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# FINAL PROGRESS REPORT

# MECHANISMS OF PHOTOREFRACTIVITY IN POLYMERIC MATERIALS

Principal Investigator: Prof. W. E. Moerner Department of Chemistry, Stanford University Mail Code 5080, 333 Campus Drive Stanford, California 94305-5080 650-723-1727 (office), 650-725-0259 (fax), e-mail: moerner@stanford.edu

# AFOSR Grant No. F49620-99-1-0032

Period Covered: 1 Apr 99 - 30 Sep 99

Date 25 Sept 2000

## 2. Objectives:

The primary goal of this research is to understand the mechanisms operative in photorefractive polymer materials. The objective of this work during the six-month grant is to explore the factors controlling the trapping dynamics and trap lifetimes. In addition, preliminary experiments aimed at identifying possible Air Force applications for the materials will be completed.

## **3. Status of Effort:**

This six month grant provided a continuation at Stanford University of AFOSR Grant No. F49620-96-1-0135, which ended 31 Mar 1999 at the University of California, San Diego (UCSD). During the period of this grant, several accomplishments are of note. A major study of the effect of nonlinear chromophore energetics on the speed of photorefractive polymers showed that rational design can improve the properties of these materials. Second, the entire laboratory moved from UCSD to Stanford University in July 1999. During this time, a major review article on photorefractive polymers for the Encyclopedia of Materials Science and Technology was completed (Pub. 171). Finally, in the new laboratories at Stanford, a first demonstration of fast image amplification with photorefractive polymers was completed.

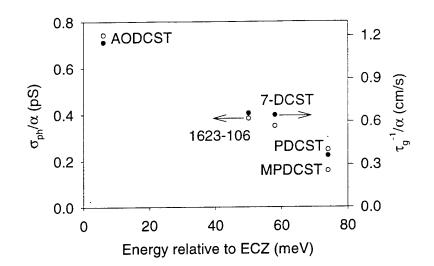
#### 4. Accomplishments/New Findings:

(publications are numbered according to the list below)

# A. Correlation between NLO energetics, speed of response, and trapping

On the materials/understanding front, we identified for the first time a strong inverse correlation between the speed of response of our photorefractive polymers with the depth of the compensating hole trap produced by the nonlinear optical chromophore (Pub. 163). In our high-speed materials, chromophore orientation was not the primary limitation on the speed of the response, rather, the speed was limited by the photoconductivity, which in turn, was affected by the compensator trap depth. As a result of this work, other investigators are now measuring the positions of NLO-induced trapping states to apply our trapping model to other classes of materials. For example, at the SPIE meeting in San Diego in July 2000, the Arizona group has presented further verification that our model based on the C<sub>60</sub> anion as the primary trap and the NLO as a compensator is correct (A. Grunnet-Jepsen, D. Wright, B. Smith, M. S. Bratcher, M. S. DeClue, J. S. Siegel, and W. E. Moerner, "Spectroscopic Determination of Trap Density in C<sub>60</sub>-Sensitized Photorefractive Polymers," *Chem. Phys. Lett.* **291**, 553-561 (1998)).

Specific measurements involved materials of the general type PVK:NLO:BBP: $C_{60}$ , in which the NLO is one of several amino-substituted dicyanostyrenes. In order to understand the specific factors controlling the speed in these materials, we have measured both the photoconductivity and the speed (inverse response time) as a function of intensity and applied electric field. In both cases, the shapes of the curves are very similar, indicating that the speed is mostly determined by the photoconductivity, not by the orientational response

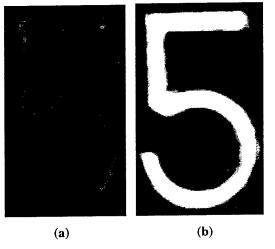


time of the NLO chromophores in these low Tg composites. We believe that these materials are fast because we have utilized NLO chromophores which have relatively shallow trapping energetics (AODCST and PDCST), so that the hindrance to the charge motion is minimized. We have obtained additional examples of this trend by correlating the normalized speed of response with the depth of the NLO compensator for every NLO in a series of DCST derivatives and find very good correlation – slower materials have deeper compensating traps (see the figure). [Publication 163] To further validate our model, we plan time-of-flight measurements of charge carrier mobility in the near future.

The significance of these results is three-fold. First, the principal trapping sites have been identified for the first time in any PR polymer. Second, the compensating centers have been identified, and they are likely to play a role in the time response of the samples. Third, these useful facts provide a framework for the rational design of new PR polymers, as the NLO chromophore is now no longer a passive component, but its energy levels must be taken into account in controlling the all-important photorefractive trap density in the final materials. A similar comment clearly applies to the plasticizer and any other component that could provide trapping sites that could help or hinder hole transport. Control of the trap density leads to control of the space-charge field, the phase shift, and the index modulation, and we are now in a position to influence these properties as required for specific applications. All this has been accomplished with a simple near-infrared spectroscopic measurement on the asmade materials, coupled with our detailed analysis of the PR characteristics.

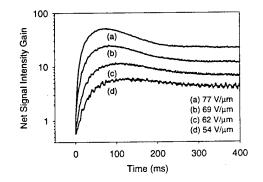
# **B.** Exploring effect of materials properties on applications of photorefractive polymers: video rate image amplification

We have demonstrated a potentially important application with our high-performance photorefractive polymer composites: video rate image amplification / novelty filtering. Here the major interest is in exploring how the materials parameters affect the suitability of photorefractive polymer materials for particular applications. In a set of preliminary experiments (recently published in Pub. 170), we have shown that energy transfer between two laser beams writing a volume hologram in a photorefractive polymer composite allows optical processing applications at video rates. For image amplification, a net increase in image intensity as high as a factor of 37 can be observed within one video frame time (33 ms) using a total beam intensity of 1 Wcm<sup>-2</sup> and 77 V $\mu$ m<sup>-1</sup> applied electric field with our PVK:AODCST:BBP:C60 composite. By interchanging the role of the image and reference beams, we also demonstrated moving object detection (novelty filtering). These first demonstrations of potentially useful applications underscore the continuing need for further research to understand and optimize this important class of optical materials.



In the figure above, the performance of our optical image amplifier is illustrated. The left image is the weak signal beam (no pump) which was passed through an Air Force resolution test chart before passing through the photorefractive polymer sample. The right image shows the amplified signal beam one frame (33 ms) later.

A plot of the gain factor as a function of time shows a slight overshoot during the initial amplification (figure below). This effect is partially due to the dynamics of space-charge formation in the material during the transit of carriers over a portion of the optical standing-wave pattern. This early, fast amplification is a desirable feature for amplification of changing scenes.



## 5. Personnel Supported:

Postdoctoral researchers: Dr. Arosha Goonesekera (Stanford)

Graduate students: Dan Wright (Stanford)

#### 6. Publications:

- 163. M. A. Díaz-García, D. Wright, J. D. Casperson, B. Smith, E. Glazer, W. E. Moerner, L. I. Sukhomlinova, and R. J. Twieg, "Photorefractive Properties of Poly(N-Vinyl Carbazole)-Based Composites for High Speed Applications," *Chem. Mater.* 11, 1784-1791 (1999).
- 165. R. J. Twieg, M. He, L. Sukhomlinova, F. You, W. E. Moerner, M. A. Diaz-Garcia, D. Wright, J. D. Casperson, R. Wortmann, C. Glania, P. Kraemer, K. Lukaszuk, R. Matschiner, K. D. Singer, V. Ostoverkhov, and R. Petschek, "Design and Optimization of Chromophores for Liquid Crystal and Photorefractive Applications," *Proc. Mater. Res. Soc.* 561, 119-130 (1999).
- 170. A. Goonesekera, D. Wright, and W. E. Moerner, "Image Amplification and Novelty Filtering in a Photorefractive Polymer," *Appl. Phys. Lett.* **76**, 3358-3360 (2000).
- 171. W. E. Moerner, "Photorefractive Polymers," appearing in *Encyclopedia of Materials* Science and Technology, D. D. Nolte, Ed. (Elsevier, Oxford, 2000).

#### 7. Interactions/Transitions:

# (a) Invited participations/presentations at meetings, conferences, seminars, etc.

- 169. W. E. Moerner, D. Wright, M. Diaz-Garcia, A. Goonesekera, J. Casperson, B. Smith, M. S. DeClue, E. Glazer, J. S. Siegel, and R. J. Twieg, "New Insights into Trapping and Compensation in Photorefractive Polymers," Material Research Society Spring Meeting Symposium F, San Francisco, California, April 5-9, 1999.
- 170. W. E. Moerner, A. Grunnet-Jepsen, D. Wright, J. Casperson, E. Glazer, M. DeClue, J. S. Siegel, and R. J. Twieg, "Understanding Trapping in Photorefractive Polymer Composites for Optical Processing Applications," Conference on Lasers and Electro-Optics CLEO '99, Baltimore, Maryland, May 23-28, 1999.
- 171. W. E. Moerner, A. Grunnet-Jepsen, D. Wright, M. S. DeClue, J. S. Siegel, and R. J. Twieg, "Understanding Photorefractivity in High-Performance Polymer Composites," Seventh Topical Meeting on Photorefractive Materials, Effects, and Devices, PR'99, Elsinore, Denmark, June 27-30, 1999.