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Citation: Appl. Phys. Lett. 85, 1877 (2004); doi: 10.1063/1.1787956
View online: http://dx.doi.org/10.1063/1.1787956
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v85/i11
Published by the American Institute of Physics.

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

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(Received 3 February 2004; accepted 30 June 2004)

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/cm^2 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. 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 during an initial uniform exposure of the sample. Unfortunately, prolonged optical exposure during operation can create an excess of traps that reduces the photoconductive response and ultimately deteriorates the temporal response of hologram formation. The accumulation of these traps correlates with an increase of the sensitizer radical anions. In PVK-based materials sensitized by C_{60}, the rate of formation and total density of C_{60} radical anions (active traps) was found to correlate with the existence of compensating radical cations formed on the chromophores (inactive traps). The formation of these radical cations is favored if the ionization potential of the chromophore is lower than that of the transport manifold matrix (i.e., 5.9 eV for PVK). Since a majority of chromophores with large photorefractive figure of merit have an I_p smaller than or comparable to that of PVK, a long-term degradation of the PR properties was observed 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 photococonductive 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.

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 cyclo-hexen (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. The synthesis of these hole-transport matrices was motivated by the possibility of having higher drift mobilities (~100 times) than in PVK, however, no significant improvement over high-speed PVK-based materials.
The inset of Fig. 1 shows that C-type samples have C\textsubscript{60} anion concentration determined spectroscopically in samples C\textsubscript{1} and C\textsubscript{2}, and R2\textsuperscript{○}. The stability of the PR response under continuous operation, two reference composites and C\textsubscript{2}, were prepared replacing PATPD with PVK but otherwise having identical composition to samples C\textsubscript{1} and C\textsubscript{2}, respectively.

The growth of the characteristic absorption band of C\textsubscript{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 W/cm\textsuperscript{2}, and biased at 57 V/\mu m, and the concentration of anions calculated as previously reported in the literature. The inset of Fig. 1 shows that C-type samples have C\textsubscript{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.

To assess the role of the accumulation of C\textsubscript{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 V/\mu m. Discrete samplings of the grating buildup and erasure were taken over the exposure time. During exposure the sample was electrically biased at 57 V/\mu 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 sample normal was tilted 60° with respect to the writing-beam bisector. The TFWM data were fitted using single-squared weighted biexponential function. The evolution of the fast time constant (\tau\textsubscript{f}) in all samples as a function of exposure is shown in Fig. 1. A remarkable stability of \tau\textsubscript{f} 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 J/cm\textsuperscript{2}. Video-rate compatible response times were observed in C-type samples even after samples were exposed beyond exposures of 4 kJ/cm\textsuperscript{2} at a field of 57 V/\mu m (see inset of Fig. 2). Typical weighting factors (m) varied from 0.63 to 0.68 for C\textsubscript{1} and from 0.74 to 0.81 for C\textsubscript{2}.

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

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-

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**FIG. 1.** Exposure dependence of the dominant time constant (\tau\textsubscript{f}) at 48 V/\mu m in samples C1(●), C2(○), R1(△), and R2(●). Total writing beam intensity 1.1 W/cm\textsuperscript{2}. Inset shows in situ exposure dependence of the C\textsubscript{60} radical anion concentration determined spectroscopically in samples C1(△), C2(○), and R2(●).

**FIG. 2.** Applied electric-field dependence of external diffraction efficiency for sample C1(△) and C2(○), after samples being exposed beyond 4 kJ/cm\textsuperscript{2}. Inset shows the applied electric-field dependence of time constants, \tau\textsubscript{f} (open symbols), and \tau\textsubscript{e} (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 kJ/cm\textsuperscript{2}. Total writing-beam intensity is 1.1 W/cm\textsuperscript{2}.

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

This work was supported in part by AFOSR, NSF Contract No. ECS-0108696 and through a CAREER Grant (B.K.), the State of Arizona through Proposition 301 Initiative and Nitto Denko Technical Corporation. It made use of STC shared experimental facilities supported by NSF under agreement No. DMR-0120967. C.F.-H. thanks CONACyT for scholarship No. 133376.