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Video-rate compatible photorefractive polymers with stable dynamic properties under continuous operation

Canek Fuentes-Hernandez,^{a)} Jayan Thomas, Roberto Termine,^{b)} Gerald Meredith, Nasser Peyghambarian, and Bernard Kippelen^{c)}
Optical Sciences Center, University of Arizona, Tucson, Arizona 85721

Steve Barlow,^{d)} Gregory Walker,^{d)} and Seth R. Marder^{d)}
Department of Chemistry, University of Arizona, Tucson, Arizona 85721

Michiharu Yamamoto, Kevin Cammack, and Kenji Matsumoto
Nitto Denko Technical Corporation, Oceanside, California 92054

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We report on photorefractive polymer composites that exhibit stable dynamic properties under continuous operation. These materials are based on a bis-triarylamine side-chain polymer matrix with a low ionization potential. The evolution of the response time for exposures up to 4 kJ/cm² was studied and compared with that obtained in poly(*n*-vinylcarbazole) (PVK) based composites. In the composites, operational stability is combined with video-rate compatible dynamics, large dynamic range at moderate fields, and long shelf lifetimes. © 2004 American Institute of Physics. [DOI: 10.1063/1.1787956]

For more than a decade, photorefractive (PR) polymers have been an active area of research because of their applications in real-time optical processing. To date, most attention was given to the study and improvement of their dynamic range, response time, and shelf lifetimes. Surprisingly, less consideration was given to the changes and degradation of essential properties, such as diffraction efficiency and response time under continuous operation. Such an operational stability is required if a PR composite is to be inserted into commercially viable optical systems.

In this letter, we report on PR polymer composites, with stable performance under continuous operation, that combine high dynamic range, video-rate compatible dynamic response, and long shelf lifetimes at room temperature. Stability improvements over previously known materials were achieved by using a bis-triarylamine side-chain polymer matrix, a polymer with a low ionization potential and good transport properties.

It is well established that photorefractive polymers can have trap densities that are changing with the sample's optical exposure history under various electric fields.¹ For instance, it has been shown that the active trap density is not constant in poly(*n*-vinylcarbazole) (PVK)-based materials and that performance can be greatly enhanced when traps are first optically generated^{1,2} during an initial uniform exposure of the sample. Unfortunately, prolonged optical exposure during operation can create an excess of traps that reduces the photoconductive response³⁻⁵ and ultimately deteriorates the temporal response of hologram formation. The accumulation of these traps correlates with an increase of the sensi-

tizer radical anions.¹ In PVK-based materials sensitized by C₆₀, the rate of formation and total density of C₆₀ radical anions (active traps) was found to correlate with the existence of compensating radical cations formed on the chromophores (inactive traps).¹ The formation of these radical cations is favored if the ionization potential (*I_p*) of the chromophore is lower than that of the transport manifold matrix (i.e., 5.9 eV for PVK).^{1,3-5} Since a majority of chromophores with large photorefractive figure of merit have an *I_p* smaller than or comparable to that of PVK,⁶⁻⁸ a long-term degradation of the PR properties was observed⁴ and is to be expected as the materials are under continuous operation. In previous work, we increased the *I_p* of the chromophore to reduce the formation of the compensating radical cations, and consequently reducing the accumulation of photoconductive traps. Unfortunately, our approach, which was to increase the *I_p* of styrene chromophores, was also accompanied by a decrease of the photorefractive dynamic range.⁴

Here, instead of adjusting the energy of the frontier orbitals of the chromophores, we designed a transport manifold with a low *I_p*. In this approach, chromophores are less likely to act as inactive traps, thus reducing the accumulation of active traps. To test this approach, we selected the chromophores: 4-homopiperidinobenzylidenemalononitrile (7DCST) with and *I_p* of 5.9 eV, and 3-(*N*, *N*-di-*n*-butylaniline-4-yl)-1-dicyanomethylidene-2-cyclohexen (DBDC), with *I_p* of 5.6 eV; and synthesized a new hole-transporting polymer matrix referred to as PATPD that has an *I_p* of 5.4 eV. This polymer consists of a polyacrylate backbone with pendant tetra-phenyl-diphenyldiamine (TPD) units attached through alkyl chains. All the electrochemical characterization was done in acetonitrile solutions. The synthesis of PATPD will be reported elsewhere. A series of similar polyacrylate TPD polymers have previously been used in PR composites.⁹ The synthesis of these hole-transport matrices was motivated by the possibility of having higher drift mobilities⁹ (~100 times) than in PVK, however, no significant improvement over high-speed¹⁰ PVK-based materials

^{a)} Author to whom correspondence should be addressed; electronic mail: canek@u.arizona.edu

^{b)} Present address: Dipartimento di Chimica, Università della Calabria, 87036 Arcavacata di Rende, Italy.

^{c)} Present address: School of Electrical and Computer Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332.

^{d)} Present address: School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332.

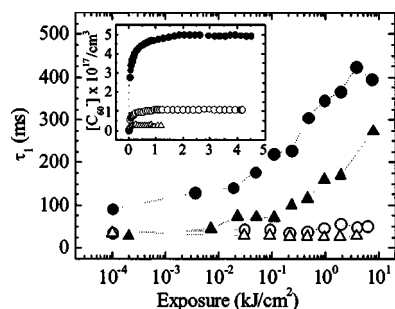


FIG. 1. Exposure dependence of the dominant time constant (τ_1) at $48 \text{ V}/\mu\text{m}$ in samples C1(Δ), C2(\circ), R1(\blacktriangle), and R2(\bullet). Total writing beam intensity $1.1 \text{ W}/\text{cm}^2$. Inset shows *in situ* exposure dependence of the C_{60} radical anion concentration determined spectroscopically in samples C1(Δ), C2(\circ), and R2(\bullet).

was found, nor have been reported following this approach.

The composites under study have the following composition: PATPD/ECZ/7DCST/ C_{60} (49.5/15/35/0.5 wt. %) and PATPD/ECZ/DBDC/ C_{60} (49.5/20/30/0.5 wt. %). Samples of both composites, referred to as C1 and C2, respectively, were prepared by laminating $105\text{-}\mu\text{m}$ -thick layers between glass slides with indium-tin-oxide electrodes. At room-temperature sample, C1 showed good phase stability for a period of several months, but at 60°C , signs of phase separation were observed after a couple of hours. In contrast, samples C2 neither have shown signs of phase separation for more than a year, nor under accelerated aging conditions at 60°C for more than a week. In differential scanning calorimetry experiments, both composites displayed a broad thermal transition indicative of a glass transition temperature T_g of around 40°C . The ability of the chromophores to reorient under the influence of an electric field was confirmed using transient ellipsometric measurements.¹¹ To compare the stability of the PR response under continuous operation, two reference composites referred to as R1 and R2, were prepared replacing PATPD with PVK but otherwise having identical composition to samples C1 and C2, respectively.

The growth of the characteristic absorption band of C_{60} near 1080 nm was followed *in situ* while a sample was exposed to a 635-nm -laser beam, providing an intensity of $0.5 \text{ W}/\text{cm}^2$, and biased at $57 \text{ V}/\mu\text{m}$, and the concentration of anions calculated as previously reported in the literature.¹ The inset of Fig. 1 shows that C-type samples have C_{60} anion densities that are significantly smaller than those of R-type samples. The latter are in good agreement with values reported in other PVK-based composites.^{1,3,4}

To assess the role of the accumulation of C_{60} anions on the dynamic response, the exposure dependence of the grating dynamics was measured. The dynamic response was determined by transient four-wave mixing experiments (TFWM) at $48 \text{ V}/\mu\text{m}$. Discrete samplings of the grating buildup and erasure were taken over the exposure time. During exposure the sample was electrically biased at $57 \text{ V}/\mu\text{m}$. Before each sampling, (except the initial one) the electric field was adjusted from the exposure to the test value on the presence of a single writing beam, then a TFWM experiment was carried out by switching on and off the second writing beam, and finally the field was adjusted back to the exposure value and exposure to a single beam continued until the next sampling was taken. A tilted-geometry configuration was used where the writing beams were incident on the sample with an interbeam angle of 20.5° in air and the surface

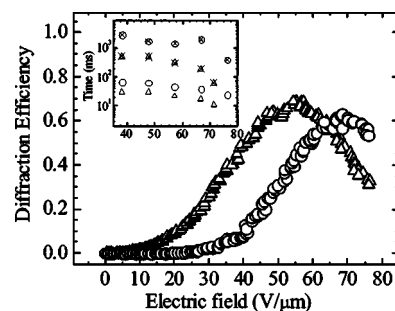


FIG. 2. Applied electric-field dependence of external diffraction efficiency for sample C1(Δ) and C2(\circ), after samples being exposed beyond $4 \text{ kJ}/\text{cm}^2$. Inset shows the applied electric-field dependence of time constants, τ_1 (open symbols), and τ_2 (crossed symbols), as determined by using a sine-squared weighted biexponential fit in samples C1 (triangles) and C2 (circles) after samples being exposed beyond $4 \text{ kJ}/\text{cm}^2$. Total writing-beam intensity is $1.1 \text{ W}/\text{cm}^2$.

sample normal was tilted 60° with respect to the writing-beam bisector. The TFWM data were fitted using sine-squared weighted biexponential function.¹¹ The evolution of the fast time constant (τ_1) in all samples as a function of exposure is shown in Fig. 1. A remarkable stability of τ_1 was observed in C-type samples as compared with the rapidly degrading response times in the PVK-based composites. The erasure of the grating under one writing beam was also fitted by a biexponential function, and yielded dominant time constants below 20 ms in C-type samples, accounting for more than 70% of the transient, for all exposure values. In contrast, R-type samples exceeded 100 ms for exposures above $100 \text{ J}/\text{cm}^2$. Video-rate compatible response times were observed in C-type samples even after samples were exposed beyond exposures of $4 \text{ kJ}/\text{cm}^2$ at a field of $57 \text{ V}/\mu\text{m}$ (see inset of Fig. 2). Typical weighting factors (m) varied from 0.63 to 0.68 for C1 and from 0.74 to 0.81 for C2.

Steady-state FWM and two-beam coupling (TBC) experiments were carried out after the samples were exposed beyond exposures of $4 \text{ kJ}/\text{cm}^2$ at $57 \text{ V}/\mu\text{m}$. External diffraction efficiencies, shown in Fig. 2, were limited by absorption, and to some extent to scattering in C1. As shown in Fig. 3, TBC experiments yielded net gain in C1 and C2 samples with absorption coefficients of 18 and 39 cm^{-1} , respectively. These gain values are similar to the ones reported in the literature for PVK-based materials.⁷

In summary, we have developed photorefractive polymer composites with stable performance under continuous operation that combine high dynamic range, video-rate compatible dynamic response, and long shelf lifetimes at room tempera-

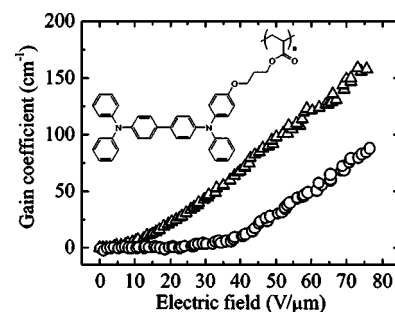


FIG. 3. Applied electric field dependence of the gain coefficient for samples C1(Δ) and C2(\circ), after samples being exposed beyond $4 \text{ kJ}/\text{cm}^2$. TBC done with 1:1 *p*-polarized beams providing a total fluence of $1.1 \text{ W}/\text{cm}^2$. Inset: structure of PATPD.

ture. Operational stability was achieved by using the low ionization potential matrix PATPD (see Fig. 3). Stable dynamic response could be maintained for exposures up to 4 kJ/cm². Considering a 50-ms write-erase cycle at an intensity of 0.5 W/cm², these samples could undergo more than 160 000 cycles without significant degradation of their PR properties. This makes them very attractive for real-time optical processing applications and brings these materials one step closer to practical applications.

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¹D. Grunnet-Jepsen, B. Wright, M. Smith, S. Bratcher, M. S. DeClue, J. S.

Siegel, and W. E. Moerner, *Chem. Phys. Lett.* **291**, 553 (1998).

²E. Mecher, F. Gallego-Gómez, H. Tillmann, H. Hörhold, J. C. Hummelen, and K. Meerholz, *Nature (London)* **418**, 959 (2002).

³E. Hendrickx, Y. D. Zhang, K. B. Ferrio, J. A. Herlocker, J. Anderson, N. R. Armstrong, E. A. Mash, A. P. Persoons, N. Peyghambarian, and B. Kippelen, *J. Mater. Chem.* **9**, 2251 (1999).

⁴J. A. Herlocker, C. Fuentes-Hernandez, K. B. Ferrio, E. Hendrickx, P.-A. Blanche, N. Peyghambarian, B. Kippelen, Y. Zhang, J. F. Wang, and S. R. Marder, *Appl. Phys. Lett.* **77**, 2292 (2000).

⁵O. Ostroverkhova and K. D. Singer, *J. Appl. Phys.* **92**, 1727 (2002).

⁶D. Wright, U. Gubler, Y. Roh, W. E. Moerner, M. He, and R. J. Twieg, *Appl. Phys. Lett.* **79**, 4274 (2001).

⁷M. A. Díaz-García, D. Wright, J. D. Casperson, B. Smith, E. Glazer, and W. E. Moerner, *Chem. Mater.* **11**, 1784 (1999).

⁸F. Würthner, R. Wortmann, and K. Meerholz, *ChemPhysChem* **3**, 17 (2003)

⁹K. Ogino, T. Nomura, T. Shichi, S. Park, H. Sato, T. Aoyama, and T. Wada, *Chem. Mater.* **9**, 2768 (1997).

¹⁰D. Wright, M. A. Diaz-Garcia, J. D. Casperson, M. DeClue, W. E. Moerner, and R. Twieg, *Appl. Phys. Lett.* **73**, 1490 (1998).

¹¹A. Herlocker, K. B. Ferrio, E. Hendrickx, B. D. Guenther, S. Mery, B. Kippelen, and N. Peyghambarian, *Appl. Phys. Lett.* **74**, 2253 (1999).