Design, Synthesis and Characterization of Novel Nonlinear Optical Polymers

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

R & T: 4132016

GRANT Number: N00014-90-J-1148

GRANT Title: Design, Synthesis and Characterization of Novel Nonlinear Optical Polymers

Principal Investigator: Dr. Sukant Tripathy

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Part I

a. Number of papers submitted to refereed journals, but not published: 3
b. Number of papers published in refereed journals (list attached): 2
c. Number of books or chapters submitted, but not published: 0
d. Number of books or chapters published (list attached): 2
e. Number of printed technical reports & non-refereed papers (list attached): 4
f. Number of patents filed: 4
g. Number of patents granted: 0
h. Number of invited presentations at workshops or professional society meetings (list attached): 2
i. Number of presentations at workshops or professional society meetings (list attached): 8
j. Honors/Awards/Prizes for contract/grant employees (list attached): 5
k. Total number of full-time equivalent graduate students and post-doctoral associates supported during this period, under this R & T project number:
   Graduate Students: 2
   Post-Doctoral Associates: 2
including the number of,
   Female Graduate Students: 1
   Female Post-Doctoral Associates: 0
the number of,
   Minority Graduate Students: 0
   Minority Post-Doctoral Associates: 0
and the number of,
   Asian Graduate Students: 2
   Asian Post-Doctoral Associates: 2

l. Other funding (list agency, grant title, amount received this year, total amount, and the period of performance, and briefly state the relationship of that research to your ONR grant):

Department of the Army, University Research Initiative
*Intelligent Materials and Structures Based on Ordered Assemblies of DNA*
co-principal investigator with Professors Kenneth Marx and Jayant Kumar
Research Grant, March 15, 1993 - March 14, 1994 - $155,000.00

American Chemical Society/Petroleum Research Fund
*Novel Photocrosslinked NLO Polymers and Related Electro-Optic Devices*
Research Grant, January 1, 1993 - December 31, 1993 - $20,000.00

University of Maryland, Baltimore
*Ultra High Speed Optical Analog-to-Digital Converter*
Research Grant, February 1, 1992 - January 31, 1993 - $5,000.00

Electric Power Research Institute
*Evaluation of Unique Solar Energy Conversion Concept*
Research Grant, October 14, 1991 - September 30, 1992 - $85,000.00

The research listed above is not related to the reported ONR grant. The Petroleum Research Foundation funding is being used to start a new line of research involving polydiacetylenes with electroactive side groups.
Part II

a. Principal Investigator: Dr. Sukant Tripathy

b. Current telephone number: 508-458-7116

c. Cognizant Scientific Officer: Dr. JoAnn Milliken

d. Brief description of the project.

The principal focus of the project is to develop new materials chemistry based on molecular level design and solid state chemistry. The goals have been to develop electroactive polymers with novel electronic, optical and nonlinear optical properties. Second and third order nonlinear optical materials have been developed based on conjugated macromolecules and asymmetric anharmonic molecular electronic dipolar oscillators.

In this multidisciplinary research effort, starting from first principle, polymeric systems have been developed with stable large nonlinear optical coefficients, ultrathin electroactive redox monolayers, molecular superlattices, etc. Sol-gel chemistry, photochemical crosslinking and photopolymerization have been employed as engineering tools in materials fabrication and to elicit new phenomenon.

e. Significant results during last year.

1. A new class of stable (temporal and thermal) second order nonlinear optical materials has been developed based on interpenetrating polymer networks.

2. Relaxation in the nonlinearity at high temperatures close to $T_g$ are related to a $\beta$ relaxation process for the IPN in contrast to the behavior for guest host systems where $\alpha$ relaxation appears to dominate the relaxation process.

3. Efficient Cerenkov Second Harmonic Generation in guided wave structures has been demonstrated using a number of candidate crosslinkable NLO polymers. Prototype frequency doubling devices have been built.
Brief summary of plans for next years work.

**Molecular Systems:** Two NLO systems will be extensively investigated. The newly developed IPN system opens up numerous possibilities. Appropriate molecular design of the components of the NLO IPN will lead to better stabilities and enhanced nonlinearities. Reactions and solid state chemistry under ordering influence of large electric fields is the subject of this study.

In the second area of research NLO chromophores will be covalently bonded to conjugated macromolecules. Second and third order optical nonlinearities are of interest in this case. Further, photovoltaic effect, photorefractive and other unusual properties will be investigated.

**Processing and Microfabrication:** We are carrying out molecular level processing and microfabrication of NLO devices in the same laboratory. Microchannel structures are being fabricated on glass substrates. Reactive IPN components are spun on and processing is carried out under large electric field. Fibers are being pigtailed at the channel ends and the whole system packaged with epoxies.

**Characterization:** Numerous solid state in situ characterization techniques are being employed. Polarized FT-IR, FT-Raman, UV-Vis-Near IR spectroscopies will be carried out as a function of photoprocessing and field induced modifications. Other linear and nonlinear optical properties will be investigated. Dynamic mechanical analysis, dielectric measurements and thermal analysis will be carried out to study molecular motion organization and property aspects. Photoconductivity and photovoltage will be measured. Second harmonic generation and EO modulation are other properties of interest.

g. Name of graduate students and post-doctorals currently working on the project.

**Post-doctoral**
Dr. Nagendra Beladakere and Dr. Thavorath Ravindran

**Graduate students (Ph.D. Candidates)**
Mr. Govindasamy Chittibabu
Mr. Dong Yu Kim

**Undergraduate students**
Mr. Craig Masse
Part II

Research Highlights
**Goal:**

- To develop novel nonlinear optical (NLO) organic/inorganic composites for second-order processes.

**Approach:**

- An NLO active organic/inorganic composite based on a polyimide and an alkoxy silane dye (ASD) is prepared.

- This hybrid material, formed by simultaneously poling and curing, exhibits excellent long term second-order NLO stability at elevated temperature.
Organic component: polyimide which is formed by imidiziation of polyamic acid.

Inorganic component: ASD will undergo sol-gel reaction leading to the formation of the inorganic network.
Temporal behavior of the second harmonic coefficient, $d_{33}$, of poled polyimide/ASD ($d_{33}(0) = 28$ pm/V).
Summary:

- A polyimide/inorganic composite was prepared as a second-order NLO material for the first time.

- The combination of the high Tg of the polyimide and the network formed by the ASD in this system promote excellent stability of the poled order in the molecular composite.
Goal:

- To develop novel electroactive polymeric systems with stable second-order nonlinear optical (NLO) property.

Approach:

- An interpenetrating polymer network (IPN) incorporating NLO active chromophores is prepared by curing and poling simultaneously at 200 °C for 1 h.

- The resulting IPN possesses excellent optical quality and large second-order NLO coefficient ($d_{33} = 33 \text{ pm/V}$). The $d_{33}$ value remains unchanged after heating at 110 °C for 168 h.
Network I: formed by an epoxy based thermocrosslinkable NLO material (BPAZO).

Network II: an NLO active phenoxy silicone polymer formed by the sol-gel reaction between ASD and THPE.
BPAZO ASD + THPE

Double bond reaction

ASD + THPE

Sol-gel reaction

curing ↓ poling

↓ NLO active chromophores

Schematic diagram for the formation of the IPN.
Temporal behavior of the second harmonic coefficient of different poled/cured samples.
Summary:

- The synergistic stability of this poled-ordered system is mainly due to the combination of high Tg, high crosslinking density, and permanent entanglements among the polymer chains of the IPN.

- The results from the IPN system have demonstrated a promising new direction for the development of new classes of NLO materials.
b. Number of papers published in refereed journals (list attached): 9


d. Number of books or chapters published (list attached): 2


e. Number of printed technical reports & non-refereed papers (list attached): 4


h. Number of invited presentations at workshops or professional society meetings (list attached): 2

"Polymers for Nonlinear Optics" (Sukant Tripathy) Indian Institute of Technology•Bombay, India, December 1992.

"Polymeric Materials Based Photonic Devices" (Sukant Tripathy) University of Alabama•Tuscaloosa, Alabama, November 1992.

i. Number of presentations at workshops or professional society meetings (list attached): 8


j. Honors/Awards/Prizes for contract/grant employees (list attached): 5

1. The American Chemical Society's Carl S. Marvel Award for Excellence in Polymer Chemistry was awarded to Professor Sukant Tripathy by the American Chemical Society in 1993.

2. The University of Massachusetts Lowell's Outstanding Graduate Faculty Award was awarded to Professor Jayant Kumar by the Graduate School of the University of Massachusetts Lowell in 1993.

3. The American Chemical Society's Division of Polymeric Materials Science and Engineering Sherwin Williams Award Competition has selected Ms. Sutiyao Marturunkakul as one of six finalists whose work will be presented at the American Chemical Society Meeting, Chicago, Illinois, August, 1993.

4. The American Chemical Society's Outstanding Undergraduate Organic Chemistry Student Award was awarded to Mr. Craig Masse by the American Chemical Society Division of Organic Chemistry in 1993.

5. The University of Massachusetts Lowell's Department of Chemistry's Mark Jonathan Elliot Scholarship Award was awarded to Mr. Jeng-I Chen for his outstanding scholarship during his graduate studies at the University of Massachusetts Lowell in 1993.