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Mark G. Kuzyk

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14. ABSTRACT

We have discovered that photo-isomerization in the simple DR1 molecule can be used for limiting in regions where the material is transparent. We have used this effect for various demonstrations of light control and beam shaping – prerequisites for making optical limiters. We have also developed a theory of what makes the maximum nonlinear response and have applied it to two photon absorption to determine

The accomplishments of our research go well beyond the original scope of the project. In addition to our work in optical limiting fibers, spillover results included making fiber-based light-sources, writing holograms in fibers, and developing the theory of the limits of the nonlinear-optical response, which has direct impact on understanding structure-property relationships in the development of new molecules. Highlights are presented in the technical report. More details can be found in our published papers.

15. SUBJECT TERMS
Polymer, Fiber, Photorefraction, organic, susceptibility, nonlinear optics

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Photorefractive Fibers

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Final Report - 2003

AFOSR Grant No. F49620-00-1-0120

Photorefractive Fibers
Mark G. Kuzyk

2. Objective

To make novel photorefractive polymer fiber devices using new materials and novel phenomena.

3. Status

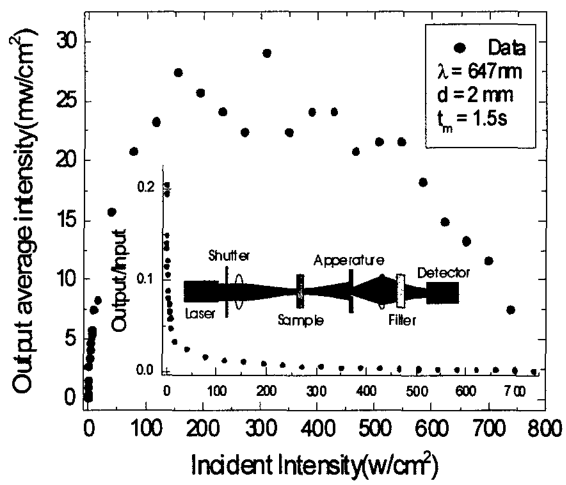
The Nonlinear Optics Laboratory at Washington State University has applied its expertise in polymer processing to making photorefractive fibers that eventually can be bundled to make an optical limiter. In addition to working with other labs to incorporate newly-synthesized materials, we have discovered that photo-isomerization in the simple DR1 molecule can be used for limiting in regions where the material is transparent. We have used this effect for various demonstrations of light control and beam shaping – prerequisites for making optical limiters. We have also developed a theory of what makes the maximum nonlinear response and have applied it to two photon absorption to determine the maximum possible response.

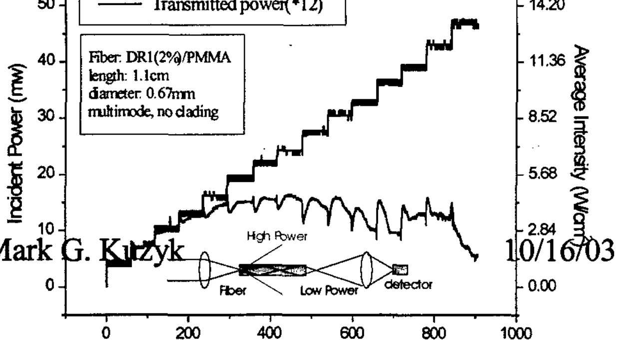
4. Accomplishments

The accomplishments of our research went well beyond the original scope of the project. In addition to our work in optical limiting fibers, spillover results included making fiber-based light-sources, writing holograms in fibers, and developing the theory of the limits of the nonlinear-optical response, which has direct impact on understanding structure-property relationships in the development of new molecules. Highlights of the work are presented below. More details can be found in our published papers.

Our first discovery was that the photo-isomerization process in DR1 can be used for optical limiting in the red. In particular, we showed that gratings formed with two-beam coupling have an 85% diffraction efficiency. This observation has led us to new studies of the cis-trans photo-isomerization process at 632nm to understand the dynamics of refractive index changes.

To test the materials in optical limiting geometries, we have done two intensity-dependent defocusing studies. The inset to the figure on the right shows a limiting apparatus in the planar sample geometry. Intensity-dependent focusing of light by the sample is limited by the aperture. The output level is limited to less than 30mW/cm^2. At higher input intensity, the output intensity falls off even more.





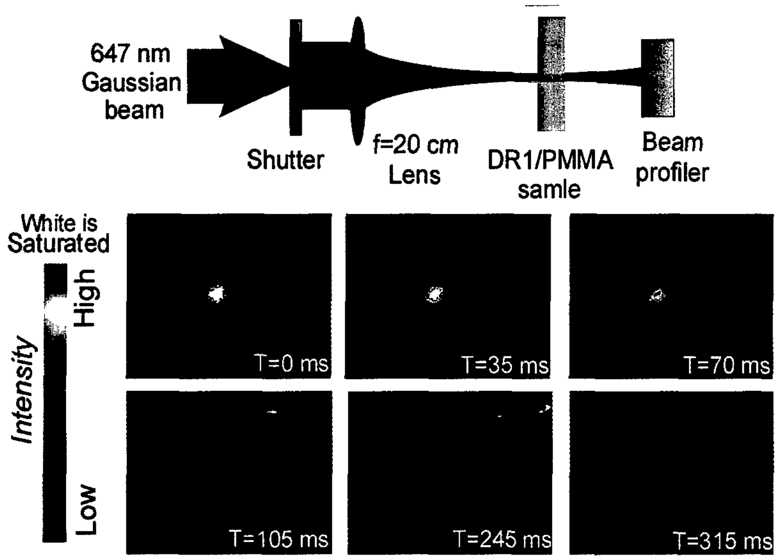
Photorefractive Fibers

Mark G. Kuzyk

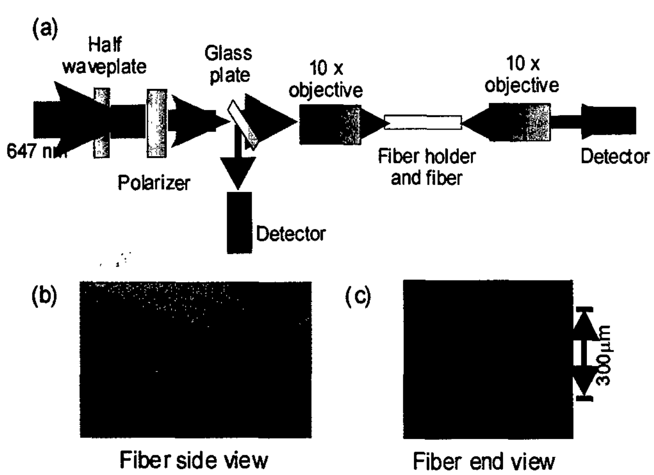
The inset in the figure to the left shows a waveguiding experiment in a polymer optical multimode fiber. The guiding condition in the fiber is analogous to the aperture in the planar experiment. As the light input is ramped up in steps, the output intensity is clearly limited. There is also evidence of interesting new physics in the time profile of the response. When the input intensity is constant immediately after a step, the output intensity dips before reaching the final equilibrium value. These fast dips may be significant in protecting against more intense short pulses. By making fibers with three different chromophores, it may be possible to make arrays of RGB fibers so that full color perception is possible.

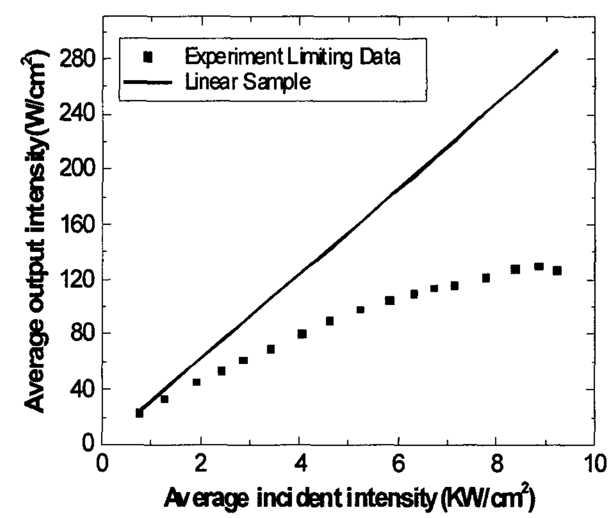
We have been using the photoisomerization mechanisms in azo-dyes to perform a series of optical limiting experiments which includes nonlinear refraction in bulk materials; two-beam coupling and four-wave mixing; and mode cut optical limiting in polymer optical fibers. The photograph below shows the beam profile of transmitted light as a function of time through an azo-dye-doped polymer. The resulting decrease in the refractive index yields beam spreading.

Beam defocusing in DR1/PMMA thick sample



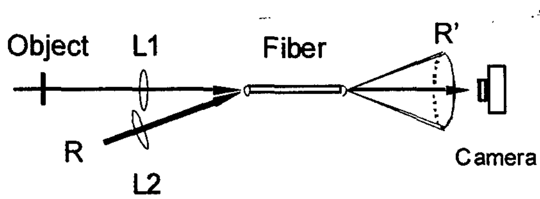
We have used this mechanism to invent the mode-cut optical limiter in a dye-doped polymer fiber, in which the light in a waveguide radiates out of the core as the intensity is increased. The figure below shows the experimental setup and the data. Light is coupled into the core of the optical fiber and the output of the fiber core is imaged onto the detector. Care is taken to paint the cladding of the fiber black so that any light that radiates out of the core does not make it back to the detector. Also displayed is a side view image of the fiber as well as the guided mode leaving the end of the fiber.

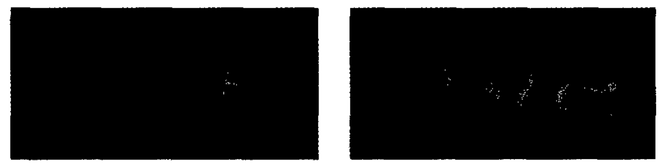




The light leaving the fiber shows the characteristic limiting effect as shown in the right part of the figure. This limiting process is being studied in detail experimentally and models are being developed and tested. These will serve to guide in the design of fiber-bundle-type arrays that will be used for optical limiting of an image.

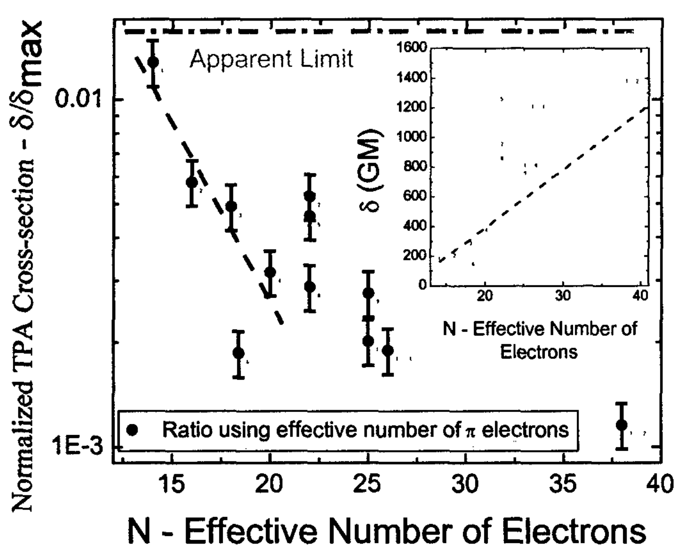
The figure below shown an experiment (left) to write holograms in a polymer optical fiber. Figure (a) shows the object, which is made of a photo-mask, and the recorded image in the fiber as it is read out with the reading beam. The fidelity of the image is very good. In addition to these studies, we have done degenerate four-wave mixing and observed phase conjugation – which can be used to compensate for beam aberration.





(a) (b)

Our most recent work has focused on understanding what make the maximum possible nonlinear optical response; and, we have applied this theory to the two-photon absorption cross-section. The results are shown below, where the measured value of the two-photon absorption cross-section is normalized to the maximum possible value. Note that all the measured values fall well below this level. In fact, most measurements are a factor of $10^{-3/2}$ below this value – meaning that there is still room for improving on existing molecules. The method for improvement, however, is not what is expected. The inset shows the raw data, which implies that larger molecules (with more π-electrons) are better. Since the normalized values fall with molecular size, the implication is that larger molecules do not use their electrons effectively. Thus, a better paradigm needs to be developed to improve on existing molecules. It is interesting to note that if we extrapolate the normalized two-photon cross-section to the 1-electron molecule, we hit the limit. While it is not possible to make a one-π-electron system, this exercise clearly show that the complications associated with having many electrons leads to a smaller two-photon absorption cross-section than is possible for that size molecule.



These results of this work were reviewed in a feature article in the September 2003 issue of IEEE *Circuits and Devices* Magazine and appeared as the cover art. Also, this work will be reviewed in the December 2003 issue of Optics and Photonic News as one of the most significant pieces of work in nonlinear optics.

Photorefractive Fibers
Mark G. Kuzyk

Please see our list of publications for a more in-depth treatment of our work.

5. Personnel Supported

(1) Number of PI and Co-PI involved in the research project : __1_____
(list on an attached page)

Kuzyk, Mark G.

(2) Number of Post Doc Supported under AFOSR:___3____

Kim, Sun Il
Bian, Shaoping
Steven Vigil

(3) Number of graduate students supported by AFOSR: ___6____

Canfield, Brian K.
Embaye, Natnael B.
Park, Jeong Joon
Zhang, Weiya
Franz,Dana
Perez-Moreno, Javier

(4) Other researchers supported by AFOSR:___3____

Hanna, Gabriel - undergraduate
Robinson, Dirk -
Dao, Khoa -

(5) Number of publications by PI refereed journals ___23____

(6) Number of publications in the last 12 months (in refereed journals only) that acknowledge AFOSR supports: ___21____

6. Publications Citing AFOSR

1. R. Kruhlak and M. G. Kuzyk, "Side Illumination Fluorescence (SIF) Spectroscopy I: Principles," **16**, 1749 (1999).
2. .R. Kruhlak and M. G. Kuzyk, "Side Illumination Fluorescence (SIF) Spectroscopy II: Applications to Squaraine dye-doped polymer optical fibers," **16**, 1756 (1999).
3. D. Sullivan, L. Liu, and M. G. Kuzyk, "Three-Dimensional Optical Pulse Simulation Using the FDTDMethods," IEEE Transactions on Microwave Theory and Techniques," **48**, 1127 (2000).
4. M. G. Kuzyk, "Fundamental limits on third-order molecular susceptibilities," Optics Letters **25**, 1183 (2000).
5. M. G. Kuzyk, "Physical Limits on Electronic Nonlinear Molecular Susceptibilities," Physical Review Letters **85**, 1218 (2000).
6. S. R. Vigil and M. G. Kuzyk, "Absolute molecular optical Kerr-effect spectroscopy of dilute organic solutions and neat organic liquids," J. Opt. Soc. Am B **18**, 679 (2001).
7. M. G. Kuzyk, "Quantum Limits of the Hyper-Rayleigh Scattering Susceptibilities," IEEE Journal on Selected Topics in Quantum Electronics **7**, 774 (2001). Invited
8. B. K. Canfield, C. S. Kwiatkowski, and M. G. Kuzyk, "Direct Deflection Method For Determining Refractive Index Profiles of Polymer Optical Fiber Preforms," Applied Optics-IP **41**, 3404-3411 (2002).
9. M. A. Diaz-Garcia, S.Fernandez De Avila, and M. G. Kuzyk, "Dye-Doped Polymers for Blue Organic Diode Lasers," Applied Physics Letters **80**, 4486-4488 (2002).
10. C. Jiang, M. G. Kuzyk, J.-L. Ding, W. E. John, and D. J. Welker, "Fabrication and Mechanical Behavior of Dye-Doped Polymer Optical Fiber," Journal of Applied Physics **92**, 4-12 (2002).
11. W. Zhang, S. Bian, S. I. Kim, and M. G. Kuzyk, "High Efficiency Volume Gratings in DR1-doped poly (methyl methacrylate)" –Optics Letters **27** (13) 1105 (2002).
12. S. Bian and M. G. Kuzyk, "Real-Time Holographic Reflection Gratings in Volume Media of Azo-Dye-Doped poly(methyl methacrylate)," Optics Letters **27**, 1761 (2002).
13. S. Bian, W. Y. Zhan, S. I. Kim, N. B. Embaye, G. J. Hanna, J. J. Park, B. K. Canfield, M. G. Kuzyk, "High-efficiency optical phase conjugation by degenerate four-wave mixing in volume media of disperse red 1-doped poly(methyl methacrylate)," Journal of Applied Physics **92,** (8), 4186-4193 (2002).
14. M. A. Diaz-Garcia, S.Fernandez De Avila, and M. G. Kuzyk, "Energy Transfer from Organics to Rare-Earth Complexes," Applied Physics Letters **81**, 3924-3926 (2002).
15. I. Vargas-Baca, A. P. Brown, M. P. Andrews, T. Galstian, Y. Li, H. Vali, and M. G. Kuzyk, "Linear and Nonlinear Optical Responses of a Dye Anchored to Gold Nanoparticles Dispersed in Liquid and Polymeric Matrixes," Can. J. Chem. **80**, 1625-1633 (2002).
16. Mark G. Kuzyk, "Fundamental limits on third-order molecular susceptibilities: erratum," Optics Letters **28**, 135 (2003).
17. M. G. Kuzyk, "Erratum: Physical Limits on Electronic Nonlinear Molecular Susceptibilities," Physical Review Letters **90**, 039902 (2003).
18. Shaoping Bian, Weiya Zhang and Mark G. Kuzyk, "Erasable holographic recording in photosensitive polymer optical fibers," Optics Letters **28**, 929 (2003).
19. M. G. Kuzyk, "Fundamental Material Limitations on Optical Devices," Circuits and Devices **19** (5), 8 (2003).
20. M. G. Kuzyk "Fundamental limits on two-photon absorption cross-sections," J. of Chem. Phys. **119**, 8327 (2003).
21. M. G. Kuzyk, "Fundamental Limits of Nonlinear Susceptibilities," Optics and Photonic News, page 24, December (2003).

7. Transitions

As a result of this grant, we have started collaborations with several researchers at Wright Patterson Air Force Base. In particular, I gave a talk at WPAFB on the theory of fundamental limits, which was of interest to the Quantum Chemists and the Physicists. Note that some of this theoretical work has spilled over to the Army research office since my talk was attended by a guest from that lab.

We are also now making samples with WPAFB materials and doing characterization studies. Our polymer processing technology has been found to be useful for making sample disks with large TPA.

We are starting collaborations with Paul Fleitz at WPAFB to make optical limiting fibers from their materials.

Note that my group and I have attended several Air Force reviews and conferences many new interactions and conference papers have resulted. Conference papers include:

1. D.J. Welker, D.W. Garvey, C.D. Breckon, B. Canfield, and M.G. Kuzyk, "Single-mode Nonlinear Electrooptic Polymer Optical Fiber," POF World '99, 23 (1999). **Invited**
2. D.J. Welker, D.W. Garvey, C.D. Breckon, and M.G. Kuzyk, "Advances in Electrooptic Fiber Devices," ACS OSA Thin Films Meeting, Santa Clara (1999). **Invited**
3. M. G. Kuzyk, "Photomechnical Fibers," Washington Technology Center Symposium on MEMS, Seattle (1999). **Invited**
4. M.G. Kuzyk, "Quantum Limits on Nonlinear Susceptibilities," ICONO'5, Switzerland (2000). **Invited**
5. M.G. Kuzyk, "Physical Limits on Nonlinear Susceptibilities," Proc. SPIE 4106, San Diego (2000). **Invited**
6. M.G. Kuzyk, "Quantum Limits of Nonlinear Susceptibilities, and Beyond," 14th Annual IEEE Lasers and Electro-Optics Society 2001 Annual Meeting, San Diego, CA (2001). **Invited**
7. M.G. Kuzyk , "Nonlinear Optics of Dye-Doped Polymers," 25th Asilomar Conference on Polymers, (2002). **Invited**
8. M.G. Kuzyk, "An Overview of Dye-Doped Polymer Optical Fibers: Fabrication, Characterization and Applications," Polymer Optical Fiber 2003, Seattle (2003) **Invited.**
9. M.G. Kuzyk, "Fundamental Limits of the Two-Photon Absorption Cross-Section," The Third International Symposium on Optical Power Limiting, Sedona (2003) **Invited.**
10. M.G. Kuzyk, "Fundamental The Sky's NOT the Limit - What Sum Rules Teach us about Nonlinear-Optical Susceptibilities," ICONO'7 and ICOPE, Sorak, Korea (2003) **Invited.**
11. B.K. Canfield and M.G. Kuzyk, "Characterization of Polymer Electrooptic Fiber," Opto-Northwest (1999).
12. R.J. Kruhlak and M.G. Kuzyk, "Photosensitivity of Squaraine Dye-doped Polymer Optical Fiber Using Side-illumination Fluorescence (SIF)," Opto-Northwest (1999).
13. B. K. Canfield, R. J. Kruhlak, and M. G. Kuzyk, "Investigation of the Third-Order Optical Susceptibility of Chromophores Through Broadband Electrooptic Spectroscopy," ICONO'5, Davos, Switzerland (2000).
14. R. J. Kruhlak and M. G. Kuzyk, "Determining the nature of Excited States Using an Inhomogeneous-Broadening Analysis of Third-Order Processes," ICONO'5, Davos, Switzerland (2000).
15. M. G. Kuzyk, "Is there a limit to Nonlinear Sucseptibilities?" ACS/OSA Thin Films Meeting, Washington D.C. (2000).
16. M. G. Kuzyk, "Fundamental Limits of Susceptibilities," Proc. SPIE **4461**, 15 (2001).
17. B. K. Canfield and M. G. Kuzyk, "Excited State Characterization of Nonlinear Optical Materials through Electrofluorescence," Proc. SPIE **4461**, 117 (2001).
18. R. J. Kruhlak and M. G. Kuzyk, "Co-Polymer and Dye-Doped Polymer Fiber and Fiber Preform Characterization," Proc. SPIE **4461**, 206 (2001).
19. S. Bian, W. Zhang, S. I. Kim, N. N. Embaye, G. J. Hanna, J. J. Park, B. K. Canfield, and M. G. Kuzyk, "Optical Phase Conjugation by Resonant Degenerate Four-Wave Mixing in Volume Media of DR1-Doped PMMA," Proc. SPIE **4798**, 44-52 (2002).
20. B. F. Howell and M. G. Kuzyk, "Amplified Spontaneous Emission and Recoverable Photodegradation in a Robust Dye-Doped Polymer," Proc. SPIE **4798**, 60-68 (2002).
21. J. J. Park, S. Bian, and M. G. Kuzyk, "Dynamics of Intensity Dependent Refractive Index Using T-Scan," Proc. SPIE **4798**, 116-122 (2002).

22. Shaoping Bian and Mark G. Kuzyk, "Photorefractive Polymer Optical Fibers," Polymer Optical Fiber 2003, Seattle (2003).
23. Shaoping Bian and Mark G. Kuzyk, "Phase conjugation generation by degenerate four-wave mixing in photosensitive polymer optical fibers," Proc. SPIE **5212**, (2002).
24. Mark G. Kuzyk, "Microscopic nonlinear susceptibilities: the sky is not the limit," Proc. SPIE **5212**, (2002).
25. Shaoping Bian, Weiya Zhang, and Mark G. Kuzyk, "Optical holographic recording by guided waves in photosensitive polymer multimode fibers," Proc. SPIE **5216**, (2002).

8. Discoveries

- Showed in a rigorous quantum calculation that there exists a well-defined upper limit to nonlinear susceptibilities.
- Demonstrated that photoisomerization can be used for optical limiting
- Demonstrated limiting in a POF
- Demonstrated holography and phase conjugation in fibers
- Demonstrated blue light sources in fibers

9. Awards and Honors

Fellow of the Optical Society of America, elected in 1999.
Executive Committee, American Society for Engineering Education, appointed in 1999.
Distinguished Member of National Society of Collegiate Scholars, elected in 2000.