A Novel Polyaryl Ether Based Photorefractive Composite

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We report the synthesis of a novel charge-transporting polymer based on the charge-transport unit *N,N*-diphenyl-*N,N*-bis(3-methylphenyl)-[1,1′-biphenyl]-4,4′-diamine (TPD). Introducing approximately 30 wt % of the liquid electro-optic molecule 4-(*N,N*-diethylamino)-2-fluoro-(*Z*)-β-methyl-(*E*)-β-nitrostyrene (FDEAMNST) and small amounts of C_{60} makes this polymer photorefractive. A full photorefractive characterization is presented. In this composite a rather large electro-optic effect is observed due to the efficient plasticization by the electro-optic molecules of the host polymer. The diffraction efficiency and gain coefficient (3.4% and 50 cm^{-1}, respectively) are rather low. This is attributed to a low space-charge field due to a very low trap density, which is in agreement with a 90° phase-shift between the illumination pattern and the refractive index grating. To increase the trap density, molecules with a low ionization energy were dispersed in the composite.

Introduction

There has been an increasing amount of research directed toward photorefractive polymers in the past few years.[1,2] The main reason for this is the potential applicability of photorefractive materials in optical data storage and dynamic holography.[3] To be photorefractive a material must contain species that can under illumination create free charges and transport and trap these charges; additionally, it should be electro-optically active. When such a material is nonuniformly illuminated, charges will be generated in the bright areas and after transport will eventually get trapped in the darker regions in the material. This redistribution of charges gives rise to a local electric field (the space-charge field) that can, through electro-optic effects, locally vary the refractive index of the material.

By far the most extensively studied class of photorefractive polymers is based on the charge-transporting polymer poly(*N*-vinylcarbazole) (PVK).[1,2,4–6] In PVK-based photorefractive polymers, very large diffraction efficiencies and gain coefficients have been observed. The strongest photorefractive responses, however, occur only in composites that have been sufficiently plasticized.[7,8] Only in low glass transition (T_g) polymers are the electro-optic molecules mobile enough to reorient

under the influence of the space-charge field. This results in a strong increase in the refractive index change, due to contributions of the orientational Kerr effect (the orientational birefringence modulation) and the modulation of the linear electro-optic coefficient to the overall electro-optic response of the material.[9] The T_g of PVK is approximately 210 °C, and although the addition of low molecular weight electro-optic molecules decreases the T_g somewhat, usually the presence of additional plasticizers is required to decrease the T_g close to room temperature. The main problem in these composites is the tendency of the electro-optic molecules to phase separate due to the insufficient amount of polymer binder. For this reason it seems interesting to design a charge-transporting polymer which has a T_g that is substantially lower than that of PVK so that the electro-optic molecules alone can cause a decrease of the T_g toward room temperature.[10]

In PVK the carbazole units are the charge-transport species, from xerography, however, it is known that there are many other and more efficient charge-transport molecules.[11] One particularly interesting example is *N,N*-diphenyl-*N,N*-bis(3-methylphenyl)-[1,1′-biphenyl]-4,4′-diamine (TPD),[12] which results when TPD is dispersed in a polymer matrix at concentrations matching the amount of carbazole units in PVK, in a

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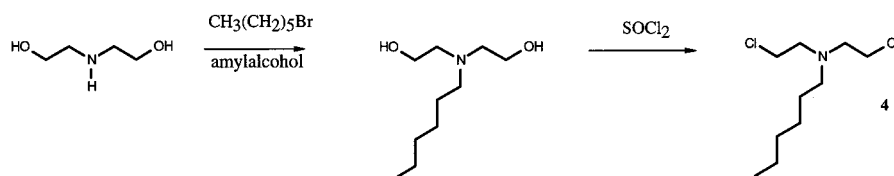(11) *Organic Photoreceptors for Imaging Systems*, Optical Engineering vol. 39; Borsenberger, P. M., Weis, D. S., Eds.; Marcel Dekker: New York, 1993.
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Scheme 1. Synthesis of the Dihydroxy-TPD
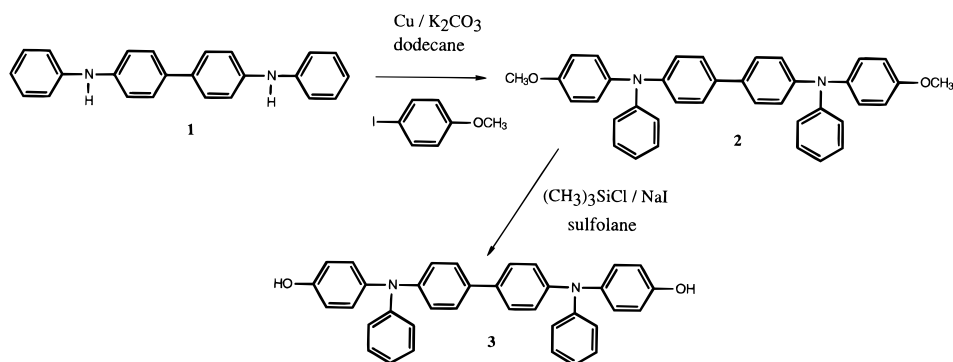
Scheme 2. Synthesis of the Dichloroalkane Comonomer

material with a higher mobility than PVK. This can, in the case of mobility-limited response times, decrease the response time of photorefractive polymers. Apart from the high mobility that is observed in materials using TPD as the charge-transport unit, in these materials the trap density is also extremely low.[13] A material with a low trap density is interesting for photorefractive applications because the trap density determines the magnitude of the saturation field and through this the phase shift and the magnitude of the photorefractive properties, diffraction efficiency, and gain coefficient.[1] For these reasons when striving for a novel charge transport polymer with a low T_g, it is interesting to prepare a polymer based on the charge-transport molecule TPD.

In this paper we describe the synthesis of a low-T_g polymer containing the charge transport molecule TPD. To provide the electro-optic effect an efficient liquid NLO molecule, 4-(N,N-diethylamino)-2-fluoro-(Z)-β-methyl-(E)-β-nitrostyrene[14] (FDEAMNST), is dispersed in this polymer. The photorefractive properties of this novel polymer composite are evaluated. Finally, an attempt was made to increase the trap density, in a controlled manner, in the polyTPD:FDEAMNST composite by adding specific molecules with low ionization energies.

Experimental Section

Synthesis. The TPD-containing monomer required for the preparation of a soluble polymer was prepared starting from N,N-diphenylbenzidine (**1**) (Scheme 1). The required bifunctionality was introduced by means of the methoxy groups of 4-iodoanisole, which was reacted with **1** in a typical Ullman-like reaction. The resulting dimethoxy-TPD (**2**) could easily be converted to the dihydroxy-TPD (**3**) by treatment with trimethylsilyl chloride and sodium iodide. This monomer can then be polymerized in various ways. The preparation of a polyether was chosen over other polymers, like polyesters or
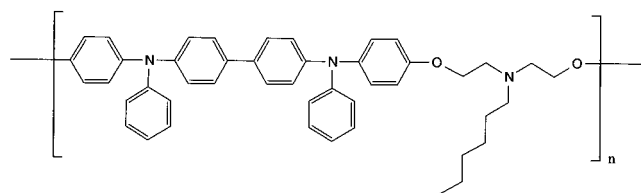

Figure 1. Chemical structure of polyTPD.

polycarbonates, due to the fact that polyethers have the most flexible backbone. Polyethers can be prepared in numerous ways; the simplest way is the reaction between a dihydroxy amine and a dihalogen alkane compound. A polymerization technique was used based on a phase transfer polyetherization.[15] Using this technique good yields (above 70%) of polymers, with moderate average molecular weights, were obtained by reacting the dihydroxy-TPD with a number of commercially available linear dihalogen alkanes. These polymers, however, did not give transparent films after solvent casting, but they were translucent. The quality of the films did improve with decreasing spacer length, but no completely transparent film could be obtained. Also the solubility of the polymers was dramatically reduced. To obtain soluble polymers a minimal spacer length is required. We overcome the minimal spacer length restriction by introducing a solubilizing side chain into the monomer unit. Such a monomer (**4**) was prepared according to Scheme 2; starting from diethanolamine, a hexyl chain was attached by nucleofilic substitution, after which the hydroxyl groups were chlorinated using thionyl chloride. The polyether based on dihydroxy-TPD and monomer **4**, hereafter referred to as polyTPD (the chemical structure is shown in Figure 1), did indeed give fully transparent films. The weight average molecular weight distribution was 31 000 and the number average molecular weight distribution was 16 000, as determined with GPC. The T_g of this polymer was 72 °C.

To be photorefractive the polymer must exhibit the electrooptic effect. In polymers the electro-optic effect is created by introducing large amounts of nonlinear optical (NLO) molecules. An interesting NLO molecule, 4-(N,N-diethylamino)-2-fluoro-(Z)-β-methyl-(E)-β-nitrostyrene (FDEAMNST), which was used before in photorefractive polymers utilizing PVK as the matrix,[14] is liquid at room temperature. This molecule could be dispersed in high concentrations without

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Scheme 3. Synthesis of the Electro-Optic Molecule FDEAMNST
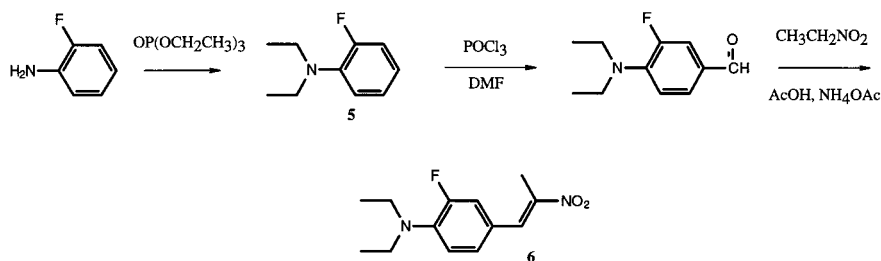
giving rise to phase separation. The synthesis of this molecule is described in Scheme 3. 2-Fluoroaniline is ethylated with triethyl phosphate. This compound **5** is then formylated in a Vielsmeijer reaction, and subsequent condensation with nitroethane gives the desired NLO molecule **6**.

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. Molecular weights were determined using a high-pressure liquid gel permeation chromatograph coupled with a multiangle laser light scattering detector (DAWN-DSP, Wyatt Technology Corp.), a refractive index detector (SHODEX RI-71), and a viscometer detector (Viscotek H502).

All reactions were performed under a dry nitrogen atmosphere. DMF was distilled over LiAlH$_4$, dichloromethane was distilled from CaH$_2$, and pentane was distilled from P$_2$O$_5$. All chemicals were obtained from either Acros Chimica or Aldrich.

Materials. *N,N-Bis(4-methoxyphenyl)-N,N-diphenyl-[1,1-biphenyl]-4,4-diamine[21]* (**2**). A solution of 10 g (0.030 mol) of *N,N*-diphenyl-[1,1'-biphenyl]-4,4-diamine, 20.9 g (0.090 mol) of 4-iodoanisole, 16.56 g (0.120 mol) of potassium carbonate, and 8.8 g of copper bronze in 40 mL of hexadecane was stirred under argon atmosphere at 210 °C for 3 days. After cooling, the excess iodoanisole was 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 11.6 g (70%) of a white solid. ¹H NMR (CDCl$_3$): δ 4.06 (s, 6H), 7.11 (dd, 4H), 7.31–7.51 (m, 18H), 7.66 (dd, 4H). ¹³C NMR (CDCl$_3$): δ 55.68 (CH$_3$O), 115.01, 122.16, 123.08, 123.25, 127.31, 127.52, 129.30 (CH-aromatic), 134.28, 140.89, 147.18, 148.28, 156.44 (C-aromatic). Mass (*m/e*): 587 (M⁺), 293.62 (M²⁺). Theoretical mass: 587.257. Found: 587.257.

N,N-Bis(4-hydroxyphenyl)-N,N-diphenyl-[1,1-biphenyl]-4,4-diamine (**3**). A solution of 10 g (0.018 mol) of *N,N*-bis(4-methoxyphenyl)-*N,N*-diphenyl-[1,1-biphenyl]-4,4′-diamine and 8.1 g (0.054 mol) of sodium iodide in 100 mL of sulfolane is heated to approximately 140 °C until the majority of the starting compounds is dissolved. After cooling to 60 °C, 6.1 g (0.054 mol) of chlorotrimethylsilane was added. The resulting mixture was refluxed for an additional 6 h, before cooling down and pouring into a large excess of water. The very viscous precipitate was isolated by careful decantation of the water layer and subsequently dissolved in methanol. After extracting twice with hexane, the methanol was evaporated, and the residue dissolved in acetone. The solution was slowly added

to a large excess of water, after which the crude product solidified. This crude product was filtrated, dried, and subsequently purified by column chromatography over silica gel using a mixture of ethyl acetate:dichloromethane (1:20) as the eluent. Evaporation of the solvent yielded 6.75 g (72%) of the pure product. ¹H NMR (DMSO-d_6): δ 6.72 (dd, 4H), 6.83–7.28 (m, 18H), 7.45 (dd, 4H). ¹³C NMR (DMSO-d_6): δ 116.38, 121.72, 121.80, 122.17, 126.72, 127.92, 129.18 (CH-aromatic), 132.66, 138.01, 146.54, 147.53, 154.56 (C-aromatic). Mass (*m/e*): 520 (M⁺), 260 (M²⁺). Theoretical mass: 520.215. Found: 520.215.

Bis(2-hydroxyethyl)hexylamine. A solution of 10 g (0.095 mol) of diethanolamine and 7.76 g (0.047 mol) of 1-bromohexane in 40 mL of isoamyl alcohol was refluxed overnight. The solvent was removed under reduced pressure and the residue was mixed with water and extracted three times with diethyl ether. The combined ether layer was washed with water (three times) and subsequently with diluted hydrochloric acid (three times). The combined hydrochloric acid layer was made basic by adding a solution of 30% NaOH in water. The oily product which was formed was extracted with ether from this basic water solution. After drying the ether layer over MgSO$_4$ and evaporating the solvent, 4.2 g (47%) of a pure oil was obtained. ¹H NMR (CDCl$_3$): δ 0.88 (m, 3H), 1.27 (m, 6H), 1.44 (m, 2H), 2.36 (s, 2H), 2.52 (t, 2H), 2.67 (t, 4H), 3.61 (t, 4H). ¹³C NMR (CDCl$_3$): δ 13.76 (CH$_3$), 22.34, 26.48, 26.77, 31.48 (CH$_2$), 54.55, 55.81 (CH$_2$N), 59.33 (CH$_2$OH).

Bis(2-chloroethyl)hexylamine (**4**). A 5 g (0.026 mol) portion of bis(2-hydroxyethyl)hexylamine was slowly added to 6.9 g (0.058 mol) of thionyl chloride and subsequently refluxed for 2 h. After cooling, the resulting mixture was poured into an excess of water, which was subsequently made basic by adding a solution of 10% NaOH in water. The product was extracted with diethyl ether. After drying over MgSO$_4$ and evaporation of the solvent, the crude product was obtained. This was purified by distillation under reduced pressure, yielding 3.5 g (60%) of a clear liquid which solidified upon standing. ¹H NMR (CDCl$_3$): δ 1.02 (t, 3H), 1.41 (m, 6H), 1.56 (m, 2H), 2.67 (t, 2H), 2.99 (t, 4H), 3.63 (t, 4H). ¹³C NMR (CDCl$_3$): δ 13.43 (CH$_3$), 21.87, 26.12, 26.97, 32.04 (CH$_2$), 42.02 (CH$_2$Cl), 54.24, 56.19 (CH$_2$N).

2-Fluoro-N,N-diethylaniline (**5**). A mixture of 22.2 g (0.200 mol) of 2-fluoroaniline and 24.3 g (0.133 mol) of triethyl phosphate was stirred for 5 h at 200 °C. The mixture was cooled to 50 °C and a solution of 25 g of NaOH in 100 mL of water was added, followed by refluxing the solution for 1 h. Upon cooling, the sodium phosphate crystallizes. The oily layer was decanted, diluted with ether, and dried over MgSO$_4$. After filtration and evaporation of the solvent, the residue was stirred overnight in acetic anhydride. A 20 mL portion of concentrated hydrochloric acid in 30 mL water was added and the clear solution was washed three times with diethyl ether. The water layer was made basic by adding a 25% NaOH solution in water and the product was collected by extracting the water layer three times with diethyl ether. After drying over MgSO$_4$, filtration, and evaporation of the solvent, 10.3 g (31%) of a colorless oil was obtained. ¹H NMR (CDCl$_3$): δ 1.10 (t, 6H), 3.24 (q, 4H), 6.84 (dd, 2H), 7.24 (dd, 2H).

3-Fluoro-4-(N,N-diethylamino)benzaldehyde. A 18.85 g (0.123 mol) sample of POCl$_3$ was slowly added to a stirred solution

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of 5.33 g (0.032 mol) of 2-fluoro-*N,N*-diethylaniline and 8.95 g (0.123 mol) of dimethylformamide in 30 mL of 1,2-dichloroethane. Subsequently the solution was refluxed for 2 h, cooled, and poured into water. The resulting mixture was extracted with dichloromethane (three times). After drying over MgSO$_4$, the solvent together with the 1,2-dichloroethane and the DMF was removed by evaporation under reduced pressure. This crude product was purified by column chromatography over silica gel using ether:hexane (1:2) as the eluent, yielding 3.1 g (50%) of a yellow oil. ^{1}H NMR (CDCl$_3$): δ 1.21 (t, 6H), 3.42 (q, 4H), 6.82 (m, 1H), 7.41−7.53 (m, aromatic, 2H), 9.72 (s, 1H).

3-Fluoro-4-(N,N-diethylamino)-(E)-β-methyl-(Z)-β-nitrostyrene (6). A mixture of 1.5 g (7.7 mmol) of 3-fluoro-4-(*N,N*-diethylamino)benzaldehyde, 0.85 g (11.3 mmol) of nitroethane, 0.40 g (5.8 mmol) of ammonium acetate, and 4.22 g of glacial acetic acid was stirred at 80 °C for 3 h. After cooling the solution was poured into water and extracted three times with dichloromethane. The combined dichloromethane layers were washed three times with water and dried over MgSO$_4$. After filtration and evaporation of the solvent, the crude product was purified by column chromatography over silica gel using dichloromethane:pentane (3:1) as the eluent, yielding 0.90 g (57%) of the pure orange oil. ^{1}H NMR (CDCl$_3$): δ 1.18 (t, 6H), 2.49 (d, 3H), 3.35 (q, 4H), 6.82 (m, 1H), 7.11−7.18 (m, 2H), 8.00 (s, 1H). ^{13}C NMR (CDCl$_3$): δ 12.76 (CH$_3$), 13.94 (CH$_3$), 45.69 (CH$_2$), 117.05, 118.23, 127.91, 133.24 (CH-aromatic), 122.06, 144.15, 144.27 (C-aromatic).

Polymerization. A mixture of 3.74 g (7.19 mmol) of *N,N'*-bis(4-hydroxyphenyl)-*N,N'*-diphenyl-[1,1-biphenyl]-4,4'-diamine, 1.6 g (7.19 mmol) of bis(2-chloroethyl)hexylamine, 0.82 g (2.4 mmol) of the phase transfer catalyst tetrabutylammonium hydrogen sulfate (TBAH), and 20 mL of chlorobenzene was stirred at 80 °C under argon atmosphere. After 15 min 12 mL of a 10 N NaOH solution was added under vigorous stirring, and the mixture was subsequently stirred for another 3 h at 80 °C. After cooling, the solution was diluted with 50 mL of dichloromethane and washed three times with brine and three times with water. The resulting dichloromethane solution was slowly added to 500 mL of methanol in which the polymer precipitated. The polymer was filtrated and reprecipitated twice from dichloromethane in methanol. Filtration and drying yielded 4.1 g (86%) of a white polymer.

Sample Preparation. The electro-optic and photorefractive measurements were performed on approximately 100 μm thick polymer films. These films were prepared from toluene solutions containing 30 wt % of FDEAMNST, 69.8 wt % of polyTPD, and 0.2 wt % of C$_{60}$. The latter was added to ensure efficient charge generation. The solutions were filtered through a 0.2 μm filter, and the solvent was allowed to evaporate. Subsequently, the obtained solid film was reduced into powder and stored overnight in a vacuum chamber to ensure maximum solvent removal. The resulting powder was pressed in a stainless steel mold at elevated temperatures. After cooling, the resulting pellets were sandwiched between two indium tin oxide (ITO) covered glass plates by applying gentle pressure at 100 °C. The thickness was fixed by Teflon spacers.

The T_g of the samples obtained in this way is approximately 30 °C, determined using DSC. The substantial lowering of the T_g with respect to that of the polyTPD can be attributed to the presence of large amounts of low molecular weight NLO molecules, which act as plasticizers.

Measurement Techniques. The electro-optic response of the samples at 1 kHz modulation frequency was evaluated with the ellipsometric technique described by Schildkraut.[16] For recording the photorefractive gratings, the tilted geometry was used, with the two beams from a He−Ne laser (λ = 633 nm) incident on the sample at external angles of 30° and 60°. The grating spacing in this configuration was approximately 1.6 μm. 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 600 mW/cm^2. For the evaluation of the gain coefficient Γ, the energy
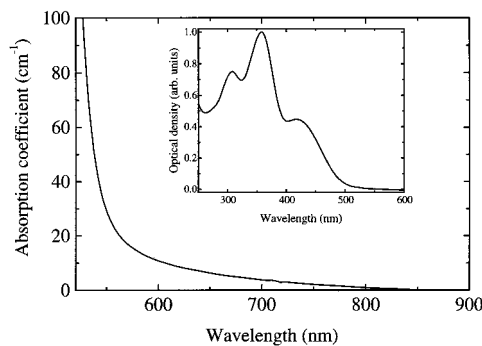

Figure 2. Tail of the absorption coefficient for a polymer film containing polyTPD (69.8 wt %), FDEAMNST (30 wt %), and C$_{60}$ (0.2 wt %). The insert shows the absorption spectrum of this composite in chloroform solution.

exchange between two *p*-polarized beams was measured. Γ was calculated according to

$$\Gamma = \left(\frac{1}{d}\right)[\ln(\gamma) - \ln(2 - \gamma)] \tag{1}$$

where γ is the ratio of the intensities of the one beam with and without the presence of the other one and d is the length of interaction. The diffraction efficiency and its decay were measured by blocking one beam after the steady-state conditions were reached.

Results and Discussion

An important feature of a photorefractive polymer is its absorption spectrum, since this determines the wavelength region in which the polymer can be used. From previous investigations it is clear that in the wavelength region of interest the NLO molecule should not absorb, as this can give rise to competing nonphotorefractive gratings.[18] Therefore, the absorption spectrum of the polymer film is measured; as depicted in Figure 2, the inset shows the absorption spectrum of FDEAMNST and polyTPD in chloroform solution. The absorption coefficient above 600 nm is very low and is most likely due to the charge-transfer complex between C$_{60}$ and polyTPD and is not caused by absorptions of FDEAMNST. Therefore, the electro-optic and photorefractive characterizations can safely be performed using a He−Ne laser which emits at 633 nm.

The magnitude of the photorefractive effect is determined by the space-charge field and the overal electro-optic effect. In polymers, the overall electro-optic coefficient depends on the concentration of NLO molecules, their molecular parameters such as hyperpolarizability and anisotropy, and their degree of alignment. The alignment of the NLO molecules is achieved by applying a large electric field (E_p) over the sample. The degree of alignment thus depends on the magnitude of the applied electric field and its frequency. A linear increase with the electric field is measured, as a result of the increase in alignment of the NLO molecules. A value of 7.2 pm/V is observed at 20 V/μm, which is a high value compared to other photorefractive host−guest polymers.[4−6] Such a high value is caused by the low intrinsic T_g of the polymer and its additional lowering by incorporating large amounts of low molecular weight NLO molecules, which can act as plasticizers.
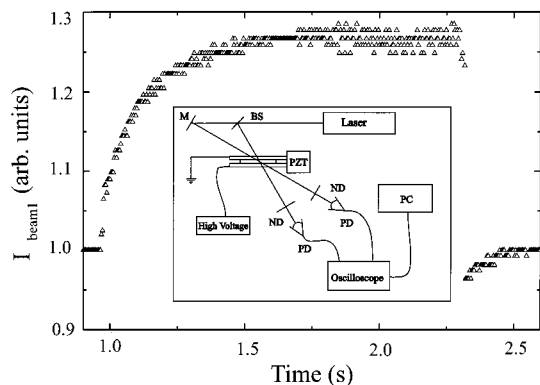
Figure 3. Asymmetric energy is observed when the second writting beam is turned on at time 1 s. At time ~2.25 s the second beam is turned off. The insert shows the experimental setup. The sample was mounted on a piezotranslator (PZT). The intensity of the two transmitted beams was reduced with neutral density filters (ND) and monitored with photodiodes and an oscilloscope (Osc) interfaced with a computer (PC). The sample was connected to a high-voltage power supply. In the picture, M is a mirror and BS a beam splitter.

Unambiguous proof for the existence of photorefractivity is provided with the demonstration of a phase-shifted refractive index grating with respect to the illumination pattern. Such a phase-shifted grating is unique for photorefractive materials and gives rise to an asymmetric energy exchange between the two laser beams that write it. In Figure 3 the energy gain of one beam is observed when the second beam is turned on in the polyTPD:FDEAMNST:C_{60} composite at an $E_p = 55$ V/μm. The second beam is turned on, at time approximately 1 s, creating the interference pattern which gives rise to the formation of the space-charge field due to the migration of the photoexcited charges. The space-charge field is converted to a refractive index grating by means of the overall electro-optic effect and energy starts to flow from beam 2 to beam 1. After approximately 0.5 s, the rise time of the grating, the gain in energy levels off, indicating that the steady-state regime has been reached. At $t \approx 2.25$ s the second beam is turned off again, which results in an immediate drop in the intensity of beam 1 even below its initial value. This is caused by the lack of energy gain from beam 2. Moreover, because the refractive index grating is still present, part of beam 1 is diffracted into the direction of beam 2. This diffracted part becomes less as the refractive index grating is erased due to the uniform illumination of the sample by beam 1.

The amplitude and phase shift, as well as information about the possible presence of complimentary absorption or refractive index gratings, were acquired with the two-beam coupling technique.[17] In Figure 4, the intensities of the two beams after translating the sample 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 two signals are 180° out of phase, indicating the dominance of the refractive index grating. From the onset of the modulation a phase shift of approximately 90° is deduced. Such a phase shift is a signature for a low trap density in the polymer.

Two important parameters that characterize the performance of photorefractive materials are the dif-
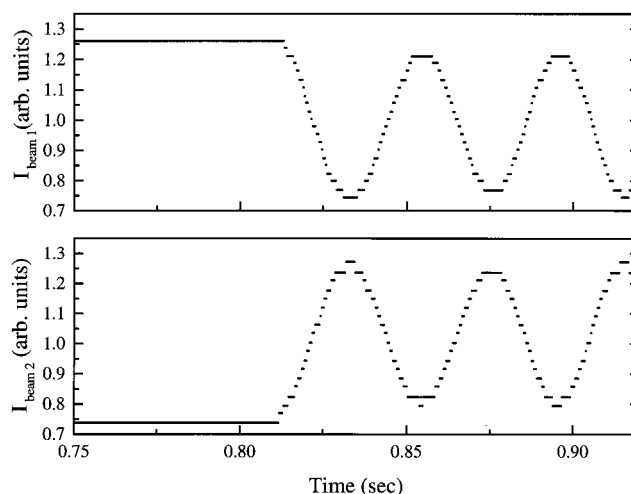

Figure 4. Time dependence of the transmitted power of the two writing beams during a two-beam coupling experiment for the sample polyTPD:FDEAMNST:C_{60} at an applied electric field of 55 V/μm.

fraction efficiency (η) and the gain coefficient (Γ). Both of them strongly depend on the overall electro-optic coefficient ($r_{overall}$) of the space-charge field (E_{sc}):

$$\eta \propto (r_{overall} E_{sc})^2 \qquad (2)$$

$$\Gamma \propto r_{overall} E_{sc} \sin \varphi \qquad (3)$$

The overall electro-optic coefficient $r_{overall}$, which describes contributions of the linear electro-optic effect, the orientational birefringence modulation, and the modulation of linear electro-optic coefficient to the refractive index modulation, is a complex function of the interaction geometry, the NLO molecules hyperpolarizability, anisotropy, and permanent dipole moment and strongly depends on the T_g of the composite. In the approximation of the small applied electric field E_p (the usual case for photorefractive polymers) the overall electro-optic coefficient $r_{overall}$ has a linear dependence on E_p.[9] It should be mentioned that the electro-optic coefficient measured with the ellipsometric technique is not exactly equal to the overall electro-optic coefficient but rather gives an order of magnitude estimate for $r_{overall}$.

In the inset of Figure 5 the gain coefficient for the polyTPD:FDEAMNST containing composite as a function of applied electric field is depicted. The maximum value of the gain coefficient is approximately 50 cm^{-1}, at an external electric field of 55 V/μm. This value is rather low, especially in view of the measured high electro-optic response. The gain coefficient increases linearly with electric field at electric fields above 30 V/μm. This is in agreement with the observation of a 90° phase shift between the illumination pattern and the refractive index grating for the composite. According to the standard model of photorefractivity, the phase shift φ is given by (in the case where the diffusion field is ignored)

$$\varphi = \arctan(E_k / E_s) \qquad (4)$$

where E_k is the projection of the applied electric field on the grating wave vector and E_s is the saturation field.
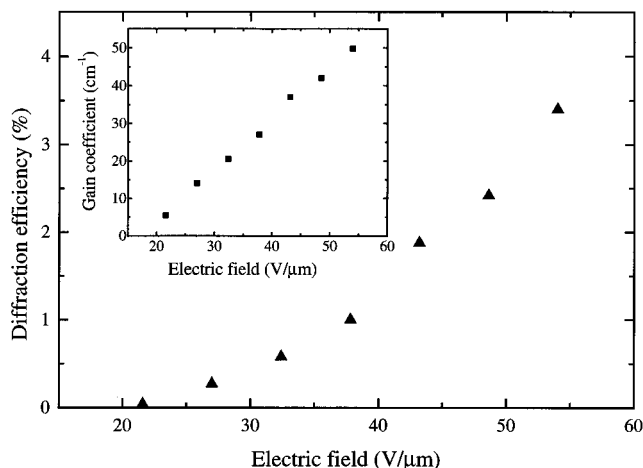
Figure 5. The diffraction efficiency of polyTPD:FDEAMNST:C_{60} as a function of applied electric field. The insert shows the dependency of the gain coefficient of polyTPD:FDEAMNST:C_{60} as a function of applied electric field.

The saturation field is determined by the effective trap density N_T and is given by

$$E_s = eN_T/\epsilon\epsilon_0 K_G \qquad (5)$$

where ϵ is the dielectric constant relative to the permittivity of free space (ϵ_0) and K_G is the grating wave vector. According to the standard model the measured 90° phase shift implies[4,5] a low value for the saturation field E_s as a result of the low trap density N_T. The low concentration of trapping sites is probably caused by the use of the TPD-based charge transport molecule. This means that the space-charge field reaches its maximum value already at low electric fields. Therefore, only at low fields do both the space-charge field and the overall electro-optic coefficient increase, resulting in the nonlinear behavior of the gain coefficient. At higher fields, the increase in the gain coefficient is solely due to an increase in the overall electro-optic coefficient, which results in the observed linear increase. Even though this linear behavior is in agreement with the standard model, fitting of the curve using the equation derived from the standard model and the overall electro-optic coefficient and using the diffusion and saturation fields as fitting parameters resulted in unrealistic values for the diffusion and saturation fields.

The dependence of the diffraction efficiency of the polyTPD:FDEAMNST-containing composite is depicted in Figure 5. The diffraction efficiency of 3.4% for the composite is again rather small. Even though the observed superlinear dependence of the diffraction efficiency with applied electric field is predicted by the standard model, it was not possible to quantitatively describe the behavior of the composites using this model. The decay of the diffraction efficiency was measured after turning of one of the two writing beams, and the typical decay time was found to be on the order of 0.5 s. This value is approximately the same as the one that can be deduced from the rise time observed in the gain experiment.

From the magnitudes of the gain coefficient and diffraction efficiency and their dependence upon electric field it is obvious that the space-charge field in this polymer composite is small. Hence, to increase the photorefractive performance it is necessary to increase the space-charge field. We were able to increase the space-charge field of a photorefractive polymer consisting of a bifunctional molecule based on TPD by introducing additional trapping sites in the form of molecules with a low ionization energy.[20] We have tried this approach again for the polyTPD-based photorefractive polymers by adding the same molecules as in the bifunctional molecule based photorefractive material, namely 4-(*N,N*-diethylamino)benzaldehyde diphenylhydrazone (DEH) and *N,N,N',N'*-tetramethyl-4-phenylenediamine (TMPD). In the polyTPD-based photorefractive polymer, however, no measurable increase in gain coefficient or diffraction efficiency was observed. This indicates that for polyTPD neither DEH nor TMPD is capable of acting as a trap. The reason for this might be that the difference in HOMO level energies between polyTPD and DEH or TMPD is not large enough. To verify this hypothesis, the ionization energies of the relevant molecules were determined by ultraviolet photoelectron spectroscopy (UPS) in the gas phase, using photons from the He I resonance line at 58.4 nm, equivalent to a photon energy of 21.22 eV. Since the HOMO energy level of polyTPD cannot be determined in the gas phase, it was assumed to be approximately equal to that of the basic unit of the polymer, dimethoxy-TPD (**2** in Scheme 1). Using UPS, ionization energies are found for DEH, TMPD, and dimethoxy-TPD (6.20, 6.15, and 6.20 eV, respectively). The energy difference between the HOMOs of DEH or TMPD and that of dimethoxy-TPD almost became negligible (0.05 eV), whereas the difference between TMPD and the bifunctional molecule from our previous investigation was approximately 0.3 eV. These data indicate that indeed the difference between the ionization potential of the charge transport and charge trapping molecule became to small for TMPD to be able to act as a trapping site in the polyTPD-based material. Attempts to incorporate molecules which have even lower ionization energies are not promising due to the unstability of such molecules with respect to oxidation.

Conclusions

We have prepared a charge-transporting polymer using the charge-transport molecule TPD. This was achieved by functionalizing this molecule with two hydroxy groups so that it could be reacted with a dichloroalkane, yielding a polyether. From the various dichloroalkanes that were investigated only bis(2-chloroethyl)hexylamine gave transparent films. The glass transition temperature of the polymer was 72 °C, which is low enough to decrease the T_g of the composite down to room temperature when electro-optic molecules are incorporated. This polymer could be made photorefractive by incorporating large amounts of FDEAMNST and small amounts of C_{60}. The high value of the electro-optic response, observed in this composite, is attributed mainly to the efficient plasticization of the FDEAMNST molecule, resulting in an almost room-temperature T_g of the composite.

The photorefractive nature of the refractive index grating was proven by the existence of a 90° phase shift between the refractive index grating and the illumination pattern. The magnitude of the photorefractive

effect expressed by the gain coefficient and the diffraction efficiency was rather small. This was attributed to a low value for the space-charge field, caused by the rather small intrinsic trap density of TPD.

The trap density did not increase with adding small amounts of low ionization energy molecule due to the small difference between the ionization energies of polyTPD and the trap molecules. This is further evidence of the intrinsically low trap density of the material, since, apparently, not many uncontrollable impurities can act as hole trap sites.

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