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AN ASSERT PROPOSAL FOR THE DEVELOPMENT OF ADVANCED POLYMERIC E-O MODULATORS

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Final Progress Report Submitted to

DR. CHARLES Y-C. LEE DIRECTORATE OF CHEMISTRY AND MATERIALS SCIENCE AIR FORCE OFFICE OF SCIENTIFIC RESEARCH BOLLING AFB, WASHINGTON, D.C. 20332-6448

by

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REVIEW OF OBJECTIVES:

The primary objective of this contract is to develop processible nonlinear optical materials and processing protocols which permit fabrication of prototype electro-optic modulator devices and integrated opto-electronic circuits. This effort provides the primary materials support for device development efforts carried out by W. H. Steier at USC, H. Fetterman at UCLA, Y. Shi at TACAN, J. Michael at PWI, W. Bischel at Gemfire, and R. Mustacich at RVM Scientific.

STATUS OF EFFORT:

A number of chromophores with $\mu\beta$ values in excess of 10,000 x 10⁻⁴⁸ esu (i.e., 30 to 70 times that of the widely used standard DANS) have been synthesized. Molecular hyperpolarizabilities have been characterized by EFISH and hyper-Rayleigh scattering (see Dalton, et al., Chemistry of Materials, 7, 1060-1081 (1995) and Dalton, Chemistry & Industry, no. 13, 510-514, 7 July 1997). Thermal properties have been evaluated by TGA. Structural characterization has been evaluated high resolution NMR, UV-Vis, FTIR, mass spectroscopy and by elemental analysis. A program has recently been set in place to evaluate photochemical and photophysical properties of chromophores at relevant wavelengths. These chromophores have been prepared with reactive functionalities which permit incorporation into various polymer processing protocols and resulting materials have been evaluated under poling and lattice hardening conditions. Macroscopic electro-optic coefficients, measured by elipsometry, attenuated total reflection and two-slit inteference modulation, have been observed in the range 15 to 83 pm/V. The fact that high $\mu\beta$ chromophores initially (without chromophore derivatization) exhibited optical nonlinearities (electro-optic coefficient and second harmonic generation coefficient) significantly below the values predicted by $\mu\beta$ /(molecular weight) scaling has been quantitatively explained. London theory has been extended to treat the competition of chromophore-electric field (acentric ordering) and chromophore-chromophore (acentric disordering or centric ordering) interactions. The shape of chromophores has been explicitly taken into account. Theoretical calculations quantitatively predict the variation of electro-optic coefficients which chromophore loading in polymeric matrices. In particular, electro-optic coefficients are observed to go through a maximum with chromophore loading (number density). Attenuation of acentric order is shown to be most problematic for prolate ellipsoidal chromophores. Chromophores of spherical shape are likely optimal for maximizing optical nonlinearity but theory predicts that oblate ellipsoidal chromophores should also be explored. The effects of electrical conductivity and photoconductivity on polinginduced acentric order has also be quantitatively investigated. In the process of this investigation chromophores have been identified which offer exciting new levels of photoconductivity and novel optical limiting properties

Three classes of electric field poling/lattice hardening reactions have been developed for preparing thermally stable nonlinear optical materials exhibiting electro-optic coefficients in excess of 15 pm/V (Dalton, et al., *Ind. Eng. Chem. Res.*, in press). Thermally stability is defined as retention of 95% or greater of optical nonlinearity after 1000 hours at 100°C. Both intra and intermolecular condensation reactions have been used to lock-in poling-induced order and to harden materials sufficiently to permit subsequent processing. These efforts have permitted the fabrication of a variety of prototype electro-optic modulator devices and the performance of these devices has been demonstrated to 113 GHz (Dalton, et al., *Appl. Phys. Lett.*, 70, 2082-4, 1997).

Both reactive ion (reactive ion etching and electron cyclotron resonance etching) and photolithographic methods have been developed for preparing buried channel nonlinear optically active waveguides. These methods have been coupled with silicon v-groove techniques to develop mechanically stable coupling of polymeric waveguides with silica fiber transmission lines. Tapered transitions have been fabricated and tested to reduce optical loss due to mode size mismatch between silica fibers and polymer EO modulator Recently processing protocols have been developed which permit waveguide. integration of polymer electro-optic devices on non-planar silicon integrated circuits (e.g., VLSI wafers). Both vertical and horizontal integration has been demonstrated (Dalton, Chemistry & Industry, no. 14, 510-514, 1997; Dalton and Harper, Polymer News, 23, 114-20, 1998; Dalton, et al., Ind. Eng. Chem. Res., in press) . Recently, London theory has been used to identify problems in poling efficiency and lattice hardening efficiency and show that these problems arise from chromophorechromophore electrostatic interactions (Dalton, et al., J. Opt. Soc. Amer. B, 15, 329-37, Problems of transient and non-transient chromophore association and 1998). aggregation can be circumvented by chromophore redesign. In particular, prolate ellipsoidal structures should be avoided in favor of spherical and oblate ellipsoidal structures. Problems associated with electrical conductivity and photoconductivity effects have been identified and insight gained has been used to develop improved active polymer waveguides and improved cladding materials. A detailed study of the effect of processing conditions upon modulator performance has been carried out. Optical loss due to material inhomogeneity associated with processing conditions has been investigated. Oligomer distributions and phase separation of crosslinking reagents in thermosetting reactions have been studied employing a variety of techniques including GPC. Not only have conditions leading to reduced optical loss been defined but the reproducibility of production of acceptable modulators has been achieved. Poling-induced optical loss has also been systematically investigated. Such loss has been shown to arise either from surface damage due to corona poling or an electrophoretic effect involving high dipole moment chromophores. Again conditions have been defined which lead to lowest possible optical loss. New femtosecond NLO spectroscpic techniques have been developed and are being used for study of DoD relevant materials including sensor protection materials being synthesized at DoD laboratories.

ACCOMPLISHMENTS/NEW FINDINGS:

Dramatic progress has been made in the development of improved second order nonlinear optical chromophores. Several chromophores exhibiting excellent thermal stability and molecular optical nonlinearities ($\mu\beta$) in the range 17,000 to 35,000 x 10⁻⁴⁸ esu have been prepared. These materials have been functionalized for incorporation into hardened polymer lattices.

Three different schemes have been devised for fabricating hardened polymeric NLO lattices. The first is a precursor route where a soluble and processible polymer containing an NLO chromophore is prepared and processed into optical quality films by spin casting. The material is then poled and a crosslinking reaction is initiated while the poling field is on. This lattice hardening reaction locks in the poling-induced noncentrosymmetric order (i.e., elevates the glass transition temperature of the polymer lattice). This process typically yields materials which retain optical nonlinearity (during dynamic assays) to temperatures greater than 170°C. The precursor route has the advantage of permitting use of solvents compatible with clean room operation and

permits reproducible poling with minimal effort. An example of the precursor route is the LD-3 material (developed under this program) currently used by TACAN/lpitek, AdTech, Radiant Research, Deacon Research/Gemfire and RVM Scientific. The second route involves the use of thermosetting materials such as in sol-gel processing. With this approach, poling and hardening processes are not well-separated and "stepped" poling protocols have been found to yield dramatically improved optical nonlinearities relative to single temperature/electric field poling. The thermosetting approach requires more effort to achieve optimal results but this approach does have the advantage of permitting high chromophore number densities to be obtained and is compatible with clean room processing. An example of this approach is the PU-DR19 material used by TACAN (Shi et al., IEEE J. Selected Topics in Quantum Electronics, 2, 289-99, 1996). The final approach started as a modification of polyimide chemistry where an intramolecular condensation (imidization) reaction is used to achieve lattice hardening. A variety of synthetic schemes were developed for incorporating chromophores into polyamic acid/polyimide polymers. This approach has the advantage of permitting excellent thermal stability of optical nonlinearity to be achieved but suffers from the requirement of harsh solvents which are difficult to use with clean room processing and which can effect chromophore stability when high $\mu\beta$ chromophores are used. These problems with the polyimide approach have been addressed recently by generalizing the synthesis of heteroaromatic polymers exploiting both intra and intermolecular condensation for lattice hardening. This generalization permits precursor polymers with improved solubility in conventional processing solvents to be prepared.

With all of the above approaches, attention must be given to chromophore aggregation associated with strong electrostatic interactions. Such interactions can be overcome by improved chromophore design and by utilization of pulsed poling protocols.

New processing techniques, e.g., laser-assisted poling and molecular selfassembly assisted poling, have been developed to improve the order parameter for noncentrosymmetric alignment of chromophores in polymeric materials. Laser-assisted poling is particularly important for development of devices (such as 100 GHz modulators) employing in-plane electrode configurations.

Major progress has been made in the area of fabrication of buried channel nonlinear optical waveguides and in the interface (coupling) of such polymeric waveguides to silica fiber optic transmission lines. The Dalton and Steier groups at USC have pioneered the use of reactive ion etching techniques and new photolithographic techniques for the fabrication of buried channel waveguides characterized by reduced optical loss. Electron cyclotron resonance etching, which facilitates greater control over plasma conditions, has been shown to permit realization of smoother channel walls (hence reduced optical loss) than can be achieved by conventional reactive ion etching. Reactive ion processing has been used to effect silicon v-groove etching which, in turn, has served as the basis for precise alignment of polymer and silica waveguides and the development of mechanically-stable, low loss couplings.

Optical loss due to mode mismatch has been dramatically reduced by fabrication of tapered transitions (A. Chen et al., Proc. SPIE, 3005, 65-76, 1997). Such tapered transitions have been generated both by reactive ion etching (RIE) and multicolor photolithography (MCP) processing methods.

The final area where major progress has been made is that of integration of polymeric optical circuitry with semiconductor electronic circuitry. We have

demonstrated that an NLO active polymeric waveguide structure can be fabricated on a planarized VLSI semiconductor wafer and that integration can be accomplished without degradation of either electronic or optical circuit function.

The above advances in processing and materials technology has permitted demonstration of electro-optic modulation to 113 GHz and has permitted the first demonstration of integration of polymeric and semiconductor circuitry. The materials effort supported by this contract has permitted fundamental questions to be answered concerning the feasibility of utilizing polymeric materials for commercial modulator applications.

As noted in the Chemistry & Industry and Polymer News articles, work under this contract has achieved for the first time polymeric electro-optic modulator materials which are competitive and even superior to lithium niobate in terms of electro-optic coefficient, permit greater bandwidth to be achieved, permit easy integration with semiconductor electronics and silica fiber optics, and exhibit excellent stability in field tests. Further material improvements (particularly further improvement in electro-optic coefficient and reduction in optical loss at various operating wavelengths) are necessary for wide scale commercial application; however, work performed under this contract has set the stage for initial niche commercial applications.

A final accomplishment to be noted is the development of new techniques in nonlinear spectroscopy. Among many new capabilities is the ability to unambiguously characterized two photon absorption coefficients. Our laboratory is currently collaborating with both Air Force and Navy laboratories on a variety of projects including serving as a reference laboratory for the definition of two photon absorption coefficients.

PERSONNEL SUPPORTED:

Teresa Axenson Rulon Joseph Larsen Andrea Hubbel

Mr. Aaron Harper, who was one of two students for which support was requested in the original application, was named to the first American Chemical Society Organic Division Fellowship.

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- 54. A. Chen, V. Chuyanov, H. Zhang, S. Garner, W. H. Steier, J. Chen, J. Zhu, M. He, S. S. H. Mao, and L. R. Dalton, "Demonstration of the Full Potential of Second Order Nonlinear Optic Polymers for Electrooptic Modulation Using a High μβ Chromophore and a Constant Bias Field," <u>Optics Lett.</u>, 23, 478-80 (1998).
- 55. S. M. Garner, V. Chuyanov, S. S. Lee, A. Yacobian, A. Chen, W. H. Steier, F. Wang, A. S. Ren, M. He, and L. R. Dalton, "Three Dimensional Integration of Polymer Electro-Optic Modulators," <u>Proc. IEEE/LEOS'98</u>, in press.
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- 58. L. R. Dalton, A. Ren, M. S. Lee, A. W. Harper, B. H. Robinson, S. M. Garner, S. S. Lee, and W. H. Steier, "Development of Opto-Chips Based on Polymeric Electro-Optic Modulators," <u>Adv. Mater.</u>, submitted.
- 59. F. P. Strohkendl, T. J. Axenson, R. J. Larsen, L. R. Dalton, R. W. Hellwarth, and Z. H. Kafafi, "Observation of the Lowest Lying Electric-Dipole-Allowed Two-Photon Resonance in C60," J. Phys. Chem. B, 101, 8802-7 (1997).
- 60. F. P. Strohkendl, T. J. Axenson, R. J. Larsen, L. R. Dalton, R. W. Hellwarth, and Z. H. Kafafi, "Two-Photon Absorption Spectra of C60 and C70 Between 0.7 and 1.7 Microns," Proc. SPIE, 3142, 2-17 (1997).
- 61. L. R. Dalton, F. P. Strohkendl, and R. J. Larsen, "Measurement of Two-Photon Absorption Coefficients Employing Femtosecond, Phase-Mismatched DFWM and nDFWM Spectroscopy," <u>Nonlin. Opt.</u>, in press.
- F. P. Strohkendl, T. J. Axenson, R. J. Larsen, L. R. Dalton, R. W. Hellwarth, and Z. H. Kafafi, "Nonlinear Optical Spectra of C70 Films Between 0.74 and 1.6 μm," Phys. Rev. Lett., submitted.
- 63. K. A. Drenser, R. J. Larsen, F. P. Strohkendl, and L. R. Dalton, "Frequency-Agile, Phase-Sensitive-Detection, Multi-Wave-Mixing, Femtosecond Nonlinear Optical Spectroscopy for the Characterization of Photonic Materials, <u>J. Phys. Chem</u>., in press.
- F. P. Strohkendl, R. J. Larsen, L. R. Dalton, R. W. Hellwarth, and Z. H. Kafafi,
 "Nonlinear Optical Spectra of Fullerene Films Between 0.74 and 1.6 μm," <u>Chem.</u> <u>Phys.</u>, submitted.

INTERACTIONS/TRANSITIONS:

INVITED LECTURES:

- 1. Third International Conference on Frontiers of Polymers and Advanced Materials, Kuala Lumpur
- 2. 28th Organosilicon Symposium, Gainesville, Florida
- 3. 1995 AČS/PMSE Symposium on Polymeric Organic Materials: Solid State Properties and Smart Materials, Anaheim, California
- 4. Materials Research Society Symposium on Thin Films for Integrated Optics Applications, San Francisco, California
- 5. National Technology Transfer Center, Technology Applications Review, Orlando, Florida
- 6. NASA Lecturer, Fifty Fourth Frontiers in Chemistry Lecture Series, Cleveland, Ohio
- 7. NATO Advanced Research Workshop on Photoactive Organic Materials: Science and Applications, Avignon, France
- 8. SPIE International Symposium on Nonlinear Optical Properties of Organic Materials VIII, San Diego, California
- 9. SPIE International Symposium of Optical and Photonic Applications of Electroactive and Conducting Polymers, San Diego, California
- 10. SPIE International Symposium on Fullerenes and Photonics II, San Diego, California
- 11. Symposium on Optoelectronic Materials and Conjugated Polymers, IV International Conference on Advanced Matierals, Cancun, Mexico

- 12. 7th International Conference on Unconventional Photoactive Systems, Stanford, California
- 13. OSA/ACS Organic Thin Films for Photonics Applications, Portland, Oregon
- 14. International Business Communications Conference on Commercial Applications for Organo Electronic Materials, Marina del Rey, CA
- 15. Society of Plastics Engineers (SPE) annual technical meeting ANTEC, Indianapolis, IN
- 16. American Chemical Society National Meeting, New Orleans, LA
- 17. American Chemical Society National Meeting, Orlando, FL
- 18. SPIE International Symposium on Fullerenes and Photonics III, Denver, CO.
- 19. ACS/OSA Symposium on Organic Thin Films for Photonic Applications, Orlando, Florida
- 20. International Conference on Nonlinear Optics 3, Marco Island, Florida
- 21. Fourth International Conference on Frontiers of Polymers and Advanced Materials, Cairo, Egypt
- 22. Symposium on Dendrimers and Hyperbranched Polymers, Spring American Physical Society National Meeting, Kansas City, Mo.
- 23. National Meeting, ANTEC, Society of Plastics Engineers, Toronto, Canada
- 24. AFOSR/ONR Photonic and Electro-Optic Polymer Review, Atlantic Beach, Florida
- 25. Sino-American Topical Meeting and Exhibit, Solid State Lasers: Materials and Applications, Tianjin, People's Republic of China
- 26. Gordon Coference on Organic Thin Films, Salve Regina
- 27. The International Society of Optical Engineering 42nd Annual Meeting, San Diego, CA.
- 28. ONR Photonic and Electro-Optic Polymer Review, Atlantic Beach, Florida.
- 29. 1998 IEEE/LEOS Summer Topical Meeting, Organic Optics and Optoelectronics, Monterey, CA.
- 30. First International Workshop on Optical Power Limiting, Cannes, France.
- 31. The International Society of Optical Engineering 43rd Annual Meeting, San Diego, CA.
- 32. American Chemical Society National Meeting, Boston, MA

INVITED SEMINARS:

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Numerous seminars at various industries, government laboratories, and universities including seminars at University of Florida, University of California at Los Angeles (UCLA), University of California at Santa Barbara (UCSB), University of Illinois, University of Washington, NASA Marshall Space Flight Center, the Max-Planck-Institut fur Polymerforschung (Mainz FRG) and the Optical Science Center of the University of Arizona.

Presentations were also made before the Board of Gemfire Corporation, senior management of Hughes Research Laboratories, the Board of the Loker Hydrocarbon Research Institute and the Board of Trustees of the University of Southern California, etc.

CONSULTATIVE AND ADVISORY PANEL SERVICE:

- 1. Blue Ribbon (Final Phase) Panel for the Selection of Presidential Faculty Fellows (National Science Foundation)
- 2. Consultant, Medical Research Service, Veterans Administration

- 3. Materials Research Science & Engineering Center Panel, National Science Foundation
- 4. Panel 15, Office of Energy Efficiency and Renewable Energy Photovoltaics Review, U.S. Department of Energy
- 5. Advisory Committee, National Institutes of Health Biomedical Technology Centers at the University of Illinois and at Dartmouth University
- 6. Consultant, Arizona Disease Control Research Commission, State of Arizona
- 7. Immunobiology Study Section, National Institutes of Health
- 8. Advisory Committee, The New York Herman F. Mark Institute for Polymers Science and Engineering at the Polytechnic University, NY, NY
- 9. Editorial Advisory Board, Chemistry of Materials, American Chemical Society
- 10. Consultant, Princeton Materials Research Center.
- 11. Board of Visitors, University of Alabama.

TECHNOLOGY TRANSITIONS:

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(1) a. Dalton, USC, b. polymeric electro-optic modulator materials, c. Pacific Wave Industries, J. Michael, (310) 753-3344, d. high frequency electro-optic modulators and integrated modulators (opto-chips).

(2) a. Dalton, USC, b. polymeric electro-optic modulator materials, c. TACAN/IPITEK, Y. Shi, (760) 438-1010 ext 3219, d. Intermediate frequency electro-optic modulators and packaged modulators.

(3) a. Dalton, USC, b. polymeric electro-optic modulator materials, c. Gemfire, W. K. Bischel, (650) 849-6877, d. large area flat panel displays.

(4) a. Dalton, USC, b. polymeric electro-optic modulator materials, c. Lockheed Martin, S. Ermer, (650) 424-3131, d. Satellite telecommunications.

(5) a. Dalton, ÚSC, b. polymeric electro-optic modulator and photochromic materials, c. RVM Scientific, R. V. Mustacich, (805) 964-3368, d. low loss waveguide fabrication and interconnection.

(6) a. Dalton, USC, b. polymeric electro-optic modulator materials, c. Radiant Research, Inc., B. M. Davies, (512) 338-4942, d. electro-optic modulators.

(7) a. Dalton, USC & UW, b. polymeric electro-optic modulator materials, c. Microvision, D. C. Bertolet, (206) 637-7055 ext 46, d. HUDs and virtual reality headsets.
(8) a. Dalton, USC & UW, b. photoactive organic materials, c. Aculight, L. Pearson, (425) 482-1100, d. Laser systems and fiber optics.

(9) a. Dalton, USC, b. photochromic materials, c. Hughes Research Laboratories, U. Efron, (310) 317-5000, d. high density optical memories.

INVENTIONS:

Patent Docket 16631-12, "New Class of High Hyperpolarizability Organic Chromophores and Process for Synthesizing the Same," L. R. Dalton, H. R. Fetterman, F. Wang, W. Steier, A. W. Harper, A. S. Ren, and J. Michael.

HONORS/AWARDS

Professional Honors (Requiring Outside Evaluation)

•1996 Richard C. Tolman Award of the Southern California Section, American Chemical Society

Paul Ć. Cross Endowed Lectureship, University of Washington, Seattle, WA (1996)
NASA Endowed Lectureship, 54th Frontiers in Chemistry Lecture Series (1995), Case Western Reserve University

•Harold & Lillian Moulton Distinguished Professorship in Chemistry (Endowed), University of Southern California, 1994

•The 1990 Univ. 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, 1976 and 1977)

•Camille and Henry Dreyfus Teacher-Scholar Award (75-77)

•Alfred P. Sloan Fellowship (74-77)

The research has been featured in the news articles in the following publications: The Baltimore Sun newspaper, Chemical & Engineering News, Research & Development Magazine, Laser World Focus, Business Week, Science, BMDO Update, Wired Magazine, Photonics Spectra, Chemistry & Industry, Polymer Science News, Photonics News, Ind. Eng. Chem. Res., etc. Note: Mr. Aaron Harper, who worked on this project was the first recipient of the American Chemical Society Organic Division Fellowship. This fellowship provided partial salary support for Mr. Harper. Mr. Harper is now an Assistant Professor of Chemistry at Texas A&M University.

ASSERT Evaluation Report (period 9/1/97 to 9/1/98 and final report)

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F49620-95-1-0450, An ASSERT Proposal for the Development of Advanced Polymeric E-O Modulators

During the support-period to 9/1/98, Theresa Axenson and Rulon Joseph Larsen received support to carry out materials synthesis, processing, and spectroscopic studies relevant to the fabrication of advanced electro-optic modulators. This research resulted in several significant improvements in polymeric electro-optic modulator technology. The evaluation of modulators fabricated employing new technology has been extended to above 120 GHz and recently vertical integration of the modulator with VLSI electronics has been demonstrated. Training of Ms. Axenson and Mr. Larsen involved laboratory research (including training in state-of-the-art synthetic methods and use of analytical instrumentation), group meetings and symposia involving graduate and undergraduate students pursuing research under the direction of Dr. Dalton, joint research group meetings involving the research groups of Professor William Steier (USC Electrical Engineering), Professor Robert Hellwarth (USC Electrical Engineering/Electrophysics), Professor Harold Fetterman (UCLA Electrical Engineering) and Professor Dalton and meetings with visiting scientists from industrial laboratories (participating in BMDO or AFOSR research programs). Visiting industrial scientists (receiving BMDO support) included Dr. Y. Shi (TACAN), Dr. Joseph Michael (PWI), Dr. William Bischel (Gemfire), Dr. H. Lacritz (Gemfire), R. Chen (Radiant) and Dr. Robert Mustacich (RVM Scientific). During this period, constant interaction was maintained with Dr. Y. Shi of TACAN Corporation, H. Lacritz (Gemfire), J. Michael (PWI), and R. Mustacich (RVM). As Ms. Axenson and Mr. Larsen have completed all formal course requirements for the Ph.D. and has passed her Ph.D. qualifying examination, they did not take formal courses but did benefit from a rich seminar program including by such distinguished visitors as Dr. F. Kajzar (CEA, France), Dr. Joseph Zyss (France Telecom), Dr. John Reynolds (Univ. of Florida), Dr. Jean Marie Lehn (Paris, France) and Dr. Robert Grubbs (Cal. Tech.). Ms. Axenson's and Mr. Larsen's research involved the first effort to incorporate high $\mu\beta$ chromophores into polymer lattices. Three different schemes were developed for stabilization of polinginduced noncentrosymmetric chromophore order. The first is a precursor polymer route where a soluble and processable polymer, containing an NLO chromophore as a pendant to the polymer main chain, is prepared and processed into optical quality films by spin casting. The material is then poled and a crosslinking reaction is initiated while the poling field is on. This lattice hardening reaction locks in the poling-induced noncentrosymmetric order (i.e., elevates the glass transition temperature of the The process typically yields materials which retain optical polymer lattice). nonlinearity to temperatures as high as 170°C (during dynamic assays). The precursor route has the advantage of permitting use of solvents compatible with clean room operation and permits reproducible poling with minimal effort. The second route involves use of thermosetting materials such as in sol-gel processing. With this approach, poling and hardening processes are not well-separated and "stepped" poling protocols have been found to yield dramatically improved optical nonlinearities relative to single temperature/electric field poling. The thermosetting approach

requires more effort to achieve optimal results but this approach does have the advantage of permitting high chromophore number densities to be realized. The final approach utilizes intramolecular crosslinking (as in the imidization reaction) to achieve lattice hardening.

Ms. Axenson and Mr. Larsen also worked on extension of London theory to provide the first quantitative understanding of the role of chromophore electrostatic interactions in defining poling efficiency and lattice hardening efficiency observed for high dipole moment/high polarizability chromophores. They also pioneered the development of new spectroscopic techniques for characterizing both optical nonlinearity and photochemical stability. Their work during the past year has already resulted in several publications (with more to follow from work already completed) and has resulted in several invited lecture presentations including an SPIE presentation and a presentation at the Naval Research Laboratories in Washington.

Ms. Axenson completed the requirements for a Ph.D. in chemistry during the period 9/97 to 9/98. After her departure for postdoctoral studies in Japan, her research activities were assumed by Mr. Larsen.

During the course of this three year grant, four students Aaron Harper (now Assistant Professor of Chemistry at Texas A&M University), Andrea Hubbel (now with USC administration), Teresa Axenson, and Rulon Joseph Larsen participated in the program.