Quasipermanent photochemical gratings in a dual use photorefractive polymer composite

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The dual nature of (3-(2-(4-(*N,N*-diethylamino)phenyl)ethenyl)-5,5-dimethyl-1,2-cyclohex-enylidene)propanedinitrile (Lemke-e) allows us to write both quasipermanent and erasable holographic gratings in the same storage volume. In the presence of a triplet excited sensitizer, Lemke-e undergoes a photochemical reaction allowing the creation of quasipermanent photochemical holographic gratings. In addition, applying an electric field to the composite allows the storage of erasable photorefractive holograms in the same location as previously stored permanent photochemical holograms. Photochemical gratings ($\eta > 10\%$) can be written in less than 1 min while photorefractive gratings ($\eta > 50\%$) can be written in less than 1 s. The photochemical gratings have a dark lifetime of several days. © *1999 American Institute of Physics.*
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Photorefractive (PR) polymers are potential replacements for PR crystals. The rapid response times and high diffraction efficiency[1] ($>86\%$) of these polymers, combined with their low cost, has led to their study for various real-time holography applications, such as phase conjugation,[2] imaging through distorting media,[3] digital data storage,[4] and the coupling of light into waveguides.[5]

A subset of the PR crystals, $Bi_{12}SiO_{20}$,[6,7] $Bi_{12}TiO_{20}$,[8] and GaP,[9] have been shown to exhibit a dual grating behavior. In these crystals, photochromic gratings are formed during the photorefractive grating formation process. These dual grating materials are useful for applications which benefit from the interaction between light diffracted from two simultaneous gratings. These applications[10] include, wave front interferometry, image synthesis, logic operations, phase object detection, holographic interferometry, and novel spatial light modulation. Here we introduce a polymer composite capable of simultaneously storing both erasable, photorefractive and quasipermanent, irreversible photochemical (PC) holograms. We have tested the photorefractive properties of our composite between 675 and 820 nm. For the PR effects, an external electric field is applied to enhance the charge generation efficiency, redistribute the photogenerated charges and to orient the nonlinear optical chromophores. We also formed PC gratings in our composite at 675 nm. Thus, gratings may be formed in the following combinations: PC only (at 675 nm with no external field); PC and PR simultaneously (at 675 nm under the application of an external field); or PR only (at wavelengths longer than 715 nm with an applied field). Our composite should prove useful in applications where two simultaneous gratings are desirable or where both long term PC data storage and real-time PR holography are needed, individually.

Our composite consists of the photoconductor poly(*N*-vinylcarbazole) (PVK), the plasticizer butyl benzyl phthalate (BBP), the sensitizer/charge generator C_{60} and the chromophore, (3-(2-(4-(*N,N*-diethylamino)phenyl)ethenyl)-

5,5-dimethyl-1,2-cyclohexenylidene)-propanedinitrile (Lemke-e).[11] Lemke-e performs two functions in our composite. First, it is a chromophore with a large PR molecular figure of merit,[12] allowing the formation of efficient PR gratings. Second, it takes part in certain photochemical reactions when triplet sensitized. These photochemical reactions can be used to write PC gratings. The photochemical reaction begins when a photon is absorbed by one of the singlet energy levels (675 nm) of C_{60}, followed by coupling of this energy into a long lived triplet state (795 nm)[13] through intersystem crossing. The C_{60} then transfers its energy to a Lemke-e molecule through triplet–triplet energy exchange. Finally, two Lemke-e molecules undergo a $2+2$ cycloaddition reaction, resulting in a change in the local absorption of the composite.[14] Interference of two coherent beams of 675 nm light inside the composite results in a local absorption grating (hologram). Recent literature has referred to this reaction as photochromic;[14,15] however, we will refer to it as photochemical or irreversible photochromic (PC) since the reaction is irreversible. The composites studied in this work consisted of Lemke-e 7%/C_{60} 1%/BBP 21%–36%/PVK 72%–56% (LCBP) by weight.

We verified the PR nature of the LCBP composites by performing asymmetric two-beam coupling (TBC) experiments and measured the diffraction efficiency of the gratings using a degenerate four wave mixing (DFWM) technique. The PR experiments were performed with either a Ti–Sapphire laser, tunable between 715 and 820 nm or a 675 nm laser diode. An electric field of 82 V/μm applied to 75-μm-thick samples yielded a TBC gain coefficient of, $\Gamma_p = 156\,cm^{-1}$, for *p*-polarized, 730 nm light. In the DFWM experiments, overmodulation occurred at 110 V/μm for 730 nm light with a maximum external diffraction efficiency of 53% (Fig. 1 inset), corresponding to an index modulation of $\Delta n_{max} = 0.0013$, according to the standard coupled wave theory.[16] Overmodulation was achieved at 80 V/μm, for 675 nm light with a maximum external diffraction efficiency of 12%. The lower diffraction efficiency was due to the high absorption of the LCBP composite at 675 nm. As expected, the PR external diffraction efficiency, η_E, of the composite

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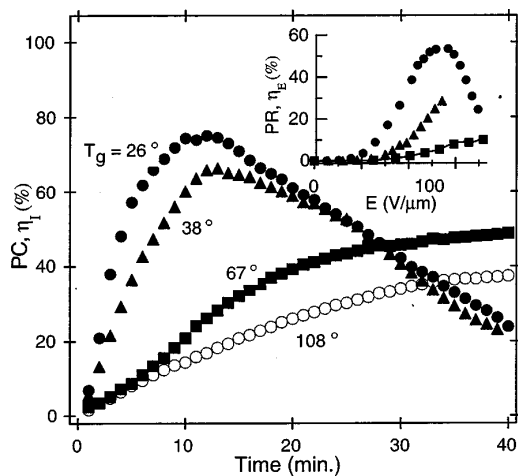[a)]Electronic mail: hayden@umbc.edu

FIG. 1. PC write times and PR diffraction efficiencies vs T_g. The T_g of the polymer composite was determined by the proportion of PVK to BBP used in the composite. The T_g of the samples were, 26 °C (BBP 36%, solid circles), 38 °C (BBP 30%, triangles), 67 °C (BBP 24%, squares), and 108 °C (BBP 21%, hollow circles). The main figure shows the internal diffraction efficiency, $\eta_I =$ (diffracted intensity/transmitted intensity with no grating), of the PC gratings as a function of write beam exposure time. The inset figure shows the T_g dependence of the PR external diffraction efficiency, $\eta_E =$ (diffracted intensity/incident intensity).

FIG. 2. Lifetime of PC holograms in Lemke-e 7%/C_{60} 1%/BBP 21%–36%/PVK 72%–56%. PC gratings were written in the various composites, using 675 nm light at 1.8 W/cm². The main figure shows grating decay during sparse reading; the inset during continuous reading. The grating decay results from the translational motion of the molecules which formed the grating.

decreases as the glass transition temperature (T_g) of the polymer increases (Fig. 1 inset). In high T_g systems, the orientational mobility of the Lemke-e dye molecules decreases, resulting in a diminished orientational enhancement[17] contribution to the grating amplitude.

The PC grating formation was probed using a DFWM configuration. For these experiments, the polymer was pressed between plain glass slides with the sample normal bisecting the two write beams. A slanted geometry was not required since no field was applied to the sample. A 675 nm laser diode was used to generate the coherent s-polarized write beams (1.8 W/cm²), as well as the p-polarized read beam (0.05 W/cm²). The initial slopes of the curves in Fig. 1 yield the sensitivities of the different composites, defined here as the square root of the diffraction efficiency divided by the exposure. The highest sensitivity, $S = 0.0006$ cm²/J ($\lambda = 675$ nm), was observed for the $T_g = 26$ °C system. The sensitivity of the material decreased as the T_g of the material increased. As a result, the time required to write a PC grating increased with the T_g. The increased write time (decreased sensitivity) is due to a decrease in the translational diffusion of the Lemke-e molecules which slows the photochemical process responsible for PC grating formation. This sensitivity is smaller than that reported by Akella, Sochava, and Hesselink[15] for a Lemke-e like chromophore sensitized with C_{60} ($S = 0.06$ cm²/J); however, the chromophore concentration of the composite studied in their paper was 45% by weight, whereas ours is only 7% by weight. As a result, their material contained over four times as many chromophores as our LCBP composites. At higher chromophore concentrations the sensitization of the chromophores and the 2+2 cycloaddition reaction should occur more frequently. We were limited to 7% dye concentration by a tradeoff between the high absorbance of Lemke-e at 675 nm and the need for 675 nm light to produce efficient photochemical gratings. Though not explicitly presented in this letter, we are cur-
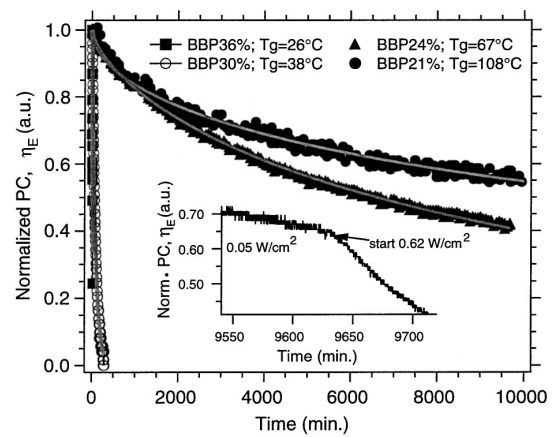
rently attempting to increase the dye concentration in our samples by either using dyes with lower absorbance at 675 nm, or by selecting a triplet sensitizer for Lemke-e that allows us to use longer wavelengths. Our early results show that by using a low absorption chromophore and simply doubling the chromophore concentration, we can increase the sensitivity to $S = 0.003$ cm²/J (sample $T_g = 67$ °C), a factor of 5 increase.

A maximum internal diffraction efficiency, $\eta_I = 74\%$ ($\eta_E = 20\%$) was reached in the BBP 36% ($T_g = 26$ °C) system after writing for 10 min. Since the photochemical grating formation process is irreversible, the decrease in η_I after reaching a maximum value in the low T_g systems is not due to overmodulation, as in the PR effect, but due entirely to the translational diffusion of the molecules that formed the grating. Thus, after a grating is formed, translational diffusion causes the grating to deteriorate in low T_g systems. The translational diffusion is reduced in the higher T_g systems. As a result, the maximum PC grating efficiency in the $T_g = 67$ and 108 °C systems are $\eta_I = 49\%$ and $\eta_I = 37\%$, respectively. Using these values we can make a rough estimate of the maximum number of write cycles that may be performed before all of the chromophores are consumed by the photochemical reaction. For example, assuming a minimum detectable diffraction efficiency of 0.01% and a maximum total diffraction efficiency of $\eta_I = 49\%$ for the 67 °C system, the maximum number of write cycles is roughly 5000.

The effect of translational diffusion on the lifetime of the PC gratings is shown in Fig. 2. After writing a PC grating to its maximum efficiency ($\eta_E \approx 20\%$), the decay in the diffraction efficiency of the grating was periodically probed with a low power density (0.05 W/cm²) read beam of the same wavelength. The exposure time of the read beam was limited to 5 s every 2 min for the 26 and 38 °C systems and to 1 min every hour for the higher T_g systems. The short exposure times minimized the grating decay caused by reading. The decay curves were fit with a Kohlrausch–Williams–Watts stretched exponential function[18,19] $\eta(t) = \eta(0) \times \exp[-(t/\tau)^\beta]$ to determine the time required for a grating to decay to $1/e$ of its original efficiency. The $1/e$ times were 24,
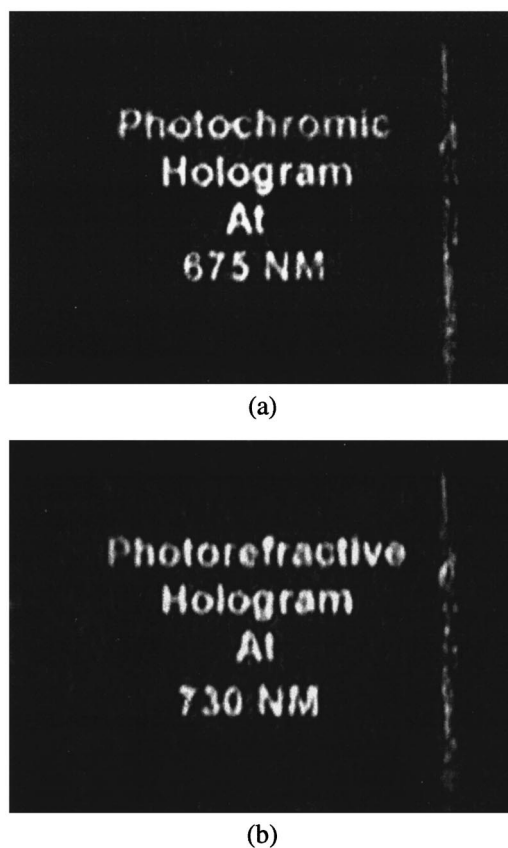
(a)

(b)

FIG. 3. PC and PR holographic storage in the same sample volume. With no electric field applied, the sample was exposed to 675 nm light for 2 min to write the PC image. Exposure for 1 s at 730 nm with 100 V/μm applied recorded the PR image. Subsequent illumination at 675 nm recovered the stored PC image (a). After reading the PC image, switching wavelengths back to 730 nm retrieved the stored PR image (b). The reading cycles could be repeated until the gratings were erased in a time similar to those seen in the DFWM experiments. The vertical lines in the ''H'' are 4 pixels wide, each pixel is 15$\times$15 μm.

91, 11 228 (7.7 days), and 26 201 minutes (18.2 days) for the 26, 38, 67, and 108 °C systems, respectively.

We also performed a short study on the effects of continuously reading a grating. After monitoring the grating decay intermittently, as above, in a $T_g = 108$ °C sample for one week, we read the grating continuously with a 0.05 W/cm^2 read beam and then with a 0.62 W/cm^2 read beam (Fig. 2 inset). We observed a small decay in the grating after 1.5 h of continuous irradiation at 0.05 W/cm^2 while reading with 0.62 W/cm^2 caused rapid erasure of the grating. This type of grating decay can be alleviated by reading with a longer wavelength. For instance, 730 nm light reconstructs PC holograms but does not photochemically alter the material and hence will not cause erasure of the PC holograms.

PC and PR holograms can also be stored in the same location. A LCBP (BBP 36%) composite was placed into a holographic storage setup which incorporated a spatial light modulator and multiple wavelength capability. We then stored and recovered holograms from the same location by illuminating the sample with the appropriate wavelength (Fig. 3). Illumination by either 675 or 730 nm light reconstructed both holograms. However, when the PC hologram was reconstructed by 730 nm light or the PR grating was reconstructed with 675 nm light, the images were diffracted

away from the camera. Besides the demonstration shown in Fig. 3, we were also able to angle multiplex and recover ten PC holograms and an erasable, dynamic PR hologram in the same volume, simultaneously.

The main advantage of our composite is that it is capable of storing both erasable and quasipermanent holograms in the same location. In addition, the grating formation processes are wavelength selective, allowing for the formation of simultaneous PR and PC gratings or each grating type individually. Using 675 nm light and an external electric field, causes the formation of both grating types, allowing applications such as holographic interferometry, image synthesis, and logic operations to be carried out. Using longer wavelengths, purely PR holographic operations such as optical switching and imaging though distorting media are possible. Finally, long term storage applications like digital data storage may be possible by writing purely PC gratings at 675 nm with no external field. Though our composite appears versatile, it may be necessary to decrease the PC write time and increase the PC storage time for the composite to find practical application. To improve the performance of our composite, we are working with structurally similar chromophores with blueshifted absorption, allowing us to incorporate a higher chromophore concentration into the polymer. Our initial results show that grating formation time decreases with chromophore concentration, as expected, since two sensitized chromophores are more likely to undergo the photochemical reaction at higher chromophore concentrations. The results of those studies will be reported at a later date.

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