

AFRL-ML-WP-TP-2007-546

**POLYMER FILM WITH OPTICALLY
CONTROLLED FORM AND
ACTUATION (Postprint)**

**Timothy Bunning, Nelson Tabiryan, Svetlana Serak,
and Xiao-Man Dai**



SEPTEMBER 2006

Approved for public release; distribution unlimited.

STINFO COPY

© 2005 OSA

The U.S. Government is joint author of this work and has the right to use, modify, reproduce, release, perform, display, or disclose the work.

**MATERIALS AND MANUFACTURING DIRECTORATE
AIR FORCE RESEARCH LABORATORY
AIR FORCE MATERIEL COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OH 45433-7750**

REPORT DOCUMENTATION PAGE				<i>Form Approved OMB No. 0704-0188</i>					
The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.									
1. REPORT DATE (DD-MM-YY) September 2006		2. REPORT TYPE Journal Article Postprint		3. DATES COVERED (From - To)					
4. TITLE AND SUBTITLE POLYMER FILM WITH OPTICALLY CONTROLLED FORM AND ACTUATION (Postprint)				5a. CONTRACT NUMBER IN-HOUSE					
				5b. GRANT NUMBER					
				5c. PROGRAM ELEMENT NUMBER 62102F					
6. AUTHOR(S) Timothy Bunning (Exploratory Development, Hardened Materials Branch) Nelson Tabiryan, Svetlana Serak, and Xiao-Man Dai (BEAM Engineering for Advanced Measurements Co.)				5d. PROJECT NUMBER 4348					
				5e. TASK NUMBER RG					
				5f. WORK UNIT NUMBER M08R1000					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> Exploratory Development, Hardened Materials Branch Survivability and Sensor Materials Division, Materials and Manufacturing Directorate Air Force Research Laboratory, Air Force Materiel Command Wright-Patterson Air Force Base, OH 45433-7750 </div> <div style="width: 45%;"> BEAM Engineering for Advanced Measurements Co. </div> </div>				8. PERFORMING ORGANIZATION REPORT NUMBER AFRL-ML-WP-TP-2007-546					
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Materials And Manufacturing Directorate Air Force Research Laboratory Air Force Materiel Command Wright-Patterson Air Force Base, OH 45433-7750				10. SPONSORING/MONITORING AGENCY ACRONYM(S) AFRL/MLPJ					
11. SPONSORING/MONITORING AGENCY REPORT NUMBER(S) AFRL-ML-WP-TP-2007-546									
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited.									
13. SUPPLEMENTARY NOTES © 2005 OSA. The U.S. Government is joint author of this work and has the right to use, modify, reproduce, release, perform, display, or disclose the work. PAO case number AFRL/WS 06-2308, 27 September 2006. Published in Optics Express, 2005, Vol. 13, No. 19. Paper contains color.									
14. ABSTRACT A low power laser beam is used to induce large and fast variations in the shape of a polymer film due to photoinduced contraction and expansion of the polymer film surface subject to the beam. The direction of the photoinduced bend or twist of the polymer can be reversed by changing the polarization of the beam. Thus the film orientation could be varied within $\pm 70^\circ$. The phenomenon is a result of optically induced reorientation of azobenzene moieties in the polymer network.									
15. SUBJECT TERMS polymers, liquid crystals, photochemistry, nonlinear optics, materials, microstructure devices									
16. SECURITY CLASSIFICATION OF: <table border="1" style="width: 100%; border-collapse: collapse; font-size: x-small;"> <tr> <td style="width: 33%; padding: 2px;">a. REPORT Unclassified</td> <td style="width: 33%; padding: 2px;">b. ABSTRACT Unclassified</td> <td style="width: 33%; padding: 2px;">c. THIS PAGE Unclassified</td> </tr> </table>			a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified	17. LIMITATION OF ABSTRACT: SAR		18. NUMBER OF PAGES 14	
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified							
19a. NAME OF RESPONSIBLE PERSON (Monitor) Timothy Bunning			19b. TELEPHONE NUMBER (Include Area Code) (937) 255-4588						
			(937) 255-4588						

Polymer film with optically controlled form and actuation

Nelson Tabiryan, Svetlana Serak, and Xiao-Man Dai

Beam Engineering for Advanced Measurements Corporation, 809 South Orlando Ave., Suite I,
Winter Park, Florida 32789, USA
nelson@beamco.com

Timothy Bunning

Air Force Research Laboratory, Wright-Patterson Air Force Base, Ohio 45433-7707, USA

Abstract: A low power laser beam is used to induce large and fast variations in the shape of a polymer film due to photoinduced contraction and expansion of the polymer film surface subject to the beam. The direction of the photoinduced bend or twist of the polymer can be reversed by changing the polarization of the beam. Thus the film orientation could be varied within $\pm 70^\circ$. The phenomenon is a result of optically induced reorientation of azobenzene moieties in the polymer network.

©2005 Optical Society of America

OCIS codes: (160.5470) Polymers; (160.3710) Liquid crystals; (260.5130) Photochemistry; (190.4400) Nonlinear optics, materials; (230.3990) Microstructure devices.

References and links

1. H. Finkelmann, E. Nishikawa, G. Pereira, and M. Warner, "New opto-mechanical effect in solids," *Phys. Rev. Lett.*, **87**, 015501-1-4 (2001).
2. J. Cviklinski, A. Tajbakhsh, and E. Terentjev, "UV isomerization in nematic elastomers as a route to photo-mechanical transducer," *Eur. Phys. J.* **E9**, 427-434 (2002).
3. P. Hogan, A. Tajbakhsh, and E. Terentjev, "UV manipulation of order and macroscopic shape in nematic elastomers," *Phys. Rev. E* **65**, 041720-1-10 (2002).
4. Y. Yu, M. Nakano, and T. Ikeda, "Directed bending of a polymeric film by light," *Nature* **425**, 145 (2003).
5. T. Ikeda, M. Nakano, Y. Yu, O. Tsutsumi, and A. Kanazawa, "Anisotropic bending and unbending behavior of azobenzene liquid-crystalline gels by light exposure," *Adv. Mater.* **15**, 201-205 (2003).
6. Y. Yu, M. Nakano, A. Shishido, T. Shiono, and T. Ikeda, "Effect of cross-linking density on photoinduced bending behavior of oriented liquid-crystalline network films containing azobenzene," *Chem. Mater.* **16**, 1637-1643 (2004).
7. M. Camacho-Lopez, H. Finkelmann, P. Palffy-Muhoray, and M. Shelley, "Fast liquid-crystal elastomer swims into the dark," *Nature* **3**, 307-310 (2004).
8. A. Makushenko, O. Stolbova, and B. Neporent, "Reversible orientational photodichroism and photoisomerization of aromatic azo-compounds," *Opt. Spectr.* **31**, 295-302 (1971).
9. M. Eich, J. Wendroff, B. Reck, H. Ringsdorf, and H. Schmidt, "Nonlinear optical self-diffraction in a mesogenic side chain polymer," *Macromol. Chem.* **186**, 2639-2647 (1985).
10. U. Wiesner, N. Reynolds, C. Boeffel, and H. W. Spiess, "An infrared spectroscopic study of photo-induced reorientation in dye containing liquid-crystalline polymers," *Liq. Cryst.* **11**, 251-267 (1992).
11. N. Holme, L. Nikolova, T. Norris, S. Hvilsted, M. Pederson, R. Berg, P. Rasmussen, and P. Ramanujam, "Physical processes in azobenzene polymers on irradiation with polarized light," *Macromol. Symp.* **137**, 83-103 (1999).
12. O. Yaroshchuk, Yu. Zakrevskyy, A. Kiselev, J. Stumpe, and J. Lindau, "Spatial reorientation of azobenzene side groups of a liquid crystalline polymer induced with linearly polarized light," *Eur. Phys. J.* **E6**, 57-67 (2001).
13. C. Kempe, M. Rutloh, and J. Stumpe, "Photo-orientation of azobenzene side chain polymers parallel or perpendicular to the polarization of red He-Ne light," *J. Phys.: Condens. Matter.* **15**, S813-S823 (2003).
14. O. Tsutsumi, Y. Demachi, A. Kanazawa, T. Shiono, T. Ikeda, and Yu. Nagase, "Photochemical phase-transition behavior of polymer liquid crystals induced by photochemical reaction of azobenzenes with strong donor-acceptor pairs," *J. Phys. Chem. B* **102**, 2869-2874 (1998).

15. H.-K. Lee, K. Doi, A. Kanazawa, T. Sciono, T. Ikeda, T. Fujisawa, M. Aizawa, and B. Lee, "Light-scattering-mode optical switching and image storage in polymer/liquid crystal composite films by means of photochemical phase transition," *Polymer* **41**, 1757-1763 (1999).
16. N. Tabiryan, S. Serak, and V. Grozhik, "Photoinduced critical opalescence and reversible all-optical switching in photosensitive liquid crystals," *J. Opt. Soc. Am. B* **20**, 538-544 (2003).
17. N. Tabiryan, U. Hrozhyk, and S. Serak, "Nonlinear refraction in photoinduced isotropic state of liquid crystalline azobenzenes," *Phys. Rev. Lett.* **93**, 113901-1-4 (2004).

1. Introduction

Polymer networks containing azobenzene liquid-crystalline (LC) moieties are capable of changing their macroscopic shape when influenced by light [1-7]. Mechanical deformation of azobenzene polymer films is a result of the effects optical radiation has on LC ordering due to photoisomerization of azo molecules that are incorporated into the chemical structure of LCs or are present in the LC network as dopants. There are two distinct processes taking place in LC due to *trans-cis* photoisomerization of azobenzene chromophores: reorientation normal to the light polarization [8-13], and decrease in the LC ordering followed by phase transition in the polymer network [14-17]. Both processes can contribute into opto-mechanical properties of azo LC networks. The relative contribution and strength of each process is determined by the wavelength of radiation. Radiation at UV wavelengths corresponds to the maximum of the absorption of azo molecules, consequently, the rate of *trans-cis* isomerization prevails on the orientational effect leading to nematic-isotropic phase transition. Radiation at longer (visible) wavelengths is at the edges of the absorption band of *trans*-isomers and is substantially absorbed by *cis*-isomers as well resulting in reverse *cis-trans* isomerization. The sequence of *trans-cis* isomerization processes followed by *cis-trans* isomerization results in orientation of the molecules perpendicular to the polarization of the beam.

Recently, Ikeda *et al.* demonstrated large UV light induced bending of a single film of LC network containing azobenzene chromophore [4]. The bend direction of the film heated to 85°C was controlled with direction of light polarization at the wavelength 366 nm, and the initial flat shape of the polymer could be restored with visible light at 540 nm wavelength. The bend was unidirectional, towards the source of radiation. The process takes place within several seconds. More than two orders of magnitude faster photomechanical response was observed in an LC elastomer doped by an azobenzene dye under the influence of argon-ion laser radiation with the wavelength 514 nm in region of the absorption maximum of the dye (495 nm) [7]. Close to 45° bending was realized at the influence of 600 mW laser beam power, and around 67° bending was achieved at 1.3 W incident power. The thermal effects should prevail in such a high power radiation in highly absorbing material as thick as 320 μm, and the apparent mechanism of bending was considered to be heating due to linear absorption in addition to photoisomerization-induced reduction of the orientational order of the LC.

In this paper we report about laser-induced variations of the form of azo LC polymer films that are characterized by: 1) the capability of being controlled with a single laser beam; 2) reversible bi-directional bending of the polymer by switching the polarization of the beam in orthogonal directions; 3) large range, over $-70^\circ < \alpha < 70^\circ$, of deformation angles; 4) high speed of photoinduced deformations (170°/s); and, finally, 5) room temperature operation. In addition, the photomechanical effect is obtained in thin polymer layers (10-50 μm) and can be controlled with low power density radiation ($\sim 0.1 \text{ W/cm}^2$).

2. Experimental results

The polymer network was made following the method described in Ref. [4]. Two monomers: 4,4'-Di(6-acryloxyalkyloxy)azobenzene and LC monomer 4-(6-acryloxy)hexyloxy-4'-ethoxyazobenzene were copolymerized at 100°C by the use of 1,1'-azobis(cyclohexane-1-carbonitrile) as thermal initiator. Polymerization was performed between two glass substrates separated by 10-50 μm thick spacers. To align the azo LC moieties, the glass substrates were

coated with poly(vinyl alcohol) and rubbed. After thermal polymerization the polymer film was separated from the substrates. Then it was sliced into rectangular pieces of different size, typically, 2 mm x 5 mm.

Such rectangular slices of the polymer, a lower edge fixed to a platform, were exposed to linearly polarized beam of a cw argon-ion laser with no mode selection. The beam was expanded to the film size and directed normal to the film. Bending deformation of the film upon exposure to the beam is observed when the film alignment is parallel ($\mathbf{E} \parallel \mathbf{n}$) or orthogonal ($\mathbf{E} \perp \mathbf{n}$) to the beam polarization, Fig. 1 (a, b). Photos of experimentally obtained deformation of the polymer film are shown in Fig. 2. The polymer film bends away from the laser when $\mathbf{E} \perp \mathbf{n}$ (Figs. 1(a), 2(b)), and it is bowing towards the laser when $\mathbf{E} \parallel \mathbf{n}$ (Figs. 1(b), 2(c)). In case the beam polarization makes 45° angle with respect to the orientation axis of the polymer film (coinciding with the LC orientation during the curing process), the film is folding clockwise or counter-clockwise depending on whether the angle made by the polarization and LC axis is 45° or -45° , Fig. 2 (e, f). The film maintains the optically-induced shapes if the beam is switched off.

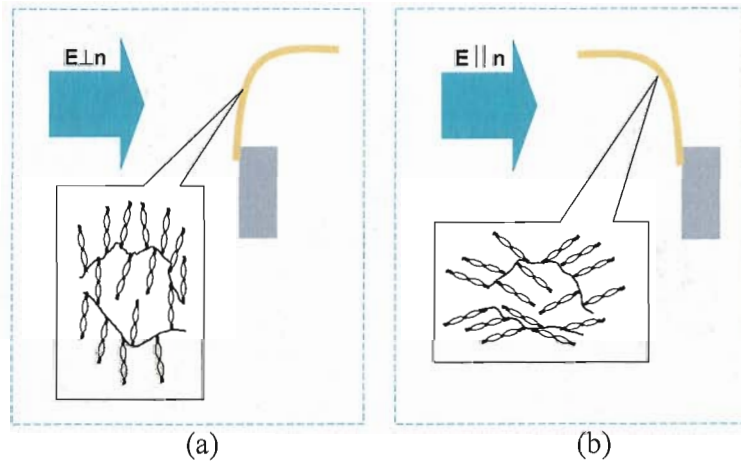


Fig. 1. Schematic of experimental geometry and the effect of laser-induced LC alignment. The block arrow shows the direction of laser beam incidence. Reorientation of azo LC molecules orthogonal to the beam polarization results in expansion (a) or contraction (b) of the input surface of the film and its bending away or towards the laser beam, correspondingly.

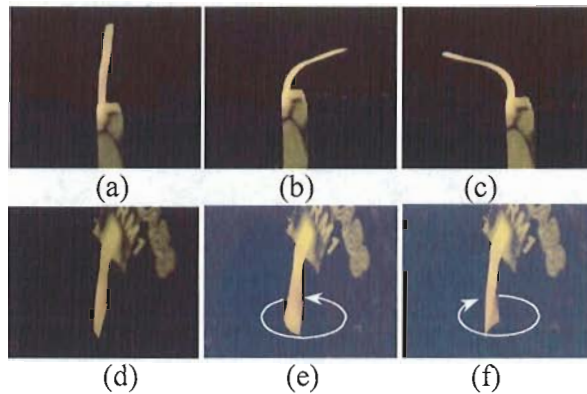


Fig. 2. Photos of optically induced polymer deformation obtained in the experiment. (a) The azo LC polymer film (1 mm x 7 mm x 20 μm) is vertically attached to a platform (side view); (b) the polymer is bent away from the laser for the beam polarized perpendicular to the film orientation; (c) and it is bent towards the laser if the polarization is along the film orientation; (d) the polymer film (2 mm x 12 mm x 20 μm) used for inducing twist deformations with a laser beam of tilted polarization; (e) counter-clockwise folding of the polymer film for -45° polarization; (f) clockwise folding of the film for 45° polarization. The power density of the laser beam is 0.25 W/cm^2 . (Movie: 1.4 Mb)

Whereas the sign of deformation is determined by the laser beam polarization, the magnitude of deformation depends on its intensity. Figure 3 shows the magnitude of the bend angle increasing with increasing power density for polarization parallel and perpendicular to the LC orientation imposed when curing the polymer. The process takes place above some threshold intensity of the beam, approximately equal to 0.1 W/cm^2 for 20 μm -thick films. The value of the threshold intensity was different for different shapes of the film, however, varying in a small range $0.1 \dots 0.3 \text{ W/cm}^2$.

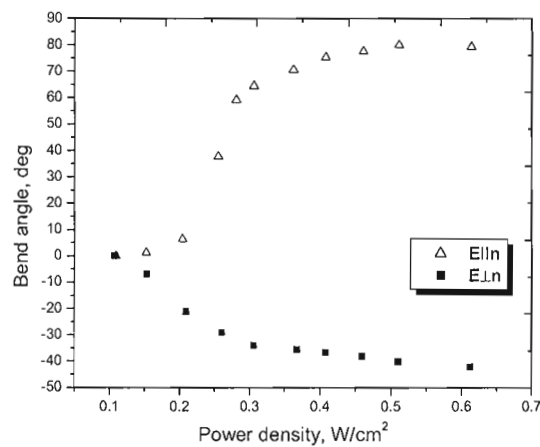


Fig. 3. Bend angle of a polymer film (3 mm x 7 mm x 20 μm) as a function of power density of the laser beam for polarization parallel and perpendicular to LC orientation imposed at curing.

The deformation of the polymer film is very fast, Fig. 4; complete 70° bending from vertical position (Fig. 2(a)) is achieved during 400 ms, which corresponds to an average

angular speed 170 degrees/s. We could swing the film back and forth at few Hz frequency by switching the beam polarization. Complete sway from negative to positive end of the bend angles (-70° rad to 70° rad) could be reached in 1.3 s by switching the beam polarization from $\mathbf{E} \perp \mathbf{n}$ to $\mathbf{E} \parallel \mathbf{n}$. Let us note that the features of optically controlled bending are not affected by the way the film is being fixed to its platform: vertically up, vertically down, or horizontally.

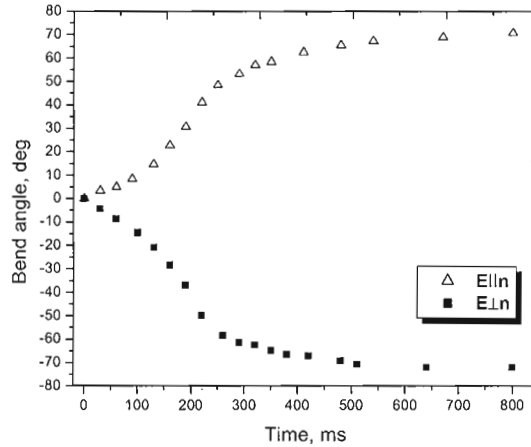


Fig. 4. Deformation dynamics of the polymer film (1 mm x 7 mm x 20 μm) at the power density of the laser beam equal to 0.25 W/cm².

3. Discussion

Polarization dependence of the deformation sign excludes laser heating (modulation of temperature - a scalar parameter) from the list of candidate mechanisms to account for the results of observations. Consider the effects of *trans-cis* photoisomerization of LC moieties which prevail in azo LC materials in the presence of low power laser beams. Photogeneration of *cis* isomers that reduces the orientational order driving the LC towards its isotropic phase is similar to the effect of heat and therefore cannot be accounted for the change of the deformation sign with switching of light polarization. The only microscopic process that changes sign with changing polarization direction is optically-induced realignment of LC chromophores and ordering of polymeric chains. This process resulting from subsequent *trans-cis-trans* photoisomerization is apparently dominant at argon-ion laser wavelengths.

The hypothesis about orientation of azo LC moieties and related polymer network perpendicular to the laser beam polarization provides a clear picture of the photomechanical effect. Orientation shrinks the volume of the polymer along the polarization direction and expands it along the direction perpendicular to it. In other words the compression force is acting along the polarization direction. By that, the changes in sizes take place most strongly in areas close to the input surface of the incident beam. The areas closer to the beam exit surface are not much affected due to strong attenuation of light caused by absorption and scattering. Thus, if the polymer film is hold in vertical direction by fixing one of its edges along a horizontal platform, and the incident beam polarization is in the vertical plane, shrinking of the input surface in vertical direction results in bending of the film towards the laser. In case the beam polarization is in the horizontal plane, the expansion of the input surface in the vertical direction bends the film backwards, away from the laser. Deformations for other states of polarization can be described from this standpoint as well.

Measurement of nonlinear transmission of the polymer film provided additional evidence about the orientational nature of underlying processes. Namely, we observed that the transmission of the film increased with increasing power density of radiation, Fig. 5. Both, decreasing order parameter and orientation of the azo LC perpendicular to the beam polarization could result in such an enhancement of transmission. The first mechanism, reduced order parameter, would, however, lead to convergence of the transmission levels for horizontally and vertically polarized beams. In our case, the transmission increases at lower power densities for perpendicular polarization of the laser beam with respect to the preferred axis of the polymer saturating at considerably higher levels compared to the transmission achieved for the beam with parallel polarization.

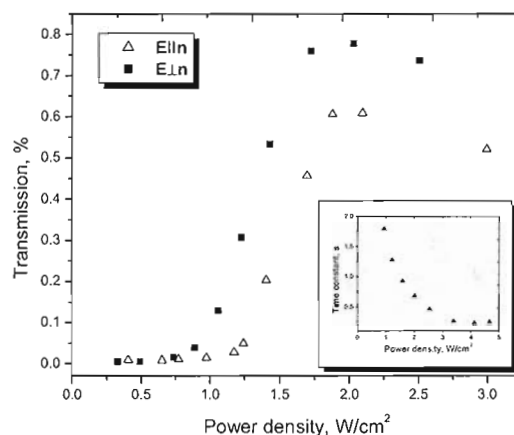


Fig. 5. Transmission and response time (inset) of the polymer film vs power density of incident beam. The film of 2 mm x 12 mm x 20 μm sizes was used in these measurements. The laser beam was not focused. The ratio of the output power to input power was registered with a power meter.

It is well known that the rubbing direction of the cell substrates induces a preferred orientation of LC molecules and the associated network. The residual anisotropy of the network in a free-standing polymer film removed from the substrate acts as an internal orienting field on mesogenic fragments of the system. Consequently, if the material is subject to a beam with polarization perpendicular to the polymer axis, the anisotropy of the network helps the molecules to orient perpendicular to the polarization and parallel to the polymer axis. In case of parallel polarization, the internal orienting field of the polymer compromises the effect of radiation that tends to orient the LC molecules perpendicular to the preferred axis of the polymer. Hence, the final transmission state is lower in this case. This type of behavior for azobenzene LCs was reported in [16] where fast and complete recovery of the planar orientation of azo LCs was observed for a laser beam polarized perpendicular to the rubbing direction of the LC cell substrates whereas the beam of parallel polarization would result in a low state of transmission. Note that all effects of photoactuation take place for low power density values, below the threshold of observations of changes in the transmission of the film.

4. Conclusions

Thus, we report about an azo LC polymer film with extraordinarily strong and fast mechanical response to the influence of a laser beam. In difference from previously develop material systems, this polymer is functional at room temperature, and its shape can be controlled by a low power single laser beam. Most importantly, the material is distinguished by the

opportunity it provides for controlling not only the magnitude but as well the sign of photoinduced deformation by the polarization state of the beam. Indeed, there are many questions that still need to be answered, quantitative models to be developed, and many interesting opportunities could be explored using such materials, including Micro-Opto-Mechanical Systems (MOMS) that could be created in a process of spatially distributed photopolymerization.

Acknowledgments

The authors are grateful to I.C. Khoo for valuable discussions and to WPAFB SBIR program for support of the work.