

Thermochromic Properties of Polythiophene Derivatives: Formation of Localized and Delocalized Conformational Defects

Claudine Roux and Mario Leclerc*

Département de Chimie, Université de Montréal, Montréal, Québec, Canada H3C 3J7

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Temperature-dependent UV-visible absorption measurements in the solid state and in solution have been performed on poly(3-butoxy-3'-decyl-2,2'-bithiophene) (PBDBT), poly(3-dodecyl-2,2'-bithiophene) (PBT12), poly(3-(octyloxy)-4-methylthiophene) (POMT), and poly(3-dodecylthiophene) (PT12). These measurements revealed the existence of two different types of thermochromism which are correlated to the substitution pattern of the polymers. A "two-phase" thermochromic behavior was found in POMT and PT12 and was related to the formation of delocalized conformational defects (twistons) upon heating. The formation of such twistons is made possible by the presence of sterically demanding substituents between each consecutive repeat unit. In contrast, the partially substituted structure of PBDBT and PBT12 allows only the formation of localized conformational defects along the polymer backbone leading to a continuous and monotonic blue shift of the absorption maximum upon heating.

Introduction

Since the discovery that unsubstituted polyacetylene can be doped to yield high electrical conductivities,¹ many studies have been devoted to conjugated polymers.² However, characterization and processing of this novel class of materials have been limited by their inherent insolubility. Their rigid-rod nature combined with strong interchain interactions prevents their melting as well as their dissolution in common organic solvents. The recent development of substituted polythiophenes,³⁻⁸ polypyrroles,^{7,9} poly(phenylenevinyls),^{10,11} and polyanilines^{12,13} have produced processable electroactive polymers which are particularly promising for many electrical and electrochemical applications.

Moreover, the presence of flexible side chains not only enhance the solubility of conjugated polymers but also can lead to novel optical effects. Indeed, in addition to their high electrical properties in the oxidized state, some

neutral polythiophene derivatives show reversible color changes, such as solvatochromism, piezochromism, and thermochromism,¹⁴⁻¹⁶ which are not found in the unsubstituted polythiophene. Some polydiacetylenes^{17,18} and polysilanes¹⁹⁻²¹ are also known to exhibit similar properties. These unusual optical effects are believed to be associated with a conformational modification of the main polymer chain since, in σ - and π -conjugated systems, there is a strong correlation between the electronic structure and backbone conformation.²²⁻²⁴ On the basis of FTIR measurements, it has been proposed that these optical effects are induced by an increase of disorder (i.e., gauche conformations) in the side chains which then forces the twisting of the main conjugated chain and, consequently, to a decrease of the conjugation length.^{25,26} This mechanism is also supported by recent studies on various polythiophene derivatives which have shown that, in the absence of sterically demanding substituents, the polythiophene backbone can retain a highly conjugated structure even at high temperatures.²⁷

* To whom correspondence should be addressed.

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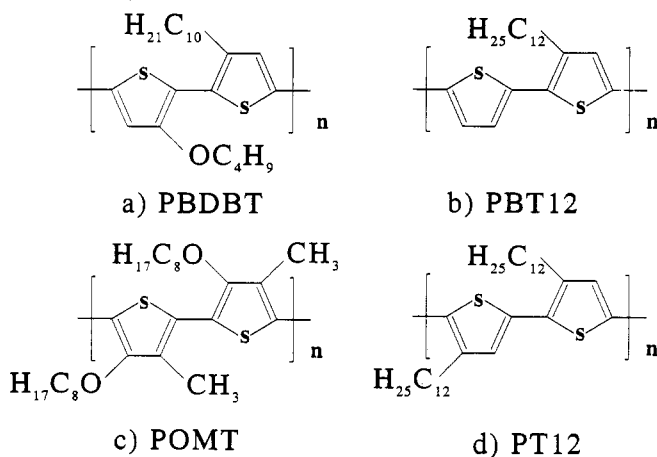


Figure 1. Scheme of the repeat unit of (a) poly(3-butoxy-3'-decyl-2,2'-bithiophene), (b) poly(3-dodecyl-2,2'-bithiophene), (c) poly(3-(octyloxy)-4-methylthiophene), and (d) poly(3-dodecylthiophene).

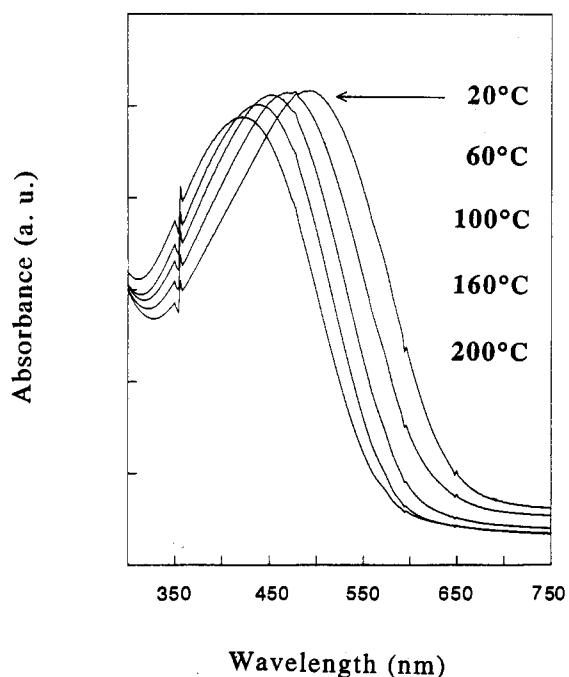


Figure 2. Temperature-dependent UV-visible spectra of PBDBT in the solid state.

On the other hand, many temperature-dependent UV-visible absorption measurements on semicrystalline poly(3-alkylthiophenes) and amorphous poly(3-alkoxy-4-methylthiophenes) in the solid state have revealed the presence of a well-defined isobestic point, indicating the coexistence of only two distinct forms for these polymers.^{6,15,25-29} This behavior seems to indicate that the conformational defects are created in a cooperative way, involving long sequences of thiophene units. However, it must be noted that these "cooperative" thermochromic effects take generally place over large temperature ranges (ca. 100–150 °C). To obtain a better understanding of the mechanisms involved in these thermochromic effects, we report here a detailed analysis of the optical properties of several polythiophene derivatives, namely, poly(3-butoxy-3'-decyl-2,2'-bithiophene), poly(3-dodecyl-

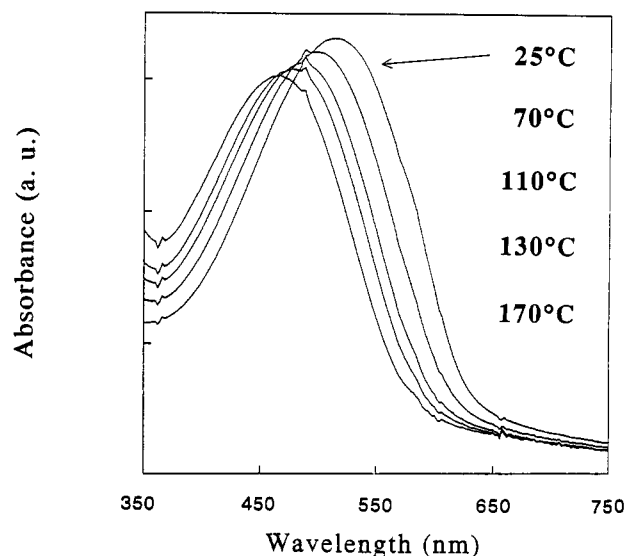


Figure 3. Temperature-dependent UV-visible spectra of PBT12 in the solid state.

2,2'-bithiophene), poly(3-(octyloxy)-4-methylthiophene), and poly(3-dodecylthiophene) (Figure 1). This study shows clearly the strong influence of the substitution pattern on the propagation of these conformational defects along the conjugated backbone.

Experimental Section

Materials. Poly(3-butoxy-3'-decyl-2,2'-bithiophene)⁸ (PBDBT), poly(3-dodecyl-2,2'-bithiophene)³⁰ (PBT12), poly(3-(octyloxy)-4-methylthiophene)⁶ (POMT), and poly(3-dodecylthiophene)³¹ (PT12) were prepared by chemical polymerization of their respective monomer or dimer unit in chloroform solution using iron(III) chloride as oxidizing agent. The resulting polymers were reduced in an aqueous solution of hydrazine (2 wt %) and were found to be soluble in common organic solvents (tetrahydrofuran, chloroform, toluene, etc.); all neutral polymers were kept in the dark. Typically, polymer exhibited a number-averaged molecular weight of ca. 20 000 and a polydispersity index of ca. 3.

Methods. Solid-state UV-visible absorption measurements were performed on a Hewlett-Packard diode array spectrophotometer (Model 8452 A). A temperature control device going from 25 to 200 °C was included in the spectrophotometer; the temperature was increased stepwise.²⁶ Low-temperature UV-visible absorption measurements (below 25 °C) were performed on a Cary 5 UV-vis-NIR spectrophotometer equipped with a cryostat (Manchester Instruments Ltd). All polymer solutions were prepared in THF and their concentrations did not exceed 5×10^{-5} M. In all cases, absorbance was lower than unity. Before each absorption spectrum was recorded, the polymer sample was kept at the desired temperature for 5 min. Differential scanning calorimetry (DSC) analyses were performed at 80 °C/min on a Perkin-Elmer DSC-4 apparatus calibrated with an ultrapure indium ($T_m = 156.6$ °C and $\Delta H_m = 28.4$ J/g) sample. After removal of traces of solvent during the first scan, the next scans were identical, within experimental error. X-ray diagrams of unoriented polymer films were obtained using a Warhus camera and Ni-filtered Cu K α radiation.

Results

Figures 2 and 3 show the temperature dependence of the UV-visible absorption spectrum of poly(3-butoxy-3'-decyl-2,2'-bithiophene) (PBDBT) and poly(3-dodecyl-2,2'-bithiophene) (PBT12) respectively, in the solid state. In

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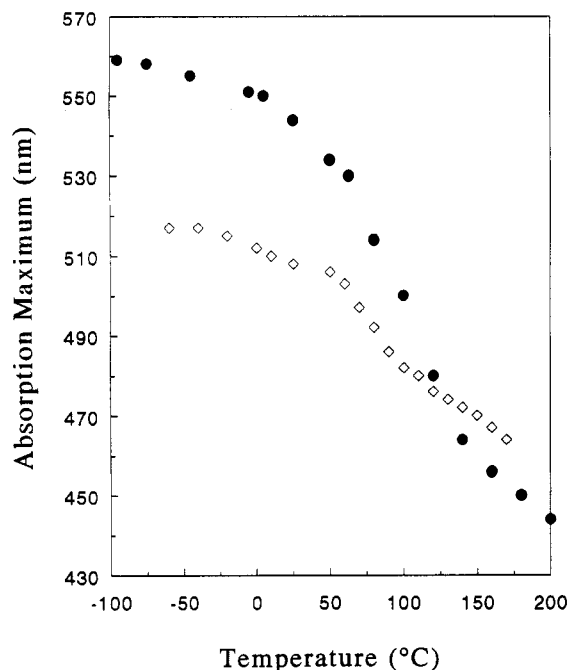


Figure 4. Variation of the absorption maximum in the UV-visible range of PBDBT (●) and PBT12 (◇) as a function of temperature, in the solid state.

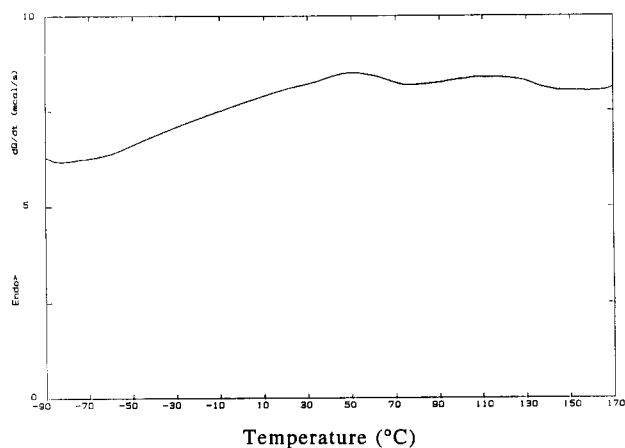


Figure 5. Differential scanning calorimetric (DSC) thermogram of PBDBT (heating scan).

both cases, the absorption maximum undergoes a blue shift upon heating (the red polymers becoming yellow), indicative of a decrease of the conjugation length. However, no isosbestic point is observed in these measurements, and therefore this phenomenon cannot be described as an equilibrium between only two distinct phases but rather as a continuous modification of the polymer backbone. Moreover, these modifications of the conjugated main chain must imply the creation of rotational defects (twisting) between some repeat units to take into account the blue shift of the absorption maximum upon heating. Figure 4 exhibits the variation of the maximum of absorption for these two polymers between -100 and 200 °C. In both cases, most important variations of the absorption maximum take place between 25 and 125 °C. These thermochromic effects have been found to be fully reversible with no hysteresis phenomenon.³²

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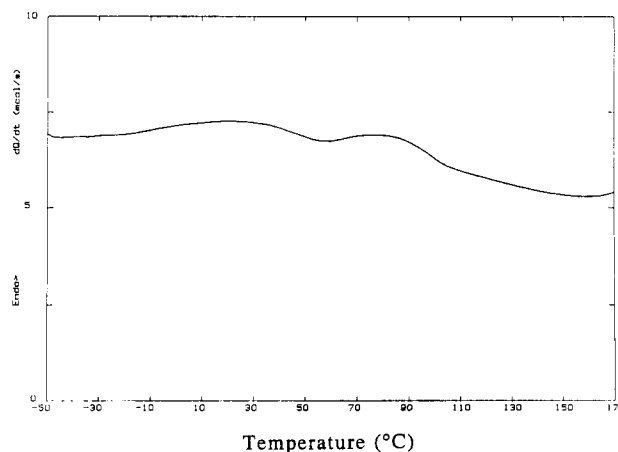


Figure 6. Differential scanning calorimetric (DSC) thermogram of PBT12 (heating scan).

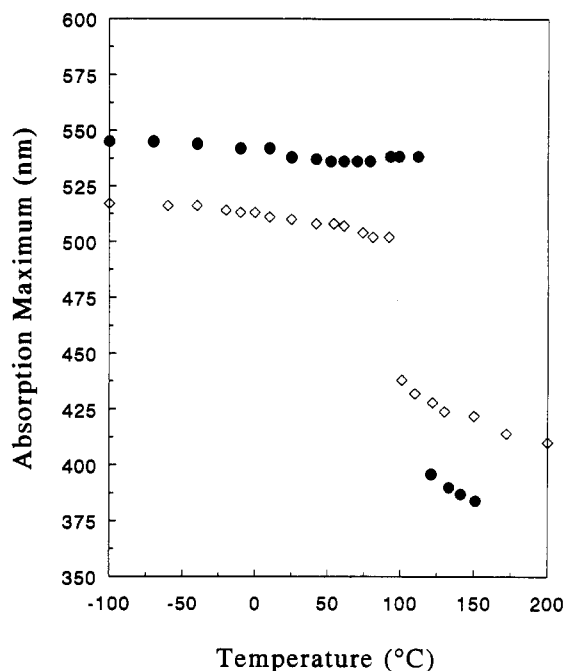


Figure 7. Variation of the absorption maximum in the UV-visible range of POMT (●) and PT12 (◇) as a function of temperature, in the solid state.

X-ray diffraction measurements have been performed on PBDBT and have revealed very weak diffraction peaks at 16.3 , 17.9 , 19.8 , and 23.8° . In agreement with this very low degree of crystallinity, calorimetric (DSC) measurements on PBDBT have shown two weak and broad endotherms: one situated between 35 and 70 °C and the second one between 85 and 145 °C (Figure 5). On the basis of previous results obtained on semicrystalline poly-(3-alkylthiophenes),³³⁻³⁵ the former endotherm can be attributed to the melting of some crystallized side chains and the latter to the melting of the main polymer chains. PBT12 exhibits a similar thermal behavior with two weak endotherms centered at 30 and 80 °C, respectively (Figure 6). Accordingly, the X-ray diffraction diagram has shown very weak peaks at 15.2 and 22.3° which indicates a very low degree of crystallinity for PBT12.

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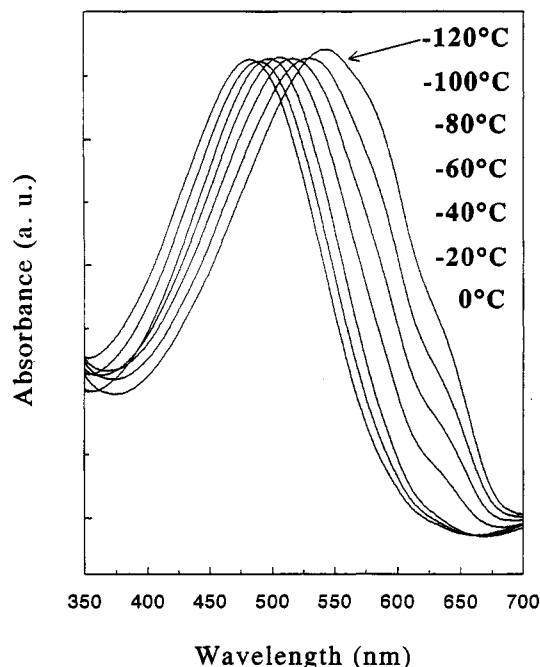


Figure 8. Temperature-dependent UV-visible spectra of PBDBT in tetrahydrofuran (cooling process).

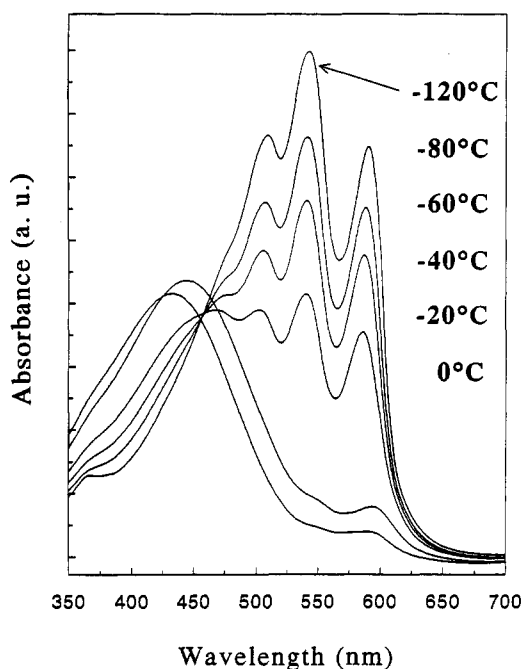


Figure 9. Temperature dependent UV-visible spectra of POMT in tetrahydrofuran (cooling process).

Figure 7 exhibits the temperature dependence of the absorption maximum of poly(3-(octyloxy)-4-methylthiophene) (POMT) and poly(3-dodecylthiophene) (PT12) in the solid state. In both cases, a discontinuous shift of the maximum of absorption can be now observed. Temperature-dependent UV-visible absorption spectra^{15,25-29} have shown the presence of a well-defined isosbestic point which is consistent with the coexistence of only two distinct conformational structures for these polymers.

Thermochromic effects have been also observed in solution and some of these results are shown in Figures 8 and 9. In Figure 8, a gradual red shift of the maximum of absorption of PBDBT in THF solution can be observed upon cooling. Once again, there is no isosbestic point,

and this thermal effect can be described as a continuous modification of the backbone conformation. These thermochromic effects are similar to those observed in the solid state but occur at lower temperatures. Experiments on PBT12 solutions revealed a similar continuous shift of the absorption maximum. No evidence of aggregation effect was observed during these measurements. It is worth noting that a "solid-state" phase would exhibit a nearly constant absorption maximum at 555 nm at such low temperatures (see Figure 4). However, aggregation and precipitation of the polymer can be observed at very low temperatures and after a long period of time. Figure 9 shows the cooling of POMT in a THF solution. It is remarkable to note that the same features that characterized the solid-state thermochromic properties of POMT²⁶ are observed again. The more conjugated form exhibits three maxima which have been explained by the presence of some vibronic peaks.⁶ A broad isosbestic point is also present during the transition, which indicates that two phases coexist simultaneously in the polymer solution. A similar "two-phase" thermochromic behavior was also observed for PT12 in THF.

Discussion

All four polymers investigated in this study are thermochromic in the solid state and in solution. Recent FTIR measurements in the solid state have revealed that a twisting of the thiophene backbone (which is responsible for the thermochromic effects) are provoked by some thermally induced steric interactions between the side chains and the main chain.^{25,26} All these polymers have similar flexible side-chains and, consequently, similar thermochromic effects were expected for this class of materials. However, it is clear that the substitution pattern has a great influence on their thermochromic properties. From these results, the thermochromic effects observed in PBDBT and PBT12 can be described as a continuous modification of the polymer chain which gives rise to a monotonic blue shift of the absorption maximum (one-phase system). On the other hand, POMT and PT12 behave like "two-phase" systems with the coexistence of two distinct chromophores (two distinct conformational structures). A two-phase system implies some cooperative effects which involves the simultaneous rotation of long sequences (if not the entire polymer chain) of thiophene units. However, in all cases, the thermochromic "transition" takes place over a large temperature domain which seems to indicate that the thermally induced twisting of the backbone is created randomly. Therefore, to explain the cooperative effects observed in POMT and PT12, it can be considered that the twisting of a first repeat unit could induce the twisting of the next repeat unit and so on. This mechanism can be alternatively described as a conformational defect delocalized over a certain number of repeat units (twiston). These so-called twistons are similar to the previously proposed "soft" conformers.¹⁶ On the other hand, these cooperative effects are not observed in PBDBT and PBT12. In this case, the thermally induced conformational defects seems to be localized and consequently, lead to a monotonic decrease of the conjugation length.

It seems that these different thermochromic mechanisms can be related to their different chemical structures. For instance, POMT and PT12 have a regular substitution pattern with one "potential" steric interaction between

each repeat unit while PBDBT and PBT12 exhibit an asymmetric structure with substituents separated by unsubstituted bithiophene unit. Consequently, it is believed that the cooperative effects observed in POMT and PT12 are made possible by the presence of a similar substitution pattern between each repeat unit which allows the formation of delocalized conformational defects (twistons). It is interesting to note that a similar discrimination between the formation of localized and delocalized conformational defects is also observed in solution. These results seem to indicate that these different behaviors are not related to different morphologies but rather to different chemical structures.

Moreover, UV-visible measurements in solution can give additional information about the nature of the driving force of this interesting conformational transition. Up to now, most studies of the thermochromic effects in solution have been performed on poly(3-alkylthiophenes)^{14,15} and, not surprisingly, a well-defined isosbestic point was observed. One major point of discussion was the discrimination between the relative importance of interchain and intrachain effects. Indeed, it was difficult to distinguish aggregation effects from pure intrachain conformational rearrangement. The results obtained with PBDBT (Figures 4 and 8) can bring valuable information about this point. As mentioned above, the formation of aggregates at such low temperatures should give an optical signature different from those reported in Figure 8. However, if it is assumed that similar intrachain interactions are responsible for the thermochromic effects in both solution and solid state, the question of their very different temperature domains must be also discussed. From spectroscopic measurements, Zerbi et al.²⁵ have found that the side chains were more disordered, for a given temperature, in solution than in the solid state and, therefore, this fact can explain the occurrence of the thermochromic effects in polythiophene solutions at lower temperatures.

On the basis of calculations performed by Cui and Kertesz,³⁶ some interchain (or polymer-solvent) interactions must be taken into account to explain the thermochromic effects in substituted polythiophenes. Indeed, their calculations seem to indicate that isolated polythiophene derivatives should adopt a nonplanar chain conformation with torsion angles of about 40°. However, as mentioned by these authors, considering also interchain

interactions, the anti-coplanar (and highly conjugated) structure is the most stable one in the solid state at room temperature. Therefore, these results could indicate that the thermochromic effects observed in some polythiophene derivatives is driven by a delicate balance between the energy of conjugation, repulsive intrachain interactions, and attractive interchain interactions.²⁷ Therefore, if aggregation is not the driving force for the thermochromic effects observed in solution for the polythiophene derivatives, some polymer-solvent interactions must stabilize a highly conjugated form at low temperatures. This point is certainly speculative and some further investigations are necessary to shed some light on this specific problem. For instance, the study of the thermochromic properties of pure and mixed polythiophene monolayers should give more information about the importance of interchain interactions.

Conclusion

Temperature-dependent UV-visible absorption measurements on various conjugated polythiophene derivatives have revealed the existence of two different thermochromic behaviors. These different mechanisms seem to be related to the substitution pattern of the polythiophene derivatives. The presence of sterically demanding substituents between each consecutive repeat unit (as found in poly(3-dodecylthiophene) and poly(3-(octyloxy)-4-methylthiophene)) allows the formation of delocalized conformational defects (twistons) upon heating. On the other hand, the partially substituted structure of poly(3-dodecyl-2,2'-bithiophene) and poly(3-butoxy-3'-decyl-2,2'-bithiophene) leads to the formation of localized conformational defects. The control and generation of these different types of conformational defects may create new opportunities for the fabrication of novel molecular devices based upon the propagation of such conformational defects along conjugated molecules or upon the resulting modification of their refractive index.

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