak, D. Spiegel, S. Hotta and A. J. Heeger, Phys. Rev.B36, 7964, (1987)

Photoinduced Absorption and Resonant Raman Scattering of Polythiophene, Synth Met. 18, 183 (1987)

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c. Books (and sections thereof) Submitted for Publication

None

d. Books (and sections thereof) Published

None

e. Technical Reports Published and Papers Published in Non-refereed Journals

None

f. Patents Filed

"Conductive Articles of Intractable Polymers and Methods of Making the Same", Inventors: P.Smith, A.J. Heeger, F. Wudl, and J. Chiang (Filed October 5, 1987)

g. Patents Granted

None

h. Invited Presentations at Topical or Scientific/Technical Society Conferences

A.J. Heeger (Invited talks specifically focused on research carried out under this ONR Contract)

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STU Workshop on Conducting Polymers, Stockholm, Sweden, April 17-18, 1988

F. Wudl

International Conference on Synthetic Metals (ICSM '88), Santa Fe, NM, June, 1988

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N. Basescu

International Conference on Synthetic Metals (ICSM '88), Santa Fe, NM, June, 1988

P. Smith

International Conference on Synthetic Metals (ICSM '88), Santa Fe, NM, June, 1988

Y. H. Kim

Brookhaven Symposium on Conducting Polymers, Brookhaven National Laboratory, October, 1987

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Soluble Substituted-PPV Conducting Polymers: Spectroscopic Studies, S. H. Askari, S.D. Rughooputh and F. Wudl

j. Honors/Awards/Prizes

NONE

k. Number of Graduate Students Receiving Full or Partial Support on ONR Contract

Ten (10)

l. Number of Postdoctoral Fellows Receiving Full or Partial Support on ONR Contract

Six (6)

PART II

a. Principal Investigators
Professor Alan J. Heeger, Professor Fred Wudl, and Professor Paul Smith

b. Cognizent ONR Scientific Officer
Dr. K. Wynne/ Dr. J. Milliken

c. Current Telephone Number
(805) 961-3184

d.Brief (100-200) description of project
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e. Significant Results During the Last Year
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We discovered a novel route for fabricating continuous fibers and films of polyacetylene. Although initially applied to polyacetylene, the methods are general, and can be used to process other so-called "intractable (conductive) polymers in pre-shaped carrier gels. Specifically, the technique involves in-situ polymerization in gel fibers containing 2% ultra-high molecular weight polyethylene. The composite polyacetylene/polyethylene fibers produced comprised up to 82% of polyacetylene; they exhibited electrical conductivities of 1,200 S/cm and 6000 S/cm. respectively for the as-polymerized and 2.2X drawn monofilaments.

f. Brief (100-200 words) summary of plans for next years work
Emphasis will be on the synthesis, characterization, processing and physical properties of polymers from the class of which poly(phenylenevinylene) is the prototype. This includes di-alkoxy

substituted (on the benzene ring) PPV derivatives, which are both more stable and have a smaller energy gap than the parent material. In addition we will work on th eanalogous family based on poly(thienylenevinylene). Initial goals will be to synthesize selected materials in sufficient quantity to allow a full range of characterization, rheological studies, and processing. Our plan is to continue to push toward high quality, chain-oriented materials in order to attempt to explore intrinsic properties.

g. List of names of graduate students and post-doctorals currently (i.e. June, 1988) working on project.

Graduate Students

C. Foster
Y. Moon
R. Souto-Maior
D. Spiegel
G. Yu

Post-doctoral Researchers

D. Moses
Y. Cao
S. Askari
Y.Kim
A. O. Patil
A. N. Patil

h. Technical Reports submitted to ONR during the year

1. Optical Properties of Conducting Polymers, A. O. Patil, A.J. Heeger and F. Wudl

2. Polarons and Bipolarons on a Conducting Polymer in Solution

Reports on the rest of the publications are in preparation.

Office of Naval Research
End-Of-The-Year Report
October 1, 1987

Publications/Patents/Presentations/Honors/Students Report

for

Contract N00014-83-K-0450

"Program for Research on Conducting Polymers"

Principal Investigators
Alan J. Heeger
Fred Wudl

Institute for Polymers and Organic Solids
University of California
Santa Barbara, CA 93106

a. Papers Submitted to Refereed Journals (not yet published)

"Intrinsic Conductivity of Conducting Polymers", S. Kivelson and A. J. Heeger (submitted to Syn. Metals).

b. Papers Published in Refereed Journals

"Chromism of Soluble Polythienylenes", S.D.D.V. Rughooputh, S. Hotta, A. J. Heeger and F. Wudl, J. Polym. Sci. Part B. Polymer Phys. Vol. 25, 1071 (1987).

"Polarons and Bipolarons on a Conducting Polymer in Solution", M. J. Nowak, S.D.D.V. Rughooputh, S. Hotta and A. J. Heeger, Macromol., Vol 20, 965 (1987).

"Semiconducting Polymers: Fast Response Non-Linear Optical Materials", A. J. Heeger, D. Moses and M. Sinclair, Syn. Metals, Vol. 15, 95 (1986).

"X-ray Scattering from Sodium Doped Polyacetylene: Incommensurate-Commensurate and Order-Disorder Transformations", M. Winokur, Y.B. Moon, A. J. Heeger, J. Barker, D. C. Bott and H. Shirakawa, Phys. Rev. Letters, Vol. 58, 2329 (1987).

"Soluble Conducting Polymers: The Poly(3-Alkylthienylenes), S.D.D.V. Rughooputh, M. Nowak, S. Hotta, A. J. Heeger and F. Wudl, Makromol. Chem., Macromol. Symp 8, 171 (1987).

"Polarons and Bipolarons on a Conducting Polymer in Solution", M. J. Nowak, S.D.D.V. Rughooputh, S. Hotta and A. J. Heeger, Macromol., Vol. 20, 965 (1987).

c. Books (and sections thereof) Submitted for Publication

None

d. Books (and sections thereof) Published

"Polyacetylene, (CH_x): New Concepts and New Phenomena, A. J. Heeger, Handbook of Conducting Polymers, Vol. 2, ed. T. Skotheim (Marcel-Dekker, N.Y., 1986), p. 729.Q.

"Electrically Conducting Polymers, A. J. Heeger and A. G. MacDiarmid, in Encyclopedia of Materials Science and Engineering, ed. Michael B. Bever (Pergamon Press, Oxford, 1986) p. 1399.

"Nonlinear Excitations and Nonlinear Phenomena in Conductive Polymers, A. J. Heeger, D. Moses and M. Sinclair, in Polymers for High Technology - Electronics and Photonics, ACS Symposium Series 346, ed. M.

J. Bowden and S. R. Turner (Amer. Chem. Soc., Washington, D.C., 1986) p. 372.

e. Technical Reports Published and Papers Published in Non-Refereed Journals

None

f. Patents Filed

"Fibers and Tapes of 'Intractable' Conducting Polymers"

g. Patents Granted

None

h. Invited Presentation at Topical or Scientific/Technical Society

A. J. Heeger

International Workshop, "Electrochemistry of Polymer Layers, Duisberg, Germany (September 1986)

Novel Microstructures Program Annual Review, Naval Research Laboratory, Arlington, Virginia (October 1986)

Seminar, University of Houston, Houston, Texas (November 1986)

Seminar, University of California, Riverside (November 1986

Materials Research Society, Boston (December 1986)

Seminar, IBM Almaden Research Laboratory, San Jose, California (January 1987)

American Chemical Society meeting, Denver, Colorado (April 1987)

International Symposium of Electrical Interactions in Complex Fluids, Colmar, France (June 1987)

Adriatico Research Conference on "One-Dimensional Organic Conductors: Chemistry, Physics and Applications" (June 1987)

Adriatico Research Conference on "High Temperature Superconductors" (July 1987)

F. Wudl

Novel Microstructures Program Annual Review, Naval Research Laboratory, Arlington, Virginia (October 1986)

Seminar, University of California, Berkeley (October 1986)

American Chemical Society meeting, Louisville, Kentucky (November 1986)

Seminar, University of California, Los Angeles (February 1987)

Seminar, University of Minnesota, (March 1987)

Seminar, University of North Dakota (March 1987)

Invited Talk, American Chemical Society meeting, Denver, Colorado (April 1987)

Seminar, University of Wyoming (April 1987)

Seminar, University of Idaho (April 1987)

Seminar, Exxon Research and Engineering Co., Annandale, New Jersey (June 1987)

Invited Talk, First International Conference on Heteroatom Chemistry, Kobe, Japan

i. Contributed Presentations at Topical or Scientific/Technical Society Meetings

A. J. Heeger

American Physical Society meeting, New York (March 1987)

American Chemical Society meeting, Denver, Colorado (March 1987)

F. Wudl

American Physical Society meeting, New York, N.Y. (March 1987)

American Chemical Society meeting, Denver, Colorado (April 1987)

j Honors/Awards/Prizes

None

k. Number of Graduate Students Receiving Full or Partial Support on ONR Contract - 4

N. Basescu
Y. B. Moon
H. Schaffer
D. Spiegel

l. Number of Postdoctoral Fellows Receiving Full or Partial Support on ONR Contract - 4

R. Friend
Y. H. Kim
Z. X. Liu
M. Winokur

Assistant Research Physicist

D. Moses

Part II

a) Principal Investigator: Alan J. Heeger
Co-Investigator: Fred Wudl

b) Cognizant ONR Scientific Officer: Dr. Kenneth Wynne

c) Current Telephone No.: (805) 961-3184)

d) Brief (100-200 words) description of project

This broad-based **Program on Conducting Polymers** is an interdisciplinary effort with roots in chemistry, physics and polymer science, and it involves a back-and-forth interpaly between the various components. Within the Institute for Polymers and Organic Solids at UCSB we have assembled a large and high quality group of graduate research students, post-doctoral researchers, technicians and Visiting Scientists working in close collaboration across these three sub-areas. The addition of the POLYMER PROCESSING effort to this program represents a major departure and a major development. To our knowlledge, we are the only academic research effort in the world which spans the full range required for continued progress in this area: --- SYNTHESIS---PHYSICAL MEASUREMENTS---POLYMER PROCESSING. Within the Institute for Polymers and Organic Solids at UCSB, we have assembled the broad base of facilities, equipment and personnel needed to carry out such a program. We are confident that this research program will lead to significant progress in the important emerging field of conducting polymers.

e) Significant results during last year (50-100 words)

We have made major progress in the synthesis, physical properties and processing of conducting polymers. We have reported electrical conductivities for polyacetylene in excess of 20,000 S/cm, and made initial progress toward identifying the intrinsic limits for the conductivity of conductive polymers. We have completed a major study of the polymer science of the soluble poly(3-alkylthiophenes) which demonstrates that these polymers can be processed, and that the concepts developed for conducting polymers in the solid state (solitons, polarons and bipolarons, etc) are applicable to conjugated polymers in solution. . The results open the way to processing this class of conjugated polymers.

f) Brief (100-200 words) summary of plans for next year's work

The main thrust of the Program of Research on Conducting Polymers for next year is to develop routes toward highly oriented fibers or films of conducting polymers.

Professor Fred Wudl and his group will synthesize the conjugated polymers for solid state structure engineering;

Professor Paul Smith and his group apply their facilities and expertise for polymer processing to the solid state structure engineering of conducting polymers;

Professor A.J. Heeger and his group will evaluate the physical porperties of the resulting polymers through a broad base of physical measurements.

Truly macromolecular materials are required for the production of very highly ordered conducting polymers. Of the many existing conducting polymer systems, we intend to initially focus on two particularly attractive systems: Polyacetylene (PA) and polyphenylenevinylene (PPV). Although PA is considered intractable, the remakable properties demand an effort directed to further improvements (lower defect density and higher degrees of orientation) toward the achievement of intrinsic properties. PPV is tractable (through the pre-polymer) and thus a particularly attractive focal point for our future research.

g) List of names of graduate students and postdoctorals currently working on project: 4

N. Basescu
Y. B. Moon
D. Spiegel
Y. M. Kim
D. Moses, Assistant Research Physicist

h) Technical reports submitted to ONR during the past year: 7

SEMI-ANNUAL REPORT

"Program for Research on Conducting Polymers"

November 1, 1986

N00014-83-K-0450

Office of Naval Research

Principal Investigators:

F. Wudl and A. J. Heeger
Department of Physics
and
Institute for Polymers and Organic Solids
University of California
Santa Barbara, CA 93106

(805)961-3184

Funding

May 1, 1986 - April 30, 1987	$105,000
May 1, 1987 - April 30, 1988	$110,000
May 1, 1988 - April 30, 1989	$130,000

1. Description of Project

This research program consists of a parallel effort directed toward the synthesis of conjugated polymers and the characterization of the polymers through a broad base of physical measurements. The approach involves step-by-step synthesis of new polymer systems using specific synthetic techniques, i.e., the design and synthesis of new conducting polymers. This involves close interaction between chemists and physicists and a constant back-and-forth interplay to characterize new materials and stimulate ideas on new systems. Continuing studies of the chemisty and physics of known conducting polymers is a critical part of the program, since future progress is limited by an in-depth understanding of successful known systems. Recent efforts in the latter area focused on the polyheterocycle, poly(thiophene), with particular emphasis on the soluble poly(3-alkylthienylenes).

2. Significant Results During Period Since Last Report

a. Spectroscopic Studies of Soluble Poly(3-alkylthienylenes)

We demonstrated that the conjugated poly(3-alkylthienylenes) can be processed from solution and subsequently used as semiconducting and metallic polymers. These polymers were synthesized by electrochemical polymerization and characterized using high pressure liquid chromatography (HPLC) and infrared (IR) spectroscopy. The HPLC data indicate a mean (weight averaged) molecular weight of about 48,000, i.e., approximately 300 monomer units. The IR spectra show that these soluble polythienylenes have a well-defined molecular structure; the data are completely consistent with linear chains of poly(3-alkyl-2,5-thineylene). Both as-synthesized and solution-cast films can be readily doped with resulting electrical conductivities which are quite high, for example, $\sigma \approx 40$ S/cm for films of poly(butylthienylene).

UV-Visible absorption spectra of these soluble polythienylenes have been obtained for solid films (as-synthesized and solution-case) and for the polymers in solution. The spectral characteristics of the solution cast films are essentially identical to those of the as-synthesized films both in the neutral state and after doping (Macromolecules, in press).

b. Chromism of Soluble Polythienylenes

Thermochromism and solvatochromism of solutions of poly(3-alkylthienylenes) were reported. The experimental results indicate the presence of two coexisting phases: polymer in solution and polymer in microcrystalline aggregates. From the concentration independence of the thermochromism, it is concluded that the transition is fundamentally driven by a single chain mechanism, and that the aggregation (microcrystallization) of the poly(3-alkylthienylene) macromolecules can occur only after the single chain conformational change has occurred (J. Poly. Sci. In press).

c. Polarons and Bipolarons on a Conducting Polymer in Solution

Electron spin resonance (ESR) measurements and spectroscopic studies have been carried out on the soluble conducting polymer, poly(3-hexylthienylene), doped in solution with $(NO)^+(PF_6)^-$. From the ESR and spectroscopic data, we have determined the nature of the charge storage configurations as a function of doping level and as a function of doped polymer concentration. The results indicate that the spinless bipolaron is the lowest energy charge storage configuration on single poly(3-hexylthienylene) macromolecules in dilute solution. Polarons are formed either as a result of an odd number of charges on a single polymer chain or as a result of interchain interactions (in the semi-dilute regime).

d. Soluble Conducting Polymers: The Poly(3-alkylthienylenes)

The conjugated poly(3-alkylthienylenes) can be processed from solution and subsequently used as semiconducting and metallic polymers. Both as-synthesized and solution-cast films can be readily doped with resulting electrical conductivities which are quite high: σ – 30-100 S/cm. UV-visible absorption spectra of the neutral and doped forms have been obtained for solid films (as-synthesized and solution-cast) and for the polymers in solution. Excitation into the π-π^* transition (peak at $\approx$ 2.8 eV) leads to photoluminescence (peak at 2.16 eV). The Stokes' shift is concistent with radiative decay from photogenerated neutral bipolarons (exciton-polarons). From electron spin resonance measurements and spectroscopic data on the doped polymer in solution, we have determined the nature of the charge storage configurations (Synthetic Metals, In press).

e. Measurement of the Third Order Susceptibility of Trans-Polyacetylene by Third Harmonic Generation

We have reported a measurement of the third order nonlinear optical susceptibility of trans-polyacetylene by third harmonic generation in thin films. The measured susceptibility is $\chi^{(3)}(3\omega = \omega + \omega + \omega) = 4 \times 10^{-10}$ esu which is comparable to the magnitude of the large nonlinear susceptibilities measured in the polydiacetylenes.

f. Picosecond Photoconductivity of Trans-Polyacetylene

Fast transient photoconductivity measurements of trans-polyacetylene as a function of temperature and photon energy indicate a relatively high quantum efficiency for the photoproduction of mobile, charged, nonlinear

excitations. Excitation by a 20 ps pulse at 590 nm with 10^{15} photons/cm^2 results in a transient photoconductivity of ~ 0.3 S/cm (at 50 ps) with time scale for decay similar to that measured in picosecond photoinduced absorption experiments. The temperature independence of the fast photoconductivity is interpreted in terms of the photoproduction of "hot" soliton excitations (Solid State Comm. 59, 343, 1986; a copy is attached).

g. Infrared Activity of Photoexcitations in Polythiophene

A careful measurement of the photinduced infrared absorption of polythiophene is reported. The observation of new spectral features below the noise level of previous doping and photogeneration experiments provides evidence for weakly infrared active bipolaron shape oscillations predicted by recent calculations based on the continuum model for conjugated polymers. In addition, four new photoinduced absorptions, not described by existing theories for defect vibrations, demonstrate the coupling of photogenerated charged nonlinear excitations to ring vibrations of the aromatic thiophene monomer (Solid State. Comm. 59, 415, 1986; a copy is attached).

h. Alkali Metal Vapor Phase Doping of Polyacetylene

A vapor phase doping process of polyacetylene by alkali metals was discovered. The existence of a threshold temperature and nucleation characterize the doping as an intercalation process. The transport and optical properties imply a high intrinsic conductivity (Solid State Commun. 58, 535, 1986; a copy is attached).

i. Phenyl-Capped Octaaniline (COA): An Excellent Model for Polyaniline

Phenyl-capped octaaniline (COA) was prepared by a decarboxylative condensation reaction between tetraaniline and 2,5-dihydroxy-3,6-dihydroterephthalic acid. The fully reduced state is a white solid, the intermediate oxication state with two quinonediimines and five phenylenediamines (B_5Q_2) in the backbone is a blue solid which exhibits all the properties ascribed to polyaniline ("emeraldine base") and the fully oxidized state (all quinoneimine) is a magenta colored solid. Protonation of B_5Q_2 produces a green solid whose room temperature conductivity is ~ 1 Scm^{-1} (J. Am. Chem. Soc. In press).

j. Poly-p-Phenyleneamineimine: Synthesis and Comparison to Polyaniline

Poly-p-phenyleneamineimine (PPAI) was prepared by a decarboxylative condensation reaction between p-phenylene-diamine and 2,5-dihydroxy-3,6-dihydroterephthalic acid. PPAI was found to be essentially idential to polyaniline (PANI) by ir, UV-vis and ESR spectroscopies. Brönsted and doping comparative studies with spectroscopy, electron spin resonance, magnetic susceptibility, conductivity and thermopower allowed us to completely describe the charge storage and transport in PANI (PPAI). Spin is generated upon protonation via an unusual proton-induced spin unjoining mechanism and transport is dominated by an interchain hopping mechanism. Therefore, althouogh PANI (when protonated) is a good conductor, it is not truly metallic (J. Am. Chem. Soc. submitted).

3. Plans for Next Year's Work

a. We will focus on the soluble poly(3-alkylthienylenes) with emphasis on exploiting their solubility and processibility. Blends and/or composites with compatible soluble saturated polymers (e.g., polystyrene) will be explored.

b. We will initiate a program directed toward conducting gels based on cross-linked poly 3ATs.

c. We will complete our in-situ studies of the evolution of the structure of Na-doped polyacetylene.

d. Synthesis plans will focus on the continuing efforts in polyacenes as well as extension of our synthesis of poly-p-phenyleneamines. Preliminary results indicate that fluorenediamine, benzidine, o-phenylenediamine, m-phenylenediamine and p,p' stilbenediamine produce polymers with 2,5-dihydroxy-3,6-dihydroterephthalic acid.

4. Faculty, Graduate Students and Postdoctoral Researchers on this Project During Report Period (May, 1986 - October, 1986

Faculty

Alan J. Heeger

Graduate Students

David Braun

Young Bin Moon

Howard Schaffer

Daniel Spiegel

Postdoctoral Researchers

Young Hoon Kim

Michael Winokur

Solid State Communications, Vol.59,No.7, pp.415-421, 1986.
Printed in Great Britain.

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Infrared Activity of Photoexcitations in Polythiophene

H. E. Schaffer and A. J. Heeger
Physics Department and Institute for Polymers and Organic Solids
University of California, Santa Barbara, CA 93106

(Received 4 April 1986 by A. A. Maradudin)

A careful measurement of the photoinduced infrared absorption of polythiophene is reported. The observation of new spectral features below the noise level of previous doping and photogeneration experiments provides evidence for weakly infrared active bipolaron shape oscillations predicted by recent calculations based on the continuum model for conjugated polymers. In addition, four new photoinduced absorptions, not described by existing theories for defect vibrations, demonstrate the coupling of photogenerated charged nonlinear excitations to ring vibrations of the aromatic thiophene monomer.

A. Introduction

The observation of photoinduced infrared absorption in the simplest conjugated polymer *trans*-polyacetylene, $(CH)_x$, has been crucial in providing a characterization of photoexcited states in this model system. The initial observation of three photogenerated infrared active vibrations (IRAV),[1,2] in one-to-one correspondence to those generated by either oxidative or reductive doping of the polymer, in conjunction with the absence of spin upon photoexcitation as seen in light-induced ESR experiments,[3] allowed an identification of the photoexcited states as spinless charged solitons, which were initially discussed in the theory of Su, Schrieffer and Heeger (SSH).[4] The IRAV spectrum as well as the Raman spectrum were both successfully explained by the "amplitude mode" (AM) formalism due to Horovitz.[5,6] Beginning with the continuum version of the SSH model,[7] this approach accounted for the observed one-to-one correspondence in the number of Raman frequencies and IRAV as well as for the difference in frequencies between doping-generated and photogenerated IRAV via the properties of the phonon response function. The key point in this treatment is that it accounted for the coupling of lattice vibrations to electronic excitations through the dependence of the electronic energy upon the amplitude of the Peierls dimerization of the carbon backbone implicit in the SSH model: hence, the term "amplitude modes".

Trans-polyacetylene is unique among semiconducting polymers in that it has a doubly degenerate ground state and thus may, in principal, have amplitude kink solitons as stable excitations. There are, however, numerous other polymers, for example, polythiophene, polypyrrole, and polyisothionaphthene, which can be doped and which exhibit optical and transport properties comparable to those of polyacetylene, but do not have a degenerate ground state and thus would not be expected to exhibit solitons as stable excitations. Rather, either polarons or bipolarons, both localized excitations which allow the chain segments on both sides of them to remain in the lower energy configuration, would be expected. The most obvious conjugated system to be probed for such excitations, the *cis*-isomer of polyacetylene, is amenable neither to doping nor to photogeneration experiments: doping isomerizes samples to *trans*-form, and optical pumping experiments have demonstrated an absence of photogenerated IRAV.[2]

Polythiophene (PT), a polymer in which the structure of cis-polyacetylene is locked in by a bridging sulfur atom, has been the subject of several recent studies. Both doping[8] and photogeneration experiments[9-11] have shown two

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PICOSECOND PHOTOCONDUCTIVITY IN TRANS-POLYACETYLENE

M. Sinclair, D. Moses, and A.J. Heeger
Institute for Polymers and Organic Solids
and
Department of Physics
University of California, Santa Barbara
Santa Barbara, California 93106

(Received 5 May 1986 by A. A. Maradudin)

Abstract

Fast transient photoconductivity measurements of trans- polyacetylene as a function of temperature and photon energy indicate a relatively high quantum efficiency for the photoproducton of mobile, charged, nonlinear excitations. Excitation by a 20ps pulse at 590nm with 10^{15} photons/cm^2 results in a transient photoconductivity of ≈0.3 S/cm (at 50 ps) with time scale for decay similar to that measured in picosecond photoinduced absorption experiments. The temperature independence of the fast photoconductivity is interpreted in terms of the photoproduction of "hot" soliton excitations.

The possible role of solitons as nonlinear photoexcitations in polyacetylene has received considerable attention[1-4] subsequent to the work of Su and Schrieffer[5], who demonstrated that an electron-hole pair evolves into a soliton-antisoliton pair within 0.1 ps after injection onto an isolated trans-$(CH)_x$ chain. Even though their calculation was based on the simple SSH model[6], their predictions were qualitatively confirmed through the experimental observation of the characteristic spectral signatures of solitons in photoinduced absorption[1-4]. Transient photoinduced absorption measurements[1,2] showed the existence of nonlinear shifts in oscillator strength associated with mobile photoexcitations on the time scale predicted by Su and Schrieffer[5]. The one-to-one correspondence[3] between the photoinduced infrared absorptions[3,4] associated with charged[3,4], spinless[7], photoexcitations and the similar features which appear on charge transfer doping indicate the photogeneration of charged solitons.

Orenstein et al[8] questioned the importance of the Su-Schrieffer mechanism and argued that the dominant initial response is the formation of a neutral exciton. In their model, charged solitons are formed only as a by-product after diffusion of a few charged polarons (which result from electrons and holes initially excited on different chains) to the neutral soliton defects already present in the sample. Although the implied decrease in the number of spins was not observed in light induced ESR experiments[7], there is no information on the charged vs neutral excitation branching ratio in the picosecond time regime.

In this letter, we present the results of a comprehensive set of measurements of transient photoconductivity in trans-$(CH)_x$. Excitation by a 20 ps pulse at 590 nm with 10^{15} photons/cm^2 results in a transient conductivity of ≈ 0.3 S/cm (at 50 ps), indicative of a relatively high initial quantum efficiency for the fast photoproduction of mobile charged excitations. These mobile charge carriers are produced within picoseconds, consistent with the Su-Schrieffer mechanism. We find that in the sub-nanosecond regime, the photoconductivity and photoinduced absorption are fully consistent; the time decay of the two are similar, and both are essentially temperature (T) independent. We interpret the large, T-independent, picosecond photoconductivity in

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ALKALI VAPOR PHASE DOPING OF POLYACETYLENE

D. Moses, N. Colaneri and A. J. Heeger
Department of Physics
and
Institute for Polymers and Organic Solids
University of California
Santa Barbara, CA 93106

(Received 10 February 1986 by A. A. Maradudin)

We have discovered a vapor phase doping process of polyacetylene by alkali metals. The existence of a threshold temperature and nucleation characterize the doping as an intercalation process. The transport and optical properties, as obtained by dc conductivity and photoabsorption studies, imply a high intrinsic conductivity.

One of the outstanding features of graphite, a material which has been studied for many decades, is the existence of well-defined intercalation compounds. Alkali-metal atoms (as well as a variety of oxidizing molecules) can be inserted into the graphite lattice by exposing it to the vapor of the intercalant.[1] These guest atoms exhibit planar ordering between the planes of the carbon atoms in the host material. The graphite intercalation compounds can be ordered in various lattice structures or, as they are called, stages. The electrical properties of the graphite intercalation compounds can be controlled by both the choice of the specific intercalant species and the degree of staging.

Conducting polymers such as polyacetylene can be doped chemically or electrochemically through oxidation (p-type) or reduction (n-type) of the polymer.[2] N-type doping with alkali ions as dopants has been achieved either chemically by dipping the polymer into a solution in which the appropriate salt (e.g., Na^+-Naphth$^-$) containing the alkali metal ions has been dissolved, or electrochemically by using the polymer as an electrode in an electrochemical cell.

We have discovered that polyacetylene can be n-type doped (i.e. reduced) by exposing it to an alkali-metal vapor. This process is especially interesting since recent electrochemical doping studies[3] have demonstrated a series of first-order phase transformations with associated counter ion ordering in specific structural phases of the alkali-metal complexes of polyacetylene. Hence, the formation of distinctive structural phases and the ability to dope $(CH)_x$ by alkali-metal vapor resemble, in many ways, the extensively investigated intercalation process in graphite.

The principal advantages of the vapor phase intercalation of $(CH)_x$ are the relative simplicity of the experimental doping procedure, the additional flexibility in controlling the process, the new possibilities that have been opened for investigating the doping mechanism and, most importantly, the improved metallic properties of the alkali-metal-polyacetylene complexes that have been found.

In the following, we describe the experimental preparations and doping procedures, and we present some initial results from studies of the optical and transport properties of the vapor phase alkali-metal intercalated polymers.

Experimental Procedures and Results

Two types of $(CH)_x$ samples were employed: thin transparent films (about 2000 Å) grown on glass substrates for the optical absorption studies

SEMI-ANNUAL REPORT

"Program for Research on Conducting Polymers"

November 1, 1985

N00014-83-K-0450

Office of Naval Research

Principal Investigators

F. Wudl and A. J. Heeger
Department of Physics
and
Institute for Polymers and Organic Solids
University of California
Santa Barbara, CA 93106

(805)961-3184

Funding

May 1, 1983 - April 30, 1984	$94,000
May 1, 1984 - April 30, 1985	96,000
May 1, 1985 - April 30, 1986	98,000

1. Description of Project

This research program consists of a parallel effort directed toward the synthesis of conjugated polymers and the characterization of these polymers through a broad base of physical measurements. The approach involves step-by-step synthesis of new polymer systems using specific synthetic techniques, i.e., the design and synthesis of new conducting polymers. This involves close interaction between chemists and physicists and a constant back-and-forth interplay to characterize new materials and stimulate ideas on new systems. Continuing studies of the chemistry and physics of known conducting polymers is a critical part of the program, since future progress is limited by an in-depth understanding of successful known systems. Recent efforts in the latter area focused on the polyheterocycle, poly(thiophene).

2. Significant Results During Period Since Last Report (May, 1985 - October, 1985)

a. X-Ray Scattering from Polythiophene: Crystallinity and Crystallographic Structure

X-ray scattering has been used to investigate the crystallinity and crystal structure of chemically coupled polythiophene. Heat treatment at elevated temperatures leads to significant increases in crystallinity (from ~ 35% as synthesized up to ~ 56% after annealing at 380 °C for 30 min) and coherence length indicative of chain growth and extension. Chemical analysis of the chain-extended polythiophene shows a major reduction in residual iodine content consistent with growth of the polymer chains to approximately 1200 thiophene rings. An initial model of the crystal structure of polythiophene is presented (Macromolecules 18, No. 10, 1985).

b. First-Order Transition to a Metallic State in Polyacetylene: A Strong-Coupling Polaronic Metal

We developed a novel theory of the first-order transition to the metallic state in polyacetylene in terms of a crossover from a lattice of charged solitons to a regular array of polaronlike distortions. The polaronic metal is shown to have a strong indirect attractive interaction, $U^* \simeq -2\Delta/3$, between electrons in the half-filled, narrow, polaron subband with the Peierls energy gap ($E_g = 2\Delta$) (Phys. Rev. Lett. 55, 308 (1985)).

c. Charge Storage in Conducting Polymers: Solitons, Polarons and Bipolarons

The results of a series of experiments demonstrate that solitons are the important excitations in trans-$(CH)_x$ and that the properties of these nonlinear excitations can be directly studied during photoexcitation or after doping. The importance of these concepts in the more general context of conducting polymers is addressed. Although the two-fold degenerate ground state of trans-$(CH)_x$ is quite special, the relevant concepts have been generalized to confined soliton pairs (bipolarons). Experimental results which demonstrate electron-hole symmetry and weak confinement in poly(thiophene) make this polyheterocycle a nearly ideal example of a model system in which the ground state degeneracy has been lifted. In the dilute doping regime, in-situ absorption spectroscopy data (during electrochemical doping) are in detailed agreement with charge storage via bipolarons with confinement parameter $\gamma \simeq 0.1 - 0.2$. These results on polythiophene demonstrate that a quantitative fundamental understanding is possible even for relatively complex systems (Polymer, 17, 201 (1985)).

d. Photogeneration of Confined Soliton Pairs (Bipolarons) in Polythiophene

From photoinduced absorption and light induced electron spin resonance, we demonstrated that the dominant photocarriers generated in polythiophene with excitation above the energy gap (E_g) are charged bipolarons (spin zero). The observation of bipolarons ($B^{2\pm}$) rather than polarons ($P^{\pm}$) as the dominant photoexcitations proves that the Coulomb contribution to the bipolaron energy (U_B) is sufficiently small that $P^{\pm} + P^{\pm} \rightarrow B^{\pm 2}$. From the analysis of the spectra, we find $(U_B/E_g) \approx 0.12$ (Phys. Rev. Lett. submitted).

e. Semiconducting Polymers: Fast Response Nonlinear Optical Materials

We have demonstrated that semiconductor polymers such as polyacetylene and polythiophene exhibit nonlinear optical processes (photo-induced absorption, photo-induced bleaching and photo-luminescence) with characteristic time scales in the picosecond range or faster. These phenomena are intrinsic and originate from the instability of these conjugated polymers toward structural distortion. The major shifts in oscillator strength due to photoexcitation of solitons, polarons and bipolarons lead to relatively large third-order nonlinear optical processes ($\chi^{(3)}$) on time scales of order 10^{-13} seconds. Largely overlooked in earlier analyses, we believe these novel photoexcitations are key to understanding the nonlinear optical properties of this growing class of semiconducting (conjugated) polymers (Comments on Solid State Physics, in press).

3. Plans for Next Year's Work

a) We will continue our research directed toward development of semiconducting polymers as <u>fast</u> electronic materials and <u>fast</u> nonlinear

optical materials. Initial experiments will focus on picosecond photoconductivity and on picosecond photoinduced absorption and picosecond photoinduced bleaching.

b) We will initiate structural studies on polyacetylene in-situ in an electrochemical cell during electrochemical doping. We will use oriented material obtained by the Durham method and by the Shirakawa method.

c) We will carry out detailed studies of the poly(3-methyl-thiophene) system as a function of doping.

d) Synthesis efforts will focus on poly(paraphenylene-amine), i.e., the polyaniline family and related systems. These plans are outlined in detail in our renewal proposal recently submitted to ONR.

4. Graduate Students and Postdoctoral Researchers on this Project During Report Period (May, 1985 - October, 1985

Graduate Students

H. Schaffer	Research Assistant	6 mos @ 50% time
M. Sinclair	Research Assistant	6 mos @ 50% time
Z. Liu	Postgraduate Research Physicist	2 mos @ 30% time

Postdoctoral Researchers

K. Lim	Assistant Research Physicist	3 mos @ avg. 67% time
M. Winokur	Visiting Postdocoral Research Physicists	2 mos @ 50% time

Faculty

A. J. Heeger	Principal Investigator	2 mos @ 50% time

Description of Project

This research program consists of a parallel effort directed toward the synthesis of conjugated polymers and the characterization of these polymers through a broad base of physical measurements. The approach involves step-by-step synthesis of new polymer systems using specific synthetic techniques; i.e. the design and synthesis of new conducting polymers. This involves close interaction between chemists and physicists and a constant back-and-forth interplay to characterize new materials and stimulate ideas on new systems.

Continuing studies of the chemistry and physics of known conducting polymers is a critical part of the program, since future progress is limited by an in-depth understanding of successful known systems. Recent efforts in the latter area focused on the polyheterocycle, poly(thiophene).

"Program for Research on Conducting Polymers" End-of-Year Report

mailed June 1, 1984

(May 1, 1983 to April 30, 1984)

N00014-83-K-0450
Office of Naval Research

Principal Investigators: Drs. A. J. Heeger and Fred Wudl
Department of Physics
University of California, Santa Barbara
Santa Barbara, California 93106
Telephone: (805) 961-2001

Effective Dates of Contract: May 1, 1983 through April 31, 1984: $94,000

✓

Significant Results During the Period May 1, 1983 - April 30, 1984

A. Studies of the Chemistry and Physics of Poly(thiophene)

Using a new method of electrochemical polymerization of poly(thiophene) from dithiophene as the starting material, we obtain a high quality film with a sharp interband absorption edge. An *in situ* study of the absorption spectrum during the electrochemical doping process has been carried out. In the dilute regime, the results are in detailed agreement with charge storage via bipolarons; weakly confined soliton pairs with confinement parameter $\gamma \sim 0.1$-0.2. At the highest doping levels, the data are characteristic of the free carrier absorption expected for a metal. From a parallel electrochemical voltage spectroscopy (EVS) study, we find evidence of charge injection near the band edge and charge removal from the bipolaron gap states. In the dilute regime, the position of the chemical potential is consistent with charge storage in weakly confined bipolarons.

Extensive earlier studies of polyacetylene have demonstrated that the coupling of electronic excitations to nonlinear conformational changes is an intrinsic and important feature of conducting polymers. Although this coupling and the degenerate ground state lead to the novel soliton excitations

in trans-$(CH)_x$, generalization of these concepts and application to the larger class of conjugated polymers has been an obvious goal of the field. The experimental evidence of electron-hole symmetry and weak confinement in polythiophene (carried out in this grant period) makes this polymer a nearly ideal example of a model system in which the ground state degeneracy has been lifted. The study of bipolarons (or confined charged solitons) in poly(thiophene) has now demonstrated that the concepts carry over in detail and that a quantitative understanding of the resulting phenomena is possible even for relatively complex systems.

B. Synthesis of New Conducting Polymers

a. Poly-ynes

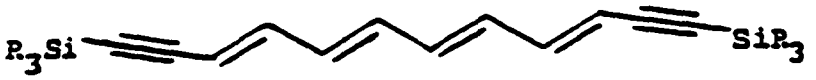
We prepared a number of precursors for the preparation of poly-ynes. These are $(CH_3)_3SiC{\equiv}CC{\equiv}CSi(CH_3)_3$ (1), $(CH_3)_3SiC{\equiv}CC{\equiv}CH$ (2), 1,6-bistrimethylsilylhex-1,5-diyne-3-ene(3) and hex-1,5-diyne-3-ene (4).

Attempts to prepare polyynes using traditional chemistry (Ullman coupling) on either acetylene, butadiyne, or 3 and 4, above, have produced polymers which are heavily contaminated with copper. These polymers are blue-black and exhibit infrared spectroscopy commensurate with a structure containing C=C (for material derived from 3 and 4, above) and C≡C bonds (for material derived from all monomers). Unfortunately the copper is tenaciously entrained in these materials so that new approaches to couple sp hybridized carbons are currently being

explored (see below).

b. Mixed Polyenes.

We have succeeded in the preparation of $(CH_3)_3SiC{\equiv}C(CH{=}CH)_4C{\equiv}CSi(CH_3)_3$ (5) and found that the yields reported in the literature are not reproducible; it has therefore been taking us longer to build up enough of this compound to submit it to further reactions. This compound is an important step in our program. In connection with designing alternate methods for the preparation of all trans polyacetylene, we found that the tetraenediyne 6 could be made in one step by an existing literature procedure.



6

While interesting polyene-polydiynes could be prepared by removing the silyl groups and Ullman coupling, the resulting tetraenediyne, a much more interesting polymer , would result if one only mono-deprotected 6 and prepared the Ullman coupling product 7.

$$R_3Si\text{-}C{\equiv}C\text{-}CH{=}CH\text{-}_4C{\equiv}C\text{-}C{\equiv}C\text{-}CH{=}CH\text{-}_4C{\equiv}C\text{-}SiR_3 \rightleftharpoons [CH_2{=}CH(CH{=}CH)_nC{\equiv}C]_2$$

7

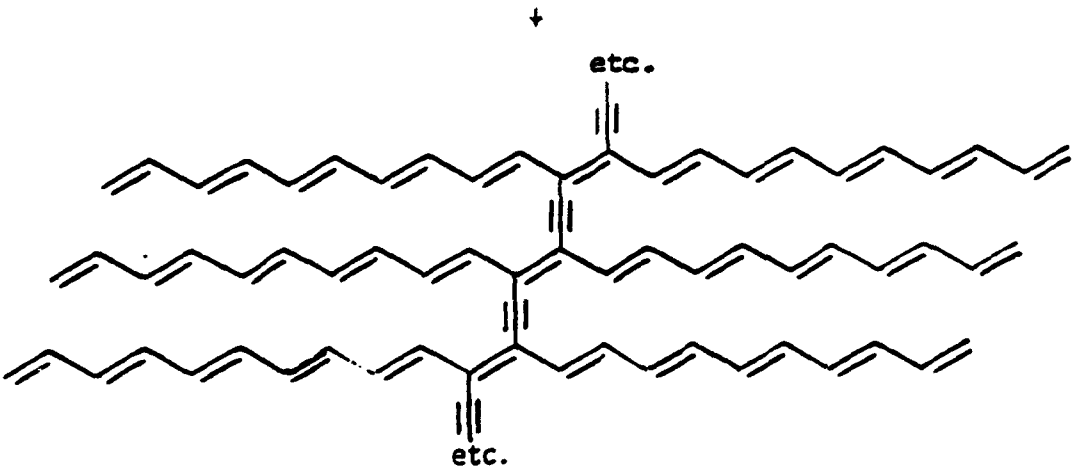
The polyene units could be extended with a little extra work on the end groups (hydrolysis, hydroboration, mercuration, lithiation and coupling with an alkene iodine via a cuprate).

Since diacetylenes polymerize in the solid state to form

crystalline polymers, monomer 7, its elongated derivative, or its deprotected, reduced product 8 would produce a polydiacetylene:

$$CH_2{=}CH(CH{=}CH)_4C{\equiv}C{-}C{\equiv}C{-}(CH{=}CH)_4CH{=}CH_2$$

8



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Recently, Planchetta et al. [Makromol. Chem., Rapid Commun. 3, 249 (1982)] have shown that RO C(O)-$(CH_2)_9$C≡C-C≡C-$(CH_2)_9$-OC(O)R polymerize under the usual conditions to form unusual polydiacetylenes of weight-average molecular weights from 8 X 10^5 to 1.3 X 10^6. Therefore, long chain appendages do not appear to interfere with the well-known Wegner-Baughman solid state polymerization reaction.

c. Polyannulenes.

This has been the most successful part of our new synthesis research so far. Through a collaboration with Professor Vogel (Koln) we have obtained 10g of methano[10]annulene and 500g

of isotetraline, a precursor to substituted methano[10]annulenes. We prepared precursors to polymers 10 and 11 (below) and very recently made a small amount of polymer 9 as well as the important dimer (bis methanoperylene) 12.

10a 10b 11

12

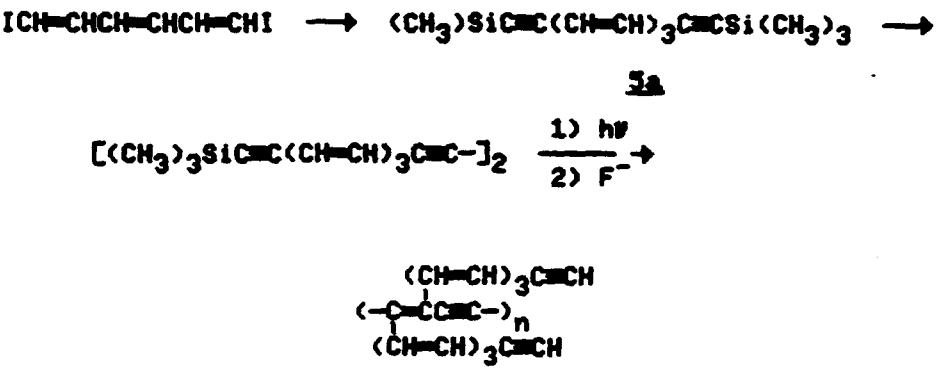
C. Plans for Next Year's Work

As implied above, there is a serious gap in synthetic organic chemical methodology for the formation of carbon-carbon bonds from sp hybridized precursors. We are, and will, study coupling reactions which are truly catalytic in added transition metal. The first attempts will involve Kumada-type chemistry using alkynyl Grignard reagents and iodoacetylenes. Preliminary results are encouraging. We have recently shown that alkynyl Grignard reagents can be coupled efficiently with alkenyl halides. This is an exciting result because it will allow us to prepare, for the first time the elusive "parent" (unsubstituted) polydiacetylene [(-CH=CH-C≡C-)$_n$].

In Scheme I, below is shown a new approach to the triene-

diyne (5a), an analog of 5, above.

Scheme I



13

This approach should allow us to pursue our attempts to prepare the intriguing crossconjugated polymer 13.

Physical measurements will support these synthetic efforts as well as continuing the current focus on the properties of carefully prepared poly(thiophene). High priority will be placed on an experimental attempt to detect photo-induced absorption in polythiophene in response to illumination by photons with $\hbar\omega > E_g$. If successful, this experiment should lead to the kind of definitive description of the photoexcitations that has been possible in polyacetylene using similar techniques (see Blanchet et al., Phys. Rev. Lett. 50, 1938 (1983); this paper was also supported by ONR during the previous grant period).

List of Reports, etc., for Period May 1, 1983 to April 30, 1984

Technical Report #1 "Charge Storage in Doped Poly(thiophene): Optical and Electrochemical Studies"

Dissertations: none

Publications: "Photoexcitations in <u>trans</u>-$(CH)_x$: A Fourier-Transform Infrared Study" by G. Blanchet, C. R. Fincher, T.-C. Chung and A. J. Heeger, Phys. Rev. Lett. <u>50</u>, 1938 (1983)

Manuscripts submitted: "Charge Storage in Doped Poly(thiophene): Optical and Electrochemical Studies" by T.-C. Chung, J. H. Kaufman, A. J. Heeger and F. Wudl, accepted for publication in Phys. Rev. B.

<u>Honors and Awards</u>

Professor A. J. Heeger received the 1983 Oliver P. Buckley Prize in Solid State Physics. Much of the research recognized by this award was supported by ONR.

Personnel Supported on this Contract During May 1, 1983 - April 30, 1984

Graduate Students

J. Chen (partial)

H. Schaffer (partial)

Postdoctorals

D. Moses (partial)

M. Boysel (partial)

Principal Investigators

A. J. Heeger (1/2 summer month)

F. Wudl (1/2 summer month)

REPORT OF INVENTIONS AND SU[illegible]ONTRACTS

(Pursuant to "Patent Rights" Contract Clause) (See [illegible]ctions on Reverse Side.)

[illegible] APPROVED
O[illegible] [illegible].0704-0016

1a. NAME OF CONTRACTOR/ SUBCONTRACTOR	c. CONTRACT NUMBER	2a. NAME OF GOVERNMENT PRIME CONTRACTOR	c. CONTRACT NUMBER	3. TYPE OF REPORT (check one)
Regents of University of California	N00014-83-K-0450	same as 1a.		☒ INTERIM ☐ FINAL
b. ADDRESS (include Zip Code)	d. AWARD DATE (YYMMDD)	b. ADDRESS (include Zip Code)	d. AWARD DATE (YYMMDD)	4. REPORTING PERIOD (YYMMDD) FROM
Santa Barbara, CA 93106	5/1/83 - 4/31/86			TO 5/1/83 -5/1/84

SECTION I - SUBJECT INVENTIONS

5. "SUBJECT INVENTIONS" REQUIRED TO BE REPORTED BY CONTRACTOR/SUBCONTRACTOR (If "None", so state) NONE

a. NAME OF INVENTOR(S) (Last, First, M.I.)	b. TITLE OF INVENTION(S)	c. DISCLOSURE NO., PATENT APPLICATION SERIAL NO. OR PATENT NO.	d. ELECTION TO FILE PATENT APPLICATIONS				e. CONFIRMATORY INSTRUMENT OR ASSIGNMENT FORWARDED TO CONTRACTING OFFICER	
			UNITED STATES		FOREIGN			
			YES	NO	YES	NO	YES	NO
	Alan J. Heeger, Principal Investigator							

f. EMPLOYER OF INVENTOR(S) NOT EMPLOYED BY CONTRACTOR/SUBCONTRACTOR.		g. ELECTED FOREIGN COUNTRIES IN WHICH A PATENT APPLICATION WILL BE FILED.	
i. NAME OF INVENTOR (Last, First, M.I.)	i. NAME OF INVENTOR (Last, First, M.I.)	i. TITLE OF INVENTION	ii. FOREIGN COUNTRIES OF PATENT APPLICATION
ii. NAME OF EMPLOYER	ii. NAME OF EMPLOYER		
iii. ADDRESS OF EMPLOYER (include Zip Code)	iii. ADDRESS OF EMPLOYER (include Zip Code)		

SECTION II – SUBCONTRACTS (Containing a "Patent Rights" clause)

6. SUBCONTRACTS AWARDED BY CONTRACTOR/SUBCONTRACTOR. (If "None", so state) NONE

a. NAME OF SUBCONTRACTOR(S)	b. ADDRESS (include Zip Code)	c. SUBCONTRACT NO.($)	d. DAR "PATENT RIGHTS"		e. DESCRIPTION OF WORK TO BE PERFORMED UNDER SUBCONTRACT(S)	f. SUBCONTRACT DATES (YYMMDD)	
			CLAUSE NO.	DATE (YYMM)		AWARD	ESTIMATED COMPLETION

SECTION III – CERTIFICATION

7. CERTIFICATION OF REPORT BY CONTRACTOR/SUBCONTRACTOR. (Not required if ☐ Small Business or ☒ Non-Profit organization.) (Check appropriate box)

a. NAME OF AUTHORIZED CONTRACTOR/SUBCONTRACTOR OFFICIAL (Last, First, M.I.)	c. I certify that the reporting party has procedures for prompt identification and timely disclosure of "Subject Inventions," that such procedures have been followed and that all "Subject Inventions" have been reported.
b. TITLE	SIGNATURE OF AUTHORIZED CONTRACTOR/SUBCONTRACTOR OFFICIAL — DATE (YYMMDD)

DD FORM [illegible]