OFFICE OF NAVAL RESEARCH

END-OF-THE-YEAR REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

GRANT: N00014-90-J-1148

R & T Code 4132016

Design, Synthesis and Characterization of Novel Nonlinear Optical Polymers

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May 31, 1993

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

Mailing Address: University of Massachusetts Lowell
Department of Chemistry
1 University Avenue
Lowell, Massachusetts 01854

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
UltraHigh 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 β relaxation process for the IPN in contrast to the behavior for guest host systems where α 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.

f. 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, photorefraction 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)	*Department*
Mr. Govindasamy Chittibabu	Chemistry
Mr. Dong Yu Kim	Chemistry

Undergraduate students	*Department*
Mr. Craig Masse	Chemistry

Part II

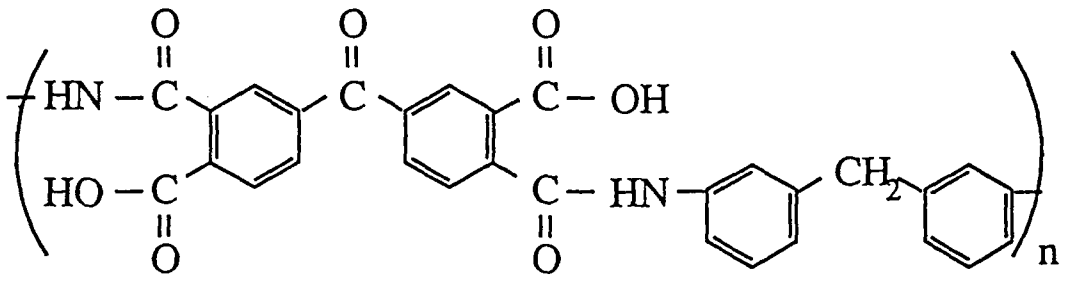
Research Highlights

Goal:

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

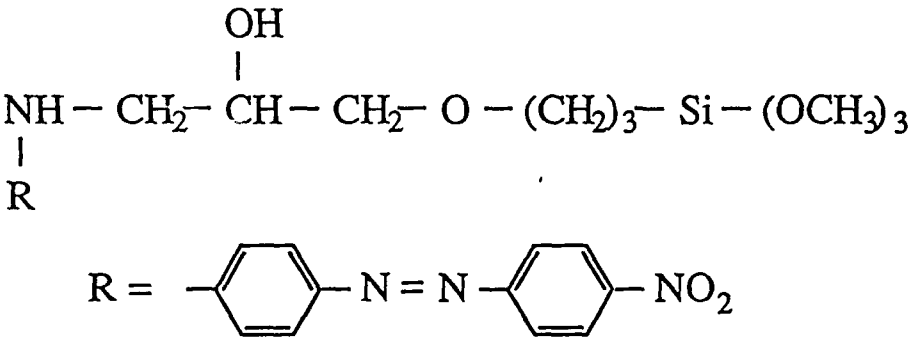
Approach:

- An NLO active organic/inorganic composite based on a polyimide and an alkoxysilane dye (ASD) is prepared.
- This hybrid material, formed by simultaneously poling and curing, exhibits excellent long term second-order NLO stability at elevated temperature.



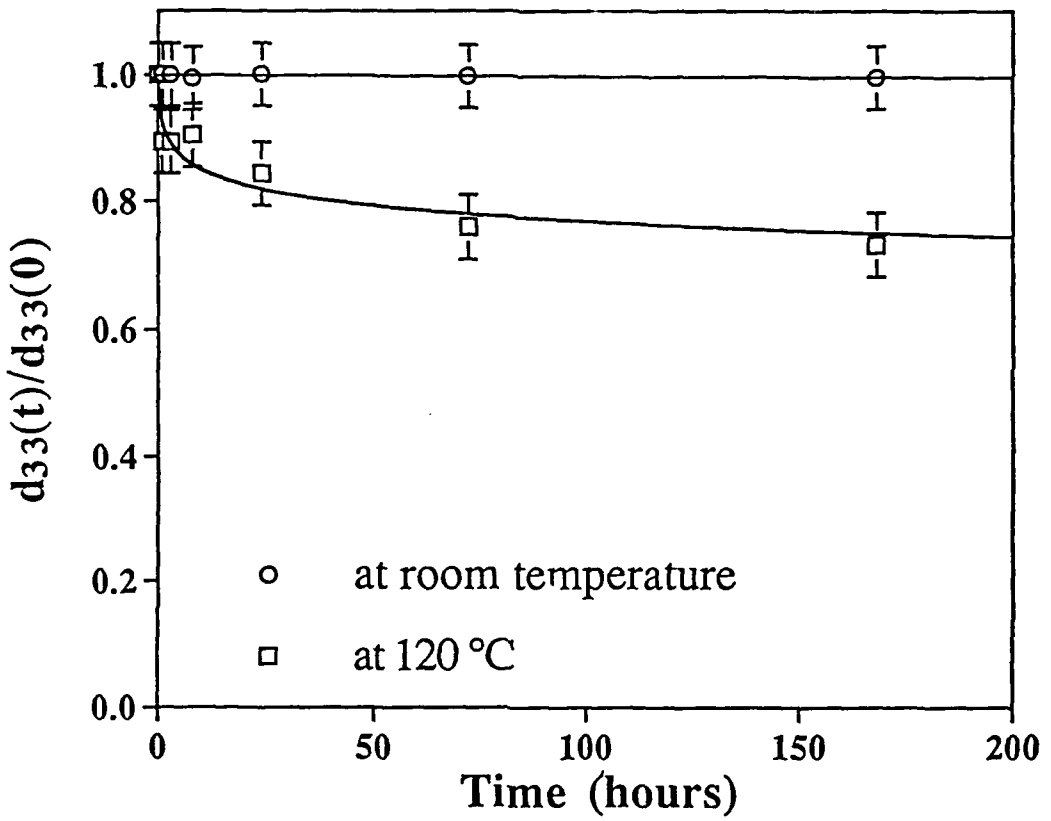
Polyamic acid

Organic component: polyimide which is formed by imidization of polyamic acid.



Alkoxysilane dye

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:

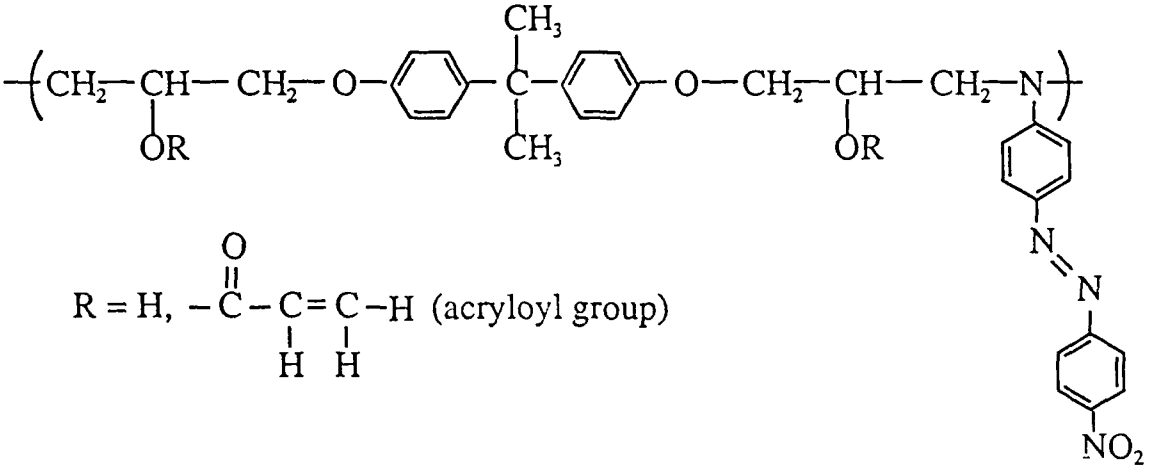
- A polyimide/inorganic composite was prepared as a second-order NLO material for the first time.
- The combination of the high Tg of the polyimide and the network formed by the ASD in this system promote excellent stability of the poled order in the molecular composite.

Goal:

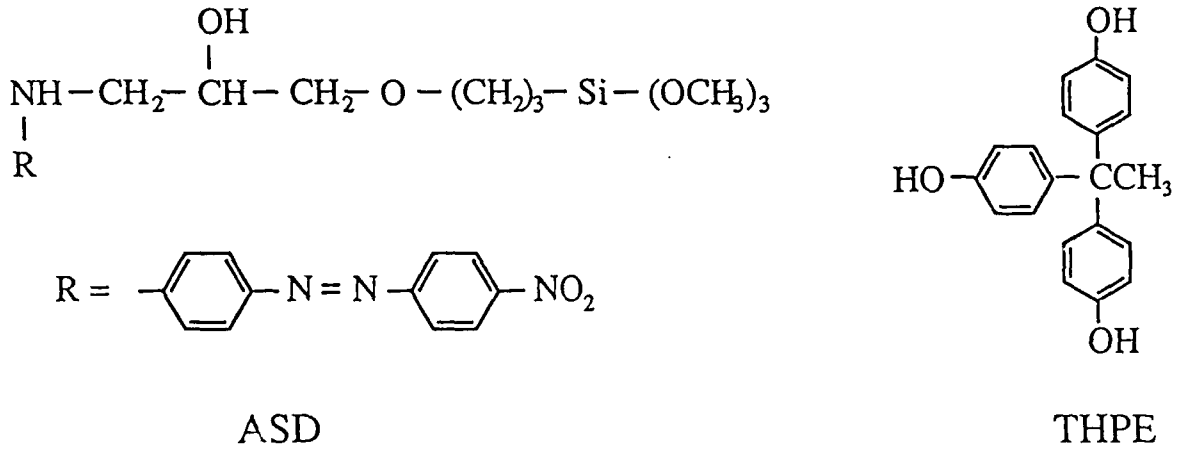
- To develop novel electroactive polymeric systems with stable second-order nonlinear optical (NLO) property.

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 pm/V). The d_{33} value remains unchanged after heating at 110 °C for 168 h.



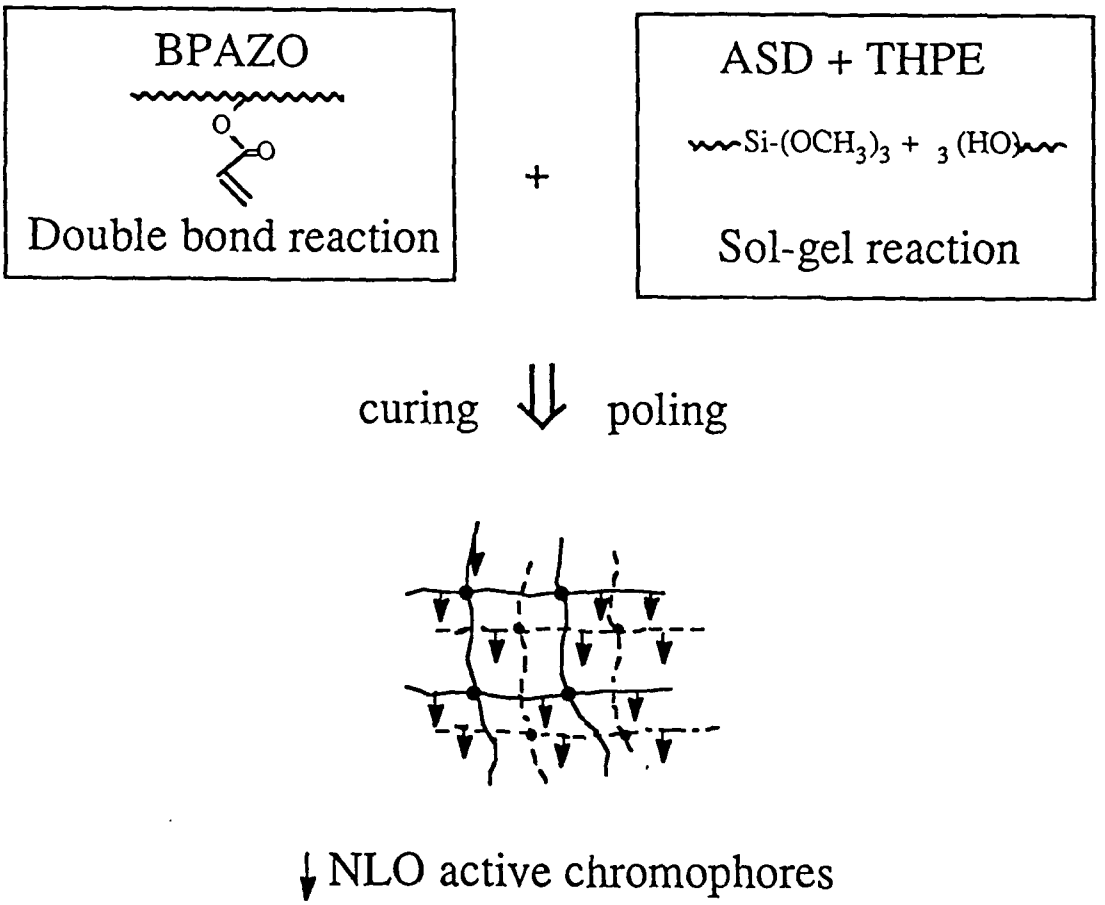
Network I: formed by an epoxy based thermo-crosslinkable NLO material (BPAZO).



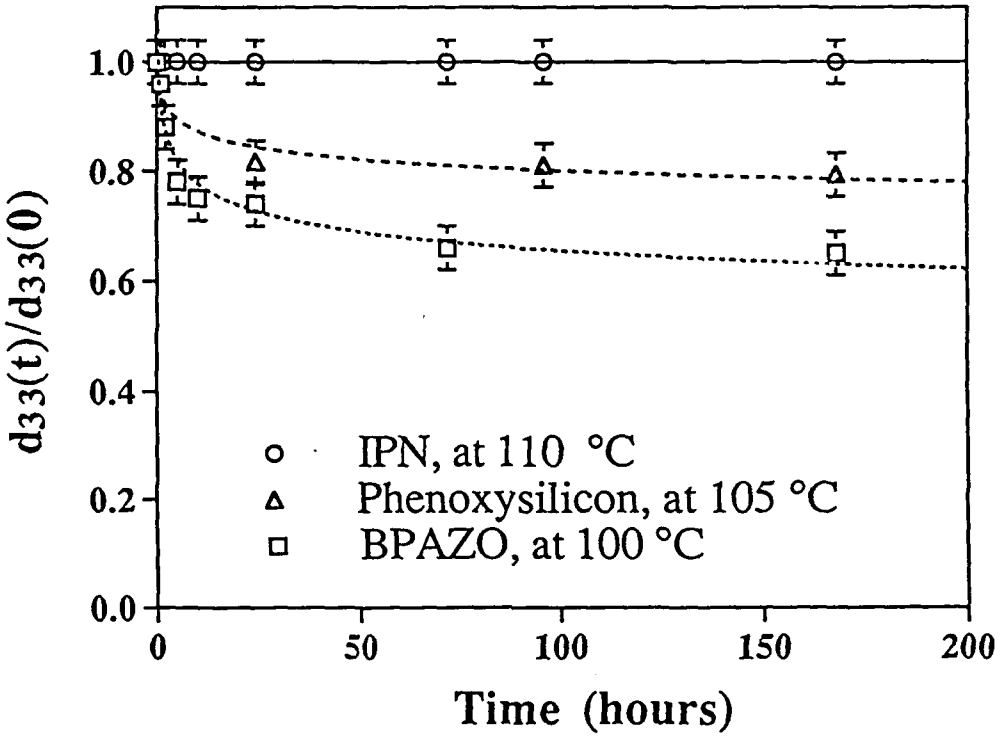
ASD

THPE

Network II: an NLO active phenoxysilicon polymer formed by the sol-gel reaction between ASD and THPE.



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**

1. "Stable Second-Order Nonlinear Optical Epoxy-Based Polymer" (Y.M. Chen, R.J. Jeng, L. Li, X.F. Zhu, J. Kumar and S.Tripathy) *Molecular Crystal Liquid Crystal Science and Technology: Section B: Nonlinear Optics* 4 71 (1993).

2. "An Interpenetrating Polymer Network as a Stable Second Order Nonlinear Optical Material" (S. Marturunkakul, J.I. Chen, L. Li, R.J. Jeng, J. Kumar and S.K. Tripathy) *Chemistry of Materials* 5 592 (1993).

3. "Phenoxy-Silicon Polymer with Stable Second Order Optical Nonlinearity" (R. Jeng, Y. Chen, J. Chen, J. Kumar and S. Tripathy) 26 2530 *Macromolecules* (1993).

4. "Nonlinear Optical Photoresponsive Polymer for Reversible Optical Data Storage" (D.Y. Kim, L. Li, R.J. Jeng, J. Kumar, M.A. Fiddy and S.K. Tripathy) in Organic and Biological Optoelectronics (P.M. Rentzepis, Ed.) SPIE 1853 (1993).

5. "Stable Second Order Nonlinear Optical Polyimide/Inorganic Composite" (R.J. Jeng, Y.M. Chen, A.K. Jain, J. Kumar and S.K. Tripathy) *Chemistry of Materials* 4 (6) 1141 (1992).

6. "Second Order Optical Nonlinearity on a Modified Sol-Gel System at 100 °C" (R.J. Jeng, Y.M. Chen, A.K. Jain, J. Kumar and S.K. Tripathy) *Chemistry of Materials* 4 (5) 972 (1992).

7. "Novel Crosslinked Guest-Host System with Stable Second Order Nonlinearity" (R.J. Jeng, Y. Chen, J. Kumar, and S. Tripathy) *Journal of Macromolecular Science-Pure and Applied Chemistry* A29 (12) 1115 (1992).

8. "Photoconductivity and Photovoltage Generation in Novel Photocrosslinkable Nonlinear Optical Polymers" (L. Li, R.J. Jeng, M. Kamath, J. Kumar and S.K. Tripathy) MRS Proceedings 277 161 (1992).

9. "Dielectric Study of a Photocrosslinkable Nonlinear Optical Polymer" (J.I. Chen, R.A. Moody, Y.M. Chen, J.Y. Lee, S.K. Sengupta, J. Kumar and S.K. Tripathy) in Electrical, Optical and Magnetic Properties of Organic Solid State Materials (L.Y. Chiang, A.F. Garito and D.J. Sandman, Eds.) MRS 247 223 (1992).

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

1. "Functionalized Polymeric Materials for Electronics and Optics" (S. Sengupta, J. Kumar, A. Jain and S. Tripathy) in Chemistry of Advanced Materials (C.N.R. Rao, Ed.) Blackwell Scientific Publications, London (1992).

2. "Nonlinear Optical Properties of New Dye Doped Photocrosslinkable Polymers" (S. Tripathy, L. Li, B.K. Mandal, J.Y. Lee and J. Kumar) in Advances in New Materials Contemporary Topics in Polymer Science 7 (J.C. Salamone and J.S. Riffle, Eds.) Plenum, New York 237 (1992).

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

1. "Investigations on a Second Order Nonlinear Optical Interpenetrating Polymer Network" (J.I. Chen, S. Marturunkakul, L. Li, R.J. Jeng, J. Kumar and S.K. Tripathy) *Polymer Preprints, American Chemical Society Division of Polymer Chemistry* 34 (1) 707 (1993).

2. "An Interpenetrating Polymer Network as a Stable Second Order Nonlinear Optical Material: Comparison with the Guest/Host Systems" (S. Marturunkakul, J. Kumar and S.K. Tripathy) *Polymer Preprints, American Chemical Society Division of Polymer Materials Science and Engineering* 69 (1993).

3. "A Stable Nonlinear Optical Material Based on a Polyimide/Inorganic Composite and Its Relaxation Study" (S. Marturunkakul, J.I. Chen, R.J. Jeng, Y.M. Chen, S. Sengupta, J. Kumar and S.K. Tripathy) *Polymer Preprints, American Chemical Society Division of Polymer Chemistry* 34 (1) 711 (1993).

4. "Poled Ordered Phenoxysilicon Polymer as Second Order Nonlinear Optical Materials" (R.J. Jeng, Y.M. Chen, J.I. Chen, J. Kumar and S.K. Tripathy) *Polymer Preprints, American Chemical Society Division of Polymer Chemistry* 34 (1) 292 (1993).

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**

1. "Investigations on a Second Order Nonlinear Optical Interpenetrating Polymer Network" (J.I. Chen, S. Marturunkakul, L. Li, R.J. Jeng, J. Kumar and S.K. Tripathy) American Chemical Society Division of Polymer Chemistry, Denver, Colorado, April, 1993.

2. "An Interpenetrating Polymer Network as a Stable Second Order Nonlinear Optical Material: Comparison with the Guest/Host Systems" (S. Marturunkakul, J. Kumar and S.K. Tripathy) American Chemical Society Division of Polymer Materials Science and Engineering Denver, Colorado, April, 1993.

3. "A Stable Nonlinear Optical Material Based on a Polyimide/Inorganic Composite and Its Relaxation Study" (S. Marturunkakul, J.I. Chen, R.J. Jeng, Y.M. Chen, S. Sengupta, J. Kumar and S.K. Tripathy) American Chemical Society Division of Polymer Chemistry Denver, Colorado, April, 1993.

4. "Poled Ordered Phenoxysilicon Polymer as Second Order Nonlinear Optical Materials" (R.J. Jeng, Y.M. Chen, J.I. Chen, J. Kumar and S.K. Tripathy) American Chemical Society Division of Polymer Chemistry Denver, Colorado, April, 1993.

5. "Poled Ordered Nanocomponents of Poly(4-Hydroxystyrene)/Alkoxysilane as Nonlinear Optical Materials" (R.J. Jeng, Y.M. Chen, J. Kumar and S.K. Tripathy) Materials Research Society, Boston, Massachusetts, December 1992.

6. "Copolymers of Thiophene Derivatives as Ordered Electroactive Polymers" (K.G. Chittibabu, M. Kamath, J. Kumar and S.K. Tripathy) Materials Research Society, Boston, Massachusetts, December 1992.

7. "Novel Solvato- and Thermochromic Transitions in a Polydiacetylene with Aromatic Sidegroups" (W.H. Kim, M.B. Kamath, J. Kumar and S.K. Tripathy) Materials Research Society, Boston, Massachusetts, December 1992.

8. "Photoconductivity and Photovoltage Generation in Novel Photocrosslinkable Nonlinear Optical Polymers" (L. Li, R.J. Jeng, M. Kamath, J. Kumar and S.K. Tripathy) Materials Research Society, Spring Meeting, San Francisco, California, Spring 1992.

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.