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

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Control of charge trapping in a photorefractive polymer

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

Modification of the trap density of the photorefractive polymer composite poly(N-vinyl carbazole) (PVK), 2,4,7-trinitro-9-fluorenone (TNF) and N,N-diethyl-*para*-nitroaniline (EPNA) was achieved with the addition of 4-(diethylamino)benzaldehyde diphenylhydrazone (DEH). Measurements of the response time, the phase shift and the amplitude of the photorefractive grating are presented. © *1995 American Institute of Physics.*

The observation of the photorefractive effect in an organic crystal[1] and later in a polymer,[2] created an alternative class of photorefractive materials. Apart from their processability, organic materials offer a promising photorefractive index change figure-of-merit $n^3 r/\epsilon$, owing to the small dc dielectric constant ϵ and reasonable linear electrooptic coefficient r and refractive index n. Photorefractivity requires charge generation, separation and trapping, together with a linear electrooptic response.[3] Photoconductivity in polymer materials is quite well explored due to their application in xerography. The electro-optic effect in polymers has also been a subject of intense research interest, due to the potential commercial exploitation of these materials in light modulators and switches.

In contrast with photoconductivity and electrooptic response, the process of charge trapping in polymers is less well studied. By definition, trapping takes place at hopping sites that require an energy substantially higher than the average energy to release the charge carriers. Thus, in a hole transport polymer, the addition of a molecule with lower ionization potential than the hopping sites is expected to give rise to trapping. This has been observed in a solid solution of N-isopropylcarbazole (NIPC) in polycarbonate when adding low concentrations of N,N′-diphenyl-N,N′-bis(3-methylphenyl)-[1,1′-biphenyl]-4,4′- diamine (TPD).[4]

Holes, which is the mobile species in all photorefractive polymers that have been reported until today, are expected to become trapped at impurities accidentally present in the polymer,[5] defects of the polymer backbone (such as chain ends),[6,7] sensitizer[8] and chromophore[7] molecules, etc. Apart from its fundamental interest, control of charge trapping has great technological importance: optimization of charge trapping might be the route towards long storage time and high diffraction efficiency required for optical data storage applications.

In an effort to explore charge trapping in photorefractive polymers, we have used the composite poly(N-vinyl carbazole) (PVK), 2,4,7-trinitro-9- fluorenone (TNF) and N,N-diethyl-*para*-nitroaniline (EPNA), for which we have recently reported photorefractivity.[9] In this Letter we will concentrate on the changes in the response time and the phase shift of the photorefractive grating as a function of doping with various amounts of 4-(diethylamino)benzaldehyde diphenylhydrazone (DEH).

The preparation of the PVK:TNF:EPNA samples has

been described in Ref. 10. DEH was prepared by condensation of 4-(diethylamino)benzaldehyde with 1,1-diphenylhydrazine. A master solution was prepared by dissolving 1.6 g PVK together with 0.624 g EPNA (39% wt relative to PVK) and 0.0016 g TNF (0.1% wt relative to PVK) in 20 ml chlorobenzene. All samples were prepared by adding different amounts of DEH to a portion of the same master solution, in order to ensure that the relative concentration of EPNA and TNF in PVK as well as the amount of impurities was exactly the same in all the samples. Five samples where prepared, with DEH concentrations equal to 0, 0.18, 1.78, 8.89 and 19.74% wt relative to PVK. The DEH/carbazole molar ratios were 0, 1/1000, 1/100, 1/20 and 1/9, respectively. The average thickness of the samples was 57 ± 7 μm.

The necessary electric field was applied on the polymer films during the experiments with a tungsten needle placed 1.5 cm away from the sample (corona discharge). For the measurements of the amplitude P and the phase shift φ of the photorefractive gratings, the two beam coupling (2BC) method[11] was used. Gratings were written using two p-polarized, mutually coherent He−Ne beams with an intensity of 600 mW/cm^2 each, incident on the sample from the ITO side with an external angle of 30 degrees. The sample was tilted 45 degrees to permit a component of the grating vector parallel to the external electric field. For the measurements of response time, one of the writing beams was blocked and the diffracted beam was monitored with a photodiode. Experimental details can be found in Ref. 9.

Charge transport in PVK has been extensively studied in the past (for a recent review see Chapter 8 of Ref. 12). Transport of holes, which is the mobile charge, takes place via hopping between localized energy levels, provided in the polymer by the carbazole units (step 1 of Fig. 1). Addition of very small amounts of another hole transport molecule with a
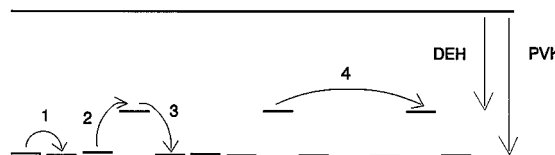

FIG. 1. Hopping transport: (1) via the high ionization potential (I_p) compound; (2) trapping at sites of low I_p; (3) detrapping; (4) hopping via the low I_p compound.
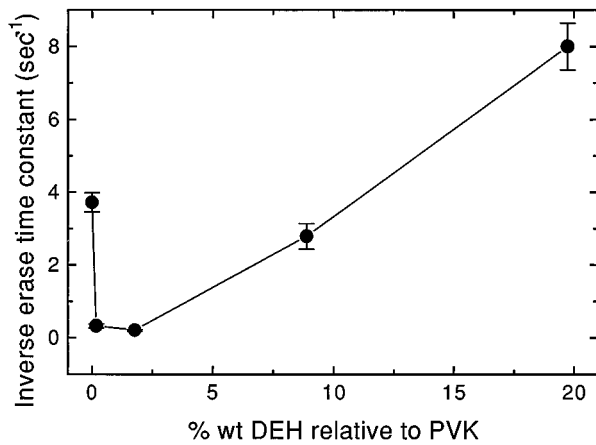
FIG. 2. Inverse erase time constant of the photorefractive grating as a function of the DEH concentration. The voltage on the needle was 10 kV and the intensity of the erasing beam, incident at 60° with the sample normal, amounted to 600 mW/cm². The line is a guide to the eye.
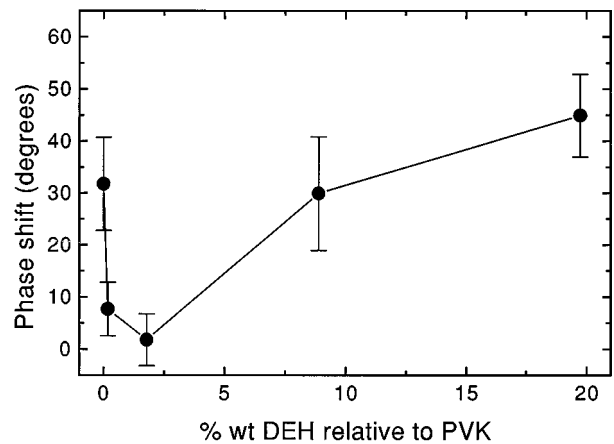

FIG. 3. Phase shift of the photorefractive grating as a function of the DEH concentration. The voltage on the needle was 10 kV. The line is a guide to the eye.

lower ionization potential is expected to give rise to hole trapping (step 2 in Fig. 1). The holes will reside at the site of these molecules, until an electron from a neighboring carbazole unit gains statistically enough thermal energy to move "uphill" to the site of the trap (step 3 in Fig. 1).

Further increase of the concentration of the molecule with lower ionization potential will create a new transport pathway for holes, as hopping between two neighboring molecules will become possible (step 4 of Fig. 1). The dependence of the macroscopic drift mobility on the concentration of the additive is thus expected to show a sharp initial decrease due to trapping, reach a minimum and then to increase as a result of transport through the low ionization potential molecules. This behavior has been observed in the case of PVK doped with TPD.[13] In this study we have used DEH instead of TPD, because it has a lower ionization potential[14] and it is therefore expected to show a more pronounced effect.

In Fig. 2 the inverse erase time constant τ^{-1} under uniform illumination (600 mW/cm²) is plotted versus the DEH concentration. A sharp decrease of τ^{-1} is observed as one DEH molecule is introduced every 1000 carbazole units in the photorefractive composite. After reaching a minimum value of 0.21 ± 0.02 sec^{-1}, τ^{-1} increases, reaching a value of 8.0 ± 0.6 sec^{-1} for the sample with the highest DEH concentration. It should be mentioned that the decay of the grating shows biexponential behavior in the samples containing DEH. However, the fast component, from which τ^{-1} was calculated, is responsible for more than 90 percent of the diffracted intensity and it decays at least an order of magnitude faster than the slow component.

This dependence of τ^{-1} on DEH concentration is in agreement with the above-mentioned arguments about trapping. Small amounts of DEH act as traps, decreasing the mobility of holes in PVK. As τ^{-1} is proportional to the mobility, it follows the same trend. As the concentration of DEH exceeds 1 per 100 carbazole units, DEH begins to contribute to charge transport and τ^{-1} increases. From Fig. 2 it is clear that there is an optimum concentration of the trapping mol-

ecules, for which the photorefractive gratings will exhibit the slowest erasure.

In order to get more insight into the influence of DEH on the charge trapping process, the phase shift of the photorefractive grating was measured as a function of DEH concentration. As can be seen in Fig. 3, it shows similar behavior with τ^{-1}. The phase shift for the PVK:TNF:EPNA composite was measured to be 32 ± 9 degrees. We have found that this value depends on the sample preparation procedure, probably due to impurities that can act as traps. As can be seen in Fig. 3, it is very sensitive to additives: addition of as little as 1 DEH molecule every 1000 carbazole units causes a steep decrease of the phase shift.

The dependence of the phase shift on the DEH concentration can be understood according to the standard theory of photorefractivity.[15] In the steady state regime, the phase shift φ of the space charge field, in the case where the diffusion field is ignored, is given by

$$\varphi = \arctan(E_o/E_q), \qquad (1)$$

where E_o is the projection of the external field along the grating wave vector and E_q the saturation field, which is proportional to the density of traps. In the case of the PVK:TNF:EPNA samples, the value of the phase shift implies that the saturation field is already comparable to the external field, indicating the presence of an already substantial amount of traps. With the addition of DEH, the trap density changes and this change can be directly probed with measurement of the phase shift. As can be estimated from Fig. 3, the trap density increases initially, as DEH is added at small amounts. When the concentration of DEH exceeds 1 per 100 carbazole units, the trap density decreases, as the DEH molecules begin to act as hole transport species instead of trapping centers. Furthermore, due to the lower ionization potential of DEH compared to PVK, hopping through DEH is expected to be less affected by trapping at impurities than hopping through PVK.

According to the same theory, the amplitude E_{sc} of the space charge field depends also on the ratio E_o/E_q:
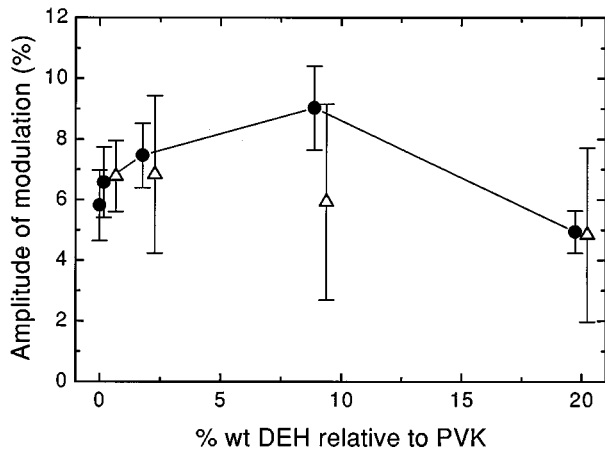
FIG. 4. Amplitude of the relative refractive index modulation as a function of the DEH concentration. Closed circles: experimental points, from the two beam coupling experiment. The voltage on the needle was 10 kV. The line is a guide to the eye. Open triangles: theoretical points, according to equation 3.

$$E_{sc} = m\, E_o\, [1 + (E_o/E_q)^2]^{-1/2}, \tag{2}$$

where m is the contrast of the light interference pattern. From the measurement of the phase shift, the amplitude P of the relative refractive index modulation can be estimated according to

$$P \sim r_{eff}\, E_{sc}\, l, \tag{3}$$

where r_{eff} is the effective electrooptic coefficient and l the thickness of the sample. In Fig. 4, the filled circles are the measured amplitudes of the relative refractive index modulation for every sample. The open triangles (which are shifted 0.5 units on the horizontal axis for clarity), are the ones calculated from the phase shift of Fig. 3. The proportionality factor of Eq. 3 was deduced from the measured values of the samples containing no DEH, and subsequently the amplitude of the relative refractive index modulation was calculated for the other samples. The large error bars are chiefly due to the distribution of thicknesses of the samples and the experimental error in the determination of the phase

shift. As can be seen in Fig. 4, the increase in diffraction efficiency with addition of DEH is not spectacular, due to the existence of an already substantial amount of traps in the PVK:TNF:EPNA polymer.

In conclusion, a change in trap density was demonstrated in the PVK:TNF:EPNA photorefractive polymer with the addition of DEH. This change affected the response time, the phase shift and the amplitude of the photorefractive grating. It seems very interesting to continue the investigation towards the improvement of the performance of photorefractive polymers by optimization of trap density.

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