

Novel Bifunctional Molecule for Photorefractive Materials

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We report on the synthesis and characterization of a novel photorefractive polymer composite that consists of a bifunctional molecule based on the charge-transport molecule *N,N*-diphenyl-*N,N*-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (TPD). It is shown that the low values obtained for the gain coefficient and the diffraction efficiency (10 cm^{-1} and 0.1%, respectively) are a result of the low intrinsic trap density. The gain coefficient and the diffraction efficiency are dramatically increased to 6% and 45 cm^{-1} , respectively, by adding only small amounts of the molecule *N,N,N,N*-tetramethyl-4-phenylene diamine (TMPD), which is shown to cause an increase in the trap density. The behavior of the diffraction efficiency, gain coefficient, response time, and phase shift upon the concentration of TMPD are discussed within the standard model of photorefractivity.

Introduction

The photorefractive effect is observed in materials that are both electrooptic and photoconducting. Non-uniform illumination of such a material results in the creation of photoexcited charges, which migrate out of the illuminated areas and eventually get trapped in the dark areas, giving rise to a spatially varying electric field (space charge field). This space charge field alters the index of refraction via the electrooptic effect. In this way, a refractive index pattern which is a replica of the illumination pattern is produced.¹ Although such a replication can also be achieved with other mechanisms, such as photochemistry, thermorefractive, etc.,² the photorefractive effect possesses a combination of characteristics which make it unique: Very high nonlinearities can be achieved with even weak laser beams, as a result of the integrating nature of the effect. The resulting refractive index gratings are reversible, as uniform illumination erases the space charge field. Another very important characteristic is the existence of spatial phase shift between the illumination pattern and the refractive index grating, which gives rise to steady-state asymmetric energy exchange between two laser beams.¹

Until recently, the main materials of interest were inorganic electrooptic crystals such as lithium niobate or barium titanate. The observation of photorefractivity in a polymer³ has led to the development of a large variety of photorefractive polymer structures (see reviews in refs 4 and 5). Most of these photorefractive polymers utilize poly(*N*-vinylcarbazole) (PVK) as the charge-

transporting material and at the same time as the polymer host in which the electrooptic molecules (which can give rise to the Pockels and or Kerr effect⁶) are dispersed. Photorefractive polymers based on PVK have a relatively high intrinsic trap density, which limits the magnitude of the phase shift that can be reached between the refractive index grating and the illumination pattern.⁷ Furthermore, the large amount of intrinsic trapping sites makes the study toward the effect of additional trapping sites more complicated.⁸ Apart from PVK there are many other alternative materials that exhibit better charge-transporting properties.⁹ Most of these materials are based on charge-transport molecules that are not covalently bound to a polymer chain but simply dispersed into an inactive polymer matrix. One of these molecules that is extensively used in photoconducting polymers is *N,N*-diphenyl-*N,N*-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (TPD).¹⁰ TPD-based photoconductors have a lower trap density than those based on PVK.¹¹ Moreover, TPD-based photoconductors exhibit a higher mobility than PVK, which in the case of mobility-limited response time can increase the speed of the photorefractive effect. These characteristics make TPD a promising transport molecule to be used in photorefractive materials.

There are several ways to incorporate TPD in a photorefractive polymer. The easiest way is to disperse TPD and the electrooptic molecules in an inactive

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polymer matrix. However, due to the fact that relatively large concentrations of these molecules have to be incorporated, composites of this kind suffer from phase separation of one or both of these molecules. One way to decrease the large amounts of low molecular weight molecule is to use a bifunctional-TPD molecule that functions not only as the charge transport species but also as the electrooptic molecule.^{12,13} In this case, only one type of molecule has to be incorporated reducing the chance of phase separation. Electrooptic molecules require a strong electron-donating and a strong electron-withdrawing moiety bound together by a conjugated bridge.¹⁴ The TPD molecule consist of two strong electron donors in the form of the amine atoms; it can thus be made electrooptically active by attaching an electron-withdrawing group to one of the two triaryl-amine moieties of which TPD consists.

In this paper we report the preparation and the characterization of a photorefractive composite consisting of a bifunctional molecule. This bifunctional molecule is based on *p*-TPD in which the methyl groups are para- instead of meta- substituted (as is the case in normal TPD) with respect to the amine atom. This was done to allow a more convenient synthesis of the bifunctional molecule by attaching a dicyanoethylene moiety on one of the triphenylamine groups of *p*-TPD. From the photorefractive characterization a low value of the trap density was deduced. The attempt to increase the trap density by adding small amounts of trapping molecules is described.

Experimental Section

General Methods. Nuclear magnetic resonance (NMR) spectra were taken with a Varian VXR 300 spectrometer. The UV-vis absorption spectra were recorded using a SLM Aminco 3000 spectrophotometer. The glass transition temperatures (T_g) were determined with a Perkin-Elmer DSC-7 series differential scanning calorimeter at a heating rate of 10 °C/min. The cyclovoltammetric analysis were performed using a EG-G Princeton Applied Research Model 273 potentiostat-galvanostat.

Materials. *N,N*-Diphenyl-*N,N*-bis(4-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (*p*-TPD, **1**).¹⁵ A solution of 10 g (0.030 mol) of *N,N*-diphenyl-[1,1'-biphenyl]-4,4'-diamine, 19.5 g (0.090 mol) of 4-iodotoluene, 16.56 g (0.120 mol) of potassium carbonate, and 8.8 g of copper bronze in 40 mL of dodecane was stirred under argon atmosphere at 210 °C for 3 days. After cooling, the excess iodotoluene is removed together with the solvent by distillation under reduced pressure. The product was extracted by refluxing in 400 mL of octane and subsequent hot filtration to remove the inorganic salts. The orange filtrate was purified by column chromatography using silica gel and dichloromethane-pentane (1:1) as the eluent. Evaporation of the solvent yielded 12.1 g (78%) of a white solid, $T_g = 52$ °C.

¹H NMR (CDCl₃) δ 2.32 (s, 6 H), 6.99–7.44 (m, 26 H) ppm. ¹³C NMR (CDCl₃) δ 20.85 (CH₃) 122.33, 123.54, 123.73, 125.00, 127.16, 129.13, 129.95 (CH aromatic), 132.84, 134.84, 145.12, 146.83, 147.88 (C aromatic) ppm.

N-(4-Formylphenyl)-*N*-phenyl-*N,N*-bis(4-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (**2**). Freshly distilled phosphoroxy chloride (1.5 g, 0.0097 mol) was slowly added to 3.9 g (0.054 mol) of dimethylformamide at a temperature between 0 and 5 °C.

After additional stirring for 1 h at room temperature, this solution was added to a stirred solution of 5 g (0.0097 mol) of *N,N*-diphenyl-*N,N*-bis(4-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine in 20 mL of 1,2-dichloroethane. This reaction mixture was stirred for another hour at 60 °C and allowed to cool to room temperature. Hereafter the mixture was poured in a solution of 10 g sodium acetate in 100 mL water, and this mixture was extracted three times with dichloromethane. The combined organic layers were washed twice with water and dried over magnesium sulfate. After filtration and evaporation of the solvent a yellow solid was obtained. The desired monoformylated product was isolated from this crude product by column chromatography using silica gel and dichloromethane as the eluent, yielding 2.7 g (51%) of a yellow solid, $T_g = 72$ °C.

¹H NMR (CDCl₃) δ 2.35 (s, 3 H), 2.39 (s, 3 H), 7.04–7.71 (m, 25 H), 9.82 (s, 1H). ¹³C NMR (CDCl₃) δ 20.85 (CH₃), 20.98 (CH₃), 118.97, 122.59, 123.22, 123.95, 125.13, 126.08, 126.59, 127.35, 127.64, 129.19, 129.98, 130.43, 131.32 (CH aromatic), 128.81, 133.06, 133.60, 135.25, 137.19, 143.41, 144.80, 144.99, 147.34, 147.52, 153.37 (C aromatic), 190.37 (CHO). Anal. Calcd for C₃₉H₃₂N₂O: C, 86.00; H, 5.92; N, 5.14. Found: C, 85.89; H, 6.07; N, 5.14.

N-(4-[2,2-Dicyanoethenyl]phenyl)-*N*-phenyl-*N,N*-bis(4-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (MDCETPD, **3**). To a solution of 1.7 g (3.1 mmol) of *N*-(4-formylphenyl)-*N*-phenyl-*N,N*-bis(4-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine and 0.4 g (6.2 mmol) of malononitrile in a mixture of tetrahydrofuran-methanol (1:1) was added one droplet of piperidine, after which the solution was stirred for 2 h at 40 °C. The solvent mixture was evaporated under reduced pressure and the residue dissolved in dichloromethane, washed with water, and dried over magnesium sulfate. The product was purified by column chromatography using silicagel and dichloromethane as the eluent, yielding 1.3 g (70%) of a red solid, $T_g = 77$ °C (see Scheme 1).

¹H NMR (CDCl₃) δ 2.33 (s, 3 H), 2.39 (s, 3 H), 7.09–7.40 (m, 19 H), 7.55–7.58 (dd, 2 H), 7.64–7.67 (dd, 2 H), 7.69 (s, 1 H), 7.86–7.89 (dd, 2 H). ¹³C NMR (CDCl₃) δ 17.78 (CH₃), 17.96 (CH₃), 71.94 (C(CN)₂), 111.11, 112.26 (CN), 119.48, 130.11, 130.16, 133.24, 135.23, 139.32, 140.62, 141.85, 144.50, 144.60, 150.41 (C aromatic), 115.17, 119.62, 120.00, 120.98, 122.15, 123.48, 123.73, 124.37, 124.75, 126.14, 126.94, 127.57, 129.95 (CH aromatic), 154.73 (CH=C). Anal. Calcd for C₄₀H₃₂N₄: C, 85.11; H, 5.44; N, 9.45. Found: C, 84.99; H, 5.48; N, 9.14. Mass (*m/e*) 592 (M⁺), 296 (M²⁺), theoretical mass 592.263, found 592.263.

Sample Preparation. Transparent films can be obtained from the bifunctional molecule since it is amorphous with a glass transition temperature of 77 °C. These films, however, were extremely brittle, making sample preparation rather difficult. Furthermore, the T_g of this material is too high to allow the alignment of the dipoles in the bifunctional molecule under the influence of an applied electric field which is necessary to obtain a net electrooptic effect. For the same reason it is not very likely that orientational enhancement⁶ can occur in this material at room temperature, which therefore also limits the magnitude of the photorefractive effect. To increase their orientational mobility, the bifunctional molecules need to be incorporated in a polymer matrix with a low T_g . Attempts to do this have been made using polybutyl methacrylate as the matrix, which has a T_g of 27 °C. However, only small amounts of the bifunctional molecules could be incorporated due to the lack of solubility. This is most likely due to the large difference in chemical nature between the bifunctional molecule, which is an aromatic compound, and the polymer which is a purely aliphatic material. We have, therefore, chosen to use polystyrene as the polymer matrix which has a much higher resemblance with the bifunctional molecule. Polystyrene has a T_g of around 100 °C, which is too high to allow for the necessary orientational freedom of the bifunctional molecules. To lower the T_g , an additional plasticizer, dioctyl phthalate (DOP), was added to the composite. In this way, concentrations up to 50 wt % of the bifunctional molecule can be incorporated in the polystyrene-DOP mixture without any apparent phase separation.

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Scheme 1. Synthesis of the Bifunctional Molecule

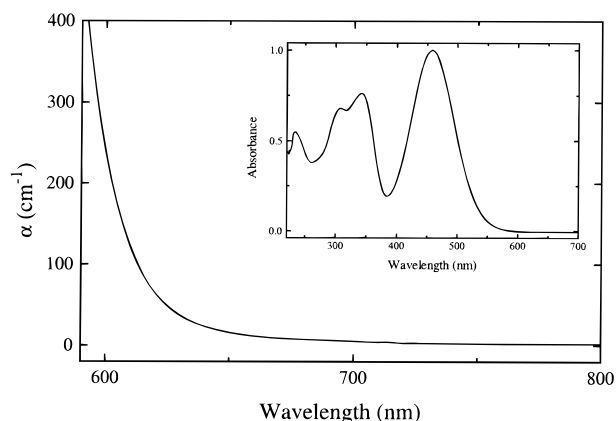
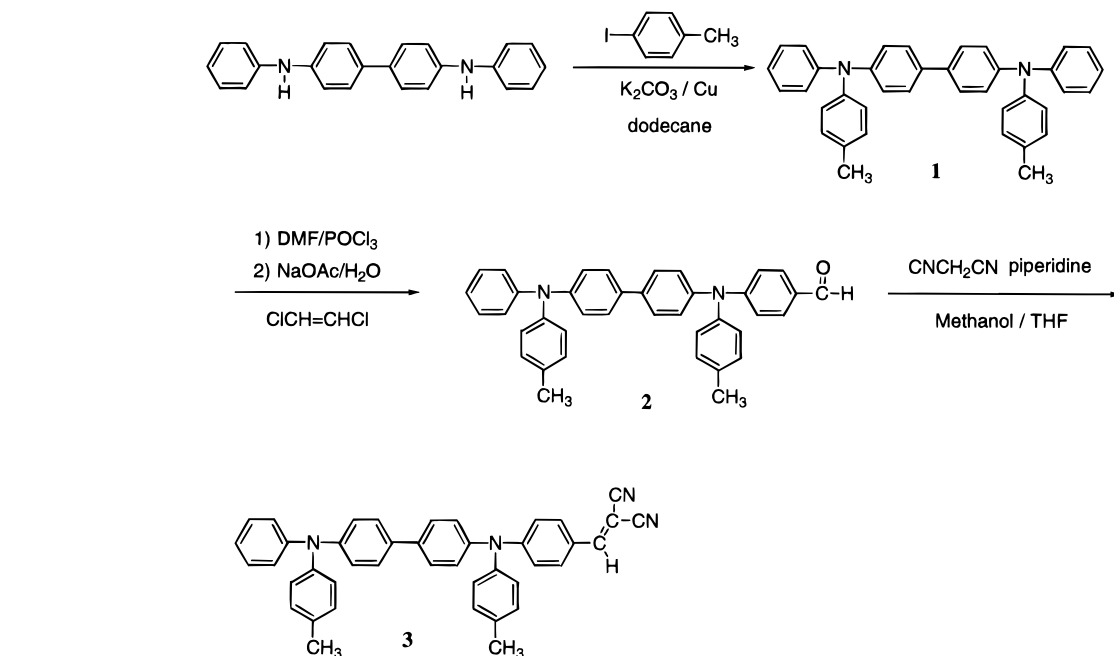


Figure 1. Tail of the absorption coefficient for a polymer film containing MDCETPD (44 wt %), polystyrene (31 wt %) and C₆₀ (0.2 wt %). The insert shows the absorption spectrum of MDCETPD in chloroform solution.

The electrooptic and photorefractive measurements were performed on approximately 100 μm thick polymer films. These films were prepared from toluene solutions containing 44 wt % bifunctional molecule, 31 wt % polystyrene, and 24.8 wt % DOP. Additionally 0.2 wt % of C₆₀ was added to allow for a more efficient photogeneration. All the concentrations mentioned in the text are with respect to the total film weight. The solutions were filtered through a 0.2 μm filter, and the solvent was allowed to evaporate under a continuous argon flow until a very viscous solution remained. Small droplets of these solutions were cast upon indium tin oxide (ITO) covered glass plates and kept for 3 days at 50 $^{\circ}\text{C}$ to ensure maximum solvent removal. The resulting rubbery solid was then covered with another ITO-covered glass plate at approximately 70 $^{\circ}\text{C}$, at which the polymeric mixture is sufficiently fluid, allowing the rubbery droplet to flow homogeneously between the ITO plates. The sample thickness was fixed around 100 μm with the help of Teflon spacers. The T_g of the samples prepared in this way is approximately 30 $^{\circ}\text{C}$ as determined with thermal analysis using DSC. In Figure 1 the tail of the absorption spectrum of the composite is depicted. At 690 nm (the wavelength of measurement) the absorption coefficient (α) is approximately 10 cm^{-1} . The inset shows the absorption spectrum of the bifunctional molecule in chloroform solution.

Measurement Techniques. All the experiments were performed under ambient conditions. The electrooptic coefficient of the samples was evaluated with the ellipsometric technique described by Schildkraut.¹⁶ For recording the photorefractive gratings, the tilted geometry was used, with two beams from a diode laser ($\lambda = 690 \text{ nm}$) incident on the sample at external angles of 30 and 60 $^{\circ}$. The grating spacing in this configuration was approximately 1.7 μm . All the photorefractive measurements were performed after applying the electric field on the sample for at least 30 s. The phase shift of the photorefractive grating was measured with the two beam coupling method,¹⁷ using two *p*-polarized writing beams with equal intensities of 100 mW/cm^2 . For the evaluation of the gain coefficient (Γ), the energy exchange between two *p*-polarized beams was measured. Γ was calculated from the equation⁴

$$\Gamma = (1/d)[\ln(\beta\gamma_0) - \ln(\beta + 1 - \gamma_0)] \quad (1)$$

where β is the ratio of the intensities of the pump and the probe before the sample, γ_0 is the ratio of the intensities of the probe beam, with and without the presence of the pump, and d is the propagation distance of the probe beam inside the sample. The diffraction efficiency and its decay were measured by blocking one beam after the steady-state conditions were reached.

The cyclovoltammometric measurements were performed using platinum working and counter electrodes and silver as the reference electrode in dichloromethane with tetrabutylammonium hexafluorophosphate as the electrolyte. The cyclovoltammograms were calibrated toward the normal hydrogen electrode (NHE) using the ferrocene/ferrocenium ion couple as an internal standard.^{18,19}

Results and Discussion

One of the important parameters for photorefractive materials is the electrooptic coefficient, since, together with the space-charge field, it determines the magnitude of the refractive index grating. The electrooptic coefficient was found to be proportional to the applied

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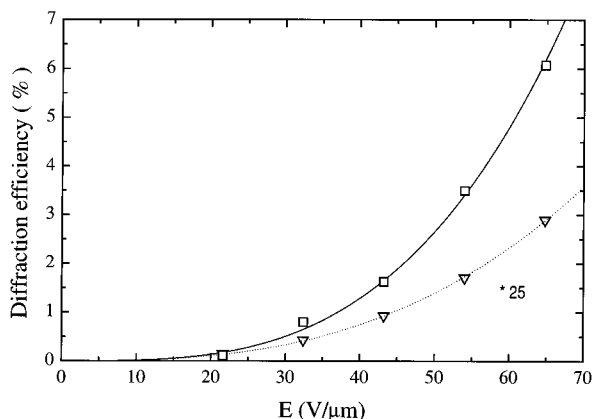


Figure 2. Electric field dependence of the diffraction efficiency of the undoped sample, multiplied by 25 (triangles) and of a sample containing additionally 0.049 wt % of TMPD (squares). The curves are fits to power laws with exponents 2.8 and 3.2 for the undoped sample (dotted line) and the sample containing TMPD (solid line), respectively.

electric field. A value of 1.5 pm/V was measured at an external electric field of 10 V/μm (modulation frequency of 1 kHz), which is lower than values obtained for photorefractive polymers based on PVK with comparable amounts of NLO molecules.^{20,21} This can be explained since in these composites more efficient electrooptic molecules were used.

Two important parameters that characterize the performance of photorefractive materials are the diffraction efficiency (η) and the gain coefficient (Γ), given by⁴

$$\eta \propto (r_{\text{eff}} E_{\text{sc}})^2 \quad (2)$$

$$\Gamma \propto r_{\text{eff}} E_{\text{sc}} \sin \varphi \quad (3)$$

where r_{eff} is the effective electrooptic coefficient, E_{sc} the space charge field, and φ the phase shift between the refractive index grating and the interference pattern.

In Figure 2 the diffraction efficiency as a function of applied electric field is depicted (triangles). The diffraction efficiency increases almost quadratically upon electric field (exponent of a power law fitting curve is 2.8). According to eq 2 such a dependence can occur only when the increase in diffraction efficiency is almost solely due to the increase of the electrooptic coefficient with electric field. The maximum value that was obtained for the diffraction efficiency at 65 V/μm was of the order of 0.1%.

The dependence of the gain coefficient on electric field is depicted in Figure 3 (triangles). The gain coefficient increases almost linearly with electric field (exponent of the fitting curve is 1.4), which again indicates that this increase is mainly due to an increase in the electrooptic coefficient. The maximum gain coefficient measured at an electric field of 65 V/μm was 10 cm⁻¹. The maximum values of both the diffraction efficiency and the gain coefficient are rather low compared to other photorefractive polymers that have approximately the same electrooptic coefficient, indicating that the space charge field is rather weak.

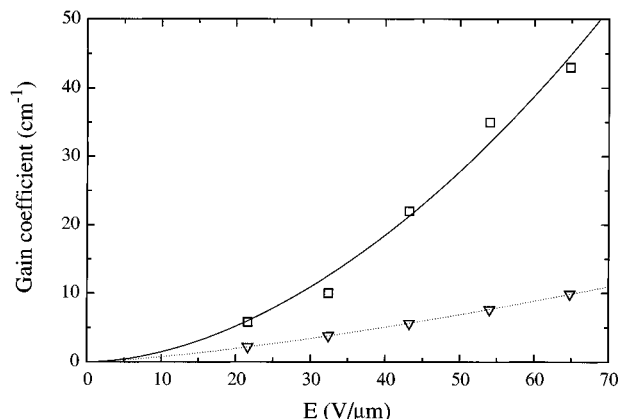


Figure 3. Electric field dependence of the gain coefficient of the undoped sample (triangles) and the sample containing additionally 0.049 wt % of TMPD (squares). The curves are fits to power laws with exponents 1.4 and 1.9 for the undoped sample (dotted line) and the sample containing TMPD (solid line), respectively.

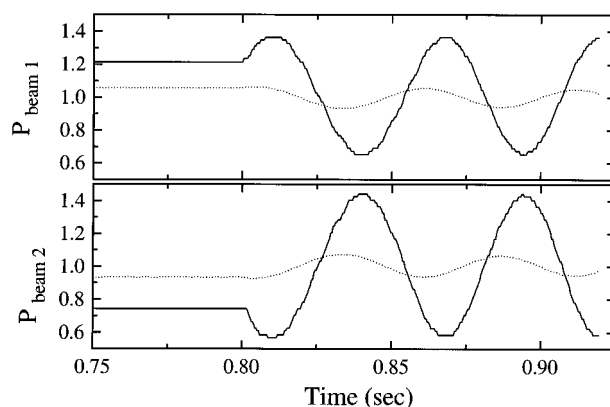


Figure 4. Time dependence of the transmitted power of the two writing beams while translating the sample during a two-beam coupling experiment, translation starts at approximately 0.8 s, for the undoped sample (dotted line) and the sample containing 0.049 wt % TMPD (solid line) at an applied electric field of 50 V/μm.

Apart from the electrooptic coefficient and the space-charge field the gain coefficient depends also on the phase shift between the illumination pattern and the refractive index grating. It is therefore an important parameter of the material, which can be determined individually. According to the standard model of photorefractivity, the phase shift, when the diffusion field is ignored, is given by⁴

$$\varphi = \arctan (E_K / E_S) \quad (4)$$

where E_K is the projection of the applied electric field on the grating wave vector and E_S the saturation field. According to eq 4, the phase shift for $E_K < E_S$ is between 0 and 45° while at high fields ($E_K \gg E_S$) the phase shift approaches 90°. In Figure 4 the dotted lines represent the intensities of the two laser beams in a typical two beam coupling experiment.¹⁸ This figure shows that the grating in this material is purely photorefractive, since the energy of one beam is transferred to the other beam while the sample is translated (translation starts at approximately 0.8 s). From the onset of the energy transfer immediately after the start of the sample translation a phase shift of approximately 90° is deduced. Such a phase shift indicates a low value for the saturation field (eq 4).

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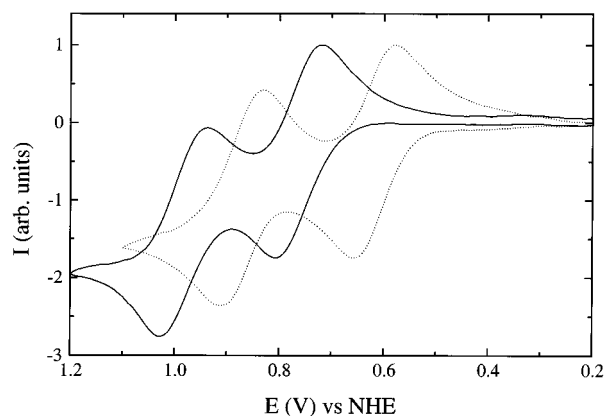


Figure 5. Cyclovoltammograms of *p*-TPD (dotted line) and MDCETPD (solid line) taken in dichloromethane solutions at a sweep rate of 50 mV/s.

From the above-described observations, the amplitude of the photorefractive grating seems to be limited by a small space-charge field. The space-charge field, in the case when the diffusion field is ignored, is given by⁴

$$E_{sc} = mE_K [1 + (E_K/E_S)^2]^{-0.5} \quad (5)$$

where m is the modulation of the illumination pattern. Since the space-charge field does not increase with increasing applied electric field (Figures 2 and 3), it can be deduced that the space-charge field is limited by the value of the saturation field (eq 5). This is corroborated by the 90° phase shift between the refractive index grating and the illumination pattern, as observed in the two-beam coupling experiment. Therefore, to increase the photorefractive performance of the material the saturation field should be increased. The saturation space charge field is described as⁴

$$E_S = eN_T(N_G - N_T)/\epsilon\epsilon_0K_GN_G \quad (6)$$

where N_T is the effective trap density, N_G is the effective concentration of generation sites, ϵ the dielectric constant relative to the permittivity of free space, ϵ_0 , and K_G the grating wave vector. One way of increasing the saturation field is to increase the trap density.

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 a lower oxidation potential than the hopping sites is expected to give rise to trapping. This has been observed in a solid solution of *N*-isopropylcarbazole in polycarbonate when low amounts of TPD were added.²² The transport molecule in our material is the bifunctional molecule *N*-(4-[2,2-dicyanoethenyl]phenyl)-*N*-phenyl-*N,N*-bis(4-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (MDCETPD, 3). This molecule is based on *p*-TPD but due to the incorporation of a strong electron accepting moiety on one side of the molecule the electronic structure has changed and therefore also the oxidation potential. The oxidation potential of the bifunctional molecule relative to that of *p*-TPD was determined using cyclovoltammetry. In Figure 5 the cyclovoltammograms of both the bifunctional molecule

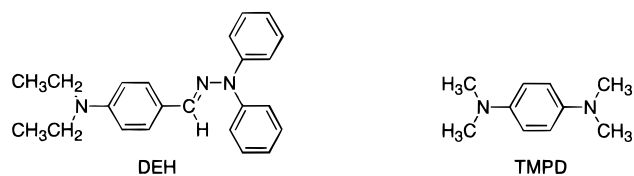


Figure 6. Chemical structures of DEH and TMPD.

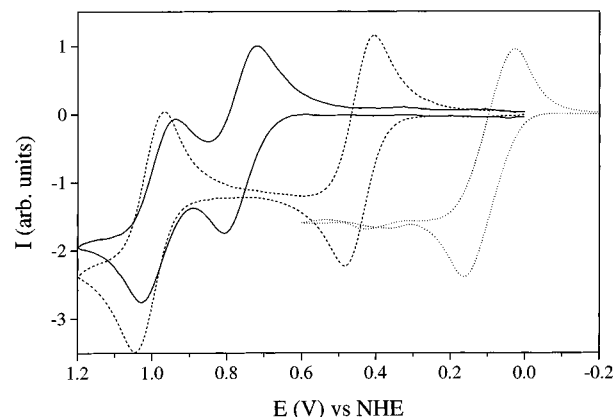


Figure 7. Cyclovoltammograms of MDCETPD (solid line), DEH (dashed line) and TMPD (dotted line) taken in dichloromethane solutions at a sweep rate of 50 mV/s.

and *p*-TPD are depicted. The oxidation potential of the bifunctional molecule has slightly shifted with respect to that of TPD (0.77 V versus 0.64 V). The process of oxidation and following reduction has not changed and is still reversible.

In a previous investigation on the effect of adding trapping molecules to a PVK based composite, we have used the charge-transporting molecule 4-(*N,N*-diethylamino)benzaldehyde diphenylhydrazone (DEH, Figure 6), which has a lower oxidation potential than carbazole, as the trapping species.⁸ The oxidation potential of DEH was determined in order to compare it with that of the bifunctional molecule. The cyclovoltammogram is depicted in Figure 7 (dashed line). An oxidation potential of 0.44 V was found, which is lower than that of the bifunctional molecule. DEH can therefore, in principle, act as a trap. Incorporating small amounts of DEH in a sample with the same composition as previously described, however, did not result in a significant change of the photorefractive performance. This leads to the conclusion that the incorporation of DEH does not effectively increase the concentration of trapping sites. One possible explanation for this result is that the difference between the oxidation potential of the bifunctional molecule and that of DEH is not large enough. For this reason we investigated another molecule, *N,N,N,N*-tetramethyl-4-phenylenediamine (TMPD, Figure 6) which has an even higher electron density than DEH. The cyclovoltammogram of TMPD is shown in Figure 7 (dotted line). The difference in oxidation potential between the bifunctional molecule and that of TMPD (0.09 V) has almost doubled with respect to that of DEH. Therefore, TMPD might act more efficiently as a trap. One disadvantage of a molecule with such a low oxidation potential is that it also easily oxidizes during sample preparation, which makes it more difficult to exactly know the amount of active (unoxidized) TMPD molecules in the material.

In Figure 2, the dependence of the diffraction efficiency on electric field is depicted (squares) for a

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sample containing 0.049% TMPD (1 TMPD molecule/250 bifunctional molecules). A large increase in diffraction efficiency is observed with respect to the sample without any additional traps, resulting in a maximum value of the diffraction efficiency of 6% at 65 V/ μm . The electrooptic coefficient of this sample is the same as that for the sample containing no additional trapping sites. This indicates that the increase in diffraction efficiency is solely due to an increase in the space charge field. Furthermore, the exponent of the power law fitting curve has increased from a value of 2.8 for the pure sample to 3.2 for the sample containing 0.049% TMPD, indicating an increased contribution from the space-charge field with increasing electric field.

The dependence of the gain coefficient on electric field for the sample containing 0.049% TMPD is depicted in Figure 3 (squares). Here also a large increase in gain coefficient is observed with respect to the sample without TMPD. The maximum gain coefficient obtained for this sample is 45 cm^{-1} at 65 V/ μm . The dependence of the gain coefficient on electric field has changed from almost linear to quadratic, which again indicates that now not only the electrooptic coefficient increases with increasing electric field but also the space-charge field. From the above-mentioned observations it is clear that the photorefractive performance of the sample has greatly improved due to an increase in space-charge field by adding small amounts of TMPD which, act effectively as trapping sites in this material.

In Figure 4, the intensities of the two laser beams during grating translation in a two-beam coupling experiment, for the sample containing 0.049 wt % TMPD (solid line) are compared with those obtained from the sample without any additional traps (dotted line). According to this figure, the nature of the grating written in the material with additional trapping sites is still purely refractive index. Together with the reversibility of the grating, this leads to the conclusion that the grating is still purely photorefractive. The phase shift, however, has dropped considerably from 90° for the pure sample to a value of approximately 30° for the sample containing TMPD. The modulation of the refractive index grating of the sample containing TMPD has increased with respect to the pure sample. These observations are in agreement with an increase of the trap density which results in a larger saturation field that causes a decrease in phase shift and an increase in the modulation in the refractive index.

The density of the trapping sites calculated from a phase shift of 30° (eqs 4 and 6) is in the order of $3 \times 10^{16} \text{ cm}^{-3}$. This is much lower than $1.8 \times 10^{18} \text{ traps/cm}^{-3}$ as can be calculated from a weight percentage of 0.049% that was added to the sample (using a density of the sample equal to 1 g/cm^3). The difference in the trapping density calculated from the phase shift and the added weight percentage we believe is due to the ease of oxidation of the TMPD molecules under the influence of oxygen. It was not possible to quantify the ratio between oxidized and unoxidized TMPD, using simple spectroscopic techniques due to the low amount of TMPD present in the samples. Furthermore, effects of the local surrounding or clustering of the trapping molecules may effect the density of active traps.

To systematically investigate the influence of additional trapping sites on the magnitude of the refractive

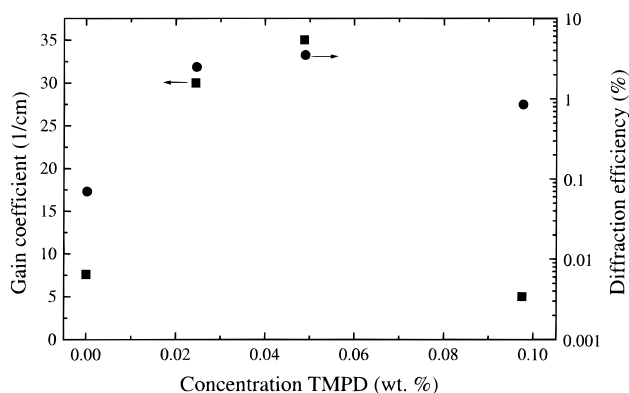


Figure 8. Gain coefficient and the diffraction efficiency of the sample containing MDCETPD (44 wt %), polystyrene (31 wt %), DOP (24.8 wt %), and C_{60} (0.2 wt %), as a function of TMPD concentration at an external electric field of 50 V/ μm .

index modulation, the diffraction efficiency, and the gain coefficient were measured for samples with different amounts of TMPD (Figure 8). The addition of trapping sites increases the space-charge field and, hence, the gain coefficient and the diffraction efficiency. An additional effect of an increased saturation field is the decrease in the phase shift between the refractive index grating and the illumination pattern, which is expected to eventually reduce the gain coefficient to zero at high trap densities. The observed decrease in diffraction efficiency after reaching its maximum value can be explained according to eq 6. Since at these high trap densities the concentration of active trapping sites approaches or even exceeds that of the concentration of effective generation sites (C_{60} in this case), which would result in a lowering of the saturation field and hence a decrease in diffraction efficiency. However, it is difficult to quantify the results because neither the effective trap nor the effective charge generator densities are known.

The response time of the different samples at an applied electric field of 5 kV ranged from approximately 500 ms for the sample containing no additional trapping sites to approximately 10 s for the sample containing the largest amount of TMPD molecules. This is in agreement with the picture of hopping controlled charge transport, as a larger concentration of trapping sites decreases the mobility of the charge carriers.

It has to be stated that the reproducibility of the dependence of the gain coefficient and diffraction efficiency on TMPD concentration is limited to an individual batch of samples. Even though the trend is the same, the absolute value of the concentration of traps at which the maximum seems to occur can be shifted with as much as 0.02% for a different series of samples prepared from a different stock solution of TMPD. This is probably caused by the ease of oxidation of the TMPD molecules under influence of light and oxygen. Even though each stock solution is prepared from freshly sublimed TMPD and the solvent is thoroughly degassed before use, the exact amount of TMPD molecules which are actively present in the resulting sample cannot be completely controlled.

Conclusions

We have prepared a novel photorefractive composite based on the new bifunctional molecule *N*-(4-[2,2-dicyanoethenyl]phenyl)-*N*-phenyl-*N,N*-bis(4-methyl-

phenyl)-[1,1'-biphenyl]-4,4'-diamine. This composite was shown to be photorefractive with a phase shift between the illumination pattern and the refractive index grating of approximately 90°. The relatively small values for the gain coefficient and the diffraction efficiency are due to a small value of the space-charge field. We have shown that the photorefractive behavior of the material can be greatly enhanced by adding small amounts of the molecule *N,N,N,N*-tetramethyl-4-phenylenediamine, which effectively increases the space-charge field. The behavior of the photorefractive parameters,

diffraction efficiency, gain coefficient and phase shift upon trap concentration, can be qualitatively explained within the standard model of photorefractivity.

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