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The research accomphlished in this project consists of four tasks each dealing with a different class of nonlinear optical (NLO) materials. Task (I): Second-order nonlinear optical materials. We developed new chromophores and processing to produce electro-optic materials with enhanced optical transparency towards the visble (~700 nm), increased chemical and thermal stability and stability of poled alignment for 1000 hours at 100'C. Several approaches showed promises and we accomplished a great deal. Also, we developed polyurethane cross-linking polymers to produce thermally stable poling alignment in both molecular-ionic type and neutral type second-order chromophores. In both cases stability up to 1000 hours at 100°C was achieved. In another approach, in collaboration with Professor Shea of University of California, Irvine, we have empolyed ormosils to produce stable poled alignments. Task (II): Third-order nonlinear optical materials. We synthesized a group of phosphoylides containing a polarizable P atom and investigated their X(3) behavior via femtosecond Kerr gate measurements. By using optically heterodyned and phase-tuned Kerr gate techniques, we obtained both the signs and the magnitudes of the

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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. Also, we investigated resonant X(3) behavior by the study of power limiter action and two-photon up-converted emission and lasing. To our knowledge we were the first to demonstrate two-photon exicited cavity lasing in organic bulk form. Task (III): Photorefractive polymers. We studied the variables in the composition and the processing of the composites to enhance the diffraction, developed techniques to fully characterize the various processes, in order to understand the kinetics of the grating formation and decay. Using a plasticizer which improved our processing and efficiency of electric filed poling, we improved the holographic diffraction efficiency to 50% and the two-beam coupling gain to 130 cm-1 in the DEANST:PVK:C60 composite. Furthermore, we studied the role of orientationally induced birefringence vs pure electro-optic effect in photo-refractive diffraction and found that the birefringence contribution is dominant. Task (IV): Sol-gel processed nonlinear optical materials. Our study focused on sol-gel processed monoliths which were impregnated with organics in the pores. We used both steady state and time-resolved fluorescence anisotropy of nonlinear chromophore, PRODAN to study the microstructure and its evolution asa function ofaging of the sol-gel processed system and found that solvent expulsion from the sol-gel matrix is a step-wise process in that removal of water followed by the removal of water. In addition, we used the sol-gel method to prepare multiphasic nanostructured composites where the phase separation is of nanometer scale. Such a composite containing two different noninteracting phases (for example C60 and a two-photon absorbing dye) in the nanometer scale shows optical power limiting at different wavelengths characteristic to different phases.

FINAL REPORT

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

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ABSTRACT

The research accomplished in this project consists of four tasks each dealing with a different class of nonlinear optical (NLO) materials. **Task (I):** Second-order nonlinear optical materials. We developed new chromophores and processing to produce electro-optic materials with enhanced optical transparency towards the visible (≥700 nm), increased chemical and thermal stability and stability of poled alignment for 1000 hours at 100°C. Several approaches showed promises and we accomplished a great deal. Also, we developed polyurethane cross-linking polymers to produce thermally stable poling alignment in both molecular-ionic type and neutral type second-order chromophores. In both cases stability up to 1000 hours at 100°C was achieved. In another approach, in collaboration with Professor Shea of University of California, Irvine, we have employed ormosils to produce stable poled alignments. **Task (II):** Third-order nonlinear optical materials. We synthesized a group of phosphoylides containing a polarizable P atom and investigated their $\chi^{(3)}$ behavior via femtosecond Kerr gate measurements. By using optically heterodyned and phase-tuned Kerr gate techniques, we obtained 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. Also, we investigated resonant $\chi^{(3)}$ behavior by the study of power limiter action and two-photon up-converted emission and lasing. To our knowledge we were the first to demonstrate two-photon excited cavity lasing in organic bulk form. **Task (III):** Photorefractive polymers. We studied the variables in the composition and the processing of the composites to enhance the diffraction, developed techniques to fully characterize the various processes, in order to understand the kinetics of the grating formation and decay. Using a plasticizer which improved our processing and efficiency of electric filed poling, we improved the holographic diffraction efficiency to 50% and the two-beam coupling gain to 130 cm^{-1} in the DEANST:PVK:C_{60} composite. Furthermore, we studied the role of orientationally induced birefringence vs pure electro-optic effect in photo-refractive diffraction and found that the birefringence contribution is dominant. **Task (IV):** Sol-gel processed nonlinear optical materials. Our study focused on sol-gel processed monoliths which were impregnated with organics in the pores. We used both steady state and time-resolved fluorescence anisotropy of nonlinear chromophore, PRODAN to study the microstructure and its evolution as a function of aging of the sol-gel processed system and found that solvent expulsion from the sol-gel matrix is a step-wise process in that removal of water followed by the removal of water. In addition, we used the sol-gel method to prepare multiphasic nanostructured composites where the phase separation is of nanometer scale. Such a composite containing two different noninteracting phases (for example C_{60} and a two-photon absorbing dye) in the nanometer scale shows optical power limiting at different wavelengths characteristic to different phases.

DETAILS OF THE TECHNICAL PROGRESS

Task I: Second-Order Materials

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, β, 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. *Ab initio* time-dependent coupled perturbed 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 showed that with this type of chromophore one can use a thiophene oligomer, in place of a thiophene monomer, to amplify the nonlinearity.

Also, we carried out linear and nonlinear optical properties of three different classes of basic heterocyclic organic structures using *ab initio* time-dependent coupled perturbed Hartree-Fock-Roothan method. We showed that for the α and γ coefficients, the calculated orders thiophene > Pyrrole > furan for the five membered rings; Pyridine > pyrazole > s-triazene for the aromatic bases; and benzothiazole > oxazole for fused ring systems indicating a qualitative relationship with the corresponding order in $\Delta\epsilon$(HOMO - LUMO) of the respective group of molecules. The β values did not appear to show a discernible trend. The dispersion of $\alpha(-\omega;\omega)$ and those of $\gamma(-\omega;0,0,\omega)$, $\gamma(-\omega;\omega,\omega,-\omega)$, $\gamma(-2\omega;0,\omega,\omega)$ and $\gamma(-3\omega;\omega,\omega,\omega)$ in the case of the five-membered rings were fond to be consistent with our previous findings. Accordingly, the out-of-plane component of α tensor shows nearly parallel dispersion, indicating a benzene like structure. In another study we investigated NLO properties of series of primary heterocyclic structures. We calculated the linear and NLO properties of *cis* and *trans* isomers of diphenylbenzobisoxazole (PBO) and diphenylbenzobisthiazole (PBT) by *ab initio* time-dependent coupled perturbed Hartree-Fock method with the use of a *split-valence* basis set. We found that the second-order nonlinear optical susceptibilities of the *trans* isomers to be larger by a factor of 1.5 than that of *cis* isomers over a wide range of optical frequencies. Between two homologues, PBT exhibits slightly higher nonlinear optical susceptibilities, supporting the experimental findings.

We 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.

Also, we investigated a new class of second-order nonlinear optical polymer (PU-TPh) based on polyurethane back-bone with a molecular-ionic nonlinear optical chromophore in the side-chain. A bulky counter-ion, tetraphenylborate, was used to effectively pole this type of chromophore. This polymer structure provides both high second-order optical nonlinearity and extended room temperature stability. The high second-order activity was achieved by incorporating 100 % (molar) of chromophores into the polymer chain; it means each structural unit of this polymer carries one nonlinear optical moiety. The high temporal stability, even as for the relative low glass transition temperature 121 °C, is due to extensive formation of hydrogen bonds stabilizing the poling induced alignment. In our on-going experiment we monitored the $\chi^{(2)}$ value of a 1 μm thick Pu-TPh film for a period of 31 days without any noticeable decay. The $\chi^{(2)}$ value of Pu-TPh we can obtain was ~3×10^{-7} esu with $\lambda_{max} = 478$ nm. We observed a clear relation between the thickness of PU-TPh films and poling efficiency. Generally, the thinner the film the higher the poling efficiency can be observed.

Also, we synthesized and characterized a new thermally curable optically second-order active material based on polyurethane derived from poly[(phenylisocyanate)-co-formaldehyde] and 4-[N-(2-hydroxyethyl)-N-methylaminophenyl]-4'-(6-hydroxyhexylsulonyl)azobenzene. In this approach a liquid polymer, poly[(phenylisocyanate)-co-formaldehyde], containing one isocyanate group on each phenylene ring was selected in order to increase the efficiency of the cross-linking reaction between polymer chains during the curing process. After being subjected to thermal treatment of the film at 160 °C for 30 minutes the glass transition temperature of the cross linked polymer was 142 °C. The poled and thermally cured polymer film results in a $\chi^{(2)}$ value of 3×10^{-7} esu. The film was subjected to thermal treatment in an oven at 100 °C for 2,000 hours, but no detectable relaxation was observed for the thermoset polymer.

In collaboration with Professor Shea's group at University of California, Irvine, we were able to demonstrate a sol-gel based material exhibiting both high value of macroscopic second-order nonlinear optical susceptibility, $\chi^{(2)}$ and its relatively high thermal stability. This material is synthesized by using an ormosil precursor, 4-Nitro-N-N-bis[(3-trietoxysilyl)propyl]aniline. After suitably performed hydrolysis it can be processed with excellent optical quality and after thermal curing, exhibits high rigidity, mechanical endurance and has an absorption maximum at very short wavelengths, $\lambda_{max} = 372$ nm. A relatively mild poling condition (poling field ~2.5x10-8 V/m, maximum temperature 135 °C) provided a substantial stability of the poled alignment. The $\chi^{(2)}$ value derived from the second-harmonic generation measurements was 9×10^{-8} esu. An additional parameter which correspond to the already mentioned rigidity of the cured structure is the thermal stability of the poling induced alignment of the molecular dipoles of the nonlinear optical chromophore. At temperatures below 100 °C no decay in the $\chi^{(2)}$ value of this material was observed for a period of one hour. A complete quenching of the nonlinear optical activity was achieved when the material was heated up to 175 °C. Judging from the thermal analysis (DSC) data we can assume that this threshold temperature can be elevated further if the poling temperature can be increased to 180-200 °C without causing deterioration in optical quality of the poled films.

We also performed the linear electroabsorption in a second-order nonlinear optical medium, PVK doped with DEANST. The spectral behavior of the effect was determined by the dispersion of the imaginary part of the $\chi^{(2)}(-\omega;\omega,0)$. Our measurement indicates that the induced absorption (in the spectral range from 400 to 700 nm) exhibited a single peak at 560 nm that coincides with the wavelength at which the imaginary part of electro-optic coefficient exhibits a maximum. This peak is distinctly shifted from the maximum of the linear absorption band of the films, observed at 470 nm. In addition we derivatized the nonlinear optical chromophore as to yield an amphiphilic molecule which formed stable monolayer on the air-water interface. The second harmonic generation measurements of the monolayer transferred onto silica substrate showed that LB films of this DEANST derivative consist of molecular aggregates. However, upon dilution with fatty acids LB films showed the normal second harmonic behavior of a $C_{\infty V}$ symmetry. We found that the chromophore tilt angle of DMANST mixed with fatty acid (docosanoic acid) to be 42° with respect to the surface normal. Also we investigated the SHG activity of NLO dye monolayers containing a variety of counter-ions. We found that the SHG activity in these monolayers to be dependent on the extent of aggregation which in tern depend on the conditions of the monolayer preparation. Our study showed, in the case of amphiphilic counter-ion containing NLO dyes SHG signal had a very little effect on the compression speed, due to suppression of aggregation.

Task (II): Third-Order Materials

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, γ, 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 γ/σ figure of merit (where σ 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-ethenylene pyridinium methyliodide), 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 modeled γ-enhancing features was 2,5-dimethoxyphenylene-1,4-bis(4-ethenylene pyridinium methyliodide), 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.

We have investigated the nonlinear optical performance of new UV photostable dyes, didecyl and didecyloxy substituted *para*-polyphenyl heptamers (DDPPH and DDOPPH hereafter, respectively) using the technique of degenerate four-wave mixing and optical Kerr gate. The studies were performed on the dyes dissolved in THF solution and doped in composite-glass. The magnitudes and the signs of the real and imaginary components of the complex third-order optical susceptibilities were determined independently by the heterodyned optical Kerr gate method and compared to the values obtained from concentration dependent homodyne Kerr gate and degenerate four-wave mixing measurements. The observed effective second hyperpolarizability, γ, values are dependent on optical intensity and pulse width of the pumping source beam. The optical Kerr gate measurements provide $\gamma_{real} = -1\text{x}10^{-34}$ esu and $\gamma_{im} = 3.2\text{x}10^{-35}$ esu for DDOPPH. These values were an order of magnitude lower than that obtained by degenerate four-wave mixing measurements.

Two-photon absorption is determined by the imaginary part of $\chi^{(3)}$. We have investigated two-photon absorption for an optical limiting and stabilization. The nonlinear optical material are THF solutions as well as a centimeter long epoxy rod and composite glass rod doped with the same organic dopant (2,5-benzothiazole 3,4-didecyloxy thiophene). An ultra-short laser source with 0.5 picosecond pulse width and 602 nm wavelength was employed. The transmissivity data of these two materials have been measured as a function of the input laser intensity. The obtained results can be fitted well based on the assumption that two-photon absorption is the predominant mechanism causing the observed optical limiting behavior. At 930 MW cm^{-2} input intensity level, the output intensity fluctuation is three times less than the input intensity fluctuations.

We synthesized a new lasing dye (ASPT) that possesses a much greater two-photon absorption cross-section and much stronger up-conversion fluorescence emission than common dyes (such as Rhodamine), when excited with a near infrared laser radiation. Utilizing ASPT doped bulk polymer rods two-photon pumped up-converted cavity lasing was accomplished using a Q-switched Nd:YAG laser as the pump source. The wavelength and pulse duration were

~600 nm and 306 ns, respectively, for cavity lasing; whereas the corresponding values for pump pulses were 1.06 μm and ~10 ns, respectively. For a 7 millimeter long sample rod with a dopant concentration $d_0 = 8x10^{-3}$ M L^{-1}, the conversion efficiency from the absorbed pump energy to the cavity lasing output was ~3.5% at a pump energy level of 1.3 mJ. The lasing life time, in terms of pulse numbers, was more than $4x10^4$ pulses at 2 Hz repetition rate and room temperature.

Two-photon pumped green cavity lasing was studied in a solution of a new dye, 4-[N-(2-hydroxyethyl)-N-methyl) amino phenyl]-4'-(6-hydroxyhexyl sulfonyl)stilbene (APSS) in DMF. This dye shows a strong two-photon induced fluorescence when excited at 800 nm. The molecular two-photon absorption cross section was measured to be $\sigma_2 = 1.5x10^{-19}$ cm^4/GW or $\sigma'_2 = 3.8x10^{-47}$ cm^4/photon/s and is 1 to 2 orders of magnitude higher than rhodamine 6G. The peak of the lasing spectrum was around 555 nm, and is to the best of our knowledge, the shortest wavelength obtained from a two-photon pumped dye laser. the conversion efficiency was as high as 2.8%. Also we studied blue visible emission in a solution of PRODAN when excited at 1064 nm. This up-converted emission was shown to be due to three-photon absorption followed by fluorescence with peak at 450 nm. The three-photon absorption is a resonant $\chi^{(5)}$ process. The three photon absorption was estimated to be $5.2x10^{-77}$ cm^6s^2. The optical power limiting based on three-photon was also demonstrated in this system.

Also, two-photon pumped frequency up-conversion cavity lasing at ~600 nm was accomplished in three types of dye doped solid rods pumped with ~10 ns and 1.06 μm IR laser pulses using the ASPT dye. Three different materials were chosen as solid matrices: poly-HEMA, VYCOR porous glass and sol-gel glass. Strong cavity lasing could be achieved in these solid matrices as well as in solutions in liquid cell. The spectral, temporal and spatial characteristics of the cavity lasing output were systematically investigated. Furthermore, three-photon absorption induced frequency up-conversion fluorescence emission was studied in a solution of 2,5-benzothiazole, 3,4-didecyloxy thiophene in THF, pumped with 10 ns Q-switched 1.06 μm laser pulses. The spectral peak of the emission was located in the 450-480 nm range and the intensity dependence of the visible emission on the IR excitation obeys the cubic law. At a higher solute concentration (0.18 M/L) and moderate IR excitation intensity levels (50-200 MW/cm^2) obvious optical limiting behavior was observed as a result of three-photon absorption. the measured nonlinear absorption coefficient and the corresponding molecular three-photon absorption cross-section are $\gamma = 2.7 \times 10^{-18}$ cm^3/W^2 and $\sigma'_3 = 8.8 \times 10^{-76}$ cm^6 s^2 respectively.

Task (III): Photorefractive Polymeric Composites

Polymeric composite materials constitute a new and very promising class of photorefractive materials. We have achieved a remarkable success in this new field. We developed a new polymeric composite of PVK/C_{60}/DEANST with high diffraction efficiency and asymmetric two beam coupling. 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 have showed 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 synthesis and characterization of a new, low T_g polymer exhibiting the photorefractive effect.[13] The photorefractive polymer contains a second-order nonlinear optical chromophore, a charge transporting group and a plasticizer species (n-octylmethacrylate) covalently linked to the polymer backbone. A sensitizer (C_{60}) was molecularly doped into polymer to facilitate photocharge generation. The material exhibited an r_{33} coefficient of ~6.5 pm/V at the field of 100 V/μm. The photorefractive diffraction efficiency at this field is ~ 0.8% and the two beam coupling gain is ~7.5 cm^{-1}.

Also we studied photorefractive properties of a multicomponent polymer composite PVK-TCP:C60:DEANST.[14] An efficient plasticization of the host polymer matrix with TCP and utilization of a nonlinear chromophore with large dipole moment allowed us to achieve a large poling induced electro-optic coefficient. In this composite material a diffraction efficiency exceeding 40% and a two-beam coupling gain coefficient larger than 100 cm^{-1} was observed. An example of holographic recording and retrieval of an image was demonstrated by employing a standard USAF optical resolution target. Furthermore we investigated the grating spacing dependence of photorefractive diffraction efficiency and showed that the effects resulting from orienting of the composite's optically second-order nonlinear chromophores in the period local field affect the formation of the refractive index grating.

Task (IV): Sol-Gel Processed NLO Materials

We reported steady-state and time-resolved fluorescence results for Prodan-doped TMOS derived sol-gels as a function of the 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 phenomenon 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. This systems shows great promise for second-order optical nonlinearity because PRODAN is a very good second order chromophore.

We have used polyvinylpyrrolidone (PVP) polymer processed with SiO_2 and TiO_2 to prepare planar optical waveguides.[16] In our processing, the PVP polymer is mixed with the SiO_2 precursor (tetraethoxysilane) and the TiO_2 precursor (titaniumethylhexoxide) in the solution phase and their relative ratios varied to optimize the thermal stability and desired refractive index. The alkoxides are hydrolyzed under carefully controlled conditions and the sol is allowed to reach a certain viscosity before the film is cast. The film is then thermally treated above 200 °C to induce cross-linking in PVP. We have evaluated the performance of these films in terms of their optical losses. The optimum composition appears to be 50% PVP. The relative ratio of SiO_2 and TiO_2 is varied to achieve the desired refractive index. These films can be heated up to 200 °C for densification before any deterioration of PVP occurs as evidenced by observed discoloration and a rapid increase in the optical waveguide loss.

To fabricate channel waveguides, we have used a combination of photolithography and selective laser densification.[17] It involves deposition of metal lines by using a photomask. Then the film is exposed to light which can be of any wavelength at which the $PVP:SiO_2:TiO_2$

composite does not absorb. The metal lines absorb and transfer the heat to the underlying films whereby densification occurs to produce regions of higher refractive index in the waveguide channel. We have produced channels which are 5 μm wide and 1 μm deep. The waveguide losses in these channels are 0.8 dB/cm at 633 nm which is considerably higher than that (< 0.2 dB/cm) in the planar waveguide form. We are currently improving our processing technique to explore if channel waveguide losses can be further reduced.

We have developed a multiphase composite bulk using sol-gel processing which produces large size bulks of excellent optical quality.[18] In this approach we prepare a highly porous monolith gel (in the present case silica) and thermally process it. The pores in the silica monolith under our processing conditions are in the nanoscale region (~4 nm). This allows various molecules (such as fullerene) to be adsorbed in the pores by diffusion of a solution with a polymerizable liquid such as methylmethacrylate (MMA) which is then polymerized *in-situ*. The concept of multiphasic nanostructured composite can be used to prepare a wide range of optical materials. We have been able to dope two (or more) different optically responsive materials each of which can be different phases of the matrix (the silica phase, the PMMA phase and the interfacial phase), to make multifunctional bulk materials for photonics. For example, we have doped in addition to fullerene, which is adsorbed in the interfacial phase, a fluorescent and optically nonlinear chromophore bisbenzothiazole 3,4-didecyloxy thiophene (BBTODT) in the PMMA Matrix.

Also, we have impregnated silica glasses with PMMA hosts for doping nonlinear optical chromophores.[19,20] The advantage of composite glasses are their high optical quality and mechanical strength. The narrow channels of these composite glasses are filled with longitudinal PMMA chains to form inorganic:organic composite glass. Using 6-propionyl-2-(dimethylamino) naphthalene (PRODAN), a solvent sensitive dye, we probed the local microenvironment in these PMMA:SiO_2 glasses using steady state and time-resolved fluorescence. The steady state fluorescence results clearly demonstrate that the Stokes shifts ($\Delta\nu$) obtained for PRODAN in solid matrices (composite glass, pure PMMA and pure silica gel glass) are in good agreement with the expected dependence in orientational polarizability (Δf) obtained for liquid solvents. These results also demonstrate that the dye molecules are primarily surrounded by a PMMA-like environment but there is a distinct influence of the silica skeleton and the hydrogen bonds which connect the silica matrix and PMMA. The time resolved fluorescence results also suggest a multidomain microenvironment for the PRODAN molecules within the composite glass.

Publications Resulting from the AFOSR Support

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Invited Talks and Workshops on Research Supported by AFOSR

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

2. 6th OGAMM Meeting, Los Angeles, CA, July 8, 1993: *Multifunctional Organic Heterostructures for Electro-Optics Applications.*

3. SPIE Meeting, San Diego, CA, July 12, 1993. Symposium on Nonlinear Optical Properties of Organic Materials: *Photorefractivity in Polymeric Composite Materials.*

4. Nonlinear Optics Summer School, Rochester, NY, July 18, 1993, Tutorial Course: *Nonlinear Optical Materials.*

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

6. Second International School and Topical Meeting on Applications of Nonlinear Optics, Prague, Czech Republic, August 16, 1993: *Nonlinear Optics of Novel Organic and Polymeric Materials.*

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

8. American Chemical Society, National Meeting, Polymer Chemistry Symposium on Marvel Award, August 24, 1993: *Novel Polymeric Composites for Photonics.*

9. Second 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.*
    (ii) *Measurements and Characterization Techniques for Second-Order Processes.*
    (iii) *Molecular Engineering and Materials Processing for Electro-Optic Devices.*
    (iv) *Waveguides, Interconnects and Electro-Optics Devices.*
    (v) *Current Status, New Trends and Future Directions for Materials and Applications for Electro-Optics and Photorefractivity.*

11. Polymex-93, International Symposium on Polymers, Cancun, Mexico, November 2, 1993: *Novel Polymeric Composites Materials for Nonlinear Optics and Photonics.*

12. El-Sayed Symposium, Los Angeles, CA, November 6, 1993: *Nonlinear Optical Processes in Molecules and Polymers.*

13. NLO Polymer Program Review, Washington, DC, November 8, 1993: *Recent Progress in* $\chi^{(3)}$ *Materials.*

14. NLO Polymer Program Review, Washington, DC, November 9, 1993: *Progress in* $\chi^{(2)}$ *Materials.*

15. ICONO'1, International Conference on Organic Nonlinear Optics, Val Thorens, France, January 11, 1994: *Third-Order Nonlinear Optics of Polymers and Composites.*

16. SPIE-The International Society for Optical Engineering Symposium on Organic, Metallo-Organic and Polymeric Materials for Nonlinear Optical Applications, Los Angeles, January 24, 1994: *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.*

18. Thirty-Fourth Sanibel Symposium, Sawgrass, Florida, February 18, 1994: *Nonlinear Optical Effects in Molecules and Polymers: Issues and Opportunities.*

19. American Chemical Society National Meeting, Symposium on "Organic Nonlinear Optics: Business Opportunity on Academic Curiosity", San Diego, CA, March 16, 1994: *New Chromophores and Composite Materials vs. Technological Requirements for Nonlinear Optics.*

20. American Chemical Society National Meeting, Symposium on Hybrid Organic-Inorganic Composites, San Diego, CA, March 16, 1994: *Novel Organic:Inorganic Composite Materials for Photonics.*

21. Wright-Patterson Air-Force Base, Material Division, Dayton, Ohio, April 14, 1994, Seminar: *Organic Material's Future for Nonlinear Optics and Photonics.*

22. University of New Mexico, Department of electrical Engineering, Albuquerque, New Mexico, April 15, 1994, Seminar: *Polymers for Photonics.*

23. Fourth Iketani Conference, The international conference on optically nonlinear organic materials and applications, May 18, 1994: *Polymeric Composite Materials for Nonlinear Optics and Photonics.*

24. International Symposium on Non-Linear Photonics Materials, Tokyo, Japan, May 24, 1994: *Molecular and Polymeric Material for Third-Order Nonlinear Optic*s.

25. The Society of Polymer Science, Japan, 43rd Annual Meeting, Nagoya, Japan, May 26, 1994: *New Chromophores and Composite Materials for Nonlinear Optics and Photonic*s.

26. Training School on Nonlinear Optics and Optical Design, Tehran, Iran, June 6-8, 1994: Three lectures on *Nonlinear Optical Processes in Organic Molecules and Polymers.*

27. SPIE - The International Society for Optical Engineering, Symposium on Nonlinear Optical Properties of Organic Materials VII, San Diego, CA, July 28, 1994: *Photorefractivity in Polymer Composites* M. E. Orczyk, B. Swedek, J. W. Zieba, and P. N. Prasad.

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29. American Chemical Society National Meeting, Symposium on Polymeric Thin Films for Photonic Applications, Washington, DC, August 21, 1994: *Development and Characterization of Polymeric Composites for Photorefractivity.*

30. American Chemical Society National Meeting, Symposium on Computation and Theoretical Modeling of Photonics Materials, August 21, 1994: *Nonlinear Optical Processes.*

31. Akron Polymer Lecture Group, Akron, Ohio, October 7, 1994: *Polymers as Multi-Role Materials for Photonics.*

32. BMDO Technology Applications Review, Lakewood, Colorado, October 20, 1994: *Organic Composite Photorefractive Materials and Kerr Liquid-Filled Hollow-Fiber Broadband Emission Device*s.

33. Central Glass and Ceramic Institute, Calcutta, India, November 23, 1994: *Sol-Gel Processed Organic:Inorganic Composites for Photonics.*

34. Third International Conference on Frontiers of Polymers and Advanced Materials, Kuala Lumpur, Malaysia. January 17, 1995: *Polymers as Multi-Role Materials for Photonics Technology.*

35. University of Arizona, Optical Sciences Center, Colloquium, March 9, 1995: *Polymers and Composites for Nonlinear Optics and Photonics.*

36. AFOSR ORMOSIL Program Review, Los Angeles, California, April 7, 1995: *Sol-Gel Processed Multifunctional Composites for Photonics.*

37. Korea University, Department of Chemistry, Seoul, Korea, May 8, 1995: *Multifunctional Polymers for Nonlinear Optics and Photonics.*

38. Molecular Electronic Symposium, Taejon, Korea, May 9, 1995: *Polymers as Multirole Materials for Photonics Technology.*

39. Lucky Limited Company, Taejon, Korea, May 9, 1995: *Sol-Gel Processed Multiphase Nanostructured Composites for Photonics.*

40. Korea Advanced Institute of Science and Technology (KAIST), Chemical Engineering Department, Taejon, Korea, May 10, 1995: *Multifunctional Polymers for Nonlinear Optics and Polymers.*

41. ETRI, Taejon, Korea, May 11, 1995: *Polymers as Multifunctional Materials for Photonics Technology.*

42. Han Nam University, Department of Macromolecular Science, Taejon, Korea, May 11, 1995: *Multifunctional Polymers for Nonlinear Optics and Photonics.*

43. Kulon Group Central Research Institute, Siuwon, Korea, May 12, 1995: *Polymers as Multirole Materials for Photonics Technology.*

44. Korea Institute of Science and Technology (KIST), Seoul, Korea, May 12, 1995: *Multifunctional Polymers for Nonlinear Optics and Photonics.*

45. Industrial Technology Research Institute (ITRI), Optoelectronics and Systems Laboratory, Hsinchu, Taiwan, May 15, 1995: *Polymer Composites as Multirole Materials for Photonics Technology.*

46. Industrial Technology Research Institute (ITRI), Union Chemical Laboratories, Hsinchu, Taiwan, May 16, 1995: *Multifunctional Polymers for Nonlinear Optics and Photonics.*

47. Shanghai Institute of Optics and Fine Mechanics, Jadine, Shanghai, China, May 19, 1995: *Polymer Lasers, Amplifiers and Optical Power Limiters.*

48. Southeast University, Department of Electrical Engineering, Nanjing, China, May 25, 1995: *Optical Data Storage and Photorefractivity in Polymers.*

49. Instituto di Fotochimica eRadiazioni, di Acta Energia, CNR, Bologna, Italy, June 15, 1995: *Optical Data Storage and Photochemistry in Polymers.*

50. NATO Advanced Study Institute on Spectroscopy and dynamics of Collective Excitons in Solids, Erice, Italy, June 23, 1995: *Three Lectures on Nonlinear Optical Techniques for Excitation Dynamics in Organic Solids, Fullerenes and Polymers.*

51. NATO Advanced Research Workshop on Photoactive Organic Materials, Science and Applications, Aviynon, France, June 26, 1995: *Dynamics of Third-Order Nonlinear Optical Effects in Organic Structures.*

52. DOD Photorefractive Workshop, Dayton, Ohio, August 16, 1995: *High Performance and Stable Photorefractive Polymers with Broad Optical Transparency.*

53. IV International Conference on Advanced Materials, Cancun, Mexico, August 29, 1995: *Multifunctional Polymers and Composites for Photonics.*

54. Materials Research Society Fall Meeting, Symposium on Electrical, Optical, and Magnetic Properties of Organic Solid State Materials III, Boston, Massachusetts, November 29, 1995: *Multiphasic Nanostructured Composites for Photonics.*

55. Fourth Pacific Polymer Conference, Symposium on Polymers for Advanced Optical Applications, Kauai, Hawaii, December 13, 1995: *Novel Polymeric Composites for Photonics.*

56. Fourth Pacific Polymer Conference, Symposium on Multifunctional and Smart Materials, Kauai, Hawaii, December 16, 1995: *Multifunctional Polymers and Composites for Photonics.*

57. Air Force Nonlinear Optical Polymers Contractors Review Meeting, Dayton, Ohio, February 27, 1996: *Two Lectures on*
    1. *Progress in Thermally and Temporally Stable Electro-Optic Polymers with Wide Optical Transparency.*
    2. *Resonant $\chi^{(3)}$ Processes – Two Photon Lasing and Optical Power Limiting.*

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