

Synthesis and Electrooptic Properties of a New Chromophore Dispersed or Grafted in a Carbazolyl Methacrylate Matrix

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A copolymer of [11-(*N*-carbazolyl)undecyl methacrylate] and ethyl (*E*)-2-cyano-3[5-(5-(4-methacryloyloxy)piperidino-2-thienylcarbonyl)-2-thienyl]-2-propenoate has been prepared. The photoconductivity and the electrooptic properties of a hot-pressed thin film of this copolymer have been measured and compared with the properties of the dispersion of ethyl (*E*)-2-cyano-3[5-(5-piperidino-2-thienylcarbonyl)-2-thienyl]-2-propenoate within a poly[11-(*N*-carbazolyl)undecyl methacrylate] matrix. The electrooptic coefficient has been measured by both interferometric and polarimetric techniques. The interferometric technique was not appropriated because the strong electric field applied to the electrodes changes the film thickness of these low T_g materials. A value of up to 5 pm/V for the figure of merit $n^3(r_{13} - r_{33})$ has been reported for the dispersed material, which is 10 times higher than the corresponding grafted material, and a linear relationship between the poling intensity and the electrooptic coefficient has been observed for the two materials.

1. Introduction

The growing interest in organic polymeric materials for designing electrooptic devices has led to the emergence of new classes of asymmetric π -conjugated molecules end-capped by an electron-donating group at one end and by an electron-accepting group at the other end. Stilbene-based push-pull-like structures¹ were studied first. Their molecular hyperpolarizability was however limited by a large ground-state aromaticity. The lower aromatic stabilization energy upon charge separation of heteroaromatic rings, such as thiophene, is much more favorable to the nonlinear optical properties.² This type of guest chromophores has been either dispersed within a host polymer matrix or covalently bonded to it. The alignment of the dipolar chromophores by an electric poling field can actually provide these materials with very high nonlinear optical properties.^{3,4}

We have recently studied a new class of thiophene-based chromophores, the conjugated chain of which was spaced by a semiconjugated spacer in order to tune the resonance effect.⁵ Moreover, it was found that push-pull polyenes containing a (di)methylene spacer group breaking efficiently the π -conjugation can induce very

high hyperpolarizabilities.⁶ The charge transfer in these systems was promoted by the application of an external electric field. The very large influence of the electric field, or reaction field in solution, on the molecular hyperpolarizability of a new type of carbonyl-spaced chromophores has been deeply investigated by a joint theoretical and experimental study.⁷

Carbazole containing polymers are well-known for their photoconductive properties.⁸ Poly[*N*-vinylcarbazole] (PVK) has been widely used as a photoconductive matrix and more recently in the development of a photorefractive material, which requires the combination of photoconductivity and electrooptic properties.⁹ The low miscibility of the electrooptic species in the photoconducting matrix is responsible, in some case, for the limitation of the efficiency as well as the time degradation of these materials. Copolymerization of the chromophore with the carbazole unit is a way to solve this problem. Moreover, a comparison of the same chromophore grafted or not in the photoconductive polymer can show the interactions between the matrix and the chromophore.

In this respect, free radical copolymerization of *N*-vinylcarbazole with methacrylates is not a convenient

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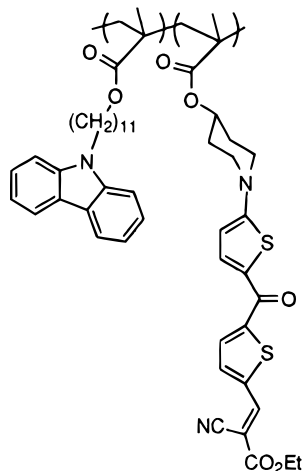


Figure 1. Structure of the carbazolyl chromophore side-chain copolymer.

route because of too different reactivity ratios.¹⁰ Very recently, new carbazole-containing polymers where the carbazolyl unit is attached onto a methacrylic backbone have been prepared by copolymerization and studied for their photoconductive and photorefractive properties.^{11,12}

This paper reports a new polymer that combines photoconductivity and electrooptic activity. Its synthesis relies upon the copolymerization of 11-(*N*-hydroxyundecyl)carbazolyl methacrylate and ethyl (*E*)-2-cyano-3[5-(5-(4-methacroyloxy)piperidino-2-thienylcarbonyl)-2-thienyl]-2-propenoate as the chromophore (see Figure 1). Attention will be paid to the effect of the electric field on the figure of merit $n^3(r_{13} - r_{33})$ as measured by the polarimetric technique applied to in situ poled polymer films. For the sake of comparison, properties of the chromophore dispersed within the poly[11-(*N*-hydroxyundecyl)carbazolyl methacrylate] matrix have also been investigated.

2. Experimental Section

2.1. General Methods. 2-Thiophenecarboxaldehyde (Acros Chimica), 11-bromoundecanol (Fluka), 2-chlorothiophene (Acros Chimica), piperidine (Janssen Chimica), lithium diisopropylamide (LDA, Aldrich, 2 M solution in a heptane-THF-ethylbenzene mixture), methacryloyl chloride (Janssen), sodium hydride (Aldrich, 60% dispersion in a mineral oil), and ethyl cyanoacetate (Fluka) were used as received. Carbazole (Aldrich) was twice recrystallized from methanol before use. Dichloromethane (CH_2Cl_2) and *N,N*-dimethylformamide (DMF) were dried over phosphorus pentoxide and distilled prior to use. Tetrahydrofuran (THF) was dried over sodium/benzophenone before distillation.

¹H NMR spectra were recorded with a Bruker AM 400 spectrometer, and the chemical shifts were referred to tetramethylsilane (TMS). *J* values are expressed in hertz. IR spectra were recorded with a Perkin-Elmer 1600 FT spectrometer. The glass transition temperature was measured by differential scanning calorimetry (DSC) with a Dupont 9000 instrument, under a nitrogen atmosphere, at a 20 °C/min heating rate. Thermogravimetric analysis was carried out under a nitrogen atmosphere with a TA Instruments TGA 51

apparatus, at a heating rate of 20 °C/min. Size exclusion chromatography was performed at 40 °C in chloroform with a WATERS 610 apparatus equipped with a WATERS 410 refractive index detector. Molecular weights were calculated with respect to a polystyrene calibration.

2.2. Synthesis of the Electrooptic Chromophore.

Synthesis of (5-chloro-2-thienyl)(2-thienylcarbonyl)methane (5): A solution of 2-thiophenecarbonyl chloride (12.36 g, 0.084 mol) and 2-chlorothiophene (10 g, 0.084 mol) in 50 mL of dry CH_2Cl_2 was added dropwise to a suspension of anhydrous aluminum trichloride (AlCl_3 , 12.1 g, 0.084 mol) in 200 mL of dry dichloromethane in a 500 mL two-necked flask and under nitrogen atmosphere. The reaction mixture, kept at room temperature in a thermostated water bath, rapidly turned red. After 1 day of stirring, the reaction mixture was poured into a water/methanol mixture (6/4, v/v). CH_2Cl_2 was evaporated until a precipitate appeared. The yellow solid was filtered off and recrystallized from ethanol/water (9/1, v/v), yielding 13.86 g of (5-chloro-2-thienyl)(2-thienylcarbonyl)methane (5) (84%), mp = 69 °C. ¹H NMR (ppm, CDCl_3) δ 7.85 (d, 1H, *J* = 3.6), 7.7 (2d, 2H, *J* = 6.0 and 4.4), 7.19 (t, 1H, *J* = 4.4) and 7.01 (d, 1H, *J* = 3.6). IR (KBr, cm^{-1}) 3099, 1603, 1525, 1422, 1294, 1052, 1003, 865, 789, 714. Elemental analysis ($\text{C}_9\text{H}_5\text{ClOS}_2$): calculated C = 47.26, H = 2.18, S = 28.04; found C = 47.25, H = 2.05, S = 28.27.

Synthesis of (5-piperidiny-2-thienyl)(2-thienylcarbonyl)methane (6a): A suspension of (5-chloro-2-thienyl)(2-thienylcarbonyl)methane (5, 2 g, 0.009 mol) in 6 mL of piperidine was heated at 120 °C overnight in a 50 mL flask. After cooling to room temperature and dilution with 50 mL of CH_2Cl_2 , the reaction mixture was washed with a 0.1 N hydrochloric acid solution and with a saturated sodium bicarbonate solution. The organic phase was dried over magnesium sulfate, and solvent was distilled off under reduced pressure, leaving 2.32 g of a yellow powder (93%), mp = 177 °C. ¹H NMR (ppm, CDCl_3) δ 7.72 (2d, 2H, *J* = 4.4), 7.56 (d, 1H, *J* = 3.60), 7.12 (dd, 1H, *J* = 3.6), 6.06 (d, 1H, *J* = 4.4), 3.36 (t, 4H, *J* = 5.2), and 1.78–1.6 (2m, 6H). IR (KBr, cm^{-1}) 3107, 3078, 2934, 2848, 1577, 1481, 1417, 1319, 1252, 1061, 782, 732. Elemental analysis ($\text{C}_{14}\text{H}_{15}\text{NOS}_2$): calculated C = 60.65, H = 5.41, N = 5.05, S = 23.07; found C = 60.47, H = 5.61, N = 5.15, S = 22.77.

Synthesis of 5-(5-piperidino-2-thienylcarbonyl)-2-thiophenecarbaldehyde (7a): In a 50 mL single-necked flask under nitrogen, a lithium diisopropylamide solution (0.9 mL, 0.0018 mol) was added dropwise to a solution of (5-piperidiny-2-thienyl)(2-thienylcarbonyl) methane (6a, 0.5 g, 0.0018 mol) in 20 mL of dry THF cooled at -40 °C. The solution immediately turned dark red. After 30 min at this temperature, dry DMF (0.5 mL, 0.006 mol) was added, and the reaction mixture was allowed to warm to room temperature. The solution turned slowly dark green. After hydrolysis with a 1 M HCl solution, the aqueous phase was extracted twice with CH_2Cl_2 and the combined organic phases were washed with 0.1 M HCl and finally with a saturated solution of sodium bicarbonate. The solvent was evaporated under reduced pressure, and the recovered red solid was purified by elution through a silica gel chromatography column (eluent: *n*-hexane/ethyl acetate, 1/1, v/v) yielding 0.25 g of 5-(5-piperidino-2-thienylcarbonyl)-2-thiophenecarbaldehyde (7a, 45%), mp = 180 °C. ¹H NMR (ppm, CDCl_3) δ 9.97 (s, 1H), 7.73 (m, 3H), 6.06 (d, 1H, *J* = 4.4), 3.38 (t, 4H, *J* = 5.2), and 1.75–1.60 (2m, 6H). IR (KBr, cm^{-1}) 2922, 2850, 1657, 1569, 1524, 1481, 1435, 1325, 1249, 1208, 1120, 1066, 1047, 1012, 795. Elemental analysis ($\text{C}_{15}\text{H}_{15}\text{NO}_2\text{S}_2$): calculated C = 59.01, H = 4.91, N = 4.59, S = 20.95; found C = 59.06, H = 5.00, N = 4.68, S = 20.42.

Synthesis of ethyl (*E*)-2-cyano-3[5-(5-piperidino-2-thienylcarbonyl)-2-thienyl]-2-propenoate (9a): Ethyl cyanoacetate (0.069 mL, 0.00065 mol) was added to a solution of 5-(5-piperidino-2-thienylcarbonyl)-2-thiophenecarbaldehyde (7a, 0.2 g, 0.00065 mol) in 10 mL of toluene. Three drops of piperidine were then added, and the solution was stirred at 60 °C for 3 h. The reaction mixture was then cooled to room temperature and hydrolyzed with water. The aqueous phase was extracted with CH_2Cl_2 , and the combined organic phases were washed

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with 0.1 M HCl before drying over magnesium sulfate. Solvent was distilled off under reduced pressure and the residue purified by elution through a silica gel column (eluent: *n*-hexane/ethyl acetate, 1/1, v/v) yielding 0.13 g of ethyl (*E*)-2-cyano-3-[5-(5-piperidino-2-thienylcarbonyl)-2-thienyl]-2-propenoate (**9a**, 50%), mp = 177 °C. ¹H NMR (ppm, CDCl₃) δ 8.30 (s, 1H), 7.87 (d, 1H, *J* = 4), 7.73 (2d, 2H, *J* = 4.4), 6.06 (d, 1H, *J* = 4.8), 4.38 (q, 2H, *J* = 7), 3.39 (t, 4H, *J* = 5.2), 1.75–1.60 (m, 6H), and 1.39 (m, 3H). IR (KBr, cm⁻¹) 2925, 2851, 2218, 1725, 1595, 1560, 1484, 1440, 1323, 1263, 1233, 1206, 1123, 793, 759, 727. Elemental analysis (C₂₀H₂₀N₂O₄S₂): calculated C = 59.92, H = 4.99, N = 6.99, S = 15.98; found C = 59.32, H = 5.02, N = 7.04, S = 15.56.

Synthesis of 5-[(4-hydroxy)piperidino-2-thienyl](2-thienylcarbonyl)methane (6b): A suspension of (5-chloro-2-thienyl)-(2-thienylcarbonyl)methane (**5**, 4 g, 0.017 mol) in 5 g of 4-hydroxypiperidine was heated at 160 °C for 2 days in a 50 mL flask. After cooling to room temperature and dilution with 20 mL of DMF, the reaction mixture was washed with a 0.1 N hydrochloric acid solution, extracted two times with 50 mL of CH₂Cl₂, and washed again with a saturated solution of sodium bicarbonate. The collected organic phases were dried over magnesium sulfate, and the solvent was distilled off under reduced pressure. After purification by elution through a silica gel chromatography column (eluent: ethyl acetate), 4.33 g of 5-[(4-hydroxy)piperidino-2-thienyl](2-thienylcarbonyl)methane (**6b**, 87%) was recovered, mp = 145 °C. ¹H NMR (ppm, CDCl₃) δ 7.74 (d, 1H, *J* = 4.4), 7.70 (d, 1H, *J* = 4.0), 7.57 (d, 1H, *J* = 4.4), 7.12 (dd, 1H, *J* = 4.0), 6.08 (d, 1H, *J* = 4.4), 3.97 (s, 1H), 3.65 and 3.21 (m, 4H), and 1.73–1.62 (m, 3H). ¹³C NMR (ppm, CDCl₃) δ 177.7, 167.7, 143.8, 137.3, 131.7, 131.6, 128.1, 127.6, 105.4, 67.0, 48.1, 33.7. IR (KBr, cm⁻¹) 3406, 3095, 2941, 2864, 1558, 1474, 1442, 1414, 1352, 1323, 1229, 1054, 784, 731. Elemental analysis (C₁₄H₁₅NO₂S₂): calculated C = 57.33, H = 5.12, N = 4.78, S = 21.84; found C = 57.34, H = 5.88, N = 5.10, S = 21.81.

Synthesis of 5-[5-(4-hydroxy)piperidino-2-thienylcarbonyl]-2-thiophenecarbaldehyde (7b): In a 500 mL single-necked flask under nitrogen, a lithium diisopropylamide solution (17 mL, 0.034 mol) was added dropwise to a solution of 5-[(4-hydroxypiperidino)-2-thienyl](2-thienylcarbonyl)methane (**6b**, 5 g, 0.017 mol) in 250 mL of dry THF cooled at -40 °C. The solution immediately turned dark red. After 30 min at this temperature, dry DMF (1 mL) was added and the reaction allowed to warm to room temperature. The solution turned slowly dark green. After hydrolysis with a 1 M HCl solution, the aqueous phase was extracted twice with CH₂Cl₂, and the combined organic phases were washed with 0.1 M HCl and once with a saturated solution of sodium bicarbonate. The solvent was evaporated under reduced pressure, and the red solid obtained was purified by elution through a silica gel chromatography column (eluent: ethyl acetate) yielding 2.07 g of 5-[5-(4-hydroxypiperidino)-2-thienylcarbonyl]-2-thiophenecarbaldehyde (**7b**, 38%), mp = 174 °C. ¹H NMR (ppm, CDCl₃) δ 9.98 (s, 1H), 7.72 (m, 3H), 6.09 (d, 1H, *J* = 4.4), 4.00 (m, 1H), 3.67 and 3.25 (m, 4H), 2.00 (m, 3H), 1.73 (m, 2H). IR (neat, cm⁻¹) 3388, 2925, 2850, 1668, 1575, 1479, 1443, 1324, 1120, 1125, 1056, 784, 752, 726. Elemental analysis (C₁₅H₁₅NO₃S₂): calculated C = 56.07, H = 4.67, N = 4.36, S = 19.93; found C = 56.07, H = 4.54, N = 4.67, S = 18.90.

Synthesis of ethyl (*E*)-2-cyano-3-[5-(5-(4-hydroxy)piperidino-2-thienylcarbonyl)-2-thienyl]-2-propenoate (8b): Ethylcyanoacetate (0.64 mL, 0.006 mol) was added to a solution of 5-[5-(4-hydroxypiperidino)-2-thienylcarbonyl]-2-thiophenecarbaldehyde (**7b**, 2 g, 0.0062 mol) in 60 mL of ethanol. Three drops of piperidine were then added, and the solution was stirred at 60 °C for 2 h. The reaction mixture was then cooled to room temperature and hydrolyzed with water. The aqueous phase was extracted with CHCl₃, and the combined organic phases were washed with 0.1 M HCl and finally dried over magnesium sulfate.

Solvent was distilled off under reduced pressure and the residue purified by elution through a silica gel chromatography column (eluent: *n*-hexane/ethyl acetate, 1/1, v/v) yielding 1.42 g of ethyl (*E*)-2-cyano-3-[5-(5-(4-hydroxy)piperidino-2-thienyl-

carbonyl)-2-thienyl]-2-propenoate (**8b**, 54%), mp = 165 °C. ¹H NMR (ppm, CDCl₃) δ 8.30 (s, 1H), 7.86 (d, 1H, *J* = 4.0), 7.73 (2d, 2H, *J* = 4.4), 6.11 (d, 1H, *J* = 4.4), 4.37 (q, 2H, *J* = 7.4), 4.01 (m, 1H), 3.39 (t, 4H, *J* = 5.2), 1.75–1.60 (m, 4H), and 1.39 (m, 3H). IR (KBr, cm⁻¹) 3416, 2925, 2218, 1721, 1592, 1480, 1443, 1324, 1261, 1225, 1128, 1054, 793, 725. Elemental analysis (C₂₀H₂₀N₂O₄S₂): calculated C = 57.69, H = 4.81, N = 6.73, S = 15.38; found C = 57.80, H = 5.01, N = 6.70, S = 15.38.

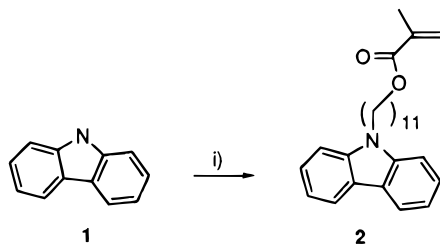
Synthesis of ethyl (*E*)-2-cyano-3-[5-(5-(4-methacryloyloxy)piperidino-2-thienylcarbonyl)-2-thienyl]-2-propenoate (9b): Methacryloyl chloride (0.28 mL, 0.0029 mol) was added to a solution of ethyl (*E*)-2-cyano-3-[5-(5-(4-hydroxy)piperidino-2-thienylcarbonyl)-2-thienyl]-2-propenoate (**8b**, 0.4 g, 0.00096 mol) in 20 mL of dry THF. Triethylamine (0.4 mL, 0.0029 mol) together with 10 mg of (*N,N*-dimethylamino)pyridine (DMAP) was then added dropwise, and the solution was stirred at 50 °C for 2 days. The reaction mixture was cooled to room temperature and hydrolyzed with water. The aqueous phase was extracted with CH₂Cl₂, and the combined organic phases were washed five times with 0.1 N NaOH before drying over magnesium sulfate. Solvent was distilled off under reduced pressure and the residue purified by elution through a silica gel chromatography column (eluent: *n*-hexane/ethyl acetate, 1/1, v/v) yielding 0.2 g of ethyl (*E*)-2-cyano-3-[5-(5-(4-methacryloyloxy)piperidino-2-thienylcarbonyl)-2-thienyl]-2-propenoate (**9b**, 45%), mp = 174 °C. ¹H NMR (ppm, CDCl₃) δ 8.30 (s, 1H), 7.87 (d, 1H, *J* = 4.0), 7.76 (d, 1H, *J* = 4.0), 7.73 (d, 1H, *J* = 4.4), 6.13 (m, 2H), 5.60 (s, 1H), 5.10 (t, 1H, *J* = 3.6), 4.38 (q, 2H, *J* = 7.4), 3.63–3.35 (2m, 4H), 2.12–1.86 (m, 8H), and 1.40 (t, 3H, *J* = 7.3). IR (KBr, cm⁻¹) 2928, 2223, 1716, 1636, 1589, 1553, 1476, 1446, 1329, 1249, 1170, 1122, 1026, 812, 792, 726. Elemental analysis (C₂₄H₂₄N₂O₅S₂): calculated C = 59.40, H = 4.96, N = 5.70, S = 13.20; found C = 58.91, H = 5.35, N = 5.34, S = 13.20.

2.3. Polymerization. Methacrylic monomers were polymerized in dry DMF in the presence of azobisisobutyronitrile (AIBN, 2 wt %) as an initiator. Air in the polymerization medium has been replaced by nitrogen twice before heating and stirring overnight at 65 °C. Reaction was stopped by pouring the polymerization mixture into methanol previously cooled to -78 °C. The isolated polymer was redissolved in THF and precipitated again in cold methanol, filtered, and finally dried under vacuum overnight.

2.4. Sample Preparation. Copolymers (or polymer/8a blends) were dissolved in THF, and the solutions were filtered through a 0.45 μm filter. The solvent was removed under reduced pressure, and the isolated material was dried overnight at room temperature under vacuum (0.1 mmHg). The polymer was then crushed in a fine powder and spread on a clean glass slide, the inner face of which is covered with an ITO electrode strip. It is then heated to 100 °C and covered with a second ITO covered glass slide. The film thickness was controlled by using a 70 μm glass spacer between the glass slides. Homogeneous films of a good optical quality and transparency were accordingly prepared.

3. Results and Discussion

3.1. Chromophore and Polymer Synthesis. 11-(*N*-Carbazolyl)undecyl methacrylate monomer **2** was prepared according to a procedure reported in the literature¹² (Figure 2). An original synthetic pathway for the carbonyl-spaced chromophores **9a** and **9b** was devised as shown in Figure 3. The first step consisted of a Friedel–Crafts acylation of 2-chlorothiophene **3** with 2-thiophenecarbonyl chloride **4**, affording (5-chloro-2-thienyl)(2-thienylcarbonyl)methane (**5**) with an 84% yield. (5-Piperidinyl-2-thienyl)(2-thienylcarbonyl)methane (**6a**) and 5-[(4-hydroxy)piperidino-2-thienyl](2-thienylcarbonyl)methane (**6b**) were easily prepared by nucleophilic substitution of the 2-chloro group by pip-



- i) 1. NaH, THF, 11-bromoundecanol
2. Methacryloylchloride, THF, NEt₃, DMAP

Figure 2. Reaction pathway for the synthesis of the carbazolylmethacrylic monomer **2**.

eridine and 4-hydroxypiperidine, respectively. The 5' position of **6a** and **6b** was formylated by LDA lithiation followed by DMF quenching. Two equivalents of LDA were however required in case of the 4-hydroxy-substituted compound **6b**, the first equivalent reacting with the hydroxyl proton. The introduction of the acceptor group by a Knoevenagel condensation on the aldehyde led to the propenoate derivatives **9a** and **8b** with 50% and 54% yield, respectively. Esterification of the hydroxyl end group by methacryloyl chloride finally led to the methacrylic monomer **9b**, i.e., ethyl (*E*)-2-cyano-3-[5-(5-(4-methacryloyloxy)piperidino-2-thienyl-carbonyl)-2-thienyl]-2-propenoate.

The corresponding homopolymer and a copolymer containing the chromophore **9b** as pendant group (10 wt %) were synthesized at 65 °C by free radical polymerization in the presence of azobisisobutyronitrile (AIBN) as an initiator. The main characteristic features of the homopolymer and the copolymer are listed in Table 1. The copolymer composition has been analyzed by ¹H NMR, by comparison with the ¹H NMR spectrum of the parent homopolymer **P2**. The glass transition temperature (*T_g*) of the (co)polymer was measured by differential scanning calorimetry (Table 1). Dispersion of 10 wt % chromophore **9a** in poly[11-(*N*-carbazolyl)undecyl methacrylate] (sample **P2-disp-9a**) only slightly decreases *T_g* of the homopolymer **P2**, although the covalent grafting of the electrooptic chromophore by copolymerization of 10 wt % monomer **9b** increases the glass transition temperature of the material from -19.0 to -6.0 °C.

The inherent thermal stability of the copolymer **P2-co-9b** and its parent dispersed blend **P2-disp-9a** was analyzed by thermogravimetric analysis. The copolymer, which starts to degrade around 300 °C, is more stable than the parent dispersed material, as shown in Figure 4. The experimental decomposition temperatures are substantially higher than the values commonly reported for thiophene-containing electrooptic materials,¹³ i.e., in the 200–250 °C range.

To measure the absorption spectra of both polymers **P2-co-9b** and **P2-disp-9a**, we made a thin film by the spin-coating technique. Transmission has been recorded by an OL Series 750 spectrometer from Optronic Laboratories Inc. The measurement of the samples thickness by a Wyko RST Plus optical profiler has allowed us to calculate the absorption coefficients presented at Figure 5. Both polymers present the same

absorption shape; however, the **P2-disp-9a** has higher levels than **P2-co-9b**. This can be explained by some diffusion of the spin-coated **P2-disp-9a** film.

The photoconduction of the two polymeric materials has been analyzed by illuminating 1 cm² of 70 μm thick films deposited on an ITO electrode with a 514 nm argon laser beam. The second electrode is constituted by a semitransparent aluminum strip deposited under vacuum. A 500 V potential is applied to the electrodes by a stabilized Fluke 415B high-voltage power supply that corresponds to an electric field of 7.1 × 10⁴ V/cm, the dark current has been measured by a solid-state electrometer Keithley 610CR, it is 5 × 10⁻⁹ A for the copolymer **P2-co-9b** and as high as 10⁻⁵ A in the case of the dispersed material **P2-disp-9a**. This significant difference in the electrical behavior of the two materials may be attributed to the lower *T_g* of the **P2-disp-9a** dispersion, which leads to a larger mobility of the chromophore and conducting impurities. The photocurrent is expressed as the difference between the dark current and the current passing through the sample under illumination (incident power of 25 mW/cm²). For the copolymer **P2-co-9b** it has been measured to be *I_{ph}* = 3 × 10⁻⁹ A, whereas no photocurrent was detected for the dispersed material **P2-disp-9a**, in a possible relation to the exceedingly high initial dark current. The photoconductivity (*σ*) and the photosensitivity (*S*) of the **P2-co-9b** sample has been calculated using the experimentally measured photocurrent (*I_{ph}*) and the eqs 1 and 2, respectively.¹¹ Here *L* is the sample thickness, *A* is the illumination area, *V* is the applied voltage and *I₀* the illumination laser power.

$$\sigma = L/AV/I_{\text{ph}} \quad (1)$$

$$S = \sigma/I_0 \quad (2)$$

A maximum value of photoconductivity $\sigma = 4.2 \times 10^{-14} (\Omega \text{ cm})^{-1}$ and a photosensitivity $S = 1.7 \times 10^{-12} (\Omega \text{ cm})^{-1}/(\text{W}/\text{cm}^2)$ are characteristic of the copolymer, which corresponds to the photosensitivity reported by Tamura et al. for a poly[methacrylate] substituted by a pendant tricyanovinylcarbazole group through an alkylene spacer.¹⁴

Since the value of the photocurrent do not exceed the dark current, both polymers could not exhibit photorefractivity as they are. However, it should be possible to enhance the photocurrent by adding a sensitizer, e.g., C60.^{15,16}

3.2. Electrooptic Measurement. 100 μm thick films have been prepared as aforementioned, coated on an ITO electrode and used for the measurement of the electrooptic properties. These prepared samples are centrosymmetric due to the randomness of the chromophore orientation and do not display any second-order nonlinear or electrooptic effect. Therefore, a continuous electric field of controlled intensity has been accordingly applied in order to align the chromophores and break down the centrosymmetry of the system.

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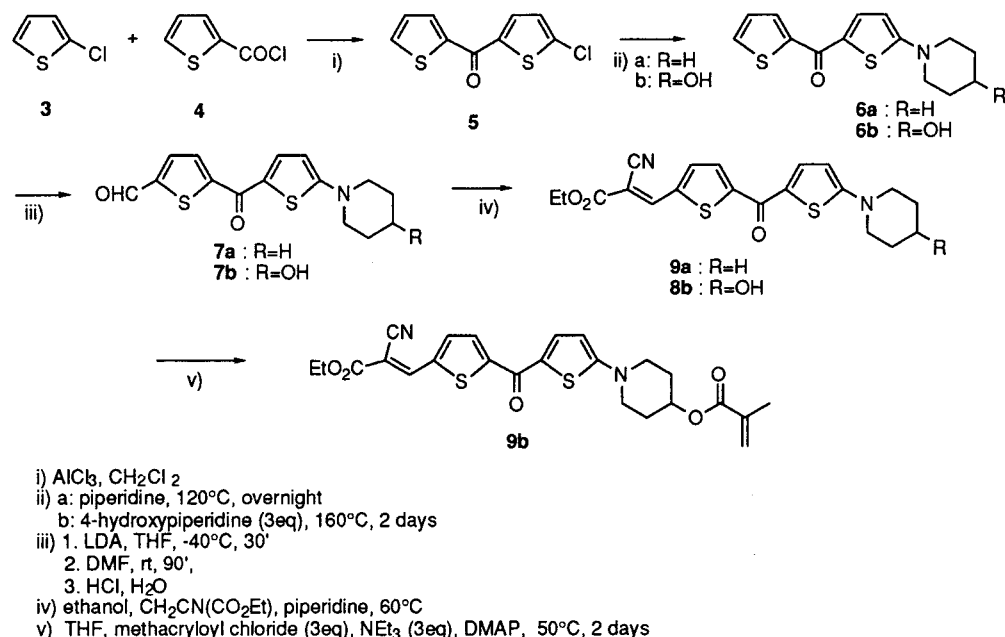


Figure 3. Reaction pathway for the synthesis of the electrooptic chromophores **9a** and **9b**.

Table 1. Homo- and Copolymer Molecular Characterization

polymer	% conversion	M_n^a	M_w/M_n	wt % NLO ^b	T_g ($^\circ\text{C}$) ^c
P2	85	16 500	1.5		-19.0
P2-disp-9a				10	-20.5
P2-co-9b	85	18 000	1.7	10	-6.0

^a SEC analysis in CHCl_3 (calibration with polystyrene standards). ^b ^1H NMR analysis (NLO: **9a** or **9b**). ^c DSC (heating rate = $20^\circ\text{C}/\text{min}$).

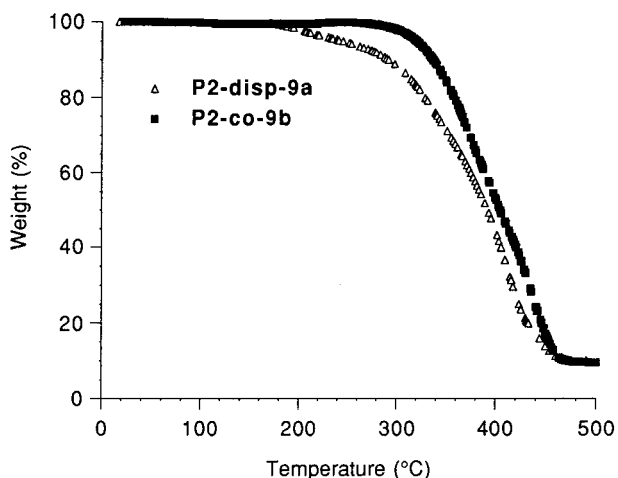


Figure 4. Thermogravimetric analysis trace of the copolymer **P2-co-9b** and the dispersed material **P2-disp-9a** (see Figure 1). Heating rate = $20^\circ\text{C}/\text{min}$.

Since the glass transition temperature of the two polymeric materials is well below the room temperature, the molecular alignment becomes rapidly random because of the thermal relaxation at this temperature and the electrooptic coefficient quickly vanishes. The poling electric field is therefore maintained all along the experiments ("in situ" poling).

The symmetry of the system under poling becomes C_{8v} , and the index modulation is given by the eq 3, where z is the direction of the applied electric field, n is the refractive index of the sample, r_{ij} is the electrooptic

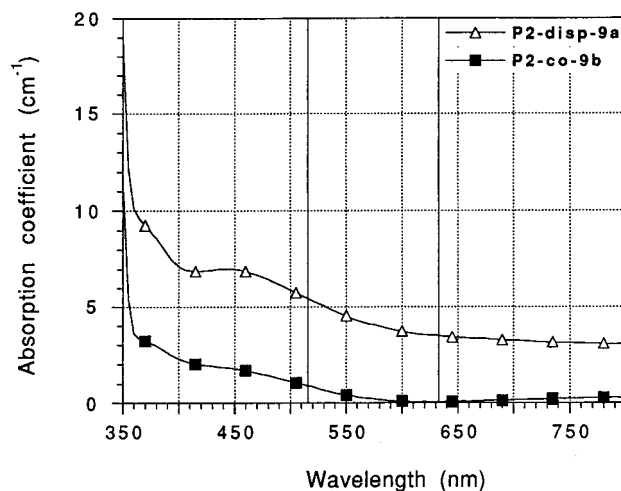


Figure 5. Absorption spectra of both polymers **P2-disp-9a** and **P2-co-9b**. The vertical lines indicate the wavelength used in our experiments (633 and 514 nm).

coefficient, and E_z is the applied external poling electric field.¹⁷

$$\Delta n_x = -\frac{1}{2}n^3 r_{13} E_z$$

$$\Delta n_y = -\frac{1}{2}n^3 r_{13} E_z \quad (3)$$

$$\Delta n_z = -\frac{1}{2}n^3 r_{33} E_z$$

The static linear electrooptic coefficient (Pockels coefficient) has been measured by two different techniques. The first method is based on interferometry^{18,19} and the second one on polarimetry.^{20,21}

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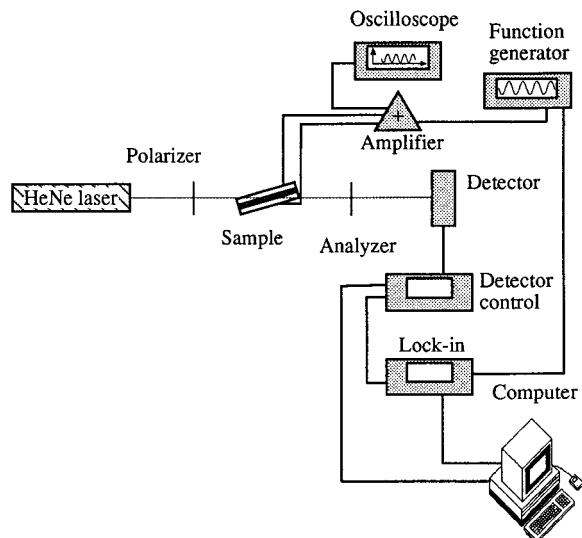


Figure 6. Polarimetric setup. The sample is turned at 70° with respect to the beam propagation; the polarizer is adjusted at 45° according to the incidence plan. The analyzer is turned at 90° according to the polarizer.

In both techniques, a sinusoidal voltage of frequency Ω is superimposed on the poling field applied to the sample. Like this, the refractive index is modulated by the electrooptic effect, and a lock-in detection system is used to extract the useful signal. To avoid the contribution from induced birefringence resulting from the orientation of the chromophores in the sinusoidal field, the frequency of this latter has been selected to 1 kHz and its amplitude has been set to $35 V_{\text{rms}}$, smaller than the poling voltage, which is at least 100 V.

The polymer sample is inserted in one arm of a Michelson interferometer used in the interferometric technique. Variation of the film refractive index in the interferometric arm led to a variation of the beam phase, which can be detected by a variation in the output intensity after recombination of the two beams. We have used a Michelson interferometer rather than a Mach-Zender one to benefit from the double pass of the beam in the sample. This method seems inappropriate to low T_g polymeric materials, since application of the poling electrical field through the electrodes is at the origin of a change in the film thickness. This deleterious effect has been confirmed by using the first ITO electrode as the interferometer mirror. The modulation recorded by the lock-in amplifier is of the same order of magnitude as that observed when the laser beam crosses the sample (10 pm/V). The values measured by this interferometric technique therefore did not correspond to the inherent Pockels effect.

The polarimetric technique has then been used since it allows the previous problem of electrostriction to be avoided. The experimental setup is shown in Figure 6. The laser beam passes through the sample localized between two crossed polarizers, under a high incidence angle. The polarization of the incident beam is fixed at 45° with respect to the incident plane. In this configuration, the polarization direction bisected the normal mode of propagation through the sample, and the electrooptic effect results in polarization ellipticity.

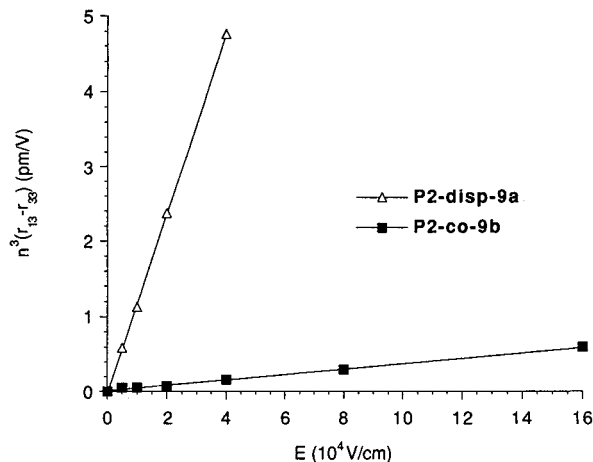


Figure 7. Electric field dependence of the electrooptic coefficient measured by the polarimetric technique.

The measurement of the light intensity that passes through the crossed analyzer allows us to calculate the electrooptic coefficient. Since the electrooptic index modulation $n^3(r_{13} - r_{33})$ is small compared to the refractive index, it can be calculated by eq 4, where

$$n^3(r_{13} - r_{33}) = \frac{2\lambda}{\pi V_{(\Omega)}^{\text{rms}}} \frac{\cos(\alpha)}{\sin^2(\alpha)} \arcsin \sqrt{\frac{I_{(\Omega)}^{\text{rms}}}{I_0}} \quad (4)$$

$I_{(\Omega)}^{\text{rms}}$ is the rms transmitted intensity modulated at the Ω frequency, I_0 is the incident intensity, and α is the refractive angle inside the sample.^{22,23} The refractive index of the polymers has not been measured but is estimated to be around 1.6 according to the usual values reported for this kind of material.¹⁴

Figure 7 shows the static electric field dependence of the electrooptic coefficient $n^3(r_{13} - r_{33})$ as measured by the polarimetric technique at the 632 nm wavelength. The linear relationship between the electrooptic coefficient and the poling field has been first reported by Prasad¹ and later on by Zhao and co-workers.¹¹ It is in line with better alignment of the chromophores and thus a higher macroscopic electrooptic response when the poling electric field is increased. It is also clear from Figure 7 that the chemical anchoring of the chromophore has a depressive effect on the electrooptic properties of the material. This is a consequence of the lower mobility of the chromophore in the copolymer **P2-co-9b** in connection with a higher T_g as well as matrix interaction with the chromophores. Higher values of the $n^3(r_{13} - r_{33})$ figure of merit could however be reached if higher voltages could be applied to thick samples without facing the problem of electrical breakdown.

In summary, new low T_g electrooptic polymers have been synthesized and characterized in terms of optical and nonlinear optical properties. The photoconductivity of the side-chain copolymer has been measured, although the value for the parent dispersed material was not within the reach of measurement, because of a very low T_g . The figure of merit $n^3(r_{13} - r_{33})$, measured by the polarimetric technique, linearly depends on the

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poling intensity and is much higher for the dispersed than for the grafted material, which is thought to reflect the higher mobility of the second-order chromophore in the physically dispersed chromophore/polymer system.

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