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6. AUTHOR(S)
Professor Alan J. Heeger
Professor Fred Wudl
Professor Paul Smith

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University of California, Santa Barbara
Santa Barbara, California 93106-5090

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13. ABSTRACT (Maximum 200 words)

Principal accomplishments during the past year related to Light Emitting Diodes fabricated from conducting polymers and to the related fundamental scientific and materials issues. Progress has been made toward passivating the low work function electron-injecting contact to the point where stable operation outside the dry box is routine. Transient electroluminescence from polymer LEDs has been reported; RC limited response with rise and fall times below 50 nanoseconds has been achieved. The absence in saturation in pulsed operation implies that such devices can be used in applications which require multiplexing (e.g. displays). Photoconductivity studies of the parent PPV material demonstrate that the absorption and emission arise directly from a π-π^* interband transition (rather than a bond excition). Work during the next year will focus on synthesis of blue emitters as well as a variety of fundamental experiments (enabled by the passivation of the devices) designed to clarify the mechanism and to enhance the efficiencies.

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OFFICE OF NAVAL RESEARCH

END-OF-THE-YEAR REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

Grant No. N00014-91-J-1235

R&T Code 4132012

Principal Investigators:
Alan J. Heeger
Fred Wudl
Paul Smith

Institute for Polymers and Organic Solids
University of California, Santa Barbara
Santa Barbara, California 93106-5090

Date Submitted: May 18, 1992

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 Investigator: Alan J. Heeger, Fred Wudl, Paul Smith

Mailing Address: Institute for Polymers and Organic Solids
University of California, Santa Barbara
Santa Barbara, California 93106-5090

Phone Number: (805) 893-3184 Fax Number: (805) 893-4755

E-mail Address:

a. Number of papers submitted to refereed journals, but not published: 2

b. Number of papers published in refereed journals (list attached): 9

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 & non-refereed papers (list attached): 1

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: 23

i. Number of presentations at workshops or professional society meetings: 7

j. Honors/Awards/Prizes for contract/grant employees (list attached): 1

k. Total number of Graduate Students and Post-Doctoral associates supported by at least 25% during this period under this R&T project number:

Graduate Students: 3

Post-Doctoral Associates: 11

including the number of,

Female Graduate Students: 1

Female Post-Doctoral Associates: 1

and, the number of

Minority* Graduate Students: 0

Minority* Post-Doctoral Associates: 0

and, the number of

Asian Graduate Students:

Asian Post-Doctoral Associates: 4

Unpublished papers submitted to refereed journals

"Electroluminescence and Electrical Transport in Poly(3-octylthiophene) Diodes, D. Braun, G. Gustafsson, D. McBranch and A. J. Heeger, J. Appl. Physics.

"Persistent Photconductivity in Poly(p-phenylenevinylene): Spectral Response and Slow Relaxation, C. H. Lee, G. Yu and A. J. Heeger, Phys. Rev. B.

Papers published in refereed journals

List attached:

"Substitution Effects on Bipolarons in Alkoxy Derivatives of Poly(1-4-phenylenevinylene)", K. F. Voss, C. M. Foster, L. Smilowitz, D. Mihailovic, S. Askara, G. Srdanov, Z. Ni, S. Shi, A. J. Heeger and F. Wudl, Phys. Rev. B 43 (6), 5109 (1991).

"Visible Light Emission from Semiconducting Polymer Diodes", D. Braun and A. J. Heeger, Appl. Phys. Lett. 58 (18), 1982 (1991).

"Highly Conductive and Stiff Fibres of Poly(2,5-dimethoxy-*p*-phenylenevinylene) Prepared from Soluble Precursor Polymer", Shizuo Tokito, Paul Smith and A. J. Heeger, Polymer 32 (3), 464 (1991).

"Improved Efficiency in Semiconducting Polymer Light-Emitting Diodes", D. Braun and A. J. Heeger, J. Elec. Mat. 20 (11)(1991).

"Synthesis, Structure and Some Properties of 2,5,7,10-Tetraiodo-1,6-methano[10]annulene", K. D. Sturm, F. Wudl and J. Lex, J. Org. Chem. 56 (3), 958 (1991).

The Higher Fullerenes: "Isolation and Characterization of C_{76}, C_{84}, C_{90}, C_{94}, and $C_{70}O$, an Axide of D5*h*-C70", Francois Diederich, Roland Ettl, Yves Rubin, Robert L. Whetten, Rainer Beck, Marcos Alvarez, Samir Anz, Dilip Sensharma, Fred Wudl, Kishan. C. Khemani and Andrew Koch, Science 252, 551 (1991).

High Molecular Weight Poly(ketene dihexyl acetal): Anion Effect in a Cationic Polymerization, K. Khemani, S. Askari and F. Wudl, Macromol. 24, 2156 (1991).

Fibres of Poly(Methoxy-2-Ethyl-Hexyloxy)Phenylenevinylene Prepared from the Soluble, Fully Conjugated Polymer, Polymer 33 1103 (5) (1992).

Tensile Drawing of Fully Conjugated Poly(2,5-thienylene vinylene), C. Zhang and Paul Smith, Synth. Met. 46, 235 (1992).

Printed Technical Reports & Non-referred Papers:

List attached:

"Improved Efficiency in Semiconducting Polymer Light-Emitting Diodes", D. Braun and A. J. Heeger, Proceedings of 1st International Workshop on NLO Active Materials, Shokuryo Kailan, Tokyo, Japan (Organic Photonics Materials Study Group, The Research Institute of Economy and Industry), October 11-12, 1991.

Honors/Awards/Prizes

Alan J. Heeger, Honorary Degree, Université de l'Etat a Mons, Belgium

Principal Investigator	Source of Support	Project Title	Award Amount	Period Covered by Award	% Effort Committed	Location Research	Co-PI
Current Support A.J. Heeger	AFOSR	Mesoepitaxy: A "Universal" Route to Oriented Materials"	$ 99,500[a]	6/15/91 6/14/92	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	"Gel-Processing as a Route to High Performance Oriented Electronic and Optical Polymer Materials: Design and Synthesis on the Supramolecular Length Scale"	$100,000[b]	3/1/91- 2/28/92	10	UCSB	P. Pincus P. Smith F.Wudl G.Fredrickson D. Pearson H. Schmidt
	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[c]	11/1/91- 10/31/92	1	UCSB	Wudl
	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	11/1/91- 10/31/92	5	UCSB	
	Hitachi	"Research Agreement"	$65,700	8/21/91- 2/21/93	1	UCSB	

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 $YBa_2Cu_3O_{7-\delta}$	$ 49,000	2/15/91-1/31/92	1	UCSB	
	ONR	"Program for Research in Conducting Polymers"	$ 90,000[d]	10/1/91-9/30/92	10	UCSB	F. Wudl P. Smith
	INCOR	"Photoinduced Metallic State and Photoinduced Superconductivity"	$ 18,000	7/1/91-6/30/92	1	UCSB	

a. Total award for this period is $198,039, shared by Heeger and Smith. This project will be funded for one more year beyond the current period at the same level.
b. The total NSF MRG award is for $650,000, shared with F. Wudl, P. Smith, P. Pincus, D. Pearson, G. Fredrickson, and H.-W. Schmidt. This project will be funded for two more years at the same level.
c. Total award is $9,250 for three years, shared by Wudl and Heeger.
d. 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.

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	"Gel-Processing as a Route to High Performance Oriented Electronic & Optical Polymer Materials: Design and Synthesis on the Supramolecular Lenth Scale"	$ 99,373[a]	3/1/91-2/28/92	10	UCSB	P. Pincus P. Smith A.J. Heeger D. Pearson H. Schmidt G. Fredrickson
	NSF	"Synthesis of New Organic Materials: Ferromagnetic Organic Metals, Cyanovinyl Acceptors and Oxydonors"	$96,000[b]	4/1/91 3/31/92 FINAL YEAR	15	UCSB	
	NSF	"High Strength Materials, Polymers for Nonlinear Optics and New Electrically Conducting Polymers"	$ 87,200[c]	8/1/91-7/31/92 FINAL YEAR	15	UCSB	
	NSF	"Molecular Atoms (Heterospherophanes)"	$53,000[d]	9/1/91 8/31/92 FINAL YEAR	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]	11/1/91-10/31/92	1	UCSB	Heeger
	ONR	"Program for Research in Conducting Polymers"	$90,000[f]	10/1/91-9/30/92	5	UCSB	A. J. Heeger P. Smith

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							
Current (Cont.)	NSF	SGER: "Functionalized Fullerenes: Unprecedented Materials Based on The New Carbon Allotrope"	$ 50,000	6/1/91-5/31/92	1	UCSB	

PART II

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

b. Current telephone number: (805) 893-3184

c. Cognizant ONR Scientific Officer: Kenneth J. Wynne

d. Brief 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 last year:

Polymer light-emitting diodes (LEDs) have demonstrated various colors (red, yellow, green and blue) with impressive efficiency, brightness and uniformity. Pulsed excitation provides important new information: the transient on/off response will ultimately limit the high frequency modulation of such light sources, and the linearity of light intensity vs. current to high injection levels will determine the potential of polymer LEDs in applications which require multiplexing (e.g. displays) or which require high levels of pumping (e.g. diode lasers). Transient electroluminescence from polymer LEDs have now been carried out: RC limited response is observed, with rise and fall times below 50 ns!. With low duty-cycle pulses (0.5%) the electroluminescence intensity remains proportional to the current at values three 1000 times greater than possible with dc operation.

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

We will continue our focus on light emitting diodes fabricated from semiconducting polymers. Synthesis efforts will be directed toward new soluble conjugated polymers with larger energy gaps: i.e. polymers for development as green and blue emitters. Although the scientific understanding of the structure/property relationships that control the magnitude of the energy gap is well developed, the structure/property relations re luminescence efficiency is less clear. Research on blends will receive greater emphasis since initial studies have demonstrated to us that dilution in glassy host polymers leads to higher photoluminescence efficiency. The question will be whether one can create a percolated (interconnected) morphology which both injects/transports the charge and has high luminescence efficiency. Transient photoluminescence decay measurements will be carried out on soluble conjugated polymers in solution, in gels in polyethylene, and in solid forms to evaluate the quantum

efficiency and to probe competing nonradiative processes. Our productive effort on photoconductivity (transient and steady state) will continue. Recent instrumentation acquisitions, resulting in improving the time resolution of our transient measurement capability by two orders of magnitude, from approximately 100 ps to approximately 1 ps, will be utilized in our photoconductivity studies of conducting polymers.

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

David Braun
Yong Cao
Kwanghee Lee
Reghu Menon
Daniel Moses
Chi Zhang
Kishan Khemani
Ruilian Wu
Kyo Jun Ihn

Part III

Nanosecond Transient Electroluminescence from Polymer Light Emitting Diodes

Initial results from semiconducting polymers employed in light–emitting diodes (LEDs) have demonstrated various colors (red, yellow, green and blue) with impressive efficiency, brightness, and uniformity. Flexible light emitting structures, which take unique advantage of the processing advantages and mechanical properties of polymers, have been fabricated.

Pulsed excitation provides important new information:

Transient on/off response will ultimately limit the high frequency modulation of such light sources,

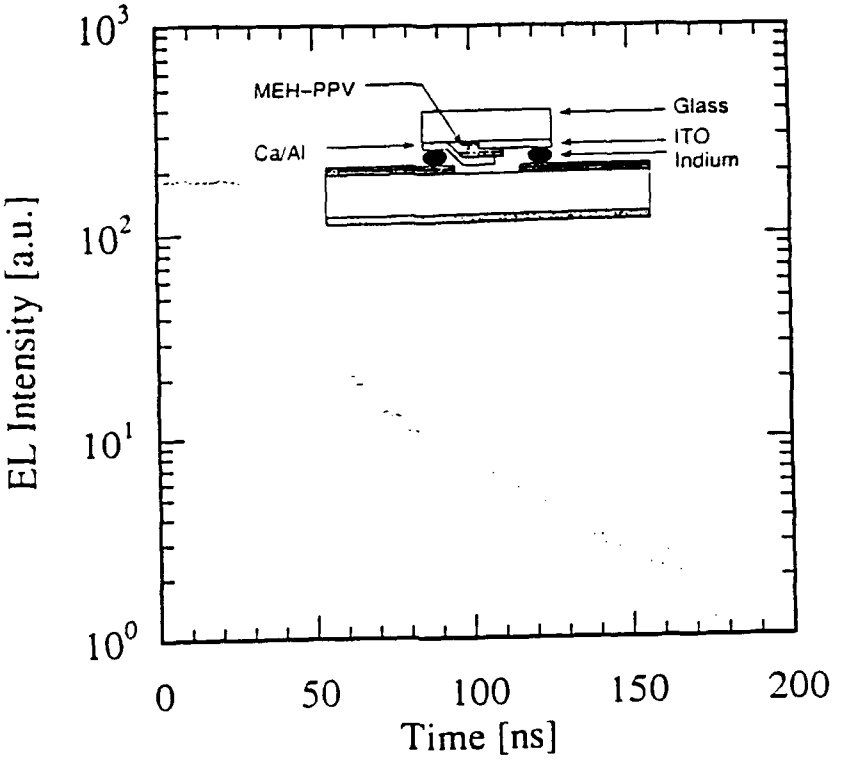
The extension of the light intensity vs. current characteristics to high injection levels will determine the potential of polymer LEDs in applications which require multiplexing (e.g. displays) or which require high levels of pumping (e.g. diode lasers).

We have succeeded with the first nanosecond time scale transient electroluminescence (EL) measurements from polymer LEDs including measurements of rise and fall times, pulsed light intensity vs current, and pulsed emission spectra.

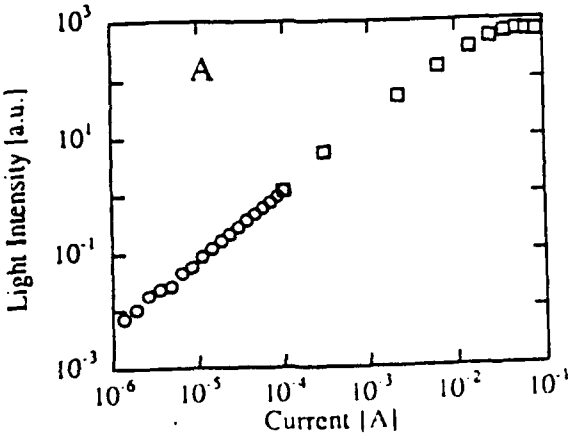
Institute for Polymers and Organic Solids
University of California at Santa Barbara

Principal investiigators
Prof. Alan J. Heeger
Prof. Paul Smith
Prof. Fred Wudl

Decay of luminescence intensity following the falling edge of an applied square voltage pulse. Inset shows the side view of the device geometry as mounted on the microstrip line.



Light emission vs. current; circles represent direct current response, and squares represent the response to a 0.5% duty–cycle square pulse with 200 μs period. Under pulsed conditions the brightness can be extended by three orders of magnitude over the maximum dc level.



Nanosecond Transient Electroluminescence from Polymer Light Emitting Diodes
(continued)

Pulsed operation of LEDs made from a soluble semiconducting polymer provides important information on the transient behavior of the electroluminescence and provides evidence that device saturation results from heating at high current densities.

When the devices are mounted on a microstrip transmission line, RC limited reponse is observed, with rise and fall times below **50 ns**!

With low duty-cycle pulses (0.5%), the EL intensity remains proportional to the current up to 10 A/cm^2, three orders of magnitude greater than possible under direct current operation.

Device switching times observed in this work compare favorably with commercially available visible LEDs made from inorganic materials.

Operation at higher current densities can be achieved by using lower duty–cycles and/or improved heat sinking.

Conclusions:

High frequency modulation of such light sources is certainly possible.

Polymer LEDs can be used in future applications which require multiplexing (e.g. displays) or which require high levels of pumping (e.g. diode lasers).

Paragraph of explanatory text:

The device geometry is displayed in the inset to Figure 1. The light–emitting diodes consist of an electron–injecting metal contact on the front surface of a poly(2–methoxy,5–(2'–ethyl–hexyloxy)–*p*–phenylene vinylene) [MEH–PPV] film on a glass substrate; the latter is partially coated with an indium–tin oxide [ITO] electrode as the hole–injecting contact. The MEH–PPV films are prepared by spin–casting from xylene solutions containing 0.5 % MEH–PPV by weight. Metal contacts (250 Å of Calcium followed by 1200 Å of Aluminum) are deposited on top of the polymer films by vacuum evaporation at pressures below 10^{-6} Torr. All processing steps are carried out in a nitrogen atmosphere. In order to improve the frequency response of the devices, small area LEDs were prepared and mounted onto a microstrip transmission line. Indium solder is used to make contact between the device electrodes and the gold microstrip line. This sophisticated design ensures that circuit elements external to the LED do not limit device response. The measurements are carried out at room temperature with the LEDs in a vacuum cryostat at pressures below 10^{-4} Torr.