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OFFICE OF NAVAL RESEARCH  
END-OF-THE-YEAR REPORT  
(FINAL REPORT)

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

**AD-A237 362**



for

GRANT: N00014-90-J-1148

R & T Code 4132016

*Design, Synthesis and Characterization of Novel Polydiacetylenes  
Using New Analytical Techniques*

Dr. Sukant Tripathy  
University of Lowell  
Department of Chemistry  
1 University Avenue  
Lowell, Massachusetts 01854



May 28, 1991

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**91-03472**



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

R & T: 4132016

GRANT Number: N00014-90-J-1148

GRANT Title: Design, Synthesis and Characterization of Novel Polydiacetylenes Using New Analytical Techniques

Principal Investigator: Dr. Sukant Tripathy

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

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*Part I*

- a. Number of papers submitted to refereed journals, but not published: **8**
- b. Number of papers published in refereed journals (list attached): **14**
- c. Number of books or chapters submitted, but not published: **1**
- d. Number of books or chapters published: **0**
- e. Number of printed technical reports & non-refereed papers (list attached): **21**
- f. Number of patents filed: **2**
- g. Number of patents granted: **0**
- h. Number of invited presentations at workshops or professional society meetings: **7**
- i. Number of presentations at workshops or professional society meetings: **13**
- j. Honors/Awards/Prizes for contract/grant employees (list attached): **1**
- k. Total number of graduate students and post-doctoral associates supported by at least 25 % during this period, under the R & T project number:
  - Graduate Students: **1**
  - Post-Doctoral Associates: **2**

including the number of,

Female Graduate Students: 0

Female Post-Doctoral Associates: 0

the number of,

Minority Graduate Students: 0

Minority Post-Doctoral Associates: 0

and the number of,

Asian Graduate Students: 0

Asian Post-Doctoral Associates: 2

During their graduate study, Dr. Daniel S. Minehan and Dr. Matior Rahman were supported during this time period under this R & T project number. However, the amount of their support was less than 25 %, as the remainder of their support was provided by University of Lowell Graduate Research Assistantships.

1. Other funding (list agency, grant title, amount received this year, total amount, and the period of performance):

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, 1991 - March 14, 1992 - \$155,000.00

Department of the Navy, Office of Naval Research  
Equipment Grant, October 1, 1990 - September 30, 1991 - \$105,000.00

Massachusetts Centers of Excellence Corporation  
*Fiber Optic Switching Using Polymer Nonlinear Optical Materials*  
Research Grant, July 1, 1990 - June 28, 1991 - \$20,000.00

Spire Corporation  
*Novel Electrically Conductive Membranes*  
Research Grant, August 1, 1990 - December 31, 1991 - \$35,000.00

University of Maryland, Baltimore  
*UltraHigh Speed Optical Analog-to-Digital Converter*  
Research Grant, February 1, 1991 - January 31, 1992 - \$19,500.00

## *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. 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. In addition, these systems are photoprocessable and the photochemistry may be carried out as almost the last step in any fabrication process. Cinnamoyl and styryl acryloyl groups are used as the photocrosslinking groups.
  - 2. Guest-host systems have been designed with complete compatibility. The second order nonlinear optical medium does not suffer from phase segregation and a very high level of dye loading may be achieved.
  - 3. Suitable design of the NLO chromophore has led to some of the largest photoconductivities in these polymers with the addition of charge transporters or dye sensitizers. Large photoconductivity, small dark conductivity, stable and large electrooptic coefficients make this class, efficient candidate photorefractive materials.
  - 4. Poling and crosslinking has led to increase in dielectric constant, decrease in dielectric loss due to molecular motion and increase in dielectric strength. Dipolar units are designed with large polarizabilities and ground state dipole moment to yield large net polarization upon poling.

f. Brief summary of plans for next years work.

Design: Molecular units with transparency to shorter wavelengths, larger dipole moment, stable holes and large figure of merit for photorefractive effects will be designed.

Dynamics simulation of these systems will be carried out to study molecular motion, packing and orientational stability. Electronic and optical properties will be estimated.

Synthesis: Above designed molecular units appropriately functionalized will be synthesized. These molecular units will be incorporated into macromolecular architecture as side chains, in the main chain and in other articulated structures. Photochemistry in thin films, in monolayers (L-B) and under orientation fields will be carried out.

Processing: Mono and multilayers and spun on films will be fabricated. Photocrosslinking will be carried out in these films under applied fields. Microfabrication and direct processing will be carried out using the photocrosslinkability by using photomasks and direct laser beam writing.

Characterization: Details of the photochemical reactions will be investigated using numerous solid state in situ characterization techniques. Polarized FT-IR, FT-NMR, 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.

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

Post-doctoral

Dr. Braja Mandal

Graduate students (Ph.D. Candidates)

Department

Mr. Jeng-I Chen	Chemistry
Mr. Yong Ming Chen	Physics
Mr. Ru Jong Jeng	Chemistry
Mr. Lian Li	Physics
Ms. Sutyao Marturunkakul	Chemistry

Undergraduate students

Department

Mr. Craig Masse	Chemistry
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*Part III*

- a. introductory viewgraph*
- b. figure*
- c. concluding viewgraph*
- d. text*

## ***Problem:***

Development of single component photorefractive polymers.

## ***Approach:***

Requirement for photorefractive behavior are second order nonlinearity and large electrooptic coefficients, photoconductivity and small dark conductivity. Good optical quality is an additional requirement to permit large path lengths.

Single component NLO system has been developed where the NLO chromophore acts as the dye sensitizer for photogeneration of carriers. The donor amino group acts as a stable hole transporter and the poled NLO system provide the required stable electrooptic coefficient. The NLO units are designed to absorb and photogenerate carriers in the visible spectrum. Tertiary amine as the donor is a stable hole and participates in the hole transport. There are no charges in the system without photoexcitation to provide dark conduction.

## *Summary:*

The only reported photorefractive polymer is a three component system. It contains;

1. An NLO polymer
2. Sensitizer
3. Hole transporter  
(IBM Labs, Ducharme et al)

This type of system suffers from phase segregation, poor optical quality and an unstable E-O coefficient. By designing a photocrosslinkable NLO unit that is also a stable hole transporter and by appropriately designing its optical absorption properties, a new class of candidate photorefractive materials has been developed.

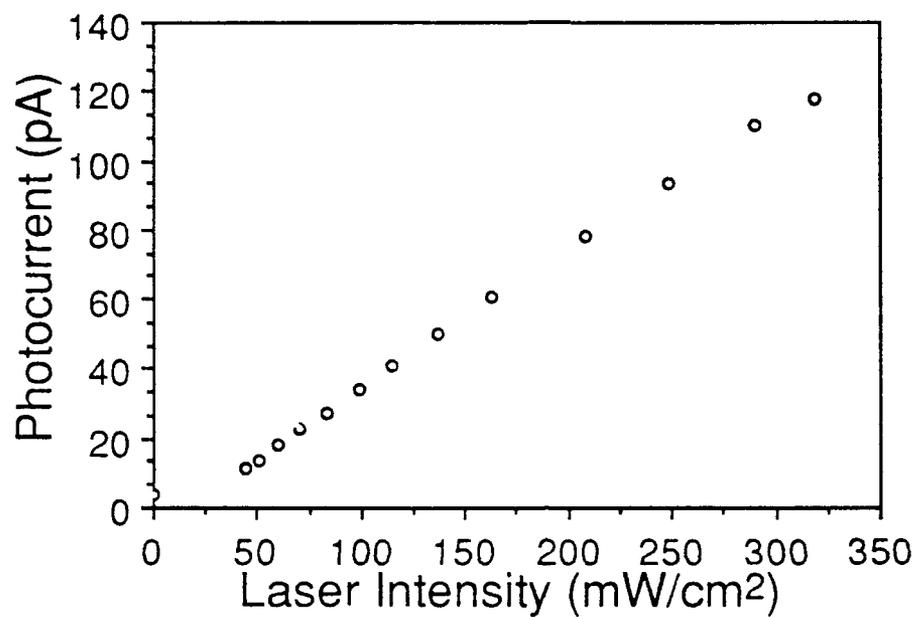


Figure 1. Photocurrent measured as a function of laser intensity at 514 nm with 10 V bias.

### ***Problem:***

Development of high dielectric, low loss polymeric materials for high energy density capacitor technology.

### ***Approach:***

At the present time poled PVDF is used for this purpose. Polyvinylidene Fluoride is a ferroelectric polymer which upon poling and alignment of the polarizable-CF<sub>2</sub> dipoles yield a large dielectric constant in a polymer with low loss and high dielectric strength.

We have designed photocrosslinkable macromolecules with highly polarizable molecular dipoles incorporated into the structures. These polymers may be poled in an analogous manner and subsequently photocrosslinked to yield a high dielectric constant polymer. Crosslinking leads to a stable network leading to extremely low loss high temperature stability and high dielectric strength.

## *Summary:*

One of the largest (possibly the largest) dielectric constant in a low loss polymer has been achieved. This is a perfectly general and versatile approach as any number of polarizable dipoles may be incorporated following the same chemistry. The poled polymer with these polarizable units will have a net polarization and have features of a ferroelectric system except there will be no Curie temperature since the crosslinked system may not relax.

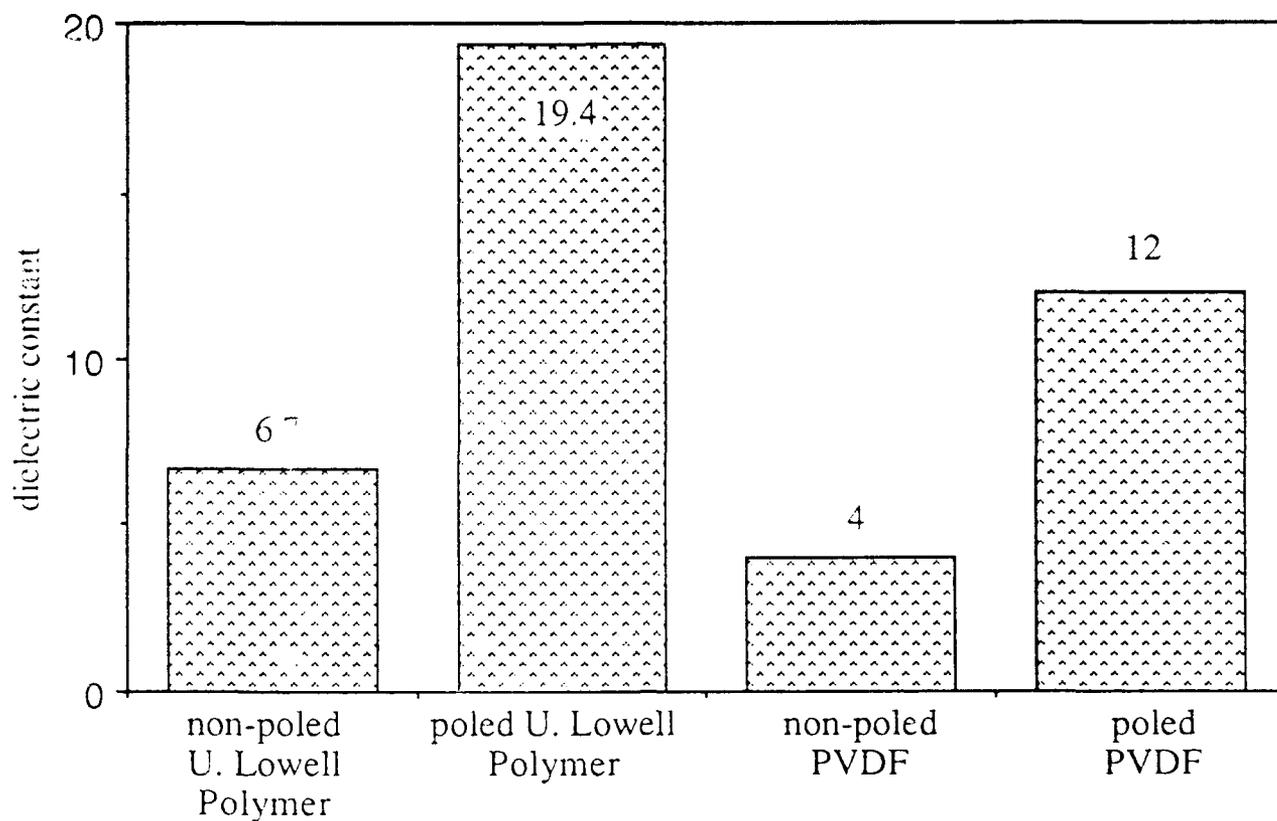


Figure 1. Comparison of the effect of poling on experimental U. Lowell UV curable polymer to current technology of poled and non-poled PVDF.

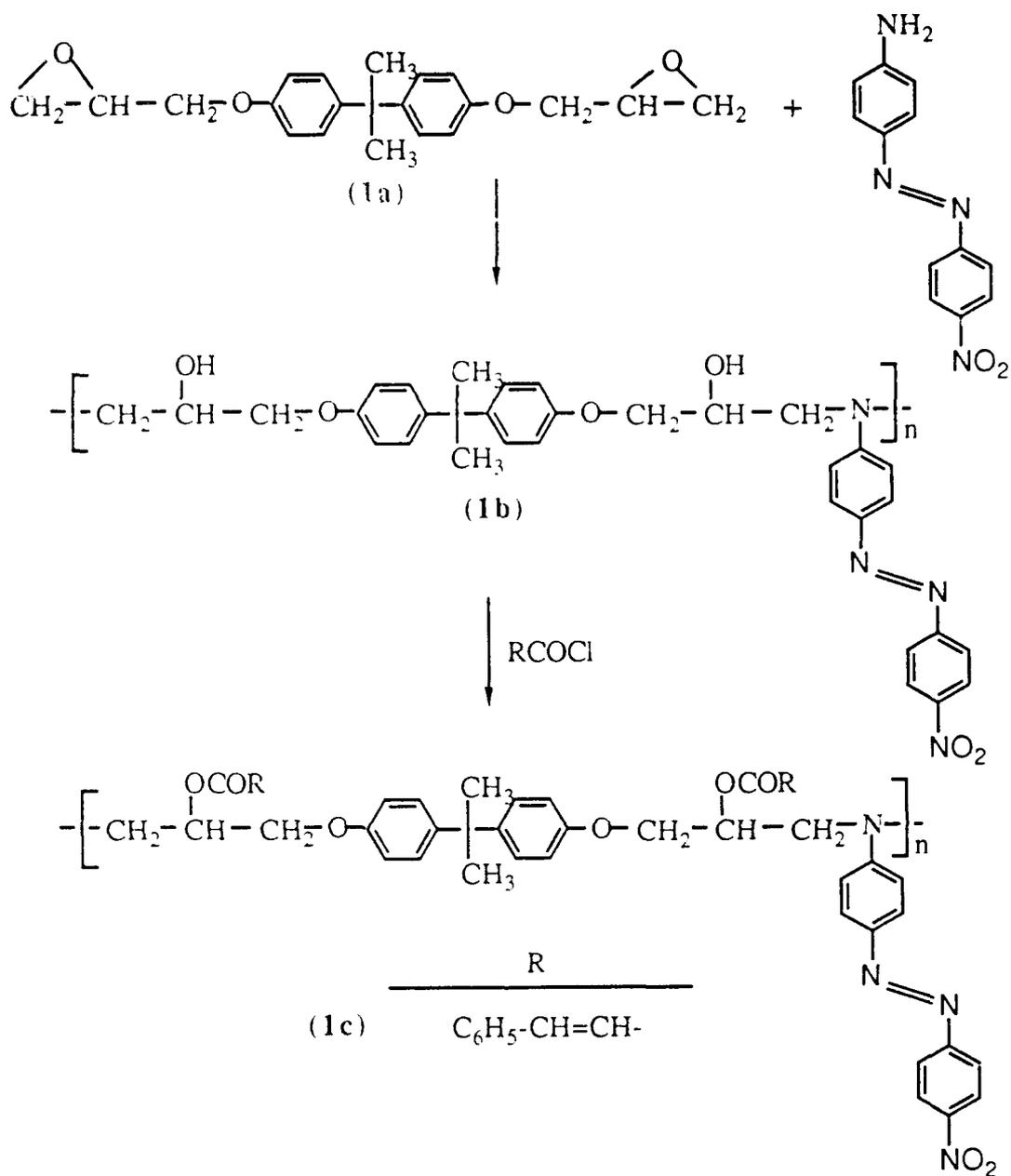


Figure 2. Photocrosslinkable nonlinear optical polymer providing large dielectric constant and low loss as a result of poling and subsequent crosslinking.

## PROBLEM

### MODIFICATION OF ELECTRONIC AND OPTICAL PROPERTIES OF POLYDIACETYLENE VIA CHANGES IN THE SIDE GROUP MOLECULAR STRUCTURE.

## APPROACH

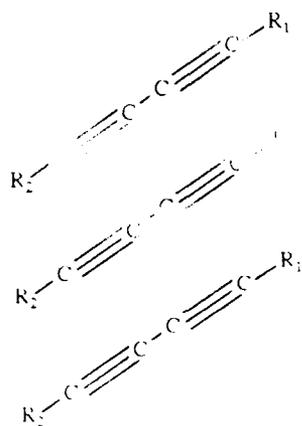
Charge carrier generation in polydiacetylene thin film single crystals, poly-PTS (2,4-hexadiyne-1,6-diol bis(*p*-toluenesulfonate)) and poly-BTFP (bis-(4-*n*-butyl-2,3,5,6-tetra-fluorophenyl) butadiyne), is studied by using steady state photoconductivity techniques. The polarization dependence of photocurrent has completely different behavior for the polydiacetylene single crystals PTS and BTFP. The results suggest that the side groups of polydiacetylene can significantly alter the material physical properties. In BTFP there is substantial  $\pi$ -overlap from the side group structure to the backbone  $\pi$ -cloud. This overlap is not present in PTS where the toluene sulfonate group is attached to the backbone by a methylene bridge ( $\sigma$ ).

The diacetylene BTFP was designed and synthesized by Nakanishi and coworkers at RIPT Japan according to our specification (from theoretical consideration).

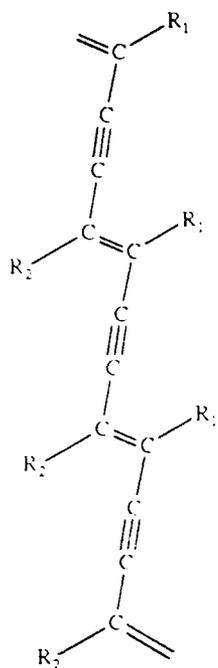
## Explanatory

The photoinduced carrier generation of polydiacetylene single crystals, poly-PTS and poly-BTFP (Figure 1), are investigated by using the steady state photoconductivity technique. Charge carriers are photoinduced by the incident light of photon energy above bandgap. Light polarization is adjusted continuously by rotating a half wave plate (Figure 2). The polarization dependence of photocurrent of PTS and BTFP are shown in Figure 3. The polarization dependence of photocurrent has completely different behavior for the polydiacetylene single crystals PTS and BTFP. PTS shows a maximum photocurrent when the incident light polarization is about 60 degree to the polymer chain and minimum when the polarization is parallel to polymer chain. A small dip is observed in the photocurrent when the polarization is exactly perpendicular to the chain direction. BTFP, on the other hand, has completely different behavior, showing a maximum in photocurrent when the polarization of incident light is parallel to the chain. It is interesting to note that the absorption in both PTS and BTFP single crystals is much higher when the incident light polarization is along the chain direction. The absorption spectrum for the two systems look similar though absorption is red shifted for BTFP compare to PTS. This suggests that the side groups play an important role not only in just shifting the bandgap but also quite significantly alter the photocarrier generation mechanism. Crystalline diacetylene polymers BTFP and PTS are important examples of solids with quasi-one dimensional band structure which behave quite differently regards photocarrier generation. This clearly establishes the importance of synthesis and design at the molecular level to elicit new phenomena in these systems. The electronic and optical properties of polydiacetylenes were assumed until now to be entirely due to the delocalized electronic structure of the backbone. The side groups were assumed to play only a mechanical (structural) role in the system.

\* MONOMER

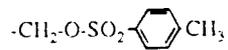


POLYMER

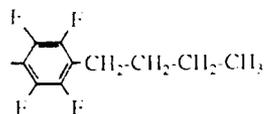


SIDE GROUP

R<sub>1</sub>=R<sub>2</sub>=



PTS



BTFP

Figure 1 Solid-state polymerization scheme and the chemical structure of PTS and BTFP

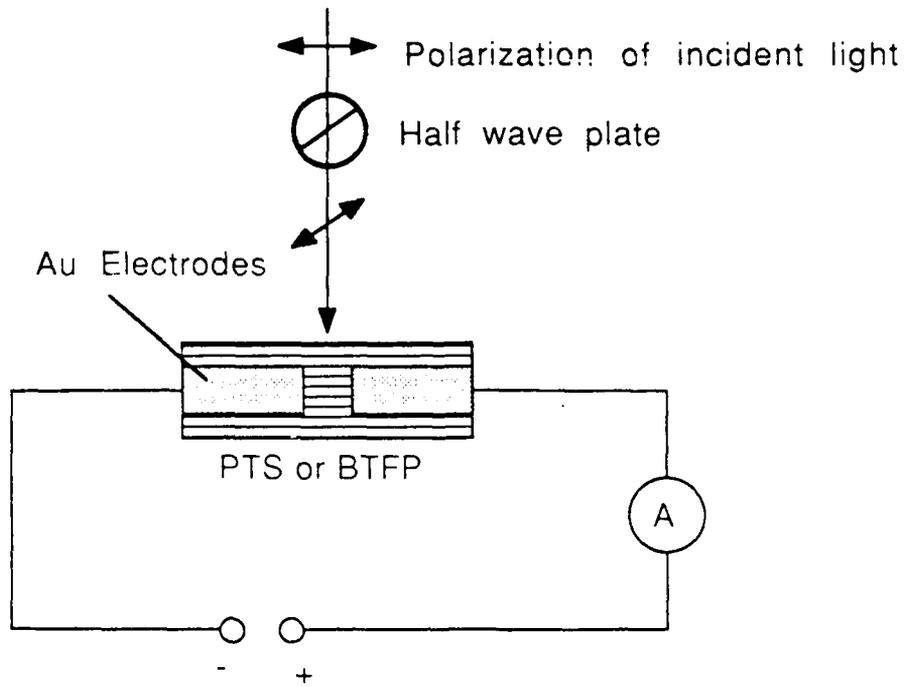


Figure 2 The experimental setup for the measurements of polarization dependence of photocurrent.

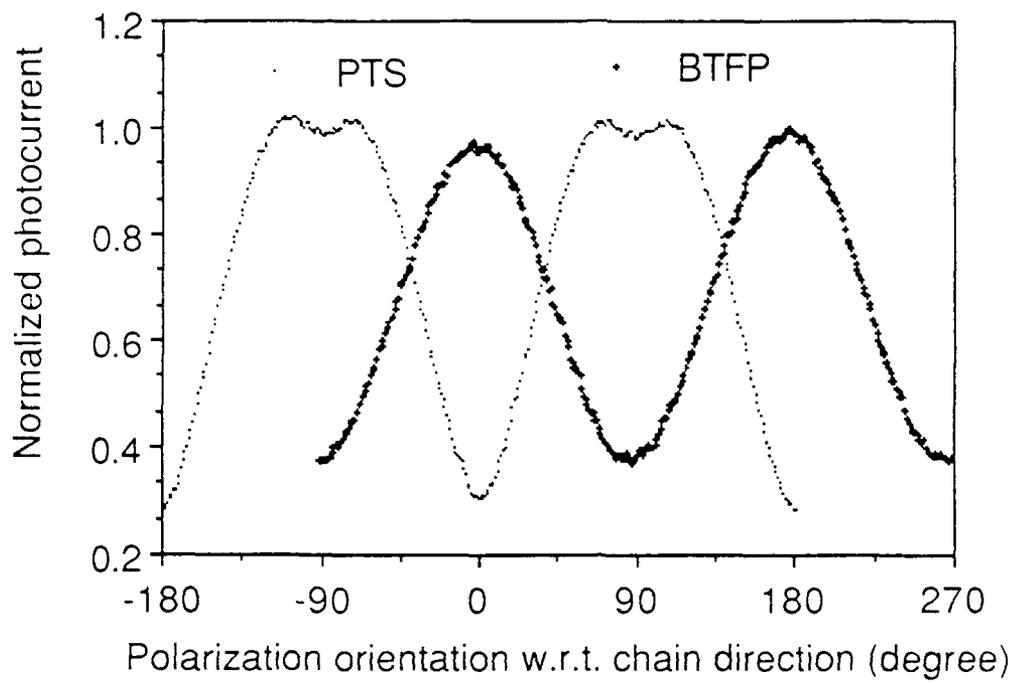


Figure 3 The polarization dependence of photocurrent of PTS and BTFP

Attachment page 1

b. Number of papers published in refereed journals (list attached): 14

1. "Linear and Nonlinear Optical Properties of a Comb-Like Polymer," (Y. M. Chen, M. Rahman, T. Takahashi, B. K. Mandal, J. Y. Lee, J. Kumar and S. Tripathy), J. Appl. Phys. Japan 30 (4) April (1991).
2. "Drift velocity measurement in thin film polydiacetylene single crystals," (Y. Yang, J.Y. Lee, P. Miller, L. Li, J. Kumar and S. Tripathy), Solid State Communications 77 763 (1991).
3. "Molecular Design of Stable Second Order Nonlinear Optical Polymers," (B.K. Mandal, J. Kumar and S. Tripathy) in Optical and Electrical Properties of Polymers. (J.A. Emerson, and J.M. Torkelson, eds.) MRS 214 (1991).
4. "Optical and Electro-optical Properties of a Photocross-linkable Polymer," (A.K.M. Rahman, B.K. Mandal, X.F. Zhu, J. Kumar and S.K. Tripathy), in Optical and Electrical Properties of Polymers, (J.A. Emerson, and J.M. Torkelson, eds.) MRS 214 (1991).
5. "Optimized Processing Condition for a Photocrosslinkable Stable Nonlinear Optical Polymer," (J.Y. Lee, W.H. Kim, B.K. Mandal, J. Kumar and S.K. Tripathy), in Optical and Electrical Properties of Polymers, (J.A. Emerson, and J.M. Torkelson, eds.) MRS 214 (1991).
6. "Photocross-linked Second Order Nonlinear Optical Polymers," (Y.M. Chen, B.K. Mandal, J.Y. Lee, P. Miller, J. Kumar and S. Tripathy), in Optical and Electrical Properties of Polymers, (J.A. Emerson, and J.M. Torkelson, eds.) MRS 214 (1991).
7. "Steady State and Transient Photoconductivity of Thin Film Polydiacetylene Single Crystals," (Y. Yang, J.Y. Lee, P. Miller, L. Li, J. Kumar, S.K. Tripathy, H. Matsuda, S. Okada and H. Nakanishi), in Optical and Electrical Properties of Polymers, (J.A. Emerson, and J.M. Torkelson, eds.) MRS 214 (1991).
8. "Cross-Linked Stable Second-Order Nonlinear Optical Polymer by Photochemical Reaction," (B.K. Mandal, Y.M. Chen, J.Y. Lee, J. Kumar and S. Tripathy), Applied Physics Letters 58 (22), 3 June (1991).
9. "Dielectric Properties of Polypyrrole Doped with Tosylate Anion in the Far Infrared and Microwave," (G. Phillips, R. Suresh, J. Waldman, J. Kumar, J.I. Chen, S. Tripathy and J.C. Huang), Journal of Applied Physics, 69 (2) 899-905 (1991).
10. "A New Approach to Design of Cross-Linked Second-Order Nonlinear Optical Polymers," (B.K. Mandal, J.Y. Lee, X.F. Zhu, Y.M. Chen, E. Prakeenvincha, J. Kumar and S. Tripathy), Synthetic Metals. 43 (1-2) 2803, June 7 (1991).
11. "Novel Photocross-Linked Nonlinear Optical Polymers," (B.K. Mandal, J. Kumar, J.C. Huang and S. Tripathy), Die Makromolekulare Chemie, Rapid Communications, 12 63 (1991).
12. "Infrared Dielectric Behavior of Polypyrrole Doped With Tosylate," (G. Phillips, R. Suresh, J.I. Chen, J. Waldman, J. Kumar, S. Tripathy and J.C. Huang), Solid State Communications, 76 (7) 963 (1990).
13. "Dielectric Properties of Polypyrrole Doped with Tosylate Anion in the Far Infrared," (G.C. Phillips, R. Suresh, J.I. Chen, J. Kumar, J. Waldman, J.C. Huang and S.K. Tripathy), Mol. Cryst. Liq. Cryst., 190 27-33 (1990).
14. "Dynamics Simulation of Langmuir-Blodgett Films," (S.B. Clough, X.F. Sun, J. Kumar and S. Tripathy), Mol. Cryst. Liq. Cryst., 190 155 (1990).

Attachment page 2

- e. Number of printed technical reports & non-refereed papers (list attached): **21**
1. "Photo-Induced Charge Carrier Generation in Thin Film Polydiacetylene Single Crystals," (Y. Yang, J.Y. Lee, J. Kumar, S.K. Tripathy, H. Matsuda, S. Okada and H. Nakanishi), submitted to Physical Review Letters, 1991.
  2. "New Photocrosslinkable Polymers for Second Order Nonlinear Optical Processes," (B.K. Mandal, R.J. Jeng, J. Kumar and S. Tripathy), submitted to Die Makromolekulare Chemie, 1991.
  3. "Langmuir-Blodgett Films of Aromatic Schiff's Bases Functionalized in the Side Chains of Polymethacrylate," (T. Takahashi, P. Miller, Y.M. Chen, L. Samuelson, D.M. Galotti, B.K. Mandal, J. Kumar and S.K. Tripathy), submitted to Journal of Polymer Science, 1991.
  4. "Optical Characterization and Patterning of Nonlinear Optical Polymers With Photocrosslinking Groups," (P. Miller, J.Y. Lee, R.J. Jeng, W.H. Kim, S. Broude, B.K. Mandal, S. Tripathy and J. Kumar), submitted to Applied Physics A, 1991.
  5. "Molecular Dynamics Simulation of Substituted Polyacetylenes," (X.F. Sun, S.B. Clough, S.K. Tripathy and G.L. Baker), To be published in Macromolecules, 1991.
  6. "Second Harmonic Properties of Aromatic Schiff's Bases Functionalized in the Side Chains of Polymethylmethacrylate," (T. Takahashi, B.K. Mandal, Y.M. Chen, J.Y. Lee, L. Samuelson, D. Galotti, J. Kumar, A. Blumstein and S.K. Tripathy), to be published in Proceedings of International Symposium on Non Linear Optical Materials, University of Texas at El Paso, held October 28 - November 2, 1990.
  7. "Linear and Nonlinear Optical Properties of a Comb-Like Polymer," (Y. M. Chen, M. Rahman, T. Takahashi, B. K. Mandal, J. Y. Lee, J. Kumar and S. Tripathy), J. Appl. Phys. Japan 30 (4) April (1991).
  8. "Drift velocity measurement in thin film polydiacetylene single crystals," (Y. Yang, J.Y. Lee, P. Miller, L. Li, J. Kumar and S. Tripathy), *Solid State Communications* 77 763 (1991).
  9. "Molecular Design of Stable Second Order Nonlinear Optical Polymers," (B.K. Mandal, J. Kumar and S. Tripathy) in Optical and Electrical Properties of Polymers, (J.A. Emerson, and J.M. Torkelson, eds.) MRS 214 (1991).
  10. "Optical and Electro-optical Properties of a Photocross-linkable Polymer," (A.K.M. Rahman, B.K. Mandal, X.F. Zhu, J. Kumar and S.K. Tripathy), in Optical and Electrical Properties of Polymers, (J.A. Emerson, and J.M. Torkelson, eds.) MRS 214 (1991).
  11. "Optimized Processing Condition for a Photocrosslinkable Stable Nonlinear Optical Polymer," (J.Y. Lee, W.H. Kim, B.K. Mandal, J. Kumar and S.K. Tripathy), in Optical and Electrical Properties of Polymers, (J.A. Emerson, and J.M. Torkelson, eds.) MRS 214 (1991).
  12. "Photocross-linked Second Order Nonlinear Optical Polymers," (Y.M. Chen, B.K. Mandal, J.Y. Lee, P. Miller, J. Kumar and S. Tripathy), in Optical and Electrical Properties of Polymers, (J.A. Emerson, and J.M. Torkelson, eds.) MRS 214 (1991).
  13. "Steady State and Transient Photoconductivity of Thin Film Polydiacetylene Single Crystals," (Y. Yang, J.Y. Lee, P. Miller, L. Li, J. Kumar, S.K. Tripathy, H. Matsuda, S. Okada and H. Nakanishi), in Optical and Electrical Properties of Polymers, (J.A. Emerson, and J.M. Torkelson, eds.) MRS 214 (1991).
  14. "Cross-Linked Stable Second-Order Nonlinear Optical Polymer by Photochemical Reaction," (B.K. Mandal, Y.M. Chen, J.Y. Lee, J. Kumar and S. Tripathy), Applied Physics Letters 58 (22), 3 June (1991).
  15. "Dielectric Properties of Polypyrrole Doped with Tosylate Anion in the Far Infrared and Microwave," (G. Phillips, R. Suresh, J. Waldman, J. Kumar, J.I. Chen, S. Tripathy and J.C. Huang), Journal of Applied Physics, 69 (2) 899-905 (1991).
  16. "A New Approach to Design of Cross-Linked Second-Order Nonlinear Optical Polymers," (B.K. Mandal, J.Y. Lee, X.F. Zhu, Y.M. Chen, E. Prakeenvincha, J. Kumar and S. Tripathy), Synthetic Metals, 43 (1-2) 2803, June 7 (1991).

Attachment page 3

17. "Novel Photocross-Linked Nonlinear Optical Polymers," (B.K. Mandal, J. Kumar, J.C. Huang and S. Tripathy), Die Makromolekulare Chemie, Rapid Communications, 12 63 (1991).
18. "Infrared Dielectric Behavior of Polypyrrole Doped With Tosylate," (G. Phillips, R. Suresh, J.I. Chen, J. Waldman, J. Kumar, S. Tripathy and J.C. Huang), Solid State Communications, 76 (7) 963 (1990).
19. "Dielectric Properties of Polypyrrole Doped with Tosylate Anion in the Far Infrared," (G.C. Phillips, R. Suresh, J.I. Chen, J. Kumar, J. Waldman, J.C. Huang and S.K. Tripathy), Mol. Cryst. Liq. Cryst., 190 27-33 (1990).
20. "Dynamics Simulation of Langmuir-Blodgett Films," (S.B. Clough, X.F. Sun, J. Kumar and S. Tripathy), Mol. Cryst. Liq. Cryst., 190 155 (1990).
21. "Design and Synthesis of a New Class of Photocrosslinkable Nonlinear Optical Polymers," (S.K. Tripathy, B.K. Mandal, R.J. Jeng, J.Y. Lee and J. Kumar) to be published in Proceedings of ACS Symposium on Polymeric Materials for Photonic and Optical Applications New York, August, 1991.

Attachment page 4

- j. Honors/Awards/Prizes for contract/grant employees (list attached): **1**
- 1. The Mark Jonathon Elliot Scholarship Award was awarded to Dr. Xiao-Fang Sun, in 1990, for his outstanding scholarship, during his graduate studies at the University of Lowell.