This project consisted of four tasks each dealing with a different class of nonlinear optical materials. Task (I): Second-Order Materials. During the past year we used theoretical and experimental studies to develop a new class of materials in which a commonly used electron donor chromophore was replaced by a thiophene ring. To efficiently pole a second-order ionic chromophore, the use of a bulky counter-ion in order to reduce ionic conductivity was demonstrated. We also investigated the imaginary part of $X(2)$ by electro-absorption. Task (II): Third-Order Materials. We synthesized a group of phosphorylides which contain a polarizable P atom. Their $X(3)$ behavior were experimentally investigated using femtosecond Kerr gate. Using our new method of optically heterodyned and phase-tuned Kerr gate method, we investigated both the signs and the magnitudes of the real and the imaginary components of $X(3)$. We showed that in the case of one-photon saturation, the sign of imaginary part is negative, while for two-photon absorption, this sign is positive. A very efficient two-photon induced fluorescence was also found for another nonlinear chromophore, diethylaminonitrostyrene, in the crystalline form. Task (III): Photorefractive polymeric composites.
plasticizer which improved our processing and efficiency of electric field poling, we were able to improve on the efficiency of holographic diffraction efficiency to 50% and the two-beam coupling gain to 120 cm\(^{-1}\) in the DEANST: PVK:C60 composite. In order to understand the kinetics of the process, we studied the dynamics of grating formation and decay and their dependence on the electric field and the light intensity. Task (IV): sol-gel processed nonlinear optical materials. The first task we undertook was to understand the microstructure of the sol-gel processed material. We used both steady state and time-resolved fluorescence anisotropy of a nonlinear chromophore, Prodan to study the microstructure and its evolution as a function of aging of the sol-gel processed system.
ANNUAL PROGRESS REPORT

PROJECT: Design, Synthesis and Characterization of Novel Nonlinear Optical Materials

PERIOD: April 1, 1993 to March 31, 1994

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This project consisted of four tasks each dealing with a different class of nonlinear optical materials. Task (I): Second-Order material. During the past year we used theoretical and experimental studies to develop a new class of materials in which a commonly used electron donor chromophore was replaced by a thiophene ring. To efficiently pole a second-order ionic chromophore, the use of a bulky counter-ion in order to reduce ionic conductivity was demonstrated. We also investigated the imaginary part of $\chi^{(2)}$ by electro-absorption. Task (II): Third-Order Materials. We synthesized a group of phosphoylides which contain a polarizable P atom. Their $\chi^{(3)}$ behavior were experimentally investigated using femtosecond Kerr gate. Using our new method of optically heterodyned and phase-tuned Kerr gate method, we investigated both the signs and the magnitudes of the real and the imaginary components of $\chi^{(3)}$. We showed that in the case of one-photon saturation, the sign of imaginary part is negative, while for two-photon absorption, this sign is positive. A very efficient two-photon induced fluorescence was also found for another nonlinear chromophore, diethylaminonitrostyrene, in the crystalline form. Task (III): Photorefractive polymeric composites. Using a plasticizer which improved our processing and efficiency of electric field poling, we were able to improve on the efficiency of holographic diffraction efficiency to 50% and the two-beam coupling gain to 120 cm$^{-1}$ in the DEANST:F-- composite. In order to understand the kinetics of the process, we studied the dynamics of Ag$^+$ formation and decay and their dependence on the electric field and the light intensity. Task (IV): sol-gel processed nonlinear optical materials. The first task we undertook was to understand the microstructure of the sol-gel processed material. We used both steady state and time-resolved fluorescence anisotropy of a nonlinear chromophore, Prodan to study the microstructure and its evolution as a function of aging of the sol-gel processed system.
We reported experimental and theoretical studies of the nonlinear optical properties of a new class of compounds which differ from traditional second-order molecules in the sense that a commonly used electron donor chromophore is replaced by a thiophene ring. The molecular second-order nonlinear optical coefficients, \( \beta \), as determined by the electric field-induced second-harmonic generation technique, for 2-nitro-1-(2-thienyl)ethene and 4-nitro-1-(2-thienyl)-1,3-butadiene are, respectively, one and three times that of para-nitroaniline. \textit{Ab initio} time-dependent correlated Hartree-Fock results are in agreement with the experimental findings. A Mulliken population analysis indicates that the sulfur atom in the thiophene ring acts as an electron donor. Both the experimental and the theoretical results confirm that a thiophene ring acts as an efficient donor, giving rise to highly efficient second-order nonlinear optical properties. We also show that with this type of chromophore one can use a thiophene oligomer, in place of a thiophene monomer, to amplify the nonlinearity.

We have synthesized new glassy methacrylate polymers containing a molecular-ionic (N-methylpyridinium) nonlinear optical chromophore in the side chain. A bulky tetraphenylborate (TPB) counterion was substituted at the salt unit in order to reduce the migration of the counterion during the process of poling. The poling-induced chromophore alignment of the TPB-containing polymer is significantly improved compared to that of the iodide or bromide containing polymers. The second-order nonlinear optical susceptibility, \( \chi^{(2)}(-2\omega;\omega,\omega) \), of the poled TPB-containing polymer is approximately five times larger than that of the corresponding iodide analogue. Also, the temporal stability of the poled structure of the TPB-containing polymer is found to be considerably improved over that of the analogous iodide containing polymer.

We investigated the linear electroabsorption in a second-order optically nonlinear medium. The spectral behavior of the effect is determined by the dispersion of the imaginary part of the second order susceptibility, \( \chi^{(2)}(-\omega;\omega,0) \). Experimentally, we performed spectral measurements of both the dispersion of the complex linear electro-optic coefficient and the electroabsorption in poly[vinyldiazobenzyl bromide] doped with a second order active molecule, 4-(N,N-diethylamino)-\( \beta \)-nitrostyrene, in the range from 400 to 700 nm. The induced absorption is linear in the applied field and exhibits a single peak at 560 nm that coincides with the wavelength at which the imaginary part of electro-optic coefficient exhibits maximum. This peak is distinctly shifted from the maximum of the linear absorption band of the films, observed at 470 nm.

Third-order nonlinear optical susceptibility of solutions of a triphenodithiazine derivative in dichloromethane was measured at several different wavelengths utilizing sub-picosecond degenerate four-wave mixing. The values of the second hyperpolarizability, \( \gamma \), for the neutral and for the oxidized form (dication) are reported. The measurements performed at the wavelengths corresponding to the absorption maxima of the neutral and the dication forms (578 nm and 800 nm, respectively) indicate a twofold increase of the \( \gamma/\sigma \) figure of merit (where \( \sigma \) is
the absorption cross section) for the dication molecule. Time resolved experiments reveal different dynamics of photoexcitation relaxation in the neutral and the oxidized molecules. The photoexcited dication returns to the ground state following a single-exponential decay law, whereas the photoexcited neutral molecule exhibits a more complex dynamics. Analysis of the heterodyned optical Kerr effect as well as the transient absorption experiment performed with a 90 fs resolution indicates an intermediate state generated during the fast decay of the primary photoexcited neutral molecules.

We analyzed the merits of the new method of phase-tuned optically heterodyned femtosecond Kerr gate relatively to the inner reference method in relation to obtaining the magnitudes and the signs of both the real and the imaginary components of the third-order optical susceptibility. The results obtained on several representative dyes showed that, as expected, near a one-photon resonance, the saturation effect leads to a negative imaginary component while near a two-photon resonance the sign of the imaginary component is positive.

The $\chi^{(3)}$ resonant behavior of two model compounds, one of them being a representative of the newly synthesized group of phosphoylide chromophores, was investigated. The results of femtosecond phase tuned optically heterodyned OKG at the wavelength of 796 nm and DFWM at 602 nm were reported. A representative phosphoylide, triphenylphosphinium cyclopentadiene-2,5-bis(4-ethylenylene pyridinium methylidide), abbreviated here to as TPCEPM, was investigated at the wavelength of 602 nm using the inner reference method in conjunction with the degenerate four-wave mixing technique. We derived $\gamma_{RE} = 8.1 \times 10^{-32}$ esu and $\gamma_{IM} = 22.3 \times 10^{-32}$ esu for the chromophore. Another chromophore which incorporates some of the earlier modelled $\gamma$-enhancing features was 2,5-dimethoxyphenylene-1,4-bis(4-ethylenylene pyridinium methylidide), referred to as DMPEPM. We investigated this chromophore at the wavelength of 796 nm, where it is virtually transparent, and two-photon absorption is the resonantly enhancing mechanism. Using the technique of phase-tuned optically heterodyned Kerr gate we derived at that wavelength: $\gamma_{RE} = 1.6 \times 10^{-32}$ esu and $\gamma_{IM} = 2.1 \times 10^{-32}$ esu, in agreement with the 2-photon contribution predictions.

Polymeric composite materials constitute a new and very promising class of photorefractive materials. The results of experimental and theoretical studies in newly developed photorefractive polymeric composite of PVK/C$_{60}$/DEANST were analyzed. In the design of Polymeric Photorefractive Materials we use a multicomponent composites in which each necessary functionality can be independently optimized. The investigated composite was devised of charge transporting polymeric matrix of poly[N-vinylcarbazole] (PVK), C$_{60}$ fullerene photosensitizing molecules, and optically second-order active molecules of diethylaminonitrostyrene (DEANST), and dibutyl phthalate as the plasticizer.
Photorefractive properties of the material were investigated using erasable volume holography in a non-degenerate four-wave mixing geometry and two-beam coupling techniques. A previously developed model of space-charge field grating formation in photoconductive polymers was used to explain the field dependence of four-wave mixing diffraction efficiency. The model takes into account the field dependence of three important parameters for polymeric materials: (i) charge photogeneration quantum yield, (ii) carrier field mobility, and (iii) electro-optic coefficient. Necessary information about these parameters was obtained from the results of photoconductivity and electro-optic modulation experiments. Two-beam coupling gain of 4 cm\(^{-1}\) and diffraction efficiencies of 2\% were measured. With improved processing, we have successfully increased the two-beam coupling to 120 cm\(^{-1}\) and the diffraction efficiency to 50\% at 6328 Å.

Special attention was focused on the kinetics of photorefractive response in the composite. It was found that a very effective switching of diffraction efficiency induced by dc electric field occurs in this system. Electric field induced switching in the tens of millisecond time scale is possible. Also the results of kinetic studies of the index grating writing and its subsequent light-induced erasure are reported. Light-induced grating erasure times of 30 ms were observed at standard light intensities of 1W/cm\(^2\). Experimental and theoretical effort has also been devoted to the influence of the slanted grating experimental geometry on holographic diffraction efficiency measurements performed in poled polymeric composite thin films. The dependence of the diffraction efficiency on the grating slant angle, as well as the difference between the two fundamental s- and p-polarized readouts were investigated. We show and discuss the influence of the poling-induced anisotropy of the second-order nonlinear optical activity and the birefringence of the medium on the angular dependence of the diffraction efficiency.

We reported steady-state and time-resolved fluorescence results for Prodan-doped TMOS derived sol-gels as a function of aging time. The steady-state results show that the microenvironment of sol-gels remains constant well beyond the gelation point. The fluorescence emission characteristics of Prodan indicate that the expulsion of solvent is a step-wise process, in which the removal of ethanol is followed by that of water. Our previous work using R6G did not observe this phenomena because R6G is not nearly as environmentally sensitive compared with Prodan. There is significant rotational freedom of the entrapped probe even after drying the sol-gel under ambient conditions. Time-resolved fluorescence results are in agreement with steady-state measurements. The excited-state intensity decay of Prodan is best described by a unimodal continuous Gaussian distribution throughout the entire sol-gel process. Earlier work with R6G did not reveal such a distribution mainly because R6G's decay kinetics are not easily affected by the physicochemical properties of its local environment. The expulsion of solvent changes the Prodan lifetime distribution, finally resulting in a microenvironment that is intermediate between that of water and ethanol. The microenvironment of the sol-gels is
heterogeneous immediately after the onset of gelation. This heterogeneity increases upon expulsion of ethanol but decreases as water is removed from the sol-gel matrix. One possible interpretation of the recovered intensity decay data is a corresponding distribution of microviscosities. We have shown that the microviscosity change is minimal until the removal of solvent. The recovered final mean microviscosity sensed by Prodan is significantly lower than that previously reported for the bulk viscosity of sol-gels but agrees well without previous R6G results. This result again demonstrates that there is mobility of some dopants within the sol-gel network. The non-linear optical properties of Prodan doped in a sol-gel matrix is currently under investigation. This systems shows great promise for second-order optical nonlinearity.
Publications Resulting from AFOSR Support


Invited Lectures on Work Supported by AFOSR

1. University of Michigan, Department of Chemistry, Ann Arbor, MI., April 15, 1993. "Nonlinear Optical Effects in Molecules and Polymers".


5. University of Hyderabad, School of Physics, Hyderabad, India, August 6, 1993. "Nonlinear Optical Processes in Organic Molecules and Polymers".


7. BASF, Ludwigshafen, Germany, August 19, 1993. "Novel Trends in the Field of Molecular, Polymeric and Composite Materials for Nonlinear Optics".


9. 2nd Brazilian Polymer Conference, Sao Paulo, Brazil, October 6, 1993. "Polymers for Photonics".

10. A series of five lectures at Telebras, the telecommunication company of Brazil, Campinas, Brazil, October 8-14, 1993.
    Titles: (i) Organic and Polymeric Materials for Nonlinear Optics and Photonics: An Overview.
    (iii) Molecular Engineering and Materials Processing for Electro-Optic Devices.
    (iv) Waveguides, Interconnects and Electro-Optics Devices.
"Novel Polymeric Composites Materials for Nonlinear Optics and Photonics".

"Nonlinear Optical Processes in Molecules and Polymers".

"Recent Progress in $\chi^{(3)}$ Materials".

"Progress in $\chi^{(2)}$ Materials".

"Third-Order Nonlinear Optics of Polymers and Composites".

"Polymeric Composite Photorefractive Materials for Nonlinear Optics Applications".

17. The University of Southern Mississippi, Department of Chemistry and Biochemistry, Hattiesburg, Mississippi, Seminar, February 11, 1994.  
"Polymers for Photonics".

"Nonlinear Optical Effects in Molecules and Polymers: Issues and Opportunities".

"New Chromophores and Composite Materials vs. Technological Requirements for Nonlinear Optics".

"Novel Organic: Inorganic Composite Materials for Photonics".

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