

Ionochromic and Thermochromic Phenomena in a Regioregular Polythiophene Derivative Bearing Oligo(oxyethylene) Side Chains

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Structural, thermal, and optical studies on regioregular poly[3-oligo(oxyethylene)-4-methylthiophene] have revealed interesting thermochromic and ionochromic effects related to a planar/nonplanar transition of the conjugated backbone. This first-order-like conformational transition (formation of twistons) seems driven by side-chain disordering induced by an increase of temperature or through noncovalent interactions with specific cations. The twisting of one repeat unit of this regioregular polythiophene derivative provokes the twisting of a large number of adjacent thiophene units (a domino effect) which leads to an amplification of the resulting optical (i.e., absorption or emission band) signal. These features are particularly promising for the development of novel affinitychromic and photochromic sensors based on new regioregular poly(3-alkoxy-4-methylthiophene)s.

Introduction

Conjugated polymers (e.g., polyacetylenes, polypyrroles, polythiophenes, polyanilines, etc.) are now well-known as highly conducting materials in the doped (oxidized, reduced, or protonated) state.¹ The delocalized electronic structure of these polymers is, in part, responsible for the stabilization of the different charge carriers created upon doping. In most cases, the conjugated electronic structure involves a relatively small π – π^* bandgap together with a strong absorption in the UV–visible range. The strong coupling between the electronic structure and the UV–visible absorption of these polymers has led to the development of interesting electrochromic devices, based on reversible doping–dedoping redox processes.¹

On the other hand, it is also possible to modify the UV–visible absorption spectrum of neutral conjugated polymers by varying their conformational structure. For instance, Brédas et al.^{2,3} have fully described the dependence of the electronic structure of conjugated polymers upon their conformation. This correlation between electronic structure and backbone conformation can then explain the intriguing thermochromic features found in several substituted polydiacetylenes,^{4–6} polysilanes,^{7–9} and polythiophenes.^{10–14} In most cases,

these optical changes have been attributed to a thermally induced planar/nonplanar conformational transition of the conjugated backbone. The strong dependence of these thermochromic phenomena upon the position and the bulkiness of the substituents seems to indicate that side-chain disorder could be the driving force of these optical effects; side-chain disordering increasing their steric hindrance which then forces the backbone to adopt a nonplanar conformation.¹⁵ This assumption is in agreement with FTIR measurements which have revealed that some disorder are created in both the side chains and the main chain upon heating.^{13,14} Moreover, if side-chain disorder is the driving force of a planar/nonplanar conformational transition of the backbone, it can be considered that any modification of the side-chain organization could induce some chromic effects. Following these concepts, recent studies have indicated that noncovalent interactions between metal ions and some ether^{16,17} or crown ether^{18,19} functionalized polythiophenes can induce a blue-shift of their absorption maximum in solution.

In this respect, we have recently shown that regioregular poly(3-alkoxy-4-methylthiophene)s can undergo a thermally induced first-order-like conformational transition (both in solution and in the solid state) of the backbone (formation of twistons) which leads to dramatic color changes.^{14,20,21} The coexistence of long

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sequences of twisted and planar thiophene units in these regioregular polymers has been put in evidence by the presence of a clear isosbestic point in temperature-dependent optical absorption measurements. In contrast, this cooperative conformational transition of the main chain did not occur in nonregioregular polymers, where only the formation of weak and localized conformational defects along the backbone together with a continuous and monotonic blue-shift of the absorption maximum has been observed.²¹ Using these properties, it could be then possible to design regioregular polythiophene derivatives where the ratio between the twisted and planar chromophores can lead to a colorimetric determination of various external stimuli. Moreover, it is believed that this cooperative twisting of the regioregular conjugated polymers (which can be compared to a domino effect) could lead to an amplification of the detection where the twisting of a first unit would induce the twisting of a large number of adjacent repeat units along the backbone. As an example of these novel possibilities for conjugated polymers, regioregular poly[3-oligo(oxyethylene)-4-methylthiophene] has been recently synthesized,²² and we report herein an extensive characterization of its thermochromic and ionochromic properties. Moreover, the unusual substitution pattern (side chains of different lengths) of this polymer can give useful information about the mechanisms involved in the formation of delocalized conformational defects (twistons).

Experimental Section

Materials. Following a procedure developed by El Kassmi et al.,²³ 3-oligo(oxyethylene)-4-methylthiophene was synthesized from a coupling reaction between 3-bromo-4-methylthiophene²⁴ and poly(ethylene glycol) methyl ether (PEG, MW 350, Aldrich). PEG was previously dried under vacuum at 70 °C for 24 h. Size exclusion chromatography measurements (SEC) on poly(ethylene glycol) methyl ether (MW 350) revealed that the side chains vary from 3 to 10 oxyethylene units with a weight-average molecular weight of 350 (average of 7 oxyethylene units) and a polydispersity index of 1.08. The resulting monomer was dried under vacuum at 50 °C for 24 h.

3-Oligo(oxyethylene)-4-methylthiophene: yield 65%. ¹H NMR (300 MHz, CDCl₃, ppm) 2.09 (s, 3H), 3.38 (s, 3H), 3.55 (m, 2H), 3.65 (m, 19H), 3.69 (m, 2H), 3.86 (m, 2H), 4.11 (m, 2H), 6.16 (d, 1H), 6.81 (m, 1H). ¹³C NMR (75 MHz, CDCl₃, ppm) 12.48, 58.75, 58.80, 69.35, 69.42, 70.24, 70.31, 70.34, 70.36, 70.39, 70.62, 71.53, 71.66, 96.23, 119.65, 128.82, 155.60.

The polymer was prepared by chemical polymerization in chloroform using iron trichloride as an oxidizing agent.²⁴ The mixture was stirred for 24 h. Chloroform was then evaporated and the resulting black oxidized polymer was collected on a Büchner funnel and washed with methanol. It was subsequently washed with water using a soxhlet apparatus. It was then rinsed with methanol at room temperature to eliminate the low molecular weight fraction. The polymer was dissolved in chloroform, filtered, slowly evaporated to produce a free-standing thin polymer film, and finally dried under vacuum at 45 °C for 1 day (30% yield). This polymer is completely soluble in chloroform and tetrahydrofuran at room temperature and is soluble in methanol when heated. The polymer

reveals a number-average molecular weight of 22 500 with a polydispersity index of 5.9.

Physical Methods. NMR spectra measurements were performed in deuterated chloroform solutions on Bruker AMX 300, ARX 400, or Varian 600 instrument. 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) measurements were carried out with a Waters apparatus (Model 410) equipped with ultrastaygel columns, in tetrahydrofuran. The calibration curve was obtained with monodispersed polystyrene standards. The absorption spectra were obtained with a Hewlett-Packard diode array UV-vis spectrophotometer (Model 8452A). For the solid-state measurements, the spectrophotometer was provided with a temperature control unit that allows measurements over a temperature range 25–250 °C with a maximum error of ± 2 °C. 1-cm quartz cells were used for solution measurements. The polymer concentration was 1.0×10^{-4} M (based on the average molecular weight of one repeat unit). Solution temperature-dependent measurements (15–50 °C) were performed using a methanol–water cryostat. Low temperature (down to –100 °C) UV-visible spectra were performed on a Cary 5 UV-vis-NIR spectrophotometer equipped with a cryostat (Manchester Instruments Ltd.). Fluorescence measurements were recorded on a Spex Fluorolog-2 spectrophotometer, using a 1-cm path length quartz cell. The polymer concentration in methanol was 5.0×10^{-6} M, giving absorbances always less than 0.05 to avoid any filter effect. The solutions (with and without KCl) were excited at 434 nm. The KCl concentration varied between 1.0×10^{-6} and 1.0×10^{-2} M. The fluorescence excitation spectra were found to be equivalent to their absorption spectra. The temperature-dependent measurements (10–55 °C) were performed using a methanol–water cryostat. X-ray diffraction patterns of polymer samples were recorded by a scintillation counter coupled with a pulse-height analyzer as detector using Ni-filtered Cu K α radiation from a Rigaku rotating anode generator (Rotaflux RU200). Collimation was done at wide angles with a Soller slit and a 1.0 mm pinhole. The temperature was controlled by a water-cooled copper block oven with Mylar windows.

For the preparation of polymer–salt mixtures, the salts (KCl, NaCl, LiCl, NH₄Cl, KSCN) were previously dissolved in methanol. Similarly, the polymer was dissolved in methanol. Identical volumes of a salt solution and the polymer solution were mixed together. The polymer–salt mixtures were let to stabilize for at least 1 day before any measurement. In absence of light, these solutions were stable for weeks.

Results

Thermochromism. NMR analyses have revealed that poly(3-oligo(oxyethylene)-4-methylthiophene) is regioregular with a head-to-tail content higher than 95%. For instance, ¹³C NMR spectrum of this polymer exhibits only four sharp peaks for the aromatic carbon atoms of the thiophene ring (Figure 1). Accordingly, the ¹H NMR spectrum shows one sharp peak at 2.3 ppm (related to the protons of the methyl group at the 4-position) which indicates a highly regioregular substitution pattern along the backbone.^{21,24} This highly regioregular structure is consistent with previous results obtained with other poly(3-alkoxy-4-methylthiophene)^{20,21,24,25} and can be related to an asymmetric reactivity of the oxidized monomer.²⁶ As observed with similar polythiophene derivatives, this polymer exhibits a reversible thermochromic behavior both in the solid state and in solution. In the solid state and at room temperature, an absorption peak is found at 550 nm

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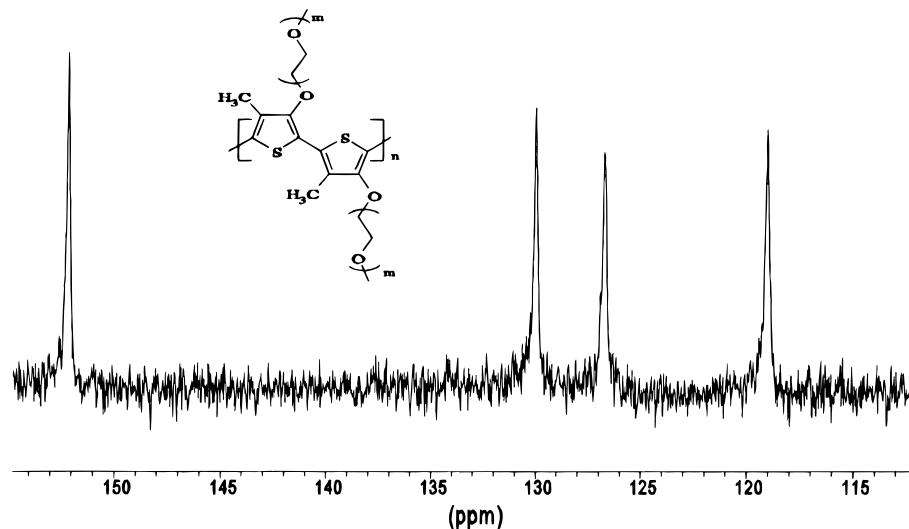


Figure 1. Aromatic region of a 150 MHz ^{13}C NMR spectrum of poly[3-oligo(oxyethylene)-4-methylthiophene] in CDCl_3 .

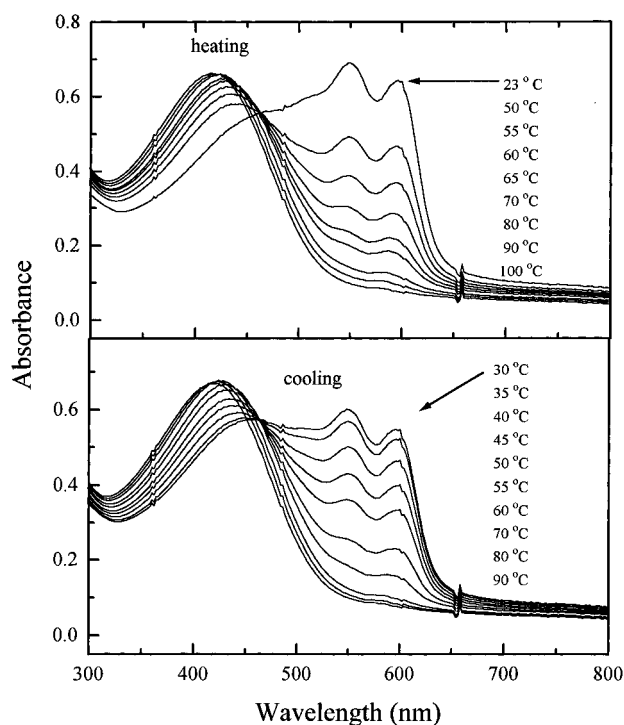


Figure 2. Temperature-dependent UV-visible absorption spectra of poly[3-oligo(oxyethylene)-4-methylthiophene] in the solid state.

which can be related to a planar (or nearly planar) conjugated backbone, while the other peak at 594 nm stands for a vibronic fine structure (Figure 2). At higher temperatures, there is a decrease of the 550 nm band, whereas the absorption peak at 426 nm increases. This absorption band centered at 426 nm is characteristic of a delocalized twisted (less conjugated) form of the backbone. The presence of an isosbestic point reveals the coexistence of two conformational structures (planar and nonplanar). The solid-state planar/nonplanar transition of this polymer appears at very low temperatures for this class of materials and can be related to the presence of highly flexible side chains. In fact, the transition is already in progress at room temperature. By plotting the absorbance at 550 nm as a function of the temperature, one can see that the thermochromic transition is reversible but with some hysteresis.

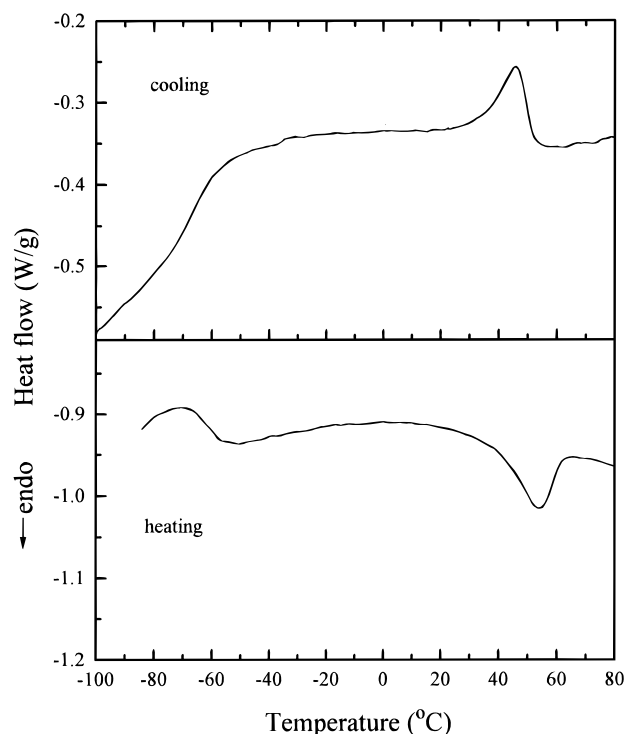


Figure 3. Thermograms of poly[3-oligo(oxyethylene)-4-methylthiophene].

This thermally induced conformational transition can be also characterized by differential scanning calorimetry (DSC, Figure 3). In the heating scan, a relatively broad endothermic transition appears with a maximum at 53 °C. In the cooling scan, the corresponding exothermic peak is observed at 46 °C. The enthalpy of both thermal transitions is about 0.7 kcal/mol of repeat unit. There is also a second-order transition around -60 °C which can be attributed to a glass transition. At this point, it is clear that the calorimetric measurements have indicated a first-order-like transition in a temperature range where most important optical (conformational) changes take place. In correlation with these optical and thermal transitions, X-ray diffraction data have revealed some short-range organization for this polymer with a interlamellar spacing of about 2.7 nm and a stacking distance of 0.41 nm at room temperature (Figure 4). Upon heating (at 100 °C), the

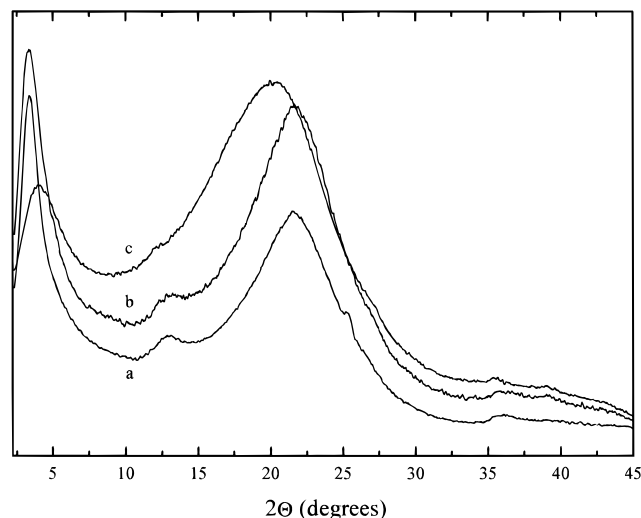


Figure 4. X-ray diffraction spectrum of poly[3-oligo(oxyethylene)-4-methylthiophene] at (a) 25 °C, (b) 25 °C after having been heated at 100 °C for 16 h, and (c) at 100 °C.

interlamellar spacing decreases to 2.15 nm while the stacking distance increases to 0.44 nm. The decrease of the interlamellar distance upon heating is consistent with a disordering of the side chain (formation of gauche conformations) while the increase of stacking spacing is consistent with a twisting of the previously planar (or nearly planar) backbone. However, it is quite evident that the thermochromic transition does not lead to a significant modification of the organization of this polymer. Similar results have been also obtained with alkoxy-substituted polythiophenes^{14,21} and polysilanes.^{27,28}

Thermochromism has been also investigated in both good and bad solvents. In a good solvent (tetrahydrofuran), at room temperature, the maximum of absorption takes place at 426 nm, meaning that the polymer is already in a twisted form. This study clearly shows that the polymer goes through a cooperative transition and turns from yellow to purple upon cooling. The transition is reversible which could indicate that no precipitation of the polymer has occurred. On the other hand, poly[3-oligo(oxyethylene)-4-methylthiophene] can be solubilized in methanol (bad solvent) only upon heating. The resulting solution is yellow but becomes violet when cooled to room temperature. This polymer solution is stable (no precipitation has been observed) and the backbone is then mostly planar. As shown in Figure 5, at room temperature, in methanol, the maximum of absorption of the polymer is at 550 nm. Upon heating, the relative concentration of the twisted form of the polymer increases. The transition is similar to that observed in tetrahydrofuran, except that it occurs at higher temperatures, and in a smaller temperature range. In both types of solvent, an isosbestic point is observed and the thermochromic transition is reversible.

Ionochromism. As mentioned in the Introduction, this new polythiophene derivative contains oxyethylene units of various lengths that are known to interact with alkali-metal cations. Accordingly, at a given temperature, some noncovalent interactions between the side chains and alkali-metal ions could modify the conformation of the side chain and induce a cooperative twisting

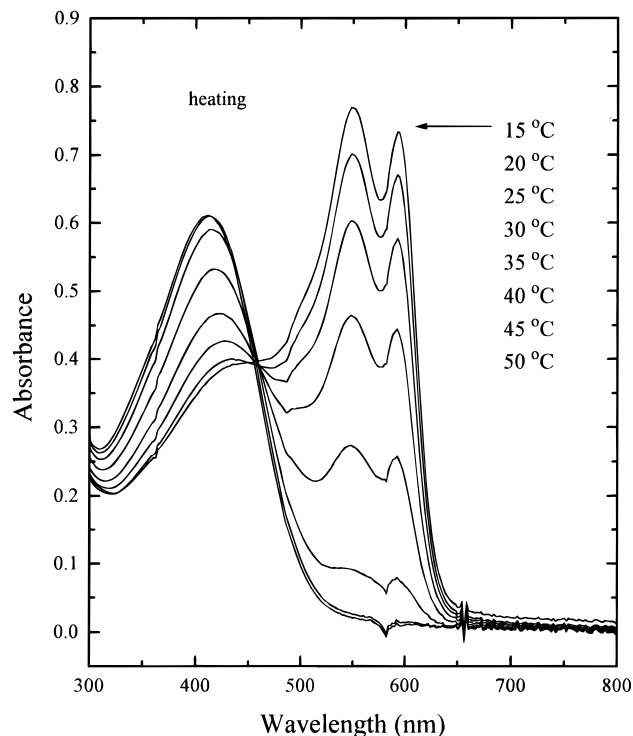


Figure 5. Temperature-dependent UV-visible absorption spectra of poly[3-oligo(oxyethylene)-4-methylthiophene] in methanol (1.0×10^{-4} M, heating scan).

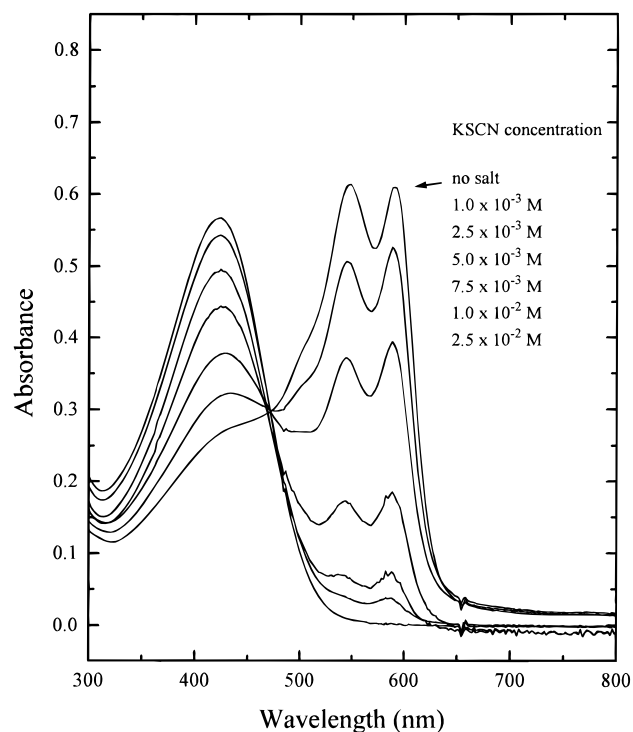


Figure 6. UV-visible absorption spectra of poly[3-oligo(oxyethylene)-4-methylthiophene] in methanol (1.0×10^{-4} M) with different KSCN concentrations.

of the main chain. To check this point, ionochromic effects have been investigated in methanol. In this solvent, as reported above, the salt-free solution contains mostly the planar form at room temperature. As shown in Figure 6, the addition of various concentrations of KSCN induces a cooperative twisting of the main chain as the salt concentration increases. Other cations (Na^+ , NH_4^+ , Li^+) have been added to the polymer

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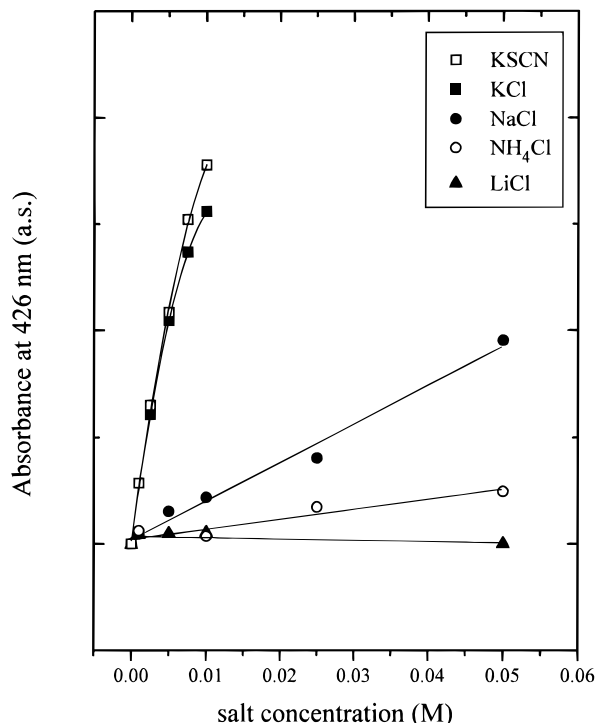


Figure 7. Variation of the absorbance of the 426 nm band of poly[3-oligo(oxyethylene)-4-methylthiophene] (1.0×10^{-4} M) in methanol as a function of the concentration of various salts at 22 °C.

solution, but most important effects have been observed with K^+ (Figure 7). This means that to induce the same effect as K^+ , more Na^+ and even more NH_4^+ must be added to the polymer solution. $LiCl$ does not produce any effect, even when the solution is saturated with this salt. The size of the alkali cations seems to be related to the ionochromic effect, K^+ being preferably solvated by the oligo(oxyethylene) side chain. The NH_4^+ cation is bigger than Na^+ , but the latter possesses a more ionic character. On the other hand, the nature of the anion is negligible since KSCN produces almost the same effect as KCl. Experiments on other poly(3-alkoxy-4-methylthiophene)s have shown that these cations can only interact with the oxygen atoms of the oxyethylene units, the side chains being then clearly responsible for this ionochromic effect. A complexation of one cation through a possible crown-ether-like conformation could explain the planar/nonplanar transition of the backbone, although these color changes could also be rationalized by a better solubilization of the polymer upon salt addition (solvatochromic effect). However, in both models, the driving force of these ionochromic effects still remains noncovalent interactions between oxygen atoms and cations.

Fluorescence Measurements. To better characterize and improve the detection of such solution thermochromic and ionochromic effects, fluorescence measurement have been carried out. Photoexcitation of the polymer in a methanol solution results in a fluorescence emission with a maximum intensity at 542 nm (Figure 8). An interesting feature is that the twisted form shows fluorescence (excitation at 434 nm) whereas the planar form (excitation at 550 nm) does not emit at all. A similar behavior has been already noted for polydiacetylenes where single crystals of perfectly coplanar polydiacetylene chain do not emit at all.²⁹ Conforma-

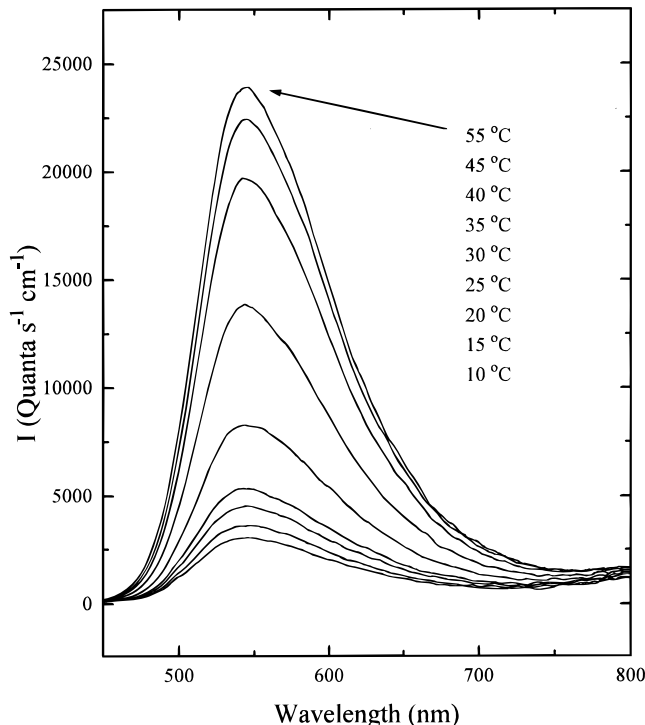


Figure 8. Temperature-dependent fluorescence spectra of poly[3-oligo(oxyethylene)-4-methylthiophene] in methanol (5.0×10^{-6} M) for a 434 nm excitation wavelength.

tional defects (a twisted conformation) can be assumed to act as traps for energy migration and therefore inhibit nonradiative decay.^{12,29,30} It is important to note that fluorescence emission in poly[3-oligo(oxyethylene)-4-methylthiophene] is insensitive to the excitation wavelength over the range of the absorption band. This indicates that the emission is really due to one chromophore only.

Intensity of emission as a function of temperature has been also measured (Figure 8). The maximum wavelength is constant (542 nm) over the entire range of temperature (10–55 °C), while the intensity of fluorescence increases as the temperature is raised. At high temperatures, there is usually an enhancement of non-radiative decay of excited species^{12,30} with, consequently, a decrease in luminescence. The opposite effect is observed, and it is clearly due to the formation of delocalized twisted structures upon heating. The constant wavelength is also an indication that the same chromophore, due to the completely twisted form of the polymer, is emitting. By plotting the emission intensity at 542 nm for a diluted solution of polymer in methanol (5.0×10^{-6} M) as a function of the temperature, and on the same figure, the absorbance at 426 nm versus the temperature for a more concentrated solution (1.0×10^{-4} M), one can see that the transition appears within the same temperature range for both polymer concentrations (Figure 9). This suggests that the thermochromic phenomenon is independent upon the polymer concentration.

Similarly, for a given temperature, the addition of alkali-metal ions modifies the conformational structure

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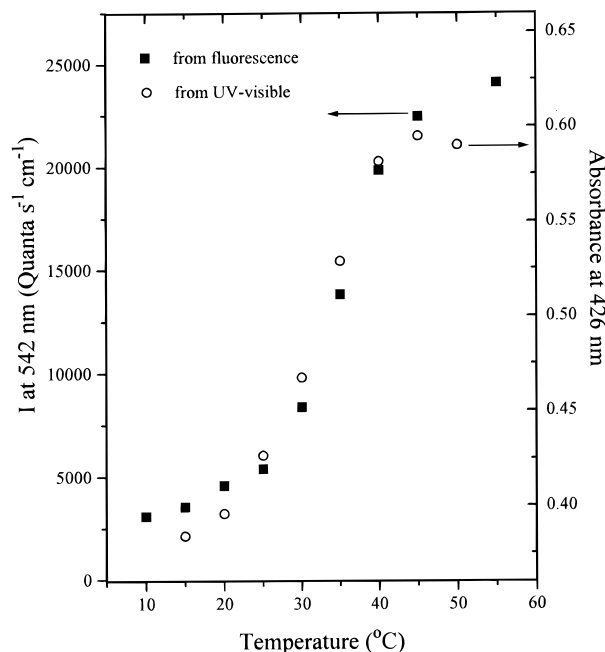


Figure 9. Temperature dependence of fluorescence at 542 nm for a 5×10^{-6} M polymer solution and of the absorbance at 426 nm for a 1.0×10^{-4} M polymer solution.

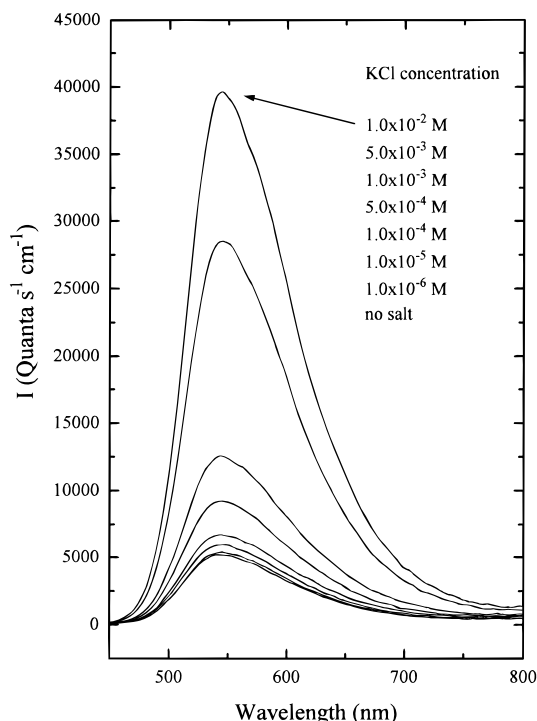


Figure 10. Fluorescence spectra of poly[3-oligo(oxyethylene)-4-methylthiophene] in methanol (5.0×10^{-6} M) for a 434 nm excitation wavelength with different KCl concentrations at room temperature.

of the polymer and its luminescence properties (Figure 10). The maximum wavelength of emission is still constant (542 nm) at all salt concentrations. This indicates that the emission is due to the same type of chromophore (delocalized twisted form) for every solution. The relative concentration of this twisted chromophore increases as the salt concentration gets higher, as observed by UV-visible measurements. As shown in Figure 10, fluorescence detection is at least 1 order of magnitude more sensitive than UV-visible measurements.

Discussion

A regioregular polythiophene derivative bearing oligo(oxyethylene) side chains has shown dramatic thermochromic and ionochromic effects. In both cases, a first-order-like conformational transition is taking place, involving a twisting of the main chain that seems driven by side-chain disordering (induced by an increase of temperature or noncovalent interactions with some cations). One particularly interesting feature of these transitions is the fact, as revealed by the presence of an isosbestic point, that the twisting of one first repeat unit seems to induce the twisting of a large number of adjacent thiophene units (e.g., a domino effect). Indeed, one can assume that disorder within the side chains is created randomly along the backbone. Therefore, one can expect that this random disordering of the side chains should lead to a continuous and monotonic blue-shift of the absorption in the UV-visible range and not to the coexistence of only two distinct chromophores. Previous studies^{21,31} have revealed that such a monotonic blue-shift of the absorption maximum (formation of localized conformational defects) occurs in nonregioregular polythiophene derivatives whereas delocalized twisted structures (twistons) can be only created in regioregular polythiophenes. Such cooperative conformational transition has then been attributed to the formation of intramolecular (through chain folding) and/or intermolecular assemblies made possible by the presence of a regioregular substitution pattern along the backbone. These assemblies would be broken through side-chain disordering. The question about the intermolecular or intramolecular nature of these chromic transitions is still a matter of debate but the independence upon the polymer concentration of these chromic effects is suggestive of a single-chain phenomenon. Similar conclusions have been also reported for polysilanes³² and polydiacetylenes.³³

However, in both intramolecular and intermolecular models, the cooperative order/disorder transition can be related either to a stacking of substituted thiophene units or to the occurrence of noncovalent interactions between the side chains forming a lamellar-like structure. The fact that the chromic polymer investigated in this study bears side chains of different lengths makes more difficult the cooperative formation of ordered lamellar-like assemblies (although a lamellar structure has been revealed in the solid state from X-ray diffraction data), and one can assume that the formation of intramolecular and/or intermolecular stacks is easier in this polymer. Moreover, the formation of stacks is consistent with results obtained with monolayers of fluorinated polythiophene derivatives which have shown thermochromic effects similar to those observed with spin-coated films.²⁰ In the monolayers, the formation of lamellar assemblies is almost impossible whereas the formation bidimensional stacks (with thiophene units perpendicular to the water subphase) is certainly possible.

On the other hand, this first report of a cooperative twisting of a regioregular conjugated polymer through

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specific noncovalent interactions between the side chains and some chemical species opens also the way to the development of novel affinitychromic sensors. The strong absorption in the visible range and the emissive properties of this chromophore allow easy detection of the signal and makes possible a quantitative determination of the analytes. Moreover, the domino effect present in these systems leads to an amplification mechanism and to an enhanced optical detection of the external stimuli. However, up to now, attempts to induce ionochromic effects in the solid state have failed. These results can be attributed to a more viscous system where side-chain disordering is rendered more difficult, although experiments have been carried out at room temperature which is much higher than the glass transition temperature of poly[3-oligo(oxyethylene)-4-methylthiophene]. It could be also possible that these ions do not diffuse easily in this matrix and induce only some chromic effects at the interface and, therefore, induce a color change of only a very small fraction of the material. For this purpose, it would be interesting to prepare monolayers from this class of materials to study the ionochromic effects in the solid state.

Conclusion

The incorporation of flexible oligo(oxyethylene) side chains to a regioregular polythiophene backbone has led to a reversible low-temperature thermochromic material. This polymer has also revealed interesting thermochromic and ionochromic effects in solution. These conformational transitions have been also characterized by fluorescence measurements at concentrations down to 5×10^{-6} M. For the first time, a cooperative twisting of the backbone (formation of twistons) has been observed towards the addition of cations such as K^+ , Na^+ , and NH_4^+ , while Li^+ did not induce any effect at all. The incorporation of substituents of different lengths did not inhibit the cooperative thermochromic and

ionochromic transitions and could indicate that the formation of assemblies is related to intramolecular and/or intermolecular stackings of substituted thiophene units regioregularly placed along the backbone. The formation of such delocalized conformational defects leads also to an amplification of the optical signal and to a quantitative and specific determination of cations. These results open the way to the development of novel affinitychromic polymers. For example, one could develop sensors based on the specific complexation of some binding sites present in the side chains from targeted chemical or biochemical species. Light could also induce chromic phenomena with regioregular polythiophene bearing photoisomerizable moieties in the side chains. Future work will focus on the development of such affinitychromic and photochromic materials and for all these purposes, the preparation of various 3-alkoxy-4-methylthiophenes is particularly attractive since from a simple chemical oxidation of these monomers, highly regioregular chromic polymers should be obtained.

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Supporting Information Available: The 300 MHz 1H NMR and 75 MHz ^{13}C NMR spectra of 3-oligo(oxyethylene)-4-methylthiophene in $CDCl_3$ and the 400 MHz 1H NMR spectrum of poly[(3-oligo(oxyethylene)-4-methylthiophene)] in $CDCl_3$ (3 pages). Ordering information is given on any current masthead page.

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