Chromic Phenomena in Regioregular and Nonregioregular Polythiophene Derivatives

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Chromic phenomena in various regioregular and nonregioregular polythiophene derivatives have been investigated both in the solid state and in solution. Some structural, thermal, and optical measurements have revealed a first-order-like conformational transition of the conjugated backbone (formation of twistons) which leads to important color changes. This thermally induced cooperative conformational transition of the main chain has been observed in both amorphous (even with branched side chains) and semicrystalline regioregular polythiophene derivatives but did not occur in nonregioregular polymers. This single-chain phenomenon is strongly dependent upon the substitution pattern but is not necessarily driven by side-chain or main-chain crystallization. Noncovalent interactions between ether-substituted regioregular polythiophenes and ionic species can be used to stabilize the coplanar form of the backbone, leading to interesting ionochromic effects.

Introduction

Conjugated polymers are well known for their excellent electrical conductivities in the oxidized (doped) state.[1] The recent development of processable conducting polymers has opened the way for large-scale industrial applications. The preparation of fusible and/or soluble conjugated polymers follows two main pathways: (i) the incorporation of relatively long and flexible side chains[2–10] or (ii) the introduction of large counterions.[11–13] Both approaches are based upon a decrease in attractive interchain interactions and the introduction of favorable interactions between the substituents (or the counterions) and the solvent. Moreover, the introduction of substituents may have a strong influence on the electronic structure of the resulting material and, conse-

quently, on its properties.[14] It may also lead to novel optical properties that are not observed in the unsubstituted parent polymer: for instance, some substituted polythiophenes exhibit intriguing thermochromic (in the solid state and in solution), solvatochromic, and piezochromic properties.[15–20] Similar effects are also observed in certain polysilanes[21–23] and polydiacetylenes.[24–26]

These unusual optical effects are believed to be related to a reversible "transition" between a coplanar (highly conjugated) and a nonplanar (less conjugated) conformation of the conjugated main chain.[27,28] Other studies have revealed the strong dependence of the thermochromic properties upon the position and the

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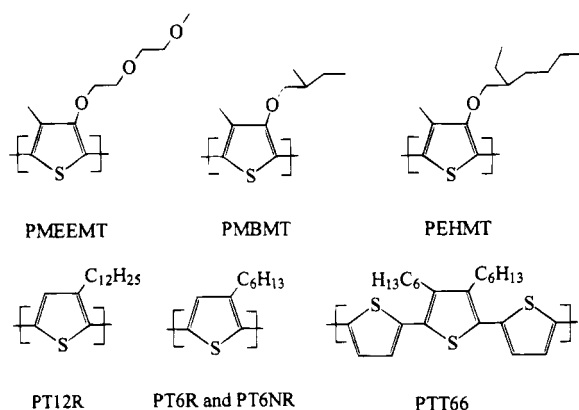
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Scheme 1

PMEEMT   PMBMT   PEHMT

PT12R   PT6R and PT6NR   PTT66

nature of the substituents.[29,30] Several explanations of the driving force of these optical phenomena have been proposed (crystallization, aggregation, thermally induced steric interactions, etc.), but a detailed description of the structural parameters involved in these optical effects is still lacking.

To shed some light on these thermochromic effects, structural, thermal, and optical measurements have been carried out on regioregular (and nonregioregular) polythiophene derivatives, namely, poly(3-(2-(2-methoxyethoxy)ethoxy)-4-methylthiophene) (PMEEMT), poly-(3-(2-methyl-1-butoxy)-4-methylthiophene) (PMBMT), poly(3-(2-ethyl-1-hexyloxy)-4-methylthiophene) (PEHMT), poly(3-dodecylthiophene) (PT12R), poly(3-hexylthiophene)s (PT6R and PT6NR), and poly(3',4'-dihexylterthiophene) (PTT66) (Scheme 1).

Experimental Section

Materials. All 3-alkoxy-4-methylthiophenes were obtained from a coupling reaction between 3-bromo-4-methylthiophene[31] and the corresponding alcohols (Aldrich) according to a procedure similar to that described by El Kassmi et al.[32] The monomers were purified by flash chromatography on silica gel.

3-(2-(2-Methoxyethoxy)ethoxy)-4-methylthiophene (MEEMT): yield: 5%. ^{1}H NMR (300 MHz, CDCl$_3$, ppm) 2.11 (s, 3H); 3.39 (s, 3H); 3.60 (m, 2H); 3.73 (m, 2H); 3.88 (m, 2H); 4.13 (m, 2H); 6.17 (d, 1H); 6.82 (m, 1H). ^{13}C NMR (75 MHz, CDCl$_3$, ppm) 17.53; 58.93; 69.45; 69.90; 70.59; 71.84; 97.42; 119.49; 124.55; 157.51. IR (neat, cm^{-1}) 3108; 2900; 1560; 1500.

3-(2-Methyl-1-butoxy)-4-methylthiophene (MBMT): yield: 28%. ^{1}H NMR (300 MHz, CDCl$_3$, ppm) 0.98 (t, 3H); 1.02 (d, 3H) 1.28 (m, 1H); 1.58 (m, 1H); 1.90 (m, 1H); 2.11 (s, 3H); 3.78 (m, 2H); 6.14 (d, 1H); 6.83 (d, 1H). ^{13}C NMR (75 MHz, CDCl$_3$, ppm) 11.37; 12.62; 16.56; 26.17; 34.73; 74.65; 95.70; 119.63; 129.22; 156.31. IR (neat, cm^{-1}) 3150; 2950; 1595; 1470; 1390; 1225; 1150; 1050; 720.

3-(2-Ethyl-1-hexyloxy)-4-methylthiophene (EHMT): yield: 31%. ^{1}H NMR (300 MHz, CDCl$_3$, ppm) 0.94 (t, 3H); 0.97 (t, 3H); 1.3–1.6 (m, 8H); 1.74 (m, 1H); 2.11 (s, 3H); 3.84 (d, 2H); 6.14 (d, 1H); 6.82 (d, 1H). ^{13}C NMR (75 MHz, CDCl$_3$, ppm) 11.16; 12.60; 14.02; 22.98; 23.96; 29.04; 30.60; 39.33; 72.32; 95.54; 119.53; 129.30; 156.38. IR (neat, cm^{-1}) 3150; 2950; 1470; 1390; 1225; 1150; 1050; 720.

The corresponding polymers (PMEEMT, PMBMT, and PEHMT) were chemically polymerized using iron trichloride as

oxidizing agent in chloroform.[33] The mixtures were stirred for 24 h at room temperature and then precipitated into methanol. The blue-black precipitates were collected on a Buchner funnel and washed with methanol. The polymers were subsequently washed by Soxhlet extraction using methanol and dried under reduced pressure. Undoped (neutral) polymers were obtained by reduction with an aqueous solution of hydrazine (Fisher Scientific Co.). These neutral polymers were dissolved in chloroform; then, the solvent was slowly evaporated to produce free-standing thin polymer films. These polymer films were purified again by Soxhlet extraction using methanol and finally dried under vacuum (50–70% yield). All poly(3-alkoxy-4-methylthiophene)s are completely soluble in chloroform or tetrahydrofuran, whereas only the low molecular weight fractions are soluble in acetone. NMR and IR spectra of the polymers were in good agreement with their expected structure. Typically, these polymers exhibit a number average molecular weight (M_n) of ca. 20 000 and a polydispersity index (M_w/M_n) of ca. 3, as determined by SEC measurements in THF using polystyrene standards.

98% head-to-tail poly(3-dodecylthiophene) (PT12R), 98% head-to-tail poly(3-hexylthiophene) (PT6R), and nonregioregular poly(3-hexylthiophene) (PT6NR) were obtained through catalyzed coupling reactions of regiospecific thiophene organozinc reagents.[34] These polymers are soluble in chloroform and tetrahydrofuran. From SEC measurements in THF against polystyrene standards, the poly(3-hexylthiophene)s have a M_n of ca. 5000 with a polydispersity index of ca. 4, whereas poly(3-dodecylthiophene) exhibits a M_n of 35 000 with a polydispersity index of 1.4. Poly(3',4'-dihexylterthiophene) (PTT66) was prepared by the chemical oxidation (using iron trichloride) of the corresponding trimer.[35] This polymer has a M_n of 9000 with a polydispersity index of 1.5.

Physical Methods. Infrared spectra were obtained by a Perkin-Elmer spectrophotometer (Model 783) using NaCl windows. NMR spectra were obtained in deuterated chloroform solutions on a 300 or 600 MHz Varian instrument. Differential scanning calorimetry (DSC) analyses were performed at 20 °C/min on a TA Instruments thermal analyst (Model 2910) calibrated with ultrapure indium. Solid-state UV–visible spectra were obtained using a Hewlett-Packard diode-array spectrophotometer (Model 8452A). A temperature control unit was installed to allow measurements over the range 25–250 °C. Low-temperature UV–visible absorption measurements (below 25 °C) were carried out on a Cary 5 UV–vis–NIR spectrophotometer equipped with a cryostat (Manchester Instruments Ltd.). 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 Kα radiation from a Rigaku rotating anode generator (Rotaflex RU200). Collimation was effected 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.

The ionochromic experiments have been carried out using 10^{-5} M solutions of PMEEMT in THF with different concentrations of KPF$_6$ (10^{-4}–10^{-6} M). Aliquots of each solution have been cooled in an acetone–dry ice bath for 5 min. The solutions were warmed to room temperature and their UV–vis spectrum then recorded.

Results and Discussion

Chemical oxidation of all 3-alkoxy-4-methylthiophenes has led to the preparation of soluble regioregular polymers with good mechanical properties. As an example, the ^{13}C NMR spectrum of PMEEMT shows four sharp peaks for the aromatic carbon atoms of the

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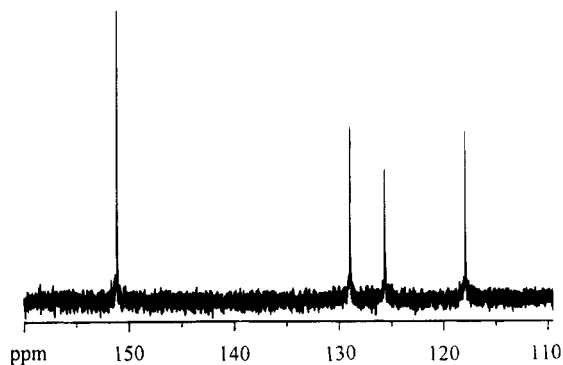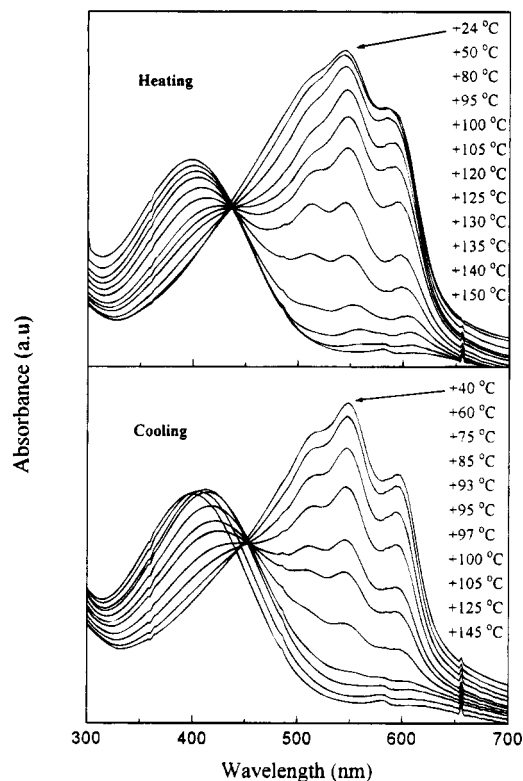
**Figure 1.** Aromatic region of a 150 MHz ^{13}C NMR spectrum of PMEEMT in CDCl$_3$.

thiophene ring (Figure 1). These results are consistent with a well-defined (>95%) head-to-tail structure.[33-38] Accordingly, ^{1}H NMR spectra of these polymers exhibit a well-defined and symmetric peak near 2.3 ppm (related to the protons of the methyl group at the 4-position) which indicates a regioregular substitution pattern along the main chain.[33] These features are characteristic of poly(3-alkoxy-4-methylthiophene)s[29b,33,36] and can be explained by an asymmetric reactivity of the oxidized monomers. It is interesting to note that this asymmetric reactivity of the oxidized monomers leads to some symmetry along the resulting polymer chain. This approach could be very useful for the easy design of regioregular polythiophenes bearing various functional groups. On the other hand, poly(3-alkylthiophenes) with only 80% of head-to-tail couplings result from a similar chemical oxidation using iron trichloride whereas highly regioregular poly(3-alkylthiophenes) can be obtained from other specific coupling procedures.[34,37,38]

Temperature-dependent optical measurements on PMEEMT were performed in the solid state, and the results are shown in Figure 2. A main absorption peak at 548 nm with two vibronic peaks at 516 and 604 nm are observed at room temperature which can be related to a planar (or nearly planar) conformation of the main chain. The presence of these well-defined vibronic peaks is another indication of the regioregularity of the polymer. Upon heating, a new absorption band appears at 398 nm at the expense of the 548 nm peak. A clear isosbestic point is observed, indicating the cooperative formation of delocalized conformational defects (twist-ons) upon heating. As shown in Figure 2, this thermochromic behavior is reversible but with some hysteresis. All these results are in marked contrast with those previously reported for similar compounds[39] and could result from a more regular structure.[19,33]

In correlation with these solid-state optical transitions, thermal transitions were observed by differential scanning calorimetry (DSC, Figure 3). Upon heating, a glass transition (near 40 °C) and a broad endothermic peak (between 75 and 135 °C) are observed, whereas an exothermic peak is observed between 100 and 50 °C upon cooling. Both peaks correspond to an enthalpic change of 0.7 kcal/mol of repeat unit, and on the basis

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Figure 2. Temperature-dependent UV−visible absorption spectra of PMEEMT in the solid state.
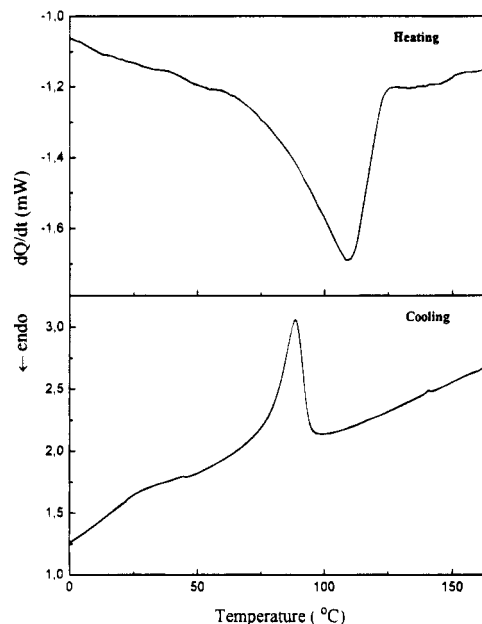
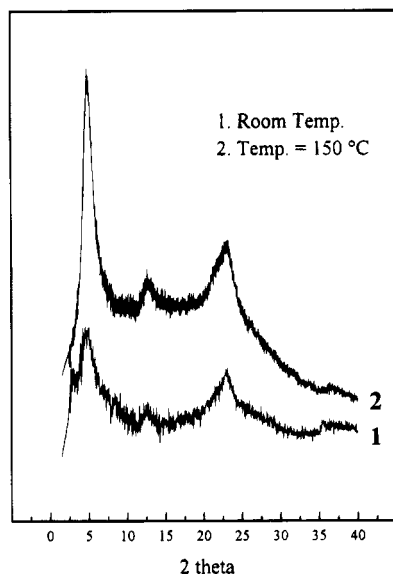**Figure 3.** DSC thermograms of PMEEMT.

of the results shown in Figures 2 and 3, it is quite evident that the thermochromic effects are directly related to these first-order-like transitions. X-ray diffraction measurements have revealed a rather amorphous structure in this polymer at room temperature which is not strongly affected by the temperature (indeed, a slightly more ordered lamellar structure is formed upon heating; Figure 4), and therefore the endothermic peak could be related to the cooperative twisting of the polymer backbone inducing a color change from a violet planar (or nearly planar) form to a yellow twisted form. These results are in good agreement with previous data reported for other amor-

Figure 4. Temperature-dependent X-ray diffraction diagrams of PMEEMT.
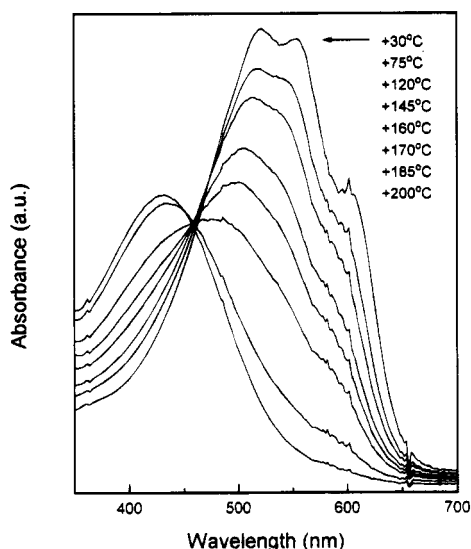
Figure 5. Temperature-dependent UV–visible absorption spectra of PT12R in the solid state (heating scan).

phous alkoxy-substituted polythiophenes[19] and polysilanes.[40,41] However, it is still intriguing to observe that regioregular poly(3-alkoxy-4-methylthiophene)s do not exhibit the expected long-range order and high conductivities,[33,36] whereas much more ordered lamellar structures have been observed in certain regioregular poly(3-alkylthiophenes).[34,42]

Regioregular and semicrystalline PT12R has been also investigated, and its solid-state thermochromic behavior is reported in Figure 5. A clear isosbestic point is also observed which indicates the coexistence of two distinct "chromophores" (conformational structures). However, the thermochromic transition is, in this case, strongly associated with the melting of the main polymer chain. Indeed, as previously observed from thermal and X-ray diffraction measurements[34,43-48] and as shown
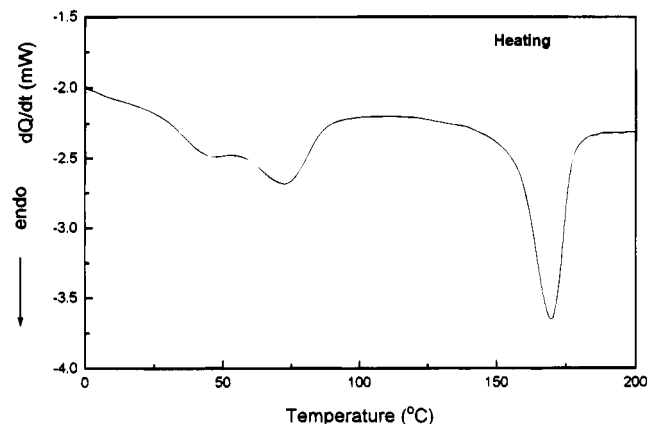
Figure 6. DSC thermogram of PT12R (heating scan).

in the present DSC analysis (Figure 6), semicrystalline PT12R shows multiple transitions upon heating. A second-order transition around +40 °C is believed to correspond to the glass transition of the polymer. The first broad endothermic peak (+75 °C) has been related to the disordering of the side chains (more than eight carbon atoms in the alkyl side chain being necessary to obtain side-chain transition in this class of materials) whereas the second endotherm (+170 °C) is related to the melting of the main chain.[34,43-48] However, from optical measurements, it is evident that the disordering of the side chains does not lead to any important chromic effects; it is only when the main conjugated chains melt that concomitant abrupt thermochromism is observed.

From these two examples, it is clear that the cooperative twisting of the main polymer chain can take place only at a temperature higher than the glass transition for an amorphous phase and above the melting temperature for a crystalline phase.[35a] On the other hand, it is worth noting that the regioregularity of the main chains is of first importance. As reported in Figure 7, nonregioregular (50% head-to-tail) PT6NR does not exhibit any cooperative thermochromic transition, whereas 70% poly(3-pentylthiophene) (PT5),[16b] 80% PT6,[16a] and 98% head-to-tail PT6R (not shown here) do. Therefore, although cooperative thermochromic effects are not necessarily driven by side-chain crystallization or even main-chain crystallization, a quite regioregular bonding seems to be an important prerequisite.

As mentioned in the introduction section, similar thermochromic properties should be observed for these materials in solution. As shown in Figure 8, 98% head-to-tail PT6R (as well as PT12R and PMEEMT) exhibits a well-defined thermochromic transition in dilute tetrahydrofuran solutions, whereas nonregioregular PT6NR shows only a weak and monotonic red shift upon cooling (Figure 9). In all cases, no dependence upon the polymer concentration (between 10^{-6} and 10^{-4} M) was observed which is suggestive of a single-chain phenom-

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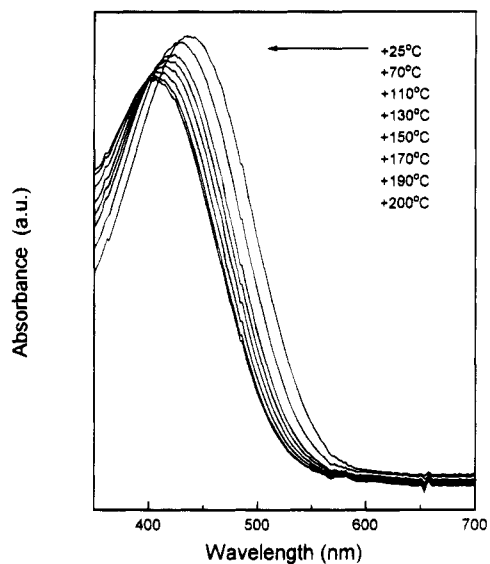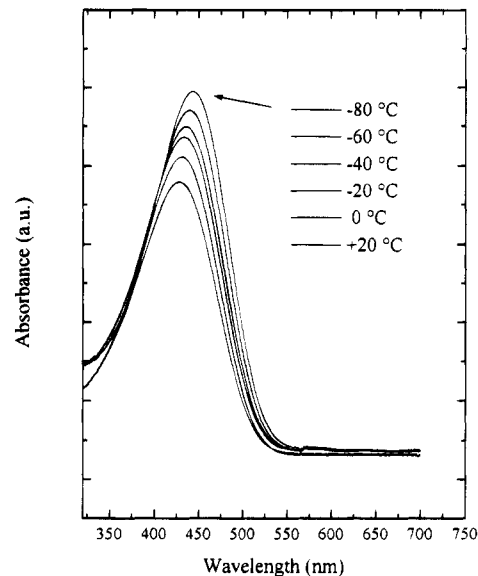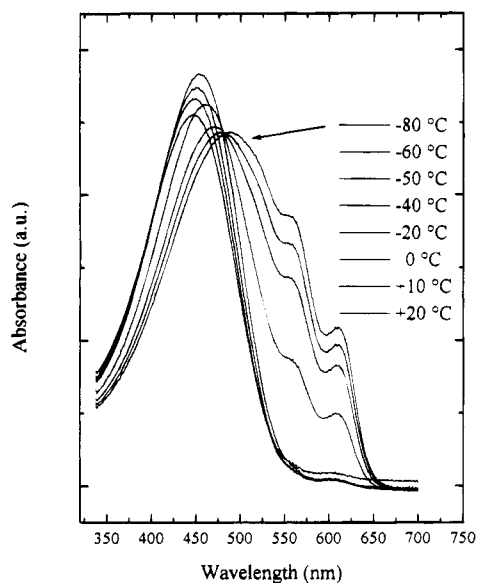(48) Bolognesi, A.; Porzio, W.; Provasoli, F.; Ezquerra, T. *Makromol. Chem.* **1993**, *194*, 817.

Figure 7. Temperature-dependent UV–visible absorption spectra of nonregioregular PT6NR in the solid state (heating scan).

Figure 9. Temperature-dependent UV–visible absorption spectra of nonregioregular PT6NR in tetrahydrofuran (cooling process).

Figure 8. Temperature-dependent UV–visible absorption spectra of regioregular PT6R in tetrahydrofuran (cooling process).
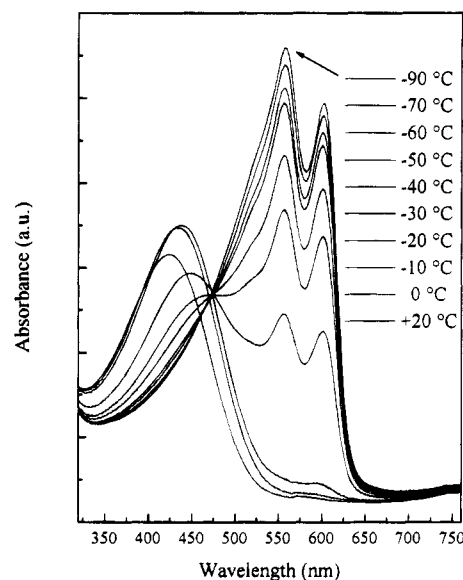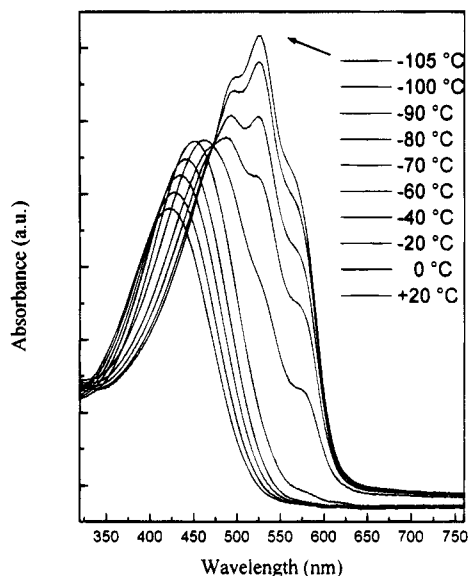

Figure 10. Temperature-dependent UV–visible spectra of high molecular weight PMEEMT in tetrahydrofuran (cooling process).

enon. Similar conclusions were previously reported for polythiophenes,[15,29,36] polysilanes,[23] and polydiacetylenes.[26]

To a first approximation, this single-chain phenomenon could consist of a kind of chain folding of the polymer chain upon cooling to adopt a lamellar-like (but not necessarily crystalline) structure similar to that found in the solid state. This chain folding would be comparable to the formation of bilayers in biomolecules and would be related to a self-assembly of the side chains made possible by the presence of a regioregular substitution pattern along the conjugated backbone. To test this hypothesis, the solution thermochromic properties of both high (chloroform soluble fraction) and low (acetone soluble fraction) molecular weight samples of PMEEMT have been studied (Figures 10 and 11). Both samples showed similar thermochromic effects but over very different temperature ranges. These results are in agreement with an intramolecular collapse of the
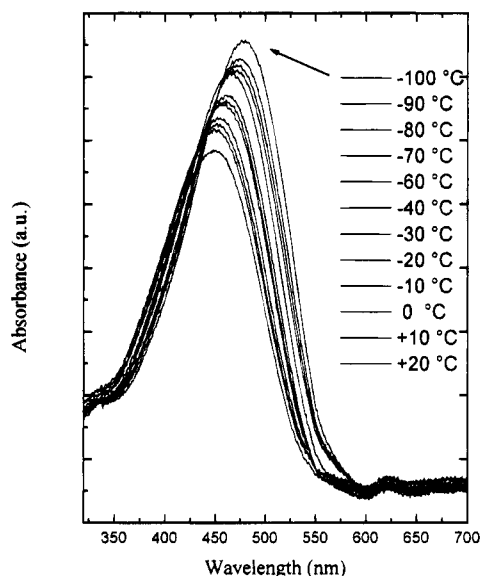
molecules where longer polymer chains show a higher propensity to chain folding than shorter ones. On the other hand, this intramolecular collapse could be related either to π-stacking of the thiophene rings or to the occurrence of noncovalent interactions between the substituents. To check this point, the thermochromic properties of PTT66 have been investigated in tetrahydrofuran (Figure 12). Although symmetric (but not with a regioregular head-to-tail structure), this polymer exhibits only a monotonic red shift of its maximum of absorption upon cooling. All these results seem to indicate that the cooperative formation of long sequences of coplanar (or nearly planar) thiophene units is mainly related to the presence of a regular head-to-tail substitution pattern. However, interdigitation of the side chains is certainly not an important criterion in this case, since thermochromic effects were also observed in regioregular polymers with branched side chains such as PEHMT (Figure 13) and PMBMT.

Regioregular and Nonregioregular Polythiophene Derivatives

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Figure 11. Temperature-dependent UV–visible absorption spectra of low molecular weight PMEEMT in tetrahydrofuran (cooling process).
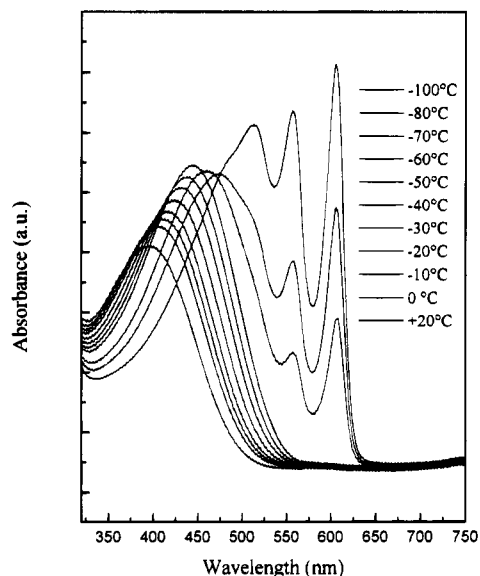
Figure 13. Temperature-dependent UV–visible absorption spectra of PEHMT in tetrahydrofuran (cooling process).

mental studies on model compounds (oligomers)[54] are needed to bring more information about the driving force of this transition.

On the other hand, in principle, with the presence of chelating side chains, it should be possible to enhance the interaction between the side chains through the addition of ionic species and thus stabilize the planar and ordered form of the polymer. This effect was studied on PMEEMT which should be sensitive to the presence of alkali-metal ions. As reported in Figure 10, pure PMEEMT undergoes a reversible nonplanar to planar transition in THF upon cooling. Upon the addition of various proportions of K^+, cooling to -70 °C for 5 min and coming back to room temperature, the ratio between the nonplanar and planar forms has been found to be dependent upon the K^+ concentration (Figure 14). It was found that the cooling procedure is required to observe this effect in this polymer, probably because of the necessity of inserting the ionic species in preorganized side chains. The nature and size of the ionic species along with that of the side chains may allow the tuning of this ionochromic effect. In contrast to previous studies where the presence of ionic species modified the average conformation of ether-substituted polythiophenes,[55,56] this process stabilizes long sequences of planar repeat units. Obviously, this approach can lead to a colorimetric determination of various chemical and biochemical species.[57] Different studies are currently being carried out based on this approach.

Figure 12. Temperature-dependent UV–visible absorption spectra of PTT66 in tetrahydrofuran (cooling process)

Another possible explanation for this phenomenon could come from the model developed by Schweizer.[49–51] According to this model, a conformational transition of the conjugated backbone is induced by a competition between attractive dispersion interaction (V_D) for the fully ordered chains and the rotational defect energy (ϵ). It is also proposed that depending upon the V_D/ϵ ratio, either cooperative twisting or weak and localized rotational defects can be created along the conjugated backbone upon heating. However, this model implies that the ordered and planar form is thermodynamically more stable, which is not obvious for substituted polythiophenes.[52,53] Clearly, further theoretical and experi-

Conclusions

Structural, thermal and optical measurements (both in the solid state and in solution) on regioregular poly-(3-alkoxy-4-methylthiophene)s and poly(3-alkylthiophe-

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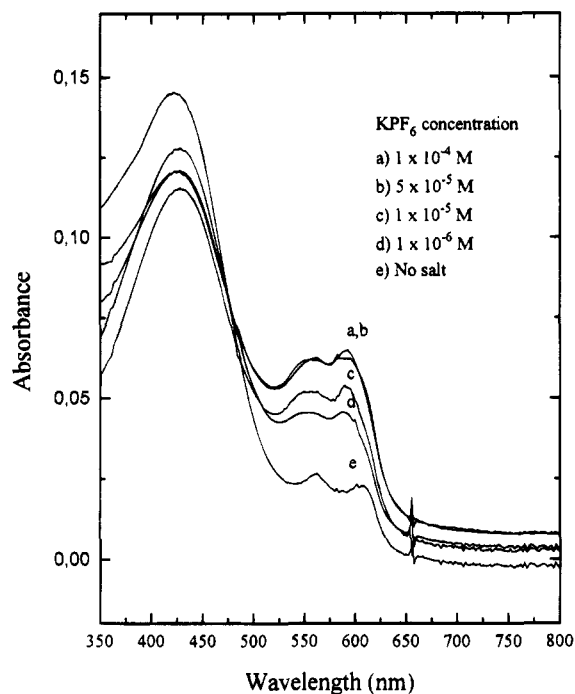(52) Cui, C. X.; Kertesz, M. *Phys. Rev.* **1989**, *B40*, 9661.
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Figure 14. UV–visible absorption spectra of PMEEMT (1 × 10^{-5} M) in tetrahydrofuran with different KPF_6 concentrations.

nes)s have revealed a first-order-like conformational transition of the thiophene backbone (formation of twistons) which leads to important thermochromic effects. This transition is not necessarily driven by side-chain or main-chain crystallization and have even been observed in amorphous poly(3-alkoxy-4-methylthiophene)s bearing branched side chains. However, nonregioregular polythiophene derivatives showed only the formation of weak and localized conformational defects. Clearly, this intriguing conformational transition is related to a single-chain phenomenon which is strongly dependent upon the substitution pattern. Finally, it is believed that this conformational transition can be induced via a large range of external stimuli and, consequently, can lead to novel chromic (ionochromic, photochromic, chemichromic, etc.) effects.