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Rod-to-Coil Transition in Alkoxy-Substituted Polythiophenes

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ABSTRACT: Temperature-dependent UV–visible absorption measurements have revealed reversible thermochromic effects (a 0.95-eV shift in the maximum of absorption) in amorphous poly[3-(octyloxy)-4-methylthiophene] (POMT). The presence of a solid-state "phase" transition was also confirmed by infrared and calorimetric analyses. All these experimental results are consistent with a conformational transition of the conjugated polymer chain from a coplanar (rod) structure at room temperature to a nonplanar (coil) form at 150 °C. According to theoretical calculations, the less conjugated form of POMT can be related to the presence of a torsion angle of ±45° between each consecutive repeat unit.

I. Introduction

In the last decade, conducting polymers have attracted great interest because of their unusual electrical, electrochemical, and optical properties.[1] Recent progress in the synthesis of new soluble conducting polymers, such as substituted polythiophenes,[2–6] polypyrroles,[6,7] poly(phenylenevinylenes),[8,9] and polyanilines[10,11] have particularly had a large impact on the study of electroactive polymers. The solubility and stability of these aromatic polymers not only allow a more complete characterization of their chemical structure but also enlarge their possibilities for industrial applications. Moreover, by the addition of different substituents, it may be possible to develop materials with improved electrical properties.

In addition to their high electrical conductivities, some polythiophene derivatives exhibit interesting reversible thermochromic,[12] solvatochromic,[13] and piezochromic[14] properties. These optical phenomena are not unique to polythiophenes and have also been reported for some polysilanes[15–17] and polydiacetylenes.[18,19] These dramatic color transitions (chromism) are associated with conformational changes since, in σ- and π-conjugated polymers, there is a strong coupling between the electronic structure and the backbone conformation.[20,21] Many studies have been carried out to explain these optical transitions, and most of them have related the color changes to an order–disorder (rod-to-coil) transition in which the planarity of the conjugated backbone is partly lost.[12,22–24]

However, no detailed descriptions of the energy and torsion angles involved in this transition have yet appeared, and, therefore, we report here some calorimetric and spectroscopic analyses on a new polythiophene derivative (e.g., poly[3-(octyloxy)-4-methylthiophene]) which give more insight into the nature of the conformational changes that accompany these thermochromic effects.

II. Experimental Section

A. Materials. Samples of poly[3-(octyloxy)-4-methylthiophene] (POMT) were chemically prepared according to the methods reported by Daoust and Leclerc.[5] The resulting blue-black doped material was reduced by using an aqueous solution of hydrazine (2% w/w). After this treatment, the neutral red-violet polymer was found to be soluble in common organic solvents (e.g., chloroform, tetrahydrofuran, toluene). NMR and IR spectra of the polymer were in good agreement with its expected structure. The molecular weight distribution was determined by size-exclusion chromatography (Waters 510) in tetrahydrofuran solution using Ultrastyragel columns calibrated with polystyrene standards. Typically, the POMT samples had a monomodal molecular weight distribution with a number-average molecular weight (M_n) of 20 000 and a polydispersity (M_w/M_n) of about 3. The neutral polymer was stable in air but must be stored in the dark.

B. Methods. Differential scanning calorimetry (DSC) analyses were performed on a Perkin-Elmer DSC-4 apparatus calibrated with an ultrapure indium (T_m = 156.6 °C and ΔH_m = 28.4 J/g) sample. Scan rates ranging from 5 to 80 °C/min were used, and transition temperatures were reproducible to ±2 °C. After removal of trace amounts of solvent during the first scan, subsequent scans gave identical results within experimental error. The enthalpies of transition were calculated by digitally integrating the area of the endotherms and exotherms and expressing these values in units of kilocalories per mole of repeat unit. Optical absorption spectra were taken from neutral polymer films cast on quartz plates from dilute solutions. The UV–visible spectroscopic measurements were carried out using a Hewlett-Packard diode array spectrophotometer (Model 8452 A) into which a temperature control unit was installed to allow measurements over a range from 25 to 200 °C. The sample temperature was measured by a thermocouple with a maximum error of ±2.0 °C. Heating and cooling rates were always close to 2.0 °C/min. Variable-temperature infrared spectra were obtained on a Bomem Fourier transform infrared (FTIR) spectrophotometer (Model DA 3) equipped with a temperature control unit similar to that used for the optical measurements. In this case, the temperature was increased stepwise. X-ray diagrams of unoriented polymer films were obtained at room temperature using a Warhus camera and Ni-filtered Cu Kα radiation.

III. Results

Figure 1 shows the UV–visible absorption spectra of poly[3-(octyloxy)-4-methylthiophene] (POMT) obtained upon heating between 25 and 150 °C. At 25 °C, POMT exhibits an absorption maximum at 548 nm and two other well-resolved absorption peaks at 598 and 520 nm, the absorption onset occurring near 640 nm. Upon heating, POMT samples did undergo an abrupt color change (from red-violet to pale yellow), the maximum of absorption shifting from 548 (2.26 eV) to 386 nm (3.21 eV). This optical transition is reversible (with the presence of hysteresis), and, upon cooling, thin polymer films recovered their initial color (Figure 2). The presence of an isosbestic point in these temperature-dependent spectra seems to indicate the coexistence of two phases, but it is impossible to determine whether these two phases are on different parts of the same polymer chain or on different polymer chains. The absorbance at the maximum of absorption (548 nm) of POMT was also recorded as a function of temperature, and, as reported in Figure 3, most important changes appeared between 105 and 145 °C in the heating scan and between 115 and 75 °C in the cooling process.

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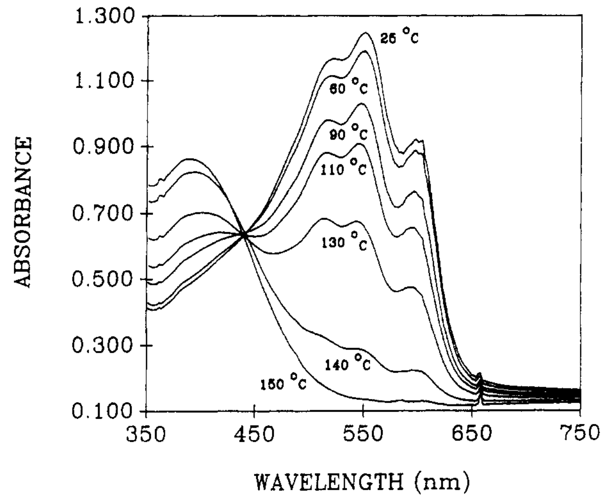

Figure 1. Temperature-dependent UV–visible absorption spectra of POMT in the solid state (heating scan).

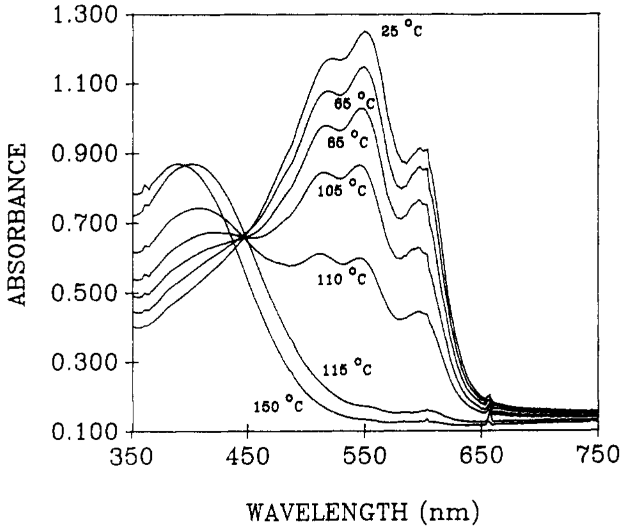

Figure 2. Temperature-dependent UV–visible absorption spectra of POMT in the solid state (cooling scan).

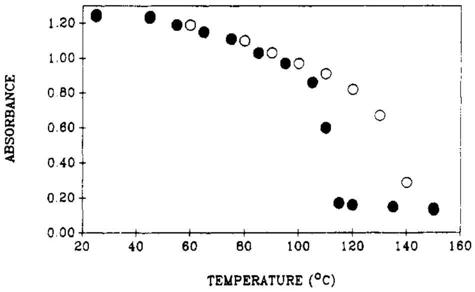

Figure 3. Temperature dependence of the absorbance at 548 nm for POMT in the solid state: (○) heating scan; (●) cooling scan.

In correlation with these optical changes, calorimetric effects were observed in POMT. As shown in Figure 4 (heating scan), the DSC curve exhibits a glass transition near 12 °C and a large endothermic peak between 105 and 145 °C. This transition cannot be attributed to the melting of any crystalline phase since X-ray diffraction measurements have revealed an amorphous structure for this unsymmetrically substituted polythiophene. Moreover, this first-order-like transition is reversible since upon cooling, an exothermic peak is observed between 115 and 75 °C (Figure 5). The endothermic peak did not show any heating rate dependence whereas the exothermic peak shifted from 90 to 105 °C by varying the scan rate from 80 to 5 °C/min. By comparing the DSC curves (Figures 4 and 5) with the optical analyses (Figure 3), it is clear that the calorimetric measurements are only sensitive to the presence of relatively important conformational changes within a narrow temperature range. Indeed, the DSC curves could be related to the derivative of the curves shown in Figure 3. On the basis of the optical results, it was calculated that 75% of the repeat units undergo a phase transition between 105 and 145 °C upon heating while, between 115 and 75 °C, 83% of the thiophene units are involved in the cooling process. Taking into account these calculations, integration of both endothermic and exothermic peaks gives an enthalpy of transition of 0.9 ± 0.1 kcal/mol of repeat unit.

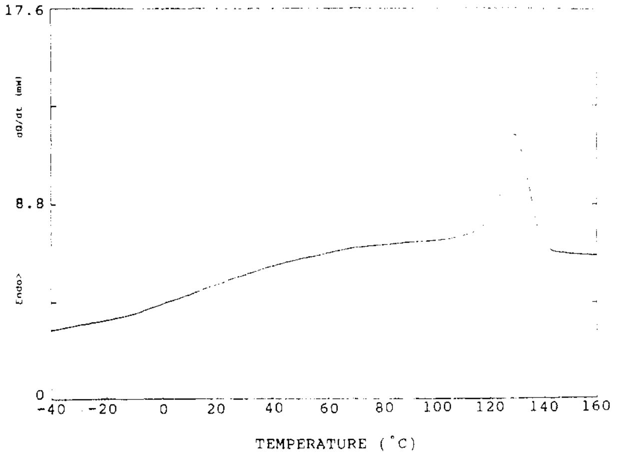

Figure 4. DSC thermogram of POMT obtained upon heating at 40 °C/min.

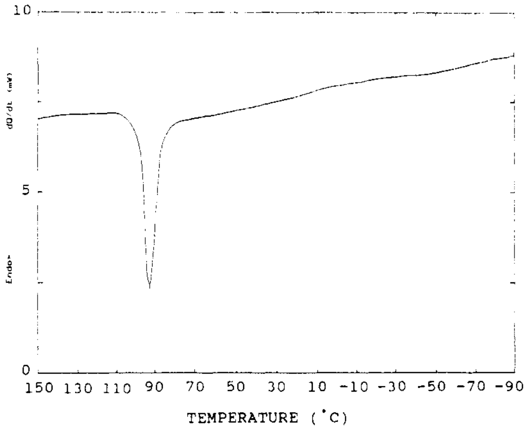

Figure 5. DSC thermogram of POMT obtained upon cooling at 40 °C/min.

In order to obtain more information on this phase transition, temperature-dependent infrared spectroscopy experiments were also performed. As shown in Figure 6, most pronounced changes appeared between 90 and 130 °C. The low-temperature (50 °C) FTIR spectrum is consistent with the presence of a regular and highly conjugated thiophene backbone; three absorption bands are related to the thiophene ring stretching modes appearing at 1468, 1510, and 1564 cm^{-1}. Similar infrared bands were also reported for the low-temperature phase of poly(3-alkylthiophenes).[25] Upon heating, the 1510- and 1564-cm^{-1} bands decreased in intensity while the 1468-cm^{-1} peak remained almost unchanged. These features are consistent with thermally induced rotational defects along the thiophene backbone. Indeed, the infrared spectrum of poly[3-octyl-4-methylthiophene] (not shown here), which is not planar at any temperature due to severe steric

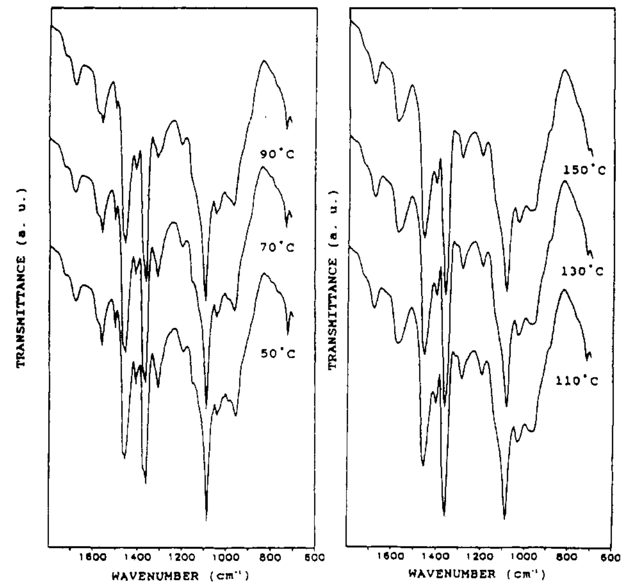

Figure 6. Temperature-dependent FTIR spectra of POMT in the solid state (heating scan).

interactions,[26] shows one broad band at 1460 cm^{-1} and no absorption bands near 1510 and 1564 cm^{-1}. Moreover, temperature-dependent infrared measurements on poly(3-alkylthiophenes)[27-29] also revealed a decrease of the oscillator strength of the ring stretching modes near 1510 and 1564 cm^{-1}. In addition to this order–disorder transition of the thiophene backbone, an increase of the conformational defects within the side chains was also observed. As reported in Figure 6, upon heating, the methylene rocking band at 720 cm^{-1} (which is intense for the trans sequence) decreased strongly in intensity while, simultaneously, the intensity of the 1200-cm^{-1} band increased. This last absorption band is due to twisting and rocking of the methylene groups.[27] These results corroborate those reported by Zerbi et al.[29] on poly(3-alkylthiophenes), which indicated an increase of the disorder in both the side groups and the main chain upon heating.

IV. Discussion

All these calorimetric and spectroscopic measurement samples are consistent with the presence of a solid-state order–disorder transition in POMT. Although the detailed conformational structure of the amorphous POMT could not be determined, its relatively low energy band gap and oxidation potential had led to the conclusion that this polymer must exist in a planar or nearly planar conformation at room temperature.[5] In fact, recently, X-ray diffraction measurements have revealed an anti coplanar conformation for poly(3-alkylthiophenes) at low temperatures,[30,31] and it is assumed that a similar conformation can also be adopted by POMT at room temperature, which is characterized by a maximum of absorption at 548 nm. Upon heating, a strong blue shift of the first optical transition (from 548 nm (2.26 eV) to 386 nm (3.21 eV)) was observed, and this behavior can be attributed to the formation of rotational defects which perturb the conjugation along the polymer chain. Brédas et al.[20] have analyzed the evolution of the electronic properties of polythiophene as a function of the torsion angle between adjacent repeat units, and, on the basis of those calculations, the 0.95-eV shift in the optical absorption maximum of POMT can be related to a solid-state order–disorder transition from a coplanar (rod) conformation at room temperature to a nonplanar (coil) form at 150 °C, characterized by a torsion angle of ±44° between each consecutive repeat unit.

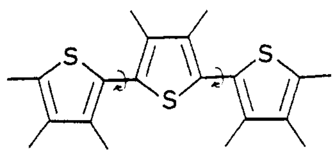

Figure 7. Schematic illustration of the conformational structure of the POMT backbone at high temperature (150 °C).

Moreover, these theoretical analyses can also be useful to analyze the conformation of polythiophene derivatives in solution. As previously reported by several authors,[12,25,32] at room temperature, poly(3-alkylthiophenes) exhibit a maximum of absorption near 510 nm (2.43 eV) in the solid state while they show an absorption maximum around 435 nm (2.85 eV) in solution (chloroform, tetrahydrofuran). Based on the previous theoretical calculations and neglecting any effect of the solvent on the position of the maximum of absorption, this 0.42-eV difference in the first optical absorption can be related to a torsion angle of 29° between each monomeric unit. This calculated torsion angle can be compared to recent neutron scattering measurements which have revealed a statistical length of 4.5 nm for poly(3-butylthiophene) in tetrahydrofuran at room temperature.[33] Using the Porod–Kratky model,[34] the statistical length (b) can be related to an angular deviation (θ) between neighboring monomer units. This is given by

$$b = 2a/(1 - \langle \cos \theta \rangle) \qquad (1)$$

where a is the monomer unit length. On the basis of X-ray diffraction measurements,[30,31] the monomer unit length was taken as 0.39 nm. Using this model, a torsion angle of 34° was found which is in good agreement with the previous theoretical calculations.

From these examples, it is then clear that the torsion angle of ±44° between each repeat unit calculated for the high-temperature form of POMT is reliable, and, moreover, this value is consistent with the calorimetric measurements. Indeed, the DSC curves have clearly indicated the presence of a first-order-like transition with an enthalpy of transition of about 0.9 kcal/mol. Recently, theoretical investigations have been carried out by Brédas and Heeger[35] on the gas-phase torsion potential of thiophene oligomers, and their calculations have clearly shown that the anti conformation is the most stable form, with an energy barrier for conversion to the syn conformation of about 3 kcal/mol. On the basis of these theoretical calculations, an energy of 0.9 kcal/mol corresponds to a torsion angle of 47°, which is in good agreement with the optical results. However, it must be noted that these calculations do not include any structural modification of the side chains. The infrared spectroscopy measurements have shown that this is not the case, but, on the other hand, the amount of energy transferred to the substituents during the phase transition is difficult to assess.

From all these considerations, it is then assumed that the thermochromic effect observed in POMT is related to a phase transition from an anti coplanar structure to a nonplanar conformation. This conformational transition is analogous to the helix–coil transition observed in biopolymers:[36] the more ordered rod has a lower internal energy, but the more disordered form has a greater entropy; therefore, at high temperatures, the latter structure has the lower free energy. The conformation of the polymer in the high-temperature phase can be compared to the form of a wormlike (Porod–Kratky) coil, the backbone being continuously deformed by an angle of about ±45° between each thiophene ring (Figure 7). The driving force of this thermochromic transition is still unclear, but the presence of an isosbestic point in the optical measurements seems to indicate that these rotational defects are created in a cooperative way, involving long sequences of thiophene units. Schweizer[37] has recently proposed that this conformational transition could be induced by attractive dispersion interactions between the delocalized electrons of the polymer backbone and the surrounding polarizable medium (including side chains). In order to verify this theory, various alkyl- and alkoxy-substituted polythiophenes are currently analyzed as well as low molecular weight model compounds.

V. Conclusion

Calorimetric and spectroscopic measurements have revealed the presence of a reversible solid-state phase transition in amorphous poly[3-(octyloxy)-4-methylthiophene] (POMT). On the basis of these experimental results and theoretical calculations, this first-order-like transition was related to a conformational change of the polymer chain from a coplanar (rod) geometry at low temperatures to a nonplanar (coil) conformation at 150 °C, characterized by a torsion angle of about ±45° between each consecutive repeat unit. The formation of these thermally induced rotational defects decreases the effective conjugation length along the thiophene backbone, and, therefore, the rod-to-coil transition of POMT is accompanied by color changes (chromism) from red-violet to pale yellow.

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