Photorefractive polymer composite with net gain and subsecond response at 633 nm

Malliaras, G. G.; Krasnikov, V. V.; Bolink, H. J.; Hadziioannou , G.

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

Photorefractive polymer composite with net gain and subsecond response at 633 nm

G. G. Malliaras, V. V. Krasnikov, H. J. Bolink, and G. Hadziioannou
Polymer Chemistry Department, Materials Science Centre, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

By combining the well-known photoconductor poly(*N*-vinyl carbazole) sensitized with 2,4,7 trinitro-9-fluorenone and the electrooptic molecule *N,N*,diethyl-substituted *para*-nitroaniline, which is transparent at 633 nm, a photorefractive polymer composite suitable for applications with He-Ne lasers was developed. Net gain of 18 cm^{-1} and 400 ms response time were measured on a 65-μm-thick sample.

In the last few years there has been observed an increasing interest in the development of photorefractive polymer materials with possible applications in image processing and reversible dynamic holographic storage.[1] Photorefractivity requires charge generation, separation, and trapping, together with a linear electro-optic response.[2] The first photorefractive polymer was an electro-optic polymer which was made photoconducting after doping with a hole transport agent.[3] Several other similar materials[4-6] as well as fully functionalized (single component) polymers[7,8] have been reported, all showing moderate efficiencies. Subsecond grating response was demonstrated in one of them.[4] More recently, net gain, high diffraction efficiencies and fast response time were observed in a photoconducting polymer, doped with electro-optic molecules.[9-11]

In all photorefractive polymers so far, π conjugated donor-acceptor molecules are used for the electro-optic effect. Although in some cases they can act as sensitizers,[12] permanent gratings with long response times observed in almost all the photorefractive polymers have been attributed to photochemical reactions involving these molecules.[13,14] Due to their strong absorption in the visible, the range of wavelengths used to study photorefractive polymers has been mainly limited to the red–near-infrared part of the spectrum.

In order to be advantageous for applications, a photorefractive material should have a large range of wavelengths where it can be used. Especially in the high density information storage devices, response in the blue side of the visible is preferable. Polymer composites offer the advantage of tailor made properties. In an effort to show that efficient photorefractive polymers can be prepared for application at common wavelengths, we have developed and studied a composite based on the well known photoconductor poly(*N*-vinyl carbazole) (PVK) sensitized with 2,4,7 trinitro-9-fluorenone (TNF), doped with the electro-optic molecule *N,N*,diethyl-substituted *para*-nitroaniline (EPNA). As a result of the lack of absorption from EPNA, net gain, and subsecond response has been measured at a wavelength of 633 nm from a He-Ne laser.

Polymer films containing 39% wt EPNA and 0.1% wt TNF on PVK were cast from solution on indium tin oxide (ITO) covered glass slides, as described in Ref. 15. For the orientation of the EPNA molecules, which is essential for the activation of the electro-optic effect, corona poling with a tungsten needle placed 1.5 cm away from the sample was used. This technique offers the advantage of easier sample preparation, as sandwiching the polymer between two ITO plates is not necessary. Furthermore, a higher electric field without total sample breakdown can be applied. One drawback of this poling technique is that the precise value of the applied electric field on the sample is not known and has to be measured separately. This value also depends on the environment (e.g., humidity of air), thus, for good reproducibility, the experiments should be done within short periods of time.

Second harmonic generation (SHG) experiments were carried out in order to probe the orientation of the EPNA chromophores. Infrared light from a *Q*-switched Nd:YAG laser was incident on the sample at an angle of 45° with the sample normal and the frequency doubled (532 nm) output was monitored as a function of the voltage on the needle. With no voltage applied, the second harmonic intensity was zero, as a result of the centrosymmetric random arrangement of the chromophores. After switching the voltage on and off several times, repeatable partial orientation of the chromophores was achieved, reaching a stable plateau value within a few seconds. No second harmonic generation was observed for needle voltages below a threshold value of approximately 2 kV. Above this value, corona discharge was possible and the plateau value of the signal had the expected quadratic behavior with the voltage. This partial orientation of the EPNA molecules at room temperature comes as a result of plasticization of the PVK due to the large loading. For all the experiments that will follow, enough time was allowed for the molecules to attain equilibrium orientation, after switching on the voltage.

Undoubtable evidence for photorefractivity is provided by the demonstration of a phase shifted refractive index grating. For this purpose, the two beam coupling (2BC) method was used. Gratings were written using two *p*-polarized, mutually coherent He-Ne beams incident on the sample from the ITO side with 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 signals were detected with regular Si photodiodes, connected with a digitizing oscilloscope to record transient signals.

Asymmetric energy transfer between the two beams was observed when the corona voltage was switched on, provid-
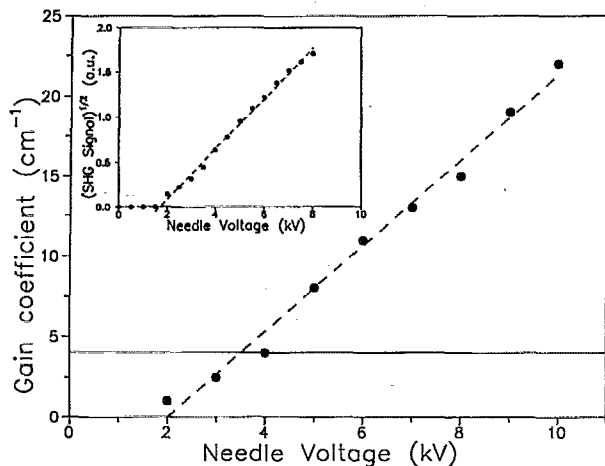
FIG. 1. Gain coefficient Γ as a function of the voltage on the needle. The solid line indicates the absorption level. The dashed line is a guide to the eye. Inset: square root of the SHG signal as a function of the voltage on the needle. The dashed line is a guide to the eye.
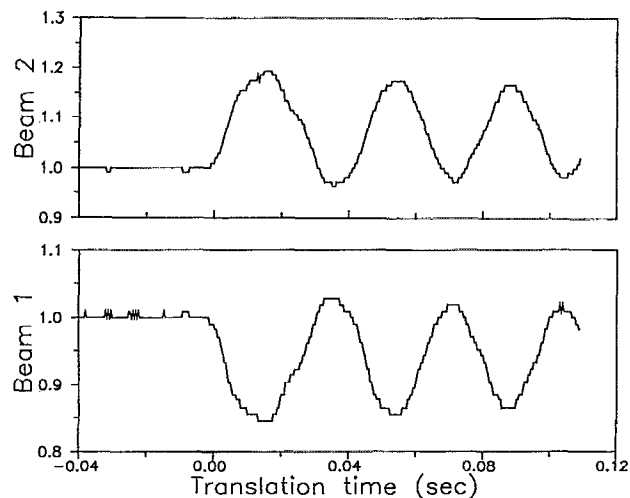

FIG. 2. The modulation of the transmitted power of the two beams due to sample translation at $t=0.0$ s indicates the existence of a phase shifted refractive index grating. The voltage on the needle was 10 kV.

ing evidence for a phase shifted grating. The same effect was observed when the intensity of one beam was monitored as the other beam was switched on and off. Using two beams of equal intensity, the gain was estimated from[16]

$$\Gamma = [\ln(\gamma_0) - \ln(2 - \gamma_0)]/L, \tag{1}$$

where L is the path length of the beam experiencing gain and γ_0 is the ratio between the power of this beam with and without the presence of the other beam.

The sample was mounted on a piezo block that could provide fast translation perpendicular to the sample normal. In this way, the two beams that write the grating can also be used to read it during translation, which provides information about the nature and the phase shift of the grating (Sutter et al.[17]).

For the measurement of response time, degenerate four wave mixing (DFWM) with two s-polarized beams for writing, and a weaker, counterpropagating, p-polarized reading beam from a separate He-Ne laser, was used. Using a separate laser for probing the grating ensures the existence of only one interference pattern inside the sample. After writing the grating, one of the writing beams was blocked and the other one was used to erase it, or both writing beams were blocked and erasing was done with the probe beam.

The majority of applications for photorefractive materials require net gain, meaning that the gain that one of the beams experiences is larger than the absorption that it suffers passing through the sample. In Fig. 1 the gain coefficient Γ is shown as a function of the corona voltage, for a 65-μm-thick sample. The absorption coefficient is also plotted on this graph, indicating the level above which net gain occurs. The offset on the horizontal axis is due to the existence of a threshold value for the establishment of the corona discharge. In the inset of Fig. 1 the square root of the second harmonic signal from the sample indicating the alignment of the EPNA chromophores is presented as a function of the needle voltage.

The external electric field influences the gain coefficient Γ through the space charge field E_{sc} and the effective linear electro-optic coefficient r_{eff}:[18]

$$\Gamma \sim r_{eff} E_{sc}. \tag{2}$$

In polymeric host-guest materials that cannot sustain any permanent orientation of the chromophores, the linear electro-optic coefficient is proportional to the externally applied electric field. According to the standard photorefractive model, the space charge field E_{sc} depends on the externally applied electric field as[18]

$$E_{sc} \sim E_{sat} \left(\frac{E_{ext}^2 + E_d^2}{E_{ext}^2 + (E_d + E_{sat})^2} \right)^{1/2}, \tag{3}$$

where E_{sat} is the saturation field that depends on the geometry of grating formation and the density of traps in the material, E_{ext} is the externally applied electric field and E_d is the diffusion field. In the case where the external field is larger than the saturation and the diffusion field, enhancement of the gain coefficient only through the linear electro-optic coefficient is expected. The linear dependence of Γ on the needle voltage (Fig. 1) indicates that the externally applied electric field on the polymer is larger than the diffusion and saturation fields and the enhancement of gain takes place only through the better alignment of the EPNA chromophores. Similar behavior has been observed in other photorefractive polymers.[6,10]

In Fig. 2, the modulation on the two beams resulting from sample translation is shown. At time equal to 0.0 s, sample translation begins and the signals on the two photodiodes are modulated as the two beams read out the grating. The signals on the two photodiodes are 180 ° out of phase, indicating the existence of a purely refractive index grating, according to Eqs. 7 of Ref. 17. Slight erasing of this grating as the sample is translated is observed. Further on, a phase shift of $50\pm5°$ with respect to the illumination pattern is revealed. Within the accuracy of our experiment, no dependence of this phase shift on the corona voltage was observed.
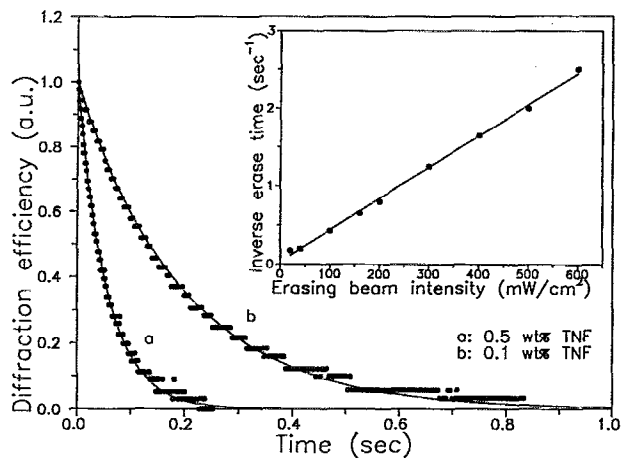
FIG. 3. Erasure of the grating for two samples with different concentrations of TNF. The solid lines are fits to Eq. 4, giving an erase time τ of 110 ms for sample a (0.5 wt % TNF) and 400 ms for sample b (0.1 wt % TNF). The erasing beam intensity was 600 mW/cm^2 and the voltage on the needle was 10 kV. Inset: inverse erase time τ^{-1} as a function of the erasing beam intensity for a sample with 0.1 wt % TNF. The voltage on the needle was 10 kV.

The same behavior was observed on all our samples, both immediately and several days after their preparation.

According to the standard photorefractive model, the phase shift should start from 90° at zero external field (pure diffusion of carriers), reach a minimum value, and then asymptotically tend to 90° as the voltage across the sample increases. A theory for photorefractive polymers taking into account the field dependence of photogeneration and mobility has been worked out,[19,20] but in the region where the external electric field is larger than all the characteristic fields, a 90° phase shift is also expected. The mechanism leading to a phase shift different from 90° is not understood at present.

In Fig. 3 the results of the DFWM experiments for two samples with different concentrations of the TNF are shown. The samples had almost the same thickness and the corona voltage was +10 kV. The solid line is a fit according to[21]

$$E_{sc} \sim e^{-t/\tau}. \tag{4}$$

The addition of TNF decreases the response time, but at the same time increases the absorption, prohibiting net gain. In the inset of Fig. 3, the inverse erase time τ^{-1} of a composite containing 0.1 wt % TNF versus the power of the erasing beam is shown, exhibiting the usual linear behavior. The corona field was 10 kV and the sample was 65 μm thick.

The diffraction efficiency was 0.2%. As the dark erase time was several minutes, no corrections were necessary. Subsecond response is observed for erasing beam power larger than 250 mW/cm^2. The erase time was found to increase almost two times when the corona voltage was decreased from +10 kV to the lowest value for which a grating was detectable.

In conclusion, we have shown that polymer composites can be tailored to show net gain and relatively fast response time by the judicious choice of the necessary components. By combining the well known photoconducting PVK:TNF polymer and the electro-optic molecule EPNA net gain of 18 cm^{-1} and 400 ms response time was observed on a 65-μm-thick sample poled at approximately 10 kV. As a result of lack of absorption from EPNA at 633 nm, no permanent photochemical grating of any kind was observed in this material.

[1] W. E. Moerner and S. M. Silence, Chem. Rev. 94, 127 (1994).
[2] P. Günter and J. P. Huignard, Eds. Topics in Applied Physics, (Springer, New York, 1988), vol. 61.
[3] S. Durcharme, J. C. Scott, R. J. Twieg, and W. E. Moerner, Phys. Rev. Lett. 66, 1846 (1991).
[4] S. M. Silence, C. A. Walsh, J. C. Scott, T. J. Mattray, R. J. Twieg, F. Hache, G. C. Bjorklund, and W. E. Moerner, Opt. Lett. 17, 1107 (1992).
[5] J. S. Schildkraut, Appl. Phys. Lett. 58, 340 (1991).
[6] M. Liphardt, A. Goonesekera, B. E. Jones, S. Durcharme, J. M. Takacs, and L. Zhang, Science 263, 367 (1994).
[7] H. J. Bolink, V. V. Krasnikov, G. G. Malliaras, and G. Hadziioannou, SPIE Proc. 2025, 292 (1993).
[8] L. Yu, W. Chan, Z. Bao, and S. X. F. Cao, Macromolecules 26, 2216 (1993).
[9] M. C. J. M. Donkers, S. M. Silence, C. A. Walsh, F. Hache, D. M. Burland, W. E. Moerner, and R. J. Twieg, Opt. Lett. 18, 1044 (1993).
[10] B. Kippelen, Sandalphon, N. Peyghmbarian, S. R. Lyon, A. B. Padias, and H. K. Hall, Jr., Electron. Lett. 29, 1873 (1993).
[11] S. M. Silence, J. C. Scott, F. Hache, E. J. Ginsburgh, P. K. Jenker, R. D. Miller, R. J. Twieg, and W. E. Moerner, J. Opt. Soc. Am. B 10, 2306 (1993).
[12] J. C. Scott, L. Pautmeier, and W. E. Moerner, Syn. Met. 54, 9 (1993).
[13] T. Kawakami and N. Sonoda, Appl. Phys. Lett. 62, 2167 (1993).
[14] B. Kippelen, K. Tamura, N. Peyghambarian, A. B. Padias, and H. K. Hall, Jr., Phys. Rev. B 48, 10710 (1993).
[15] H. J. Bolink, V. V. Krasnikov, G. G. Malliaras, and G. Hadziioannou, Adv. Mater. (in press).
[16] J. P. Hiugnard and A. Marrakchi, Opt. Commun. 38, 249 (1981).
[17] K. Sutter and P. Günter, J. Opt. Soc. Am. B 7, 2274 (1990).
[18] N. V. Kukhtarev, V. B. Markov, M. Soskin, and V. L. Vinetskii, Ferroelectrics 22, 949 (1979).
[19] J. S. Schildkraut and A. V. Buettner, J. Appl. Phys. 72, 1888 (1992).
[20] J. S. Schildkraut and Y. Chui, J. Appl. Phys. 72, 5055 (1992).
[21] G. C. Valley and M. B. Klein, Opt. Eng. 22, 704 (1983).