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13. ABSTRACT ***(Maximum 200 Words)***

The goal of this project was to produce and characterize improved organic ferroelectric materials with emphasis on improving the response time and sensitivity. We demonstrated 300-fold improvements in the mobility of photorefractive polymer composites by identifying and mitigating the dipolar disorder mobility-reducing mechanism endemic to organic photorefractive materials and choosing transport agents that were relatively insensitive to this mechanism. We also synthesized dendrimers with design features further reducing dipolar disorder and also the significant van der Waals disorder for use in improved-speed photorefractive composites.

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1. GRANT INFORMATION

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PHOTOREFRACTIVE POLYMERS FOR INTEGRATED OPTICS

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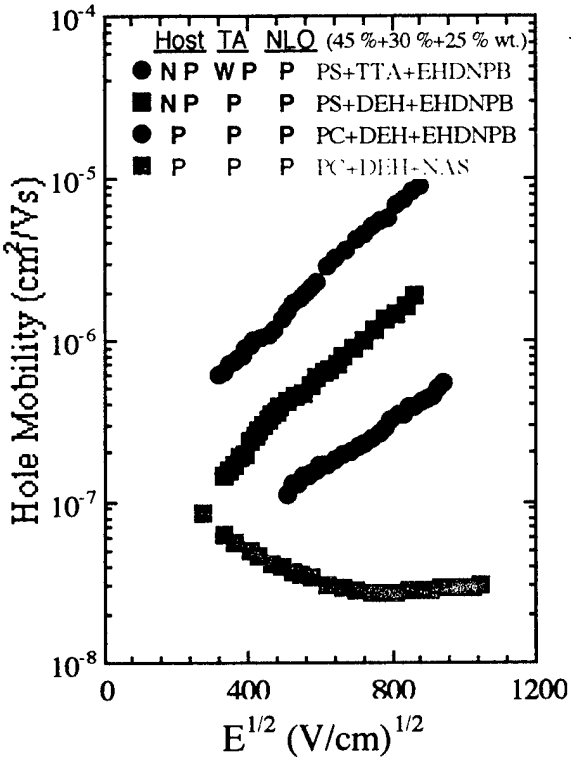
2. OBJECTIVES

To produce and characterize improved organic ferroelectric materials with emphasis on improving the response time and sensitivity.

3. STATUS



We demonstrated improvements in the mobility of photorefractive polymers and preliminary results from photorefractive dendrimers intended for further mobility improvement. Our contributions are illustrated by the mobilities (graph at right) of several photorefractive polymer composites. The Prototypical Photorefractive Polymer[1] (red squares) consists of a polycarbonate (PC) host with attached NLO chromophore 4'-nitro-4'-aminostilbene (NAS), and a hole transport agent diethylamino-benzaldehyde diphenyl hydrazone (DEH). All three functional components are polar, leading to unacceptably low carrier mobility due to the dipolar disorder effect. The Transport-Optimized Photorefractive Polymer[2] (blue circles) minimizes dipolar disorder using a nonpolar polystyrene (PS) host and using a weakly polar transport agent tri-p-tolylamine (TTA), even in the presence of the even more polar chromophore 2,5-dimethyl-4-(p-nitrophenylazo)phenol (ENDNPB). This composition shows a 300-fold improvement over the prototypical composi-

tion at 800 kV/cm. The NLO chromophore remains highly polar as is necessary to produce electrooptic or orientational birefringence effects for generation of phase gratings, but careful choice of transport agent minimizes the dipolar disorder effect while maintaining electrooptic activity.

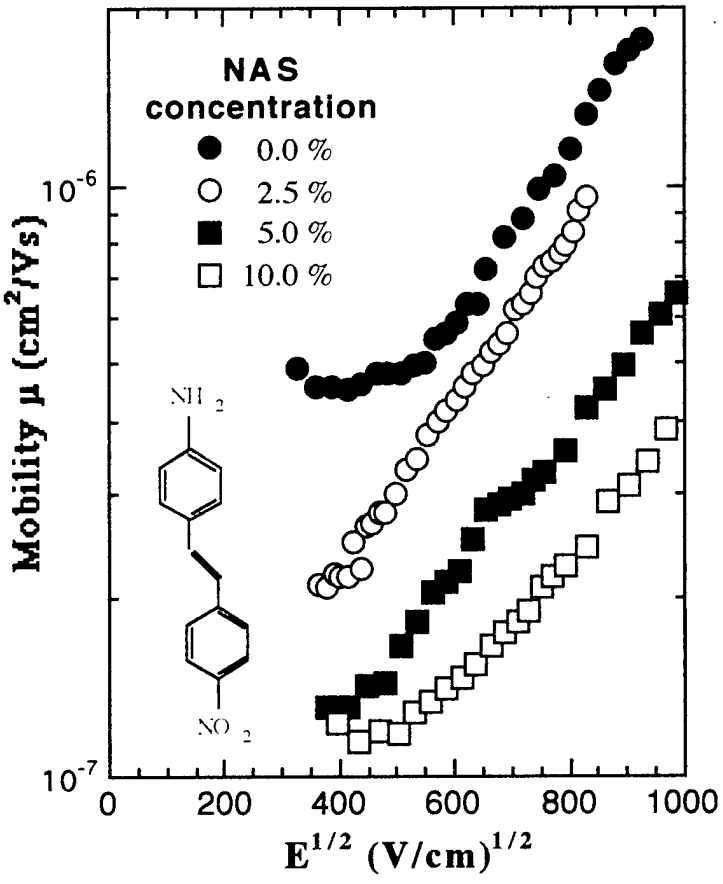
4. ACCOMPLISHMENTS

The photorefractive speed and sensitivity are proportional to, and often limited by, the charge carrier mobility, and therefore increasing the mobility is essential to the development of higher performance photorefractive materials.

a. Identification and quantification of mobility reduction mechanisms

We have shown that the main cause of mobility-reduction in organic photorefractive materials is dipolar disorder due to the polar chromophores, a necessary component of organic photorefractives. It is clear from our studies[2-4] of transport in polymer-based organic photorefractive materials that it is not reasonable to expect significantly faster operation, presently in the millisecond range at 1 W/cm^2 intensity, with conventional polymer systems.[5,6] The limitation is not in photogeneration efficiency, which can be made close to 100 %, but in carrier mobility, which is severely limited by energetic disorder in the hopping manifold. This disorder is a result of the defects and environmental inhomogeneity inherent in conventional polymer-based systems.[4] The effects of dipolar disorder on mobility were first observed in the early 1990s[7,8] in similar composites used in Xerography,[9] but our work demonstrated the distinct importance of the NLO chromophores unique to photorefractive composites.

The figure at right summarizes our results from doping a nonpolar host polymer (polystyrene, PS) with a fixed amount of a hole transport agent (30 wt. % DEH) and varying amounts of a typical high-performance NLO chromophore (4'-nitro-4'-aminostilbene, NAS). The hole mobility drops precipitously with the addition of the chromophore,[10] consistent with the predicted dependence that the mobility decreases exponentially in the square of the dipole moment.[11]

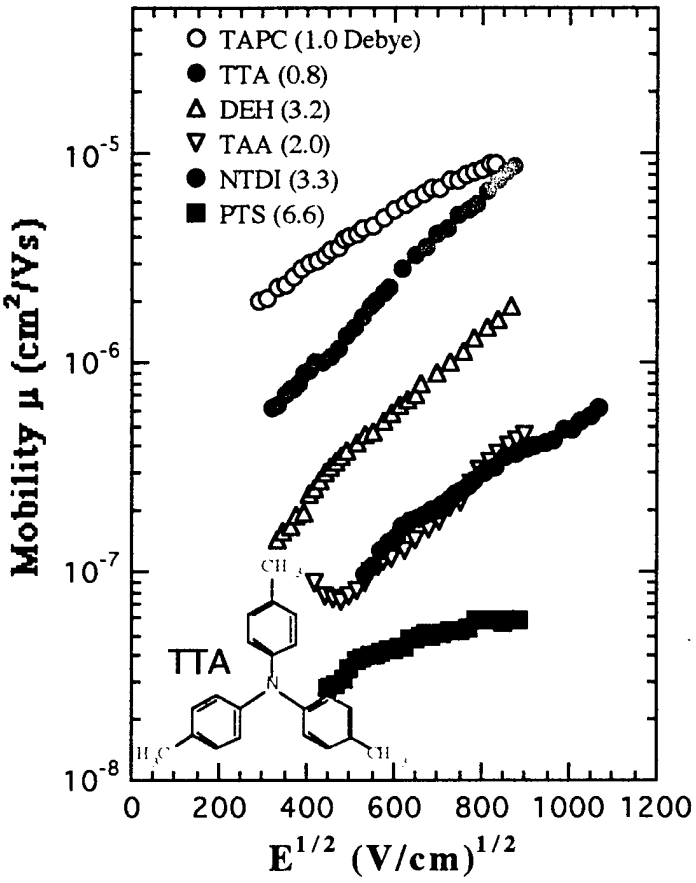


Since the polar chromophores are necessary for producing refractive-index modulation, whether through linear electro-optic (Pockles) effect[12]

or by orientational birefringence,[13] it is not possible to reduce dipolar disorder sufficiently by reduction of dipole moments or concentration of dipoles. We therefore sought transport agents with reduced sensitivity to dipolar disorder.

b. Mitigation of mobility reduction by careful choice of transport agents

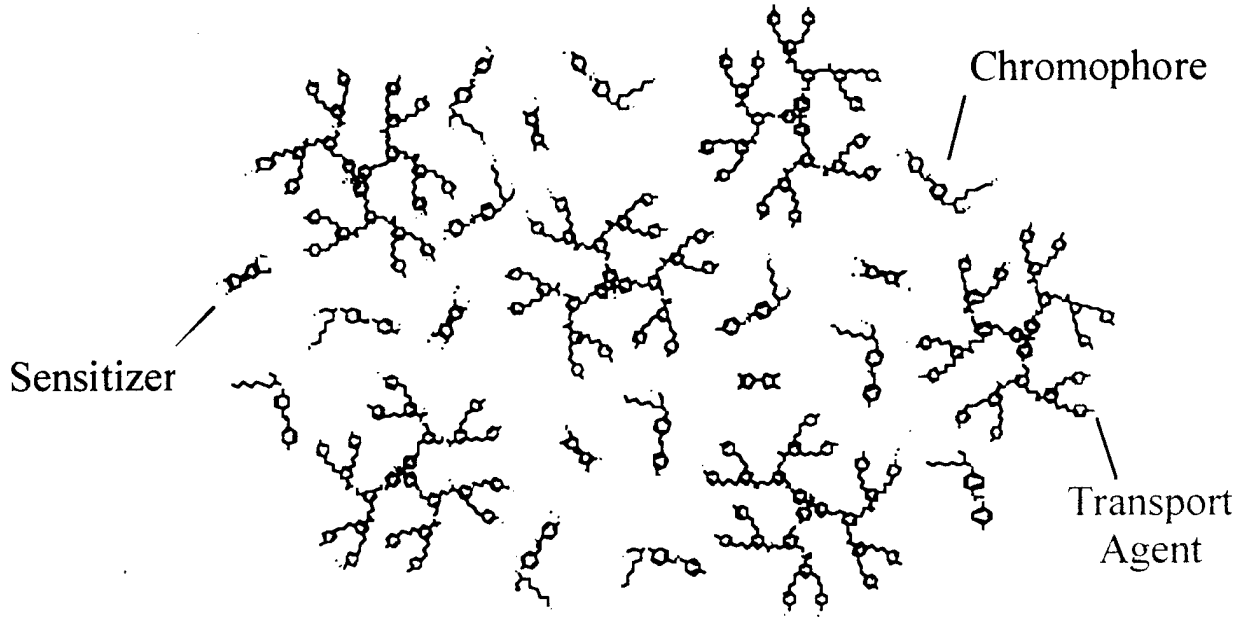
We have established methods for choosing combinations of charge transport and NLO agents to minimized the effects of dipolar disorder and increase mobilities 2-3 orders of magnitude. Transport agents with low dipole moment relatively insensitive to inhomogeneous electric fields, and therefore maintain high carrier mobility in the presence of dipolar disorder. This principle is demonstrated in the graph at right, which shows the strong dependence of the carrier mobility for both hole (open symbols) and electron (closed symbols) transport agents in the presence of a high concentration (25 wt. %) of the highly polar EHDNPB chromophore.[10] Reducing the transport agent dipole moment by a factor of 8 from PTS to TTA increases the mobility by over two orders of magnitude. The low-dipole transport agents TTA and TAPC, by virtue of their relatively small dipole moments, are insensitive to the dipolar disorder due to the chromophores, thus restoring most of the mobility reduction from addition of 25 wt. % of the highly polar EHDNPB chromophore.



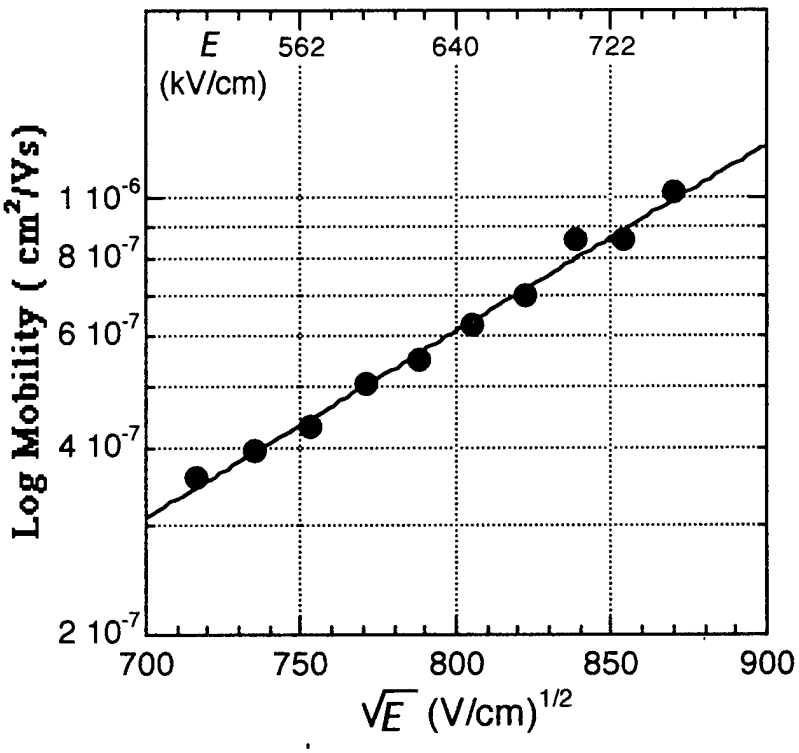
c. Development of Photorefractive Dendrimers for further mobility increases

Even after minimizing the dipolar disorder effect, carrier mobility in polymers remains unacceptably low. This is because significant energetic disorder remains, a problem inherent in the large inhomogeneities of conventional polymer-based systems.[14] To visualize the inhomogeneity problem, think about conventional linear polymers, with their unavoidable polydispersity, as an intertwined bunch of strings in a beaker, strings of varied length. Compare this picture with a beaker filled with dendrimers (dendritic or hyper-branched polymers), spheres of uniform size. In addition, physical defects introduce deep traps in the matrix, and defects at the level of a tenth of a percent or more will substantially detract from photorefractive performance. Dendrimers afford excel-

lent synthetic control over their topology by rational design; that is, we can ensure a much more homogenous (i.e., uniform and low polarity) microenvironment for charge transport.

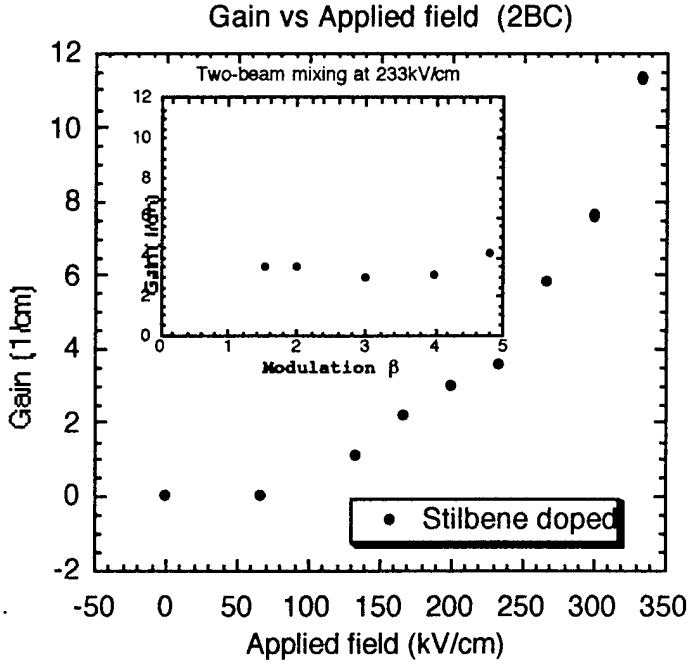


Dendrimers have received little attention, yet perhaps hold the greatest potential for understanding and optimizing photorefractive properties. Dendrimer composites like the one shown above consist of three main subunits: a **core (black)**, branches (blue), and surface groups (red). These three subunits can be independently varied to make chemically and topologically homogeneous arrays of optimal charge transport agents and/or chromophores. Dendrimers remain relatively small and are readily doped with other molecules like the chromophores (green) and **sensitizers (black)**. Such structural control allows optimization of the transport mechanisms in ways not possible in less ordered systems, while maintaining good control over thermo-physical properties. We have begun making photorefractive dendrimer systems to validate our hypotheses.

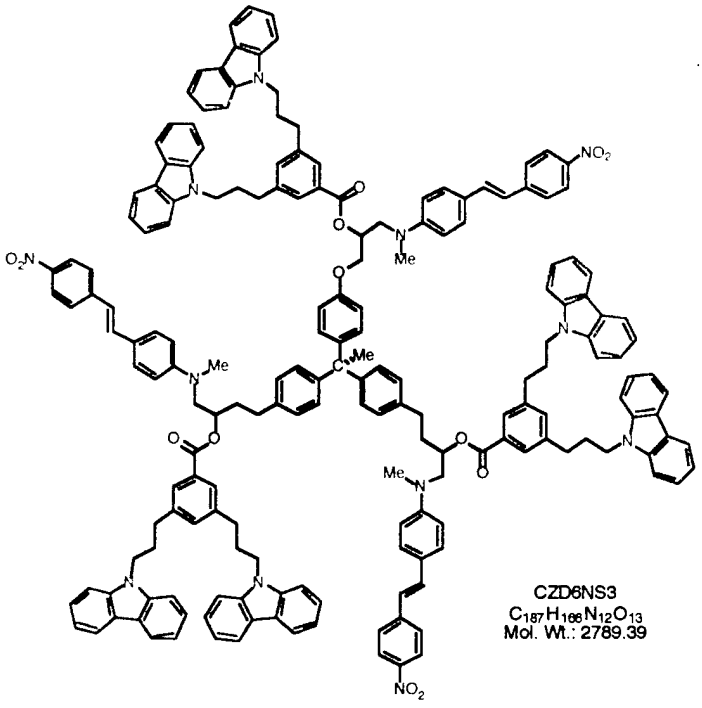


We have synthesized dendrimers capped with 4-12 carbazole endgroups as transport agents (D4, D6, D8, D8E, D12). These dendrimers were doped with an NLO chromophore

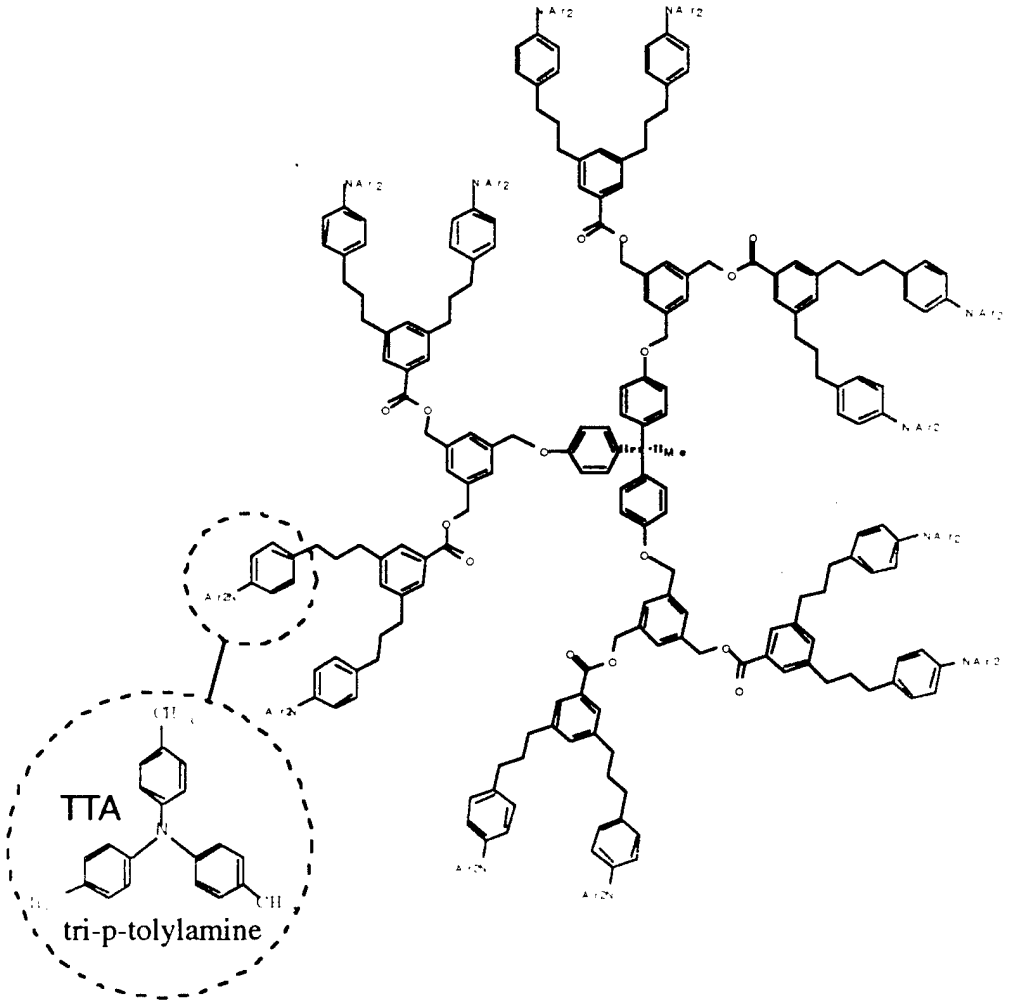
(EHDNPB) and a sensitizer (TNF). The D4 dendrimer (with carbazole end-groups) exhibits mobilities (graph at right) above 10^{-6} cm^2/Vs at 800 kV/cm electric field,[15] considerably higher than in the PVK:TNF systems the prototypical photorefractive epoxy polymer:DEH systems. The D8E carbazole dendrimer with 37 wt. % NAS chromophores exhibits reasonable photorefractive response (graph at right), with two-beam coupling gain of 12 cm^{-1} at only 350 kV/cm.[15,16] Other groups, Yu at Chicago and Wada at RIKEN,[17] made dendrimeric systems intended for photorefraction. But, while their results are encouraging, only our group has reported successful demonstration of photorefraction in a dendrimer system.



The dendrimer approach also allows us to prepare single compound (monodispersed) dual-function systems. For example, we have recently synthesized CZD6NS3 (right). We expect dual-function dendrimers to be superior due to very low electronic defect density, and by virtue of synthetic control over their topology, we can ensure a much more homogenous microenvironment for the transport states, resulting in increased mobility. In polymers, you can work to minimize polydispersity and defect density, but the dendrimeric systems are inherently superior in this respect. In addition, the dendrimeric systems permit detailed control of molecule orientations and environment so that redox potentials and photoionization energies can be adjusted without increasing disorder. For example, the electron-withdrawing group of a hole transport agent can be presented to the outside of the dendrimer structure while the remainder of the molecule is "protected" nearer the molecular core.



However, the carbazole moiety is a poor choice for photorefractive composites because it is polar and therefore very sensitive to the dipolar disorder effect, resulting in low carrier mobility and low photorefractive speed. A preferred system with a TTA transport agent (below) to increase carrier mobility is currently undergoing transport measurements.



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5. PERSONNEL SUPPORTED

Graduate Assistant Arosha Goonesekera was supported by this grant to fabricate samples and perform photoconductance and other electrical and optical characterization. Arosha completed his PhD in August 1998 and joined the Moerner group at UCSD/Stanford as a postdoctoral assistant and is now employed by Nanometrics, Inc. in Mountain View, CA. Physics PhD student Jaeil Bai continued the work on sample preparation, characterization, and photorefractive measurements for the new dendrimer systems. Chemistry postdoc Lu Liu and PhD student Alexie Leonov have been synthesizing the dendrimer systems and conducting physical and chemical characterization. Leonov has also been conducting mobility measurements of the dendrimer systems he has synthesized.

An undergraduate student, Kelly Newsome, worked one summer on dendrimer synthesis as part of the UNL/NSF Research Experiences for Undergraduates (REU) program in Nanostructured Materials Research and another undergraduate, Jennifer Webster, prepared summaries of our photorefractive polymer research for the web.

6. PUBLICATIONS

a. Refereed Journals

"Low-Field Hole Mobility in a Photorefractive Polymer," A. Goonesekera, S. Ducharme, J. M. Takacs, and L. Zhang, *J. Chem. Phys.* **107**, 8709-12 (1997).

"Measurement of the Photorefractive Grating Phase Shift in a Polymer Using an AC Phase Modulation Technique," M. Liphardt and S. Ducharme, J. Optical Society of America B 15, 2154-60 (1998).

"Effect of Dipolar Molecules on Carrier Mobilities in Photorefractive Polymers," A. Goone sekera and S. Ducharme, J. Applied Physics 85, 6506-14 (1999).

b. Conferences Proceedings

"Reduced Hole Mobility in Photorefractive Polymers Due to the Chromophore Dipole Mo ment," A. Goonesekera and S. Ducharme, in *Proceedings of the Conference on Organic Thin Films for Photonics Applications*, Long Beach, 15-17 October 1997, (Optical Society of America, Washington, DC, 1997), pp. 248-51.

"Influence of Dipole Moment of the Transport Agents on the Carrier Mobility in a Photorefrac tive Polymer," A. Goonesekera, J. Bai, S. Ducharme, J. M. Takacs, L. Lu, in Organic Pho torefractive Materials and Xerographic Photoreceptors VI, July 21-24, S. Ducharme and J. M. Stasiak, eds., SPIE Proceedings Vol. 3471 (SPIE, Bellingham, WA 1998).

"A New Organic Photorefractive Material Composed of a Charge-Transporting Dendrimer and a Stilbene Chromophore," J. Bai, S. Ducharme, L. Lu, A. Leonov, and J. M. Takacs, Organic Photorefractive Materials and Xerographic Photoreceptors V, 19-23 July, S. Ducharme, D. H. Dunlap, and R. Norwood, eds., Vol. 3799 (SPIE, Bellingham, WA 1999).

"The Synthesis and Characterization of Dendrimers for Potential Photorefractive Applications," J. Bai, S. Ducharme, A. Goonesekera, A. P. Leonov, L. Lu, and J. M. Takacs, Proceedings of the Conference on Organic Thin Films for Photonics Applications, Boston, 23-27 August 1998 (OSA, Washington, 1999).

"Charge-Carrier Mobility Studies of Potential Photorefractive Dendrimers," A. P. Leonov, Ste phen Ducharme, L. Lu, and James M. Takacs, Proceedings of the ACS/OSA *Symposium on*

Organic Thin Films for Photonics Applications, Washington, 20-25 August 2000 (OSA, Washington, DC, 2001).

c. Other Publications

Xerographic Photoreceptors and Photorefractive Polymers, S. Ducharme and P. M. Borsenberger, eds., San Diego, 10-11 July 1995, **Vol. 2526**, (SPIE, Bellingham, WA 1995), 156 pages.

Organic Photorefractive Materials and Xerographic Photoreceptors, S. Ducharme and J. M. Stasiak, eds., Denver, 7-8 August 1996, **Vol. 2850**, (SPIE, Bellingham, WA 1996), 212 pages.

Xerographic Photoreceptors and Organic Photorefractive Materials II, S. Ducharme and J. M. Stasiak, eds., San Diego, 28-29 July 1997, **Vol. 3144**, (SPIE, Bellingham, WA 1997), 248 pages.

Organic Photorefractive Materials and Xerographic Photoreceptors IV, S. Ducharme and J. M. Stasiak, eds., San Diego, 19-24 July 1998, **Vol. 3471**, (SPIE, Bellingham, WA 1998), 264 pages.

Organic Photorefractives, Photoreceptors, Waveguides, and Fibers, S. Ducharme, D. H. Dunlap, and R. A. Norwood, eds., Denver, 18-23 July 1999, **Vol. 3799**, (SPIE, Bellingham, WA 1999), 342 pages.

"Book Review: The Physics and Applications of Photorefractive Materials by Solymar, Webb, and Grunnet-Jepsen," Physics Today 50, 75-76 (October 1997).

Web Dissemination: http://physics.unl.edu/directory/ducharme/photorefrac.html

7. INTERACTIONS/TRANSITIONS

a. Meetings and Conferences

Ducharme chaired and co-edited the proceedings for the five SPIE Conference on *Organic Photorefractive Materials* 1995-99. This conferences were coordinated with the Conference on *Xerographic Photoreceptors* to enable these two communities to compare notes on the essentially similar physics underlying the different phenomenologies of photorefraction and Xerography.

Invited Conference Presentations

"Charge Transport is the Weak Link in Photorefractive Polymers," S. Ducharme, *Workshop on Transport in Organic Materials*, 2-3 November 1996, Albuquerque.

"Charge Transport in Photorefractive Polymers," S. Ducharme, *8th Annual Symposium on Materials for Electronics and Imaging*, 10-12 July 1997, Rochester.

"A Study Concerning the Effect of Polar Molecules on Carrier Mobility in Photorefractive Polymers," A. Goonesekera, *Second Workshop on Transport in Organic Materials*, 21-22 March 1998, Albuquerque.

Colloquia and Seminars

"Photorefractive Fairy Tales," Colloquium, Department of Physics, University of Missouri-Rolla, 3 October 1996.

"Charge Transport in Photorefractive Polymers," Stephen Ducharme and Arosha Goonesekera, Research Seminar, Eastman Kodak Research Laboratories, 23 October 1996.

Contributed Conference Presentations

"The Influence of Intensity on Photoconductivity in Photorefractive Polymers," A. Goonesekera, M. Liphardt, S. Ducharme, J. M. Takacs, and L. Zhang, *Optical Society of America Annual Meeting*, Rochester, 20-24 October 1996. Oral presentation.

"A Comparison of Hole Mobilities in a Photorefractive Polymer and Xerographic Photoreceptors," A. Goonesekera and S. Ducharme, *American Physical Society March Meeting*, Kansas City, 17-21 March 1997. Oral presentation.

"Reduced Hole Mobility in Photorefractive Polymers Due to the Chromophore Dipole Moment," Arosha Goonesekera, S. Ducharme, J. M. Takacs, L. Zhang, *Midwest Solid State Science Conference*, Manhattan, KS, 3-4 October 1997. Oral presentation.

"Reduced Hole Mobility in Photorefractive Polymers Due to the Chromophore Dipole Moment," Arosha Goonesekera and S. Ducharme, J. M. Takacs, L. Zhang, *Organic Thin Films for Photonics Applications Topical Meeting*, Long Beach, 15-17 October 1997. Oral presentation.

"Influence of Dipole Moment of the Transport Agents on the Carrier Mobility in a Photorefractive Polymer," Arosha Goonesekera, J. Bai, S. Ducharme, J. M. Takacs, L. Lu, SPIE Conference on *Organic Photorefractive Materials and Xerographic Photoreceptors VI*, 21-24 July 1998. Oral presentation.

"A Study Concerning the Effect of Polar Molecules on Carrier Mobility in Photorefractive Polymers," Arosha Goonesekera and S. Ducharme, *Second Workshop on Transport in Organic Materials*, 21-22 March 1998, Albuquerque. Invited Oral Presentation.

"Photorefractive Dendrimers," Kelly Newsome, J. M. Takacs, L. Liu, A. Leonov, S. Ducharme, A. Goonesekera, and J. Bai, AAPT Summer Meeting, 4-8 August 1998, Lincoln, NE. Poster presentation.

"The Synthesis and Characterization of Dendrimers for Potential Photorefractive Applications," Jaeil Bai, Stephen Ducharme, A. Goonesekera, A. P. Leonov, L. Lu, and James M. Takacs, *Organic Thin Films for Photonics Applications Topical Meeting*, Boston, 23-27 August 1998. Oral presentation.

"Photorefractive Dendrimers," J. Bai, S. Ducharme, L. Liu, A. Leonov, J. M. Takacs, *Optical Society of America Annual Meeting*, Santa Clara, 27 September-1 October 1999. Poster presentation.

"Charge-Carrier Mobility Studies of Potential Photorefractive Dendrimers," A. P. Leonov, Stephen Ducharme, L. Lu, and James M. Takacs, *Symposium on Organic Thin Films for Photonics Applications*, Washington, 20-25 August 2000. Oral presentation.

Consultative and Advisory Functions

None

c. Transitions

None

8. New Discoveries, Inventions, or Patent Disclosures

None

9. Honors/Awards

None

AFOSR Grant/Contract Summary

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PI Names: Stephen Ducharme and James M. Takacs

Institution: University of Nebraska-Lincoln

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(listed below)

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(listed below)

(3) Number of graduate students supported by AFOSR: 3
(listed below)

(4) Other researchers supported by AFOSR: 1
(listed below)

(5) Number of publications by PI's in refereed journals 3

(6) Number of publications (in refereed journals only) that acknowledge AFOSR support: 3

(7) Awards and Honors received by the PI (life-time received): 0

ADDITIONAL INFORMATION:

(1) PI and Co-PI: Assoc. Prof. Stephen Ducharme, Department of Physics and Astronomy
Prof. James M. Takacs, Department of Chemistry
(both, UNL Center for Materials Research and Analysis)

(2) Postdoc: Dr. Liu Lu, Department of Chemistry

(3) PhD Students: Arosha Goonesekera, Physics and Astronomy
Jaeil Bai, Physics and Astronomy
Alexie Leonov, Chemistry

(4) Undergraduate: Jennifer Webster, Physics and Astronomy