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Published in:
Applied Physics Letters

DOI:
[10.1063/1.114534](https://doi.org/10.1063/1.114534)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
1995

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Malliaras, G. G., Krasnikov, V. V., Bolink, H. J., & Hadziioannou, G. (1995). TRANSIENT-BEHAVIOR OF PHOTOREFRACTIVE GRATINGS IN A POLYMER. *Applied Physics Letters*, 67(4), 455 - 457. DOI: 10.1063/1.114534

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Transient behavior of photorefractive gratings in a polymer

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(Received 23 January 1995; accepted for publication 31 May 1995)

The transient behavior of photorefractive gratings in the polymer composite poly(N-vinyl carbazole) (PVK), 2,4,7-trinitro-9-fluorenone (TNF), and N,N-diethyl-*para*-nitroaniline (EPNA) doped with various amounts of 4-(diethylamino)benzaldehyde diphenylhydrazone (DEH) is presented. The influence on the hole drift mobility due to the change in the trap density induced by DEH, was directly measured. © 1995 American Institute of Physics.

Since the first observation of the photorefractive effect in a polymer,¹ considerable progress has been achieved in the performance of these materials. Subsecond grating response,² net gain,³ and diffraction efficiency of almost 100% (Ref. 4) have already been reported for diverse polymer systems. The photorefractive effect originates from the space charge field which is created after the redistribution of photogenerated carriers under nonuniform illumination. This space charge field changes the index of refraction via the electro-optic effect and in this way volume holograms can be recorded in photorefractive materials. Apart from point of view of potential applications in image processing and optical data storage, the observation of the photorefractive effect in polymers is very interesting for fundamental reasons. By measurements of photorefractive parameters with "clean" optical techniques, accesses can be gained to the processes of charge generation, transport, and trapping.

Transient photorefractivity experiments is one example, which has been used in the case of inorganic photorefractive crystals to study the dynamics of the space charge field formation⁵ and to measure the carrier drift mobility.⁶ An interference pattern from two pico- or nanosecond laser pulses creates a sinusoidal distribution of mobile carriers, which drifts under the influence of a strong dc electric field. As charge separation advances, a space charge field builds up which can be probed with a cw laser beam through the electro-optic effect. The maximum space charge field is observed when the center of the mobile charge has drifted a distance equal to half of the grating spacing (Λ). Further drift of carriers causes a decrease of the space charge field, until a distance of a full grating spacing is reached. The diffraction efficiency versus time is thus expected to show an oscillatory behavior. From the time (t_{tr}) it takes to reach the first maximum, the carrier drift mobility (μ_d) can be calculated

$$\mu_d \approx \Lambda / (2Et_{tr}), \quad (1)$$

where E is the projection of the external field along the grating wave vector. The main advantage of such a holographic time of flight technique is that the length scale (grating spacing) can be easily varied down to a micron and there is no strong restriction on the absorption length of the wavelength that is used.

Study of the transient behavior of the photorefractive gratings in polymers is very interesting, as charge transport in these materials has been shown to be very different from that in inorganic crystals, displaying a highly dispersive character, with a mobility that depends on temperature and electric field.⁷ Even though the band transport model used for semiconductors cannot be directly applied to photorefractive polymers the physical picture is qualitatively the same and therefore, the mobility could be estimated using the holographic time of flight technique.

In advance, it is not clear if any oscillation allowing an estimation of the mobility of holes will be observed in the diffraction efficiency due to the highly dispersive nature of the transport and diffusion. For this reason we have conducted transient photorefractivity experiments in the polymer composite poly(N-vinyl carbazole) (PVK), 2,4,7-trinitro-9-fluorenone (TNF) and N,N-diethyl-*para*-nitroaniline (EPNA).⁸ In a previous work⁹ we have seen that the addition of various amounts of 4-(diethylamino)benzaldehyde diphenylhydrazone (DEH) in this polymer composite results in a modification of the trap density. With transient photorefractivity experiments the effect of DEH on hole mobility can now be seen.

For the preparation of samples, proper amounts of PVK, TNF, EPNA, and DEH were dissolved in chlorobenzene and large area films were cast and allowed to dry at room temperature. After 24 h in vacuum to remove the remaining solvent, the films were reduced into powder and 200 μm thick pellets were pressed. Subsequently, the pellets were sandwiched between two ITO covered glass plates by heating above the glass transition temperature. All the films contained 39 wt % EPNA and 0.1 wt % TNF relative to PVK. Three types of films were made, the first one with no DEH, the second with 0.18 wt %, and the third with 19.74 wt % DEH relative to PVK. The DEH/PVK molar ratios were 0, 1/1000, and 1/9, respectively.

Gratings were written using two *s*-polarized, mutually coherent beams from the frequency doubled output of a single frequency Nd:YAG laser, incident on the sample at an external angle of 30°. The sample was tilted 45° to permit a component of the grating vector parallel to the external electric field. The evolution of the photorefractive grating after a single shot from the Nd:YAG laser was probed by measuring the diffraction efficiency with an attenuated, Bragg matched He-Ne laser beam. Transient photoconductivity was mea-

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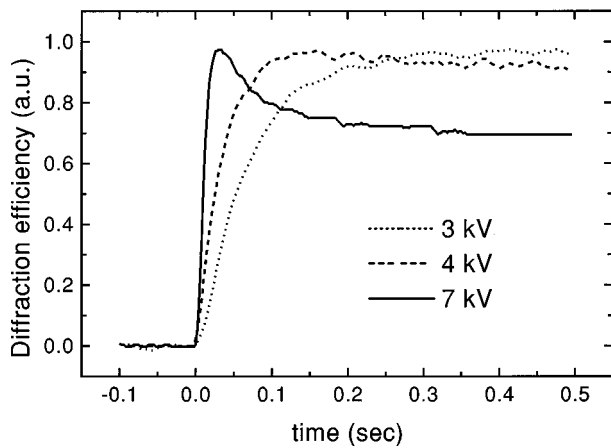


FIG. 1. Normalized diffraction efficiency vs time for various voltages applied across the PVK:TNF:EPNA sample.

sured under uniform illumination of the samples with a pulse from the same laser.

In Fig. 1 the transient behavior of the PVK:TNF:EPNA sample is shown for different voltages. A change in the behavior of the diffraction efficiency with voltage is apparent: at low voltages (3 kV), the space charge field slowly reaches saturation, which is followed by slow erasure from the probe He-Ne beam (not shown in this plot). As the applied voltage increases, a maximum appears in the diffraction efficiency (already visible in the curve for 4 kV) that becomes more pronounced at high voltages. According to the above, the presence of a maximum allows a crude estimation of the drift mobility of holes in PVK:TNF:EPNA according to Eq. (1). The influence of the space charge field on the mobility was ignored because of the low value of the space charge field compared with the external electric field. From the curve of 7 kV we estimate a hole mobility of $3 \times 10^{-8} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This value is an order of magnitude lower than values reported for pure PVK at approximately the same electric field,¹⁰ which seems to be due to the presence of large amount of EPNA in the composite.

A potential danger arises from the possible existence of an orientational enhancement of photorefractivity in polymers.¹¹ According to this mechanism, the nonlinear optical chromophores reorient to follow the space charge field, which causes an enhancement of the diffraction efficiency. Care should be taken to ensure that if any reorientation of the chromophores takes place, it follows instantaneously the dynamics of the space charge field formation. We have measured the second harmonic generation after the application of a voltage pulse in the sample and found that the orientation time of the chromophores is faster than 100 μs . This means that even if the orientational enhancement of photorefractivity takes place, it happens very fast and what we observe in Fig. 1 is indeed the formation of the space charge field.

Further evidence for the photorefractive nature of the gratings observed here is provided by transient photocurrent measurements. According to the physical picture for the space charge field formation, the change in the diffraction efficiency originates from the motion of carriers which gives rise to macroscopic current flow. The transient photocurrent,

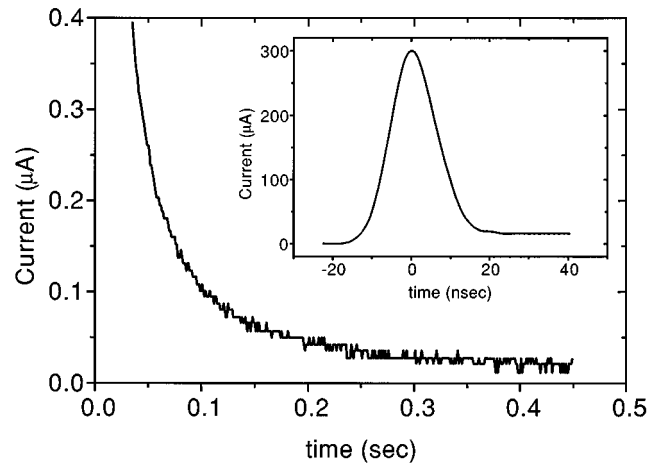


FIG. 2. Tail of the transient photocurrent for the PVK:TNF:EPNA sample. The voltage across the sample was 7 kV. Inset: the fast component of the transient photocurrent follows the shape of the nanosecond Nd:YAG laser pulse.

shown in Fig. 2, has a very fast component that follows the Nd:YAG pulse and cannot be time resolved (inset of Fig. 2), followed by a small magnitude tail. This tail still exists at time scales that correspond to grating growth time. The tail of the transient photocurrent follows an inverse power law dependence with time, which is typical for amorphous materials,⁷ in contrast with exponential decay observed in the case of inorganic photorefractive crystals.

In a previous work⁹ we have seen that addition of 1 DEH molecule every 1000 carbazole units in PVK:TNF:EPNA causes an increase in the trap density, as inferred from the decrease of the phase shift of the photorefractive grating. The presence of extra trapping centers should reduce the drift mobility of holes¹² and thus affect the rise time of the transient photorefractive grating. This is apparent in Fig. 3, where the transient behavior of the sample with 1/1000 DEH is shown. It should be stressed that in this case, the decrease of diffraction efficiency after 10 s is due to erasure of the grating by the He-Ne probe beam. An upper limit of $6 \times 10^{-11} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ can be calculated for the mobility from this plot.

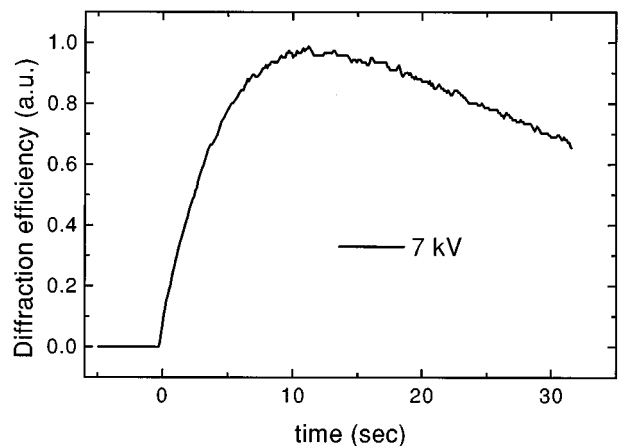


FIG. 3. Normalized diffraction efficiency vs time for the sample with 1/1000 DEH/PVK molar ratio.

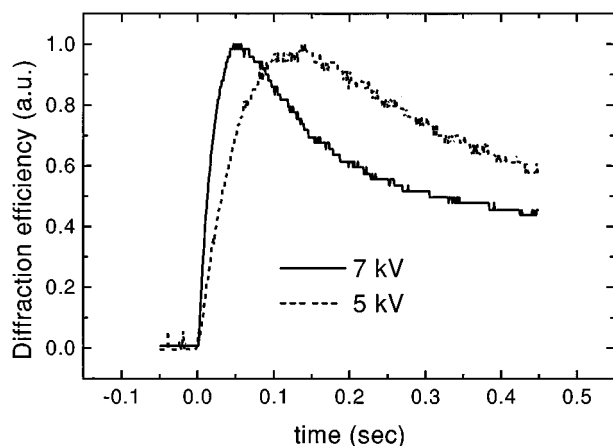


FIG. 4. Normalized diffraction efficiency vs time for various voltages applied across the sample with DEH/PVK molar ratio 1/9.

When DEH is present in large amounts in PVK:TNF:EPNA, a new pathway for hole transport is created. As DEH molecules come close enough to allow hopping of holes to become possible, the effective trap density decreases. This holds for the sample with 1 DEH molecule every 9 carbazole units. In Fig. 4 the transient behavior of this sample is shown, from which one observes that the drift mobility increases to $10^{-8} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for 7 kV applied across the sample. The decrease of the diffraction efficiency after the maximum is reached is much higher in this sample than in the PVK:TNF:EPNA sample (Fig. 1, curve for 7 kV). It is reasonable to assume that such a feature is associated with the degree of dispersion of charge transport, which seems to be different for these two samples. The absence of a second maximum is probably due to the highly dispersive nature of the charge transport.⁷ A theoretical framework tak-

ing into account the character of charge transport in polymers is needed for quantification of the results.

In conclusion, despite the dispersive character of charge transport in polymers, oscillationlike behavior was observed in the transient photorefractivity in the PVK:TNF:EPNA polymer composite. The hole drift mobility for samples with various trap densities, induced by DEH, was estimated.

Financial support from "Stichting Scheikundig Onderzoek Nederland" (SON) and "Stichting Toegepaste Wetenschappen" (STW) is gratefully acknowledged. Thanks are due to E. Kroeze and H. J. Brouwer for assistance in sample preparation, G. ten Brinke for fruitful discussions, and P. F. van Hutten for critical reading of the manuscript.

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