Multi-sensor paints have been developed for detection both physical (pressure, temperature, shear, etc.) and chemical (corrosion, explosive) phenomena. Such materials have been transitions to practical applications such as wind tunnel testing and infrastructure monitoring and have also been adopted for fundamental studies of fluid dynamics and insect flight. A variety of carbon nanotube applications have been developed including nanotube actuators for both sensing and active control of surfaces. State-of-the-art OLED and photovoltaic materials have been developed for display and renewal energy source technologies. State-of-the-art organic electro-optic materials and device concepts have been developed and adapted to a variety of defense relevant applications including sensing, information management, and guidance. Organic electro-optic materials have been integrated with silicon photonics producing a new generation of nano/microscale device technology in a thin film format. Project research is playing a critical role in enabling emerging technologies including embedded network sensing by permitting the integration of multiple functions in a thin film (smart skin) format.
Polymeric Smart Skin Materials: Concepts, Materials, and Devices

AGREEMENT #F49620-01-1-0364

4/1/01-3/31/06 REPORT

Submitted to

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DIRECTORATE OF CHEMISTRY AND MATERIALS SCIENCE
AIR FORCE OFFICE OF SCIENTIFIC RESEARCH/NL
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by

PROFESSOR LARRY R. DALTON
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Objectives:

Field-responsive polymers can be used as conformal coatings to transform mechanical structures into multifunctional and smart surfaces. Such thin film materials, or "smart skins," can be used to alter the optical signature (absorption, reflection, or emission) of a surface or object for active stealth and stealth in daylight. They can also generate signals for use in targeting alert or object identification in mobile object networks (such as orbiting nano-satellite clusters or ground-based vehicle groups). Such smart skins can employ emission or beam steering to frustrate guided munitions. They can also act as sensors for surface pressure, icing, and corrosion on aircraft and ground vehicle surfaces and for evaluating the aerodynamic performance of airframes and ground vehicle shapes in wind tunnel testing. Electroactive polymer coatings can be used to improve the performance of devices such as space deployable antenna power systems while performing a variety of additional desired functions. Other applications include laser protection via optical limiting or reflection and dynamic wavefront corrections via surface microelectromechanical actuator arrays. The research proposed here builds on an impressive track record of success in developing revolutionary conformal electro-optic thin film materials (Science, 288, 119, 2000), solar cell coatings, and pressure-sensitive aircraft paints (U.S. Patent 5,965,642, Oct. 12, 1999; now under commercial development at Boeing and Lockheed Martin and under evaluation at NASA Glenn Laboratories). With General Electric (Honeywell, Allied Signal), we have established the state-of-the-art for polymeric (e.g., single wall carbon nanotube) nano and micro-actuators. Preliminary success has been realized in developing phased-array, photonic, and optically reconfigurable radar systems. Optically tunable photonic bandgap (IEEE J. Lightwave Tech., 17, 1956, 1999) materials have been demonstrated. Recently, sub-picosecond, large angle (π radians) optical beam steering has been demonstrated (employing modest switching voltages) by combining novel polymer electro-optic and photonic bandgap materials.

We propose an aggressive program for dramatically improving the performance of electroactive polymers (and dendrimer) materials for smart skin applications. Research activities are categorized according to the following focus areas: (1) light emitting materials for sensor, remote power, and display applications; (2) two photon materials for sensor protection and photolithography; (3) electrochromic materials for ECM and optical control applications such as switching; (4) electro-optic materials for radar, ECM, sensing, display, and information processing; (5) MEMS and opto-mechanical smart materials, and (6) exploitation of the capability of organic electroactive materials to be integrated into thin film structures. In (1), we will develop nanoscale dendrimers and photonic bandgap materials to realize a new generation of smart skin sensors capable of detecting pressure, temperature, corrosion, and a variety of chemicals and biomolecules. Dendrimers will afford unprecedented specificity, processability, and stability as well as permitting optimization of sensor signal-to-noise. Photonic bandgap materials will permit amplification of sensor response and will permit a variety of new modes of detection to be explored. In (2), we will exploit dramatic improvement in two-photon absorption that has been recently achieved with dendrimer materials. In (3), a new generation of electrochromic materials including low bandgap materials will be developed. In (4), dramatic advances in electro-optic and photonic bandgap materials will be exploited for precise control of refraction phenomena. New phased array radar (EM steering) and optical spatial light modulator (optical beam steering) will be demonstrated as well a variety of other devices including optical switches and optically-based sensors. As a lower priority, we will explore the utilization of novel MEMS and opto-mechanical materials. We will also focus upon the integration of various material and device classes into 3-D structured smart skin materials. Use will be made of recent advances in reactive ion etching and two-photon photolithography for the fabrication of complex 3-D optical circuits (IEEE J. Sel. Top. Quant. Electron., 35, 1146, 1999).
Comprehensive Summary of the Significant Work Accomplished:

Substantial progress has been made toward all project objectives. State-of-the-art pressure and temperature sensing paints have been developed and have been transitioned for use in wind tunnel testing. Progress has also been made on incorporating other functionalities into paints to be used for diagnostic evaluation of aircraft, ground vehicle, and ship surfaces. Substantial progress has been realized in developing light harvesting and frequency conversion coatings and improving the efficiency of metals by exploiting the site isolation afforded by the core of dendrimers. Significant progress has been made in developing new photonic bandgap materials. The state of the art of polymeric, dendritic, and dendronized polymer electro-optic materials has been dramatically advanced to the point that these materials now significantly exceed the performance capabilities of inorganic materials, such as lithium niobate, in terms of bandwidth and drive voltage requirements. Moreover, new materials have been incorporated into novel new thin film device structures such as ring microresonators that permit novel manipulation of light including active wavelength division multiplexing (time and wavelength information encoding) and voltage controlled wavelength selective filtering. A variety of new sensors have been developed. Flexible devices have been fabricated and evaluated. Significant advances have been made in exploring the potential of carbon nanotubes for smart skin applications including the potential use of these materials for radar absorbing materials and use as MEMS devices. Advances in polymeric thin films for light emitting, electronic, and photovoltaic applications have been realized.

Accomplishments/New Findings:

A new polymeric pressure-sensitive paint based on a platinum tetra (pentafluorophenyl) porpholactone (PtTFPL) infrared active luminophor has been developed and transitioned. The new porphyrin sensor shows strong phosphorescence with a wavelength maximum 740 nm; this is sufficiently red shifted so that this pressure sensitive luminophor can be used together with a second luminophor as an intensity reference. To avoid self-absorption effects, magnesium tetra (pentafluorophenyl) porphine (MgTFPP) was prepared as an intensity reference. The compound is brightly fluorescent in the solid state; the primary luminescence at 650 nm is not self-absorbed. A dual luminophor paint results with "ideal" pressure sensitive measurement performance of 4.5% per psi and a temperature dependency of less than −0.1%/°C.
New temperature sensor paints have been developed based upon dendrimers exploiting chelation of trivalent europium. A pair of newly and independently synthesized luminescent compounds provide lifetime-based dual pressure and temperature sensing when incorporated into the same paint coating. The luminescence lifetime of the Eu luminophore incorporated into a polymer paint ranges from 50 to 500 microseconds at room temperature and shows very little quenching by oxygen. The temperature dependence of the europium paints ranges from -2.0%/°C. to -6.0%/°C. With a state of the art CCD camera with charge storage capacities of $10^5$ electrons per pixel, we estimate that 0.001°C resolution can be obtained with a one second exposure.

Significant progress has been made in the development of electroactive dendrimers, dendronized polymers, hyperbranched polymers, and phase-separating block copolymers. Development of such materials represents a fundamental objective of this research providing a systematic route to the control of intermolecular electrostatic interactions, charge perturbations, energy transport, charge transport, and electronic relaxation relevant to development of optimized electro-optic, optoelectronic (light emitting and light amplifying), photovoltaic, and sensing materials. Development of sensing materials has been discussed in the preceding two paragraphs. Significant advances in organic light emitting device (OLED) materials has also been achieved as is evident from the publications and invention disclosures cited below. New materials also appear to address the issue of pin-hole electrical shorts that was a problem with previous PLED materials. New materials for light harvesting and improved emission efficiency have also been prepared and evaluated. The successes in this area are particularly evident in the cited publications where Professor Frechet is a co-author. Improvement in the efficiency of organic photovoltaic materials has been achieved as well as dramatic improvement in the efficiency of electro-optic materials. Research of Professor Jenekhe and his students has produced blue OLEDs that define the state-of-the-art.

Efficient photoinduced charge transfer and separation accompanied by large photovoltaic power conversion efficiencies were achieved in layered nanostructures of acceptor poly(benzimidazobenzophenanthroline ladder) (BBL) and donor poly(p-phenylenevinylene) (PPV) or poly(2-methoxy-5(2'-ethyl-hexyloxy)-1,4-phenylenevinylene) (MEH-PPV) at practical sunlight intensities. A systematic study of photoinduced electron transfer and photovoltaic properties of donor/acceptor bilayers containing donor PPV or MEH-PPV and a series of acceptor polymers with electron affinities in the range 2.7 – 4.0 eV show that both the charge transfer efficiency at the polymer/polymer interface and the power conversion efficiency of the devices were maximized when the highest electron affinity acceptor polymer BBL (EA = 4.0 eV) was used. The observed power conversion efficiencies of 1.5 – 4.6 % for ITO/PPV/BBL/Al cells under white light illumination of 1 – 80 mW/cm$^2$ are among the largest achieved to date in polymer solar cells. Optimization of the bilayer film thicknesses and
improvements in the hole mobility and photooxidative stability of the donor polymers can be expected to increase the power conversion efficiency of polymer solar cells at high illumination intensities. The observed photovoltages originate from the HOMO–LUMO energy levels in the donor/acceptor bilayer cells. Our results demonstrate that the layered donor/acceptor heterojunction is a promising architecture for developing efficient polymer thin film solar cells.

Organic electro-optic dendrimers and dendronized polymer materials have been developed that exhibit electro-optic coefficients exceeding 400 pm/N at telecommunication wavelengths. An important correlated theoretical and experimental (synthesis, characterization, and application) effort has been developed that has the potential for realizing even larger electro-optic coefficients while permitting the optimization of auxiliary properties.

A number of new thin film device structures have been explored including ring microresonator structures that have great potential for active wavelength division multiplexing, voltage-controlled wavelength selective filtering, voltage controlled laser wavelength tuning, and ultra-sensitive sensors. Such devices can play multiple and critical roles in smart skin applications including that of sensing, signal routing, information encoding and multiplexing. Such devices can play a critical role in information management on airborne platforms and in embedded network sensing. Flexible electro-optic devices have also been prepared and evaluated with observation of extraordinary properties. Polymeric electro-optic materials clearly avoid the development of conformal thin film devices—an opportunity that cannot be achieved with inorganic electro-optic or electro-absorptive materials.

Preliminary success has been achieved in exploring carbon nanotubes as microwave absorbing materials. Carbon nanotubes have also been used to develop MEMS devices including optical switches based on single wall carbon nanotube actuation.

We have demonstrated angle-dependent tuning of reflectivity and color of emissive photonic crystals. Such materials can be used in conjunction with adaptive surfaces (i.e. MEM arrays) to alter the optical signature (reflectivity, perceived color) of the surface. These materials may be useful in developing adaptive low-visibility coatings or total immersion environments, both areas of interest to the Air Force.

A new family of organolanthanide coordination complexes that emit at near-infrared wavelengths are promising candidates for optical amplification and electroluminescence have been developed. These materials and their associated devices can be used in a variety of Air Force relevant applications, including optical signal amplification, and on-chip light sources. The long
excited-state lifetimes of these materials may be advantageous for developing solid-state polymeric lasers.

Substantial progress has been made demonstrating that sophisticated integration of active organic (and inorganic) elements (devices and circuits) can be achieved in a polymeric thin film motif. This represents significant progress toward our objective of integrated smart skin function where sensing, information routing, information processing, response, and power generation are all integrated in a single smart skin structure. In particular, the integration of organic electro-optic materials into silicon photonic circuitry permits active control of light to be effected in devices of nano/microscopic dimensions. Never before achieved phenomena have been demonstrated. Slotted waveguide silicon photonic ring microresonators have been used both for electrical-to-optical signal transduction and for optical-to-electrical signal transduction. A significant advance has been achieved in increasing the functionality of thin film materials adding significant capability to smart skin materials. Integration of novel materials in a thin film format has permitted dramatic advances in specific performance characteristics, e.g., single molecule detection can be carried out.
Personnel Supported:

❖ Professor Larry Dalton
   Number of PI(s) and Co-PI(s) Involved: 2
   Number of Post Docs Supported: 5
   Number of Graduate Students Supported: 7
   Other Researchers Supported: 4
   PIs and Co-PIs Supported:
     • Larry Dalton
     • Bruce Robinson
   Postdoctoral Fellows Supported:
     • Joseph K. Amend
     • Bruce Eichinger
     • Arumugasamy Elangovan
     • Kimberly Firestone
     • William P. Weber
   Graduate Students Supported:
     • Amit Babel
     • Joshua A. Davies
     • Llewellyn R. Lawson
     • Ivan Shuvalov
     • Daniel Sluss
     • Jocelyn Y. Takayesu
     • James Westphal
   Other Researchers Supported:
     • Kolby Allen
     • Alvin Chang
     • Shih-hao Liu
     • Eric A. Woodcock

❖ Professor Alex K-Y. Jen
   Number of PI(s) and Co-PI(s) Involved: 1
   Number of Post Docs Supported: 4
   Number of Graduate Students Supported: 5
   Other Researchers Supported: 0
   Postdoctoral Fellows Supported:
     • Jingdong Luo
     • Shi Liu
     • Baoquan Chen
     • Qingmin Xu
   Graduate Students Supported:
     • Petra Herguth
     • Tae Dong Kim
Polymeric Smart Skin Materials: Concepts, Materials, and Devices
Statistical Report

- Sen Liu
- Richard Schofield
- Lixin Zheng

❖ Professor Younan Xia
Number of PI(s) and Co-PI(s) Involved: 1
Number of Post Docs Supported: 7
Number of Graduate Students Supported: 2
Other Researchers Supported: 0
Postdoctoral Fellows Supported:
- Sang Hyuk Im
- Unyong Jeong
- Xuchuan Jiang
- Kaori Kamata
- Xianmao Lu
- Yugang Sun
- Yuliang Wang
Graduate Students Supported:
- Byron Gates
- Jesse McCann

❖ Professor Alan Heeger
Number of PI(s) and Co-PI(s) Involved: 1
Number of Post Docs Supported: 9
Number of Graduate Students Supported: 1
Other Researchers Supported: 2
Postdoctoral Fellows Supported:
- Glenn Bartholomew
- Giovanni Bellomi
- Anoop Dhoot
- Xiong Gong
- Youngjin Kim
- Raluca Negres
- Cesare Soci
- Cuiying Yang
- Qinghua Xu
Graduate Students Supported:
- Glenn Bartholomew
Other Researchers Supported:
- Kwanghee Lee
- Daniel Moses
Polymeric Smart Skin Materials: Concepts, Materials, and Devices

Statistical Report

Professor Jean Frechet
Number of PI(s) and Co-PI(s) Involved: 1
Number of Post Docs Supported: 5
Number of Graduate Students Supported: 8
Other Researchers Supported: 0
Postdoctoral Fellows Supported:
  - Zachary Ball
  - Katya Kadnikova
  - Christine Luscombe
  - Claire Pitois
  - Xavier Schultze
Graduate Students Supported:
  - Paul Armstrong
  - Lan Deng
  - Paul Furuta
  - Stefan Hecht
  - David Kavulak
  - Justin Mynar
  - Jason Serin
  - Kevin Sivula

Professor Aaron Harper
Number of PI(s) and Co-PI(s) Involved: 1
Number of Post Docs Supported: 0
Number of Graduate Students Supported: 4
Other Researchers Supported: 0
Graduate Students Supported:
  - Patrick J. Case
  - Michael D. Julian
  - Cory G. Miller
  - Asanga B. Padmaperuma

Professor S.A. Jenekhe
Number of PI(s) and Co-PI(s) Involved: 1
Number of Post Docs Supported: 2
Number of Graduate Students Supported: 1
Other Researchers Supported: 1
Postdoctoral Fellows Supported:
  - M. M.(Faruk) Alam
  - T. W. Kwon
Graduate Students Supported:
  - Jessica Schendel
Polymeric Smart Skin Materials: Concepts, Materials, and Devices  
Statistical Report

❖ **Professor James M. Tour**  
Number of PI(s) and Co-PI(s) Involved: 2  
Number of Post Docs Supported: 4  
Number of Graduate Students Supported: 8  
Other Researchers Supported: 2  
PIs Supported:
- James M. Tour  
- James Roberts  
Postdoctoral Fellows Supported:
- Christopher Dyke  
- Bo Chen  
- Yubao Li  
- Yuxing Yao  
Graduate Students Supported:
- Dell Doyle  
- Jared Hudson  
- Tim Imholt (UNT)  
- Joshua Jurs  
- David Price  
- Katherine Price  
- Arnab Mukerjee  
- Jason Stephenson  
Other Researchers Supported:
- Christy Steger  
- Adilah Guiseppi-Wilson

❖ **Professor William Steier**  
Number of PI(s) and Co-PI(s) Involved: 1  
Number of Post Docs Supported: 4  
Number of Graduate Students Supported: 2  
Other Researchers Supported: 0  
Postdoctoral Fellows Supported:
- She-Won Ahn  
- H-C Song  
- C. Wang  
- C. Zhang  
Graduate Students Supported:
- Y-H Kuo  
- Reem Song

❖ **Professor Surya Prakash**  
Number of PI(s) and Co-PI(s) Involved: 1  
Number of Post Docs Supported: 0  
Number of Graduate Students Supported: 2
Polymeric Smart Skin Materials: Concepts, Materials, and Devices

Statistical Report

Other Researchers Supported: 0
Graduate Students Supported:
- Ryan DeSousa
- Sujith Chacko

Professors Martin Gouterman and Gamal Khalil
Number of PI(s) and Co-PI(s) Involved: 2
Number of Post Docs Supported: 0
Number of Graduate Students Supported: 3
Other Researchers Supported: 0
Graduate Students Supported:
- Kimberly Lau
- Fletcher Kimura
- Wayne Shinoki

Publications:

Summary all years
Total number of publications in refereed journals: 771
Total number of publications which acknowledge AFOSR support: 274

Professor Larry Dalton
Number of Publications in Refereed Journals: 148
Number of Publications Which Acknowledge AFOSR Support: 94

Publications Which Acknowledge MURI Support


78. S. Grenoble, M. Gouterman, G. Khalil, J. Callis, and L. Dalton, "Pressure Sensitive Paint (PSP): Concentration Quenching of Platinum and

❖ Professor Alex K-Y. Jen
Number of Publications in Refereed Journals: 119
Number of Publications Which Acknowledge AFOSR Support: 38

Publications Which Acknowledge MURI Support


**Professor Younan Xia**
Number of Publications in Refereed Journals: 91
Number of Publications Which Acknowledge AFOSR Support: 19
Publications Which Acknowledge MURI Support

7. Use of Electrospinning to Directly Fabricate Hollow Nanofibers with Functionalized Inner and Outer Surfaces Li, D.; McCann, J. T. and Xia, Y., Small 2005, 1, 83-86.
**Polymeric Smart Skin Materials: Concepts, Materials, and Devices**

**Statistical Report**


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**Professor Alan Heeger**

Number of Publications in Refereed Journals: 55

Number of Publications Which Acknowledge AFOSR Support: 23

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**Publications Which Acknowledge MURI Support**


v Professor Samson A. Jenekhe
Number of Publications in Refereed Journals: 45
Number of Publications Which Acknowledge AFOSR Support: 9

Publications Which Acknowledge MURI Support


Polymeric Smart Skin Materials: Concepts, Materials, and Devices

Statistical Report

- **Professor Jean Frechet**
  - Number of Publications in Refereed Journals: 158
  - Number of Publications Which Acknowledge AFOSR Support: 34

Publications Which Acknowledge MURI Support
630


❖ Professor James M. Tour 
Number of Publications in Refereed Journals: 60 
Number of Publications Which Acknowledge AFOSR Support: 19

Publications Which Acknowledge MURI Support


❖ Professor William Steier
Number of Publications in Refereed Journals: 55
Number of Publications Which Acknowledge AFOSR Support: 13

Publications Which Acknowledge MURI Support

*Professor Surya Prakash*
Number of Publications in Refereed Journals: 44
Number of Publications Which Acknowledge AFOSR Support: 0

*Professor Aaron W. Harper*
Number of Publications in Refereed Journals: 4
Number of Publications Which Acknowledge AFOSR Support: 8
Publications Which Acknowledge MURI Support


---

**Professors Martin Gouterman and Gamal Khalil**

Number of Publications in Refereed Journals: 16

Number of Publications Which Acknowledge AFOSR Support: 17

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**Publications Which Acknowledge MURI Support**


7. “Dual Luminophor Pressure Sensitive Paint II: Lifetime Based Measurement of Pressure and Temperature,” Biniam Zelelow, Gamal E.
Interactions/Transitions:

Participation/Presentations:

- **Professor Larry Dalton**

1. March 1, 2002—Dinner meeting and presentation with Seattle Mayor Greg Nichols, community leaders, and UW President McCormick.
6. April 29, 2002—Invited Seminar, Washington State University, Pullman, WA. "Electro-Optic Materials and Devices".
7. June 10, 2002--3 presentations in the Palo Alto, CA area
11. Conference--June 20, 2002--Invited presentation at the IBM Workshop on Organic Electronic and Photonic Materials (T. J. Watson Research Center, Yorktown Heights, NY)
16. August 12-13, 2002--PNNL Nanoscience and Technology Advisory Committee Meeting, Richland, WA.

18. August 19-29, 2002—STC Director's Meeting, Atlanta, GA. Overview of UW STC.


24. October 9, 2002—Seminar, Norfolk State University, Norfolk Virginia. "Implementing the New Information Technology Age: Exploiting the Best of Photonics and Electronics".


Polymeric Smart Skin Materials: Concepts, Materials, and Devices


35. February 13, 2003—Florida International University, Miami, FL. Invited Seminar:"Technology for the 21st Century: Exploiting the Best of Photonics and Electronics".


42. May 5-7, 2003--PNNL Nanoscience and Technology Advisory Committee Meeting, Richland, WA

43. May 17-18, 2003—NSF “Chemical Bonding Centers” Workshop, NSF Headquarters, Arlington, VA


45. NASA Space Grant Program on Research for Undergraduates—July 3,
2003—Delivered Education Component including lecture on Space Based Applications of Organic Electro-Optic Modulators.


49. September 26, 2003—Provided day long Orientation for the incoming Freshman Class at the University of Washington under the auspices of a new program developed by the Dean of Undergraduate Education to introduce students to unique educational opportunities at UW.

50. October 1, 2003—Presentation to the National Reconnaissance Office on the status of organic electro-optic materials, Univ. of Washington, Seattle.


52. October 27-31, 2003---AFRL/Materials and Manufacturing Directorate (ML) Scientific Advisory Board (SAB) Science and Technology (S&T) Quality Review

53. November 4, 2003—Eastman Lecture at the Department of Chemistry, University of Akron

54. September 14-15, 2004 — 2 Lectures, DARPA MORPH Review, Redmond, WA


56. September 29, 2004 — Invited Lecture, Universite Pierre & Marie Curie, Paris France

57. October 4-6, 2004 — Invited Lecture, MWP 2004 International Topical Meeting on Microwave Photonics, Qunguquit, Maine


59. October 22-26, 2004 — Invited Lecture, Symposium on Organic Thin Film for Photonic Applications, 229th ACS National Meeting, Philadelphia, PA


61. November 6-7, 2004 — Invited Lecture, Tobinstock, Northwestern University, Evanston, IL


64. January 22-27, 2005 — Invited Lecture, SPIE Photonics West, San Jose, CA

65. March 7-11, 2005 — Invited Lecture, International Conference on Organic Photonics and Electronics 2005 (ICOPE2005) & The 8th International Conferences on Organic Nonlinear Optics (ICONO'8), Matsushima, Japan


67. May 14, 2005 — Invited Lecture, Stanford Photonics Research Center Annual Symposium, Stanford, CA

68. May 22-27, 2005 — 1 Tutorial and 1 Invited Lecture, CLEO/QELS/PhAST Conference, Baltimore, MD


70. April 5-7, 2005 — 2 Lectures, Graduate Course: Introduction to Advanced Photonic Materials and Devices, Norfolk State University, Norfolk, VA

71. June 3-5, 2005 — Unconventional Magnetic and Electronic Materials Conference, Columbus, OH


73. July 11-14, 2005 — Invited Lecture, IQEC and CLEO-PR Conference, Tokyo, Japan


76. July 31-August 4, 2005 — 3 Invited Lectures, SPIE Optics & Photonics Conference, San Diego, CA

77. August 8-13, 2005 — Air Force Office of Scientific Research, Chemistry & Life Sciences Directorate, Polymer Chemistry & Polymer Matrix Composites Program Review, San Diego, CA

78. September 24, 2005, the Dow/Karabatosos & Distinguished Alumni Lectureship, Michigan State University, East Lansing, MI

79. November 7, 2005, Invited Lecture, Symposium on Exploratory Research for Advanced Technology (ERATO)—Koike Photonics Polymer Project, Japan Science Technology Agency (JST), Tokyo, Japan


81. January 15-20, 2006, Invited Lecture, 3rd ICPOP and 2nd KF-PMD, Val Thorens, France

82. March 8, 2006, Corporate-wide invited seminar, Intel Corporation

83. March 13, 2006, Invited seminar, Corning Corporation, Corning, NY

84. March 14, 2006, Invited seminar, CIBA Corporation, Tarrytown, NY

Invited Presentations and Seminars by Alex Jen:

1. "Nanoscale Architectural Control of Organic Functional Materials for Photonics & Molecular Electronics", Lawrence Berkeley Lab., Univ. of California, Berkeley, CA, 8/03.


5. "Functional Self-Assemblies with Nanoscale Ordering for Molecular Electronics and Biomaterials", in the Symposium of "Organic and Polymeric Materials for Plastic and Molecular Electronics", ACS Annual Meeting, New York, NY, 9/03.


8. "Nanoscale architectural control of dendrimers and polymers for photonics and molecular electronics", Institute of Chemistry, Academia Sinica, Taiwan, 12/02.

9. "Nanoscale architectural control of dendrimers and polymers for photonics and molecular electronics", National Tsing Hua University, Taiwan, 12/02.

10. "Recent progress in developing highly efficient nonlinear optical chromophores and side-chain dendronized polymers for electro-optics", in the Symposium on "Organic Photonic Materials and Devices VI", Photonic- West: Optoelectronics San Jose, CA, 1/03.
11. "Nanoscale tailoring of dendrimers and polymers for electro-optic devices" in the Photonics Initiative Workshop, University of Arizona, Tucson, AZ, 1/03.

12. "Nanoscale tailoring of organic functional materials for photonics and molecular electronics", Chinese University of Hong Kong, Hong Kong, 2/03.


Invited Presentations and Seminars by Younan Xia


7. Inorganic Chemistry Seminar, Department of Chemistry, University of California, Santa Barbara, CA, October, 2002.


Invited Presentations and Seminars by Alan Heeger

Polymeric Smart Skin Materials: Concepts, Materials, and Devices

Statistical Report


7. “Progress in “plastic” electronics,” DOE Workshop; DOE Basic Energy Sciences Personnel, Salt Lake City, UT.

Invited Presentations and Seminars by Aaron W. Harper


10. Efficient energy harvesting of conjugated polymers by direct coordination

Invited Presentations and Seminars by S.A. Jenekhe:

Invited Presentations and Seminars by William Steier:
3. "Polymer Micro-resonator Technology," Presentation at PECIO’03 Conference, Prague, Italy.

Invited Presentations and Seminars by Gamal Khalil and Martin Gouterman
Polymeric Smart Skin Materials: Concepts, Materials, and Devices

Statistical Report


Consultative/Advisory Functions:

Professor Larry Dalton

Recent Representative Advisory Positions, Non-Federal

• Member, Editorial Board, Materials Today (2002-)
• Chairman/Member, External Advisory Committee, Center for Research and Education on Advanced Materials, Norfolk State University, (2002-)
• Member, External Advisory Committee, NSF RISE Center, Alabama A&M University (2005-)
• Member, Scientific American 50 Awards Advisory Committee (2003)
• Board of Visitors, Chemistry Department, University of Alabama (98-2002)
• Guest Editor, Special Issue of the Journal of Physical Chemistry (2003-2004)
• Academic Technology Advisory Committee, University of Washington (2003-)

Recent Representative Recent Federal and State Advisory Panel Service

• Member, NSF ACGPA (Advisory Committee for the Government Performance and Results Act) (2006-)
• Member, Advisory Committee, Mathematical and Physical Science Directorate, National Science Foundation (2005-2008)
• Member, Advisory Group on Electron Devices (AGED), Office of the Undersecretary of Defense (2006-)
• Member, Committee of Visitors, Division of Materials Research, National Science Foundation (2005)
• Member, MPS/EHR (Education Human Resources) Subcommittee on Broadening Participation, National Science Foundation (2005)
• Member, Engineering and Physical Sciences Research Council (EPSRC), England
• Chairman, Arizona Biomedical Research Commission (formerly, Arizona Disease Control Research Commission) Review Panel for Biomedical Engineering, Imaging, and Sensing (2005-)
Polymeric Smart Skin Materials: Concepts, Materials, and Devices
Statistical Report

- Member, National Science Foundation Panel on the Technological Challenges of Organic Electronic and Photonic Materials (2004)
- Member, National Science Foundation Panel on Sensors and Sensor Systems (2003)
- Member, National Science Foundation Workshop on Chemical Bonding Centers (2003)
- Member, National Science Foundation "Grand Challenges Workshops" for the National Nanotechnology Initiative (2003)
- Member, Air Force Scientific Advisory Board (2003)
- Member, Department of Energy Peer Review Panel for the Energy Science and Technology Directorate (2003-)
- Member, Department of Energy Peer Review Panel for the Nanotechnology Initiative (2002-2004)
- Member, National Science Foundation NIRT Review Panel (2002)
- Member, National Science Foundation Panel on Information Technology Research (ITR)
- Member, National Science Foundation SBIR/STTR Peer Review Panel (2001)
- Member, National Science Foundation IGERT Review Panel (2001, 2006)
- Member, National Science Foundation Nanotechnology Review Panel (2001)
- Reviewer, Arizona Biomedical Research Commission (formerly, Arizona Disease Control Research Commission) for Annual Review of Proposals (1995-present)

Recent Invited Lectures at Federal, British Government, and Corporate Workshops

- Institute for Defense Analyses Nanosensor Technology Tutorial (Gomac Tech 06, San Diego, March 20, 2006)
- DARPA Workshop on Molecular Photonics/Engineering (2002)
- Corning Corporate-wide Workshop on Organic Electro-Optic Materials (2001)
- 2006 Corporate-wide lectures at Intel, CIBA, GE, and Corning

Other Knowledge/Technology Transitions:
Transition 1
a. Dalton, UW, b. Data for organic electro-optic materials, c. William Krug/Boeing
Polymeric Smart Skin Materials: Concepts, Materials, and Devices

Statistical Report

Phantom Works., 253-657-8018 d. For a development of a research program for handling both digital and analog data exploiting WDM techniques and explicitly wavelength selective filter and beam steering concepts.

Transition 2
a. Dalton, UW, b. Data relating to polymeric electro-optic materials and processing protocols, c. Susan Ermer/Lockheed Martin Corporation, 650-424-3131 d. For prototyping high frequency, low drive voltage modulators.

Transition 3

Transition 4
a. Dalton, UW, b. Polymeric electro-optic materials and processing protocols, c. Todd McIntyre/Lumera Corporation, 425-415-6616 d. For electro-optic device fabrication and consideration for establishing an electro-optic materials production facility.

Transition 5
a. Dalton, UW, b. Polymeric electro-optic materials and processing protocols, c. Ray Chen/UT-Austin Microelectronics Center and Radiant Photonics, 512-338-4942 d. For electro-optic device fabrication and evaluation.

Transition 6
a. Dalton, UW, b. Polymeric electro-optic materials and processing protocols, c. James G. Grote/AFRL/MLPO, 937-255-4474 ext 3263 d. For use with conducting cladding materials developed by AFRL.

Transition 7

Transition 8

Transition 9
a. Dalton, UW, b. Polymeric electro-optic materials and processing protocols, c. Paul Ashley/Army Missile Command, Redstone Arsenal, 205-876-7484 d. Polymeric electro-optic materials for gyro development.
Transition 10

Transition 11
a. Dalton, UW, b. Light harvesting solar cell coatings, c. Paul Hausgen/Kirtland AFB, paul.hausgen@kirtland.af.mil d. Improved solar cell technology.

Transition 12

Transition 13

Transition 14

Transition 15

Transition 16
a) Tour, Rice University, b) Functionalization of single wall carbon nanotubes, c) Morley Stone, Program Manager, DARPA, 571-218-4504, d) For preparation of new polymer composites.

Transition 17
a) Tour, Rice University, b) Functionalization of single wall carbon nanotubes, c) MURI Smart Skin Review at University of Washington d) For preparation of new polymer composites.

Transition 18
a) Tour, Rice University, b) Functionalization of single wall carbon nanotubes, c) TiiMS URETI meeting, NASA Langley, d) For preparation of new polymer composites.

Transition 19
Polymeric Smart Skin Materials: Concepts, Materials, and Devices

Statistical Report

Honeywell FM&T, 505-661-1207, d. For improving the damage threshold of optical devices.

Transition 20
a) Xia, U. Wash., b) Electrospinning with co-axial capillaries, c) M. Marquez, Kraft Foods, 847-646-3357, d) For fabrication of hierarchically, multifunctional materials related to drug delivery and controlled release.

Transition 21
a) Pl. Jen, Univ. of Washington, b) highly efficient E-O polymers and NLO chromophores, c) Professors Steier (USC) and Yariv (CalTech), and Dr. Bill Krug (Boeing), d) for the fabrication of low \( V_{\text{r}} \) modulators and active ring resonators. We have already supplied both the high \( r_{\text{33}} \) guest/host polymers and Diels-Alder reversibly crosslinkable polymers to Bill Steier's group (USC) for evaluation of making E-O devices. Their initial approach will be to fabricate stripline Mach-Zehnder modulators and also micro ring resonator because the latter devices can tolerate higher loss. In addition, we have worked with Amnon Yariv's groups (Caltech) and Bill Krug (Boeing) to incorporate these newly developed reversibly crosslinkable polymers into their ring-resonator device structures and photonic bandgap structures using soft lithography or nanoimprinting.

Transition 22
a) Pl. Jen, Univ. of Washington, b) highly efficient E-O polymers and NLO chromophores, c) Professors Steier (USC), Peyghambarian anf Fallahi (UA), and Scherer (CalTech), and Dr. Bill Krug (Boeing), d) for the fabrication of low \( V_{\text{r}} \) modulators and active ring resonators. We have already supplied both the high \( r_{\text{33}} \) guest/host polymers and Diels-Alder reversibly crosslinkable polymers to Bill Steier's and Fallahi/Peyghambarian groups for evaluation of device fabrication. Their have fabricated low drive voltage (\( V_{\text{r}} = 1.7 \) V) stripline Mach-Zehnder modulators and very low insertion loss sol-gel/polymer hybrid modulators (~7 dB fiber-to-fiber which is the lowest among all polymer-based E-O devices). In addition, we have worked with Axel Scherer's groups (Caltech) and Bill Krug (Boeing) to incorporate these newly developed reversibly crosslinkable polymers into their ring-resonator device structures, nano slot waveguide structures, and photonic bandgap structures using nanoimprinting.

Transition 23
a. Jen, U. Washington, b. new E-O materials, c. Dr. Geoffrey Linday (NAVY), d. to provide detailed synthetic schemes and procedures for them to develop new E-O materials for DoD's applications.

Transition 24
a. Khalil & Gouterman, UW, b. Pressure Sensitive Films, c. James Bell /NASA Ames, ihbell@mail.arc.nasa.gov d. Performance of low speed pressure steady measurements.
Polymeric Smart Skin Materials: Concepts, Materials, and Devices

Statistical Report

Transition 25
a. Khalil & Gouterman, UW, b. Pressure Sensitive Films, c. Youssef Mebarki /The Institute for Aerospace Research, Youssef.Mebarki@nrc-cnrc.gc.ca  
d. Performance of automotive model pressure measurement.

Transition 26
a. Khalil & Gouterman, UW, b. Pressure Sensitive Films, c. Jim Crafton/ISSI, jwcrafton@innssi.com  
d. Successful evaluation of the “dual paint”.

Transition 27
a. Khalil & Gouterman, UW, b. Fiber-optic Sensors, c. Roger Wolthuis/RJC Enterprises, roger@ricenterprises.net  
d. Development of fiber optic oxygen sensor - medical application.

Transition 28
a. Khalil & Gouterman, UW, b. Pressure Sensitive Films, c. Timothy Bencic/NASA Glenn, Timothy.J.Bencic@grc.nasa.gov  
d. Research into ice wind tunnel performance.

Transition 29
a. Khalil & Gouterman, UW, b. Dual luminophor Pressure Sensitive Paint, c. James Bell /NASA Ames, jhbell@mail.arc.nasa.gov  
d. Applications in wind tunnel testing

Transition 30
a. Khalil & Gouterman, UW, b. Dual luminophore Pressure Sensitive Paint, c. Youssef Mebarki /The Institute for Aerospace Research, Youssef.Mebarki@nrc-cnrc.gc.ca , d. For low speed wind tunnel testing for automotive designs.

Transition 31
a. Khalil & Gouterman, UW, b. Dual luminophor Pressure Sensitive Paint, c. Jim Crafton/ISSI, jwcrafton@innssi.com , d. For licensing evaluation

Transition 32
a. Khalil & Gouterman, UW, b. Oxygen sensor material, c. Roger Wolthuis/RJC Enterprises, roger@ricenterprises.net , d. For fiber optic oxygen sensor, medical application

Transition 33
a. Khalil & Gouterman, UW, b. Temperature sensitive dye c. Donald Oglesby, NASA Langley, Hampton, Virigina  
d. For cryogenic wind tunnel testing.

Transition 34
a. Khalil & Gouterman, UW, b. Pressure and Temperature Sensitive Paints c.
Jim Callis, UW, d. For insect flight research

Transition 35
a. Khalil & Gouterman, UW, b. Oxygen sensitive dye c. Ian Sweet, UW, d. For islets viability research

Transition 36
a. Khalil & Gouterman, UW, b. Oxygen, zinc, pH sensitive dyes c. Masoud Ghandehari, Polytechnic University, d. For infrastructure corrosions sensing and gaseous leak detections.

Transition 37
a) Khalil, University of Washington, b) "Highly Stable NIR Dyes for Photonic Applications: Tetra(pentafluorophenyl)porphodilactone and trilactone" 3rd, c) International Conference on Porphyans and Phthalocynines, New Orleans, LA, July 11-16, 2004, d) presented findings

Transition 38
a) Lau, University of Washington, b) "Highly Stable NIR Dyes for Photonic Applications: effects of light and oxygen on the synthesis of Tetra(pentafluorophenyl)porphodilactone", c) 3rd International Conference on Porphyans and Phthalocynines, New Orleans, LA, July 11-16, 2004, d) presented findings

Transition 39
a) Gouterman, University of Washington, b) "Platinum Porphyin Luminescence: Oxygen Sensing and Pressure Sensitive Paint (PSP)", c) Chemistry Department, LSU, Baton Rouge, LA, July 19, 2004, d) presented findings

Transition 40
a) Khalil, University of Washington, b) "Dynamic surface pressure measurements, Pressure measurement in fluid phase Shear stress measurement, oxygen lung physiology", c) James Callis, Department of Chemistry, University of Washington (206) 543 1208

Transition 41
a) Khalil, University of Washington, b) "Instrumentation for shear stress measurement", c) Werner Kaminsky, Department of Chemistry, University of Washington (206) 543 7585

Transition 42
a) Khalil, University of Washington, b) "Lung oxygen physiology studies", c) Michael P Hlastala, Department of Physiology and Biophysics University of Washington (206) 543-3166
Polymeric Smart Skin Materials: Concepts, Materials, and Devices

Statistical Report

Transition 43
a) Khalil, University of Washington, b) “Pressure measurement in fluid phase”, c) Dana Dabiri, Department of Aeronautics, University of Washington (206) 543 6067

Transition 44
a) Khalil, University of Washington, b) “Synthesis of porpholactones NIR dyes”, c) Christian Bruckner, Department of Chemistry, University of Connecticut, Storrs, Connecticut (860) 486-2743

Transition 45
a) Khalil, University of Washington, b) “Sensors for in situ monitoring of geo-environmental and infrastructure materials, Gas leak detection”, c) Masoud Ghandehari, Department of Civil Engineering, Polytechnic University, Brooklyn, New York (718) 260 3441

Transition 46
a) Khalil, University of Washington, b) “Optical Measurements in Wind Tunnel Testing: application to delta wings”, c) Mebarki, Youssef, The Institute for Aerospace Research, National Research Council, Ontario, Canada (613) 998 8994

Transition 47
a) Khalil, University of Washington, b) “Improved Pressure- and Temperature-Sensitive Paint, Shear stress measurement” c) Jim Crafton, ISSI, Dayton, Ohio, (937) 429 4980

Transition 48
a) G. Khalil, Univ. of Washington, b) Developed and transferred a leak detection system to Professor Masoud Gandahari of Civil Engineering Department, Polytechnic University, Brooklyn, New York, c) Collaborating with the New York Gas Institute the leak detection system can be used to capture and measure in real time gas leaks from refineries as well as oil, gas and chemical processing equipment.

Transition 49
a) G. Khalil, Univ. of Washington, b) Developed and transferred pressure sensitive particles production system for fluid flow measurement to Professor Dana Dabiri, Department of Aeronautics, University of Washington. The system is capable of producing airborne polystyrene beads. The beads are small enough to follow fluid flow accurately and function as pressure-sensitive air-born micro-particles.

Transition 50

Transition 51

Transition 52
a) Prakash, University of Southern California, b) Functionalization of Crosslinked Polystyrene Nanospheres, c) 227th National American Chemical Society Meeting, Anaheim CA, March 28-April 1, 2004, d) Presented findings to organic division

Transition 53
a) Frechet, University of California, Berkeley, b) electroactive copolymers and terpolymers for highly efficient solution processible light emitting diodes, c) transition to Prof Mark Thompson, University of Southern California, (213) 740-6402, d) application: highly efficient solution processed light emitting diodes.

Transition 54
a) J.M.J. Frechet, University of California, Berkeley. b) electroactive copolymers and terpolymers for highly efficient solution processible light emitting diodes c) transition to Prof Mark Thompson, University of Southern California, (213) 740-6402 d) application: highly efficient solution processed light emitting diodes.

Transition 55
a) J.M.J. Frechet, University of California, Berkeley. b) Low bandgap polymers c) Transition to Nanosolar Inc. d) application in photovoltaics

Transition 56

Transition 57

Transition 58

Transition 59
a. Heeger, UC Santa Barbara, b. New hole injectionlayer for polymer LEDs, c. DuPont Displays, Dalen Keyes and Ian Parker d. Polymer LED displays
Polymeric Smart Skin Materials: Concepts, Materials, and Devices

Statistical Report

Transition 60
a. Heeger, UC Santa Barbara, b. New hole injection layer for polymer LEDs, c. Ritdisplay (Taiwan), D.C. Wang CEO, Note: Ritdisplay is a joint venture with DuPont to manufacture polymer LED displays, d. Polymer LED displays

Transition 61
a. Heeger, UC Santa Barbara, b. Polymer solar cell technology transfer, c. Board of Directors and consultant to Konarka Technologies, d. Polymer solar cell technology

Transition 62
a. Heeger, UC Santa Barbara, b. Goodyear; Contact: Dr. A Saleem, c. May 9, 2003, d. Progress in “plastic” electronics

Transition 63
a. Heeger, UC Santa Barbara, b. VEECO, Dr. C. Prater, CTO, c. May 29, 2003, d. Progress in “plastic” electronics

Transition 64
a) Heeger, University of California, Santa Barbara, b) polymer LEDs, c) Dalen Keys abnd Ian Parker, DuPont Displays, d) Polymer LED displays

Transition 65
a) Heeger, University of California, Santa Barbara, b) Polymer LEDs, c) Ritdisplay (Taiwan), D.C. Wang CEO (Ritdisplay is a joint venture with DuPont to manufacture polymer LED displays), d) Polymer LED displays

Transition 66
a) Heeger, University of California, Santa Barbara, b) Polymer solar cell technology transfer, c) Board of Directors and consultant to Konarka Technologies (Howard Berke, CEO), d) Polymer solar cell technology

Transition 67
a) Heeger, University of California, Santa Barbara, b) Polymer diodes and polymer Field effect transistors, c) B. Nilsson (b.nilsson@ieee.org) d) Formation of a new start-up company to develop “plastic electronics”

Transition 68
a) Heeger, University of California, Santa Barbara, b) Venture Partner for evaluation of new materials concepts, c) NGEN (Santa Barbara), d) Peter Grubstein, (805) 896-4614

Transition 69
a) Heeger, UC Santa Barbara, b) The solar cell technology (see B under Accomplishments/Findings section) has been licensed by Konarka Technologies,
Polymeric Smart Skin Materials: Concepts, Materials, and Devices

Statistical Report

headquarters in Lowell MASS. Konarka is developing the technology for plastic solar cells for commercialization. Konarka recently announced a commercialization plan that schedules Pilot Plant production in 2007 with the manufacturing of commercial products in 2008.

Transition 70

Transition 71

Transition 72
a. Steier, USC, b. Materials and Devices, c. Paul Payson/Air Force Research Laboratory, Rome, NY, Paul.Payson@rl.af.mil d. A materials and device collaboration has been established. A recent graduate of my group has now joined the Air Force Research Laboratory.

Transition 73
a. Steier, USC, b. Resonators, c. Mike Morse/Intel, mike.morse@intel.com d. Development of polymer ring resonators for computer backplane interconnections.

Transition 74
a. Steier, U. South. Calif. b. polymer device technology. c. A. Szep, F. Haas, P. Payson, AFRL, 315-330-4069 d. visit on 7/31/03 to discuss linearization of EO modulators

Transition 75
a. Steier, U. South. Calif. b. polymer device technology. c. J. Grote, AFRL, (937) 255-4474 x3263 d. visit 5/20/03 to review waveguide technology and present seminar

Transition 76
a. Steier, U. South. Calif. b. polymer device and material technology. c Timothy Parker, R. Dinu, T. Mino, Lumera Corp. (425) 398-6526 d. visit on 8/28/03 to review EO modulator work and several materials and device exchanges.

Transition 77
Polymeric Smart Skin Materials: Concepts, Materials, and Devices

Statistical Report

Transition 78

Transition 79

Transition 80

Transition 81

Transition 82
a. Steier, U. South. Calif. b. polymer device and material technology, c. JPL, Dr. Serge Dubovitsky 818 354 9796 d. Integration of polymer devices with high speed electronics.

Transition 83
a) Steier, University of Southern California, b) Polymer device technology, c) M. Morris, B. Block, Intel, 408-455-6403, d) Discuss integration of polymer devices.

Transition 84
a) Steier, University of Southern California, b) Polymer device technology, c) L. Maleki, JPL, 818-354-3688, d) Review polymer resonator technology.

Transition 85
a) Steier, University of Southern California, b) Polymer device and material technology, c) Timothy Parker, R. Dinu, Lumera Corp., 425-398-6526, d) Review EO modulator work and several materials and device exchanges.

Transition 86
a) Steier, University of Southern California, b) Polymer device and material technology, c) G. Lindsay Naval Weapons Ctr. China Lake, 760-939-1630, d) Exchange information on materials and waveguide fabrication.

Transition 87
Polymeric Smart Skin Materials: Concepts, Materials, and Devices

Statistical Report

a) Steier, University of Southern California, b) Polymer device and material technology, c) Lockheed Martin, W. Anderson, 650-424-2224, d) Flexible polymer modulator technology and applications to Lockheed systems.

Transition 88
a) Steier, University of Southern California, b) Polymer device and material technology, c) photonic Systems, Inc., C. Cox, 780-272-1819, d) Review integration of polymer components and discuss joint programs.

Transition 89
a) Steier, U. South. California b) Polymer device and material technology c) Presentation at AAAS Symposium, Seattle WA, 2/15/04, d) Review status of high speed modulator technology and polymer micro-resonator technology.

Transition 90
a) Steier, U. South. California b) Polymer device and material technology c) Presentation at SPIE Conference, San Jose, 1/28/04, d) Review technology for polymer photonic devices

Transition 91

Transition 92
a) Steier, U. South. California b) Polymer device and material technology, c) LEOS meeting, Tucson, 10/29/03, d) reviewed polymer photonic device program

Transition 93
a) Steier, U. South. Calif. b) polymer device technology. c) M. Morris, B. Block, Intel, (408) 455 6403 d. program review during the year to discuss integration of polymer devices.

Transition 94
a) Steier, U. South. Calif. b) polymer device technology. c) L. Maleki, JPL, 818-354-3688 d. established cooperative program on polymer resonator technology

Transition 95
a) Steier, U. South. Calif. b) polymer device and material technology. c) Timothy Parker, R. Dinu, Lumera Corp. (425) 398-6526 d. continued coolaboration on EO modulator work using Lumera materials.

Transition 96
a) Steier, U. South. Calif. b) polymer device and material technology. c) G. Lindsay Naval Weapons Ctr. China Lake, 760-939-1630 d. Exchange
information on materials and waveguide fabrication.

Transition 97
a) Steier, U. South. Calif. b) polymer device and material technology. c) Lockheed Martin, W. Anderson, 650 424 2224, d. Reviewed bias technology and flexible polymer modulator technology and applications to Lockheed systems.

Transition 98
a) Steier, U. of Southern California, b) Applications of polymers to tunable filters, c) LightSmyth Technologies, Dr. C. M. Greiner, d. Submitted joint STTR proposal.

Transition 99
a) Steier, U. of Southern California, b) Applications of polymers to rf links, c) Regolux Technologies, Dr. Kanti Jain, d. Submitted joint STTR proposal.

Transition 100
a. Steier, U. South. Calif. b. polymer device technology. c. M. Morris, B. Block, Intel, (408) 455 6403 d. program review during the year to discuss integration of polymer devices.

Transition 101
a. Steier, U. South. Calif. b. polymer device technology. c. L. Maleki, JPL, 818-354-3688 d. established cooperative program on polymer resonator technology

Transition 102

Transition 103

Transition 104

Transition 105
a. Steier, U. of Southern California, b. Applications of polymers to tunable filters, c. LightSmyth Technologies, Dr. C. M. Greiner, d. Submitted joint STTR
Polymeric Smart Skin Materials: Concepts, Materials, and Devices

Statistical Report

proposal.

Transition 106

New Discoveries, inventions, or patent disclosures:

| OTL Ref #: | 2636-3380 |
| Inventor(s): | Larry R. Dalton |
| Title of Work: | Hyperpolarizable Organic Chromophores and Electro-optic Materials |
| Patent Title: | Hyperpolarizable Organic Chromophores |
| Provisional Filed: | 7/24/2000 |
| PCT App. Filed: | 7/24/2001 |
| Elect title: | Yes |
| Lics. to the Gov: | 8/24/2001 |

•OTL Ref#: 2727-3487
| Inventor(s): | L. R. Dalton, W. B. Carlson, Gamal-Eddin, Khalil, M. Gouterman |
| Title of Work: | Fourierinated Acrylic Polymer based upon 2-[ethyl(heptadecafluorooctyl)sulfonyl]amino]ethyl methacrylate (FAB) |
| Date Disclosed: | 5/1/2001 |

• OTL Ref: 2765-3533
| Inventor(s): | Larry R. Dalton, W. Brenden Carlson, Gamal-Eddin Khalil, Gregor D. Phelan |
| Title of Work: | Temperature sensing europium chelates |
| Date Disclosed: | 8/13/2001 |

• OTL Ref: 2766-3534
| Inventor(s): | Larry R. Dalton, W. Brenden Carlson, Gamal-Eddin Khalil, Martin Gouterman |
| Title of Work: | Novel iridium luminophores for use as oxygen sensors and pressure sensing paint based upon FAB, FTB, acrylic polymers, acrylic/silicone polymers, polydimethylsiloxane, and trimethylsilyl-1-propyne |
| Date Disclosed: | 8/13/2001 |

• OTL Ref: 2790-3581
<p>| Inventor(s): | Larry R. Dalton, W. Brenden Carlson, Alex Kwan-yue Jen, Xuezhong Jiang |</p>
<table>
<thead>
<tr>
<th>Title of Work</th>
<th>Date Disclosed</th>
<th>OTL Ref</th>
<th>Inventor(s)</th>
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<tbody>
<tr>
<td>based OLEDs.</td>
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<tr>
<td>Title of Work: Highly efficient and thermally stable electro-optic polymers</td>
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<td></td>
<td></td>
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<tr>
<td>from reversibly crosslinkable process</td>
<td>12/27/2002</td>
<td>2799-3935</td>
<td>Younan Xia, Yugang Sun, Brian Mayers</td>
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<tr>
<td>Title of Work: Highly efficient and thermally stable electro-optic polymers</td>
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<td></td>
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<tr>
<td>from reversibly crosslinkable process</td>
<td>01/09/2004</td>
<td>4098DL</td>
<td>Khalil, Callis, Kaminsky, Kimura</td>
</tr>
<tr>
<td>Title of Work: Shear Sensitive Paint for High-resolution 2-Dimensional Shear</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Stress Measurements Over Dynamic Surfaces</td>
<td>4/7/2004</td>
<td>7027DL</td>
<td>Khalil, Callis, Gouterman, Hankins</td>
</tr>
<tr>
<td>Title of Work: Simple Visual Test for Packaging Integrity</td>
<td>5/27/2004</td>
<td>7061DL</td>
<td>Khalil, Callis, Chang, Dalton, Gouterman</td>
</tr>
</tbody>
</table>
Polymeric Smart Skin Materials: Concepts, Materials, and Devices
Statistical Report

• OTL Ref: 7184D
Inventor(s): Gregory D. Phelan, William Brenden Carlson, Larry R. Dalton
Title of Work: Rhodium Based Luminescent Materials
Date Disclosed: 03/15/2005

• OTL Ref: 7185D
Inventor(s): William Brenden Carlson, Gregory D. Phelan, Larry R. Dalton
Title of Work: Platinum Luminescent Materials for Use as an Emission Source
Date Disclosed: 03/14/2005

• OTL Ref: 7186D
Inventor(s): William Brenden Carlson, Gregory D. Phelan, Larry R. Dalton
Title of Work: Osmium Based Oxygen Sensors and Pressure Sensing Paint (PSP)
Date Disclosed: 03/14/2005

• OTL Ref: 7191D
Inventor(s): William Brenden Carlson, Gregory D. Phelan
Title of Work: Polymeric Host Materials for Use in Organic Light Emitting Devices
Date Disclosed: 03/25/2005

• OTL Ref: 7217D
Inventor(s): William Brenden Carlson, Gregory D. Phelan
Title of Work: Platinum based near infrared emitters for use in organic light emitting devices
Date Disclosed: 04/14/2005

• OTL Ref: 7261D
Inventor(s): Younan Xia, Sang-Hyuk Im
Title of Work: Polystyrene Hollow Particles with Deliberate Holes in Their Surface
Date Disclosed: 06/20/2005

• OTL Ref: 7272D
Inventor(s): Younan Xia, James B. Callis, Gamal-Eddin Khalil
Title of Work: Polystyrene beads loaded with dual luminophors for self referenced optical sensing
Date Disclosed: 07/13/2005

• Patent No: 3426P.1US
<table>
<thead>
<tr>
<th>Inventor(s)</th>
<th>Title of Work</th>
<th>Date Disclosed</th>
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<tbody>
<tr>
<td>Xia, Callis, Dalton, Khalil,</td>
<td>Dual-Luminophor Compositions and Related Methods</td>
<td>07/19/2005</td>
</tr>
<tr>
<td>Gouterman, Costin, Im</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alex Kwan-yue Jen, Shi Michelle</td>
<td>Crosslinkable Hole-transport Layer on p-doped Hole-injection Layer for High</td>
<td>11/29/2005</td>
</tr>
<tr>
<td>Liu, Yuhua Niu</td>
<td>Efficiency Polymer Light-emitting Diodes</td>
<td></td>
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<td></td>
<td>Cathode</td>
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<tr>
<td>Gregory D. Phelan</td>
<td>(PSP)</td>
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<tr>
<td>Gregory D. Phelan</td>
<td>New Ligand Design for the Creation of Luminescent Metal Complexes for Use in</td>
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<td>Sensors and Organic Electronics that Emit Light.</td>
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</table>
Polymeric Smart Skin Materials: Concepts, Materials, and Devices

Statistical Report

RICE UNIVERSITY

Tech ID#: 24044
Inventor(s): James Tour, Christopher Dyke, Francisco Maya, Michael Stewart, Bo Chen, Austen Flatt
Title of Work: Use of Functionalized Carbon Nanotubes for Covalent Attachment of Nanotubes to Silicon
Date Disclosed: 05/10/2005

Tech ID#: 24040
Inventor(s): James Tour, Christopher Dyke, Jared Hudson
Title of Work: Functionalization of Carbon Nanotubes in Super Acid Medium
Date Disclosed: 03/01/2004

POLYTECHNIC UNIVERSITY / CITY UNIVERSITY OF NEW YORK, NEW YORK

Inventor(s): Khalil, Callis, Gouterman, Ghandehari, Spellane
Title of Work: Porphyrin Compound Based Corrosion Sensors
Date Disclosed: 7/9/2003

Honors/Awards:

Awards and Honors Received by Larry Dalton:
- 2006 IEEE/LEOS William Streifer Scientific Achievement Award
- Fellow, American Association for the Advancement of Science (2006)
- Senior Member, IEEE (2006)
- QEM (Quality Education for Minorities)/MSE (Mathematics, Science, and Engineering) Network 2005 Giants in Science Award
- Dow/Karabatsos Lecture Series and the Alumni Distinguished Lectureship, Michigan State University, 2005
- AFRL Materials, Manufacturing & Enabling Technologies Lecture Series, Dayton, 2004
- 2003 Chemistry of Materials Award of the American Chemical Society
- 2003 Eastman Lecturer, University of Akron
- 2002 Lecturer, Distinguished Lecture Series of the National Science Foundation
- 2000 Distinguished Alumni Award of Michigan State University
- 1996 Richard C. Tolman Medal of the American Chemical Society
- Paul C. Cross Lectureship, University of Washington, Seattle, WA (1996)
Case Western Reserve University

- The 1990 University of Southern California Associates Award for Creativity in Research and Scholarship
- 1986 Burlington Northern Foundation Faculty Achievement Award
- NIH Research Career Development Awards (Two Awards, one at Stony Brook, one at Vanderbilt, 76-81)
- Camille and Henry Dreyfus Teacher-Scholar Award (75-77)
- Alfred P. Sloan Fellowship (74-77)

Awards and Honors Received by A. K-Y Jen

- Fellow, American Association for the Advancement of Science (2006)
- Boeing-Johnson Endowed Chair University of Washington, 1999-
- Industrial fellow (rank as full professor) Northwestern University, 1995-2000
- Founder’s Award ROItech, 1995
- Outstanding Achievement Award EniChem America, 1994
- President’s Award EniChem America, 1989

Awards and Honors Received by Y. Xia:

- Camille Dreyfus Teacher Scholar, the Camille and Henry Dreyfus Foundation, 2002
- Fellow in Science and Engineering, the David and Lucile Packard Foundation, 2000
- Research Fellow, the Alfred P. Sloan Foundation, 2000
- Faculty Early Career Development Award, the National Science Foundation, 2000
- Victor K. LaMer Award, the American Chemical Society (ACS), 1999
- Oversea Young Investigator Award, the Chinese Natural Science Foundation, 1999
- New Faculty Award, the Camille and Henry Dreyfus Foundation, 1997
- ICI Student Award Finalist, the American Chemical Society (ACS), 1997

Awards and Honors Received by Alan Heeger:

- Presidential Chair, UC Santa Barbara, 2003
- Doctor of Philosophy (h.c.) Bar-Ilan University, Israel, 2002
- National Academy of Engineering (USA), 2002
- Korean Academy of Science (Foreign Member), 2001
- University of California, Santa Barbara, Chancellor’s Medal, 2001
- University of Pennsylvania, President’s Medal for Distinguished Achievement, 2001
- National Academy of Sciences (USA), 2001
- Doctor of Science (h.c) South China Institute of Science and Technology, 2001
Polymeric Smart Skin Materials: Concepts, Materials, and Devices

Statistical Report

- Doctor of Science (h.c.) Japan Advanced Institute for Science and Technology, 2001
- Nobel Prize in Chemistry, 2000
- Doctor of Science (h.c.), Univ. of Nebraska, 2000
- Doctor of Humane Letters (h.c.), Univ. of Mass-Lowell, 1999
- Doctor of Technology (h.c.) Abo Akademi University, Finland, 1999
- Doctor of Technology (h.c.) University of Linköping, Sweden, 1996
- Doctor of Science (h.c.) Université d'Etat a Mons, Belgium, 1992
- John Scott Award for 1989
- Oliver E. Buckley Prize for Condensed Matter Physics, 1983
- Fellow, American Physical Society, 1968
- Alfred P. Sloan Foundation Fellow, 1963-1965

Awards and Honors Received by Samson Jenekhe
- Honeywell Star Inventor Award, 1986.
- 21ST Annual New Horizons in Physics Lecturer, SUNY –, New Paltz, Fall 1990.
- Boeing-Martin Professor of Engineering, University of Washington, 2000.
- Fellow, American Physical Society, 2003
- Fellow, American Association for the Advancement of Science, 2003
- Chemistry of Materials, Editor of Special Issue on Organic Electronics, 2004.

Awards and Honors Received by Jean Frechet:
- IUPAC Canadian National Committee Award, 1983.
- Polymer Society of Japan Lecture Award, 1986.
- American Chemical Society, Cooperative Research Award in Polymer Science 1994.
- American Chemical Society, ACS Award in Applied Polymer Science, 1996
- Society of Imaging Science and Technology, Kosar Memorial Award, 1999
- American Chemical Society, ACS Award in Polymer Chemistry, 2000
- Elected Member of the National Academy of Sciences, 2000
- Elected Fellow of the American Association for the Advancement of Science,
2000
- Elected Fellow of the PMSE Division of the American Chemical Society, 2000
- Elected Member National Academy of Engineering, 2000
- Elected Fellow of the American Academy of Art and Sciences, 2000
- American Chemical Society, Cope Scholar Award, 2001
- American Chemical Society, 2001 Salute to Excellence Award.
- Honorary doctorate, University of Lyon (France) 2002
- Honorary Doctorate, University of Ottawa (Canada) 2004

(b) Honors and major Lectures & Series (2001-2004 only)
- The John Stauffer Lectures, Stanford University 2001
- The Bayer Lectures, University of Pittsburgh 2001
- The George Fisher Baker Lectures in Chemistry, Cornell University 2001
- The Walter J. Chute Distinguished Lectures in Chemistry, Dalhousie University 2002
- The Merk-Frosst Lecture, University of Alberta, 2002
- The Chambers Lectures, University of Rochester, 2002
- Opening Lecture, International Symposium on Nanobiochemistry, Taiwan, 2002
- Plenary lecture: International Symposium of the Molecules of the Future, Lyon, 2002
- Plenary Lecture “Polymeric Nanomaterials 2002”, California 2002
- Keynote Lecturer IUPAC conference on mission and Challenges of Polymer Science & Technology Kyoto 2002
- Plenary Lecture International Symposium on Soft Materials, Tokyo 2002
- The Xerox Distinguished Lectures, Xerox Corp. and McMaster Univ. 2003
- Opening Plenary Lecturer International Dendrimer Symposium, Berlin 2003
- Opening Plenary Lecturer Australian Polymer Symposium, 2003
- Plenary Lecturer IUPAC World Congress, Ottawa, 2003
- Plenary Lecturer Nanotechnology Symposium Yokohama Japan, 2003
- Plenary Lecturer Okamoto Symposium 2004 Nagoya
- Plenary Lecturer Epi-6 Ithaca, 2004
- Plenary Lecturer POC-2004 Prague
- Plenary Lecturer IUPAC Macro-2004 Paris

Awards and Honors Received by James M. Tour:
- Advisory Board, NIRT at U. South Carolina Philosophical and Social Dimensions of Nanoscale Research, 2003-present.
- Distinguished Faculty Associate, Hanszen College, Rice University, 1999-2000.
- Chemical Reviews, American Chemical Society, Editorial Advisory Board, September 1999 to 2003.
Polymeric Smart Skin Materials: Concepts, Materials, and Devices

Statistical Report

- Abbott Distinguished Lecturer, Colorado State Univ., March 1997
- Governor's Mathematics and Science Advisory Board for South Carolina, September 1996-98.
- National Science Foundation, Materials Research Centers Advisory Committee, April 1996.
- National Science Foundation, CAREER Program Advisory Committee, March 1995.
- Exxon Educational Foundation Research and Training Award, 1994.
- National Science Foundation Presidential Young Investigator Award in Polymer Chem., 1991-96.
- Office of Naval Research Young Investigator Award in Polymer Chemistry, 1989-92.
- IBM Corp. One Week Visiting Lecturer, Polymer Division, Almaden Research Center, June 1988.
- National Institutes of Health Postdoctoral Fellow, 1987-88.
- IBM Corporation Full Graduate Fellowship in Polymer Chem., Purdue Univ. 1985-86.
- Celanese Corporation Graduate Fellowship in Chemistry, Purdue Univ., 1981-82.
- American Institute of Chemists Award, 1981.

Awards and Honors Received by William Steier:
- School of Engineering Faculty Service Award
- School of Engineering Senior Research Award
- Fellow IEEE
- Fellow Optical Society of America
- William M. Hogue Professor of Electrical Engineering
- USC Associates Award for Creativity in Research and Scholarship
- Distinguished Alumnus Award, University of Illinois Department of Electrical and Computer Engineering

Awards and Honors Received by Surya Prakash:
- 2004, Elected Member, Phi Kappa Phi Honor Society
- 2004, NASA Space Act Board Award for NTR no. 19227, New Fuels For Direct Oxidation Fuel Cells
- 2004 American Chemical Society Award for Creative Work in Fluorine Chemistry.
- Appointed Member of the Editorial Board, The Journal of Organic Chemistry,
Polymeric Smart Skin Materials: Concepts, Materials, and Devices
Statistical Report


- USC Associates Award for Creativity in Research and Scholarship, University of Southern California, 2000.
- Appointed Member of the Editorial Board, Indian Journal of Chemistry, Section B, 1999.
- Visiting Professor, University of Pierre et Marie Curie, Paris 6, France, April - May 1998.
- First Holder of the George A. & Judith A. Olah Nobel Laureate Chair in Hydrocarbon Chemistry.
- Guest Editor, Research on Chemical Intermediates, Issues 7, 8 and 9, 1996.
- Visiting Researcher, National Institute for Resources and Environment (MITI), Tsukuba, Japan, January 16-26, 1996.
- JPL/TAP Group Achievement Award for Direct Oxidation Methanol Fuel Cells, November 1994.
- Phi Kappa Phi Faculty Recognition Award for Research and Scholarship, University of Southern California, 1986.
- Research Excellence Award by the University of Southern California, 1984.
- Case Western Reserve University Graduate Fellowship, 1974-1978.

Awards and Honors Received by Martin Gouterman:
- Liberal Arts Professor, 1993-94
- Faculty Excellence Award, Minority Science and Engineering Program, 1991
- Received an award certificate for "creative and enduring theoretical contributions to the chemistry of porphyrins..." presented by an indebted porphyrin community, assembled in Los Angeles, California, Sept., 1988.
- NSF Pre-Doctoral Fellow, 1954-58
- PhD student, Roald Hoffmann shared the 1981 Nobel Prize in Chemistry

Awards Received by Under-Graduate Students Working on This Project: 1
Status of Effort:

In the past year, we have made major breakthrough in electro-optic (E-O) materials and polymer light-emitting diodes (PLEDs). Both ultrahigh electro-optic coefficient (> 180 pm/V @ 1300nm) and highly efficient red-emitting LEDs (maximum external quantum efficiency of 7.9% and a maximum brightness of 15800 cd/m²) have been demonstrated for potential applications in ultrahigh-speed modulation/signal processing and flat panel displays.

Highly efficient electro-optic materials development

(1) Materials exhibiting electro-optic activity ($r_{33}$) of greater than 180 pm/V have been achieved. Moreover, new chromophores have been prepared that possess improved molecular hyperpolarizability that should be capable of being translated into even higher electro-optic activity. Efficient synthetic techniques, including microwave-assisted synthesis, have also been used to improve reaction yields and reduce reaction times in the production of new materials. The chromophore development include the following:

(a) Replacement of methyl groups on the tricyanodihydrofuran (TCF) acceptor with one trifluoromethyl group and one alkyl-phenyl-substituted group leads to a factor of 1.5-2.0 in improving molecular hyperpolarizability ($\beta$).

(b) Development of new acceptors (e.g., replacement of the TCF acceptor with a tricyanopyrrolinevinylene (TCP) or a dicyanopyrrolineketone (DCPK) acceptor leads to significantly improved (a factor of 2 improvement) molecular first hyperpolarizability.

The above advances have already led to record EO activity (>180 pm/V at 1.3 micron telecommunication wavelength). When implemented together with supramolecular assembly, these chromophore modifications may lead to further improvement in E-O activities. Long-term stability at 85°C has also been demonstrated for these chromophores in a high glass transition polycarbonate host polymer. Future research will focus on combining the above-mentioned strategies together with synthesizing of more efficient conjugating bridges. This activity should lead to further improvements in molecular first hyperpolarizability. Chromophores will be incorporated into a variety of hardened lattice structures and the resulting materials will be transitioned to device prototyping after synthetic production has been optimized.

(2) We have developed a novel lattice-hardening method using the Diels-Alder reaction. To overcome the nonlinearity-stability trade-off in poled polymers, the lattice-hardening process should ideally be separated from the poling process that requires high rotation freedom of chromophores. In addition, since most of the highly efficient NLO chromophores possess only moderate chemical and thermal stability, very mild conditions should be employed for
lattice hardening. Taking into account all of these requirements, we have developed an efficient crosslinking method using the Diels-Alder [4+2] cycloaddition reaction. The Diels-Alder (DA) reaction generally involves the coupling between a "diene" with a "dienophile". Among many features of the DA reaction is that the resultant adducts can be reversibly thermally cleaved to give back the starting materials. By taking these process advantages in hardening NLO polymers, it allows us to achieve both very high nonlinearity (76 pm/V at 1.3 μm) and thermal stability at 70 °C.

Highly efficient red light-emitting diodes

Highly efficient red-emitting electrophosphorescent devices were fabricated by doping a novel Iridium (Ir)-complex containing trifluoromethyl (CF₃)-substituted pyrimidine ligand into a conjugated bipolar polyfluorene with triphenylamine and oxadiazole as side chains. The device efficiency was enhanced through effective exciton confinement using a layer of 1,3,5-tris(N-phenylbenzimidazol-2-yl)benzene on the cathode side and a layer of in-situ polymerized tetraphenyldiamine-perfluorocyclobutane on the anode side. For a blend with 5 wt % of the Ir-complex, a maximum external quantum efficiency of 7.9 photon/electron % and a maximum brightness of 15800 cd/m² are reached with Commission Internationale de L'Eclairage chromaticity coordinates of x = 0.65, y = 0.34. To our knowledge, these results are among the best for red LEDs using a phosphorescent emitter as dopant in conjugated polymer.
Polymeric Smart Skin Materials: Concepts, Materials, and Devices

Individual PI: Dr. Younan Xia, University of Washington

Accomplishments/New Findings:

MURI Final Report, Xia Group (UW), 8/2006

In the last five years (5/1/2001-4/30/2006), my group has extensively explored a broad range of approaches related to the design and fabrication of smart skin materials capable of detecting, amplifying, and responding to external stimuli. In most of these studies, our efforts were focused on the ability to tune the optical properties of nanostructured materials, and thus to demonstrate the "smart skin" concept. Three accomplishments are highlighted below.

1. Colloidal Crystals with Tunable Stop Bands and Colors

Colloidal crystals whose stop bands could be tuned through the application of a liquid have been fabricated and demonstrated for use as smart photonic coatings. Such a colloidal crystal was generated by infiltrating the voids within an opaline lattice of polystyrene beads with a liquid prepolymer to poly(dimethylsiloxane), followed by thermal curing. When a liquid (e.g., a silicone fluid, hexane, or octane) capable of swelling the elastomer matrix was applied to the surface of this crystal, the lattice constant and thus the wavelength of Bragg-diffracted light was increased. For instance, the color of light diffracted from a colloidal crystal made of 175-nm polystyrene beads could be varied from violet through green and orange to red by swelling it with different solvents. Based on this mechanism, we further demonstrated a photonic paper/ink system where colored patterns could be conveniently generated on the surface of such a colloidal crystal by writing with a Pilot pen, by screen printing, or by microcontact printing with an elastomer stamp. To fully illustrate the potential of this paper/ink system, we have demonstrated the fabrication of photonic papers as large as 75 cm² in area, both supported on rigid substrates and flexible Mylar films. By judiciously choosing the size of the polystyrene beads, it was possible to adjust the color initially displayed by a photonic paper to any wavelength within the spectral region from the ultraviolet to the near infrared. These photonic papers can be fabricated to appear colorless while the regions patterned with the inks will display a shiny color, or vice versa. Such thin films coating are also potentially useful for color coding. For more details, see the publications in Advanced Materials (2003, 15, 892-896) and Langmuir (2003, 19, 9653-9658).

2. Multifunctional Nanofibers by Electrospinning

Electrospinning is a simple and inexpensive technique for the production of fibers with nanoscale
diameters and long lengths. Traditionally this method is used to create randomly-oriented non-woven mats of organic fibers from polymer solutions or melts. By co-spinning sol-gel precursors with an ethanol soluble polymer, we have extended this system to spin composite fibers with excellent size control down to tens of nanometers. Additionally, we have made two important modifications to the electrospinning setup. Using a coaxial spinneret, we have been able to manufacture porous, hollow, and core-sheath nanofibers and control the surface chemistry of resultant fibers by tuning the core and sheath solutions. We have also used patterned collectors to uniaxially align nanofibers into parallel arrays. These arrays could be readily assembled into structures for device fabrication. In a recent study, we have directly fabricated porous nanofibers by immersing the collector in a bath of liquid nitrogen. As a result of thermally induced phase separation, between solvent-rich and solvent-poor regions in the fiber, porous nanofibers were obtained when the solvent was removed in vacuo. This method is versatile in that it can be readily used with non-volatile solvents and does not require selective dissolution of phase-separated polymers. The porosity and resultant morphology of the fibers can be controlled by altering the collection distance and freeze-drying protocol. As this method is dependent on the presence of residual solvent to induce phase separation, it is also applicable to electrospray in order to generate hollow and/or porous particles in a simple and inexpensive fashion. In addition, the fibers are porous throughout, thus making them suitable for encapsulation of active substances or catalysts. By altering the surface properties of the fibers, it is possible to control the adhesion and growth of cells to the fibers, thus enhancing the properties of nanofiber assemblies for applications such as smart fabrics. In addition, the increased surface area of the fibers can be used to create superhydrophobic coatings. For details, see a comprehensive review on this subject published in Advanced Materials (2004, 16, 1151-1170), as well as a recent communication in Journal of the American Chemical Society (2006, 128, 1436-1437).

3. Polymeric Capsules with Controllable Holes in the Surface

Polymer hollow particles with deliberate holes in their surfaces were prepared by swelling solid beads with a good solvent, followed by freeze-drying with liquid nitrogen. The void size of such a hollow particle is controlled by the solubility parameter of the solvent while the hole diameter is determined by the flux of solvent evaporation. This novel class of hollow particles can serve as mesoscale containers to encapsulate various types of functional materials that include organic chromophores, fluorescent proteins, superparamagnetic iron oxide nanoparticles, and spherical polymer beads. As a major advantage of this system, the functional material to be encapsulated can be directly loaded...
through the holes, which will then be closed by heating the sample above the glass transition
temperature of the polymer. This novel class of capsules is immediately useful in the fabrication
of self-healing composites as well as other types of smart materials. A report on this finding was
Status of Effort:

We have continued to focus on the achievement of improved performance for light emitting diodes fabricated from semiconducting polymers (polymer based electroluminescent devices) and from blends of semiconducting polymers with Ir-based metal-organic complexes (electrophosphorescent devices). A number of specific steps forward were demonstrated including the following:

- Demonstration that end-capping could be used to introduce localized impurity levels that function to improve carrier injection
- Demonstration of white emitting electrophosphorescent devices in which the color coordinates, color temperature and color rendering index are insensitive to the brightness
- Demonstration of “printable” --- water soluble conjugated polymer layer --- electron-transporting in polymer LEDs.

A continuing theme was that the energy transfer from the semiconducting polymer host to the emitting moiety (e.g. the Ir-complex, or the fluorenone defect) occurs by sequential charge trapping and not by Förster resonance energy transfer (FRET).

Accomplishments/New Findings:

White Light Electrophosphorescence from Polyfluorene-based Light-Emitting Diodes: Utilization of Fluorenone Defects

Poly(9,9-dioctylfluorene-co-fluorenone) with 1% fluorenone, (PFO-F(1%)), was synthesized as a model compound in order to investigate the optical and electrical effects of fluorenone defects in poly(9,9-dioctylfluorenyl-2,7-diyl), PFO. Photoluminescence (PL) and electroluminescence (EL) measurements demonstrate that PFO-F(1%) emits stable green light. PL and EL studies indicate that Förster energy transfer to and charge carrier trapping on fluorenone defects (with subsequent fluorenone emission) are responsible for the color degradation typically observed with the polyfluorenes. By utilization of “fluorenone defects” in PFO – fluorenone copolymers (PFO-F), white electrophosphorescent light-emitting diodes were fabricated. Polymer blends were spin-cast from solution containing PFO, PFO-F (1%) and tris[2,5-bis-2’-(9’,9’-dihexylfluorene)pyridine-κ²NC₃]Iridium(III), Ir(HFP)₃. The white emission turns on at approximately 5V, with a luminance (L) of 6100 cd/m² at 17 V. The luminous efficiency is 3 cd/A at current density of 8.5 mA/cm² (L= 255 cd/m²).
(a) EL spectrum obtained from white emitting electrophosphorescent PLEDs and (b) the same spectrum as in (a) but renormalized to the sensitivity of the human eye. The white light exhibits stable color coordinates, stable color temperature and has a high color rendering index.

Authors: Xiong Gong, D. Moses and Alan J. Heeger and Steven Xiao

Water Soluble Conjugated Copolymer as Electron-Transport Layer in Polymer Light Emitting Diodes

The principal criteria for a polymer based electron transport layer (ETL) for use in polymer light-emitting diodes (PLEDs) are the following: (1) The lowest unoccupied molecular orbital (LUMO) of the ETL must be at an energy close to, or even within the π*-band of the emissive semiconducting polymer; and (2) The solvent used for casting the electron injection material must not dissolve the underlying emissive polymer. Although a few attempts to satisfy these criteria have been reported, \cite{11,12} none has succeeded in avoiding interfacial mixing in multi-layer PLEDs.

In this study, we reported the fabrication of multi-layer PLEDs using a semiconducting polymer (red, green or blue emitting), cast from solution in an organic solvent, as the emissive layer and a water-soluble (or methanol-soluble) conjugated copolymer as electron-transport layer (ETL) in the device configuration: ITO/PEDOT/emissive polymers/ETL/Ba/Al. To our knowledge, there are no previous reports on the fabrication of multi-layer PLEDs using a water-soluble conjugated polymer as ETL to solve the interfacial mixing problem. The results demonstrate that devices with the ETL have significantly lower turn-on voltage, high brightness and improved luminous efficiency.
The current density (mA/cm²), applied voltage (V) and luminance (cd/m²) vs. applied voltage (V) for devices made using blue-emitting PFO with and without the ETL. Note that with the ETL, the devices turn on at a significantly lower voltage and the brightness at all voltages is increased by orders of magnitude.

Authors: W. Ma, X. Gong, P. Iyer, B. Liu, G. C. Bazan*, D. Moses* and A. J. Heeger*
Double heterojunction photovoltaic cells were prepared from the acceptor polymer poly(benzimidazobenzophenanthroline ladder) (BBL) and the donor poly(p-phenylenevinylene) (PPV) or poly(2-methoxy-5(2'-ethyl-hexyloxy)-1,4-phenylenevinylene) (MEH-PPV). Although the photovoltage was almost doubled as expected, the photocurrent and fill factor were low and thus photovoltaic power conversion efficiencies of only up to 1.35 % were achieved. This power conversion efficiency is significantly lower that the single heterojunction solar cells, suggesting that there is a major problem in coupling the two cells. This is believed to be due to the poor conductivity of the conducting polymer used as a metallic electrode between the two heterojunction cells. A new class of n-type fullerodendrimers with high electron affinity (4.0 eV) were synthesized and explored in photovoltaic devices. A maximum fill factor of 42 % and a power conversion efficiency of 0.15 % were obtained at 10 mW/cm² illumination for initial ITO/C₆₀-G1:MEH-PPV/AI photovoltaic cells. In collaboration with Younan Xia we have prepared a mesh of conjugated polymer nanofibers by electrospinning as an approach to control the interface of polymer solar cells.

**Accomplishments/New Findings:**

1. **Double Heterojunction Polymer Photovoltaic Cells.** It has been recognized that photoinduced electron transfer between donor and acceptor polymers with significantly different energy levels leads to the most efficient exciton dissociation at a donor/acceptor interface. As we reported last year, layered donor/acceptor heterojunctions of poly(p-phenylenevinylene) (PPV) and poly(benzimidazobenzophenanthroline ladder) (BBL) gave very promising photovoltaic conversion efficiencies of about 1.5-4.6 %. One limitation of this layered architecture is the small interface between the donor and acceptor polymers. A double heterojunction device of the type ITO/PPV/BBL//conductor//PPV/BBL/AI represents a potential improvement by doubling the interfacial area. In this case, the individual cells are sufficiently thin to allow for a large fraction of the photogenerated excitons to reach a donor/acceptor interface, while the complete stack is sufficiently thick to absorb most of the incident photons. Furthermore, the photovoltage of a double heterojunction cell should, in principle, be equal to the sum of the photovoltages of the individual heterojunction cells and thus result in an increased open-circuit voltage. We used a conducting polymer thin layer (BBL:PSSA) as the conductor between adjacent...
cells to serve as efficient recombination sites for electrons and holes generated in the neighboring cells and ensuring a minimal loss of photovoltage.

The current density-voltage (J-V) curves of the PPV/BBL double heterojunction devices in the dark and under AM1.5 simulated solar light illumination are shown in Figure 2a. Under dark condition, the J-V curve revealed excellent rectifying semiconductor diode characteristics. Upon illumination, a larger photocurrent was observed in this device. Short-circuit current density ($J_{SC}$) and open-circuit voltage ($V_{OC}$) of the photodiode were 0.045 mA/cm$^2$ and 1.11 V at the 10 mW/cm$^2$ illumination, whereas $J_{SC} = 0.97$ mA/cm$^2$ and $V_{OC} = 1.35$ V at 80 mW/cm$^2$ light illumination. A maximum fill factor of 27 % and power conversion efficiency ($\eta_p$) of 1.35 % were obtained at 10 mW/cm$^2$ illumination. The open-circuit voltage (1.11 V) was much greater than that of single heterojunction cell (0.74 V) as expected. However, the photocurrent and fill factor were much lower and thus the photovoltaic power conversion efficiency was significantly lower than that of the single heterojunction devices. The MEH-PPV/BBL double heterojunction photocell had a short-circuit current density ($J_{SC}$) of 0.172 mA/cm$^2$ and open-circuit voltage ($V_{OC}$) of 0.75 V (Figure 2b) resulting in a fill factor of 29 % and power conversion efficiency of 0.37 % at 10 mW/cm$^2$ illumination. The poor results are mainly attributed to the poor conductivity of the conducting polymer layer used as a metallic electrode between the two heterojunction cells. Further improvements of this architecture, e.g., optimization of the layer thickness for each cell and the contact layer and the use of other interlayers which are less optically absorptive and have better conductivity, are currently under investigation.

2. New Fullerodendrimers for Photovoltaic Devices. Since C$_{60}$ is a strong acceptor (n-type) with long exciton diffusion length and appears to be a versatile building block, fullerene-functionalized dendrimers which dramatically improve the solubility of the fullerenes have attracted much attention in photovoltaic applications. Here we have successfully prepared a new class of n-type quinoline-based fullerodendrimers (Figure 3) for use as good electron acceptors in photovoltaic cells.
We investigated the photovoltaic properties of these fullerodendrimers by blending with MEH-PPV. The photophysical and electrochemical properties of the dendrimers were reported last year. The molecular structures of two dendrimers and a schematic diagram of G1C60:MEH-PPV blend photovoltaic device are shown in Figure 3.

The current density-voltage (J-V) curves of the photovoltaic device made from G1C60:MEH-PPV blend (ITO/G1C60:MEH-PPV/Al) in the dark and under AM1.5 simulated solar light illumination are shown in Figure 4. Short-circuit current density ($J_{SC}$) and open-circuit voltage ($V_{OC}$) of the photodiode were 62 $\mu$A/cm$^2$ and 0.58 V at the 10 mW/cm$^2$ illumination, whereas $J_{SC} = 168$ $\mu$A/cm$^2$ and $V_{OC} = 0.66$ V at 80 mW/cm$^2$ light illumination. A maximum fill factor of 42 % and power conversion efficiency of 0.15 % were obtained at 10 mW/cm$^2$ illumination. The power conversion efficiency is better than that of the single-layer PPV Schottky-barrier device ITO/PPV/Al which had a power conversion efficiency of 0.03 % at 10 mW/cm$^2$ illumination. These results demonstrate that the new quinoline-based fullerodendrimers are promising n-type (electron-transport) materials for polymer photovoltaic applications.
3. Polymer Blend Solar Cells via Electrospinning. Charge recombination between the separated holes and electrons needs to be minimal to better utilize the photogenerated excitons in polymer-based solar cells. The exciton dissociation is most efficient at a donor-acceptor (p-type polymer/n-type polymer) interface, where a donor with a low IP and an acceptor with a high EA can drive the separation of the bound photogenerated exciton into free charges. The nanostructured interface heterojunctions (Figure 5) will increase the donor-acceptor interfacial area which will lead to better exciton dissociation and will alleviate the problems of generally small exciton diffusion lengths in organic materials. In collaboration with Younan Xia we propose to use electrospinning technique to make such nanostructured heterojunctions. Figure 6 shows an SEM micrograph of a mesh of nanofibers of MEH-PPV (p-type polymer) made via electrospinning. An n-type polymer layer can then be spin coated on top of this mesh to achieve large interfacial area heterojunction between the donor and acceptor polymers.

Figure 5. Nanostructured interface heterojunction polymer solar cell schematic

Figure 6. SEM Image of MEH-PPV Nanofibers by electrospinning.
Status of Effort:

We have focused on electroactive polymeric “smart skins” that fulfill functions of light emission and/or light absorption and/or charge transport for new generations of highly efficient polymer-based light emitting systems, photovoltaics, and organic field-effect transistors. While our polymer targets are based on fundamentally new molecular concepts, their designs are also user-friendly as they are solution processible: they can be applied by classical spin-coating, drop-casting, or ink-jetting techniques as opposed to more complex vacuum evaporation/deposition procedures. In addition to fundamental synthetic developments we have also demonstrated that the new smart skins can be incorporated into working polymer-based devices with state of the art efficiencies of over 10% in light emitting diode configuration and 2% in photovoltaic mode.

Accomplishments/New Findings:

Novel copolymers incorporating both electron transport (ET) and hole transport (HT) moieties, or terpolymers containing emitter as well as ET and HT moieties, have been designed and their structure optimized for solubility and electronic properties from a small library of novel monomers with a variety of structures. The new polymers can be spin-coated onto appropriate substrates to produce highly efficient light emitting diode devices. Particularly noteworthy is the fact these polymers are highly soluble and can be handled in air to produce spin-coated OLED devices with efficiencies as high as 11% under unoptimized processing conditions.

Similarly, we have designed novel functionalized electroactive polymers that provide excellent “electronic communication” with semiconducting inorganic components such as nanocrystals, nanowires, or bulk surfaces for the preparation of polymer-based photovoltaics. Once again the polymers are designed for their ease of use as their intrinsic solubility enables spin-coated for device preparation. In early tests, these novel polymers have demonstrated vastly improved photovoltaic performance over conventional electroactive polymers with efficiencies of 2% achieved in unoptimized devices.

Most Recent Research: Design and applications of functionalized polythiophenes films as field effect transistor with increased air stability: We have achieved the synthesis of new polythiophenes containing electron-withdrawing alkyl carboxylate substituents, which exhibit high charge mobility (Figure A). We have found that the regularity of the alkyl carboxylate substitution in our polythiophene can induce and facilitate molecular self-assembly in a fashion similar to that exhibited by regioregular poly(3-hexylthiophene) P3HT. Due to the electron-withdrawing properties of the carboxylate substituents, the new polymers have lower HOMO energy levels (by approximately 0.5 eV) than P3HT, and therefore provide better oxidative doping stability than conventional solution-processible polythiophenes such as P3HT. The new materials are highly crystalline and exhibit very small π-π stacking distances.
in the solid state. High charge mobilities are observed as a result of the close ordering of the polymer chains, and top-contact organic thin-film transistors (OTFTs) fabricated entirely in air had measured mobilities averaging 0.06 cm²/V·s with on/off ratios >105. Off currents in these devices remained low over a period of months demonstrating the low propensity of these materials towards p-doping by molecular oxygen. We have also prepared novel oligothiophenes with excellent solubility and electronic properties than can be used to print transistors using an ink-jet printer.

Figure A. Synthesis of the regioregular polythiophene 5 with low HOMO.
Status of Effort:

We have developed the covalent functionalization of single-wall carbon nanotubes (SWNTs) in fuming sulfuric acid to afford unbundled individual SWNT-arylsulfonic acids that are soluble in water; the process does not require surfactant or polymer-based pre-wrapping, centrifugation or sonication. SWNTs are promising building blocks for high performance composite materials. An obstacle to fully exploiting the materials properties of SWNTs is their tendency to spontaneously form bundles and/or flocculate in their unfunctionalized state due to the extraordinary 0.5 eV/nm intermolecular cohesive interaction between neighboring SWNTs.

It has recently been reported that SWNTs disperse as individuals in superacids with SWNT concentrations of up to 10 wt %. Exploiting the solubility of SWNTs in oleum, (H2SO4, 20% free SO3), we have modified our diazonium functionalization chemistry to produce efficient functionalizations of nanotubes in that solvent. The aryl rings sulfonate under the reaction conditions thereby imparting the unusual water solubility to the final compounds. We achieved the functionalization using sodium nitrite and diverse anilines to covalently attach arenes to the HiPco-produced SWNTs that had been oxidatively purified (p-SWNT). Previous diazonium functionalization methods required the presence of a radical source for functionalization to ensue. In superacids it is proposed that SWNTs are surrounded by a double layer of protons and counterions, thus the tube is unlikely to inject an electron into the diazonium salt. Interestingly, we found that the reaction in superacid does proceed in the presence of a radical initiator and affords a similar degree of functionalization when compared to previous diazonium methods. However, in the superacid process, the functionalization results in individual SWNTs, not bundles.

Accomplishments/New Findings:

We have developed methods of functionalizing single wall carbon nanotubes (SWNTs) in SDS solution such that they do not rebundle once the SDS is removed. We have also developed methods of functionalized SWNTs in oleum, and have examined the physical characteristics of blends of nanotubes in various polymer matrixes (see publications). The functionalization of carbon nanotubes will allow the blending of the functionalized tubes into materials of aircraft construction, reducing weight and increasing strength.
Status of Effort:

We have been investigating optical waveguides made with ordered 3D arrays of polymer spheres (PBG) as the waveguide walls. By incorporating analytes in or on the spheres, the band gap properties of the arrays can become sensitive to numerous environmental components such as gasses, temperature, strain, moisture, etc. By combing this with the waveguide slow wave properties, a sensitive polymer detector could be realized. We have developed the technology of self alignment of the arrays and used the band gap properties for temperature detection. However the loss per reflection from the arrays is too large for an effective slow wave structure. We have therefore redirected our efforts. We are now preparing a theoretical paper that shows the trade off between slow wave velocity and loss in real media.

Accomplishments/New Findings:

As part of the "smart skins" program, we have analyzed and developed a new class of fiber based polymer micro-resonator strain sensors. The flexible sensors are fabricated using a lift off process and are based on the distortion of the micro-ring by strain and the subsequent shift of the resonant wavelength. For the demonstration, a controlled strain was achieved by flexing the sensor.

A. Polymer Micro-Resonator Strain Sensors

Fiber based sensors have been demonstrated and their advantages of EMI immunity, optical multiplexing, and relatively high sensitivity have been discussed widely in the literature. Fiber grating sensors have the added advantage that they can be used for distributed sensing and multiple sensors can be addressed in serial fashion over one fiber. We report here on a new type of fiber-based sensor that is based on the polymer micro-resonator technology and that has all of the advantages of fiber grating sensors including high sensitivity and wavelength multiplexing. These detectors are small (100-500 µm dimensions) and could be embedded into materials for the detection of two-dimensional patterns for "smart structures". The sensors we report on here are strain sensors but the concepts can be expanded to real-time temperature, vibration, and load sensing. With the use of selected polymers, the micro-resonator sensors can also be used for chemical and environmental sensing.

Figure 1 shows a schematic of a waveguide coupled micro-ring resonator and the effect of strain on the ring. The resonant wavelength of the ring is given by

$$\lambda = \frac{n_{eff} L}{m}$$

(1)

and the free spectral range is given by

$$FSR = \frac{\lambda^2}{n_{eff} L}.$$  

(2)

In these expressions $L$ is the path length around the ring ($L=2\pi R$ if the ring is a circle of radius $R$), $n_{eff}$ is the effective index of refraction of the optical mode in the ring waveguide, and $m$ is an integer. The unloaded $Q$ is given by
where $\alpha$ is the waveguide loss, including material, scattering, and bending loss in dB/cm and $\lambda$ is in microns. At resonance, power is coupled from the input guide and the output drops. At critical coupling all of the power is removed from the input guide.

If the substrate upon which the polymer micro-resonator is fabricated is strained, the shape of the ring will be distorted and as L changes, the resonant wavelength shifts. Since these can be high Q devices ($\sim 10^5$), small resonant shifts and small strains can be detected.

For small strain, the diameter becomes larger in the direction of the strain and smaller in the perpendicular direction and a circular ring becomes an ellipse. The change in path length around the ring can be written as

$$\frac{\Delta L}{L} \approx \frac{\varepsilon(1-\nu)}{2}$$

where $\varepsilon$ is the strain and $\nu$ is Poisson’s ratio. For a circular ring, the direction of the strain does not matter.

The index of refraction of the polymer, $n$, is also affected by the strain through the strain-optic effect. For light propagating the direction of the strain, for either polarization

$$\frac{\Delta n}{n} = -\frac{n^2\varepsilon}{2}[P_{12} - \nu(P_{11} + P_{12})].$$

For light propagating perpendicular to the strain with the polarization in the direction of the strain

$$\frac{\Delta n}{n} = -\frac{n^2\varepsilon}{2}[P_{11} - 2\nu P_{12}].$$

For light polarization perpendicular to the strain the expression is the same as Equation (5). In these expressions $P_{11}$ and $P_{12}$ are the stress-optic coefficients. The calculation of the effect on the resonant wavelength due to $\Delta n$ requires a weighted integral around the circular path but if the values for polystyrene, a typical polymer, ($\nu=1.55$, $P_{11}=0.3$, $P_{12} = 0.31$, $\nu=0.4$) are used in Equations 4, 5, and 6, we find $\Delta n/n$ varies from $-0.06$ to $-0.085\Delta$. This effect is smaller than $\Delta L/L = 0.3\varepsilon$ and in this first demonstration we will therefore assume the average effect of the index change around the ring is the average value of $-0.072\varepsilon$. If we assume that $\Delta n_{\text{eff}} \approx \Delta n$, the change in the resonant wavelength, $\Delta \lambda$, due to strain is therefore

$$\frac{\Delta \lambda}{\lambda} = \frac{\Delta L}{L} + \frac{\Delta n}{n} = 0.228\varepsilon$$

The resonant wavelength is also temperature sensitive

$$\frac{\Delta \lambda}{\lambda} = \frac{\Delta L}{L} + \frac{\Delta n}{n} = \left[\alpha + \left(\frac{dn}{dT}\right)\right] \Delta T$$

where $\alpha$ is the coefficient of thermal expansion of the substrate and $dn/dT$ is the thermal index coefficient of the core polymer. For typical polymers, $dn/dT$ is approximately $-10^{-4}$. The thermal wavelength shift will therefore depend on the
substrate to which the ring is attached.

The fabrication of the micro-resonator strain sensor is based on a lift-off process used to fabricate flexible polymer electro-optic modulators. It is based on the low adhesion between Au films and SU-8, a photo-resist. The fabrication process is shown in Fig 2A and the cross-section and photograph of the sensor are shown in Fig.3A. The Si fabrication substrate is patterned with the Au lift-off pattern and the separation occurs at the SU-8/Au interface. After lift-off, the 150 μm thick UV15-7 film becomes the device substrate. Si pads are left on each end of the device to serve as mounting pads for the coupling fibers.

To apply a controlled strain, the Si pads were mounted on separated movable micro-stages as shown in Fig 4A. When the pads are moved closer together, the flexible device bends upward and from the measured vertical displacement Δy, the radius of curvature, R, of the flexed device is calculated and from the radius and thickness, d of the film, the strain on the upper surface is calculated. The vertical displacement was measured optically using a CCD camera. The total length of the sensor, L, between the mounting pads was 11 mm. If the flexed shape is assumed to be a sigmoid and the horizontal movement, Δx, is much smaller than 11 mm, the radius of curvature R is approximately given by

\[
R \approx \frac{L^2}{16\Delta y} = \frac{7.6}{\Delta y}
\]

where R and Δy are in millimeters. If the Young’s moduli of the various polymers used in the sensor are assumed equal, the strain on the upper surface where the micro-ring is located is approximately given by

\[
e = \frac{d}{2R}.
\]

The measurements were done with a tunable 1310nm laser and the shift in the resonant wavelength of one of the modes of the ring was measured as a function of the bending of the ring. The measurements were done at room temperature and no attempts were made to closely control the temperature of the sensor. We believe the resonator was under coupled. The observed Q was 4.5 x 10³ and there was no observable change in the Q when the sensor was flexed.

Fig 5A shows the measured change in resonant wavelength compared to the calculated change given by Eq 7 as a function of the strain. The comparison is quite good; the measured slope is 0.32 x 10⁻³ nm/με and eq. (11) at 1310 nm gives 0.30 x 10⁻³ nm/με.

The sensitivity of the micro-resonator strain gauge is about 30% of that reported for fiber Bragg and fiber Fabry-Perot strain gauges. The micro-resonator strain gauge sensitivity can be increased to about the same as these sensors by using a race track design. In this design, the sensitivity is greatest for strain along the long axis of the resonator and by using two orthogonal race tracks, the direction of the strain can also be sensed. If two nominally identical race track resonators have their long axes perpendicular to each other and are coupled to the same waveguide, the difference between their resonant wavelengths is independent of temperature changes. The difference however is a function of the strain except in the special case where the strain is at 45° to the resonator axes. This is a possible way to eliminate the problem of these gauges being sensitive to both strain and temperature.
Fig. 1A Schematic of the waveguide coupled micro-ring resonator and the effect of strain on the ring.

Fig. 2A Fabrication process of the micro resonator strain sensor based on a lift-off process.

Fig. 3A Cross-section and photograph of the sensor.
B. Polymer optical waveguide vertically coupled to high Q Whispering–Gallery resonators.

In conjunction with JPL, we implemented a new approach to bringing very high Q disc resonators into an integrated circuit technology and smart skins based on polymer waveguides. The polymer optical waveguide is vertically coupled into the whispering gallery modes of a fused silica resonator disk. Vertical coupling between high Q WGM resonator disks with a polymer waveguide specially has potential benefits for many photonic applications such as: integrated circuits, power switching, wavelength selection, filters and modulator. This can potentially have a significant benefit for integrated photonic circuits and many other applications. We obtained the loaded quality factor $Q \approx 3.43 \times 10^6$.

Fused silica sphere and disc micro-resonators have been reported with Q’s exceeding $10^9$. Tapered fibers, side polished fibers and frustrated total internal reflection prisms are typically used to couple to these whispering gallery modes. On the other hand, ring waveguide and disc micro-resonators have been integrated with coupling bus waveguides in several materials systems. The highest reported Q’s in these integrated devices are $\sim 10^5$ usually limited by scattering from side-walls.

In this work, the fused silica (Suprasil F300) disc, radius 1.7 mm, thickness 35 $\mu$m, is fabricated with the sides optically flat and the edge optically polished. On a separate Si substrate
a group of straight polymer waveguides are fabricated. The waveguides are designed to have the same effective index of refraction at $\lambda = 1550$ nm as the mode in the fused silica disc. One of the waveguides is vertically coupled to the mode of the disc by careful alignment of the waveguide near the perimeter of the disc and adjusting the vertical air gap between the disc and the waveguide as shown in Fig. 1B.

Efficient coupling from the polymer waveguide to the fused silica disc requires a velocity match between the waveguide mode and the whispering gallery mode of the disc. The effective index of the lowest order radial mode of the disc was estimated as using in and the results are shown in Fig. 2B for a wavelength of 1550 nm. The estimated effective index of a 1.7 mm radius disc is 1.4384.

The single mode polymer waveguides were fabricated on a Si substrate using a 7 $\mu$m thick lower cladding of ZPU13-R1 [3] with a refractive index of 1.4053 @ 1550 nm. The core material is ZPU12-R1 with a refractive index of 1.4701 @ 1550 nm. The upper cladding is air and a ridge waveguide is used for lateral confinement. The effective index method was used to design the waveguide with an effective index close to the effective index of the disc and with a width the same as our existing masks. With a waveguide width of 3.5 $\mu$m, a ridge height of 0.5 $\mu$m and a core width (outside the ridge) of 1.4 $\mu$m, the calculated effective index is 1.4376.

Over the estimated effective coupling length between the waveguide and the disc of $\sim 150$ $\mu$m, this index mismatch is negligible.

The disc was glued by wax on top of the brass holder post and the waveguides were mounted on a micro-manipulator for both horizontal and vertical adjustment. The waveguides were placed under the disc. One of the waveguides (as shown in Fig. 1B) was positioned near the perimeter of the disc and the lateral position fine tuned for maximum coupling. A tunable 1550 nm laser was fiber butt coupled into the correct waveguide and the waveguide output was fiber coupled to a photo-detector. The vertical coupling gap between the waveguide and the disc was adjusted with a micro-manipulator and piezo-electric movements to maximize the coupling.

Fig 3Ba shows the output power vs. detuning frequency and shows coupling to two longitudinal modes and two different radial modes of the disc. The frequency spacing between the sets of the same radial modes is consistent with calculated free spectral range (FSR) of 19.5 GHz, where $\text{FSR} = c/2 \pi n_{\text{eff}} R$. Figure 3Bb shows one mode on an expanded frequency scale. The measures loaded $Q$ is \(3.43 \times 10^6\). The coupling is near critical coupling. We calculate the percentage of power coupling from the waveguide into disc about 0.7 % [4]. The unloaded $Q$ of \(6.86 \times 10^8\), thus the total propagation loss (the sum of scattering loss due to roughness, absorption loss of material and radiation loss due to bending) is about \(8.5 \times 10^{-3}\) cm$^{-1}$ that leads to the roundtrip loss 0.9% in the disc.

We installed piezo-electric actuator with low drive voltage of 3 VDC per 100 nm displacement into the manipulator to control the air gap between disc and the waveguide. Through the microscope we can observe the contact fringes when we closely set the top of waveguide’s ridge touching parallel with the bottom surface of the disc. The surface roughness of polished disc can be estimated about nm range [6]. The power coupled to one of the modes as measured and Fig 4B shows the transmission to the output guide as a function of the air gap when the wavelength is tuned to resonance. The critical coupling is obtained when the gap is about 0.45 $\mu$m compare to the estimated gap of 0.5 $\mu$m by using the coupled mode theory.
Fig. 1B The top and cross section view of polymer waveguide vertically coupled to the WGM in resonator disk.

Fig. 2B The effective refractive index of WGM in resonator disk as a function of its radius at wavelength of 1550 nm.

Fig. 3B The optical transmission spectrum for the polymer waveguide - fused silica resonator disk system at $\lambda = 1550$ nm.

a) Output power vs Laser detuning frequency, $FSR = 19.54$ GHz.

b) Expanded frequency scale show that $FWHM = 56.4$ MHz, so the $Q_{loaded} = 3.43 \times 10^6$

Fig. 4B The transmission factor vs the gap between the polymer waveguide and resonator disk.
Polymeric Smart Skin Materials: Concepts, Materials, and Devices

Individual PI: Dr. Surya Prakash, University of Southern California

Status of Effort:

- Polystyrene nanospheres were doped with charged dyes.
- Poly(pentafluorostyrene) nanospheres and poly(pentafluorostyrene) grafted polystyrene nanospheres were surface functionalized by novel nucleophilic aromatic substitution chemistry.

Accomplishments/New Findings:

Doping of polystyrene nanospheres with charged dyes
The infrared region of the electromagnetic spectrum between 1300 nm and 1550 nm is in the telecommunication wavelength region. Many of the dyes emissive in the infrared region are either positively or negatively charged. The polystyrene nanospheres prepared by emulsifier free emulsion polymerization technique have overall surface negative charge. Positively charged Basic Fuchsin dye was found to attach to the surface of the nanospheres strongly by electrostatic interactions as indicated UV-Vis spectroscopy.

Functionalization poly(pentafluorostyrene) (PFS) nanospheres and poly PFS grafted polystyrene nanospheres.
Monodispersed poly(pentafluorostyrene) nanospheres and poly(pentafluorostyrene) grafted polystyrene nanospheres fabricated in our previous work were functionalized by nucleophilic aromatic substitution chemistry. The nanospheres were surface functionalized with para-aminophenoxide and 2-(4-aminophenyl)ethoxide nucleophiles. The surface amino groups were diazotized and diazocoupled to interesting dye molecules. Furthermore, thiol group containing nucleophiles gave nanospheres that strongly complexed gold colloidal particles. Hydroxy as well as carboxylic acid group containing nanospheres were also prepared. All the surface functionalized nanospheres were characterized by DRIFT, XPS and diffuse reflectance UV spectroscopy.
Status of Effort:

(1) **Highly Stable NIR Dyes for Photonic Applications: Tetra(pentafluorophenyl)porphodilactone and trilactone.** Kim Lau, 4th year graduate student

The goal of this research is to synthesize and characterize stable NIR dyes from the porpholactones family. These photostable dyes will be used to develop oxygen, pressure, pH, CO₂, temperature sensors and potential photovoltaic materials. Density Functional Theory calculations suggested that opposite porphodilactones should be significantly red shifted in comparison to the porphomonolactone and the porphotrilactone should have absorption bands greater than 1000 nm. We have varied the reaction conditions and observed that light and oxygen are critical factors. We have adopted a new synthetic approach, designed by Bruckner and Dolphin, to separately synthesize the dilactone isomers.

(2) **High resolution, 2-dimensional shear stress measurements from imaging polarimetry.** Fletcher Kimura, 3rd year graduate student

This project involves the development of a novel method for obtaining high-resolution, 2-dimensional shear stress measurements over aerodynamic surfaces, based upon the dynamic birefringence of a shear sensitive, liquid crystal coating. We developed a new imaging device that can make quantitative birefringence measurements at the rate of 30 Hz. The resolution of the resulting shear stress maps are limited only by the CCD imager. We made considerable progress fabricating liquid crystal coatings that are robust yet remain responsive to shear stress.

(3) **Pressure Measurement Using Singlet Oxygen Emission.** Alvin Chang, 2nd year graduate student

We are developing an alternative luminescence method to measure pressure / oxygen concentrations based on the 1270 nm singlet oxygen emission, which can be imaged with an InGaAs NIR camera. This direct measurement of oxygen emission complements and further validates the indirect oxygen measurement. Initial success at obtaining a high negative correlation between 650 nm and 1270 nm emissions under solution conditions has led us to additional two dimensional film studies. We are in the process of evaluating NIR cameras from different vendors.

(4) **Continuous Gas Leak Detection System.** Alice Chin, senior, chemistry student

A novel gas leak detector has been developed based on continuous monitoring of the oxygen concentration surrounding a natural gas pipeline. Any gas leaking from a pipeline and the associated displacement of oxygen by the
leaking gas can then be detected through fiber optic evanescent field spectroscopy via an oxygen sensitive based sensor. Once optimized, the detector system will capture and measure in real time large leaks from refineries and other oil and gas or chemical process equipment flanges, valves, and pump leaks. Grant proposal has been presented to the New York gas group for further development.

Accomplishments/New Findings:

- In collaboration with ISSI awarded phase I STTR Air Force grant to develop Pressure- and Temperature-Sensitive Paint.
- Developed a new imaging instrument for high resolution, 2-dimensional shear stress
- Progress has also been made towards the development of robust liquid crystal coating to adhere to an airfoil surface, yet remain responsive to shear stress.
- Successfully evaluated the gas leak detector system. Including > 30 days of continuous detection of methane gas leaks by the oxygen sensor embedded in wet sand.
- Identified a synthetic procedure to make the NIR dye dilactone at higher yield.
ACCOMPLISHMENTS/FINDINGS:

The Dalton research group has participated in many of the activities described by other individual investigators in the preceding paragraphs. Most particularly, they have been involved in the design and development of sensor paints (with Gouterman and Khalil). Activities of the final year resulted in development of chem./bio. thin film sensor paints and the integration of these materials into ring microresonator devices for enhanced sensitivity of detection. Another major theme of the Dalton research group has been the integration of multi-component diverse material technology into a single thin film (smart paint) format. This has included the integration of organic and silicon materials.

The Dalton research group has also actively collaborated with the Steier and Jen groups on the development of thin film materials with exceptional optoelectronic and sensor properties.

The Dalton research group helped pioneer the development of carbon nanotube actuators and other carbon nanotube based technologies.