Synthesis of Azobenzene-Containing Polythiophenes and Photoinduced Anisotropy

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ABSTRACT: Three new polythiophenes containing an azobenzene moiety in the side-chain were synthesized and characterized. Two of them, which are slightly soluble in tetrahydrofuran to allow the preparation of thin films from solution casting, were used to investigate the photoinduced anisotropy arising from the photoisomerization of azobenzene in this type of polymer. The results show that, unlike other amorphous azobenzene polymers, only an extremely small anisotropy can be induced on excitation with an Ar^+ laser at 488 nm in these azobenzene-containing polythiophenes, and that this photoinduced anisotropy is observable only by heating the polymer to some temperatures below glass transition temperature. It is suggested that the inability for azobenzene polythiophenes to display a significant photoinduced anisotropy may be caused by some structural constraints and/or a severe interference from conjugated thiophene chains that absorb strongly in the visible region. © 2004 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 42: 3445–3455, 2004

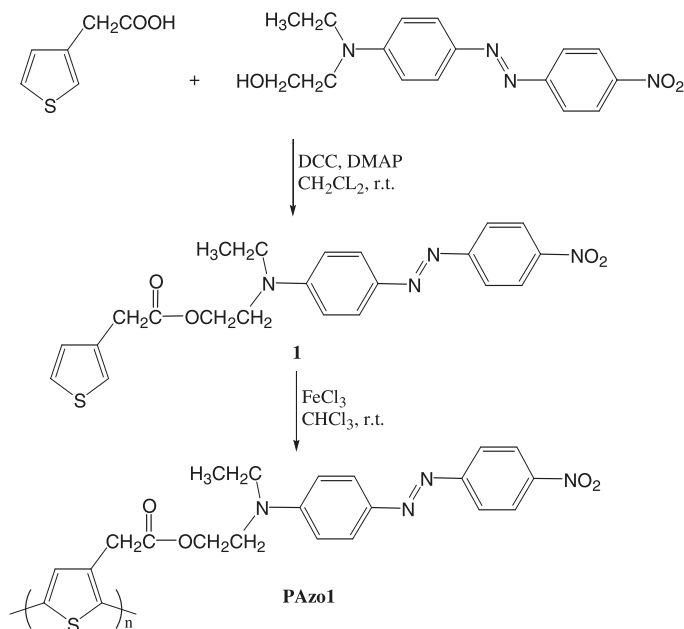**Keywords:** azo polymers; polythiophene; photoinduced anisotrophy

INTRODUCTION

Over the past decade or so, the reversible photoisomerization of the azobenzene chromophore, between stretched trans and bent cis isomers, has been extensively used in the design and exploitation of various types of functional polymers.[1–6] These include amorphous polymers, side-chain liquid crystalline polymers, block copolymers,[7,8] thermoplastic elastomers,[9,10] dendrimers,[11] and polymer-stabilized liquid crystals.[12,13] The great interest on azobenzene polymers is driven by their potential utility for optical and photonic applications. There has been relatively less attention given to π-conjugated polymers carrying an azobenzene moiety in their structures.[14–18] In the

few reports on polythiophenes with azobenzene in the side-chain, the authors studied the influence of the photoisomerization of azobenzene on the conductivity,[15,16] on the conformation of the conjugated chain backbone,[17] and on the thermochromic properties of the polymers.[18] Quite surprisingly, to the best of our knowledge, no investigation has been reported on the photoinduced anisotropy (birefringence) in azobenzene-containing polythiophenes, which is a prominent feature of azobenzene polymers.

As part of our research efforts on azobenzene polymers,[8–10,12,13] we have conducted an investigation on azobenzene polythiophenes. The purpose of the study was to look at the photoinduced anisotropy in this type of polymer as well as the possibility of recording surface relief gratings (SRGs) using an interference pattern produced by two coherent laser beams.[2,3] Optical recording of SRGs was first discovered for amorphous azobenzene polymers[19,20] as a result of mass transport

Scheme 1. Synthetic route to poly[2-[ethyl-[4-(4-nitro-phenylazo)-phenyl]-amino]-ethane (3-thienyl)ethanoate] (PAzo1).

on the surface of the film, and has been the subject of numerous studies.[2,3] Our interest in azobenzene polythiophenes came from the idea that if SRGs could be effectively formed, this may provide the basis for the development of an all-optical micropatterning method for π-conjugated polymers, which is of interest.[21] In this article, we report on the synthesis of three new polythiophenes bearing an azobenzene moiety in the side-chain and the surprising finding that the photoinduced birefringence for azobenzene polythiophenes was extremely small and, consequently, no SRG was observed. Analyses of the results suggest that the difficulty in inducing significant anisotropy through Ar$^+$ laser irradiation may represent a general feature of azobenzene polythiophenes.

EXPERIMENTAL

Materials

Disperse Red 1 (95%), 1,3-dicyclohexylcarbodiimide (DCC, 99%), 3-thiopheneacetic acid (98%), 4-(dimethylamino)pyridine (DMAP, 99%), 4-aminobenzonitrile (98%), 2-(3-thienyl)ethanol (99%), acetonitrile (anhydrous, 99.8%), triphenylphosphine dibromide (96%), 6-chloro-1-hexanol (96%), calcium hydride (powder, 90–95%), sodium (cube,
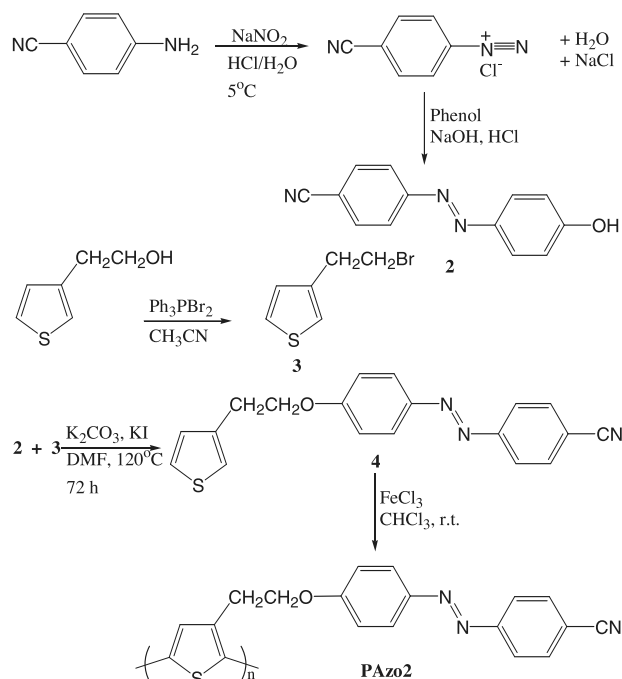
in mineral oil, 99.95%), and benzophenone (99%) were used as received from Aldrich. Ferric chloride (FeCl$_3$, anhydrous; Fisher), hydrochloric acid (HCl, 36–38%; EMD), sodium nitrite (NaNO$_2$, 99.7%; Fisher), sodium hydroxide (NaOH, 97%; EM Science), potassium carbonate (K$_2$CO$_3$, 99%; EM Science), and potassium iodide (KI; BDH) were used as received. Methylene chloride (CH$_2$Cl$_2$) was distilled with calcium hydride and tetrahydrofuran (THF) with sodium and benzophenone.

Synthesis of Azobenzene Polythiophenes

Three azobenzene-containing polythiophenes were synthesized in this study, and denoted hereafter as PAzo1, PAzo2, and PAzo3. Their chemical structures and synthetic routes are shown in Schemes 1–3, respectively. Because they are more or less different in chemical structure from the azobenzene polythiophenes already reported in the literature,[15–18] the synthetic details are reported below.

Synthesis of Poly[2-[ethyl-[4-(4-nitro-phenylazo)-phenyl]-amino]-ethane (3-Thienyl)ethanoate] (PAzo1)

2-[Ethyl-[4-(4-nitro-phenylazo)-phenyl]-amino]-ethane (3-Thienyl)ethanoate (1). Under an nitrogen atmosphere, *N,N'*(DCC) (3.58 g, 17.4 mmol)
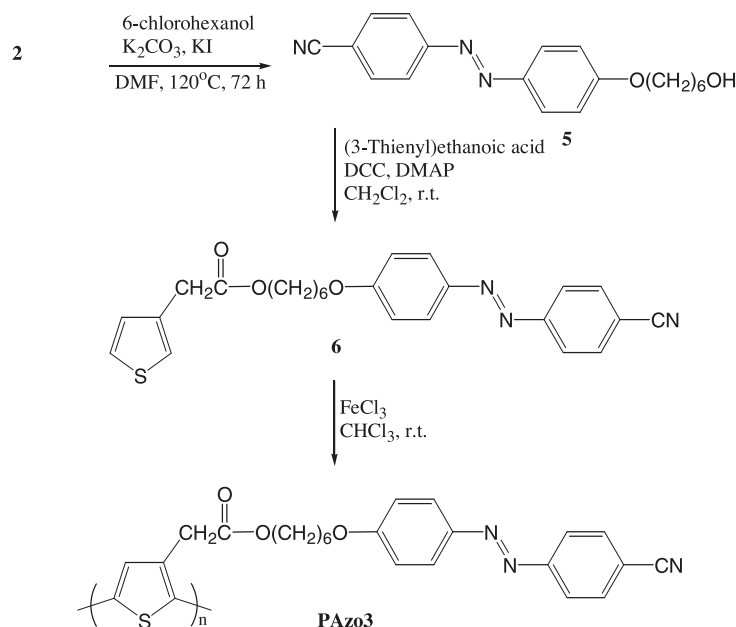
Scheme 2. Synthetic route to poly[4-[4-(2-thiophen-3-yl-ethoxy)-phenylazo]-benzonitrile] (PAzo2).

room temperature, and the reaction was monitored by thin-layer chromatography. The dicyclohexylurea was eliminated by filtration, and the solvent in the remaining solution was removed under reduced pressure. Purification by column chromatography on silica gel (eluent, $CHCl_3$) gave 2.23 g of (**1**) as a red solid (yield: 84%). mp: 120 °C. MS (m/z): 438 (M^+). ^1H NMR ($CDCl_3$, 300 MHz, ppm): 1.21 (t, 3H, J = 7.4 Hz, N—CH_2—**CH$_3$**), 3.45 (q, 2H, J = 7.6 Hz, N—**CH$_2$**—CH_3), 3.63 (t, 2H, J = 7.6 Hz, COO—CH_2—**CH$_2$**—N), 3.71 (s, 2H, Th—**CH$_2$**—COO—), 4.32 (t, 2H, J = 7.5 Hz, CH_2—COO—**CH$_2$**—CH_2), 6.78 (d, 2H, J = 7.2 Hz, aromatic H *ortho* to amine), 7.00 (d, 1H, J = 5.4 Hz, Th-4-H), 7.12 (s, 1H, Th-2-H), 7.29 (d, 1H, J = 3.2 Hz, Th-5-H), 7.90 (t, 4H, J = 8.1 Hz, aromatic H *ortho* to N=N), 8.32 (d, 2H, J = 7.9 Hz, aromatic H *ortho* to NO_2). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): 12.1, 35.6, 45.5, 48.6, 61.7, 111.4, 122.5, 124.6, 126.2, 128.3, 133.0, 143.8, 147.3, 151.1, 156.6, 170.9. FTIR (KBr, cm^{-1}): 3024, 2975, 1736, 1601, 1592, 1517, 1392, 1341, 1136, 1004, 860, 730.

PAzo1 synthesis. Polymerization of (**1**) was conducted by chemical oxidation of the monomer using ferric trichloride.[22] To the mixture of (**1**) (1.39 g, 3.16 mmol) and $FeCl_3$ (2.12 g, 12.7 mmol), anhydrous $CHCl_3$ (50 mL) was slowly added. The

in 100 mL of CH_2Cl_2 was added to a solution of Disperse Red 1 (2.00 g, 6.36 mmol), 3-thiophene-acetic acid (0.90 g, 6.4 mmol), and DMAP (0.080 g, 0.64 mmol). The mixture was stirred for 24 h at

Scheme 3. Synthetic route to poly[6-[4-(4-cyanophenyldiazenyl)phenoxy]hexyl (3 thienyl)ethanoate] (PAzo3).

resulting solution was stirred at room temperature under nitrogen for 24 h, and then precipitated into methanol (1 L). The black precipitate was collected on a Büchner funnel and washed with methanol. Afterward, the solid was washed by Soxhlet extractions using methanol, acetone, and hexane. This treatment gave rise to the undoped polymer appearing brown-red after the removal of the iron chloride species. The loss of the black color of the precipitate was indicative of the removal of $FeCl_3$. The polymer was purified by precipitation of THF solution into methanol, resulting in 0.12 g of PAzo1 (yield: 9%). ^{1}H NMR (THF-d_8, 300 MHz, ppm): 1.29 (m, 3H, N—CH$_2$—**CH$_3$**), 3.44 (m, 2H, N—**CH$_2$**—CH$_3$), 3.70 (m, 4H, **CH$_2$**—COO—CH$_2$—**CH$_2$**), 4.31 (m, 2H, CH$_2$—COO—**CH$_2$**—CH$_2$), 6.80 (m, 2H, aromatic H *ortho* to amine), 7.10 (s, 1H, Th-4-H), 7.79 (m, 4H, aromatic H *ortho* to N=N), 8.22 (m, 2H, aromatic H *ortho* to NO$_2$). FTIR (KBr, cm^{-1}): 3104, 2973, 1744, 1598, 1587, 1516, 1385, 1335, 1136, 1001, 859, 730

Synthesis of Poly[4-[4-(2-thiophen-3-yl-ethoxy)-phenylazo]-benzonitrile] (PAzo2)

4-(4-Hydroxy-phenylazo)-benzonitrile (2).[17] 4-Aminobenzonitrile (2.00 g, 17.0 mmol) was dissolved in a warm mixture of 80 mL of water and 20 mL of hydrochloric acid. This solution was then cooled in an ice–salt bath (0–5 °C) with vigorous stirring. A cold solution of 16.00 g of NaNO$_2$ in 25 mL of water was added slowly to the mixture until the solution became neutral. Then phenol (1.63 g, 17.0 mmol) was dissolved in a solution of NaOH (10% in water) and cooled in an ice bath. The diazotized solution was slowly added to the cooled phenol mixture. Concentrated hydrochloric acid was added to the solution until it became strongly acidic. The precipitate was then filtered and washed with water until it became free of the acid. The product was recrystallized in a mixture of methanol and water to give 3.50 g of (**2**) as an orange solid (yield: 92%). mp: 204 °C. MS (*m/z*): 223 (M$^+$). ^{1}H NMR (CDCl$_3$, 300 MHz, ppm): 5.49 (broad, OH), 6.97 (d, 2H, *J* = 6.7 Hz, aromatic H *ortho* to OH), 7.78 (d, 2H, *J* = 8.6 Hz, aromatic H *ortho* to CN), 7.93 (t, 4H, *J* = 8.3 Hz, aromatic H *ortho* to N=N). FTIR (KBr, cm^{-1}): 3350, 3022, 2225, 1603, 1590, 1433, 1405, 1138, 849.

3-(2-Bromo-ethyl)thiophene (3).[23] 2-(3-Thienyl)-ethanol (3.00 g, 23.4 mmol) was added at 0 °C to an anhydrous acetonitrile solution (50 mL) of

triphenylphosphine dibromide (9.94 g, 23.6 mmol) as a bromination reagent. The solution was refluxed for 2–3 h, then cooled to room temperature, diluted with diethylether, and washed three times with water to eliminate triphenylphosphine oxide. The organic phase was dried over magnesium sulfate and the solvent was evaporated under reduced pressure. The crude product was chromatographed on silica gel (eluent: 20% ethyl acetate and 80% hexane) to give 3.61 g of (**3**) as a clear yellow liquid (yield: 81%). MS (*m/z*): 192 (M$^+$). ^{1}H NMR (CDCl$_3$, 300 MHz, ppm): 3.21 (t, 2H, *J* = 7.6 Hz, CH$_2$—CH$_2$—Br), 3.57 (t, 2H, *J* = 7.5 Hz, CH$_2$—CH$_2$—Br), 6.98 (d, 1H, *J* = 5.2 Hz, Th-4-H), 7.07 (s, 1H, Th-2-H), 7.29 (t, 1H, *J* = 3.5 Hz, Th-5-H position). FTIR (KBr, cm^{-1}): 3062, 2985, 1592, 1485, 1310, 856, 730, 540.

4-[4-(2-Thiophen-3-yl-ethoxy)-phenylazo]-benzonitrile (4).[24] First, 3.00 g (15.7 mmol) of (**3**) and 4.24 g (19.0 mmol) of (**2**) were added to 100 mL of dry acetone. An excess of K$_2$CO$_3$ (7.10 g) and a catalytic amount of KI (0.45 g) were added. The mixture was heated under a reflux for about 72 h. The solution was cooled to room temperature and the precipitate was filtered. It was washed with acetone and then with water to solubilize the salts. Afterward, it was recrystallized in methanol. This reaction gave 2.50 g of (**4**) as an orange solid (yield: 48%) mp: 156.5 °C. MS (*m/z*): 333 (M$^+$). ^{1}H NMR (CDCl$_3$, 300 MHz, ppm): 3.18 (t, 2H, *J* = 6.9 Hz, **CH$_2$**—CH$_2$—O), 4.28 (t, 2H, *J* = 7.0 Hz, CH$_2$—**CH$_2$**—O), 7.02 (d, 1H, *J* = 7.1 Hz, Th-4-H), 7.05 (d, 2H, *J* = 6.2 Hz, aromatic H *ortho* to O—CH$_2$—CH$_2$), 7.11 (s, 1H, Th-2-H), 7.30 (t, 1H, *J* = 4.1 Hz, Th-5-H), 7.78 (d, 2H, *J* = 8.2 Hz, aromatic H *ortho* to CN), 7.94 (d, 4H, *J* = 8.6 Hz, aromatic H *ortho* to N=N). ^{13}C NMR (CDCl$_3$, 75 MHz, ppm): 30.1, 68.4, 114.9, 118.6, 121.7, 123.1, 125.5, 128.4, 133.1, 138.0, 146.9, 154.8, 162.3. FTIR (KBr, cm^{-1}): 3024, 2969, 2225, 1602, 1589, 1493, 1463, 1238, 1136, 1018, 853, 730.

PAzo2 Synthesis. The same procedure as described for PAzo1 was used. As an example, a polymerization using 1.01 g (3.03 mmol) of monomer and 1.99 g (12.1 mmol) of FeCl$_3$ resulted in 0.43 g of PAzo2 as a brown-red solid before purification. This polymer was found to be insoluble in organic solvents.

Synthesis of Poly[6-[4-(4-cyanophenyldiazenyl)phenoxy]hexyl (3-Thienyl)ethanoate] (PAzo3)

4-(4-(6-Hydroxyhexyloxy-phenylazo)-benzonitrile) (5).[16] KI (0.27 g, 1.6 mmol), the compound (**2**) (0.34 g, 1.5 mmol), 6-chloro-1-hexanol (0.20 mL, 1.5 mmol), and K_2CO_3 (0.22 g, 1.6 mmol) were dissolved in 50 mL of dimethylformamide and stirred at 120 °C for 72 h. The reaction was monitored by thin-layer chromatography. Upon addition of water (200 mL), an orange solid was precipitated. The precipitate was dissolved in CH_2Cl_2 and washed with water. The organic layer was dried ($MgSO_4$) and evaporated under reduced pressure. The crude product was purified by recrystallization from hexane to give 0.35 g of (**5**) as an orange solid (yield: 72%). mp: 144 °C. MS (*m/z*): 324 (M$^+$). ^{1}H NMR (CDCl$_3$, 300 MHz, ppm): 1.27 (broad, OH), 1.49 (m, 4H, Ph—O—CH$_2$—**CH$_2$**—**CH$_2$**—CH$_2$—CH$_2$—CH$_2$—OH), 1.58 (m, 2H, CH$_2$—**CH$_2$**—CH$_2$—OH), 1.84 (m, 2H, CH$_2$—**CH$_2$**—CH$_2$—O—Ph), 3.68 (t, 2H, J = 7.5 Hz, CH$_2$—CH$_2$—**CH$_2$**—OH), 4.05 (t, 2H, J = 7.2 Hz, CH$_2$—CH$_2$—**CH$_2$**—O—Ph), 7.01 (d, 2H, J = 6.4 Hz, aromatic H *ortho* to O—R), 7.78 (d, 2H, J = 8.3 Hz, aromatic H *ortho* to CN), 7.92 (d, 4H, J = 8.4 Hz, aromatic H *ortho* to N═N). FTIR (KBr, cm^{-1}): 3020, 2932, 2225, 1600, 1500, 1471, 1405, 1255, 1139, 848.

6-[4-(4-Cyanophenyldiazenyl)phenoxy]hexyl (3-Thienyl)ethanoate (6). The same procedure as for (**1**) was utilized, using 1.54 g (4.74 mmol) of (**5**), 0.69 g (4.8 mmol) of 3-thiopheneacetic acid, 2.64 g (12.8 mmol) of DCC, and 0.060 g (0.48 mmol) of DMAP. After purification on silica gel chromatography (eluent: CHCl$_3$), 1.74 g of the monomer (an orange solid) was obtained (yield: 82%). mp: 221.7 °C. MS (*m/z*): 447 (M$^+$). ^{1}H NMR (CDCl$_3$, 300 MHz, ppm): 1.35 (m, 4H, COO—CH$_2$—CH$_2$—**CH$_2$**—**CH$_2$**—CH$_2$—CH$_2$—O—Ph), 1.65 (m, 2H, COO—CH$_2$—**CH$_2$**—CH$_2$), 1.90 (m, 2H, Ph—O—CH$_2$—**CH$_2$**—CH$_2$), 3.63 (t, 2H, Th—**CH$_2$**—COO—CH$_2$), 4.02 (t, 2H, J = 7.7 Hz, Ph—O—**CH$_2$**—CH$_2$—CH$_2$), 4.09 (t, 2H, J = 7.3 Hz, COO—**CH$_2$**—CH$_2$—CH$_2$), 7.01 (d, 2H, J = 6.3 Hz, aromatic H *ortho* to OR), 7.04 (d, 1H, J = 6.8 Hz, Th-4-H), 7.18 (s, 1H, Th-2-H), 7.32 (d, 1H, J = 3.9 Hz, Th-5-H), 7.78 (d, 2H, J = 8.4 Hz, aromatic H *ortho* to CN), 7.92 (d, 4H, J = 8.5 Hz, aromatic H *ortho* to N═N). ^{13}C NMR (CDCl$_3$, 75 MHz, ppm): 25.6, 28.4, 28.9, 35.8, 64.7, 68.1, 114.8, 118.5, 123.0, 125.4, 128.4, 133.7, 146.6, 154.7, 162.5,

171.1. FTIR (KBr, cm^{-1}): 3017, 2930, 2225, 1732, 1654, 1600, 1524, 1453, 1254, 1139, 849, 730.

PAzo3 Synthesis. The same procedure as for PAzo1 and PAzo2 was used. As an example, the use of 0.82 g (1.84 mmol) of monomer and 1.19 g (7.36 mmol) of FeCl$_3$ gave rise to 0.06 g of PAzo3 as a brown-orange solid (yield: 7%). ^{1}H NMR (THF-d_8, 300 MHz, ppm): 1.35 (m, 4H, COO—CH$_2$—CH$_2$—**CH$_2$**—**CH$_2$**—CH$_2$—CH$_2$—O—Ph), 1.65 (m, 2H, COO—CH$_2$—**CH$_2$**—CH$_2$), 1.90 (m, 2H, Ph—O—CH$_2$—**CH$_2$**—CH$_2$), 3.63 (m, 2H, **CH$_2$**—COO—CH$_2$), 4.02 (m, 2H, Ph—O—**CH$_2$**—CH$_2$—CH$_2$), 4.09 (m, 2H, COO—**CH$_2$**—CH$_2$—CH$_2$), 7.01 (m, 2H, aromatic H *ortho* to OR), 7.12 (s, 1H, H position 4 of thiophene), 7.78 (m, 2H, aromatic H *ortho* to CN), 7.92 (m, 4H, aromatic H *ortho* to N═N). FTIR (KBr, cm^{-1}): 3049, 2937, 2227, 1738, 1600, 1581, 1502, 1468, 1253, 1138, 1001, 848, 730.

Characterizations

All samples were characterized by a number of techniques including differential scanning calorimetry (PerkinElmer DSC-7), ^{1}H NMR (Bruker-AC300), infrared (Bomem MB-200 FTIR) and ultraviolet–visible (UV-vis) (HP-8452A) spectroscopy. DSC measurements were conducted at a heating or cooling rate of 10 °C/min, and the glass transition temperature (T_g) was taken as the midpoint of the step change in the heat capacity. Molecular weights and polydispersities of the polymers were measured by gel permeation chromatography using a Waters system equipped with a refractive index and a photodiode array detector; THF was used as eluent (elution rate: 0.5 mL/min) and polystyrene standards were used for calibration. X-ray diffraction measurements were conducted on a Bruker diffractometer with a two-dimensional position-sensitive wire-grid detector (Bruker AXS). For photoisomerization observations, a UV–vis curing system (Novacure), combined with monochromatic filters (10-nm bandwidth; Oriel), was used to irradiate either solutions or thin films of the polymers (the irradiation intensity was about 23 mW/cm^2 for UV light at 360 nm and 14 mW/cm^2 for visible light at 440 nm). For these measurements, polymer films were obtained by spin coating from THF solution.

For the photoinduced birefringence measurements, an optical set-up similar to that described elsewhere[25] was used. Typically, a thin film about 1-μm thick, prepared from solution casting, was placed between two crossed polarizers. A linearly

polarized Ar^+ laser ($\lambda = 488$ nm) was used as the excitation beam, whose propagation direction was set at a small angle to the normal to the film plane. Unless otherwise mentioned, the intensity of the excitation beam was adjusted to be 50 mW/cm^2 and the polarization of the laser was 45° to the crossed polarizers. A low-power He-Ne laser ($\lambda = 633$ nm, 4 mW) was used as the probe light, with normal incidence. A photodiode detector behind the crossed polarizers monitored the transmission of the probe light. Any photoinduced anisotropy due to the alignment of azobenzene moieties would result in changes in transmission of the probe light, which can be measured and used to calculate the photoinduced birefringence.[25] For all measurements, a second photodiode detecting changes in intensity of the probe light before passing the second polarizer was used to make sure that the measured transmission changes were not caused by scattering or absorption of the sample. A home-made temperature-controllable optical oven was used for the variable temperature measurements. The attempts of recording SRGs were made using an interference pattern produced by two laser beams using basically the same set-up.[25]

RESULTS AND DISCUSSION

Among the three azobenzene polythiophenes, PAzo1 and PAzo3 are slightly soluble in THF, whereas PAzo2 is completely insoluble in organic solvents and could not be purified properly. This is why PAzo2 was characterized only by DSC. The yield of polymerization is very low for both PAzo1 (9%) and PAzo3 (7%), which is consistent with the low yields reported for other azobenzene polythiophenes.[16] In our case, the main reason for this seems to be the limited reactivity of the azobenzene monomers under the used conditions. The characteristics of the polymers are summarized in Table 1. They all appear to be amorphous; the T_g's

Table 1. Characteristics of the Azobenzene Polythiophenes

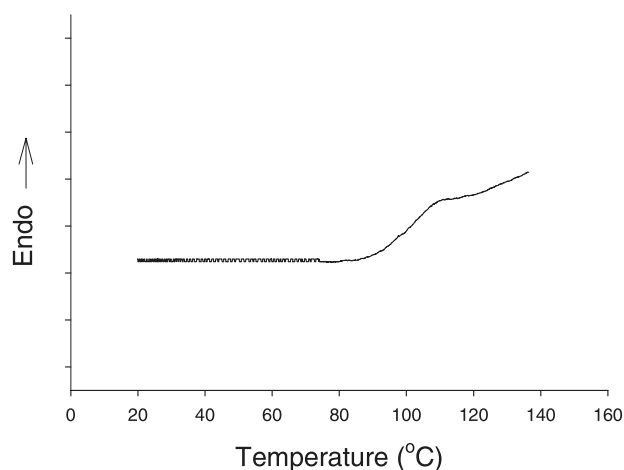| Polymer (Acronym)	T_g (°C)	M_n	M_w/M_n	λ (nm, THF)
PAzo1	102	20,300	2.3	468
PAzo2	73			
PAzo3	64	11,800	2.0	365

Figure 1. DSC heating curve (10 °C/min, second scan) for poly[2-[ethyl-[4-(4-nitro-phenylazo)-phenyl]-amino]-ethane (3-thienyl)ethanoate] (PAzo1).

were measured from the second heating scan (10 °C/min). As an example, the DSC heating curve and ^{1}H NMR spectrum of PAzo1 are given in Figures 1 and 2, respectively.

Unlike azobenzene polythiophenes reported in the literature,[15–18] the azobenzene moiety in the side-chain of PAzo1 contains strong electron-donor and electron-acceptor groups. As expected, this shifts the maximum absorption into the visible region, as shown by the UV–vis spectra of PAzo1 in THF solution and in the solid state (Fig. 3). The spectrum of the thin film is significantly broader than that of the solution, with a new absorption component appeared at higher wavelengths around 530 nm, which comes from the increased conjugation of chain backbone in the solid state.[26] To investigate the photoisomerization behavior of PAzo1, both dilute solution and thin film were exposed to visible light at $\lambda = 440$ nm; no decrease in the absorption of trans azobenzene was observed even with prolonged irradiation (up to 40 min). This, however, should not be taken as an indication of the absence of any photoisomerization of azobenzene in PAzo1. For this polymer, the absorption of trans azobenzene (π-π*) is almost superimposed with that of cis azobenzene (n-π*) so that the visible light irradiation may activate the trans–cis isomerization as well as the reverse cis–trans isomerization process in the same time. This situation is known to favor the induction of photoalignment of azobenzene moieties in the direction perpendicular to the polarization of light due to the fast trans-cis-trans isomerization cycles.[3]
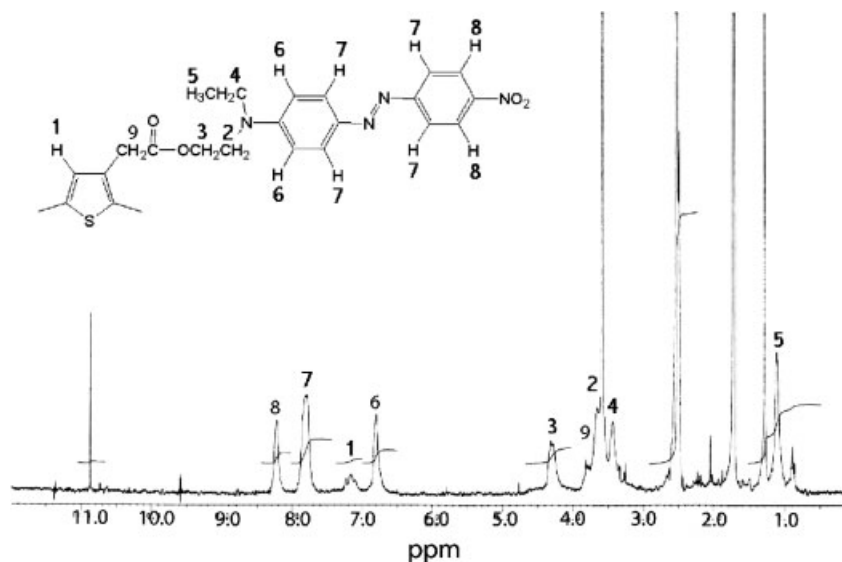
Figure 2. ^{1}H NMR spectrum of poly[2-[ethyl-[4-(4-nitro-phenylazo)-phenyl]-amino]-ethane (3-thienyl)ethanoate] (PAzo1) in THF-d_8.

In contrast with PAzo1, PAzo3 contains an azobenzene group that absorbs in the UV region. In this case, the reversible photoisomerization of azobenzene on UV light irradiation is observable from changes in absorption of trans azobenzene. This is clear from Figures 4 and 5 for solution and thin film of PAzo3, respectively. Several observations can be made. First, in both cases, the maximum decrease in absorption of trans azobenzene is obtained after 10 min of irradiation with UV light reaching the photostationary state (spectra with shorter irradiation times are not shown).

Second, after a subsequent 10-min visible light irradiation at 440 nm, the reverse cis–trans isomerization process is almost complete in solution but seems to be partial for the film. Thermal relaxation of cis azobenzene are much slower, taking several hours to complete. Third, the apparent maximum absorption of trans azobenzene shifts from around 370 nm in solution to about 390 nm in the solid state because of the overlapping with the absorption band of conjugated thiophene chains. Fourth, whereas the absorption of trans azobenzene decreases on UV irradiation, no
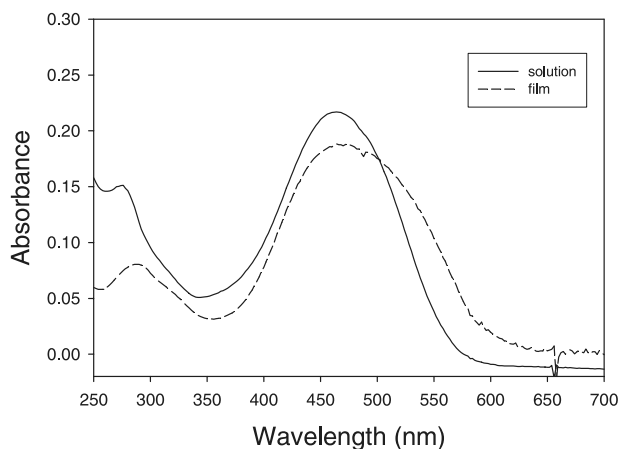

Figure 3. UV–vis spectra of poly[2-[ethyl-[4-(4-nitro-phenylazo)-phenyl]-amino]-ethane (3-thienyl)ethanoate] (PAzo1) in THF solution and in the solid state (thin film prepared from spin coating).
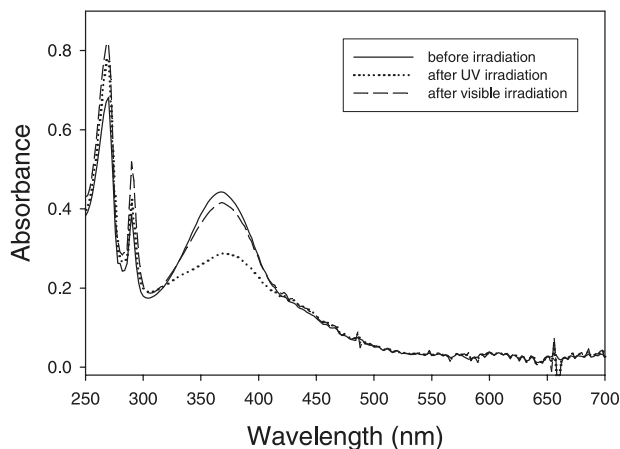

Figure 4. UV–vis spectra of poly[6-[4-(4-cyanophenyl-diazenyl)phenoxy]hexyl (3-thienyl)ethanoate] (PAzo3) in solution before irradiation, after 10 min of UV light irradiation, and after 10 min of visible light irradiation.
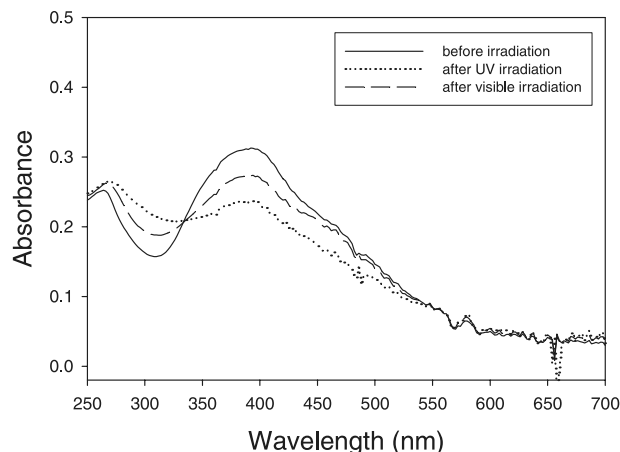
Figure 5. UV–vis spectra of a thin film of poly[6-[4-(4-cyanophenyldiazenyl)phenoxy]hexyl (3-thienyl)ethanoate] (PAzo3) before irradiation, after 10 min of UV light irradiation, and after 10 min of visible light irradiation.

clear increase in absorption of cis azobenzene around 450 nm can be noticed. The absorption of thiophene in this region would probably hide any increase of the weak absorption band of cis azobenzene, especially in the case of thin films.

As mentioned earlier, the main purpose of making new azobenzene polythiophenes was to use them for investigations of photoinduced anisotropy related to the photoalignment of azobenzene moieties as well as the possibility of inscribing SRGs with this type of π-conjugated polymers. Surprisingly, we found that unlike most azobenzene polymers, only very weak birefringence could be induced on irradiation with an Ar^+ laser at $\lambda = 488$ nm in these azobenzene polythiophenes. Actually, no photoinduced birefringence was obtained when the excitation laser was applied at room temperature and at temperatures close to T_g of the polymer. The photoinduced birefringence was observed only at some intermediate temperatures. Figure 6 shows an example of data for both PAzo1 and PAzo3, using an irradiation intensity of 50 mW/cm², with the film of PAzo1 heated to 60 °C and that of PAzo3 heated to 40 °C. For the sake of clarity, the data for PAzo3 were magnified by a factor of 10. It should be emphasized that despite the extremely small values for the anisotropy and the low signal-to-noise ratio, the change in birefringence was really induced by the excitation laser beam, because the polymers showed no response at all to the excita-
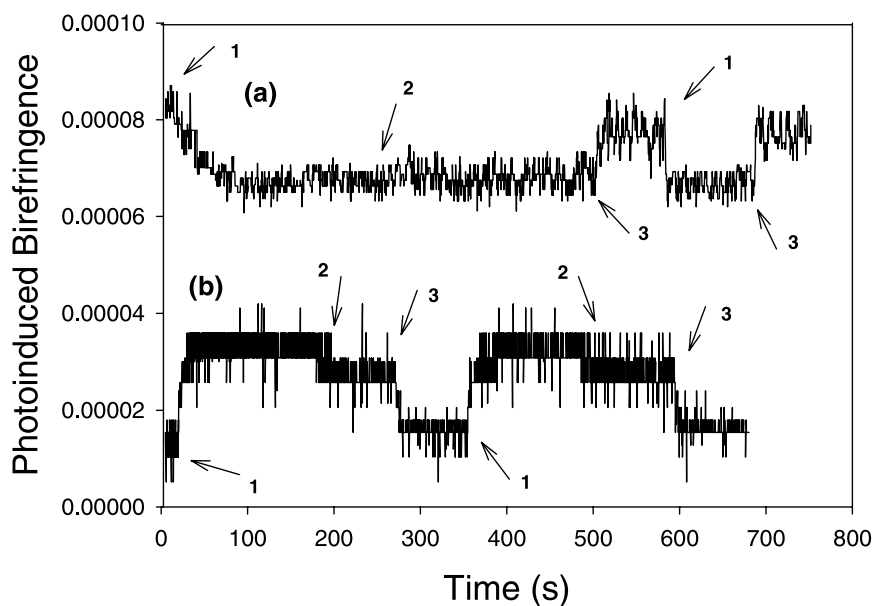

Figure 6. Photoinduced birefringence in thin films of undoped polymers: (a) poly[2-[ethyl-[4-(4-nitro-phenylazo)-phenyl]-amino]-ethane (3-thienyl)ethanoate] (PAzo1) at 60 °C; and (b) poly[6-[4-(4-cyanophenyldiazenyl)phenoxy]hexyl (3-thienyl)ethanoate] (PAzo3) at 40 °C. (1) Linearly polarized Ar^+ laser (50 mW/cm²) is applied; (2) linearly polarized Ar^+ laser is turned off; and (3) circularly polarized Ar^+ laser is applied. Data for PAzo3 are magnified by a factor of 10.
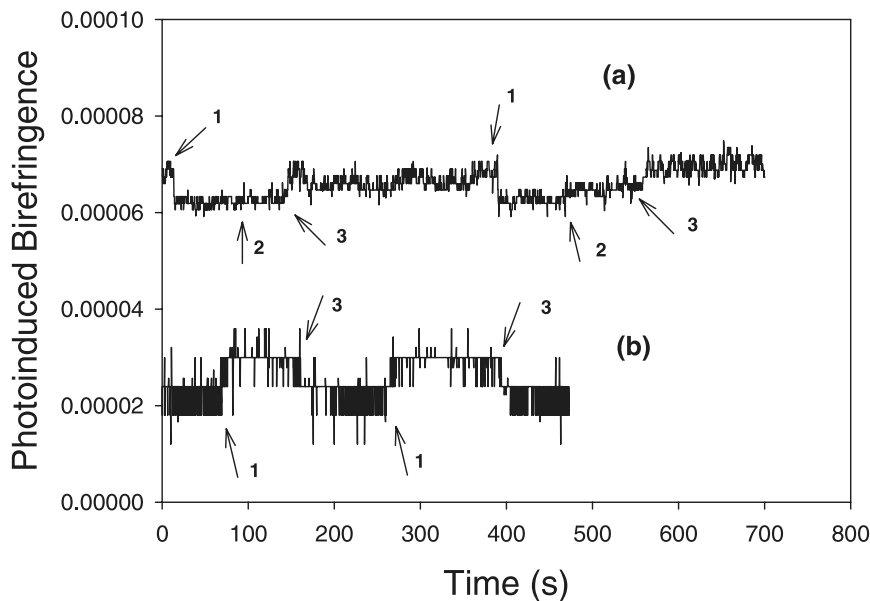
Figure 7. Photoinduced birefringence in thin films of doped polymers: (a) poly[2-[ethyl-[4-(4-nitro-phenylazo)-phenyl]-amino]-ethane (3-thienyl)ethanoate] (PAzo1) at 60 °C; and (b) poly[6-[4-(4-cyanophenyldiazenyl)phenoxy]hexyl (3-thienyl)ethanoate] (PAzo3) at 40 °C. (1). Linearly polarized Ar$^+$ laser (50 mW/cm^2) is applied; (2) linearly polarized Ar$^+$ laser is turned off; and (3) circularly polarized Ar$^+$ laser is applied. Data for PAzo3 are magnified by a factor of 5.

tion laser when the experiments were conducted at temperatures about 10 °C lower or higher. As a matter of fact, in both cases, the behavior of the photoinduced birefringence is typical to amorphous azobenzene polymers.[3] That is, when the linearly polarized Ar$^+$ laser is applied (indicated by arrows labeled with 1), a change in birefringence is induced, and reaches a plateau value after some time. On the first irradiation, the rate of birefringence induction seems slower for PAzo1 than PAzo3, but becomes similar for both polymers on the second irradiation. When the linearly polarized excitation laser is turned off (indicated by arrows labeled with 2), there is a thermal relaxation of the induced birefringence, which is clearer for PAzo3 than PAzo1. Finally, the remaining birefringence can be erased by applying the Ar$^+$ laser that is circularly polarized (indicated by arrows labeled with 3). Such a cycle of optical induction and erasure of anisotropy can be repeated. Two observations from Figure 6 need to be addressed. On one hand, on excitation, PAzo1 displays apparently a negative change in birefringence, which is possible at such a small level of birefringence if the photoinduced movement of azobenzene perturbs (reduces) the initial anisotropy in the polymer film. On the other hand, the

photoinduced birefringence of PAzo3 is even smaller than that of PAzo1 by almost an order of magnitude. This may be explained by the lack of strong electron-donor and electron acceptor groups on the azobenzene moiety in PAzo3, which is known to result in less efficient photoalignment.[3] Another contributing factor may be the excitation wavelength of 488 nm that is far from the absorption maximum of azobenzene in PAzo3.

We also performed experiments of photoinduced birefringence on doped PAzo1 and PAzo3. To make doped samples, films were dipped in a FeCl$_3$/methanol solution for 2 h under nitrogen atmosphere; they were then washed with methanol and dried in a vacuum oven (the doped films had a metallic appearance). The measurements gave rise to very similar results. The slight photoinduced birefringence could only be observed in the same range of temperatures, that is, around 60 °C for PAzo1 and 40 °C for PAzo3. For comparison, the results on doped polymers recorded under the same conditions as in Figure 6 for undoped polymers are shown in Figure 7 (the data for PAzo3 were magnified by a factor of 5). Basically the same analysis can be made. Because of such extremely small photoinduced anisotropy, it was no surprise to find that all attempts of record-

ing SRGs on films of these azobenzene polythiophenes failed.

The inability to display a significant photoinduced birefringence by azobenzene polythiophenes is unexpected. The peculiar temperature dependence of the photoinduced anisotropy may be related to some sort of structural constraint on the photoisomerization or movement of azobenzene moieties. Typically for amorphous azobenzene polymers, the highest birefringence is generally obtained at room temperature. This is because when temperature is increased, even though the mobility of azobenzene moieties increases, which may favor the alignment, the greater thermal relaxation has a dominant opposing effect that results in decease in photoinduced birefringence. By contrast, no photoinduced birefringence was observed for these azobenzene polythiophenes, even with higher irradiation intensities of 75–100 mW/cm^2. The absence of photoinduced anisotropy at room temperature may imply the lack of the mobility required for photoalignment of azobenzene moieties at room temperature. As the temperature is increased, the mobility of azobenzene may increase but the increasing thermal relaxation prevents the photoinduced anisotropy from developing. The consequence of the two competing effects would be the appearance of a small anisotropy at some intermediate temperatures. In addition to DSC (Fig. 1), the amorphous nature of these polymers was also confirmed by polarizing optical microscope showing no birefringence, and X-ray diffraction. Given in Figure 8 are the X-ray diffraction patterns of PAzo1 recorded at room temperature, 60 and 120 °C, which are almost identical. The broad peak characteristic of amorphous polymers is visible around $2\theta = 19°$ (the apparent peak at $2\theta \approx 4.5°$ is from unsubtracted baseline, and the diffusion due to traces of solvent in the sample was believed to cause the sharp increase at $2\theta < 2°$). If some structural constraints were at the origin of the behavior of these azobenzene polythiophenes (Figs. 6 and 7), we do not know what they are at this point. Actually, significant photoinduced anisotropy is generally observed at room temperature even for high-T_g amorphous and semi-crystalline azobenzene polymers.[3]

Another possible explanation for the great difficulty in developing photoinduced anisotropy by azobenzene polythiophenes is based on an inherent feature of polythiophenes. As a matter of fact, thiophene is also a chromophore and polythiophenes may absorb strongly in the visible region.
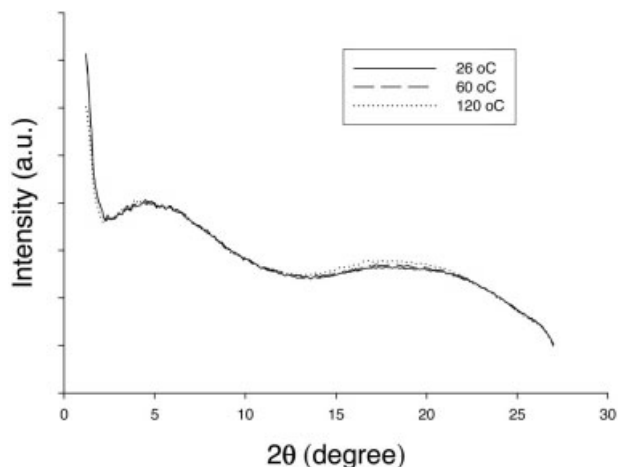

Figure 8. X-ray diffraction patterns of poly[2-[ethyl-[4-(4-nitro-phenylazo)-phenyl]-amino]-ethane (3-thienyl)ethanoate] (PAzo1) recorded at room temperature, 60°C, and 120 °C.

At the used excitation wavelength of $\lambda = 488$ nm of the Ar$^+$ laser, the absorption of polythiophenes is very important in PAzo1 (Fig. 3) and dominant in PAzo3 (Figs. 4 and 5). This may result in a severe interference by thiophene units which considerably reduces the efficiency of activation of azobenzene moieties or/and diminishes the quantum yield for the trans–cis isomerization. More investigations are needed to understand the results of this study.

Finally, we want to mention several other experiments that confirm the inability of azobenzene polythiophenes for photoinduced anisotropy. On the one hand, because PAzo2 is insoluble in organic solvents, we synthesized some random copolymers using the monomer of PAzo2 and 3-hexyl thiophene, and they are fairly soluble in THF. But similar to PAzo1 and PAzo3, no photoinduced birefringence was observed in these copolymers at room temperature on excitation with the Ar$^+$ laser. On the other hand, using a UV–vis curing system, thin films of PAzo1, PAzo3, as well as the copolymers of PAzo2 with poly(3-hexyl thiophene) were exposed to linearly polarized UV or visible light. In all cases, no alignment of azobenzene moieties was observed from polarized UV–vis and infrared spectroscopic measurements.

CONCLUSIONS

Three polythiophenes containing an azobenzene group in the side-chain were synthesized and

characterized and two of them were used to investigate the photoinduced anisotropy by irradiation with an Ar^+ laser at 488 nm. The results are unexpected and quite surprising. Unlike other amorphous azobenzene polymers, no birefringence can be induced on laser excitation at room temperature, and only an extremely small anisotropy appears at some higher temperatures below T_g of the polymer. On the one hand, this peculiar temperature dependence seems to suggest the lack of mobility of azobenzene moieties at room temperature. On the other hand, the interference from the strong absorption of thiophene backbone in the visible region may also be the cause of the inability of azobenzene polythiophenes to display significant photoinduced anisotropy. Because of this behavior, no SRGs could be inscribed on films of these polymers. Therefore, to explore the use of SRGs for all-optical micropatterning of π-conjugated polymers, it would be necessary to incorporate azobenzene moieties into π-conjugated polymers that do not interfere with azobenzene. Possible candidates include polyparaphenylenes and polyfluorenes.

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