1406 *Chem. Mater.* **1999,** *11,* 1406−1408

Side-Chain Nonlinear Optical Polymers Containing a Styrylfuran-Based Chromophore with Large Electro-optic Properties

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Received March 4, 1999

Organic nonlinear optical (NLO) materials have been the subject of intense research because of their potential applications in the electro-optic modulation of optical signals, telecommunication, and data storage.[1] Major emphasis has been focused on developing NLO polymers that possess large nonlinearity, high thermal stability, and good processability.[2,3] Very recently, we reported that 2-(*p*-diethylaminostyryl)furan derivatives have large first hyperpolarizabilities.[4] For a given donor−acceptor pair, the $\beta(0)$ value was larger for the furan compound than for the thiophene analogue. An examination of the physical properties revealed that 5-[5′-(*p*-diethylaminostyryl)furfurylidene]-*N*,*N*′-diethylthiobarbituric acid ($\beta(0) = 75 \times 10^{-30}$ esu) is a promising NLO chromophore.

In this work, we have synthesized novel methyl methacrylate (MMA) and maleimide copolymers **P1** and **P2** that contain 5-[5′-(*p*-diethylaminostyryl)furfurylidene]-*N*,*N*′-diethylthiobarbituric acid in the side chain. The synthetic routes for the copolymers **P1** and **P2** are shown in Scheme 1. 5-[*p*-(*N*-hydroxyethyl-*N*-methylamino)styryl]furan-2-carboxaldehyde (**I**) was synthesized by a Wittig reaction of (2-furylmethyl)triphenylphosphonium bromide with *p*-(*N*-hydroxyethyl-*N*-methylamino)-benzaldehyde followed by a Vilsmeier formylation as reported previously.[4] Reactions of **I** with methacryloyl chloride and 3-isopropenyl-α,α-dimethylbenzylisocyanate afforded the corresponding furaldehydes **IIa** and **IIb** in high yields.[5,6] Condensation reactions of **IIa** and **IIb** with *N*,*N*′-diethylthiobarbituric acid in DMF proceeded quantitatively to produce monomers **IIIa** and **IIIb**.[7] Copolymers **P1** and **P2** were prepared from **IIIa** and **IIIb**, respectively, under typical free-radical polymerization reaction conditions.[5,8]

Copolymers **P1** and **P2** were soluble in polar solvents such as tetrahydrofuran (THF), *N*,*N*-dimethylformamide (DMF), cyclohexanone, and 1,1,2,2-tetrachloroethane. **P1** had a weight-average molecular weight M_w = 10 000 with a polydispersity index of 1.38, while copolymer **P2** had a slightly higher M_w = 13 000 with

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(6) Compounds **IIa** and **IIb** were synthesized by the following procedure: **Methacrylate monomer IIa**: Methacryloyl chloride (0.93 g, 8.92 mmol) was added to a stirred solution of 5-[*p*-(*N*-hydroxyethyl-*N*-methylamino)styryl]-2-furaldehyde (**I**) (2.20 g, 8.11 mmol) in anhydrous THF (30 mL) under nitrogen. To this solution, Et_3N (0.92 g, 8.92 mmol) in 10 mL of THF was added dropwise in a 10-min period. The mixture was stirred overnight (18 h) at room temperature. The solution was evaporated to produce an oil. The crude product was taken up in 100 mL of ethyl acetate and the organic layer was washed several times with saturated aqueous $NaHSO_4$. The solvent was evaporated and the product was purified by column chromatography with ethyl acetate/hexane (1/6) as the eluent to obtain a bright-orange solid. Yield 2.25 g (81.7%); mp 85~86 °C; IR (KBr, cm^{-1}) 1707, 1663, 1603, 1549; NMR (200 MHz, DMSO-d_6) δ 9.53 (s, 1H), 7.40 (d, 2H, $J = 8.6$), 7.33 (d, 1H, $J = 16.2$), 7.24 (d, 1H, $J = 3.5$), 6.73 (d, 2H, $J = 8.6$), 6.72 (d, 1H, $J = 16.2$), 6.43 (d, 1H, $J = 3.5$), 6.06 (s, 1H), 5.56 (s, 1H), 4.33 (t, 2H, $J = 5.8$), 3.70 (t, 2H, $J = 5.8$), 3.05 (s, 3H), 1.90 (s, 3H). Anal. Calcd for $C_{20}H_{21}NO_4$: C, 70.8; H, 6.20; N, 4.1. Found: C, 70.8; H, 6.27; N, 4.01. [Caution: methacryloyl chloride is a highly toxic and flammable liquid and must be used in a well-ventilated fume hood with special precautions.] **(3-Isopropenylphenyl-1-methylethyl)carbamate monomer IIb**: A trace of dibutyltin dilaurate (DBTDL, 0.15 mol %) was added to a solution of 5-[*p*-(*N*-hydroxyethyl-*N*-methylamino)styryl]-2-furaldehyde (**I**) (3.20 g, 11.8 mmol) in 30 mL of dry DMF under nitrogen. To this mixture, 3-isopropenyl-α,α-dimethylbenzylisocyanate (*m*-TMI, 2.61 g, 13.0 mmol) in 15 mL of DMF was added dropwise in a 15-min period. The mixture was stirred for 8 h at room temperature. The product mixture was poured into cold water (~1 L). The orange solid that precipitated was filtered and dissolved in a small amount of THF. This solution was poured into hexane to obtain shiny orange crystals. Yield 4.20 g (75.3%); mp 93~96 °C; IR (KBr, cm^{-1}) 1731, 1655, 1603, 1523; NMR (200 MHz, $CDCl_3$) δ 9.52 (s, 1H), 7.46 (s, 1H), 7.39 (d, 2H, $J = 8.6$), 7.33 (d, 1H, $J = 16.3$), 7.25~7.29 (m, 3H), 7.24 (d, 1H, $J = 3.6$), 6.71 (d, 1H, $J = 16.3$), 6.70 (d, 2H, $J = 8.6$), 6.43 (d, 1H, $J = 3.6$), 5.35 (s, 1H), 5.13 (s, 1H), 5.08 (s, 1H), 4.18 (br t, 2H), 3.58 (br t, 2H), 3.00 (s, 3H), 2.15 (s, 3H), 1.64 (s, 6H). Anal. Calcd for $C_{29}H_{32}N_2O_4$: C, 73.7; H, 6.8; N, 5.9. Found: C, 73.7; H, 6.87; N, 5.88. [Caution: DBTDL and *m*-TMI must be used in a well-ventilated fume hood with special precautions because the former is corrosive and toxic and the latter a toxic lachrymator.]

(7) The NLO monomers **IIIa** and **IIIb** were prepared by dissolving **IIa** or **IIb** (4.23 mmol) in 25 mL of DMF with *N*,*N*′-diethylthiobarbituric acid (0.84 g, 4.32 mmol) and stirring for 2 h at room temperature. The products were isolated by the usual workup procedure and purified by crystallization from ethanol. **IIIa;** Yield 2.12 g (96.2%); mp 151 °C (by DSC); IR (KBr, cm^{-1}) 1717, 1688, 1659, 1596; NMR (200 MHz, $CDCl_3$) δ 8.85 (d, 1H, $J = 4.0$), 8.36 (s, 1H), 7.43 (d, 2H, $J = 8.6$), 7.37 (d, 1H, $J = 16.2$), 6.74 (d, 1H, $J = 16.2$), 6.73(d, 2H, $J = 8.6$), 6.67 (d, 1H, $J = 4.0$), 6.06 (s, 1H), 5.56 (s, 1H), 4.57 (q, 4H, $J = 6.9$), 4.34 (t, 2H, $J = 5.7$), 3.71 (t, 2H, $J = 5.7$), 3.07 (s, 3H), 1.90 (s, 3H), 1.31 (t, 6H, $J = 6.9$). Anal. Calcd for $C_{28}H_{31}N_3O_5S$: C, 64.5; H, 6.0; N, 8.1. Found: C, 64.6; H, 6.04; N, 8.12. **IIIb**: Yield 2.65 g (95.5%); mp 170 °C (by DSC); IR (KBr, cm^{-1}) 1697, 1653, 1597; NMR (200 MHz, $CDCl_3$) δ 8.86 (d, 1H, $J = 4.2$), 8.37 (s, 1H), 7.47 (s, 1H), 7.42 (d, 2H, $J = 8.6$), 7.38 (d, 1H, $J = 16.2$), 7.27−7.33 (m, 3H), 6.73 (d, 1H, $J = 16.2$), 6.71 (d, 2H, $J = 8.6$), 6.68 (d, 1H, $J = 4.2$), 5.34 (s, 1H), 5.12 (s, 1H), 5.10 (s, 1H), 4.58 (q, 2H, $J = 6.9$), 4.19 (br t, 2H), 3.61(br t, 2H), 3.02 (s, 3H), 2.15 (s, 3H), 1.64 (s, 6H), 1.32 (t, 6H, $J = 6.9$).

(8) Freshly distilled methyl methacrylate (192 mg, 1.92 mmol) and 1-methyl-2-pyrrolidinone (NMP) (10.0 mL) were introduced into a vacuum ampule along with NLO monomer **IIIa** (1.00 g, 1.92 mmol) and 2, 2′-azobisisobutyronitrile (AIBN) (31.0 mg, 0.192 mmol). The solution was degassed repeatedly using the freeze−vacuum−thaw technique and then sealed. The ampule was heated for 72 h at 65 °C. Copolymer **P1** was dissolved in THF and purified by precipitation from ether followed by vacuum-drying at 100 °C for 24 h. Yield 0.88 g (73.8%). Copolymer **P2** was synthesized using the same procedure except that *N*-phenylmaleimide (0.63 g, 3.67 mmol)[9] was added as a comonomer. Yield 1.70 g (56.0%).

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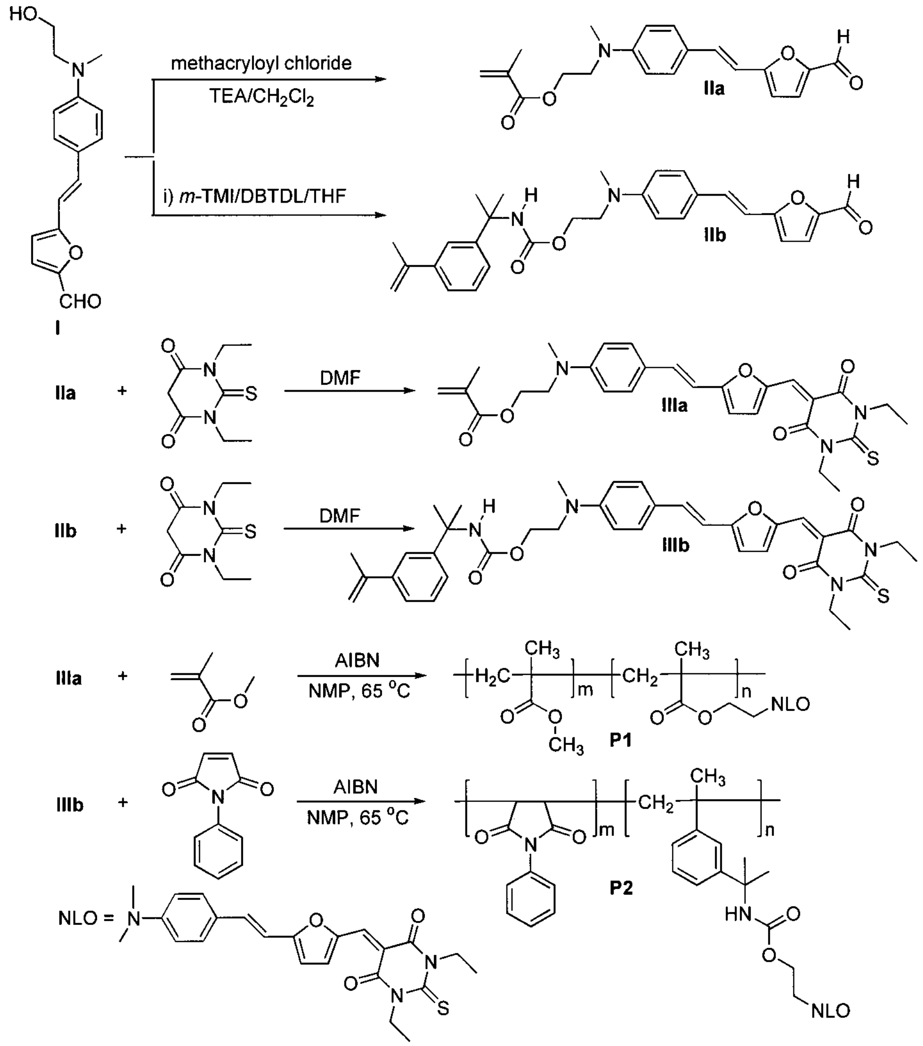
Scheme 1



a polydispersity index of 1.71.[10] The low molecular weight may be due to an undesirable radical trap effect by the NLO chromophore.[11] The UV−vis spectra of the copolymers as thin films exhibited strong absorption bands at λ_{max} = 568 and 594 nm for **P1** and **P2**, respectively. These bands are significantly blue-shifted from that observed in dimethylsulfoxide (DMSO) (λ_{max} = 630 nm), presumably because of the less polar environment of the polymer matrix compared to DMSO.[4] The glass-transition temperatures (T_g) measured by differential scanning calorimetry (DSC) were 150 and 160 °C for **P1** and **P2**, respectively.

An optical-quality thin film (1∼1.5 μm) was prepared by spin coating the filtered polymer solution in 1,1,2,2-tetrachloroethane (∼10 wt %) onto a glass substrate precoated with indium tin oxide (ITO). The film was vacuum-dried at 100 °C overnight and the upper gold electrode was vapor-deposited onto the polymer film. Dipole alignment in the NLO side-chain copolymer was achieved by contact poling at T_g. The electro-optic coefficient r_{33} was measured by the reflection technique reported by Teng.[12]

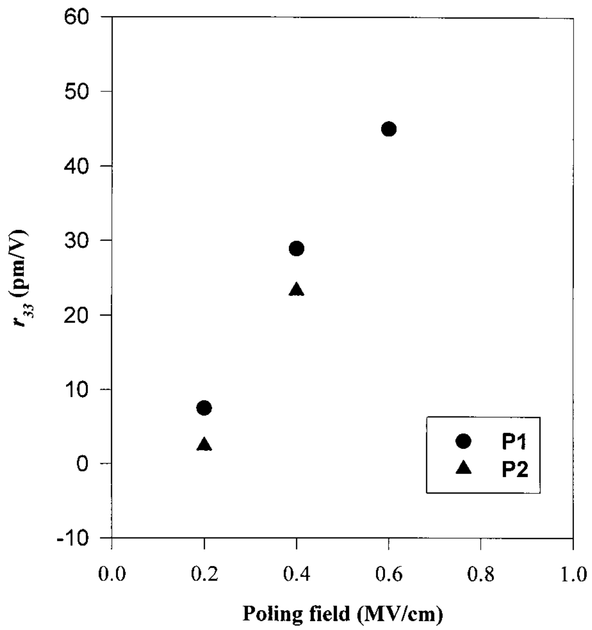


Figure 1. Poling field dependence of r_{33} for copolymers **P1** and **P2**.

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[10] The molecular weight and polydispersity (relative to polystyrene standard) were determined by a Waters 515 GPC using Styragel HR 1, 2, and 4 columns at room temperature and THT as the eluent.

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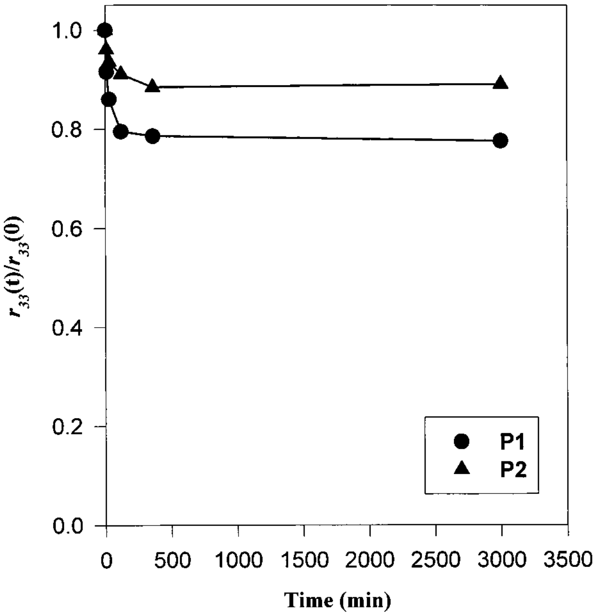

Figure 2. Decay of r_{33} values in the electrode-poled copolymer films upon heating at 80 °C.

Figure 1 shows that the r_{33} value increases linearly with the applied electric field. Copolymer **P1** exhibited preliminary r_{33} values of 2.4, 28.9, and 45.1 pm/V at 1.3 μm with poling fields of 0.2, 0.4, and 0.6 MV/cm, respectively. Copolymer **P2** gave r_{33} values of 2.4 and 23.3 pm/V at 1.3 μm with poling fields of 0.2 and 0.4 MV/cm, respectively. The r_{33} values of copolymers **P1** and **P2** retained 80% and 90% of the original values, respectively, after heating at 80 °C for 50 h (Figure 2). To our knowledge, the $r_{33} = 45$ pm/V for copolymer **P1** is the largest value observed under comparable conditions.

In conclusion, we have synthesized side-chain second-order NLO copolymers containing a styrylfuran derivative as the chromophore. These copolymers exhibit an electro-optic coefficient $r_{33} = 23{\sim}45$ pm/V at 1.3 μm with poling fields of 0.4~0.6 MV/cm and have good thermal stability. This result demonstrates the utility of furan-containing stilbene derivatives as promising NLO chromophores with enhanced NLO properties. We are currently synthesizing higher molecular weight NLO polymers containing the same chromophore with the objective of improving the physical properties.

Acknowledgment. This research was supported by the Korean Council for University Education (1997).

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