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<small>Abstract (Maximum of 200 words)</small> Our program involves development and applications of second-order optical materials which are also multifunctional, i.e., they exhibit more than one functionality and in some cases, new properties derived from a combination of more than one functionality. We specifically focused on applications in electro-optic modulation and photorefractivity. Our effort has focused on developing electro-optic chromophores which offer extended transparency in the visible (to 633 nm), large r-coefficient, as well as high thermal and temporal stability of electrically poled alignment. Earlier we have developed an electro-optic chromophore, APSS, which was processed using an isocyanate containing liquid polymer to produce a thermally stable electrically poled polyurethane based electro-optic polymer. In order to further improve on optical losses in the visible range (633nm), enhance thermal stability and achieve a better control of the poling process, we have made chemical modifications and synthesized a related chromophore APSAS. This chromophore containing linkable four hydroxy sites, permits the usage of a smaller isocyanate, tolylene diisocyanate, with broader optical transparency, to produce rigid cross-linked polyurethane structures. In addition, we tested waveguide parameters of these chromophores. A waveguide				
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modulator was fabricated using APSS to study processing optimization of this modulator. APSS and APSAS also exhibit multifunctionality: A strong two-photon absorption, photobleaching and up-converted emission. APSS exhibits photobleaching when illuminated with high peak power femtosecond pulse lasers. Utilizing this photobleaching 3D optical data storage was illustrated with a Bugs Bunny cartoon video in which each movie frame was stored in layers 5 μm apart. The two-photon excited photosensitization using APSS was also used for a new approach of two-photon photodynamic therapy which can allow treatment of deeper tumors. The use of this chromophore also permitted us to develop a photorefractive composite with broad spectral response from 488 nm to red. In addition, we demonstrated the concept of thermal fixing of photorefractive hologram to enhance the storage time.

FINAL REPORT

PROJECT: Processing of Novel Chromophores for Electro-Optic Applications

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ABSTRACT

Our program involves development and applications of second-order optical materials which are also multifunctional, i.e. they exhibit more than one functionality and in some cases, new properties derived from a combination of more than one functionality. We specifically focused on applications in electro-optic modulation and photorefractivity. Our effort has focused on developing electro-optic chromophores which offer extended transparency in the visible (to 633 nm), large r -coefficient, as well as high thermal and temporal stability of electrically poled alignment. Earlier we had developed an electro-optic chromophore, APSS, which was processed using an isocyanate containing liquid polymer to produce a thermally stable electrically poled polyurethane based electro-optic polymer. In order to further improve on optical losses in the visible range (633 nm), enhance thermal stability and achieve a better control of the poling process, we have made chemical modifications and synthesized a related chromophore APSAS. This chromophore containing linkable four hydroxy sites, permits the usage of a smaller isocyanate, tolylene diisocyanate, with broader optical transparency, to produce rigid cross-linked polyurethane structures. In addition, we tested waveguide parameters of these chromophores. A waveguide modulator was fabricated using APSS to study processing optimization of this modulator.

APSS and APSAS also exhibit multifunctionality: a strong two-photon absorption, photobleaching and up-converted emission. APSS exhibits photobleaching when illuminated with high peak power femtosecond pulse lasers. Utilizing this photobleaching 3D optical data storage was illustrated with a Bugs Bunny cartoon video in which each movie frame was stored in layers 5 μm apart. The two-photon excited photosensitization using APSS was also used for a new approach of two-photon photodynamic therapy which can allow treatment of deeper tumors. The use of this chromophore also permitted us to develop a photorefractive composite with broad spectral response from 488 nm to read. For photorefractivity we developed a new composite with broad spectral response. In addition, we demonstrated the concept of thermal fixing of photorefractive hologram to enhance the storage time.

The objective of our project supported by BMDO has been to produce low optical loss, efficient and thermally stable electro-optic materials having usable optical transparency extending to the visible wavelength range. We successfully developed a suitable chromophore APSS (structure shown below in Figure 1). A novel approach was developed to fabricate EO material wherein an isocyanate containing liquid polymer and APSS chromophore are reacted to produce a thermally stable electrically poled polyurethane based electro-optic polymer. The poled alignment in this polymer was found to be stable even after 1,000 hours of continuous heating at 100 °C. In order to further improve optical quality in the visible range (633 nm), enhance thermal stability, and achieve a better control over the poling process, we have modified the chemical structure of the chromophore and synthesized it. This modified chromophore, APSAS, contains four hydroxyl groups accessible for crosslinking and permits the use of a smaller isocyanate molecule to react with e.g. tolylene diisocyanate; it also has broader optical transparency, and can produce a rigid cross-linked polyurethane structure. Figure 1 compares the chemical structures of APSS and APSAS. Lower optical losses at 633 nm and better thermal stability of poled alignment for this new polymer at temperatures higher than that for the APSS polymer have already been achieved. Table 1 compares the properties of these two chromophores evaluated so far.

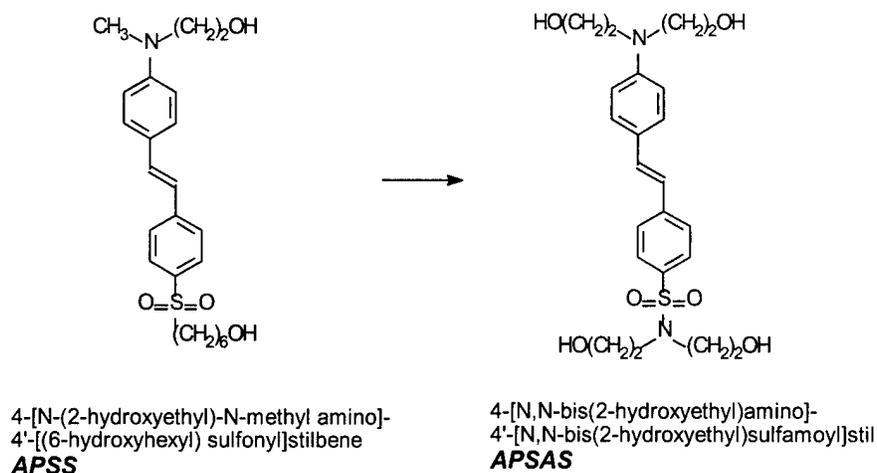


Figure 1: Molecular structures of two novel chromophores, APSS and APSAS.

Table 1: Optical properties of the APSS- and APSAS-based NLO polymers.

Parameters	APSS system	APSAS system
χ^2 [esu]	1.76×10^{-7}	9.1×10^{-8}
r_{33} [pm/V]		
633 nm	12.3-18.5	(to be determined)
812 nm	8.2-8.9	(to be determined)
T_g [°C]	131	137
Optical loss [dB/cm]		
633 nm, TM	8.30	6.25
TE	7.52	6.12
823 nm, TM	1.19	1.03
TE	1.09	0.98
Absorption peak [nm]	390	384
Absorption edge [nm]	490	480

Since waveguide modulators form an important class of electro-optic devices, a considerable effort was spent on novel methods of waveguide preparation. An inorganic-organic optical composite material of polyvinylpyrrolidone(PVP) and SiO₂, prepared by using the sol-gel technique, was introduced, evaluated and optimized for waveguide application. In the optimized condition, 50% PVP/SiO₂ composite film had optical propagation loss of 0.2 dB/cm at 633 nm, and showed no change of index of refraction at 110 °C for one thousand hours after initial slight increase. A unique technique, that utilizes photolithography and laser densification with longer-wavelength-laser than that for conventional laser densification, was then used to fabricate a channel waveguide from this slab waveguide. This approach produced waveguides with propagation losses as low as 0.9 dB/cm.

In order to formulate optimum conditions for waveguide devices we have also conducted waveguide electro-optic modulation studies in APSS using a Mach-Zehnder interferometric arrangement. An optical phase modulator utilizing the APSS based 0.5-

μm -thick electro-optic polymer layer was prepared as a single-mode edge coupled waveguide. Figure 2 shows the schematic drawing of the modulator. The good quality end facets of the modulator were achieved by using a dicing procedure. We were able to obtain waveguide modulation even at 633 nm. At this wavelength, a half-wave-voltage of our device is 38 V.

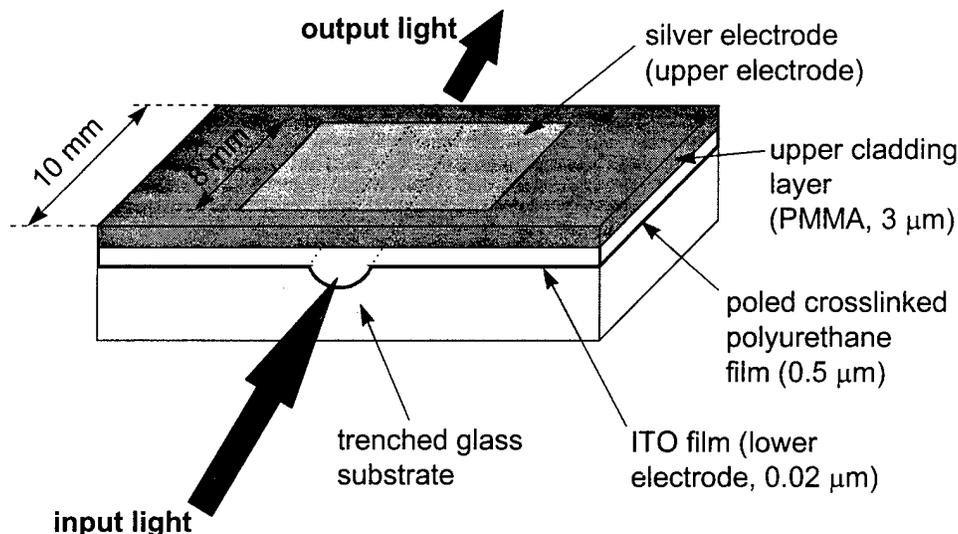


Figure 2: Prototype of a single-mode phase modulator operating at 633 nm.

The APSS chromophore is a truly multifunctional molecule because, in addition to its 2nd order NLO properties, it also exhibits a strong two-photon absorption (around~800nm) and an efficient up-converted emission. It also exhibits two-photon induced photobleaching at higher peak intensities. The efficiency of the up-converted emission is so strong that two-photon pumped lasing has been achieved. This strong two-photon pumped emission has permitted us to use this chromophore as a fluorescent probe to produce 3-dimensional volume image of polymeric materials, dental materials, and biological tissues in a confocal microscopic arrangement.

The up-conversion lasing has also allowed us to observe a new phenomenon. “Phase Conjugation Using Backward Stimulated Up-Converted Emission.” This phenomenon appears to hold promise for high contrast and aberration corrected IR-to-visible image up-conversion and intensification.

We have used the two-photon induced photobleaching to produce high density 3-dimensional optical data storage of WORM type. This method allows both digital and analog storage using a one beam geometry. Figure 3 shows different frames of a Bugs Bunny Cartoon, each stored in a different layer at a spacing of 5 microns. The Bugs Bunny Cartoon is written in a space of 50 microns.

An important biophotonic application is two-photon induced photodynamic therapy. In photodynamic therapy, a photosensitizer is light activated to produce singlet oxygen which destroys tumor cells. Normally, one photon absorption is used for this purpose allowing only superficial penetration. It thus cannot be used to treat tumors located deep in body tissue. The use of two-photon processes allows deeper penetration. In this approach the two-photon chromophore (APSS) absorbs a near infrared photon, up-converts and transfers energy to a photosensitizer. Preliminary study using APSS together with photofrin as the photosensitizer has been successful.



Figure 3: Different frames of the Bugs Bunny Cartoon stored in the layers spaced by 5 μm .

Photorefractive polymers have emerged as an important class of materials for holographic optical data storage and for optical signal processing. However, the photorefractive polymers reported in the past have had limited transparency in the visible (usable only in the red). The broader transparency of APSS in the visible range has permitted us to prepare an efficient photorefractive polymeric composite-PVK:TCP:C₆₀:APSS. Figure 4 shows the absorption spectra of the unsensitized PVK:TCP:APSS (dashed line) and the C₆₀ sensitized PVK:TCP:C₆₀:APSS (solid line) composites materials. As one can see, the unsensitized PVK:TCP:APSS composite shows high transparency in the blue and green region of the visible spectrum. Small absorption of the chromophore assures low background losses of the composite and minimizes formation of non-photorefractive gratings (i.e. photochromic gratings, absorption gratings, etc.). Upon addition of the photocharge generator C₆₀, absorption coefficients of the material reach values of 34.5, 21 and 5 cm⁻¹ at the wavelengths of 488, 514.5 and 632.8 nm respectively.

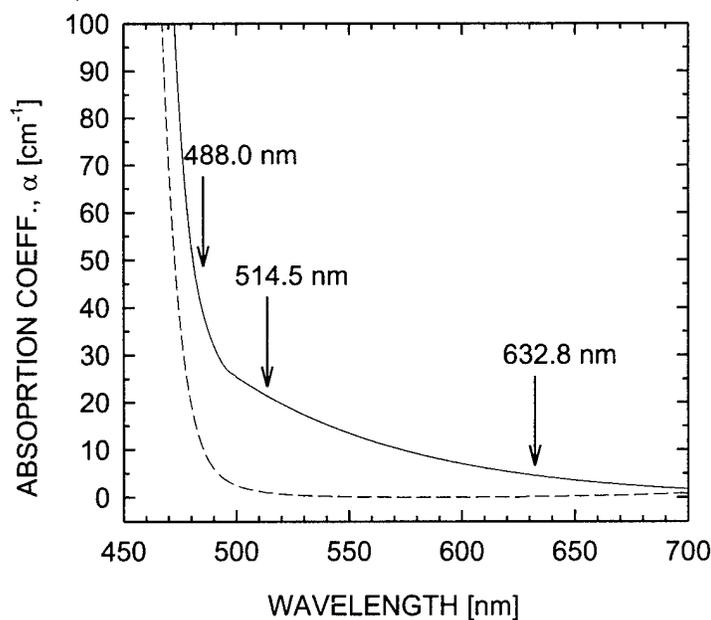


Figure 4: Absorption spectra of the unsensitized (dashed line) and the C₆₀ sensitized (solid line) PVK:TCP:C₆₀:APSS photorefractive composite.

The PVK:TCP:C₆₀:APSS composite shows high photorefractivity over a broad wavelength range. Figure 5 presents the electric field dependence of the diffraction efficiency measured for this material at three different wavelengths. Also, efficient two-beam gain coefficients, exceeding absorption losses, have been demonstrated for this photorefractive material. The net gain coefficients, $\Gamma - \alpha$, obtained were 15,37 and 43 cm⁻¹ at the same wavelengths respectively.

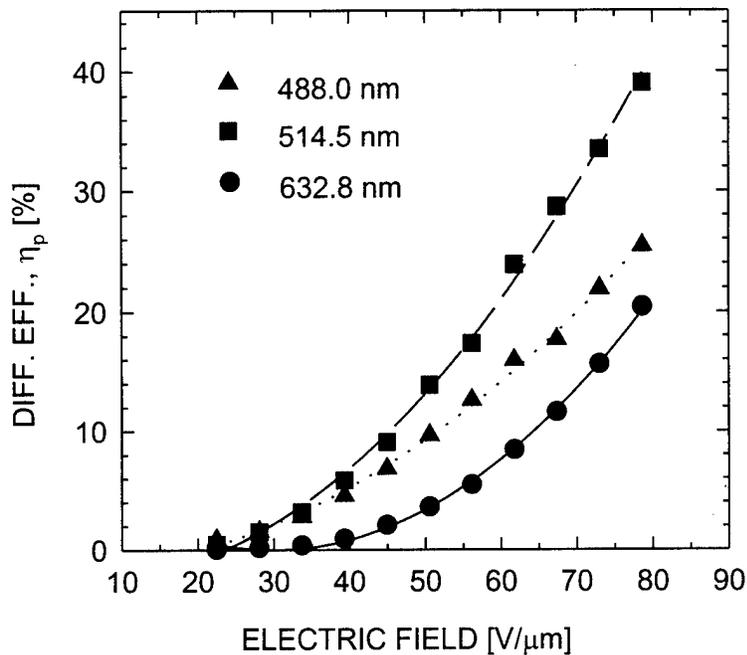


Figure 5: Electric field dependence of the diffraction efficiency in the PVK:TCP:C₆₀:APSS polymeric composite measured at 488, 514.5 and 632.8 nm.

In addition to the demonstration of the efficient broadband photorefractive response in a polymeric material, we have succeeded in developing a new approach of thermal fixing to enhance the storage time for a holographic grating in a photorefractive

polymer. A significant increase in storage time by thermal fixing of photorefractive gratings in a polymeric composite of PVK, TCP, C₆₀, and 4-N,N-diethylamino- β -nitrostyrene (DEANST) is demonstrated. The fixing of the volume holograms is created by quasifreezing the orientation of the linearly anisotropic chromophore molecules. The fixed photorefractive gratings can be easily erased by elevating the sample's temperature to the glass transition temperature (T_g) of the composite. The readout of the thermally fixed first-order ($1K_G$) grating does not require the presence of an external electric field. Figure 6 shows the long term decay of the thermally fixed refractive index grating in the PVK:TCP:C₆₀:DEANST polymeric composite.

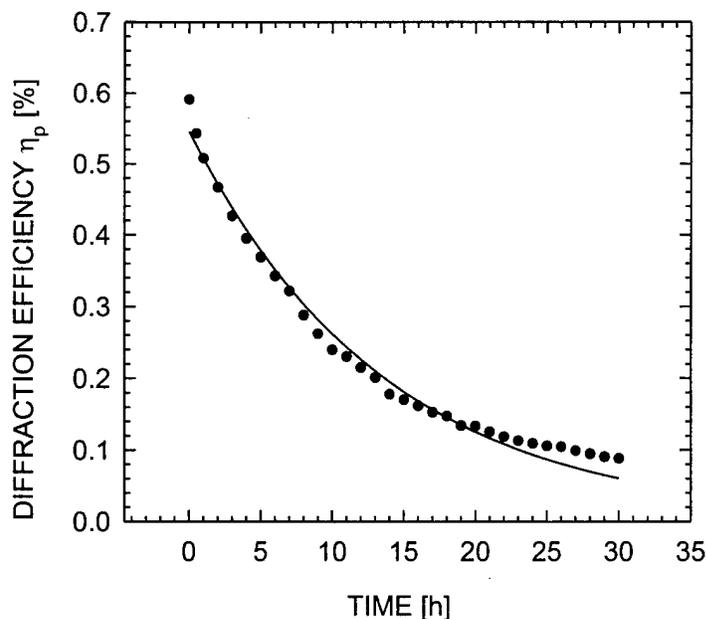


Figure 6: Long time decay of the thermally fixed grating in the PVK:TCP:C₆₀:DEANST polymeric composite stored at room temperature. The solid line is the fit to the stretched-exponential equation.

PUBLICATIONS RESULTING FROM CURRENT BMDO/AFOSR SUPPORT

1. "Fast-Photorefractive Effect in PVK:C₆₀:DEANST Polymer Composite" J. Zieba, M. E. Orczyk, and P. N. Prasad, *J. Phys. Chem.* 98, 8699 (1994).
2. "Optically-Induced Nonlinearities in Fullerenes and Fullerene Doped Polymer Composites," P. N. Prasad, G. Huang, M. E. Orczyk, J. Swiatkiewicz, J. Zieba, M. Berrada and S. Miyata, *SPIE Proceeding* 2284, 228 (1994).
3. "Enhanced Photorefractive Performance in a Photorefractive Polymer Composite," M. E. Orczyk, B. Swedek, J. Zieba and P. N. Prasad., *J. Appl. Phys.* 76, 4995 (1994).
4. "Development and Characterization of Polymeric Composites for Photorefractivity," P. N. Prasad, M. E. Orczyk, J. Zieba and B. Swedek, *Polym. Prepr.* 35, 97 (1994).
5. "Holographic Diffraction in Photorefractive Polymeric Thin Films: Influence of a Slanted Grating Experimental Geometry," M. E. Orczyk, J. Zieba and P. N. Prasad, *Int. J. Nonlinear Optics* 12, 153-163 (1995).
6. "Novel Organic-Inorganic Composite Materials for Photonics," P. N. Prasad, F. V. Bright, U. Narang, R. Wang, R. A. Dunbar, J. D. Jordan and R. Gvishi in *Hybrid Organic-Inorganic Composites*, eds. J. E. Mark, C. Y.-C. Lee, and P. A. Bianconi, ACS Symposium Series (1995) p. 317.
7. "Materials for Nonlinear Optics," W. M. K. P. Wijekoon and P. N. Prasad in "Perspectives in Optoelectronics," ed. S. S. Jha, World Scientific (Singapore, 1995) p. 607-677.
8. "Highly Crosslinked Polyurethane with Very Stable Second-Order Nonlinear Optical Property," C. K. Park, J. Zieba, C. F. Zhao, B. Swedek, W. M. K. P. Wijekoon and P. N. Prasad, *Macromolecules* 28, 3713 (1995).
9. "Non-Electrooptic Non-Local Photorefractive Effect in a Polymer Composite," M. E. Orczyk, J. Zieba and P. N. Prasad, *Appl. Phys. Lett.* 67, 311-313 (1995).
10. "Sol-Gel Derived PVP:SiO₂ Composite Materials and Novel Fabrication Technique of Channel Waveguides," M. Yoshida and P. N. Prasad, *Mat. Res. Soc. Symp. Proc.* 392, 103-108 (1995).
11. "Fabrication of Channel Waveguides from Sol-gel Processed PVP:SiO₂ Composite Materials," M. Yoshida and P. N. Prasad, *Appl. Optics* 35, 1500-1506 (1995).
12. "Sol-gel Processed SiO₂/TiO₂/Polyvinylpyrrolidone Composite Materials for Optical Waveguides," M. Yoshida and P. N. Prasad, *Chem. Mat.* 8, 235-241 (1995).
13. "Two-photon Pumped Cavity Lasing in a Dye Solution Filled Hollow Fiber System," G. S. He, J. D. Bhawalkar, C. F. Zhao, C.-K. Park, and P. N. Prasad, *Opt. Lett.* 20, 2393-2395 (1995).

14. "New Application for a Well-known Molecule: Prodan as an Attractive Optically-second Order Nonlinear Chromophore," J. D. Bhawalkar, J. Zieba, M. Kazmierczak, P. N. Prasad, Y. Zhang, S. Ghosal, M. K. Casstevens, and R. Burzynski, *Int. J. Nonlinear Optics* 16, 95-107 (1996).
15. "Nonlinear Multiphoton Processes in Organic and Polymeric Materials," J. D. Bhawalkar, G. S. He, and P. N. Prasad, *Rep. Progress of Physics* 59, 1041-1070 (1996).
16. "Two-Photon Generated Photo-Bleached Patterns in a Polymer Matrix," P. C. Cheng, J. D. Bhawalkar, S. J. Pan, J. Swiatkiewicz, J. K. Samarabandu, W. S. Liou, G. S. He, G. Ruland, N. D. Kumar, and P. N. Prasad, (*Proceedings of SCANNING 96*), *Scanning* 18, 129-131 (1996).
17. "Phase-Conjugate Backward Stimulated Emission from a Two-Photon Pumped Lasing Medium," G. S. He, Y. Cui, M. Yoshida, and P. N. Prasad, *Opt. Lett.* 22, 10-13 (1997).
18. "Photorefractivity in a Novel Polymer Composite with High Diffraction Efficiency and Broad Optical Transparency," Y. Cui, B. Swedek, K.-S. Kim, and P. N. Prasad, *J. Phys. Chem. B* 101, 3530-3534 (1997).
19. "Highly Efficient Upconverters for Multiphoton Fluorescence Microscopy," P. C. Cheng, J. D. Bhawalkar, S. J. Pan, A. Shih, T. M. Suchyna, K-S. Kim, W. S. Liou, J. Swiatkiewicz, and P. N. Prasad, submitted to *Journal of Microscopy*.
20. "Thermal Fixing of Refractive Index Gratings in a Photorefractive Polymer" N. Cheng, B. Swedek, and P. N. Prasad, *Appl. Phys. Lett.*, appearing in September 1997.