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Novel Dual Photochromism in Polythiophene Derivatives

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ABSTRACT: The synthesis of azobenzene-substituted polythiophenes (poly[3-(2-(4-((4′-ethoxyphenyl)-azo)phenoxy)ethoxy)-4-methylthiophene] (P3A), poly[3-((6-(4-((4′-ethoxyphenyl)azo)phenoxy)hexyl)oxy)-4-methylthiophene] (P3B)) and poly[3-(((6-(4-((4-ethoxyphenyl)azo)phenoxy)ethyl)tri(ethoxy)oxy)-4-methylthiophene] (P3C) has led to the development of novel photochromic polymers where the isomerization of the photoactive side chains not only modifies their own UV−visible absorption but also induces a modification of the optical features associated with the conjugated backbone. These results seem to indicate that any perturbation of the side-chain organization in poly(3-alkoxy-4-methylthiophenes) could lead to a modification of the conformation of the main chain and, consequently, to chromic effects both in solution and in the solid state.

Introduction

The recent development of various functionalized polythiophenes has led to processable materials with interesting electrical and optical properties.[1] The addition of side chains onto the aromatic backbone does not only allow an easier processing of the polymeric materials but can also modify the electronic properties of the resulting polymers. For instance, striking thermochromic, solvatochromic, and piezochromic phenomena have been reported in some polythiophene derivatives (principally, poly(3-alkylthiophenes) and poly(3-alkoxy-4-methylthiophenes)).[2] These optical effects are not exclusive to polythiophenes but were, indeed, first observed in some polydiacetylene and polysilane derivatives.[3] In most cases, these color changes are believed to be related (at least partially) to a conformational transition from a highly conjugated planar (or nearly planar) conformation to a nonplanar and less conjugated conformational structure.[4] Indeed, in conjugated polymers, there is a strong correlation between the electronic structure and the backbone conformation, any twisting of the backbone conformation leading to a modification of the effective conjugation length associated with a shift of the absorption in the UV−visible range. However, studies on different polythiophene derivatives have suggested that this conformational modification of the main chain could be induced by order−disorder transitions of the side chains,[5] side-chain disordering disrupting planar polythiophene assemblies.

On the basis of these results, it was then believed that various external stimuli could perturb the side-chain organization and, consequently, induce some chromic phenomena. For instance, noncovalent interactions between some metallic ions and certain ether or crown-ether functionalized polythiophenes induce a blue shift of their maximum of absorption in solution.[6] Moreover, in the case of regioregular ionochromic polythiophene derivatives, a cooperative conformational transition can take place which may lead to an amplification mechanism (i.e. a domino effect).[5,6] These concepts have also led to the design of novel biochromic polythiophenes,[7] where the specific complexation of a protein (avidin) to a biotinylated water-soluble polythiophene results in a strong modification of the optical absorption of the solution. From all these results, it could be then assumed that photoinduced order−disorder transition within the side chains could also lead to a modification of the main chain and, consequently, to a photochromic behavior. Indeed, a similar approach was recently used to photo-induce the inversion of the helical twist sense in chiral polyisocyanates.[8] Moreover, these novel photochromic materials could give more information about the cooperative mechanisms observed in regioregular polythiophenes. Therefore, we report here the synthesis and characterization of azobenzene-substituted polythiophenes, azobenzene compounds being well-known as reversible photo-isomerizable units.[8,9]

Experimental Section

Materials. 4-Hydroxy-4′-ethoxyazobenzene (1) was synthesized according to literature procedures.[10] Then 1.02 g (7.44 mmol) of phenetidine (Aldrich) was dissolved in a warm mixture of 2.5 mL of water and 2.5 mL of hydrochloric acid. This solution was then cooled in an ice−salt bath (0−5 °C) with vigorous stirring. A cold solution of 1.85 g of $NaNO_2$ in 4 mL of water was added to the mixture until the solution became neutral. Then 0.69 g (7.33 mmol) of phenol (Aldrich) was dissolved in a solution of 1.50 g of NaOH in water and cooled in ice. 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 from the acid. The product was recrystallized in a mixture of methanol and water. A brown powder was recovered with a yield of 67%.

M_p: 117−120 °C.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 1.44 (t, 3H), 4.10 (q, 2H), 6.03 (broad, OH), 6.88 (d, 2H), 6.98 (d, 2H), 7.80 (d, 2H), 7.85 (d, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 14.71, 63.82, 114.71 (2C), 115.83 (2C), 124.35 (2C), 124.53 (2C), 146.77, 147.02, 157.91, 161.02.

Anal. Calcd for $C_{14}H_{14}N_2O_2$: C, 69.4; H, 5.8; N, 11.6. Found: C, 68.6; H, 5.8; N, 11.8.

3-Methoxy-4-methylthiophene was synthesized as previously described.[7,11]

3-(2-Bromoethoxy)-4-methylthiophene (2a) was synthesized as follows[7,11] 1.03 g (8.0 mmol) of 3-methoxy-4-methylthiophene and 2.77 g (22 mmol) of bromoethanol (Aldrich) were added to 10 mL of toluene which contained 1.00 g of $NaHSO_4$. The azeotrope (methanol/toluene) was distilled until the temperature reached 108−110 °C. The solution was cooled, and 10 mL of toluene was added and then distillation continued. The solution was cooled again, and 1.25 g of 2-bromoethanol was added with 10 mL of toluene. The

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distillation was pursued a third time, and the residual toluene was removed under vacuum.

The product was purified by distillation (bp 84 °C at 300 μTorr) to give a yellow oil; yield 44%.

^{1}H NMR (CDCl$_3$, 300 MHz, ppm): 2.11 (s, 3H), 3.64 (t, 2H), 4.26 (t, 2H), 6.17 (m, 1H), 6.83 (m, 1H).

^{13}C NMR (CDCl$_3$, 75 MHz, ppm): 12.71, 29.20, 69.65, 97.23, 120.33, 129.18, 155.06.

Anal. Calcd for C_7H_9BrOS: C, 38.0; H, 4.1. Found: C, 37.6; H, 4.1.

3-(2-(4-((4-Ethoxyphenyl)azo)phenoxy)ethoxy)-4-methylthiophene (3a) was synthesized following a procedure described by Reck et al.[12] First, 153 mg (0.7 mmol) of 3-(bromoethoxy)-4-methylthiophene (**2a**) and 0.249 g (1 mmol) of **1** were added to 6 mL of dry acetone. An excess of K_2CO_3, finely powdered (0.31 g), and a catalytic amount of KI were added (0.019 g). The mixture was heated under a gentle reflux for about 60 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, and then it was recrystallized in methanol. The soluble part in acetone was recrystallized in methanol twice and washed with methanol. This reaction gave an orange powder (yield 60%) with a melting point of 143−146 °C.

^{1}H NMR (CDCl$_3$, 400 MHz, ppm): 1.45 (t, 3H), 2.10 (s, 3H), 4.12 (q, 2H), 4.34 (m, 2H), 4.41 (m, 2H), 6.24 (d, 1H), 6.84 (m, 1H), 6.99 (d, 2H), 7.06 (d, 2H), 7.87 (d, 4H).

^{13}C NMR (CDCl$_3$, 100 MHz, ppm): 12.74, 14.79, 63.78, 66.76, 68.52, 96.89, 114.65 (2C), 114.90 (2C), 120.16, 124.31 (2C), 124.39 (2C), 129.28, 146.94, 147.33, 155.65, 160.62, 161.06.

Anal. Calcd for $C_{21}H_{22}N_2OS$: C, 65.9; H, 5.8; N, 7.3. Found: C, 65.5; H, 5.9; N, 7.3.

3-((6-chlorohexyl)oxy)-4-methylthiophene (2b) was synthesized following a procedure similar to that described above using 6-chlorohexanol (Aldrich) and 3-methoxy-4-methylthiophene. It was purified by distillation (bp 122 °C at 75 μTorr) to give a yellow oil with a yield of 71%.

^{1}H NMR (CDCl$_3$, 400 MHz, ppm): 1.50 (t, 4H), 1.83 (m, 4H), 1.89 (t, 2H), 2.11 (s, 3H), 3.57 (t, 2H), 3.98 (t, 2H), 6.17 (d, 1H), 6.85 (m, 1H).

^{13}C NMR (CDCl$_3$, 100 MHz, ppm): 12.55, 25.35, 26.52, 28.94, 32.41, 44.85, 69.57, 95.83, 119.64, 128.97, 156.03.

Anal. Calcd for $C_{11}H_{17}ClOS$: C, 56.8; H, 7.4; S,13.8. Found: C, 56.7; H, 7.5; S, 13.3.

3-((6-iodohexyl)oxy)-4-methylthiophene (2b′) The iodation was performed according to a synthesis described by Bailey et al.[13] To a solution of 2.06 g (14 mmol) of sodium iodide in 10 mL of anhydrous acetone was added 1.68 g (7.23 mmol) of 3-chlorohexanoxy-4-methylthiophene. The mixture was heated under a gentle reflux for 16 h. Diethyl ether was added, the precipitate was filtered, and then the product was extracted with a mixture of diethyl ether/water. The solvent was evaporated, and the residue was dissolved in chloroform and the precipitate filtered again. The product was a yellow oil and was used without further purification. Yield: 85%.

^{1}H NMR (CDCl$_3$, 300 MHz, ppm): 1.29 (t, 4H), 1.50 (t, 2H), 1.85 (t, 2H), 2.12 (s, 3H), 3.22 (t, 2H), 3.96 (t, 2H), 6.15 (d, 1H), 6.84 (m, 1H).

^{13}C NMR (CDCl$_3$, 75 MHz, ppm): 6.95, 12.65, 25.04, 28.92, 30.16, 33.31, 69.61, 95.86, 119.69, 129.06, 156.06.

Anal. Calcd for $C_{11}H_{17}IOS$: C, 40.8; H, 5.3; S, 9.9. Found: C, 41.9; H, 5.5; S, 9.8.

3-((6-(4-((4-Ethoxyphenyl)azo)phenoxy)hexyl)oxy)-4-methylthiophene (3b) was synthesized following a procedure similar to that used for **3a**, coupling compound **1** and compound **2b′**. It was then recrystallized in dimethylchloride/methanol to obtain an bright yellow powder. Yield: 79%. Mp: 104−106 °C.

^{1}H NMR (CDCl$_3$, 300 MHz, ppm): 1.44 (t, 3H), 1.55 (m, 4H), 1.81 (m, 4H), 2.09 (s, 3H), 3.94 (t, 2H), 4.03 (t, 2H), 4.08 (t, 2H), 6.12 (d, 1H), 6.80 (m, 1H), 6.97 (d, 4H), 7.86 (d, 4H).

^{13}C NMR (CDCl$_3$, 75 MHz, ppm): 12.68, 14.75, 25.80, 25.89, 29.10, 29.12, 63.70, 68.07, 69.73, 95.91, 114.58 (2C), 114.60 (2C), 119.73, 124.30 (4C), 129.13, 146.87 (2C), 156.16, 160.93, 161.07.

Anal. Calcd for $C_{25}H_{30}N_2O_3S$: C, 68.5; H, 6.9; N, 6.4; S, 7.3. Found: C, 68.8; H, 7.0; N, 6.6; S, 7.1.

3-Methyl-4-(tetraethoxy)thiophene(2c) was synthesized using a procedure similar to that described by Faid and Leclerc.[7] First 2.01g (11.4 mmol) of 3-bromo-4-methylthiophene, 1.96 g (13.6 mmol) of CuBr, and 12 mL of NMP were added to an excess (20.43 g, 0.1 mol) of tetraethylene glycol (Aldrich) that had previously reacted with 0.70 g (30 mmol) of Na(s). The mixture was heated to 110 °C for 36 h. The solution was allowed to cool to room temperature and filtered on a Buchner funnel, and the filtrate was extracted with diethyl ether. The product was purified on silica gel using ethyl acetate (yield 43%, light yellow oil).

^{1}H NMR (CDCl$_3$, 400 MHz, ppm): 2.08 (s, 3H), 2.88 (broad, OH), 3.58 (t, 2H), 3.66−3.74 (m, 10H), 3.84 (t, 2H), 4.10 (t, 2H), 6.16 (d, 1H), 6.80 (m, 1H).

^{13}C NMR (CDCl$_3$, 100 MHz, ppm): 12.58, 61.55, 69.49, 69.57, 70.21, 70.48, 70.52, 70.73, 72.37, 96.45, 119.79, 128.99, 155.72.

Anal. Calcd for $C_{13}H_{22}O_5S$: C, 53.8; H, 7.6; S, 11.0. Found: C, 54.1.; H,7.7; S, 10.5.

3-(((2-Iodoethyl)triethoxy)oxy)-4-methylthiophene (2c′) was synthesized following a procedure described by Barbarella et al.[14] First, the mesylate derivative was obtained by adding 13 mL of pyridine to 1.53 g of **2c** at −20 °C. Then 0.95 mL of methanesulfonyl chloride were slowly added to this cooled solution, and the mixture was then allowed to sit at room temperature for 48 h. The mixture was poured onto 150 g of ice, stirred for 10 min, and extracted with chloroform. The product was added to a saturated solution of NaI in acetone (32 g of NaI in 64 mL of acetone), stirred for 24 h, and evaporated. The residue was dissolved in CH_2Cl_2 and washed with water (yellow oil, yield 45%).

^{1}H NMR (CDCl$_3$, 400 MHz, ppm): 2.11 (s, 3H), 3.23 (t, 2H), 3.67−3.70 (m, 6H), 3.73−3.78 (m, 4H), 3.87 (t, 2H), 4.12 (t, 2H), 6.17 (d, 1H), 6.82 (m, 1H).

^{13}C NMR (CDCl$_3$, 100 MHz, ppm): 2.86, 12.60, 69.50, 69.55, 70.08, 70.49, 70.59, 70.75, 71.81, 96.44, 119.78, 128.95, 155.71.

Anal. Calcd for $C_{13}H_{21}O_4SI$: C, 39.0 ; H, 5.3 ; S, 8.0. Found: C, 40.1.; H, 5.4; S, 7.7.

3-(((6-(4-((4-Ethoxyphenyl)azo)phenoxy)ethyl) Triethoxy)oxy)-4-methylthiophene (3c) was synthesized by coupling compound **1** and compound **2c′** following a procedure similar that used for **3a**. It was washed with water and methanol and then recrystallized in acetone/hexanes to obtain a dark yellow powder with a yield of 75%. Mp: 87−89 °C.

^{1}H NMR (CDCl$_3$, 400 MHz, ppm): 1.45 (t, 3H), 2.10 (s, 3H), 3.7−3.74 (m, 8H), 3.85−3.90 (m, 4H), 4.10−4.12 (m, 4H), 4.20 (t, 2H), 6.16 (m, 1H), 6.82. (d, 1H), 7.01 (m,4H), 7.88 (m, 4H).

^{13}C NMR (CDCl$_3$, 100 MHz, ppm): 12.65, 14.70, 63.68, 67.64, 69.56, 69.58, 69.63, 70.62, 70.64, 70.82 (2C), 96.50, 114.57 (2C), 114.74 (2C), 119.85, 124.20 (2C), 124.28 (2C), 129.06, 146.84, 147.07, 155.81, 160.69, 160.95.

Anal. Calcd for $C_{27}H_{34}N_2O_6S$: C, 63.0; H, 6.7; N, 5.4; S, 6.2. Found: C, 63.4.; H,6.8; N, 5.5; S, 6.0.

Poly[3-(2-(4-((4-ethoxyphenyl)azo)phenoxy)ethoxy)-4-methylthiophene] (P3A). **3a** was chemically oxidized with $FeCl_3$ in chloroform for 24 h.[15] It was then washed in a Soxhlet apparatus with methanol, then with acetone.

$M_w = 7.5 \times 10^3$. $M_w/M_n = 1.5$ against polystyrene standards.

Poly[3-(6-(4-((4-ethoxyphenyl)azo)phenoxy)hexyloxy)-4-methylthiophene] (P3B). **3b** was polymerized using the same synthetic procedure as for P3A.

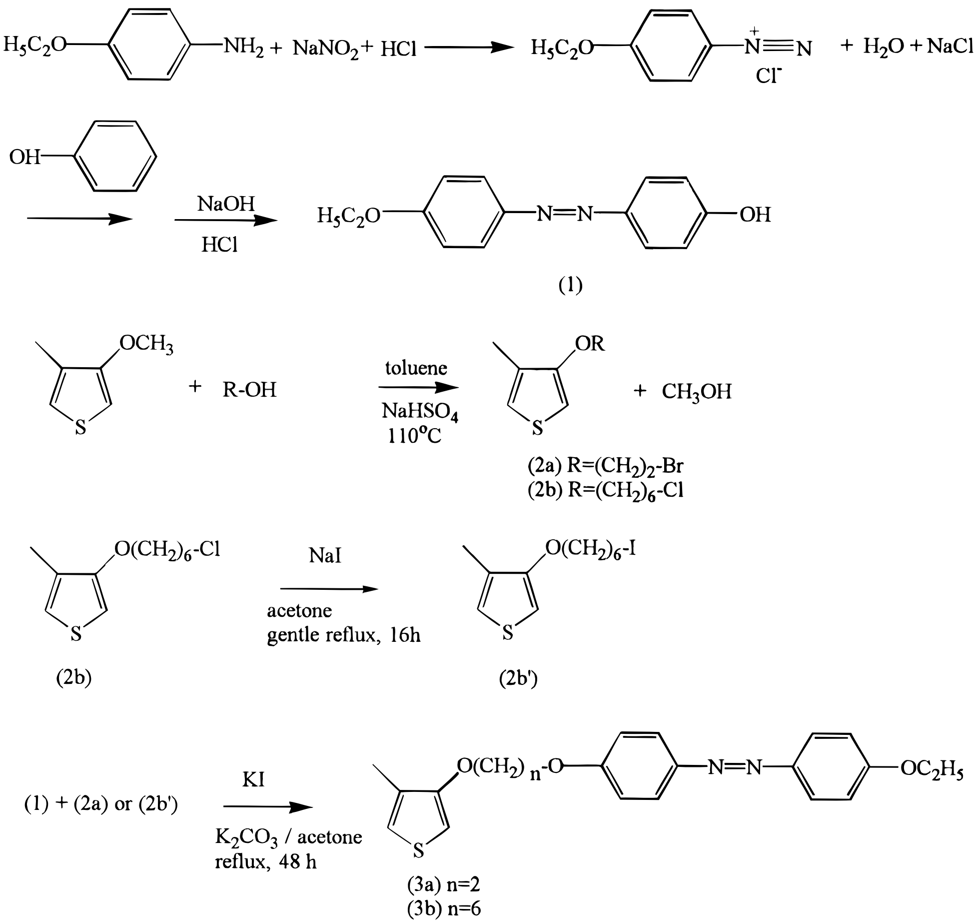
$M_w = 9.0 \times 10^3$. $M_w/M_n = 1.7$ against polystyrene standards.

Poly[3-(((6-(4-((4-ethoxyphenyl)azo)phenoxy)ethyl) Tri(ethoxy)oxy)-4-methylthiophene] (P3C). **3c** was chemically oxidized with $FeCl_3$ in chloroform for 4 h. It was washed in the same manner as the other polymers.

$M_w = 7.5 \times 10^4$; $M_w/M_n = 1.6$ against polystyrene standards.

Physical Methods. NMR spectra measurements were performed in deuterated chloroform solutions on Bruker AMX 300 and ARX 400 instruments. Differential scanning calorimetry (DSC) analyses were performed at 10 °C/min on a TA Instruments thermal analyst (Model 2910) calibrated with ultrapure indium. Size exclusion chromatography (SEC)

Scheme 1



measurements were carried out with a Waters apparatus equipped with ultrastyragel columns, in tetrahydrofuran. The calibration curve was obtained with monodispersed polystyrene standards. UV−visible spectra were obtained using a Hewlett-Packard diode-array spectrophotometer (Model 8452A). The photochromic experiments were carried out using a Xe lamp (150W, ICL LX-150 UV) as the source. The light was filtered by passing through a $CuSO_4$ solution and an UG1 filter (Schott), to get a maximum of emission at 350 nm. The samples were dissolved in the appropriate solvents and then allowed to sit for 24 h in the dark before irradiation.

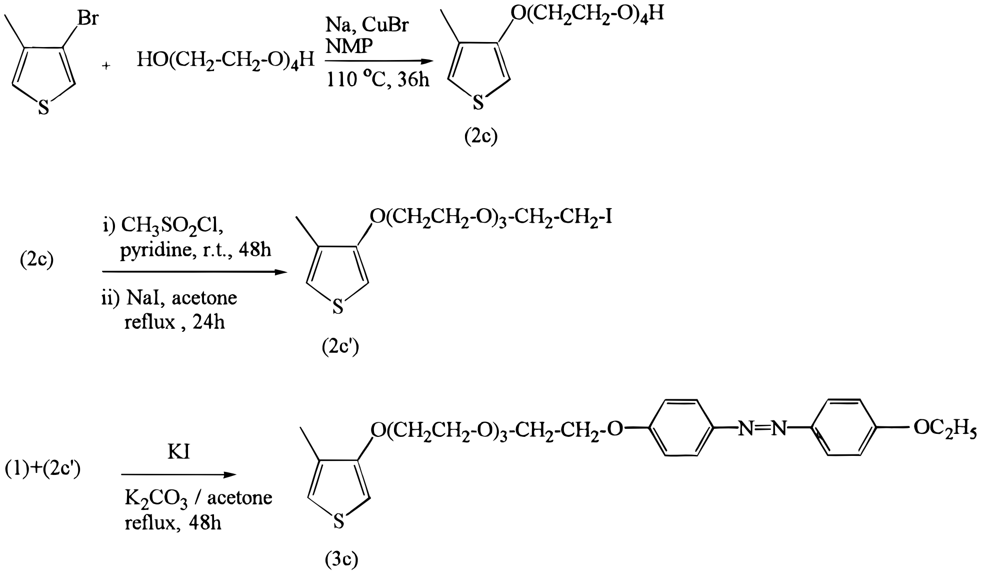
Results

As shown in Schemes 1 and 2, 3-alkoxy-4-methylthiophenes bearing azobenzene moieties have been easily prepared: the first monomer has two methylene units between the photoresponsive unit and the thiophene ring (monomer **3a**), the second one, has six methylene units as a spacer group (monomer **3b**), and the third one has four oxyethylene units as a spacer (monomer **3c**). The photochemical properties of all these monomers were evaluated in chloroform solutions. As an example, monomer **3a** exhibits an absorption maximum at 365 nm which is related to a $\pi-\pi^*$ transition of the azobenzene trans configuration. Upon UV irradiation, a trans−cis isomerization is induced, leading to new absorption bands centered near 320 and 450 nm, respectively (Figure 1). The first absorption band is related to a $\pi-\pi^*$ transition while the latter is associated with a $n-\pi^*$ transition.[9] Under our experimental conditions, the photoinduced isomerization reaction of the monomers is almost complete after 30 s (as revealed by the disappearance of the 365 nm absorption band). The presence of two isosbestic points clearly indicates the coexistence of both configurational structures during this photochromic process. It is also reversible, and after UV irradiation, in visible light, the initial absorption spectrum, related to the more stable trans configuration, is recovered within 60−90 min. Once again, two clear isosbestic points are observed during the reverse cis−trans isomerization. Similar results have been obtained with monomers **3b** and **3c** within the same time scale.

Since all these monomers are photoresponsive, the thiophene units have been chemically polymerized using iron trichloride as an oxidizing agent in chloroform.[15] The resulting polymers are soluble in common organic solvents. However, it has been found that P3C, bearing a highly flexible oxyethylene spacer group, has a much higher solubility than P3A and P3B. This higher solubility can explain its higher molecular weight, since precipitation of the growing chains can be limited, in this case, during the oxidative polymerization reaction. Because of this higher solubility in chloroform, clear NMR spectra of P3C were obtained (Figures 2 and 3). Both NMR spectra reveal a well-defined regioregular structure for this polymer. In particular, the presence of a sharp peak at 2.3 ppm (related to the protons of the methyl group attached to the thiophene ring) in the ^1H NMR spectrum (Figure 2) and the presence of only four aromatic peaks related to the carbon atoms of the thiophene ring (Figure 3) are a clear indication of a high (>95%) head-to-tail content (5,15). Moreover, these spectra show no sign of cross-linking between the aryl substituents.

In a poor solvent (chloroform−methanol 1:1), all polymers exhibit an absorption band centered at 360

Scheme 2



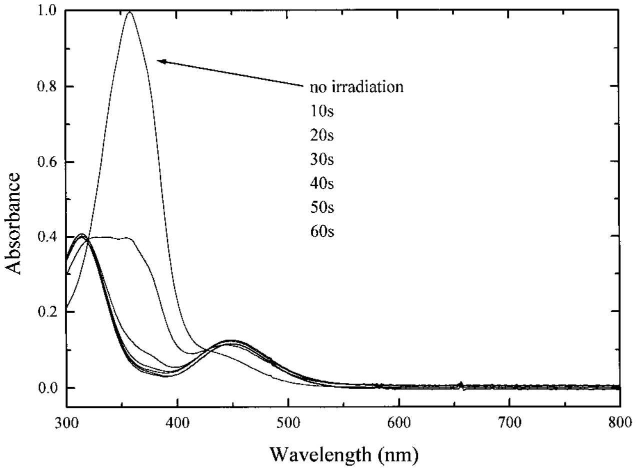


Figure 1. UV–visible absorption spectra of monomer **3a** as a function of time of UV irradiation, in chloroform solution, at room temperature.

nm which is related to the $\pi-\pi^*$ transition of trans configuration of the azobenzene moieties together with a large absorption band around 540 nm associated to the $\pi-\pi^*$ transition of the highly conjugated polythiophene units (as an example, see Figure 4). On the basis of previous studies,[5–7] this highly conjugated form of the thiophene backbone would be the result of the formation of intramolecular (through chain folding) and/or intermolecular assemblies. Indeed, very similar absorption spectra are observed for these polymers in the solid state at room temperature. Upon UV irradiation, a trans–cis isomerization reaction of the azobenzene unit is induced as revealed by the decrease of the absorption near 365 nm and the increase of the absorption near 325 and 440 nm. These UV–visible absorption modifications associated with the azobenzene moieties are essentially the same as those observed with the monomers. However, it is clear that the photoinduced isomerization reaction is not complete (there is still the presence of an absorption band near 365 nm), and that could be related to a screening effect of the polymers. However, this point is highly speculative and many more experiments have to be carried out to understand this limitation of the trans–cis isomerization reaction in the polymers.

Interestingly, this isomerization reaction in the side chains also induces a modification of the absorption features associated with the conjugated backbone. Indeed, the violet solution becomes yellow upon UV irradiation, and this major color change can be related to a conformational transition of the main chain. On the basis of previous results obtained with other chromic poly(3-alkoxy-4-methylthiophenes),[5,15] the decrease of absorption between 500 and 650 nm should be associated with the growth of a new absorption band centered around 420–440 nm which, in this case, is added to the absorption band related to the n–π^* transition of the cis configuration of the azobenzene substituent. As observed with the monomers, this photoinduced process is reversible and, after irradiation, the polymers slowly recover their initial absorption features. Consequently, a novel dual-photochromic behavior is found in these materials, where the trans–cis isomerization of azobenzene moities not only leads to a strong modification of its UV–visible absorption features but also leads to a strong modification of the absorption features of the backbone to which it is attached. This phenomenon does not seem strongly influenced by the distance between the photoactive moities and the backbone, since a polymer with six methylene units (P3B) or four oxyethylene units (P3C) as the spacer between photoactive units and the backbone shows essentially the same behavior as the analog with only two methylene groups as the spacer unit. These results seems to indicate that a modification of the side-chain organization and not necessarily a significant increase of the steric hindrance in the vicinity of the backbone could be sufficient to induce a conformational transition of the conjugated backbone.

On the other hand, it is very intriguing to observe a broad isobestic point near 460–480 nm in Figure 4. Indeed, in a first approximation, it can be assumed that the photoinduced isomerization reaction involves individual and randomly located azobenzene units which could affect, in principle, the thiophene units next to them. Therefore, a continuous shift of the absorption maximum related to the $\pi-\pi^*$ transition of the backbone should be observed. This is not the case, and as found in all previous studies on regioregular poly(3-alkoxy-4-methylthiophenes),[5,7] a cooperative twisting of the several thiophene units (a domino effect) seems to

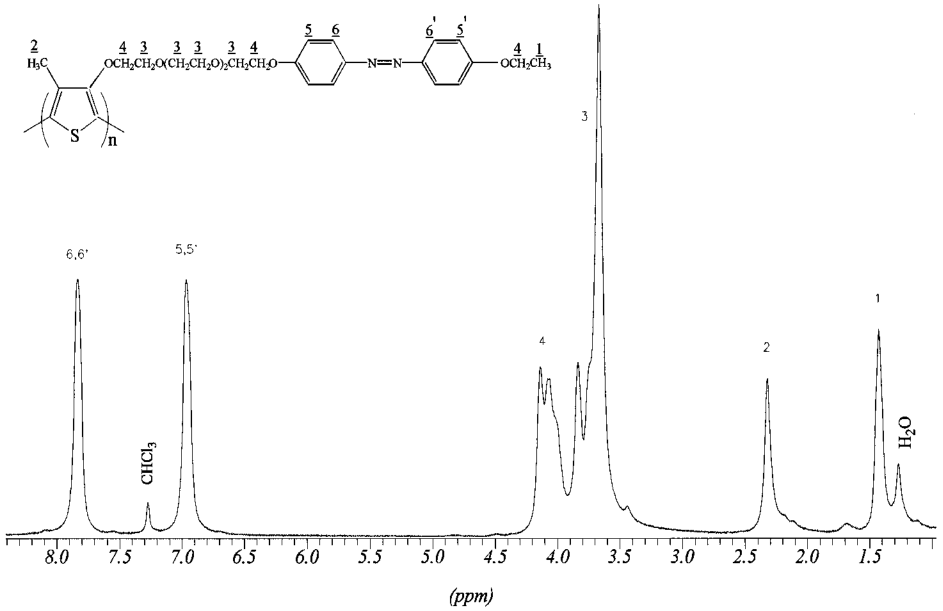


Figure 2. ^{1}H NMR spectrum of P3C in CDCl$_3$.

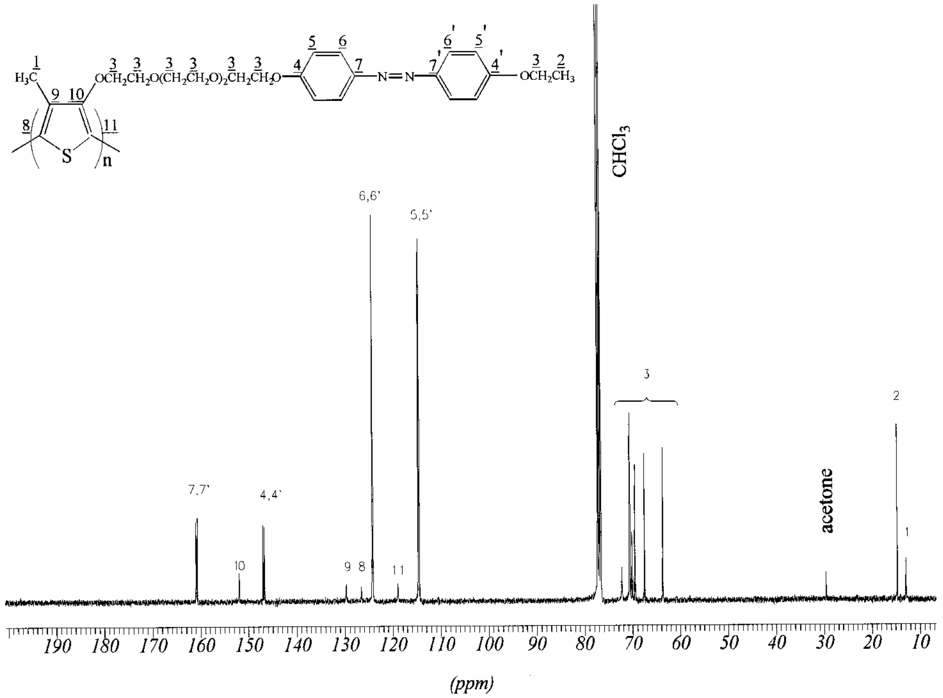


Figure 3. ^{13}C NMR spectrum of P3C in CDCl$_3$.

be induced by one side-chain configurational (and conformational) modification. This amplification phenomenon will be further investigated by the preparation of random copolythiophenes bearing photoactive and nonphotoactive side-chain units.

For practical applications, such as photochromic and optical recording materials, it could be interesting also to analyze these photochromic behaviors in the solid state. All polymers were first heated and quenched before irradiation to remove any crystallinity. As shown in Figure 5, trans—cis isomerization of the azobenzene unit is possible in the solid state, at room temperature. In correlation with this modification of the side-chain organization, the absorption related to the backbone is also affected. Once again, a cooperative twisting of backbone seems to take place upon UV irradiation. Indeed, these photochromic effects are very similar to those observed in solution although they are not complete. The study of UV—visible absorption as a function of temperature for this polymer in the solid state has revealed that it is possible for these polymers to adopt a completely disorganized (and yellow) form upon heating (Figure 6). However, since the glass transition temperature of these polymers is around 25—50 °C, that could explain why long-range conformational modification of the backbone is hindered at room temperature. However, on the basis of these promising results, new homopolymers and copolymers with lower glass transition temperatures will be developed in the near future.

Conclusions

Azobenzene-substituted polythiophenes have revealed a novel reversible dual photochromic behavior where the photoisomerization of the side chains leads to a change of the UV—visible absorption bands of both the side

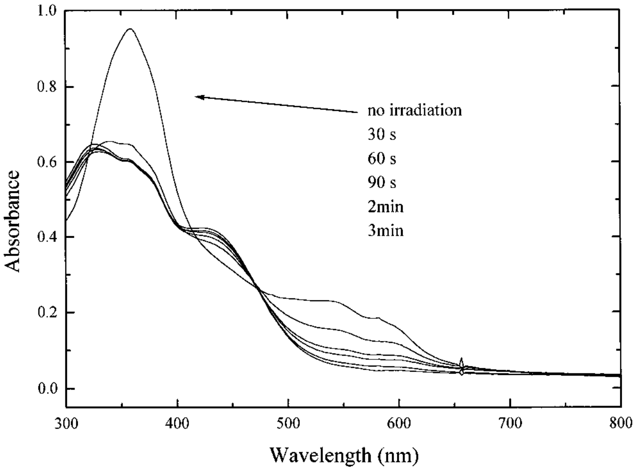


Figure 4. UV−visible absorption spectra of polymer P3A, as a function of time of UV irradiation, in chloroform−methanol (1:1) solution, at room temperature.

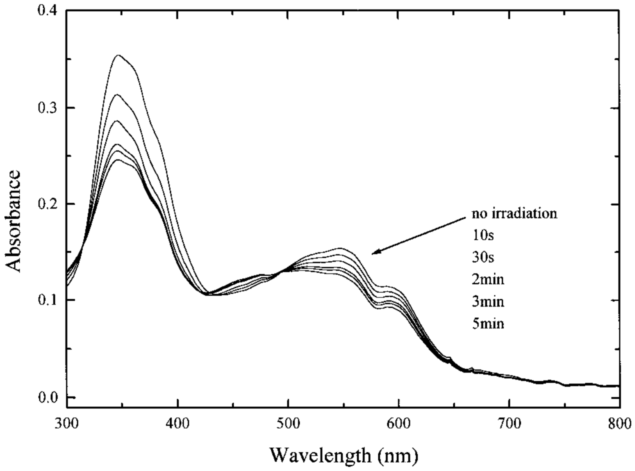


Figure 5. UV−visible absorption spectra of polymer P3C, as a function of time of UV irradiation, in the solid state, at room temperature.

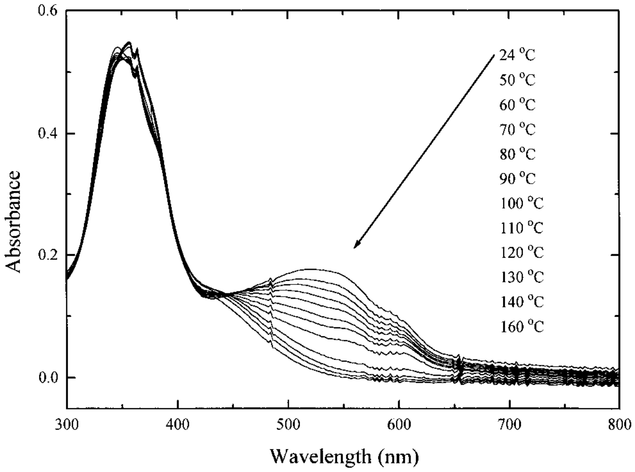


Figure 6. UV−visible absorption spectra of polymer P3C, as a function of temperature, in the solid state.

chains and the main chain. This dual photochromic effect does not seem to depend upon the distance between the photoactive units and the backbone and has been observed both in solution and in the solid state. These results combined with our previous studies on ionochromic and biochromic poly(3-alkoxy-4-methylthiophene)s seem to indicate that many external stimuli could be used to induce a conformational transition of the conjugated backbone and correlated optical changes. Moreover, the presence of a cooperative effect could lead to an amplification mechanism and, therefore, could be useful to develop highly sensitive photochromic or affinity chromic materials.

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Supporting Information Available: Figures showing ^{1}H NMR and ^{13}C NMR spectra for all monomeric compounds (18 pages). Ordering information is given on any current masthead page.

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