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**Title of Project**: Nonlinear Organic Materials for Optical Devices

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## Background:

Although polymers have been under development for nonlinear optics applications for about two decades, it is only in the last 5-7 years that serious efforts have been made towards device applications. Their unique properties in terms of electron conjugation and efficient charge transfer have led to very large nonlinearities. However, the challenges to using these materials are very different from the more standard nonlinear materials, for example semiconductors, and these challenges have to be overcome before organics will truly be used in devices. This research program dealt with supplying some of the necessary knowledge base and developing new device concepts, for both second and third order nonlinear optics in polymers.

Second Order NLO

The primary thrust into polymer nonlinear optics over the last few years has been into second order nonlinearities, especially for electro-optics applications. Progress has been very impressive indeed and issues of long term stability due to thermal and photoinduced degradation have been in the forefront. Although high temperature polymer matrices and chromophores have been successfully developed, problems due to multiphoton absorption and photobleaching had not been addressed prior to this program.

Second order nonlinearities can also be used for frequency conversion processes such as second harmonic generation. However, in polymers the trade-off between nonlinearity and loss (via the location of $\lambda_{max}$) are unfavorable for the efficient generation of blue light in standard geometries. There are, however, novel geometries previously explored in semiconductors and ferroelectrics which could circumvent this problem and they have been investigated here in polymers. Furthermore, it is generally believed that second order nonlinear interactions are not useful for signal processing because they involve a frequency-shifted output signal. Here we showed that there are niche applications of second order NLO to operations such as wavelength demultiplexing which can be implemented in poled polymers.

Third Order NLO

This field has been dominated for many years by the development of new molecules and the measurement of their molecular hyperpolarizabilities, aimed at a better understanding of structure-property relations. However, device applications require solid state materials which satisfy well-defined device figures of merit. This program has addressed solid state materials instead of individual molecules, device figures of merit and the application of polymers to NLO phenomena and devices.

To date the test of prevailing theories of nonlinearities in conjugate polymers has been limited to scaling relations or to a few isolated nonlinear optical measurements. During this program some of the first spectroscopic investigations of third harmonic generation (THG), and later non-degenerate three wave mixing (NDTWM) were carried out and two prevailing theories tested.

From previous work on nonlinearities in semiconductors it has been known that two photon absorption is one of the most important factors which limits device operation, especially in waveguides. This question was addressed here for the first time in organics. Detailed measurements did establish spectral windows in which very large nonlinearities exist with minimal multiphoton absorption. In fact, an ideal material was found for operation in the communications windows.

## Executive Summary of Achievements: Third Order Effects

1. Physics and Nonlinear Characterization of Poly-4BCMU

Two models for the nonlinearities in conjugated polymers have been stringently tested by measuring $\chi^{(3)}$ in three independent series of experiments with different frequency inputs over broad spectral ranges. Third harmonic generation (THG) and non-degenerate three wave mixing (NDTWM) techniques were used. It was concluded that neither the essential states nor anharmonic oscillator model fully explains all of the thin film poly4-BCMU data. This indicates that molecular models are not appropriate for describing solid state nonlinearities (required for devices) and effects like local fields, intramolecular interactions etc. need to be explicitly included.

Multiphoton absorption has been found to be very important, dominant in the near infrared with 65 psec and 3 psec pulses. Only with femtosecond pulses (200) have we resolved the true two photon coefficients. For longer pulses, excited states effects dominate multiphoton absorption. We have concluded that poly4-BCMU is not a useful material for applications, partly because of the excited state effects, and most importantly because of its degradation with time.

2. Spectroscopic Investigation of DANS Molecules

The electronic states responsible for the third order nonlinearities in the classic charge transfer molecule DANS (in a side-chain polymer) were investigated using THG and NDTWM. There were puzzling features in the spectra, for example a shift of the $3\omega$-resonance to wavelengths longer than $\lambda_{max}$, the peak of the one photon absorption spectrum. This has now been explained as due to transitions between vibrational sub-levels (in collaboration with Jean-Luc Bredas). We conclude that the origin of the nonlinearities in this class of molecules, when included as side-chains to a polymer backbone, are reasonably well understood. However, they are not large enough for practical devices operating at reasonable power levels.

3. Spectroscopic Investigation of Miscellaneous Polymers

The physics of the nonlinearity in a number of polymers and polyenes have been studied with nonlinear spectroscopy. The linear conjugated polymer polythiophene was investigated with multiple nonlinear spectroscopic techniques, namely THG and NDFWM. For polythiophene we again found that neither of the prevailing models could adequately explain all of the spectra. This reinforces the conclusions drawn from the poly4-BCMU work about the inadequacy of existing models. Finally, the magnitudes of the nonlinearities are not large enough for devices.

4. Wavelength Dispersion of the Complex Nonlinear Refractive Index in PTS

The two-photon absorption coefficient $\alpha_2$ ($\Delta\alpha = \alpha_2 I$, I≡intensity) and the intensity dependent refractive index $n_2$ ($\Delta n = n_2 I$) of the prototype conjugated polymer PTS has been measured over the ranges 750 to 1600 nm, and 1060 to 1600 nm respectively. This allowed all of the important two-photon states to be identified and the two-photon figure of merit to be evaluated for the first time in an organic material. Two spectral regions, coinciding with the two communications windows at 1300 and 1550 nm, were found in which this material is useful for all-optical devices. Furthermore, at 1330 nm the material was found to have minimal thermo-optic nonlinearities. The non-resonant value for the nonlinear refractive index coefficient is the largest known for any material. We judge that this material is ideal for nonlinear optical devices operating at sub-watt power levels.

5. Dark Spatial Solitons for Optical Interconnects

Thermal nonlinearities in DANS molecules in solution have been used to demonstrate new dark soliton phenomena such as the generation of periodic soliton arrays, the guiding of light beams in them and their all-optical scanning in space.

6. Prototype Guided Wave Devices

We tested organic materials in prototype device configurations in order to determine material limitations. We studied DANS in distributed feedback gratings and directional couplers at 1550 nm. Thermal nonlinearities were dominant, reinforcing our previous conclusion that this class of materials is not suitable for all-optical applications.

## Executive Summary of Research Achievements: Second Order Effects

7. Counterpropagating SHG

Considerable progress has been made in the application of poled polymers to this process. In-plane poling of the DANS side-chain polymer has reached record levels with fields up to 370 V/μm before breakdown. This clearly reduces the maximum activity needed for molecules in second-order, for example electro-optic, devices. Strong second harmonic generation has been shown to radiate normal to the waveguide surface when counterpropagating beams are inputted. The performance of multilayer GaAs-based devices has already been surpassed. This process has considerable promise for efficient doubling into the blue part of the spectrum. Furthermore, we project efficient WDM demultiplexing operation, ultimately at 10-100 mW power levels.

8. Two-Photon Absorption and Photobleaching in DANS

The two-photon absorption spectrum of the side-chain polymer DANS used in AKZO's electro-optical devices was measured. The peak value of 5 cm/GW occurs at 930 nm and there

is no measurable (< 0.2 cm/GW) multiphoton absorption at 1300 and 1500 nm where e-o device operation is desirable. Degradation in the refractive index due to multiphoton photobleaching was measured and projected to limit the lifetime of devices operated at wavelengths near the peak in $\alpha_2$ to less than one year. This has serious repercussions to future electro-optic devices relying on larger $\lambda_{max}$ than DANS when operated at 1300 nm.

## Detailed Research Achievements:

1. Physics and Nonlinear Characterization of Poly-4BCMU

Poly4-BCMU is a classic example of a linear conjugated polymer which can be made into high optical quality films. The origins of its nonlinearity are generic to linear conjugated polymers. How the physics of the nonlinearity determines the details of the third order nonlinearity $\chi^{(3)}$ depends on the particular nonlinear interaction process used to measure it. For example the frequency dispersion for THG (third harmonic generation) of $\chi^{(3)}(3\omega;\omega,\omega,\omega)$ is different from that of $\chi^{(3)}(\omega;\omega,-\omega,\omega)$, and from that for NDTWM (non-degenerate three wave mixing) of $\chi^{(3)}(2\omega_2-\omega_1;\omega_2,\omega_2,-\omega_1)$ etc. However, the underlying physics is the same and if one has the correct model, then one should be able to predict all of these spectra from one consistent set of parameters. This was our goal.

We have made three separate series of measurements of the spectral dispersion of different $\chi^{(3)}$s as a test of the physics of the nonlinearities of conjugated polymers. Specifically we measured the magnitude and phase for THG and NDTWM (with two different fixed values of $\lambda_1$, 1.06 μm and 1.92 μm). We then tried to fit all three spectra simultaneously to a single theory.

We were able to fit one, rarely two spectra with a single set of parameters using
(a) either the essential states model with four states, a $1A_G$ ground state, two one-photon states $1B_U$ and $nB_U$, and one two-photon state $mA_G$
(b), or the anharmoic oscillator model.
The gross features of the spectra were in reasonable agreement with theory, the details were not. This indicates that these molecular based theories are not sufficient to treat the solid state case. Obviously missing are important details associated with "dense" media such as local field effects, intramolecular interactions etc.

Multiphoton absorption presents a serious limitation to using the third order nonlinearity of any material such as poly4-BCMU for all-optical devices. Two-photon absorption, proportional to Imaginary$\{\chi^{(3)}(\omega)\}$, limits the effective length of a sample at high intensities. Furthermore, excited state absorption can increase the effective absorption coefficient with time for continuous pulse trains, reaching much larger values than those produced by two-photon absorption. Therefore locating and measuring the strength of two-photon absorption and the corresponding states involved in the two-photon transition is very important.

We measured using Z-scan the multiphoton absorption spectrum using
(a) 65 picosecond pulses from an OPG at Dupont
(b) 4 and 0.2 psec pulses from a Ti:sapphire laser operating either cw mode-locked or with single pulses.
For all of the experiments, data was taken as a function of pulse energy in order to probe the presence of higher order nonlinear effects. The TPA coefficient could only be measured accurately with femtosecond pulses in the near infrared and these experiments are expected to be completed in Fall 1994. For the 4 psec pulses, the extrapolation to zero intensity also gave

the true two-photon coefficient, and the energy dependent component can be either due to a higher order nonlinearity ($\chi^{(5)}$), or to excited absorption.

Strong excited state absorption was found at 900 nm. The picture which emerges for the observed multiphoton absorption is two-photon excitation to a two-photon state in the singlet spectrum, energy crossing to an excited state in the triplet spectrum, and then resonant linear absorption to an excited state in the triplet manifold.

2. Spectroscopic Investigation of DANS Molecules

DANS is a classical example of a charge transfer molecule with donors and acceptors engineered to have large molecular second order nonlinearity. There is some degree of electron delocalization and a large change in the dipole moment between the ground and excited states. Therefore a large nonlinearity was expected.

THG and NDTWM broad spectral scans have been done on DANS. It was clear at the outset that a simple two-level model would not suffice. For example, the principal THG peak was red-shifted to longer wavelengths than $\lambda_{max}$. This fact has now been explained as due to the excited states electronic displacement induced by strong vibrational modes (in collaboration with J.L. Bredas) The theory is based on an INDO/MRD-CI (Intermediate Neglect of Differential Overlap/Multi-Reference-Determinant-Configuration Interaction) calculation applied to the optimized DANS geometry. Comparison between our experiments and the theory produced excellent agreement. We conclude that the origin of the third order nonlinearity is reasonably well-understood and can be predicted by the above-mentioned quantum molecular calculations.

One of the spectral regions of prime interest for nonlinear materials is 1.3 μm because it is useful for communications. Using a nonlinear Mach-Zehnder interferometer we have measured $n_2$ in DANS channel waveguides to be $n_2 = +0.8\pm0.2\times10^{-13}$ cm$^2$/W for a 35% DANS loading. An upper limit to the two photon coefficient of 0.1 cm/GW was also measured.

Additional nonlinearity measurements by Z-scan were performed at a few other wavelengths. At 1.06 μm we measured $n_2 = -0.9\times10^{-13}$ cm$^2$/W and $\alpha_2 = 4$ cm/GW, in good agreement with our previous measurements at this wavelength using nonlinear grating coupling. At 0.69 μm we found $n_2 = -4.5\times10^{-13}$ cm$^2$/W and $\alpha_2 = 2$ cm/GW. Therefore, ignoring linear loss (which is also an issue), the two photon figure of merit $T = \lambda\alpha_2/n_2$ is 0.3 at 0.69 μm and is 4 at 1.06 μm. $T < 1$ is required for useful device operation. The linear loss at 0.69 μm is still quite high, of the order of 10 cm$^{-1}$ which means that the $W = \Delta n/\alpha\lambda = 1$ for an incident intensity of 1.5 GW/cm$^2$. ($W > 1$ is needed.) We estimate that DANS may be useful at both 0.69 μm and 1.32 μm from a figure of merit point of view. However, the nonlinearities are still too small.

3. Spectroscopic Investigation of Miscellaneous Polymers

We investigated polythiophene with multiple nonlinear spectroscopic techniques. It is also a classic example of a nonlinear conjugated polymer, just like poly4-BCMU. Again, THG and NDTWM (with two fixed wavelengths) were used. To date only Mazumdar's four level essential states model was available for fitting to the data. In general, the fits to all of the spectra were better than for poly4-BCMU, but still not satisfactory. These results reinforce our conclusions drawn from the poly4-BCMU experiments, i.e. that the models need to improved to better take into account molecular interactions which take place in the solid state.

Working with Seth Marder of CalTech, we have been exploring what happens to a linear conjugated polyene when a side group with a small dipole moment is added to break the reflection symmetry about the molecule's center, i.e. the linear conjugation is perturbed. We had previously measured the THG spectrum of β-carotene. THG results on apo-carotenal show that

the nonlinearity (THG style) is increased in this material relative to β-carotene. Measurements on materials with increasing donor or acceptor strength are planned to quantify this effect. This could be a route to increasing third order nonlinearities.

4. Wavelength Dispersion of the Complex Nonlinear Refractive Index in PTS

Since large nonlinearities were first reported in single crystal PTS by Chance and coworkers in 1976, it has been the prototype nonlinear conjugated polymer with the largest documented nonlinearity. However, it is not known if two-photon states will limit the actual application of this material. The key parameter is the ratio of $T = \alpha_2\lambda/n_2$, the two-photon figure of merit, which must be less than unity for efficient all-optical device applications. We have measured the multiphoton absorption spectrum of PTS with 65 psec pulses between 750 and 1600 nm using Z-scan techniques, and the corresponding $n_2$ from 1060 to 1600 nm.

There are four distinct two photon peaks, implying two two-photon states above the energy of the excitonic $1B_u$ state and two in the gap below. No existing theory has predicted this number of states. Experiments have now been repeated in the 700-970 nm region with 3 and 0.2 psec pulses showing an instantaneous response. The existence of two two-photon states in the gap indicates very strong electron correlation effects. One possible explanation for some of the features observed is that some of the peaks are due to transitions between vibrational sub-levels in the ground and excited states.

We also measured higher order nonlinear effects over almost the complete wavelength range studied. Detailed studies in the 700-970 nm region could be interpreted as due to saturation of the two photon states, followed by a rapid transition to the $1B_u$ state (one exciton state) and then subsequent absorption of another photon from the input beam.

We also measured the wavelength variation in $n_2$. Noteworthy is that dispersion occurs near each two-photon absorption peak. At 1600 nm no measurable two-photon absorption occurs and $n_2 = 2.2\ (\pm 0.3)\ cm^2/W$, the non-resonant value for PTS. This is the largest non-resonant nonlinearity measured in any material. Also, the two photon figure of merit T is less than unity there. The key result is that there are two spectral windows, one on each side of the 1500 nm two-photon peak, where the two-photon figure of merit is very attractive. This material looks like the best bet for organic all-optical devices.

5. Dark Spatial Solitons for Optical Interconnects

Research into dark spatial solitons was performed because one of our visitors expressed an interest in such an investigation based on organic materials. Needed is a self-defocussing nonlinear medium ($n_2<0$) and a plane wave field with an intensity minimum which has a $\pi$ phase shift across it. Over a small range of input powers, nonlinear refraction and diffraction are balanced and the intensity minimum propagates without change. Because $n_2$ is negative, the intensity minimum region has a higher index than the illuminated region and acts like an optical waveguide for another beam. Since the direction of propagation (angle) can be controlled externally, dark spatial solitons can be used as dynamic interconnects.

We have discovered how to generate ideal arrays of dark spatial solitons, guide signal beams in them and steer them all-optically in space. Two plane waves are incident on a nonlinear medium create an interference pattern which can evolve into a periodic array of dark spatial solitons. Adiabatic amplification of the signal is necessary for stable soliton generation, for example by gently focussing the beam in one dimension. This effect has been demonstrated using the negative nonlinearity of DANS molecules in solution at 5145 nm.

These periodic arrays produce a higher refractive index in their dark zone. We have

demonstrated that signals (He-Ne laser) can be guided without diffraction in these induced waveguides. Furthermore, by varying the relative power of the two input interfering beams, "grey" solitons (non-zero intensity minima) are generated which can also guide signal beams (also demonstrated experimentally). Furthermore, changing the relative powers of the input plane waves leads to scanning (changing) the propagation direction in space (also observed) of both the spatial solitons and beams guided in them.

Although new soliton phenomena were discovered, it is clear that bright, not dark, solitons are most useful for optical interconnects. In fact, PTS is the ideal material in which to implement such dynamic interconnects.

6. Prototype Guided Wave Devices

We tested organic materials in prototype device configurations in order to uncover and understand the limitations inherent to this material system. We studied DANS in distributed feedback gratings and directional couplers.

The directional coupler consists of two parallel channel waveguides, spaced closely enough so that power oscillates back and forth between the channels with propagation distance. In the nonlinear version, a high field inputted into one of the channels stops this power transfer. We verified that at low powers the output power emerged through the adjacent (non-incident) channel at 1.3 μm. As the power is increased we did observe some growth in the incidence channel and depletion from the adjacent channel with increasing power. However, we destroyed the entrance face of the waveguide at high powers with the 80 psec pulses used.

A distributed feedback grating device was fabricated for operation at 1555 nm. Using a cw mode-locked color center laser with 6 psec pulses we measured the throughput as a function of input power. The transmission increased with increasing input power as the Bragg condition was detuned by an optically induced change in refractive index. However, when the laser repetition rate was reduced from 76 MHz to 0.3 MHz using a $LiTaO_3$ modulator, no switching was observed at the same peak power level. Clearly the nonlinear response observed was thermal.

7. Counterpropagating SHG

A new idea was investigated for ultrafast demultiplexing of optical signals based on second order nonlinearities. It utilizes the mixing of two contra-propagating guided waves in a $\chi^{(2)}$-active optical waveguide. The direction into which the sum frequency mixing signal is generated out of the waveguide depends on the wavelength difference between the two signals. Therefore, different wavelengths in an input data stream can be separated out. The key technological problem which we faced is the fabrication of appropriately poled channel waveguides.

In-plane poling was used to achieve large in-plane second order coefficients in DANS. A series of technological improvements led to record poling fields of 370 V/μm before material breakdown. At 300 V/μm, a nonlinearity of 150 pm/V was measured. Since the peak absorption in DANS occurs at 430 nm, this value is somewhat resonantly enhanced. However, because the SHG signal traverses only the film thickness, the additional linear losses normally associated with resonance enhancement in second harmonic generation are not important here.

The second harmonic signal radiated normal to the surface was measured for samples with poling fields up to 200V/μm. The radiation was highly directional, as expected. Extrapolating this result to the highest poling voltages achieved, for 100 mW input we should obtain 100 μW outputs, more than sufficient for the purpose of demultiplexing. With various

material and film geometry improvements, it appears that we can improve on the output signal to 10 mW for operation at 1550 nm! This signal can also be used for efficient generation of blue light.

8. Two-Photon Absorption and Photobleaching in DANS

Trans-cis isomerization is known to occur in many charge-transfer molecules used in electro-optic applications. It results in a drastic reduction in the nonlinearity as well as a change in the refractive index. It occurs when the state corresponding to the main absorption peak is excited either by one or multiphoton absorption processes. Although operation at wavelengths > 600 nm excludes one photon excitation in DANS, two- photon excitation leading to photobleaching is possible, depending on the location and strength of the two-photon states.

The two-photon absorption coefficient was measured for DANS side-chain polymer with both 65 and 4 psec pulses. No excited state absorption was found, i.e. the induced absorption scaled linearly with input intensity. It is noteworthy that the peaks of the one and two-photon spectra did not coincide. Since there is no inherent symmetry to the DANS molecule one would expect no distinct one or two-photon states, just mixed states with both one and two-photon character. Recent calculations by Bredas' group has identified this shift to be due to transitions involving different vibrational sub-levels in the ground and excited states.

We also measured the induced multiphoton photobleaching. By monitoring the coupling angle for grating coupling into thin film DANS waveguides, the index change induced was measured. Extrapolating the results to continuous operation at the milliwatt level, we estimate 7 month device lifetimes at the peak of the two photon absorption curve, i.e. for $\alpha_2 = 5$ cm/GW. This is clearly not an issue for DANS-based devices at 1300 nm. However, some of the new, high temperature chromophores have $\lambda_{max}$'es of 600 nm and longer which will result in some two photon absorption and photobleaching at 1300 nm. This effect needs to be studied carefully in such molecules.

**Publications**:

(a) Papers


1. G.I. Stegeman, "Waveguiding and waveguide applications of nonlinear organics" in Materials for Nonlinear Optics, ACS tutorial series #455, edited by S.R. Marder, J.E. Sohn and G.D. Stuckey, (American Chemical Society, Washington, 1991) pp113-127
2. W.E. Torruellas, K.B. Rochford, R. Zanoni and G.I. Stegeman, "The cubic susceptibility dispersion of poly-4BCMU thin films: third harmonic generation and two photon absorption measurements", Opt. Comm., 82:94-100 (1991).
3. W.E. Torruellas, R. Zanoni, M.B. Marques, G.I. Stegeman, G.R. Mohlmann, E.W.P. Erdhuisen and W.G.H. Horsthuis, "The cubic susceptibility dispersion of MONS and DANS side chain substituted polymers: comparison with the two level model", J. Chem. Phys., 94:6851-6 (1991).
4. M.B. Marques, G. Assanto, G.I. Stegeman, G.R. Mohlmann, E.W.P. Erdhuisen and W.H.G. Horsthuis, "Intensity dependent refractive index of novel polymer materials: measurements by nonlinear grating coupling", Appl. Phys. Lett., 58:2613-5 (1991)
5. G.I. Stegeman, "Nonlinear Optical Devices: Current Status of Organics", Proceedings of Organic Materials for Nonlinear Optics II, edited by R.A. Hann and D. Bloor, (Royal Soc. Chemistry, London, 1991) pp 311-23
6. S. Aramaki, W. Torruellas, R. Zanoni and G.I. Stegeman, "Tunable third harmonic generation of trans-β-carotene", Opt. Comm., 85:527-35 (1991).
7. G.I. Stegeman, W. Torruellas, K.B. Rochford, R. Zanoni, W. Krug, E. Miao and M.W. Beranek, "Material requirements for all-optical devices: Nonlinear properties of poly-4BCMU", in Materials for Optical Information Processing, edited by C. Warde, J. Stamatoff and W.I. Wang, Proceedings of the 1991 MRS Spring Meeting, 228:3-15 (1991)
8. G.I. Stegeman, "Nonlinear Optical Devices: Relative Status of Polymeric Materials", in Materials for Optical Information Processing, edited by C. Warde, J. Stamatoff and W.I. Wang, Proceedings of the 1991 MRS Spring Meeting, **228**:27-39 (1991)
9. G.I. Stegeman, "Material requirements for nonlinear third order phenomena in waveguides", Proceedings of Toyota Conference in Nonlinear Optics, edited by S. Miyata, (North Holland, Amsterdam, 1992), pp 337-53
10. G.I. Stegeman, " Nonlinear Optical Devices: Relative Status of Polymeric Materials", Frontiers of Polymer Research, edited by P.N. Prasad and J.K. Nigam, (Plenum Press, New York, 1991), pp63-70
11. D. Guo, S. Mazumdar, G.I. Stegeman, M. Cha, D. Neher, S. Aramaki, W. Torruellas and R. Zanoni, "Nonlinear optics of conjugated polymers", Proceedings of the Fall 1991 MRS Meeting on Electrical, Optical and Magnetic Properties of Organic Solid State Materials, Vol. 247 edited by L.Y. Chiang, A.F. Garito and D.J. Sandman, pp151-162
12. T.-M. Lee, S. Mittler-Neher, D. Neher, G.I. Stegeman, C. Roux and M. Leclerc, "Side-chain dilution effects on the optical properties of pol[3-alkylthiophene]s", Optical Materials, 1:65-70 (1992)

13. K.B. Rochford, R. Zanoni, G.I. Stegeman, W. Krug, E. Miao and M.W. Beranek, "Pulse-Modulated Interferometer for Measuring Intensity-Dependent Phase Shifts", IEEE J. Quant. Electron., 28:2044-2050 (1992)
14. G. Assanto, D. Neher, G.I. Stegeman, W.E. Torruellas, M.B. Marques, W.H.G. Horsthuis and G.R. Mohlmann, "The enhancement of third-order nonlinearities in organic polymers via microscopic cascading of second-order hyperpolarizabilities", Proceedings of 14'th International Conference on Liquid Crystals and Organics, Mol. Cryst. Liq. Cryst., 222:33-43 (1992)
15. D. Neher, W.E. Torruellas, K.B. Rochford, G. Assanto, R. Zanoni and G.I. Stegeman, "Nonlinear optical probes of conjugated polymers", Synthetic Metals, 49:21-35 (1992)
16. S. Aramaki, G. Assanto, G.I. Stegeman, W.H.G. Horsthuis and G.R. Mohlmann, "Integrated Bragg reflectors in polymeric channel waveguides", Opt. Comm., 94:326-30 (1992)
17. S. Mittler-Neher, A. Otomo, G.I. Stegeman, C.Y.-C. Lee, R. Mehta, A.K. Agrawal and S.A. Jenekhe, "Waveguiding in substrate supported and freestanding films of insoluble conjugated polymers", Appl. Phys. Lett., 62:115-7 (1993)
18. A. Otomo, S. Mittler-Neher, G.I. Stegeman, W.G. Horsthuis and G.R. Mohlmann, "Adiabatic Focusing Structures in Low Loss DANS Polymer Waveguides", Electron. Lett., 29:129-30 (1993).
19. M. Cha, D. Neher, F.W. Embs, S. Mittler-Neher and G.I. Stegeman, "Determination of the two first non-trivial orientational order parameters in LB films of rod-like molecules by third order sum frequency mixing", Chem. Phys. Lett., 202:44-50 (1993).
20. A. Aramaki, G. Assanto, G.I. Stegeman and M. Marciniak, "Realization of integrated Bragg reflectors in DANS-polymer waveguides", J. Lightwave Techn., 11:1189-1195 (1993).
21. A. Otomo, S. Mittler-Neher, C. Bosshard, G.I. Stegeman, W.H.G. Horsthuis and G.R. Mohlmann, "Second harmonic generation by counter propagating beams in DANS side chain polymer channel waveguides", Appl. Phys. Lett., 63:3405-7 (1993).
22. M. Cha, W. Torruellas, G.I. Stegeman, H.X. Wang, A. Takahashi and S. Mukamel, "Spectroscopic Investigation of the Nonlinear Optical Response of Poly(4BCMU)", Chem. Phys. Lett., in press
23. G. I. Stegeman, A. Otomo, C. Bosshard and R. Flipse, "Recent progress in nonlinear optical photonic devices made from organic materials", Proceedings of 2nd International Conference on Frontiers of Polymers and Advanced Materials, P. Prasad ed., (Plenum, NY, 1993), in press
24. Ch. Bosshard, P.V. Mamyshev and G.I. Stegeman, "All-optical steering of dark spatial soliton arrays and the beams guided by them", Opt. Lett., 19:90-2 (1994).
25. S. Mittler-Neher, D. Neher, G.I. Stegeman, F.W. Embs and G. Wegner, "Polarization dependent resonant THG on Langmuir-Blodgett multilayers of rod like polysilanes during annealing", J. Chem. Phys., 161:289-97 (1992).
26. D.Y. Kim, M. Sundheimer, A. Otomo, G.I. Stegeman, W.G.H. Horsthuis and G.R. Mohlmann, "Third order nonlinearity of DANS waveguides at 1319 nm", Appl. Phys. Lett., 63:290-2 (1993).
27. Ch. Bosshard, A. Otomo, G.I. Stegeman, M. Kupfer, M. Florsheimer and P.

Gunter, "Surface emitted green light generated in Langmuir-Blodgett film waveguides", Appl. Phys. Let., 64:2076-8 (1994).

28. B. Lawrence, M. Cha, J.U. Kang, W. Torruellas, G.I. Stegeman, G. Baker, J. Meth and S. Etemad, "Large Purely Refractive Nonlinear Index of Single Crystal P-Toluene Sulfonate (PTS) at 1600 nm", Electron. Lett., 30:447-8 (1994).
29. A. Otomo, G.I. Stegeman, C. Bosshard, S. Mittler-Neher, W.H.G. Horsthuis and G.R. Mohlmann, "Fabrication of Poled Polymer DANS Waveguides and First Observation of SHG by Counter-Propagating Guided Waves", Proceedings of MRS Symposium on Electrical, Optical, and Magnetic Properties of Organic solid State Materials, edited by A. F. Garito, A. K-Y. Jen, L.R. Dalton and C. Lee, Vol. 328, 631-6 (1993).
30. G.I. Stegeman and W. Torruellas, "Issues in Organic Materials for Nonlinear Optics", Proceedings of MRS Symposium on Electrical, Optical, and Magnetic Properties of Organic solid State Materials, edited by A. F. Garito, A. K-Y. Jen, L.R. Dalton and C. Lee, Vol. 328, 397-412 (1993).
31. B.L. Lawrence, M. Cha, W.E. Torruellas, G.I. Stegeman, S. Etemad and G. Baker, "Measurement of the nonlinear refractive idnex and two photon absorption coefficient of PTS at 1064 nm", Appl. Phys. Lett., 64:2773-5 (1994).
32. P.V. Mamyshev, C. Bosshard and G.I. Stegeman, "Generation of a periodic array of dark spatial solitons in the regime of effective amplification", JOSA B, 11:1254-60 (1994).
33. D. Guo, S. Mazumdar, D. Neher, G.I. Stegeman and W. Torruellas, "A new essential state model for the nonlinear optical response of 1D conjugated organic systems", in Organic Materials for Nonlinear Optics III, edited by G.J. Ashwell and D. Bloor, (The Royal Society of Chemistry, Serial Publication No. 136, 1993), pp. 13-18.
34. B. Lawrence, W. Torruellas, M. Cha, G.I. Stegeman, J. Meth, S. Etemad and G. Baker, "Identification and Role of Two Photon Absorption in the $\pi$-Conjugated Polymer Paratoluene-Sulfonate", Phys. Rev. Lett, 73:597-600 (1994).
35. M. Cha, D. Neher, F.W. Embs, S. Mittler-Neher, G.I. Stegeman, "Determination of the orientational order parameter in polysilane LB-films by measuring third order susceptibility tensor components", SPIE Proceedings on Nonlinear Optical Properties of Advanced Materials, 1852:151-161 (1993).
36. M. Cha, W. Torruellas, D. Neher, G.I. Stegeman and M. LeClerc, "Measurement of $\chi^{(3)}(-\omega_3; \omega_1, \omega_1, -\omega_2)$ spectra for poly[3-tetradecylthiophene]", SPIE Proceedings on Nonlinear Optical Properties of Advanced Materials, 1852:106-112 (1993).
37. G.I. Stegeman, "Material figures of merit and implications to all-optical switching", SPIE Proceedings on Nonlinear Optical Properties of Advanced Materials, in press
38. A. Otomo, Ch. Bosshard, S. Mittler-Neher, G.I. Stegeman, M. Kupfer, M. Florsheimer, P. Gunter, W.G.H. Horsthuis and G.R. Mohlmann, "Second Harmonic Generation by Counterpropagating Beams in Organic Thin Films", Proceedings of ICONO1, in press
39. B.L. Lawrence, M. Cha, W.E. Torruellas, G.I. Stegeman, S. Etemad and G. Baker, "Z-Scan Measurement of Third and Fifth Order Nonlinearities in Single Crystal PTS at 1064 nm", J. Nonlinear Optics, in press

40. D.Y. Kim, B,L. Lawrence, W.E. Torruellas, G. Baker and J. Meth, "Assessment of Single Crystal PTS as an All-optical Switching Material at 1.3 μm", Appl. Phys. Lett., in press
41. M. Cha, W.E. Torruellas, G.I. Stegeman, W.H.G. Horsthuis, G.R. Mohlmann and J. Meth, "Two Photon Absorption of DANS (Di-alkyl-amino-nitro-stilbene) Side Chain Polymer", Appl. Phys. Lett., submitted
42. G. Vitrant, L. Mayollet, B. Vogele, A. Rameix, R. Reinisch, G.I. Stegeman, G.R. Mohlmann, W.H.G. Horsthuis, P.A. Chollet and F. Kajzar, "Measurements of Large Nonresonant Nonlinearities in Doped Polymers", J. Nonlin. Opt., submitted
43. A. Otomo, G.I. Stegeman, W. Horsthuis and G. Möhlmann, "Second Harmonic Generation By Counter-Directed Guided Waves In Poled Polymer Waveguides", ACS tutorial series, edited by G. Lindsay, (American Chemical Society, Washington, 1994), in press
44. A. Otomo, G.I. Stegeman, W.H.G. Horsthuis and G.R. Mohlmann, "Strong Field, In-Plane Poling for Nonlinear Optical Devices in Highly Nonlinear Side Chain Polymers", Appl. Phys. Lett., submitted
45. M. Cha, W.E. Torruellas, S.H. Yuan and G.I. Stegeman, "Third Order Optical Spectroscopy of Polythiophene", J. Opt. Soc. Am. B, submitted

(b) Conference Presentations (* denotes invited)

1.* "some topic on nonlinear organics", ICONO'2, Japan, July 1995
2.* "Nonlinear Optics in Polymer Waveguides", Erice Summer School on Electroactive Polymers and Their Applications", July 1995
3.* "Nonlinear Optical Materials for Information Processing", Royal Society Meeting on "Nonlinear Optics for Information Processing", London, March 1995
4.* "A Novel Geometry for Second Harmonic Generation in Poled Polymers", Third International Conference on Frontiers in Polymers and Advanced Materials, Kuola Lampour (Malasia, January 1995)
5.* "Nonlinear Optics of Conjugated Polymers: Physics and Applications, Fifth Annual Symposium of the NSF Center for Photoinduced Charge Transfer", Rochester, August 1994
6.* "Efficient Second Harmonic Generation by Counterpropagating Input Beams in a Poled Polymer Waveguide", ACS/OSA Meeting, Washington, August 1994
7.* "Second Harmonic Generation in DANS Waveguides", SPIE Meeting, San Diego, July 1994
8.* "Perspectives on Third Order Nonlinear Materials for Devices", MITI Conference on Nonlinear Photonics Materials, Tohoku University Japan, May 1994
9.* "Recent Advances in Non-Resonant Nonlinearities in Organic Materials", Iketani Conference on Optically Nonlinear Organic Materials, Hawaii, May 1994
10.* "Nonlinear Refraction and Absorption in Polydiacetylenes", 2nd Conference on Optical Probes of Conjugated Polymers", Salt Lake City, February 1994
11.* "Spectral Dispersion of the Complex Nonlinear Refractive Index of PTS", International Conference on Organic Nonlinear Optics", Val Thorens France, January 1994
12.* "Nonlinear Spectroscopy in Organic Molecules", SPIE Meeting, Los Angeles,

January 1994

13.* "Issues in Organics for Nonlinear Optics", MRS Fall Meeting, Boston, December 1993

14.* "Nonlinear Polymers for All-Optical Processes", Int. Symposium on Polymers for Microelectronics, Tokyo, (1993)

15.* "Nonlinear Spectroscopy of Thin Organic Films", OSA Topical Meeting on Nonlinear Organic Films, Toronto, October 1993

16.* "Nonlinear Spectroscopic Studies of Polydiacetylenes", SPIE, San Diego, July 1993

17.* "Nonlinear Spectroscopy Of Conjugated Polymers", MRS Spring Meeting, San Francisco, April 1993

18.* "Current Status of Nonlinear Materials and Their Applications to Waveguide Devices", (plenary paper), Integrated Photonics Research, Palm Springs, March 1993

19.* "Linear and Nonlinear Optical Properties of Polymers", American Institute of Chemical Engineering, Miami, November 1992

20.* "Device Considerations for Nonlinear Optical Materials", US-France Workshop on the Chemistry of Optical Materials, Maubuisson France, Sept. 29-Oct. 2, 1992

21.* "Nonlinear Organics: Will they be used for Devices?", Gordon Conference on Transport and Nonlinearities in Organic Materials", New Hampshire, July 26-31, 1992

22.* "Nonlinear Optics of Polymers", INOE 50'th Anniversary Lectures, Mexico, April 1992

23.* "Characterization of Organic Materials for All-Optical Switching Devices", given by Dieter Neher, Workshop on Organic Optoelectronic Materials, Monterey, March 1992

24.* "Nonlinear Organics: Will they be used for Devices?", American Physical Society Spring Meeting, Indianapolis, March, 1992

25.* "Nonlinear Optics of Conjugated Polymers", MRS Meeting, Boston, December 1991

26.* "Overview of Nonlinear Characterization Techniques", Ceramic Society, Washington, October 1991

27.* "Material Requirements for Nonlinear Third Order Phenomena in Waveguides", Toyota Conference on Nonlinear Optics, Nagoya, October 6-9, 1991

28.* "Nonlinear Optics of Polymers", ILS-VII, Monterey, CA, September 1991

29.* "Prospects for Nonlinear Organics in Waveguides", Topical Meeting on Nonlinear Guided Wave Phenomena", Cambridge UK, September 1991

30.* "Nonlinear Optical Probes of Conjugated Polymers", (given by Dieter Neher) Optical Probes of Conjugated Polymers, Salt Lake City, August 1991

32.* "Material Requirements for All-Optical Devices: Nonlinear Properties of Poly4-BCMU", MRS Meeting, Anaheim, April 1991

33.* "Nonlinear Optical Devices: Status of Polymeric Materials", MRS, Anaheim, April 1991

34. "First Demonstration of SHG by Oppositely Propagating Guided waves in DANS Waveguides", Conference on Lasers and Electro-Optics (CLEO), Anaheim, May 1994

35. "Two-Photon Absorption Spectrum of a Side-Chain Polymer", IQEC, Anaheim,

May 1994

36. "Fabrication of Poled Polymer DANS Waveguides and First Observation of SHG by Counter-Propagating Guided Waves", MRS 1993 Fall Meeting, Boston, November 1993
37. "Measurement of the Nonlinear Refractive Index and Two Photon absorption coefficient of PTS at 1064 nm", ACS/OSA, Toronto, Canada, 1993
38. "Measurement of the Two Photon Absorption Spectrum in PTS from 800 to 1600 nm", Quantum Electronics and Laser Science Conference (QELS), Baltimore, May 1993
39. "Third Order Nonlinear Spectra of a Polydiacetylene; the quasi-particle exciton representation", QELS, Baltimore, May 1993
40. M. Cha, G.I. Stegeman, D. Neher, M. LeClerc, G.R. Mohlmann and W.G. Horsthuis, "Determination of two-photon and Raman contribution to the third-order susceptibility of nonlinear polymers", SPIE Symposium on the Nonlinear Properties of Advanced Materials, January 1993
41. W.E. Torruellas, M.L. Sundheimer, M. Cha, G.I. Stegeman, S. Etemad, G.L. Baker, "Search for two-photon states in $\pi$-electron conjugated systems", SPIE Symposium on the Nonlinear Properties of Advanced Materials, January 1993
42. D.Y. Kim and G.I. Stegeman, "Direct nonlinear index measurement in DANS polymer waveguide", Opt. Soc. Am. Annual Meeting, September 1992
43. M.Cha, D.Neher, G.I.Stegeman C.Roux, M.Leclerc, "Two-photon spectroscopy in poly(3-alkylthiophene) thin films by resonant three-wave mixing", OMNO'92, August 1992
44. D.Guo, S.Mazumdar, D.Neher, G.I.Stegeman, W.Torruellas, S.Aramaki, R.Zanoni, "A new essential state model for the nonlinear optical response of 1D conjugated organic systems", OMNO'92, August 1992
45. G.I. Stegeman, D. Neher, W. Torruellas and S. Aramaki, "Role of two photon states in conjugated polymer nonlinearities", IQEC'92, June 1992
46. G. Assanto, D. Neher, G.I. Stegeman, W.E. Torruellas, M.B. Marques, W.H.G. Horsthuis and G.R. Mohlmann, "Third-order nonlinearities in organic polymers and the role of microscopic cascading of second order hyperpolarizabilities", International Conference on Optics of Liquid Crystals, August 1991