Fully Functionalized Photorefractive Polymethacrylates with Net Gain at 780 nm

David Van Steenwinckel,*,† Christiaan Engels,‡ Elke Gubbelmans,‡ Eric Hendrickx,† Celest Samyn,‡ and André Persoons†

Laboratory for Chemical and Biological Dynamics, Center for Research on Molecular Electronics and Photonics, University of Leuven, Celestijnenlaan 200D, B-3001 Leuven, Belgium, and Laboratory of Macromolecular and Physical Organic Chemistry, University of Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium

Received December 14, 1999; Revised Manuscript Received March 14, 2000

ABSTRACT: We report on the synthesis and characterization of three fully functionalized photorefractive polymethacrylates containing different chromophores. Carbazole- and NLO-functionalized methacrylate monomers in a 1:1 ratio were polymerized with 20 mol % of dodecyl methacrylate to obtain photorefractive polymers. The resulting polymers had glass transition temperatures of 48, 47, and 52 °C, respectively. Asymmetric two-beam-coupling and four-wave-mixing experiments at 780 nm and three different temperatures pointed out that the resulting polymers, doped with 1 wt % (2,4,7-trinitro-9-fluorenylidene)-malononitrile (TNFDM), showed good photorefractive properties. A net two-beam coupling gain and a diffraction efficiency of 60% were observed at 58 V/μm.

Introduction

The photorefractive effect involves the modulation of the refractive index by a space charge field via the Pockels effect and birefringence.[1,2] The materials used for photorefractive applications are multifunctional, combining photoconductivity and electrooptic activity. Optical signal processing, information storage, real-time holography, image amplification, and optical phase conjugation are among the practical applications of photorefractive (PR) materials.[1] Because of this widespread range of applications, PR materials have received considerable attention the past few years. Great progress has been made in the field of organic photorefractive polymers (e.g. composites based on poly(*N*-vinylcarbazole) (PVK) and fully functionalized polymers).[3−5] Compared to the inorganic crystals, where the photorefractive effect was originally discovered, organic polymers have the advantages of a better processability, lower cost, larger electrooptic coefficients, and lower dielectric constants. An additional advantage of these polymers was the extension of the optical wavelength at which charge generation and photoconductivity occur to the near-IR region. This wavelength determines which laser system can be used, and for the near-IR region several low-cost laser diodes are available. In the well-known PVK composites, the wavelength of absorption of the PVK-sensitizer charge-transfer complex was extended to the near-IR by replacing 2,4,7-trinitro-9-fluorenone (TNF) by (2,4,7-trinitro-9-fluorenylidene)-malononitrile (TNFDM), and characterization of photorefractive materials was possible up to 830 nm.[4]

A drawback of the intensely studied photorefractive PVK-based composite materials is the phase instability these materials suffer.[6,7] The polar chromophores that are dispersed in the apolar PVK matrix have a tendency toward crystallization, because of the dipolar interactions and the high melting points of the chromophores. Crystallization, however, should be avoided since it reduces the dielectric strength and the fringe contrast in the samples. This makes it difficult to obtain stable photorefractive composite materials with a chromophore load of 40 wt % or higher. The plasticizer material that is often used, *N*-ethylcarbazole (ECZ), tends to crystallize from the PVK matrix as well, when used in concentrations above 40 wt %.

Since fully functionalized polymers offer the best perspectives in terms of stability,[8,9] we have prepared three photorefractive polymethacrylates in which the chromophore unit is polymerized along with the charge transporting unit. An additional plasticizer was incorporated to obtain lower glass transition temperatures (T_g) and hence to enable poling of the chromophores at room temperature. Each polymer consists of the same charge transport and plasticizing units in identical molar concentrations but with different chromophores.

Results and Discussion

Synthesis of the Photorefractive Polymethacrylates and Sample Preparation. The synthetic routes for preparation of the polymers are depicted in Scheme 1. The polymers were prepared by a polymerization of three types of methacrylates, functionalized with carbazole, a D-π-A-chromophore, and a dodecyl group, respectively. The composition of the polymers reflects the multistep process of photorefractivity: Photoconductivity is brought about by the carbazole groups, and charge generation can be easily accomplished by the selective excitation of a carbazole−TNFDM charge-transfer complex up to wavelengths in the near-IR region. The D-π-A-chromophores are necessary to obtain electrooptic activity and to induce birefringence. The chromophores all have strong electron donors and acceptors, which enhances the dipole moment μ, the polarizability anisotropy $\Delta\alpha$, and the first hyperpolarizability β. This improves the photorefractive figure of merit[10] (FOM $= N\Delta\alpha\mu^2 + \beta\mu$, where N equals $^9/_2kT$) and enlarges the refractive index modulation. The dodecyl group, finally, acts as an internal plasticizer and lowers

† Laboratory for Chemical and Biological Dynamics.
‡ Laboratory of Macromolecular and Physical Organic Chemistry.

10.1021/ma992093e CCC: $19.00
Published on Web 04/25/2000

Scheme 1. Synthetic Routes for Photorefractive Polymethacrylates

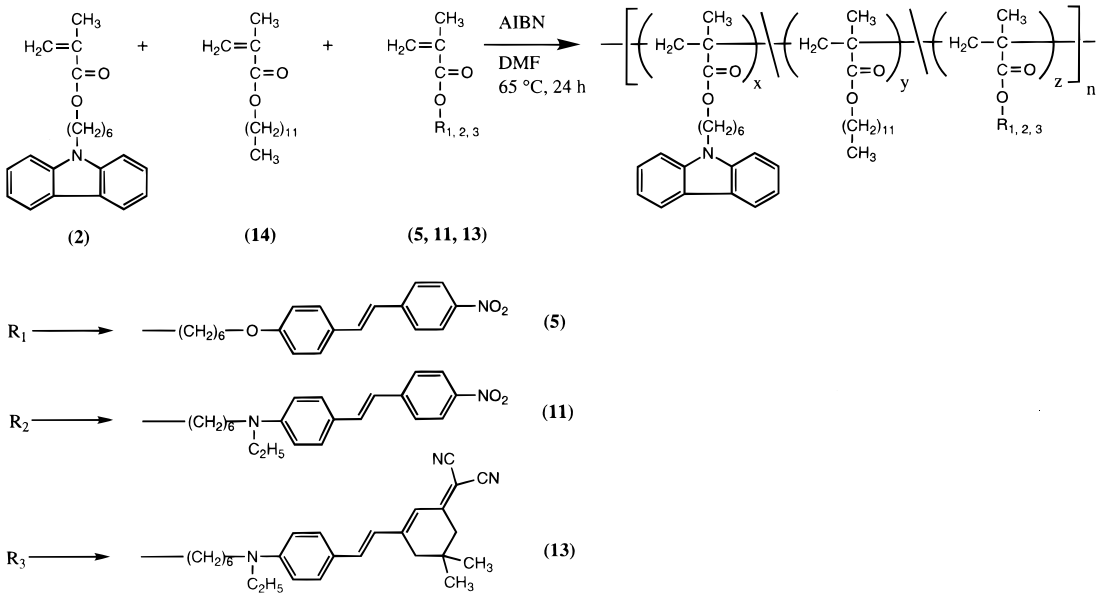

Table 1. Composition of the Synthesized Polymethacrylates

		x/*y*/*z*[b]		
polymer	chromophore[a]	feed	composn[c]	yield/%
1a	**5**	0.50/0.0/0.50	0.45/0.0/0.55	92
1b	**5**	0.40/0.20/0.40	0.42/0.22/0.36	70
2	**11**	0.40/0.20/0.40	0.46/0.23/0.31	94
3	**13**	0.40/0.20/0.40	0.45/0.18/0.37	77

[a] The chromophore incorporated in the polymer. The chromophore number refers to the Experimental Section. [b] The molar ratios of carbazole-, dodecyl-, and chromophore-functionalized methacrylates, respectively. [c] The polymer composition was determined by ^{1}H NMR.

Table 2. Number Average and Mass-Average Molar Mass and Glass Transition Temperatures of the Synthesized Polymethacrylates

polymer	$\bar{M}_n$/g mol^{-1}	$\bar{M}_w$/g mol^{-1}	$\bar{M}_w/\bar{M}_n$[a]	T_g/°C
1a	20 000	70 000	3.5	66 ± 2
1b	26 000	100 000	3.8	48 ± 2
2	14 000	40 000	2.8	47 ± 2
3	8 000	20 000	2.5	52 ± 2

[a] Polydispersity.

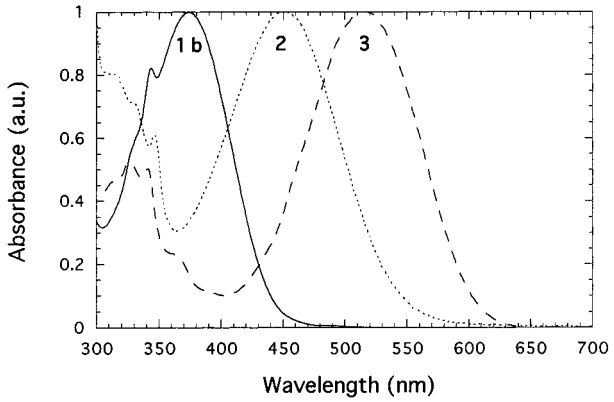

Figure 1. Absorption spectrum for polymers **1b**, **2**, and **3** in chloroform. The curves were normalized at the wavelength of maximum absorption. The λ_{max} for the chromophores in polymers **1b**, **2**, and **3** are 375, 451, and 515 nm, respectively. The peaks around 328 and 343 nm, observed in the 3 polymers, are due to a weaker absorption from the carbazole moieties.

the T_g value of the polymer. This is very important for photorefractive polymers, because lowering the T_g of the polymers allows the chromophores to take full advantage of the orientational enhancement effect,[11] as they are given the necessary rotational mobility to reorient along the total electric field (i.e. the superposition of the applied electric field and the space-charge field). Having a nonzero polarizability anisotropy, the chromophores translate the periodic total electric field into a refractive index modulation additional to the Pockels effect, and the photorefractive performances of the material are greatly enhanced by this birefringence contribution. The carbazole moieties and the D-π-A-chromophores both were separated from the methacrylate backbone by a flexible hexyl chain. This also results in a lower glass transition temperature and provides more rotational flexibility for the chromophores.

The compositions of the polymers were determined with ^{1}H NMR and are listed in Table 1. The results were consistent with the monomer feed. The physical properties of all prepared polymers are listed in Table 2. In a first approach, a copolymer containing only the charge transport agent and chromophore was prepared (**1a**). Because the glass transition temperature (T_g) of the resulting polymer **1a** was relatively high, terpolymerizations were performed with dodecyl methacrylate. As shown in Table 2, 20 mol % of this internal plasticizer lowered the T_g sufficiently for our purposes. Therefore, all polymers were prepared with 20 mol % of dodecyl methacrylate. High yields and reasonable molecular weights were obtained. The polymers had good film forming properties and showed remarkable good resistance toward dielectric breakdown. In addition, the photorefractive polymer samples were of a high optical quality. Absorption spectra of polymers **1b**, **2**, and **3** in chloroform are shown in Figure 1. Next to the three chromophore absorption peaks for the respective polymers, each polymer showed weak absorption bands at 328 and 343 nm, due to absorption from the carbazole group.

In preparation of the photorefractive samples, an external sensitizer (TNFDM) was added in 1 wt % concentration to create the charges necessary for the photorefractive effect, by selective excitation of the

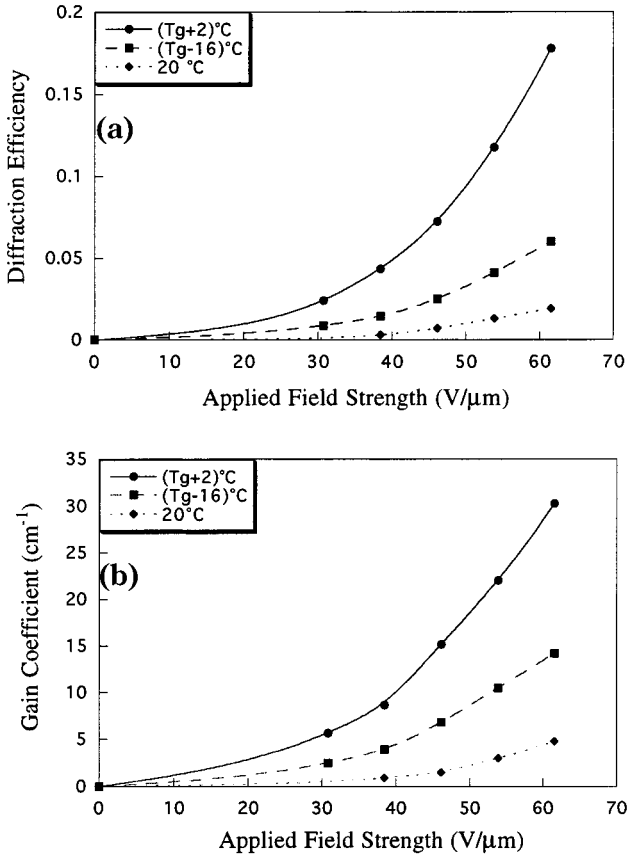

Figure 2. (a) Diffraction efficiencies for polymer **1b** at 20 °C (28 °C below T_g), at 16 °C below T_g, and at 2 °C above T_g versus applied electric field. (b) Gain coefficients (cm^{-1}) for polymer **1b** at 20 °C (28 °C below T_g), at 16 °C below T_g, and at 2 °C above T_g versus applied electric field.

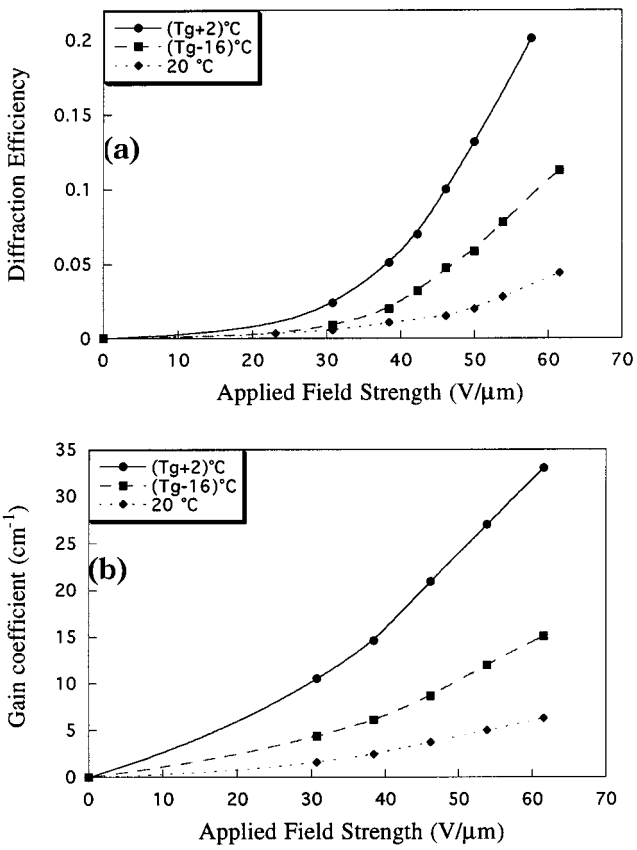

Figure 3. (a) Diffraction efficiencies for polymer **2** at 20 °C (27 °C below T_g), at 16 °C below T_g, and at 2 °C above T_g versus applied electric field. (b) Gain coefficients (cm^{-1}) for polymer **2** at 20 °C (27 °C below T_g), at 16 °C below T_g, and at 2 °C above T_g versus applied electric field.

carbazole−TNFDM charge-transfer complex at 780 nm. The sensitizer was not incorporated in the polymer structure because crystallization of this unit is not likely due to its small concentration.

Photorefractive Characterization. The photorefractive performances of the polymers were investigated by two-beam coupling as well as degenerate four-wave mixing. The latter technique provides information about the amplitudes of the photorefractive space-charge field and of the resulting refractive index modulation.[12] Real proof of the photorefractive effect, however, can only be obtained by asymmetric two-beam coupling,[13] which outrules other possible grating forming mechanisms as photochromic or thermal gratings. For films of the three polymers, reversal of the applied electric field was followed by a reversal of the direction of energy transfer, which proves the nonlocal and the photorefractive nature of the grating. Diffraction efficiencies for polymers **1b**, **2**, and **3** at 20 °C, at 16 °C below T_g, and at 2 °C above T_g are presented in Figures 2a, 3a, and 4a, respectively, while the observed gain coefficients for polymers **1b**, **2**, and **3** at 20 °C, at 16 °C below T_g, and at 2 °C above T_g are shown in Figures 2b, 3b, and 4b, respectively. Since the buildup times of the photorefractive effects in these materials are rather large (a few tens of seconds), measurements were performed in steady-state conditions. This means that, at a certain bias field, the photorefractive effects were allowed to build up for 5 min, before increasing the voltage with 1 kV. At 20 °C, the polymers show good results, as shown in the lower curves of Figures 2−4, respectively. However, when the temperature of the samples is increased, large improvements in diffraction efficiency as well as in gain coefficient are observed. This enhancement can, to a large extent, be attributed to the orientational enhancement effect.[10] When the temperature of the samples approaches the glass transition temperature of the polymer mixture, the chromophores gain orientational mobility and reorient into the direction of the total electric field. If the chromophores have a nonzero polarizability anisotropy, this periodic orientation produces a modulated birefringence, which gives rise to an additional refractive index modulation. Therefore, if one wants to compare the photorefractive efficiencies of different polymer materials, it is very important that measurements are performed at equal distances from the respective glass transition temperatures ($T - T_g$). The measurements in this work were performed at 2 °C above T_g, at 16 °C below T_g, and at 20 °C. The trends seen upon raising the temperature have been explained above. Note that the performances of the polymers are good, although the concentration of the charge transporting unit (carbazole) is much lower than in the photorefractive PVK-based composite materials. For polymer **3**, for example, the 45 mol % of carbazole units that are incorporated into the polymer are equivalent to 20 wt % of carbazole groups. In the photorefractive PVK-based composites often more than 60 wt % of carbazole groups is used. Also important is that the three polymers, when measured at 2 °C above T_g, show net gain $\Gamma-\alpha$ (Γ is the gain coefficient, and α is the absorption coefficient; both are in cm^{-1}). This net gain is an important feature for incorporation of these

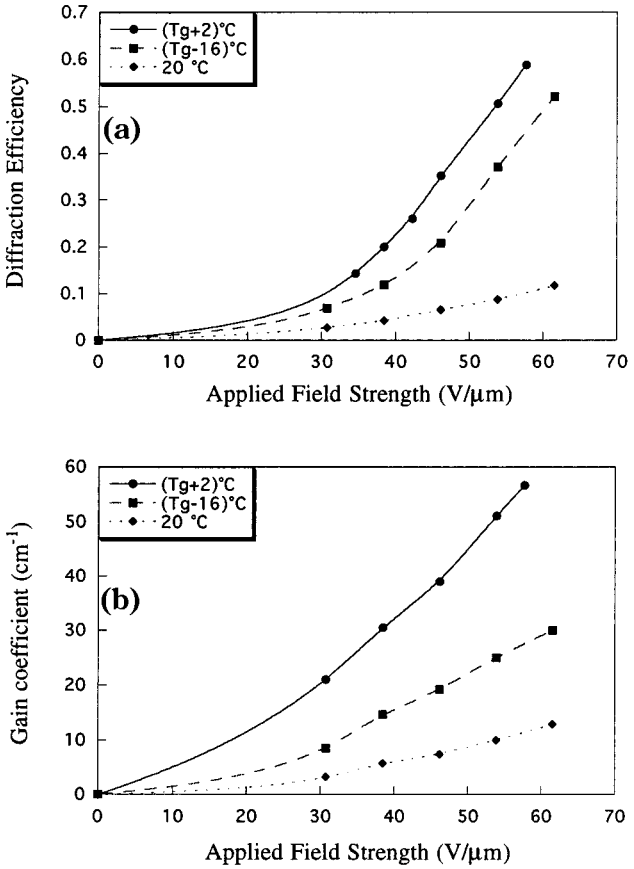

Figure 4. (a) Diffraction efficiencies for polymer 3 at 20 °C (32 °C below T_g), at 16 °C below T_g, and at 2 °C above T_g versus applied electric field. (b) Gain coefficients (cm^{-1}) for polymer **3** at 20 °C (32 °C below T_g), at 16 °C below T_g, and at 2 °C above T_g versus applied electric field.

materials into photorefractive applications. The absorption coefficients for polymers **1b**, **2**, and **3** at 780 nm are 16, 25, and 43 cm^{-1}, respectively.

It can be easily seen that both diffraction efficiencies and gain coefficients for polymer **3** are much better than for polymer **2** and polymer **1b**, respectively. This tendency can be explained in terms of the photorefractive figures of merit for the chromophores that are incorporated in the respective polymers. The D-π-A-chromophore in polymer **1b** is 4-methoxy-4′-nitrostilbene (MONS), while the D-π-A-chromophore in polymer **2** is 4-(*N*,*N*-dimethylamino)-4′-nitrostilbene (DANS). The latter chromophore has a higher dipole moment (6.6 ± 0.5 D)[14] than MONS (5.7 ± 1.5 D).[15] The first hyperpolarizabilities for the two chromophores show the same tendencies. Therefore, the chromophore of polymer **2** has a higher photorefractive figure of merit than that of polymer **1b**, which explains the higher diffraction efficiencies observed in this material. The chromophore in polymer **3** contains a longer conjugated bridge, and the dicyano moiety is a stronger electron acceptor than the nitro groups in polymers **1** and **2**. Both elements contribute to a higher dipole moment (8.7 ± 0.5 D)[16] as well as to a larger polarizability anisotropy, and the figure of merit for this chromophore is again enhanced, producing a better polymer in terms of photorefractive performance. The amplitude of the refractive index moduation amplitude Δn can be calculated from the internal diffraction efficiency η using eq 1

$$\eta = \sin^2(564\Delta n) \qquad (1)$$

Equation 1 was obtained from the coupled wave theory for thick holograms developed by Kogelnik, after filling in all absorption and geometry factors.[12] The refractive index modulation amplitude is proportional to the figure of merit for photorefractive chromophores. Above T_g, $N\Delta\alpha\mu^2$ is the dominant term in the figure of merit. As an example, we have calculated the refractive index modulation amplitude for polymers **1b**, **2**, and **3**, at an applied field of 55 V/μm, at $T_g + 2$ °C. Under these conditions, the values of Δn were (6.5 ± 0.3) × 10^{-4}, (7.8 ± 0.4) × 10^{-4}, and (14.6 ± 0.7) × 10^{-4}, respectively. These values agree with the μ^2 dependence of the figure of merit and of Δn, within the experimental errors. Although the gain coefficients show the same trends as the diffraction efficiencies, such a quantitative comparison cannot be made, since the gain coefficient is proportional to both Δn and the sine of the photorefractive phase shift. The phase shifts in these polymers are the subject of a next study.

For polymer **3**, a diffraction efficiency of 60% and a gain coefficient of 57 cm^{-1} were measured with an externally applied field of 58 V/μm. To our knowledge, these are the highest values reported to date for fully functionalized polymers at 780 nm.[17]

In conclusion, we have prepared three fully functionalized polymethacrylates containing different chromophore groups, showing good photorefractive performances at 780 nm. Films of good optical quality and high resistance against dielectric breakdown were prepared. Qualitatively, the magnitude of the photorefractive effects was observed to be proportional to the photorefractive figure of Merit for the chromophore that is incorporated. Elevation of the measurement temperature invoked a large increase in the photorefractive performances for all polymers, mainly due to a higher rotational mobility of the chromophores. The polymers contained only 20 wt % carbazole groups, much less than the concentration of the charge transporting units in PVK-based polymer composites. Net gain was observed at 780 nm for the three polymers, and polymer **3** showed a diffraction efficiency of 60% and a gain coefficient of 57 cm^{-1} at 58 V/μm.

Experimental Section

General Methods. All reagents are commercially available and used as received. All synthesized products were characterized by a Bruker WM-250 (250 MHz) ^{1}H NMR; the polymer composition was studied by a Bruker AMX-400 (400 MHz) ^{1}H NMR. The molecular weights were determined by gel permeation chromatography (Waters HP/GPC), using THF as eluent and toluene as internal reference; polystyrene standards of known molecular weights were used for calibration. The polymers were detected by differential refractometry and by UV absorption. The glass transition temperatures of the polymers were measured by differential scanning calorimetry (DSC), using a Perkin-Elmer DSC-7. All samples were heated at a rate of 20 °C/min.

9-(6-Hydroxyhexyl)carbazole (1). To a solution of 16.7 g (0.1 mol) of carbazole were added 34.1 g (0.15 mol) of 6-iodohexanol, 1.1 g (3.3 mmol) of tetrabutylammonium hydrogen sulfate (TBAHS) in dry acetone (100 mL), and 6.0 g (0.15 mol) of sodium hydroxide, and the mixture was stirred under reflux for 24 h, cooled, poured into iced water, filtered, and then purified by column chromatography (silica gel) with chloroform as eluent. Yield: brown solid **1**, 13.3 g (39%), mp 133−136.2 °C. NMR: δ_H ($CDCl_3$) 8.1 (d, 2H), 7.5 (m, 4H), 7.3 (d, 2H), 4.3 (t, 2H), 3.5 (t, 2H), 1.5 (m, 4H), 1.4 (m, 4H), 1.0 (br s, 1H).

4-[(6-Hydroxyhexyl)oxy]benzaldehyde (3). A stirred solution of 18.3 g (0.15 mol) of 4-hydroxybenzaldehyde, 20.5 g

(0.15 mol) of 6-chlorohexanol, 44.6 g (0.323 mol) of K_2CO_3, and 2.0 g (5.4 mmol) of tetrabutylammonium iodide in DMF (600 mL) was refluxed for 24 h under argon. After filtration, the solvent was removed in vacuo to obtain the pure white solid **3** (26.9 g, 80%), mp 30.2−31.7 °C. NMR: δ_H ($CDCl_3$) 9.1 (s, 1H), 7.8 (d, 2H), 7.0 (d, 2H), 4.1 (t, 2H), 3.7 (t, 2H), 1.8 (m, 4H), 1.4 (m, 4H).

6-[(4-(2-(4-Nitrophenyl)ethenyl)phenyl)oxy]hexanol (4). A mixture of 5.6 g (25 mmol) of 4-[(6-hydroxyhexyl)oxy]-benzaldehyde, **3**, 6.8 g (37 mmol) of 4-nitrophenylacetic acid, and 1.7 mL (17 mmol) of piperidine was stirred for 12 h at 130 °C. After cooling, water was added, and the reaction mixture was filtered. The yellow solid **4** was finally recrystallized from ethyl acetate. Yield: 3.9 g (46%), mp 159.4−162 °C. NMR: δ_H ($CDCl_3$) 8.2 (d, 2H), 7.7 (d, 2H), 7.6 (d, 2H), 7.5 (d, 1H), 7.2 (d, 1H), 6.9 (d, 2H), 4.4 (br s, 1H), 4.0 (t, 2H), 3.4 (t, 2H), 1.7 (m, 4H), 1.4 (m, 4H).

***N*-Ethyl-*N*-(6-hydroxyhexyl)aniline (6).**[18] A stirred solution of 60.6 g (0.5 mol) of distilled *N*-ethylaniline, 68.0 g (0.5 mol) of 6-chlorohexanol, 76.0 g (0.55 mol) of K_2CO_3, and 0.99 g (15 mmol) of KI in *n*-butanol (300 mL) was refluxed under argon for 4 days. After cooling and filtration, the solvent was removed and the crude reaction product was distilled under reduced pressure to obtain a slightly yellow liquid **6**. Yield: 53.0 g (48%), bp 140 °C (0.4 mmHg). NMR: δ_H ($CDCl_3$) 7.2 (m, 2H), 6.8 (m, 3H), 3.6 (m, 2H), 3.2 (m, 4H), 2.9 (br s, 1H), 1.3 (m, 8H), 1.1 (t, 3H).

***N*-Ethyl-*N*-(6-acetoxyhexyl)aniline (7).** A stirred solution of 44.0 g (0.2 mol) of *N*-ethyl-*N*-(6-hydroxyhexyl)aniline, **6**, in acetic acid anhydride (60 mL) was refluxed for 10 h. The solvent was removed in vacuo, and the product was purified by distillation to yield a slightly yellow liquid **7**. Yield: 48.4 g (98%), bp 150 °C (2.0 mmHg). NMR: δ_H ($CDCl_3$) 7.2 (t, 2H), 6.8 (d, 3H), 4.0 (t, 2H), 3.4 (q, 2H), 3.3 (t, 2H), 2.0 (s, 3H), 1.5 (m, 8H), 1.1 (t, 3H).

4-[(*N*-Ethyl-*N*-6-acetoxyhexyl)amino]benzaldehyde (8). A 18.1 mL (0.194 mol) volume of $POCl_3$ was added dropwise to ice-cooled DMF (55 mL) and stirred for 4 h at 0 °C. A solution of 48 g (0.18 mol) of *N*-ethyl-*N*-(6-acetoxyhexyl)aniline, **7**, in DMF (5 mL) was then added dropwise. The reaction mixture was then stirred for 3 h at 90 °C and poured into an ice-cooled solution of water (600 mL) and 10 g of sodium acetate, extracted with dichloromethane, and dried ($MgSO_4$). After removal of the solvent, the product was distilled to obtain **8** as a yellow liquid. Yield: 39.9 g (75%), bp 205 °C (0.1 mmHg). NMR: δ_H ($CDCl_3$) 9.7 (s, 1H), 7.7 (d, 2H), 6.7 (d, 2H), 4.1 (t, 2H), 3.4 (m, 4H), 2.1 (s, 3H), 1.5 (m, 8H), 1.2 (t, 3H).

4-[*N*-Ethyl-*N*-(6-hydroxyhexyl)amino]benzaldehyde (9). A stirred solution of 15.5 g (0.05 mol) of 4-[(*N*-ethyl-*N*-6-acetoxyhexyl)amino]benzaldehyde, **8**, and 3.0 g (75 mmol) of NaOH in water−ethanol (1:1 v/v, 120 mL) was heated for 24 h at 90 °C. After cooling, the reaction mixture was extracted with chloroform, washed with water, and dried ($MgSO_4$); then the solvent was removed in vacuo and the product was distilled to yield a yellow liquid **9**. Yield: 9.5 g (76%), bp 213 °C (1 mmHg). NMR: δ_H ($CDCl_3$) 9.7 (s, 1H), 7.7 (d, 2H), 6.7 (d, 2H), 3.6 (t, 2H), 3.4 (q, 2H), 3.3 (t, 2H), 1.6 (m, 4H), 1.4 (m, 4H), 1.2 (t, 3H).

6-[*N*-Ethyl-*N*−(4-(2-(4-nitrophenyl)ethenyl)phenyl)-amino]hexanol (10). A stirred mixture of 4.7 g (19 mmol) of 4-[*N*-ethyl-*N*-(6-hydroxyhexyl)amino]benzaldehyde, **9**, 5.2 g (28 mmol) of 4-nitrophenylacetic acid, and 1.3 mL (13 mmol) of piperidine was heated for 12 h at 120 °C. After cooling, chloroform was added, the solution was washed out with water and dried ($MgSO_4$), and the solvent was removed in vacuo. The orange solid **10** was purified by recrystallization from ethanol. Yield: 4.3 g (61%), mp 94.5−96.9 °C. NMR: δ_H ($CDCl_3$) 8.2 (d, 2H), 7.6 (d, 2H), 7.4 (d, 2H), 7.1 (d, 1H), 6.9 (d, 1H), 6.7 (d, 2H), 3.7 (t, 2H), 3.5 (m, 4H), 1.7 (m, 4H), 1.5 (m, 4H), 1.3 (t, 3H).

2-[3-(2-(4-(*N*-Ethyl-*N*-(6-hydroxyhexyl)amino)phenyl)-ethenyl)-5,5-dimethylcyclohex-2-ene-1-ylidene]-1,3-propanedinitrile (12). A mixture of 4.7 g (19 mmol) of 4-[*N*-ethyl-*N*-(6-hydroxyhexyl)amino]benzaldehyde, **9**, 3.5 g (19 mmol) of 2-(3,5,5-trimethylcyclohex-2-ene-1-ylidene)-1,3-propanedinitrile, which was prepared according to ref 19, 1.7 mL of acetic acid, 1.7 mL of acetic anhydride, and 3.5 mL of piperidine in DMF (17 mL) was stirred at ambient temperature for 30 min and 12 h at 80 °C. After cooling, the reaction mixture was poured into iced water and extracted with chloroform and then washed with water and dried ($MgSO_4$), and the solvent was removed in vacuo to yield the purple oily substance **12** which was purified by column chromatography (silica gel) using ethyl acetate as eluent. Yield: 3.8 g (48%). NMR: δ_H ($CDCl_3$) 7.4 (d, 2H), 7.0 (d, 1H), 6.8 (d, 1H), 6.7 (s, 1H), 6.6 (d, 2H), 3.7 (t, 2H), 3.5 (q, 2H), 3.4 (t, 2H), 2.6 (s, 2H) 2.4 (s, 2H), 1.5 (m, 4H), 1.3 (m, 4H), 1.2 (t, 3H), 1.1 (s, 6H).

Monomer Synthesis: General Procedure.[20] A mixture of 0.02 mol of one of the above synthesized alcohols (**1**, **4**, **10**, **12**), 4.0 g (0.04 mol) of triethylamine, 20 mg (0.18 mmol) of hydroquinone, and 150 mL of dichloromethane was cooled to 0 °C; 3.1 g (0.03 mol) of methacryloyl chloride in 15 mL of dichloromethane was added dropwise under stirring. The reaction mixture was kept at 0−5 °C for 48 h under stirring and washed with water. The organic layer was dried ($MgSO_4$), and the solvent was removed under reduced pressure. The remaining reaction product was purified by column chromatography (silica gel) using ethyl acetate or dichloromethane as eluent.

6-(9-Carbazoyl)hexyl Methacrylate (2). Yield: 5.4 g (80%). NMR: δ_H ($CDCl_3$) 8.1 (d, 2H), 7.5 (m, 4H), 7.3 (d, 2H), 6.1 (s, 1H), 5.9 (s, 1H), 4.3 (t, 2H), 4.1 (t, 2H), 1.9 (s, 3H), 1.5 (m, 4H), 1.4 (m, 4H).

6-[4-(2-(4-Nitrophenyl)ethenyl)phenyloxy]hexyl Methacrylate (5). Yield: 3.7 g (79%). Mp: 90.4 °C. NMR: δ_H ($CDCl_3$) 8.3 (d, 2H), 7.6 (d, 2H), 7.5 (d, 2H), 7.2 (d, 1H), 7.1 (d, 1H), 7.0 (d, 2H), 6.1 (s, 1H), 5.6 (s, 1H), 4.2 (t, 2H), 4.0 (t, 2H), 1.9 (s, 3H), 1.8 (m, 8H).

6-[*N*-Ethyl-*N*-(4-(2-(4-nitrophenyl)ethenyl)phenyl)amino]hexyl Methacrylate (11). Yield: 3.2 g (73%). Mp: 75.3−78.9 °C. NMR: δ_H ($CDCl_3$) 8.2 (d, 2H), 7.6 (d, 2H), 7.5 (d, 2H), 7.1 (d, 1H), 6.9 (d, 1H), 6.7 (d, 2H), 6.1 (s, 1H), 5.6 (s, 1H), 4.2 (t, 2H), 3.4 (m, 4H), 1.9 (s, 3H), 1.7 (m, 4H), 1.5 (m, 4H), 1.3 (t, 3H).

6-[*N*-Ethyl-*N*-(4-(2-(3-(dicyanomethylidenyl)-5,5-dimethylcyclohex-1-ene)ethenylphenyl)amino]hexyl Methacrylate (13). Yield: 2.8 g, 64%). Mp: 59.4−60.7 °C. NMR: δ_H ($CDCl_3$) 7.4 (d, 2H), 7.0 (d, 1H), 6.8 (d, 1H), 6.7 (s, 1H), 6.6 (d, 2H), 6.1 (s, 1H), 5.6 (s, 1H), 4.1 (t, 2H), 3.5 (q, 2H), 3.4 (t, 2H), 2.6 (s, 2H) 2.4 (s, 2H), 1.9 (s, 3H), 1.5 (m, 4H), 1.3 (m, 4H), 1.2 (t, 3H), 1.1 (s, 6H).

Dodecyl methacrylate (14) was purchased from Aldrich Chemical Co. and purified by column chromatography (silica gel) using chloroform as eluent.

Polymer Synthesis: General Procedure.[20] The polymerizations were carried out in DMF solution under argon atmosphere at 65 °C in the presence of 1 wt % AIBN for 24 h. The resulting polymer solution was cooled and poured into methanol to precipate the polymer. The precipitated polymer was filtered, redissolved and reprecipitated, filtered, and finally dried under reduced pressure.

Photorefractive Sample Preparation. Samples for photorefractive measurements were prepared by dissolving the polymer in chloroform and by adding TNFDM up to 1 wt % concentration. After passage of this solution through a 0.2 μm PTFE membrane filter, the solvent was allowed to evaporate for 3 h at 80 °C. The resulting homogeneous mixture was then molten between two ITO-coated glass slides, and the thickness of the samples was controlled by glass spacers of 125 μm diameter.

Photorefractive Characterization. Two-beam coupling experiments and four-wave mixing experiments were done using a setup similar to the one described in ref 21. All data were reproducible within 5% of the experimental values. The laser was a diode laser operating at a wavelength of 780 nm. The angle between the two writing beams outside the samples was (14 ± 1)°, and the angle between the bisector and the surface normal was (50 ± 2)°. For the two-beam coupling experiments, the two beams were p-polarized, had a power of 2.8 mW each, and were collimated to (250 ± 10) μm diameter

in the sample. The analysis of the data was done using the equation

$$\Gamma d = \cos \alpha_1 \left(\ln \frac{I_1^t(I_2 \neq 0)}{I_1^t(I_2 = 0)} \right) - \cos \alpha_2 \left(\ln \frac{I_2^t(I_1 \neq 0)}{I_2^t(I_1 = 0)} \right) \quad (2)$$

I_1^t and I_2^t are the transmitted intensities of writing beams 1 and 2. Beam 1 is the beam closest to the surface normal, α_1 and α_2 are the angles between the writing beams and the surface normal in the sample, d is the sample thickness, and Γ is the gain coefficient.

Four-wave mixing experiments were performed using s-polarized writing beams and a p-polarized probe beam, counterpropagating to writing beam 1. The power of the writing beams was the same as in the two-beam coupling experiments, and the probe beam, collimated to $(150 \pm 10)\ \mu$m, had a power of $(2 \pm 0.1)\ \mu$W. The internal diffraction efficiencies were calculated using the formula

$$\eta = \frac{I_{\text{diff}}}{I_t} \quad (3)$$

where I_{diff} is the intensity of the light diffracted upon the photorefractive grating and I_t is the total amount of light transmitted through the sample, that is, the sum of the diffracted and transmitted intensities.

Acknowledgment. D.V.S. is a research assistant and E.H. is a research associate of the Fund for Scientific Research-Flanders (Belgium) (FWO). This research was supported by research grants from the FWO (G.0308.96 and S 2/5-AV. E 8), the University of Leuven (GOA/95/01), and the Belgian Government (IUAP P4/11).

References and Notes

(1) Günter, P.; Huignard, J.-P. In *Photorefractive Materials and Their Applications*; Springer-Verlag: Berlin, 1988−1989; Vols. I and II.
(2) Kukhtarev, N. V.; Markov, V. B.; Odulov, S. G.; Soskin, M. S.; Vinetskii, V. L. *Ferroelectrics* **1979**, *22*, 949.
(3) Meerholz, K.; Volodin, B. L.; Sandalphon; Kippelen, B.; Peyghambarian, N. *Nature* **1994**, *371*, 497.
(4) Kippelen, B.; Marder, S. R.; Hendrickx, E.; Maldonado, J. L.; Guillemet, G.; Volodin, B. L.; Steele, D. D.; Enami, Y.; Sandalphon, Yao, Y. J.; Wang, J. F.; Röckel, H.; Erskine, L.; Peyghambarian, N. *Science* **1998**, *279*, 54.
(5) Meerholz, K.; De Nardin, Y.; Bittner, R.; Wortmann, R.; Würthner, F. *Appl. Phys. Lett.* **1998**, *73*, 4.
(6) Hendrickx, E.; Volodin, B. L.; Steele, D. D.; Maldonado, J. L.; Wang, J. F.; Kippelen, B.; Peyghambarian, N. *Appl. Phys. Lett.* **1997**, *71*, 1159.
(7) Meerholz, K.; Bittner, R.; De Nardin, Y.; Bräuchle, C.; Hendrickx, E.; Volodin, B. L.; Kippelen, B.; Peyghambarian, N. *Adv. Mater.* **1997**, *9*, 1043.
(8) Hendrickx, E.; Van Steenwinckel, D.; Persoons, A.; Watanabe, A. *Macromolecules* **1999**, *32*, 2232.
(9) Yu, L.; Chan, W. K.; Peng, Z.; Gharavi, A. *Acc. Chem. Res.* **1996**, *29*, 13.
(10) Kippelen, B.; Meyers, F.; Peyghambarian, N.; Marder, S. R. *J. Am. Chem. Soc.* **1997**, *119*, 4559.
(11) Moerner, W. E.; Silence, S. M.; Hache, F.; Bjorklund, G. C. *J. Opt. Soc. Am. B* **1994**, *11*, 320.
(12) Kogelnik, H. *Bell Syst. Techn. J.* **1969**, *48*, 2909.
(13) Kippelen, B.; Meerholz, K.; Peyghambarian, N. In *Nonlinear Optics of Organic Molecules and Polymers*; Nalwa, H. S., Miyata, S., Eds.; CRC Press: Boca Raton, FL, 1997; p 465.
(14) Cheng, L.-T.; Tam, W.; Stevenson, S. H.; Meredith, G. R.; Rikken, G.; Marder, S. R. *J. Phys. Chem.* **1991**, *95*, 10631.
(15) Huijts, R. A.; Hesselink; G. L. J. *Chem. Phys. Lett.* **1989**, *156*, 209.
(16) Ermer, S.; Lovejoy, S. M.; Leung, D. S.; Warren, H.; Moylan, C. R.; Twieg, R. J. *Chem. Mater.* **1997**, *9*, 1437.
(17) Peng, Z.; Gharavi, A. R.; Yu, L. *J. Am. Chem. Soc.* **1997**, *119*, 4622.
(18) Robello, D. R. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 1.
(19) Lemke, R. *Synthesis* **1974**, 359.
(20) Rondou, P.; Van Beylen, M.; Samyn, C.; s'Heeren, G.; Persoons, A. *Makromol. Chem.* **1992**, *193*, 3045.
(21) Volodin, B. L.; Sandalphon; Meerholz, K.; Kippelen, B.; Kukhtarev, N. V.; Peyghambarian, N. *Opt. Eng.* **1995**, *34*, 2213.

MA992093E