Journal of Materials Chemistry

Cite this: J. Mater. Chem., 2012, 22, 12220

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Millisecond photorefractivity with novel dicyanomethylenedihydrofurancontaining polymers

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Received 2nd March 2012, Accepted 23rd April 2012 DOI: 10.1039/c2jm31320k

New multifunctional copolymers containing carbazole units and high loads of dicyanomethylenedihydrofuran (DCDHF) were synthesized and used to prepare blends for photorefractive (PR) purposes. The materials response, which is strongly dependent on the glasstransition temperature (T_g) , was thoroughly analyzed by holography, conductivity and ellipsometry measurements in order to both determine the limiting factors and optimize the performance. Materials that have a T_{σ} around room temperature show strongly hindered chromophore orientation, which is avoided by lowering the T_g down to 6 °C, without compromising the PR effect or the material stability. A further DCDHF-containing homopolymer without carbazole was synthesized and characterized, showing an inferior PR response, which is attributed to a beneficial role for charge generation and transport of the attached carbazole in the copolymers. The new blends strongly improve the structural properties of previous DCDHF-based materials, allowing application of fields well above 100 V µm⁻¹ and preventing beam fanning. Outstanding PR performance was achieved, with fast buildup and erasure times of a few tens of milliseconds (even at low recording intensities), large refractive index modulation (over 10^{-2}) and two-beam coupling gain (above 350 cm⁻¹). Such performance is among the best reported for PR materials based on multifunctional and nonlinear polymers and comparable to standard PR composites.

Introduction

The photorefractive (PR) effect is a nonlinear optical (NLO) process that induces a change in the material refractive index by nonuniform illumination, arising from the coexistence of charge photogeneration, carrier transport and trapping and electrooptic (EO) response.¹ PR materials could be useful for applications like high-density holographic data storage, image processing, phase conjugated mirrors and lasers and real-time imaging. Among them, organic PR materials (mainly polymers) offer low cost and easy processability and benefit from their typically low dielectric constants (allowing for stronger internal fields) and versatile composition.² The complex nature of the PR effect makes it necessary to combine all required functionalities in the same material. Particularly suitable are materials with, first, high

load of NLO moieties (chromophores) for large EO modulation, and, second, low glass-transition temperatures (T_g) in order to profit from birefringence (BR) modulation, which also contributes to photorefractivity (orientational enhancement mechanism,³ OEM). All of these requisites make the design of an optimized material a challenging task.

So far, composites, in which a host polymer is doped by the distinct functional species, allowing the separate improvement of each molecule type and easy $T_{\rm g}$ adjustment, are the most successful approach.^{4,5} However, being a physical mixture, composites can undergo crystallization and phase separation, which restricts the use of a high percentage of NLO chromophores and limits the mechanical stability against electrical breakdown. Alternatively, monolithic materials, like fully functionalized (FF) polymers⁶ and low molecular weight glasses,^{7,8} are formed by one single component combining all of the required functionalities, so that instability problems are greatly reduced. Nevertheless, besides the need for important synthetic effort, the price to be paid is a much lower tunability of their properties, especially charge generation (with adequate photosensitizing groups) and Tg. As an intermediate option, multifunctional polymers,9,10 containing both charge transporting and NLO subunits, also prevent phase separation (even at high

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chromophore contents) through a much less demanding synthesis. Photogeneration and T_g can be adjusted by separately adding a photosensitizer (in low amounts) and a plasticizer (normally a nonpolar molecule) without compromising the material stability. However, in spite of notable research work, these strategies are generally in clear disadvantage in comparison to the standard composite approach.

Here, we undertake the synthesis of two multifunctional methacrylate copolymers, 1 and 2 (Fig. 1), that have an attached carbazole, as a widely used hole-conducting molecule,¹¹ and hydroxyl derivatives of 2-dicyanomethylene-3-cyano-4-styryldihydrofuran, taking advantage of the high hyperpolarizability of dicyanomethylenedihydrofuran (DCDHF).12 DCDHF-based glasses are among the best PR monolithic materials reported to date, generally showing high optical gain coefficients Γ (up to 250 cm⁻¹ at \sim 30 V μ m⁻¹)^{13,14} and diffraction efficiencies (near total diffraction at ~ 25 V μ m⁻¹).^{14,15} However, they exhibit a slow PR response (in the best cases with buildup times of ~ 1 s at 30 V μ m^{-1 13,16,17} and erase times of several seconds^{13,15}), low dielectric breakdown (often below 50 V μ m⁻¹) and frequently strong beam fanning^{7,13,16} or thermal instability.^{7,13} Only one PR polymer bearing DCDHF has been reported so far;18 a FF polymer exhibiting good steady-state performance (Γ = 180 cm⁻¹ and total diffraction at 50 V μ m⁻¹), but a slow response (>1 s) and low dielectric breakdown. Since the typical slow response is attributed to limited chromophore orientation,8,13,18 we focus on the achievement of relatively soft polymers and subsequent preparation of PR blends with optimized T_{g} . Fast erasure, as a relevant technological parameter, was also aimed for. High polymer solubility and processability, which should minimize beam fanning and dielectric breakdown, were also targeted. We further synthesized homopolymer 3 (Fig. 1), which is identical to 2 but without carbazole, to evaluate the convenience of anchoring together charge transport and NLO moieties. A detailed analysis of the PR performance, supported by photoconductivity and ellipsometric experiments, was performed in order to understand the mechanisms at play and the improving factors of our materials

Experimental

Synthetic procedures

NMR spectra were taken on a 300 MHz Bruker AC-300, using deuterated chloroform as the solvent and tetramethylsilane as the internal reference. UV-vis absorption measurements were taken on a Thermo Spectronic Helios γ spectrophotometer with chloroform as the solvent. Ultraviolet data were used to determine copolymer composition. Infrared measurements were taken with a Fourier Transform Thermo Nicolet IR 200 spectrometer in ATR mode with a germanium window. Glass transition temperatures (T_{α}) were measured by differential scanning calorimetry (DSC) with a PerkinElmer Pyris 1 analyzer during the second heating run (20 K min⁻¹) under nitrogen. Gel permeation chromatography (GPC) was carried out using Agilent Zorbax PSM silanized columns. N,N-Dimethylformamide (DMF) with 0.1% of LiBr was used as the solvent and the measurements were done at 70 °C with a flow rate of 1.0 mL min⁻¹ using a diode array detector. The columns were calibrated with narrow distribution standards of polystyrene. The methacrylate of 2hydroxyethylcarbazole was synthesized as reported in the literature.19

(*E*)-2-{4'-[2''-(4'''-Cyano-5'''-dicyanomethylene-2''',2'''dimethyl-2''',5'''-dihydrofuran-3'''-yl)vinyl]-2',5'-dimethylphenoxy}ethyl methacrylate (5). Compound 4^{20} (1.04 g, 2.8 mmol) was dissolved in 25 mL of dry THF under an argon atmosphere. Then, methacryloyl chloride (0.41 g, 4.4 mmol) and dry triethylamine (0.37 g, 3.6 mmol) were added and the reaction mixture was held at room temperature for 96 hours. The reaction mixture was filtered and THF was removed under reduced pressure. The crude solid was dissolved in ethyl acetate and the solution was washed twice with 2 M sodium hydroxide solution, then with 0.1 M HCl and finally with distilled water. The organic layer was dried over anhydrous sodium sulfate and filtered, and the solvent was removed under reduced pressure. The product was purified by chromatography through a silica gel column (dichloromethane). Yield: 51%. Melting point: 115–116 °C.



Fig. 1 Chemical structures of polymers 1–3 synthesized in this work.

¹H-NMR δ : 7.56 (d, 1H, J = 16.1 Hz), 7.16 (s, 1H), 6.96 (s, 1H), 6.85 (d, 1H, J = 16.1 Hz), 6.14 (br, 1H), 5.59 (br, 1H), 4.53 (t, 2H, J = 5.2 Hz), 4.32 (t, 2H, J = 5.2 Hz), 2.58 (s, 3H), 2.17 (s, 3H), 1.95 (br, 3H), 1.40 (s, 6H). IR: 2930, 2231, 1709, 1584, 1528, 1507, 1455, 1305, 1264, 1165, 1098, 963, 855 cm⁻¹.

(E)-6-{4'-[2''-(4'''-Cyano-5'''-dicyanomethylene-2''',2'''dimethyl-2''',5'''-dihydrofuran-3'''-yl)vinyll-2'-hexyloxyphenoxy}

hexyl methacrylate (7). Compound 6^{21} (0.9 g, 1.8 mmol) was dissolved in 15 mL of dry THF under an argon atmosphere. Then, methacryloyl chloride (0.56 g, 6.1 mmol) and dry triethylamine (0.57 g, 5.5 mmol) were added and the reaction mixture was held at room temperature for 96 hours. The reaction mixture was filtered and THF was removed under reduced pressure. The crude solid was dissolved in ethyl acetate and the solution was washed twice with 2 M sodium hydroxide solution, then with 0.1 M HCl and finally with distilled water. The organic layer was dried over anhydrous sodium sulfate and filtered, and the solvent was removed under reduced pressure. The product was purified by chromatography through a silica gel column (dichloromethane). Yield: 59%. Melting point: 132-133 °C. ¹H-NMR δ : 7.57 (d, 1H, J = 16.2 Hz), 7.22 (dd, 1H, $J_1 = 8.5$ Hz, $J_2 =$ 1.7 Hz), 7.10 (d, 1H, J = 1.7 Hz), 6.91 (d, 1H, J = 8.5 Hz), 6.85 (d, 1H, J = 16.2 Hz), 6.09 (br, 1H), 5.55 (br, 1H), 4.16 (t, 2H, J = 6.6Hz), 4.08 (t, 2H, J = 6.6 Hz), 4.05 (t, 2H, J = 6.5 Hz), 1.91–1.25 (br, 25H), 0.91 (t, 3H, J = 6.9 Hz). IR: 2928, 2866, 2226, 1736, 1562, 1540, 1461, 1380, 1317, 1261, 1149, 1142, 1117, 1015, 756, 634 cm^{-1} .

6-(9'H-Carbazol-9'-yl)hexyl methacrylate (8). This compound was prepared using a slightly modified procedure from that described elsewhere.9,22 Carbazole (2 g, 12 mmol), sodium hydride (0.56 g, 14 mmol) and a catalytic amount of potassium iodide were dissolved in dry DMF (42 mL) under an argon atmosphere. After twenty minutes stirring at room temperature, 6-chlorohexanol (1.64 g, 12 mmol) dissolved in dry DMF (8 mL) was added dropwise. The reaction mixture was heated at 90 °C for 21 hours. After cooling to room temperature, water was added to the reaction mixture to remove excess sodium hydride. The mixture was extracted twice with ethyl acetate and the organic layer was washed with diluted hydrochloric acid, then with water, and dried over anhydrous sodium sulfate before removal of solvent under reduced pressure. The crude product was purified by chromatography through a silica gel column (nhexane-ethyl acetate, 2/1 v/v). The yield of 6-(9'H-carbazol-9'-yl) hexan-1-ol was 1.97 g (61%). Melting point: 110-111 °C. ¹H NMR δ : 8.10 (d, 2H, J = 7.8 Hz), 7.44 (m, 4H), 7.23 (m, 2H), 4.31 (t, 2H, J = 8.1 Hz), 3.60 (t, 2H, J = 6.2 Hz), 1.47 (m, 8H). IR: 3346, 2937, 2862, 1710, 1453, 1326, 1277, 1237, 1074, 1054, 1033, 1002, 752, 725, 650 cm⁻¹. This product (1.3 g, 4.8 mmol) was dissolved in dry THF (50 mL) under an argon atmosphere. Then, methacryloyl chloride (1.53 g, 14.6 mmol) and dry triethylamine (1.47 g, 14.6 mmol) were added and the reaction mixture was heated at 50 °C for 72 hours. After cooling, the reaction mixture was filtered and THF was removed under reduced pressure. The crude solid was dissolved in ethyl acetate and the solution was washed twice with 2 M sodium hydroxide solution, then with 0.1 M HCl and finally with distilled water. The organic layer was dried over anhydrous sodium sulfate and filtrated, and the solvent was removed under reduced pressure. The product was purified by chromatography through a silica gel column (dichloromethane). Yield: 1.43 g (89%). Boiling point > 350 °C (dec.). ¹H-NMR δ : 8.10 (d, 2H, J = 7.5 Hz), 7.44 (m, 4H), 7.23 (t, 2H, J = 7.8 Hz), 6.08 (br, 1H), 5.54 (br, 1H), 4.37 (t, 2H, J = 7.2 Hz), 3.54 (t, 2H, J = 6.7 Hz), 1.93 (br, 3H), 1.85–1.35 (m, 8H). IR: 2936, 2858, 1717, 1637, 1597, 1485, 1454, 1324, 1296, 1164, 1120, 1031, 941, 815, 751, 725, 651 cm⁻¹.

General procedure for polymerization. Azobisisobutyronitrile (AIBN, 2 wt%) was added to a 1 M solution of methacrylic monomers (in the case of copolymers, the ratio carbazole/chromophore was 1.0/1.2) in dry DMF. The polymerization medium was bubbled with an argon stream for 10 minutes before heating at 60 °C for 24 hours. The reaction was stopped by cooling to room temperature. Cold methanol was added to precipitate the polymers from the obtained gels. Polymers 2 and 3 were dissolved in THF and reprecipitated with MeOH. Finally, they were filtered and dried overnight in an oven at 90 °C under reduced pressure. Polymer 1, being insoluble, had to be mechanically broken and was washed for 24 hours with cold methanol. Finally, it was filtered and dried overnight in an oven at 90 °C under reduced pressure.

Polymer 1. Yield: 72%. IR: 2227, 1729, 1674, 1570, 1528, 1504, 1460, 1311, 1261, 1095, 753, 726 cm⁻¹. *T*_g: 152 °C.

Polymer 2. Yield: 64%. ¹H-NMR δ: 7.99, 7.36, 7.14, 7.00, 6.72, 4.11, 3.92, 3.83, 1.68, 1.43, 1.29, 1.01, 0.86 ppm. IR: 2940, 2863, 2231, 1729, 1574, 1538, 1465, 1274, 1150, 756, 731 cm⁻¹. UV-vis λ (log ε): 243 (1.20), 265 (1.08), 296 (0.94), 333 (0.53), 347 (0.60), 475 nm (0.95). $T_{\rm g}$: 75 °C. $M_{\rm n}$: 28 000 g mol⁻¹. $M_{\rm w}$: 66 000 g mol⁻¹. $M_{\rm w}/M_{\rm n}$: 2.3.

Polymer 3. Yield: 43%. ¹H-NMR δ: 7.57, 7.22, 7.10, 6.91, 6.85, 4.16, 4.08, 4.05, 1.91, 1.73, 1.62, 1.55, 1.33, 1.25, 0.91 ppm. IR: 2927, 2860, 2227, 1726, 1567, 1532, 1465, 1382, 1327, 1267, 1153, 1143, 1111, 1020, 615 cm⁻¹. UV-vis λ (log ε): 240 (1.04), 277 (0.83), 350 (0.64), 474 nm (1.08). *T*_g: 80 °C. *M*_n: 62 000 g mol⁻¹. *M*_w: 84 000 g mol⁻¹. *M*_w/*M*_n: 1.3.

Materials preparation and samples fabrication

Different blends were prepared by separately dissolving each component in dry dichloromethane and mixing them in adequate proportions. The solvent was evaporated by slow dropping on two glass plates heated at 50 °C. Thereafter, composites were homogenized by mechanical pounding between the two plates at 90–120 °C. Material T_g 's were measured by DSC in a Mettler Toledo TGA/DSC 1 apparatus during the second heating cycle (20 K min⁻¹) under static air. Sandwich-like samples of thickness $d = 37 \,\mu\text{m}$ were fabricated at ~100 °C by pressing the material between two indium tin oxide (ITO) electrodes and prompt cooling down to room temperature. The thickness was guaranteed using fiber-glass spacers. The moderate thickness ensured optical quality and high transmittance of the samples. Absorbances, A, were measured on fresh samples with a Helios Gamma UV-vis spectrophotometer to obtain the absorption coefficient α according to $\alpha = \ln 10 A/d$.

Photoconductivity and ellipsometry measurements

DC conductivities were measured by applying a field of 22 V μm^{-1} to the sample in the dark (σ_{dark}) and under illumination (σ_{light}) with a He–Ne laser beam (633 nm, full-width half-maximum of 10 mm² and intensity of 50 mW cm⁻²). The current, *i*, was measured after 200 s with a Keithley 600B electrometer to calculate the conductivities from $\sigma_{dark, light} = id/(VS)$, where $S = 4.2 \text{ mm}^2$ is the electrode area and $d = 37 \mu \text{m}$ is the sample thickness. Photoconductivity was defined as $\sigma_{ph} = \sigma_{light} - \sigma_{dark}$ and conductivity contrast as $M = (\sigma_{light} - \sigma_{dark})/\sigma_{light}$.

Field-induced birefringence was measured by null-transmission ellipsometry.²³ A weak 785 nm beam impinged on the sample (at internal incidence angle of 32°) placed between two crossed polarizers (set at $\pm 45^{\circ}$ with respect to the plane of incidence). The transmitted beam intensity by applying an external field to the sample was monitored. Time-dependent birefringence curves were fitted by a monoexponential function with time constant τ_{BR} .

Holographic characterization

The composites were characterized by standard degenerate fourwave-mixing (DFWM) and two-beam coupling (TBC) experiments at room temperature (~ 22 °C). Thereby, gratings were written by two p-polarized 633 nm write beams (WB's) with equal internal intensities (160 mW cm⁻² each) in a typical tilted recording geometry with internal WB angles $\theta_1 = 26.7^\circ$ and $\theta_2 =$ 33.3° (grating tilt angle $\Psi = 30^{\circ}$ and grating spacing $\Lambda = 3.2 \,\mu\text{m}$). Gratings were read out by a weak (1.2 mW cm⁻²) p-polarized 633 nm read beam (RB), counterpropagating to WB₁. Timeresolved measurements were standardly carried out by pre-illuminating the sample with the fringe pattern (i.e., both WB's on) in the absence of an external field for 15 min and switching the field on/off to write/erase the grating (*E-switch method*). Alternatively (see below subsection on Photorefractive Characterization), the sample was pre-poled by applying the field in the presence of only one write beam (WB₂) for 15 min and WB₁ was switched on/off to write/erase the grating (WB_1 -switch method). Grating values reached after 200 s were taken as steady-state data.

The PR performance was characterized by the internal diffraction efficiency η (ratio of the diffracted RB intensity to the sum of the diffracted and the transmitted RB intensities) and the gain coefficient Γ calculated according to¹

$$\Gamma = \frac{1}{d} \left[\cos\theta_1 \ln \left(\frac{I_1}{I_1(0)} \right) - \cos\theta_2 \ln \left(\frac{I_2}{I_2(0)} \right) \right]$$
(1)

where $I_{1(2)}(0)$ and $I_{1(2)}$ are the WB₁₍₂₎ intensities after the sample before and during grating recording, respectively. η and Γ are related to the refractive index modulation Δn of the PR grating by^{1,24}

$$\eta = \sin^2 \left(\frac{\pi d\Delta n}{\lambda (\cos\theta_1 \cos\theta_2)^{1/2}} \right)$$
(2)

and

$$\Gamma = \frac{2\pi}{\lambda} \Delta n \sin \Theta \tag{3}$$

where Θ is the PR phase-shift, *i.e.*, the phase difference between the index grating and the light interference pattern, and λ is the light wavelength. In low- T_g PR materials,³ Δn is proportional to the external field *E* and the developing space-charge field E_{SC} , the latter being in turn proportional to the conductivity contrast M.¹

 Δn was obtained from η according to eqn (2). For evaluation of the PR dynamics, the resulting time-dependent Δn curves were fitted by a bi-exponential function, with fast and slow time constants τ_{fast} and τ_{slow} .

Results and discussion

DCDHF-containing polymers

Polymers were prepared by radical polymerization of the corresponding methacrylates, using AIBN as the initiator. In a first attempt, we selected polymer 1 as the target expecting that the short alkyl chains would ensure enough solubility while minimizing the weight of inert material. In this way, chromophore 4²⁰ was acylated in 51% yield by treatment with methacryloyl chloride in THF. The resulting ester 5 was copolymerized with 2-(carbazol-9'-yl)ethyl methacrylate¹⁹ to afford 1 in 72% yield (Scheme 1). Polymer 1, which presented ethyl connectors, happened to be insoluble, thus precluding complete characterization and any further material preparation. We decided to introduce longer alkyl chains to improve the solubility of the resulting polymers while lowering the T_{g} , although this would reduce the percentage of active moieties in the material. This strategy proved to be correct and allowed us the preparation of the readily soluble polymer 2 (Scheme 2). Thus, reaction of chromophore 6^{21} with methacryloyl chloride yielded ester 7, which was copolymerized in the same conditions as earlier,⁹ leading to 2 in 64%. In order to study the effect of attaching the carbazole units to the polymer backbone, we also synthesized the soluble polymer 3 in 43% starting from 7 (Scheme 2).

The ¹H NMR spectra of both **2** and **3** showed the disappearance of the olefinic protons (at *ca.* 6.1 and 5.5 ppm) present in the starting methacrylates (Fig. 2). UV-vis spectra of polymers **2** and **3** resembled those of the constitutive monomers (Fig. 3). Polymer **3**, which has a higher quantity of chromophore (DCDHF) per concentration unit, showed higher absorption in the 400–600 nm range than copolymer **2**. The comparison with the spectra of the starting methacrylates allowed for the calculation of the composition of copolymer **2**, yielding a carbazole/chromophore



Scheme 1 The synthesis of insoluble polymer 1.



а 50 40 ل<mark>ہ وس</mark>ا 3 الہ و 0 b 15 300 - M2-54 - M3-42 ່ ຮູ້ 200 ε [L g⁻¹ cm⁻¹] 2 10 100 0 600 650 700 750 λ [nm] 5 0 300 400 500 600 700 800 900 200 λ [nm]

Fig. 3 Absorption spectra of (a) monomers 7 and 8, and (b) copolymer 2 and homopolymer 3. Inset: absorption coefficients of composites M2-54 and M3-42 measured at 37 μ m samples.



Fig. 2 ¹H NMR spectra of copolymer 2 and homopolymer 3.

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ratio of 1.0/1.9. The insolubility of polymer 1 precluded the estimation of the composition by UV-vis. In this case, we used the intensity of selected IR bands, obtaining a carbazole/chromophore ratio of 1.0/0.9. The solubility of polymers 2 and 3 allowed for the determination of their molecular weights. Thus, 2 exhibited values of 66 000 and 28 000 for M_w and M_n , with a polydispersity of 2.3. On the other hand, 3 showed a M_w value of 84 000 and a M_n value of 62 000, being the polydispersity 1.3. From the M_n values, we estimated that 3 was statistically composed of chains of 116 units, while the chains of 2 contained around 21 carbazole and 40 chromophore units.

Composite materials

PR materials M2 with varying T_g 's close to room temperature were prepared by mixing polymer 2 with different amounts of the plasticizer N-ethylcarbazole (ECZ), which also contributed to photoconduction. All materials were sensitized with 1% of 2,4,7trinitro-9-fluorenone (TNF), which provides efficient carrier photogeneration via charge transfer with the carbazole units. The resulting composites were named after the polymer percentage (Table 1). A further composite was analogously prepared from polymer 3 (M3-42, Table 1) for direct comparison with the best performing M2 material (M2-54), both having similar T_g 's (6-8 °C) and, simultaneously, equally large percentages of both carbazole (\sim 45 wt%) and NLO (\sim 30 wt%) units. Note that some percentage of carbazole units in the M3 composite was provided by the addition of poly(N-vinylcarbazole) (PVK) in order to, first, match the T_g of the M2 blend and, second, achieve a similar percentage of polymeric matrix (\sim 50 wt%). It is remarkable that, despite the high loads of the strongly polar DCDHF (up to ${\sim}40$ wt%), samples exhibited neither phase separation nor aggregation over more than two years. This represents a clearly superior stability compared to most host-guest materials, typically restricted to a few weeks or months.²

Photorefractive characterization

We investigated the PR performance of M2 materials by DFWM and TBC experiments. Both grating strength and dynamics strongly varied between composites, some of them exhibiting high and fast diffraction and optical gain at moderate applied fields (Fig. 4). The PR refractive index modulation Δn was calculated from DFWM measurements since η exclusively depended on Δn (eqn (2)). Buildups of Δn could be fitted by biexponential functions, with a fast and a slow time constants (τ_{fast} and τ_{slow} , respectively). The resulting Δn and best-fit time



Fig. 4 Temporal evolution of (a) diffraction efficiency and (b) gain coefficient of gratings in **M2** composites with different T_g 's (Table 1). Gratings were recorded using the E-switch method (with an applied field of 60 V μ m⁻¹).

constants are displayed in Fig. 5(a) and (b) against the materials' $T_{\rm g}$, which evidently was a crucial parameter for the PR performance. Indeed, gratings in harder composites showed lower Δn and slower rates (larger buildup times, both τ_{fast} and τ_{slow}) while, by lowering the material's T_{g} , both grating strength and speed improved due to enhanced chromophore motion. However, by further decreasing the Tg towards 0 °C the speed barely increased, while the grating modulation Δn worsened. Such behavior indicates that chromophore orientation was hindered in the harder materials ($T_g > 20$ °C, although being slightly above RT), leading to restricted OEM (i.e. poor BR contribution to the grating) and slow response. In the softer materials, chromophore mobility clearly improved, allowing larger modulation Δn with faster speed. The saturation of the speed improvement suggests that chromophore orientation was no longer a limiting factor for $T_{\rm g} = 6 \,^{\circ}{\rm C}$ or less. This was confirmed by the dynamics of chromophore alignment from transient ellipsometry, described by the time constant τ_{BR} (Fig. 5b); τ_{BR} was comparable to τ_{slow} in the harder composites ($T_g = 23$ and 31 °C) and further decreased in the softer composites, being even lower than τ_{fast} . Thus, by softening the material, the PR response speed was increasingly determined by the space-charge field buildup, rather than by the chromophore orientational speed.

Table 1 Composition, glass-transition temperature (T_g) and absorption coefficient (α) of the PR blends characterized in this work. Weight percentages of chromophore (calculated excluding the hexamethylenic connecting bridge) and total carbazole (calculated excluding the hexamethylenic connecting bridge in **2** and the ethyl group in ECZ) units in each composite are also shown

Composition (wt%)				Functional components (wt%)				
2	3	PVK	ECZ	TNF	Chromophore	Carbazole	$T_{g} [^{\circ}C]$	$\alpha [\mathrm{cm}^{-1}]$
71.0	_	_	28.0	1.0	38.2	32.1	31	110
64.0			35.0	1.0	34.4	37.3	23	105
54.0			45.0	1.0	29.0	44.6	6	93
50.0			49.0	1.0	26.9	47.6	-1	82
_	42.4	7.6	49.0	1.0	29.9	48.1	8	115
	Compos 2 71.0 64.0 54.0 50.0 —	Composition (wt%) 2 3 71.0 64.0 54.0 50.0 42.4	Composition (wt%) 2 3 PVK 71.0 64.0 54.0 50.0 42.4 7.6	Composition (wt%) 2 3 PVK ECZ 71.0 28.0 64.0 35.0 54.0 45.0 50.0 49.0 42.4 7.6 49.0	Composition (wt%) 2 3 PVK ECZ TNF 71.0 28.0 1.0 64.0 35.0 1.0 54.0 45.0 1.0 50.0 49.0 1.0 42.4 7.6 49.0 1.0	Composition (wt%) Functional composition 2 3 PVK ECZ TNF Chromophore 71.0 - - 28.0 1.0 38.2 64.0 - - 35.0 1.0 34.4 54.0 - - 45.0 1.0 29.0 50.0 - - 49.0 1.0 26.9 - 42.4 7.6 49.0 1.0 29.9	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	Composition (wt%) Functional components (wt%) 2 3 PVK ECZ TNF Chromophore Carbazole T_g [°C] 71.0 - - 28.0 1.0 38.2 32.1 31 64.0 - - 35.0 1.0 34.4 37.3 23 54.0 - - 45.0 1.0 29.0 44.6 6 50.0 - - 49.0 1.0 26.9 47.6 -1 - 42.4 7.6 49.0 1.0 29.9 48.1 8



Fig. 5 Dependence on the **M2** composites' $T_{\rm g}$ of (a) the PR refractive index modulation Δn , (b) time constants $\tau_{\rm fast}$ and $\tau_{\rm slow}$ (both from Δn fitting) and $\tau_{\rm BR}$ (from ellipsometry fitting) and (c) conductivities $\sigma_{\rm light}$ and $\sigma_{\rm dark}$ (left axis) and conductivity contrast M (right axis). PR gratings were recorded using the E-switch method (applied field of 60 V μm^{-1}). Ellipsometry was performed at 60 V μm^{-1} , while conductivities were measured at 22 V μm^{-1} . Lines connecting points are to guide the eye.

In particular, τ_{slow} decreased by lowering the T_g more strongly than τ_{fast} . This would agree with the usual assumption that the slower component is mainly related to the chromophore orientation (BR modulation), while the fast component is due to the formation of the space charge field upon charge generation and transport (EO modulation). This is, however, an oversimplified description and both fast and slow components are also affected by the different trapping sites, especially with T_g below RT.²⁵ Indeed, τ_{slow} drastically dropped from $T_g = 31$ to 23 °C (in more than one order of magnitude), while it decreased moderately for $T_{\rm g}$'s below RT. On the other hand, $\tau_{\rm fast}$ was also influenced to some extent.²⁶ The worsening of Δn at the lowest T_g is explained by the conductivity behavior (Fig. 5c), as σ_{light} barely improved by decreasing T_{g} 's, while σ_{dark} increased over more than 2 orders of magnitude. This led to a drastic reduction of the conductivity contrast M (down to 0.68) in the softest composite, causing the lowering of Δn . Similar deterioration of both M and photorefractive Δn has previously been observed by operating at temperatures well above the material's T_{g}^{27} and, in particular, in DCDHF glasses.²⁸ In general, DCDHF-based materials with a T_g below room temperature exhibited inferior PR performance,13,14,18 despite an improved orientational rate. In this work, we achieved the best performance at $T_g = 6$ °C (M2-54) and profited from the enhanced speed, keeping good material processability.

Further insights into the physical processes governing the material PR response can be gained from the dependence of the grating dynamics on the recording/erasure scheme. By writing the grating with either the *E-switch* or WB_{I} -switch method (see

Experimental section), the sample conditions prior to recording can strongly vary.²⁹ Fig. 6, left, compares these two writing schemes in both the relatively hard M2-71 and the soft M2-54 composites. In the harder material, sample pre-poling (WB_{I}) switch method) allowed a much faster response as chromophores only needed to slightly reorient under the effect of the developing $E_{\rm SC}$ (instead of reorient from a random distribution), which mitigated the handicapped chromophore mobility. By contrast, pre-poling barely improved the recording in the soft M2-54, corroborating that the PR response was not orientation-limited when the $T_{\rm g}$ was low enough. The distinct limiting factors depending on the material's T_g was further evidenced by the dependence of the PR buildup speed on the total recording intensity I (insets in Fig. 6). Indeed, the speed τ_{fast}^{-1} was weakly Idependent in the harder material, indicating orientation-limited dynamics,^{7,13} but nearly proportional to I in the soft composite, as the speed became rather photoconductivity-limited.²⁸ It is worth noting that the little influence of sample pre-illumination in the soft material demonstrates that the photogeneration of uniform charge density prior to measurement did not enhance the PR speed, which would occur, by contrast, in case of a charge-generation-limited response.^{5,30} This suggests that our material was efficiently sensitized by carbazole/TNF so that the grating speed was rather limited by charge redistribution, which is consistent with the typically low hole mobility in carbazolebased systems. Thus, the clear intensity-dependence of the buildup speed (inset in Fig. 6b) indicates that higher irradiance led to improved charge transport, maybe due to modification of the trap landscape, although this aspect is unclear at this point. On the other hand, pre-illumination did not induce speed slowdown, suggesting that no optical trap activation³¹ occurred.

The grating decay gave further information as the erasure conditions strongly varied in each scheme, having a distinct effect depending on the composite's T_g (Fig. 6, right). On the one hand, in the *E*-switch method the BR modulation relaxed as the aligned



Fig. 6 A comparison of η transient behaviors upon two different recording/erasure schemes (*E*- and *WB*₁-switch methods) performed in (a) hard **M2-71** and (b) soft **M2-54** composites. The recording intensity *I* was 320 mW cm⁻². Arrows indicate the beginning of grating buildup/ erasure (*E* or *WB*₁ on/off). Insets: *I*-dependence of the experimental speed τ_{fast}^{-1} (symbols) and fit functions *I*^{β} with $\beta = 0.20$ (a) and 0.89 (b) (lines). The external field was 60 V μ m⁻¹ in all cases.

chromophore spontaneously randomized in absence of an external field while the EO component decreased parallel to E_{SC} , mainly due to recombination of the present charge carriers. This erasure scheme was much slower in the hard material M2-71, strongly limited by the inefficient chromophore reorientation. Besides, the relatively fast decay in the soft material M2-54 indicated rather fast charge recombination in the material. On the other hand, the WB_1 -switch method consists in optical erasure, in which E_{SC} decreased mainly through uniform charge photogeneration upon the homogeneous illumination (opposite to dark decay) followed by slight chromophore re-orientation in the progressively uniform total field. The decay in this case, which was increasingly effective at higher E due to the fielddependent photogeneration in organic materials,³² achieved clearly faster rates with this scheme. Once again, the decay was slower in the hard material due to inefficient relaxation of the BR modulation. In any case, optical erasure exhibited faster dynamics than writing, which is an important technical feature for real applications. Interestingly, resulting Δn decay curves (calculated from eqn (2)) could be fitted by mono-exponential functions in the soft composite, but bi-exponential in the hard one, which manifests the existence of one predominant process and two competing ones, respectively.

The PR grating field-dependence, governed by the raise of $E_{\rm SC}$ and Δn with increasing *E*, was also characterized (Fig. 7, displaying **M2-54** data). η exhibited a sinusoidal dependence (eqn (2)), with near total diffraction at 65 V μ m⁻¹ in the relatively thin 37 μ m samples (maximum Δn of 0.024 was achieved at 120 V μ m⁻¹). Γ monotonously increased (eqn (3)), up to 350 cm⁻¹ at

1.0- **a**

0.8

0.6

0.4

0.2



Fig. 7 Field-dependence of steady-state η and Γ and buildup time constant τ_{fast} , measured in **M2-54** and **M3-42**. Inset in (b): normalized total transmitted WB intensity ($I_1 + I_2$) against the applied field. Lines connecting points are to guide the eye.

120 V μ m⁻¹, although some saturation was evident above 50 V μ m⁻¹. Such deterioration of TBC has been typically caused by strong beam fanning in other DCDHF-based materials.^{7,13,16} However, this detrimental effect was not significant in our composites, as the total transmitted WB intensity decreased only slightly at high voltages (inset in Fig. 7b). Thus, Γ saturation was probably caused by loss of grating contrast (due to unequal WB intensities within the sample resulting from the high TBC). Regarding the dynamics, the buildup response speeded up for increasing fields (Fig. 7c), as expected due to enhanced charge photogeneration/transport and chromophore alignment, and buildup times (τ_{fast}) as low as 35 ms at 120 V μm^{-1} were achieved. Erasure times (*WB*₁-switch) were as low as 20 ms at 120 V μ m⁻¹. The high electrical breakdown of the soft composite M2-54 is remarkable (and even higher, up to 170 V μ m⁻¹, in the harder M2-71), which reveals the high structural stability of our multifunctional polymers. These figures of merit are superior to most of those reported in previous DCDHF-based PR materials and are among the best data found in multifunctional polymers and even standard composites.

Several composites based on homopolymer 3 were also prepared and their PR properties were characterized, which also allowed us to evaluate the convenience of anchoring the carbazole to the copolymer 2 together with the chromophore. Qualitatively, PR performance in M3 materials exhibited same dependence on T_g and recording/erasure schemes as that in M2, which manifests analogous physical properties in both polymers. This suggests that the attached carbazole groups did not sterically hindered the chromophore orientability in copolymer 2. The best M3 composite (M3-42, $T_g = 8 \degree C$) is directly compared in Fig. 7 with the best M2 material (M2-54, $T_g = 6$ °C). M3-42 showed very similar field dependence as that of M2-54 but an inferior PR effect, which was more evident in Γ than in η , implying a larger phase-shift Θ in the M2 material (according to eqn (3)). Again, significant beam fanning was ruled out, as shown in the inset of Fig. 7b. Concerning the dynamics, grating buildup rates were lower (about two-fold) in the M3 material (Fig. 7c), as well as the erasure rates. Assuming no orientation-limited performance, those facts suggest a somewhat more effective charge photogeneration and transport in copolymer 2, favoring charge migration (large Θ) and fast E_{SC} formation. This is further supported by the smaller photoconductivity measured in the M3 composites ($\sigma_{ph} = 2.4$ and 3.1 pS cm⁻¹ in M3-42 and M2-54, respectively, measured at 22 V μ m⁻¹). A possible explanation could be that the well-distributed carbazole units attached to the copolymer 2, in which the NLO units act as spacers, would help the charge transfer with TNF molecules and the subsequent hole transport. The totally random distribution of carbazole in M3 materials may also lead to increased disorder of the density of states (more dispersive charge transport³²) or some π -stacking of the planar carbazole groups,³³ in both cases resulting in decreasing photoconductivity.

Conclusions

Photorefractive low- T_g DCDHF glasses and fully functionalized copolymers have previously been reported, generally showing very slow PR response due to hindered chromophore orient-ability. Unfortunately, further lowering of the T_g led to a faster

but smaller effect, or to material instability. Here, we synthesized two new multifunctional DCDHF-containing copolymers, with attached carbazole units, one of them (2) being suitable for the preparation of efficient low- T_g PR blends. Composites' T_g , progressively lowered by adding plasticizer, governed the material PR response, which turned from orientation-limited to photoconductivity-limited, and finally suffered strong deterioration due to increased dark conductivity. Nevertheless, an optimum T_g was found at 6 °C that enabled a fast response before significant PR strength reduction occurred. Furthermore, the composite exhibited higher structural stability than prior DCDHF-based materials, preventing electrical breakdown or beam fanning even at applied fields above 100 V μm^{-1} . Outstanding PR performance was achieved ($\Delta n = 0.024$, $\Gamma =$ 350 cm^{-1} and buildup (erase) times of 35 (20) ms at 120 V μm^{-1} and low intensity 320 mW cm⁻²), which is promising for practical applications. In addition, a NLO homopolymer (3), identical to copolymer 2 but without carbazole, was synthesized and characterized in PR composites. Although their qualitative behavior was similar, the homopolymer exhibited inferior PR performance, which suggests a favorable role of the carbazole units attached to the copolymer, contributing to better charge generation/transport.

Acknowledgements

We thank support from the Spanish Government MEC and the European Community (FEDER) (grants MAT2008-06648-C01, MAT2011-28167-C02-01, CTQ2008-05901/BQU and Consolider-Ingenio 2010 project HOPE CSD2007-00007). FGG thanks the Juan de la Cierva program of the Spanish Government MEC (grant JCI-2006-3029-2615) for support.

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