

Main Chain-Containing Azo-Tetraphenylidiaminobiphenyl Photorefractive Polymers

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The design of polymeric materials with optimized photoconductivity and nonlinear optical properties is of major interest for emerging optical applications using photorefractive properties. This paper reports the synthesis and preliminary optical characterization of a series of novel, fully functionalized, photorefractive polymers. They were synthesized by a post azo coupling reaction of a polyether carbonate polymer based on the charge transport N,N,N',N'-tetraphenyl-diaminobiphenyl group with 4-nitrobenzene-diazonium tetrafluoroborate by phase transfer catalysis. The amount of the inserted 4-nitro-phenyl-azo group was between 0.1 and 1.7 per structural unit. These polymers absorb in the UV–vis range, because of the presence of donor–acceptor substituted azobenzene chromophores. Light induced change of the refractive index was studied by birefringence measurements ($\lambda_{\text{probe}} = 632.8$ nm) as a function of azo content in thin films with thickness ranging from 200 to 500 nm. Surface relief grating inscription was also demonstrated in the same polymer thin films, with a weak surface relief amplitude and a low diffraction efficiency (<1%). These results indicate a relatively low mobility of the azobenzene chromophores. Photoconductivity was studied by measuring the photocurrent through 40 μm thick samples where a metal-free phthalocyanine layer deposited on electrodes served as charge generator. These samples have exceptionally high photoconductivity compared to other composite materials. In addition, preliminary two-beam coupling experiments demonstrated unambiguously the photorefractive effect under low poling field (2.5 V/ μm) at room temperature, but no net gain was obtained because of a high absorption coefficient at 632.8 nm.

Introduction

Photorefractive polymers^{1,2} are the subject of intense study because of the possibility of adjusting properties by changing the polymer structure and because of the variety of possible applications. Such applications include dynamic and reversible holographic data storage, real-time image processing, optical connectors and many others.^{3,4}

Initially studied in a mixture of guest–host polymer systems, the current molecular design strategy is to optimize and synthesize fully functionalized polymers in order to take advantage of the structural and compositional flexibility of polymers which allows higher diffraction efficiency, faster responses, and longer term stability. Such parameters can be optimized by improv-

ing the ordering of photoconductors and electrooptic chromophores, by reducing the optical loss due to the absorption and scattering, and also by avoiding the formation of aggregates and improving the lack of miscibility. The concentration of components can be easily tuned in order to find the optimum balance between the photoconductive and electrooptic groups.⁵

The main strategy is multiple side-chain functionalization,⁶ but a combination of all properties within a single structural unit was also demonstrated.^{7–9} In our research, azocarbazole units were designed to contain the photoconductive carbazole group substituted at the 3 position by a 4'-nitroazobenzene group, which provides the electrooptic activity. This active component was bound to a methacrylate backbone through a spacer of variable length, allowing the adjustment of the polymer

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film properties. However, no net gain was reported, since the polymers have strong absorption coefficients ($\alpha = 2200 \text{ cm}^{-1}$ and $\Gamma = 240 \text{ cm}^{-1}$).

The N,N'-diphenyl N,N'-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (**TPD**) molecule and some of its derivatives are extensively used as hole transport conductors. It exhibits better charge-transport mobility than carbazole derivatives such as poly(N-vinylcarbazole) (PVK), which are commonly used as charge-transporting components in composite photorefractive materials. It is noteworthy that in PVK, the carrier mobility and the activation energy of hole transport mobility are dependent on the poling field, while for **TPD**-doped polymers with high concentration, high mobilities have been measured at room temperature and $1 \text{ V}/\mu\text{m}$.^{10,11}

In this context, incorporating **TPD** units in polymeric materials could potentially lead to an increase of photoconduction and therefore of photorefractive efficiency. Recently, a photorefractive composite polymer obtained by the dispersion of a bifunctional **TPD**-based molecule in a polymer matrix was reported by Hadzioannou et al.¹² Sato and co-workers have reported the preparation of acrylate-type homo- and copolymers that are efficient as charge transport components in a composite photorefractive material.^{13,14}

We report here the synthesis and characterization of the first fully functionalized polymer where the electrooptic chromophore is covalently linked to the photoconductive moiety (**TPD**). As in most of our previous work,^{15,16} we will demonstrate photoinduced orientation and surface relief gratings in this new polymer, followed by a preliminary demonstration of the photorefractive properties.

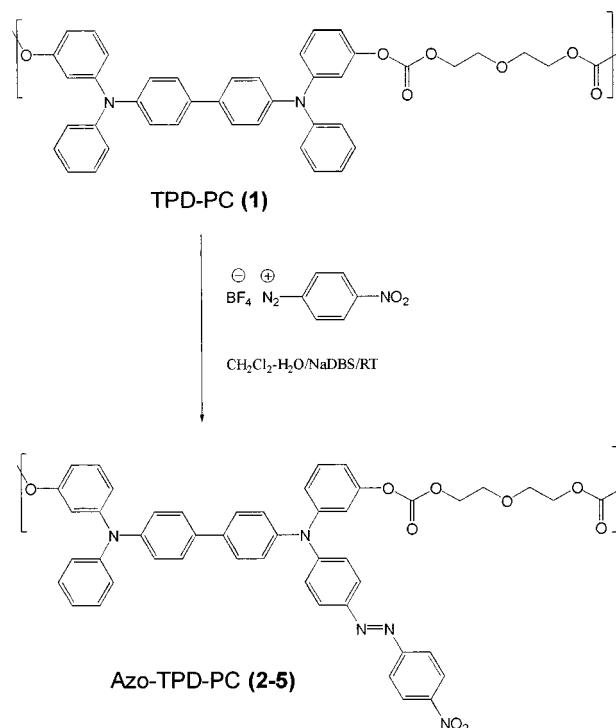
Experimental Section

Synthesis and Polymer Characterization. The synthesis of TPD-PC (**1**) (Scheme 1) was previously reported.¹⁷ ¹H NMR spectra of the copolymers were measured on a Bruker AC-F 200 MHz spectrometer in deuterated dichloromethane solutions. Glass transition temperatures (T_g) were measured on second heating scans on a Mettler TA-30 DSC instrument equipped with a TA-3000 processor at a scan rate of $10 \text{ }^\circ\text{C}/\text{min}$. UV-vis spectra of solutions and films of polymers were measured on a Shimadzu 1201 spectrophotometer. The average molecular weights (M_w) and polydispersities of the polymers were estimated by gel permeation chromatography (polystyrene standard calibration), in THF, on a Waters liquid chromatograph equipped with a R410 differential refractometer.

General Procedure for Azo Coupling Reactions. Polymer 2: 4-nitrobenzenediazonium tetrafluoroborate (0.69 g; 2.9 mmol), freshly prepared and dried, was dissolved in distilled water (100 mL). The mixture was stirred at $0 \text{ }^\circ\text{C}$ for 15 min,

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Scheme 1



then sodium dodecylbenzenesulfonate (NaDBS; 0.150 g) was added. A solution containing TPD-PC (**1**) (2.00 g; 2.9 mmol) in 200 mL of methylene chloride was added to the previous mixture. The resulting mixture was stirred vigorously at room temperature for 2 days to give a dark-brown color. The methylene chloride was removed by evaporation causing the precipitation of the polymer in the remaining aqueous phase. The polymer was separated by filtration, washed several times with water, further purified by reprecipitation (twice) from methylene chloride-methanol, and dried under vacuum overnight. The same procedure was used for the other polymers **3–5**, in the experimental conditions described in Table 1.

Sample Preparation. Thin films for birefringence and grating inscription were prepared by spin-coating from a THF solution of the polymer onto clean glass microscope slide (Corning 2947) and subsequently dried in an oven at $120 \text{ }^\circ\text{C}$ for 1 h.

Film thicknesses were determined with a Dektak profilometer and ranged from 200 to 500 nm. Optical anisotropy was induced using a linearly 488 nm Ar^+ laser line with an irradiance set at $100 \text{ mW}/\text{cm}^2$. Birefringence was measured out of resonance at 674 nm; additional information can be found in related references.¹⁸

Photoconductivity and asymmetric two-beam coupling experiments were performed on thicker samples. Dried polymer powder was compressed between two glass slides precoated with indium thin oxide (ITO). A thin layer (80 nm) of metal-free phthalocyanine in a polymer binder had been previously spun-cast on the top of each electrode, and dried at $110 \text{ }^\circ\text{C}$ for 15 min (Figure 1). The preparation of a dispersion of the X form of metal-free phthalocyanine (X–H₂Pc) followed the literature.^{19,20} The cells are then heated to $150 \text{ }^\circ\text{C}$ for 2 h and cooled slowly to room temperature. The films are homogeneous on a large surface (5 mm^2) and the film thickness is determined by the interference fringes method and by profilometry after opening the cell. More details about preparation of these samples can be found in Barrett et al.⁹

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Table 1. Synthesis and Characterization of the Azo-TPD-PC Polymers 2–5^a

polymer	azo amount in polymer	diazonium salt (equiv.)	reaction time (days)	M_w	PDI	T_g	λ_{max}/nm ($\epsilon/\text{L.g}^{-1}.\text{cm}^{-1}$)
1				100600	1.98	113	
2	0.13	1	2	12300	1.96	107	422 (4.3)
3	0.50	1.5	2	5500	1.59	100	442 (6.6)
4	0.65	2	6	6600	1.67	109	444 (8.3)
5	1.67	4	6	3700	1.58	113	470 (19)

^a UV-vis in CHCl_3 , for solutions with the same concentration of polymer ($c = 1.98 \times 10^{-2}$ g/L).

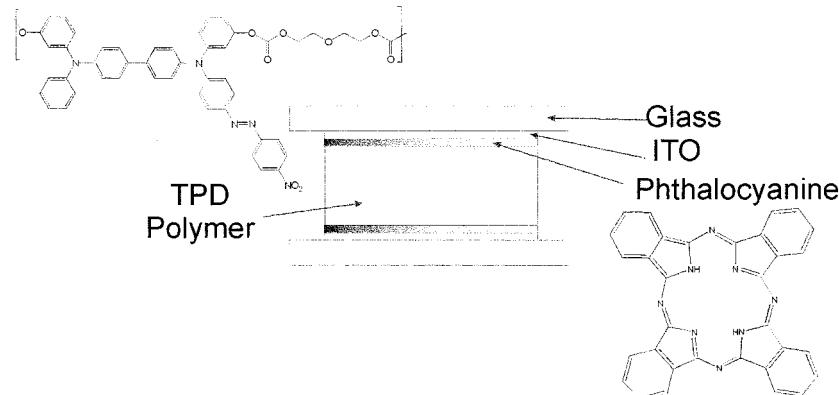


Figure 1. Cell for photoconduction and two-beam coupling experiments.

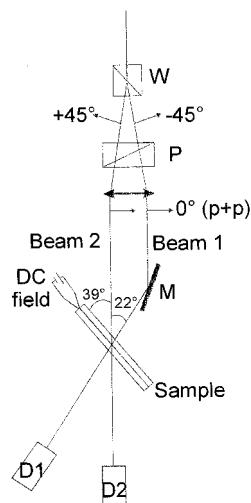


Figure 2. Experimental setup for two-beam coupling, depicting the position of Wollaston prism (W), Glan Taylor polarizer (P), mirror (M), and photodiode detectors (D).

Photoconductivity and Two-Beam Coupling Experiments. Photoconductivity measurements were carried out using a Keithley 617 electrometer. Photoconductivity is determined by measuring the difference between the dark current and the current during irradiation for electric fields varying from 0.5 to 10 $\text{V}/\mu\text{m}$. Irradiation was performed with a 10-mW He-Ne laser (632.8 nm) on a spot of 2-mm diameter ($I = 0.3 \text{ W}/\text{cm}^2$).

For two-beam coupling experiments, gratings were written using two coherent beams from a He-Ne laser (632.8 nm) with a tilted geometry. The setup is shown in Figure 2. From a linearly polarized laser, two linearly polarized beams with $+45^\circ$ and -45° orientation with respect to the incident plane emerge after passing through a Wollaston prism. A Glan Taylor polarizer sets the same p polarization to the two beams that are then collected with a 10-cm focal lens, and have parallel propagation directions. The sample holder is mounted on a goniometer and the angle between the mirror and the sample is adjustable. The p polarized writing beams have an irradiance of 110 mW/cm² each and are focused on a 200- μm diameter spot. The incidence of the bisector defined by the two

beams is set at 50° and the interbeam angle is 22° in air. The interference light pattern has a spacing of $2.7 \mu\text{m}$ in the polymer for $n_{\text{glass}} = 1.515$.

Both pump beams were chopped at the same frequency ($f = 700$ Hz) and two identical amplified photodiodes in conjunction with two numerical lock-in amplifier (Stanford SR830) were used for detection. Poling was initially achieved at 110 °C for 30 min with a poling field of 100 V. The sample was then cooled slowly to room temperature while maintaining the poling field on. Two-beam coupling experiments were done by maintaining a poling voltage between 5 and 100 V for samples with a maximum thickness of 40 μm .

Results and Discussion

A. Synthesis and Characterization. Post azo coupling reaction of a polymer with a diazonium salt was previously used for single step synthesis of polymers incorporating a push-pull azo group in the polymer. This was reported on functionalization of a copolymer of methyl methacrylate and a methacrylate ester of N-ethyl-N-(hydroxyethyl)aniline in organic acid media as solvents.^{21,22} There are only few polymers that display good solubility in organic acids. More recently it was found that the coupling reactions between polymer and diazonium salt can be efficiently carried out in polar solvents such as dimethylformamide and dimethylacetamide.^{23,24} In all these reactions, the starting polymer material contained N-dialkyl-aniline units, known as reactive coupling components in the 4-position for the azo coupling. Our starting material, TPD-PC (**1**) has a lower reactivity because it contains triphenyl-amino groups. For organic molecules with low reactivity for the azo coupling reactions, the most promising procedure

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reported in the literature, is phase transfer catalyzed (PTC) coupling. The catalyst described as being the most efficient on standard substrates is sodium tetrakis[3,5-di-(trifluoromethyl)phenyl]-borate (NaTFPB).^{25,26} We obtained it in two steps from 3,5-bis-(trifluoromethyl)-1-bromobenzene, as previously described.²⁷ It was reported that this phase transfer catalyst is the most efficient when used in dried solvents.²⁸ However, all attempts of reaction of the polymer **1** with 4-nitrobenzenediazonium tetrafluoroborate, freshly prepared and dried, in dried chloroform with the exclusion of air and water failed to give azo polymers. This catalyst is highly sterically crowded and this is believed to be the reason for its high efficiency on organic molecules. The low yield on polymer **1** is probably due to the fact that polymer **1** is sterically crowded as well, so that the access of the diazonium salt, mediated by the catalyst to the active sites of the polymer is hindered.

Post azo coupling reaction of the TPD-PC (polymer **1**) with 4-nitrobenzene-diazonium tetrafluoroborate worked in a two phase system (methylene chloride-water) at room temperature, using 4-sodium 4-dodecylbenzenesulfonate (NaDBS) as phase transfer catalyst. This procedure was reported previously as giving good yields on functionalization of less reactive aromatic amines.²⁹ It was more recently used for the functionalization of the well-known unreactive carbazole derivatives.^{7,9} Details of the functionalization are given in Table 1. The reaction was carried at room temperature. By varying the reaction time and the concentration of the diazonium salt, different amounts of azo groups could be attached to the TPD structural unit of polymer **1**. The degree of functionalization was determined by ¹H NMR spectroscopy, from the peak areas for the protons *ortho* to nitro group (at about 8.4 ppm) and the area of all other aromatic protons. The coupling reaction was slow. For example, if one equivalent of diazonium salt was used, polymer **2** contained only 0.1 of bound azo groups per structural unit. To obtain larger amounts of azo groups in the polymers, long reaction times were needed (2 to 6 days) and the amount of diazonium salt had to be increased up to 4 equiv (Table 1). In turn, this allowed us to synthesize polymers with various amounts of azo groups. By ¹H NMR spectroscopy it is difficult to assign the position of azo substitution on the TPD unit. However, given the bulkiness of the substrate, it is reasonable to assume that the substitution takes place on the initially unsubstituted phenyl rings of the TPD-PC (**1**), in *para* position, as shown in Scheme 1. It should be emphasized that the resulting polymers, after functionalization, are copolymers containing up to three different structural units: mono- or disubstituted azo-containing structural units, and unreacted TPD structural units. For example, in polymer **5**, an amount of 1.67 azo structural units means that the polymer contains structural units that were functionalized at both unsubstituted phenyl rings of the TPD moiety,

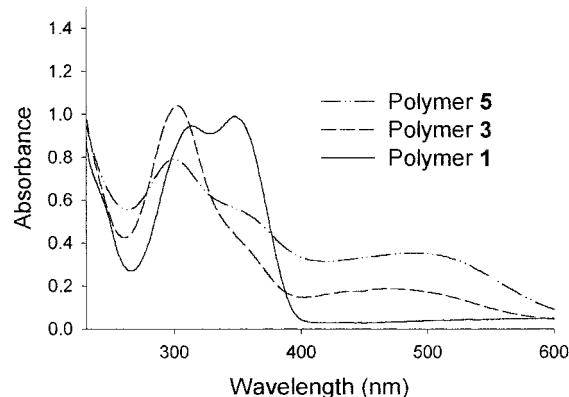


Figure 3. UV-vis spectra of polymer thin films.

probably together with units functionalized only once, and maybe with some unreacted units.

The GPC measurements suggested that the obtained Azo-TPD-PC polymers **2–5** have lower M_w than the starting material (TPD-PC, polymer **1**). During the synthesis, it is likely that the polymer chains are partly broken by hydrolysis of the carbonate groups in the acidic conditions. This tendency increased with the increase of the amount of diazonium salt used in synthesis: $M_w = 12300$ for 1 equiv (polymer **2**) to $M_w = 3700$ when 4 equiv of diazonium salt were used (polymer **5**). All the polymers show T_g 's close to that of the starting material (about 110 °C). It is difficult to obtain well-defined structural units by this method. However, this azo post-functionalization procedure is attractive because of its simplicity (single-step reaction) and the mild conditions employed, which work with well-known unreactive substrates such as triarylamines.

B. Absorption Spectra. The Azo-TPD-PC polymers **2–5** are colored and the absorption bands, due to the presence of the azo groups, appear in the range of 442 to 470 nm (chloroform solution, Table 1). This absorption band is due to the vibronic coupling of $n-\pi^*$ and $\pi-\pi^*$ electronic transitions.³⁰ The extinction coefficient of this band increases with the amount of azo groups in polymers, as expected. The electronic spectra of the polymer films are shown in Figure 3. The polymers **2–5** show a systematic shift of the absorption maxima to longer wavelength as the concentration of azo groups increases. This is in contrast with the behavior of side chain azo polymers, where an increase of the concentration of azobenzene groups usually induces a blue shift for the absorption maxima. For side chain azobenzene polymers, this was previously explained by an antiparallel arrangement of the side chain azo chromophores in film or solution.³¹ In polymers **2–5** the azo groups are placed in the main chain. It is thus possible that the polymer is not flexible enough to allow an antiparallel arrangement of the azo chromophores along the main chain.

C. Photoinduced Birefringence. Birefringence measurements were performed on polymers **2** to **5** during orientation and relaxation periods. Because of the presence of substituted azobenzene chromophores, the

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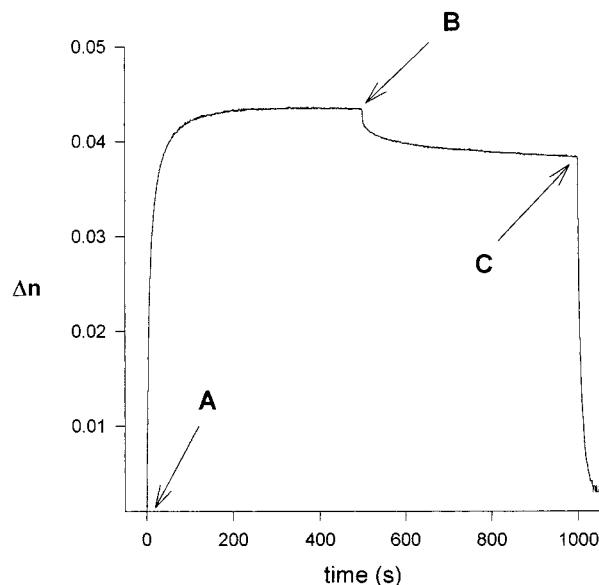


Figure 4. Typical sequence of photoinduced birefringence followed by relaxation and “erasing” for polymer 5. (A) Writing beam on; (B) write beam off; (C) erasing beam on.

Table 2. Photoinduced Birefringence Characteristics for Polymers 2–5

polymer	maximum birefringence	stable birefringence	stable birefringence (%)
2	0.001		
3	0.020	0.014	70
4	0.022	0.017	77
5	0.045	0.038	84

materials are highly sensitive to the polarization of the actinic light and become anisotropic when irradiated with a linearly polarized light. This is a consequence of the polarization-sensitive rodlike trans azobenzene chromophores. After irradiation with a linearly polarized light, the azobenzene groups undergo a *trans-cis* photoisomerization followed by an angular reorientation of the chromophore in a perpendicular direction with respect to the incident polarization. This anisotropic molecular reorientation induces both birefringence and dichroism properties in the material.

A typical birefringence variation during illumination, followed by a relaxation and an “erasing” period is presented in Figure 4 for polymer 5. Birefringence is induced to a saturated level by a linearly polarized laser beam (488 nm, 100 mW/cm²) that is turned on at point A for 500 s. The relaxation starts at point B, when the laser beam is turned off for 500 s. At point C, the residual birefringence is then erased with a circularly polarized 488-nm laser beam.

Birefringence values are given in Table 2. The level of photoinduced birefringence increases with the amount of azo groups in the polymer. For example, the maximum of birefringence is almost 2 orders of magnitude higher for polymer 5 (1.7 azo groups per structural unit) compared to polymer 2 (0.1 azo groups per structural unit). This is expected, because the photoorientation process is more efficient when the amount of chromophore is higher, since collective orientation of the chromophores has been demonstrated to occur.

The stability of the optically induced birefringence (after 500 s of relaxation) increases with the azo content and almost 90% of the induced birefringence is con-

served in the case of polymer 5. For comparison, in polymer 3, only 70% of the induced birefringence is conserved after the same time. The stability of the birefringence is related to the ability of the azo groups to reorient and randomize their distribution by thermal relaxation. The T_g of the polymers is one of the important factors that governs the ability of the polymers to reorient. In the case of high- T_g polymers such as polyimide, the level of induced birefringence is low but the remnant orientation of the chromophores is very high.³² Our polymers have similar glass transition temperatures (about 110 °C), and their relaxation behavior cannot be exclusively explained on the basis of T_g . It is more likely that the relaxation process is reduced by cooperative interactions of the neighboring azo groups. This trend is more pronounced as the amount of azo groups in the polymer increases.

D. Optically Induced Diffraction Gratings. Surface gratings were formed by the interference of two co- and contra-circularly polarized laser beams (488 nm) on the surface of a film of polymer 5. The evolution of the diffraction efficiency was monitored by the intensity of the first diffracted order using a laser diode operating at 674 nm.⁷ The grating profile exhibits a sinusoidal shape, with a grating spacing of about 1 μm and a depth of about 30 nm after 2 h of writing. The depth obtained on polymer 5 is small when compared to other polymers reported by our group,³³ and consequently the diffraction efficiency is relatively low (about 0.4%). However, this proves that it is possible to inscribe surface modulation of a polymer thin film by simple holographic methods. Polymers 2 to 4 were not tested for surface grating inscription, as it is expected that their efficiency will be lower than that of the polymer 5, because of their lower azo group content.

Photoconductivity and the Photorefractive Effect. Photoconductivity in response to a 632.8-nm laser beam was studied for polymer 3, but for higher azo content we could not fabricate thick films of good quality. A beam with an irradiance of $I_{\text{pump}} = 0.3 \text{ W/cm}^2$ impinges the film through the ITO-phthalocyanine coated glass in 30-s cycles. The photocurrent generated with 5, 10, 50, and 90 V applied between the electrodes is shown in Figure 5. The conductivity is calculated as the difference between dark current state (I_0 when the light off) and with the pump beam on (I_1 when the light on) divided by the thickness of the sample (e) and by the applied voltage U . Its expression is given by $\phi = (I_1 - I_0)/Ue$. For a film of 40 μm, the photoconductivity normalized by the laser irradiance ($\rho = \phi/I_{\text{pump}}$) increases slightly with the applied field ($\rho_{90V} = 1.25 \times 10^{-7} \text{ S}\cdot\text{cm}/\text{W}$, $\rho_{50V} = 1.11 \times 10^{-7} \text{ S}\cdot\text{cm}/\text{W}$, $\rho_{10V} = 1.01 \times 10^{-7} \text{ S}\cdot\text{cm}/\text{W}$, $\rho_{5V} = 0.97 \times 10^{-7} \text{ S}\cdot\text{cm}/\text{W}$).³⁴ These values have to be compared with previous measurements on pCAR-BA-based polymers^{7,9} in which photoconductivity is 5 orders of magnitude lower in similar experimental conditions ($\rho \approx 1 \times 10^{-12} \text{ S}\cdot\text{cm}/\text{W}$ and $I_{\text{pump}} = 0.2 \text{ W/cm}^2$). Also, composite polymers of poly(vinyl carbazole)/trinitrofluorenone/Disperse Red 1 exhibit weaker

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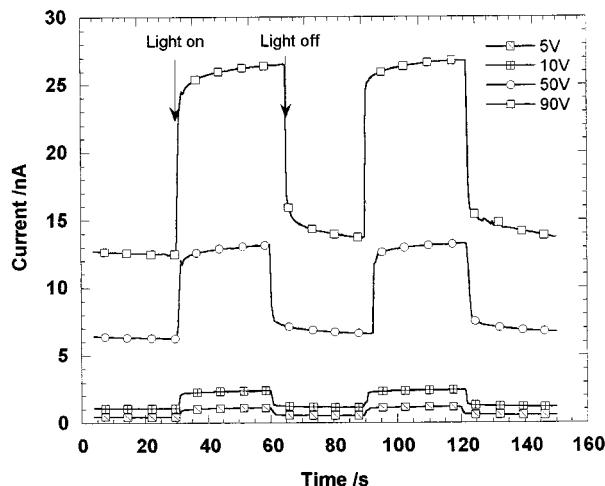


Figure 5. Cycles of photocurrent for an applied voltage ranging from 5 to 90 V. At $t = 30$ s and $t = 90$ s, a light beam (0.3 W/cm^2 at 632.8 nm) is applied for 30 s.

photoconductivity at higher electric field ($50 \text{ V}/\mu\text{m}$, $\rho \approx 1.6 \times 10^{-9} \text{ S}\cdot\text{cm}/\text{W}$).³⁵ In agreement with Stolka et al.,¹⁰ this proves the exceptional ability of photoconduction of the TPD-based polymer in conjunction with the use of a layer of phthalocyanine based charge generator. As discussed earlier by Moerner et al.,¹ the rate-limiting step in the formation of the photorefractive (PR) space charge field is charge generation. If the charge generation is efficient, mobility and trapping are assumed to be efficient enough and lead to the formation of the PR grating.

To ascertain the photorefractive properties, asymmetric energy exchange under poling condition was measured using beam coupling experiments. The poling field is applied normal to the film surface and varies from 0.5 to $10 \text{ V}/\mu\text{m}$, which is weak compared to values found in the literature ($U \leq 90 \text{ V}/\mu\text{m}$). Films have thicknesses of $10\text{--}40 \mu\text{m}$ and are pre-poled at 110°C for 30 min. The intensities of the two p-polarized beams are displayed in real time while two shutters are controlling separately the two beams. In Figure 6, the top trace is the signal detected by detector 1. When beam 2 is introduced, a signal gain is clearly observed. In the second part of the graph (i.e. after $t = 35$ s) the introduction of beam 1 induces a loss of signal on detector 2. This experiment is an evidence of asymmetric signal transfer from beam 1 to beam 2. From steady-state behavior, the optical gain coefficient Γ can be evaluated using the equation:

$$\Gamma = \frac{\cos \theta}{d} \left[\ln \left(\frac{\gamma_0 \beta}{\beta + 1 - \gamma_0} \right) \right]$$

where d is the film thickness, β is the ratio of the beam intensities measured independently in front of the sample, and $\gamma_0 = P/P_0$ is the power ratio of the two writing beams after passing through the sample. P_0 is the detected signal from beam 1 (beam 2) when beam 2 (beam 1) is off, and P the signal of beam 1 (beam 2) when beam 2 (beam 1) is on; $\theta = \theta_1$ or θ_2 is the incidence angle of the beam inside the material. In these condi-

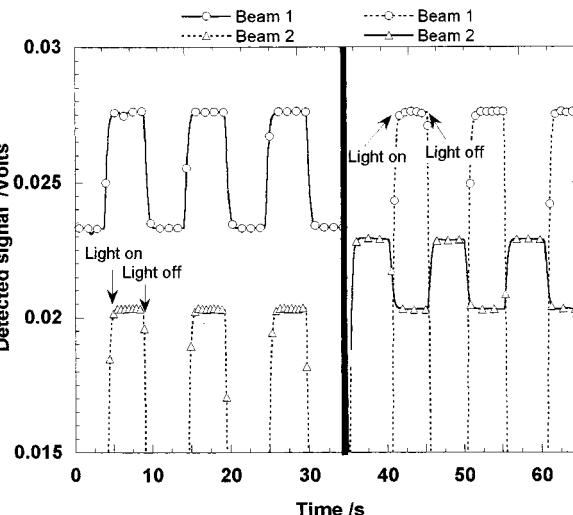


Figure 6. Asymmetric two-beam coupling in polymer 3. With a poling field of $2.5 \text{ V}/\mu\text{m}$, beam 1 intensity (upper trace, circles) increases when beam 2 (lower trace, triangles) is turned on (up to 35 s), while beam 2 intensity decreases when beam 1 is introduced (after 35 s).

tions, the maximum gain coefficient measured in a p-p polarization configuration is 70 cm^{-1} for an external electric field of $E = 2.5 \text{ V}/\mu\text{m}$. This gain value is the same order of magnitude that Hadzioannou reported for a higher poling field.¹² Furthermore, because of the strong optical absorption extending into the red range, no net gain is observed since the absorption coefficient is 250 cm^{-1} at a wavelength of 632.8 nm . It is noteworthy that this absorption coefficient is underestimated since it neglects the absorbance of the phthalocyanine layer which has an intense absorption band at the working wavelength, corresponding to the Q transition.^{36,37} Stable phthalocyanine dyes have been well studied as organic semiconductors and more details concerning the mechanism of the photoconduction step can be found elsewhere.²⁰

In Figure 7, the growth and decay of the energy exchange between beam 1 and beam 2 were fitted by single-exponential curves to estimate the rate of energy exchange. The argument τ of the exponential function ($\exp(\pm t/\tau)$) is the characteristic growth or decay time. When the two pump beams are on, the growth response time is estimated to $0.46\text{--}0.47 \text{ s} (\pm 2\%)$ while the decay time is slightly longer (0.48 s). In their TPD-based polymer, Sato et al. have measured a response time of the order of 10 ms , which is fast compared to composite doped polymers ($\tau = 1 \text{ s}$).¹³ This shows that the extrapolated value for our polymer is also better than that of the composite polymers.

The high absorption of the azo chromophores, the low poling electric field, and especially the room-temperature poling of these preliminary experiments are the main sources of such low gain. Better experiments done in collaboration with a specialist in photorefractivity are in progress. The exceptional photoconduction is the major feature of this polymer. Polymers with higher

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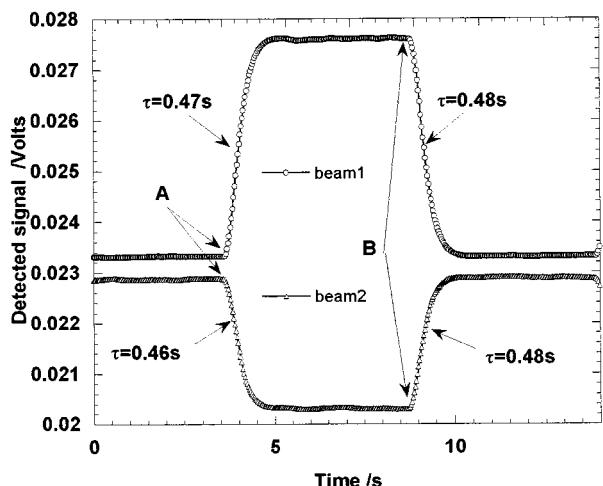


Figure 7. Fitting curves during growth and decay of energy exchange. A monoexponential function was used as a fitting function ($y(t) = A(1 - \exp(-t/\tau))$), where τ is the characteristic response time ($\pm 2\%$) of the polymer when the two pump beams are on (A), and when only one beam is impinging the sample (B). The time constant of the lock-in amplifier is fixed at 30 ms.

content of azo-chromophores (polymer **5**) have not yet been studied because of the difficulty of obtaining thin films of good optical quality. However, we can expect to achieve higher electrooptic coefficient leading, under higher poling field, to a net orientational enhancement mechanism and therefore a higher gain.

Conclusions

Post azo coupling reaction was successfully applied to synthesize a series of functionalized photorefractive

polymers. The polymers contain an aromatic diamine (TPD) as charge transport component, and an azobenzene chromophore as the electrooptic group. This method does not afford azo polymers with a well-defined structural unit. Further work is in progress on the design of azo-TPD polymers containing well-defined photoactive structural units by starting with the functionalized TPD moiety.

Because of the presence of azobenzene groups, these polymers are suitable materials for reversibly photoinducing birefringence. Surface relief gratings can also be inscribed in a film of polymer **5**, but the diffraction efficiency is relatively low, indicating the low mobility of the azo moieties. Photoconductivity measurements on polymer **3** provide verification of the high conduction as hole transport of the conjugated **TPD** polymer.

Energy transfer is also proven on polymer **3** using a two-beam coupling technique. However, no net gain is reported, since the poling conditions were not optimal. Efforts to optimize poling of the electrooptic azo chromophore on the whole copolymer series are in progress.

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