Planar-to-Nonplanar Conformational Transition in Thermochromic Polythiophenes: A Spectroscopic Study

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ABSTRACT: The thermochromic transition in regioregular poly(3-(2-methyl-1-butoxy)-4-methylthiophene) was characterized by UV−vis, FTIR, and Raman spectroscopies. The nonplanar yellow form of this polymer can be planarized at room temperature upon treatment with acetone vapor to yield a red polymer film. Upon heating, combined spectroscopic measurements have revealed important irreversible color changes (from red to yellow) between 75 and 95 °C induced by both side-chain and main-chain disordering. These measurements, in particular Raman spectroscopy, clearly indicate a significant planar-to-nonplanar conformational transition of the polythiophene backbone during the thermochromic transition.

Introduction

The past 25 years have witnessed the emergence of conjugated polymers as an important class of electroactive and photoactive materials for both academic and industrial laboratories.[1−5] The development of this research field has been sustained by the judicious utilization of a variety of synthetic strategies to prepare well-defined polymers with optimized physical properties. Along these lines, the initial problem of processability was resolved by the attachment of relatively long and flexible side chains since the unsubstituted parent polymers are not melt- or solution-processable, owing to strong interchain interactions and chain stiffness. Interestingly, some of these substituted conjugated polymers exhibit intriguing color changes (chromism) such as thermochromism, solvatochromism, piezochromism, and affinitychromism.[6−10] In other words, with appropriate substituents, some functionalized conjugated polymers can detect and transduce physical or chemical information into an optical signal.

In most cases, these optical changes have been described by a conformational transition of the backbone in the presence of external stimuli. Indeed, there is a strong correlation between the electronic structure of conjugated polymers and their backbone conformation, any change in the main-chain conformation leading to a modification of the so-called effective conjugation length associated with a concomitant shift in the UV−vis absorption. However, it may also be postulated that chromic phenomena can partly (or even only) reflect temperature-dependent interchain interactions (excitons, $\pi-\pi$ interactions, etc.) that accompany the formation (or disruption) of small aggregates or microcrystallites. Planarization always leads to a red shift, but the direction of shift caused by aggregation depends on the details of the molecular packing.[11] Recently, many studies have been devoted to the analysis of the relative contribution of chromophore aggregation and planarization on the optical properties of various chromic conjugated polymers.[11−20] Among these studies, a series of analyses (in dilute solutions, in the solid state, and as isolated molecule in alkane matrices) on oligothiophene model compounds have revealed that the chromic effects observed in substituted oligothiophenes are mainly due to conformational changes instead of electronic interchain interactions.[18−20] These observations would therefore support the model that explains chromism in polythiophenes by the formation of planar assemblies that are disrupted upon side-chain and/or main-chain disordering, an important twisting of the backbone being involved with this diassembly.[21,22] However, such a twisting of the conjugated polythiophene backbone has never been clearly determined, and only indirect effects have been observed. In this regard, we report here a detailed spectroscopic investigation of chromic regioregular poly(3-(2-methyl-1-butoxy)-4-methylthiophene). This polymer can be obtained in either a highly (red) or less conjugated (yellow) form at room temperature, depending upon film preparation, and should therefore allow a better understanding of the molecular mechanisms involved in chromic polythiophenes.

Experimental Section

Chemicals. All reagents were purchased from Aldrich Co. 2-Methyl-1-butanol was previously dried by distillation over Mg + I_2. Regioregular poly(3-(2-methyl-1-butoxy)-4-methylthiophene)[23] (PMBMT) and poly(3,4-dihexylthiophene)[24] (PDHT) were prepared following published procedures.

Physical Methods. Differential scanning calorimetry (DSC) analyses were performed on a Perkin-Elmer (DSC-7) instrument at a heating rate of 10 °C/min under a nitrogen flow. Fourier transform infrared (FTIR) experiments were performed with a Nicolet Magna 560 spectrometer on thin films deposited on NaCl disks for ex situ experiments or BaF_2 disks for in situ experiments. For in situ measurements, a calibration curve was obtained by measuring the “real” temperature in the center of a BaF_2 disk with a thermocouple vs the displayed temperature on the temperature control unit. The

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subsequent linear regression formula calculated was then used to obtain the real temperature around the sample. UV−vis in the solid state was performed on polymer films deposited from $CHCl_3$ on a quartz cell, with a Hewlett-Packard diode array spectrophotometer (model 8452) equipped with a temperature control unit. The temperature was measured with a thermocouple, with $\Delta T \sim 3$ °C. Surface-enhanced Raman scattering (SERS) FT spectra were recorded with a RFS 100 Bruker spectrometer (excitation wavelength 1064 nm). In the visible range, a multichannel Jobin-Yvon T64000 spectrophotometer connected to a CCD detector was used, with the following excitation lines available: 457, 514, 647, and 676 nm. In situ Raman experiments were carried out by increasing the temperature by 10 deg steps between 60 and 110 °C. SERS spectra quality is very dependent on the treatment of Ag surface. The silver films were deposited on glass following a special preparation.[25] A vacuum evaporation technique with a deposition rate of 1 nm/s at pressure lower than 10^{-5} Torr was used. By controlling the evaporation geometry and the quantity of evaporated metal, a good reproducibility of the roughness of the films was ensured. The SERS technique allows a fast recording of the spectra, with a reasonable signal/noise ratio. Finally, the polymer thin films were deposited from $CHCl_3$ on these Ag supports.

Results and Discussion

UV−vis Measurements. At room temperature, a thin film of regioregular poly(3-(2-methyl-1-butoxy)-4-methylthiophene) (PMBMT) cast from a chloroform solution is yellow, exhibiting a maximum of absorption at 410 nm. After washing with acetone or in the presence of vapor of acetone, it becomes red and shows a maximum of absorption at 502 nm with vibronic sidebands at 534 and 582 nm. A broad shoulder around 400 nm is also observed. Interestingly, a similar solvent-induced ordering in the solid state was reported for regioregular poly(3-(4-octylphenyl)thiophene).[26] This unusual chromic effect could be attributed to a possible decrease of the glass transition induced by the “momentary” presence of acetone, which then allows a reorganization of the backbone in its more stable conformation. Indeed, dry PMBMT shows a glass transition near 50 °C, which gives a glassy state at room temperature with limited motion along the backbone.

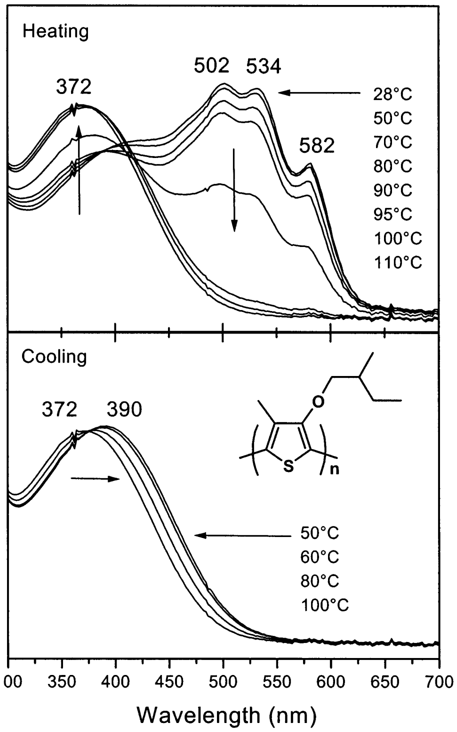

Figure 1. UV−vis absorption spectra of cast PMBMT thin film as a function of the temperature. Arrows indicate the evolution of the absorption bands upon heating (top) or cooling (bottom).

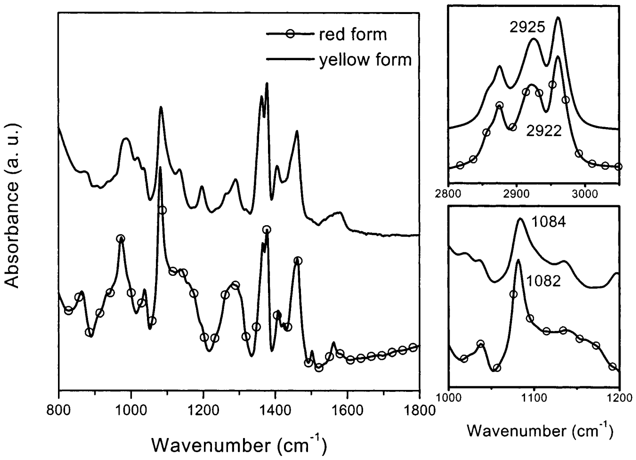

Figure 2. FTIR spectra of red (40 °C) and yellow (100 °C) PMBMT.

Figure 1 shows the thermochromic behavior of such a dry, red, polymer film. No significant optical change is observed below 50−70 °C, which can be related to the glass transition of the polymer which inhibits any important modification of the conjugated backbone below these temperatures. Then, the intensity of the absorption bands at 502, 534, and 582 nm decreases upon heating, a near-isosbestic point being visible around 400 nm. At 95 °C, the conversion is complete; the yellow poly(3-(2-methyl-1-butoxy)-4-methylthiophene) (PMBMT) shows then a maximum of absorption at 372 nm. Most significant optical changes occur around 90 °C. This conjugation loss seems irreversible; upon cooling, this polymer does not return to its previous state (the maximum of absorption only red shifts by about 18 nm), and even after several days, the films were still yellow. Accordingly, in addition to a glass transition at 50 °C, DSC measurements have revealed a broad endothermic peak (1.5 kcal/mol of repeat unit) between 75 and 110 °C. A second heating only shows the glass transition, confirming the irreversibility of the endothermic (chromic) transition. This strong hysteresis could be useful for the design of irreversible temperature detectors. However, as mentioned above, presence of vapor of acetone can restore the initial optical spectrum.

FTIR Measurements. On the basis of some models described in the Introduction section, this thermochromic transition would be driven by thermally induced disordering of both the side chain and the main chain. To shed some light on this feature, an in situ FTIR absorption experiment on a thin film of PMBMT was carried out. Following procedures developed for UV−vis measurements, a polymer film was cast onto a NaCl disk, which was then immersed in acetone and dried before measurements. Figure 2 shows the spectra of PMBMT at 40 °C (“red” conformation) and 100 °C (“yellow” conformation). Only slight differences between both conformations were observed in the FTIR spectra. The main modifications upon heating are the following: (i) the peaks at 1561 and 1503 cm^{-1} and the shoulders at 1306, 1175, and 1160 cm^{-1} disappear; (ii) the broad band centered around 1280 cm^{-1} gradually decreases in intensity, and its shape is modified, to

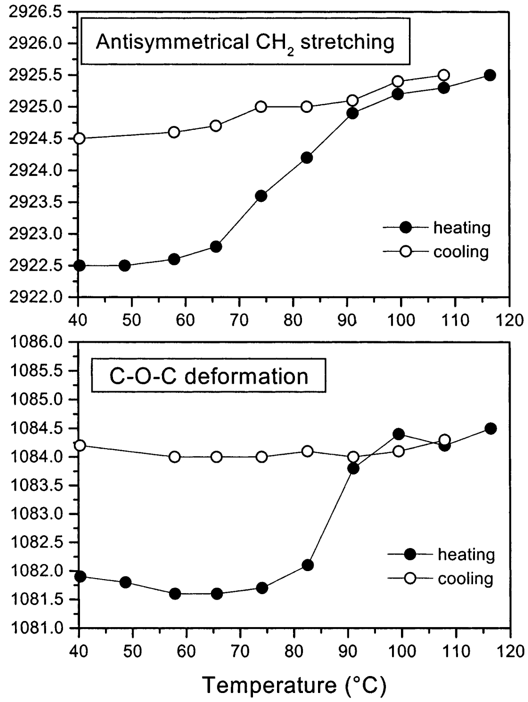

Figure 3. Temperature dependence of the position of two IR absorption bands of PMBMT.

give only two well-defined bands at 1290 and 1262 cm^{-1}; (iii) the bands at 974 and 1038 cm^{-1} are finally overlapped by two other bands that grow around 994 and at 1020 cm^{-1}; (iv) peaks at 1198 and 881 cm^{-1} appear.

A more detailed analysis of the spectra revealed interesting behaviors. The band at 1377 cm^{-1} remains totally unchanged; it can be assigned to the umbrella deformation of the CH_3 group.[27] The weak band located at 1503 cm^{-1} and characteristic of the $C_\alpha{=}C_\beta$ out-of-phase stretching starts to decrease in intensity from 75 °C to vanish at 100 °C. This vibration mode is usually called antisymmetric stretching; it refers to the antisymmetrical stretching of the two C=C bonds, relative to the symmetry plan in the thiophene unit. In nonsymmetrically substituted polythiophene derivatives, this term is also used, but it can be considered incorrect. In the rest of this paper, we will refer as out-of-phase and in-phase (for the "symmetric" mode) stretching modes. Around 3000 cm^{-1}, the bands assigned to the CH_3 stretching vibrations (2960 and 2874 cm^{-1}) are not shifted upon heating, whereas the antisymmetrical CH_2 stretching band undergoes a significant shift (Figure 3). Its maximum of absorption moves from 2922 to 2925 cm^{-1}, slightly up to 65 °C, then more pronouncedly between 65 and 90 °C, and slightly afterward. It was not possible to determine whether the symmetrical stretching band (shoulder, around 2850 cm^{-1}) followed the same tendencies, its maximum of absorption being difficult to point out precisely. This shift of the CH_2 stretching band is known to reflect the transformation of the methylene group from a "trans" conformation toward a "gauche" conformation, as shown for example in phospholipids.[28-30] Upon cooling, it slightly shifts toward lower wavenumbers, but without retrieving its initial position. In the 1000−1200 cm^{-1} region, the strong band located at 1082 cm^{-1}, which is assigned to the C−O−C deformation mode (Figure 3, bottom), remains unchanged in position up to 75 °C. Between 75 and 95 °C, it is shifted to 1084 cm^{-1} and then stays close to this position, even upon cooling. It is worth noting that the temperature range where changes occur in the FTIR spectra is in good agreement with the optical absorption experiments, discussed above.

These different behaviors of the IR bands allow us to assume that the positions of bands corresponding (i) to CH_3 vibrations would be unaffected, (ii) to CH_2 vibrations would continuously shift, with a larger shift between 65 and 90 °C, (iii) to vibrations of bonds linked to the thiophene ring would remain unaffected up to 75 °C and then undergo a clear shift, and (iv) to the thiophene ring would decrease in intensity between 75 and 95 °C.

Considering these assumptions, and with the help of previous studies performed on some polythiophene derivatives,[31-37] we assigned the main bands of our IR spectra, and these assignments are reported in Table 1. From these FTIR experiments, some important points must be kept in mind. The gradual thermally induced changes of the CH_2 groups conformations are visible, denoting a disordering of the side chains during heating. Between 75 and 95 °C a drastic change occurs: the thiophene bands disappear, and the bands assigned to chemical bonds directly linked to the thiophene rings undergo a clear shift in position. Upon cooling, the side chains seem to tend to their initial conformation, but all these results confirm that the polymer remains blocked in this "disordered conformation", even when cooled to room temperature. All these FTIR measurements corroborate our UV−vis absorption results.

Raman Spectroscopy. To continue this spectroscopic investigation on the structural evolution and planarity behavior of conjugated PMBMT, Raman spectroscopy was utilized. Group theory predicts that polythiophene has a D_{2h} symmetry and that the regioregular substituted polythiophenes possess a C_{2h} symmetry. In the C_{2h} and D_{2h} symmetries, the in-plane "gerade" modes are Raman-active, whereas the "ungerade" modes are infrared-active. So, Raman spectroscopy is usually a complementary tool to infrared absorption. If twisting of the thiophene backbone takes place, i.e., if adjacent thiophene units are no more coplanar (dihedral angle different from 0° or 180°), the delocalization of the π-electrons decreases and affects the perfect symmetry of the chain. The symmetry changes to the C_2 structure. This should be visible in the Raman spectra. Consequently, the main effect on the frequencies and intensities in the Raman spectra depends on the changes in the effective conjugation length. It is an intrinsic property of these macromolecular systems.

Moreover, when using the resonance Raman effect (excitation wavelength corresponding to an electronic transition in the studied material), it is known that the totally in-phase modes are preferably enhanced and that the position of the bands related to the π-bonding system depends on the excitation wavelengths, as already shown for polyacetylene.[38] As a result, the recorded Raman spectra depend on the position of the excitation line with respect to the observed electronic transitions. As has already been stated, solvents or thermal effects induce a shift of the absorption bands in the visible part of the spectrum. Thus, different excitation wavelengths should be used for the studies of the planar polymer and for its twisted form. With all these considerations, the near-IR (1064 nm) excitation line is the most suitable for the studies of PMBMT, because we are out of resonance for all conformations

Table 1. Assignment of Experimental Infrared Bands of PMBMT and Parent polythiophenes

polythiophene[31]	poly(3,3′-dihexyl-2,2′-bithiophene)[34]	poly(3-decylthiophene)[32]	poly(3,4-dihexylthiophene)	poly(3,3′-dibutoxy-2,2′-bithiophene)[33]	PEDOT[31]	PMBMT red	PMBMT yellow	proposed assignments
1488	1535	1510	1515	1486	1488	1561, 1503		C═C o.o.ph stretching
	1465					1461	1462	CH_3 a.s. bending
	1450	1465	1461			1454	1453	CH_2 bending
					1427	1423	1423	C═C−O in-ph stretching
1441	1447	1438	1435					C═C(−H or −C) in-ph stretching
						1409	1406	CH_2 bending
	1379		1367			1377	1377	CH_3 "umbrella def"
		1377	1378	1389	1366	1366	1363	CH_2 wagging
1224	1261	1208, 1182, 1156	1257			1280, 1175, 1160	1290, 1262	C−C inter-ring stretching + C_β−H bending
	1180		1215				1198, 1136	CH_2 twisting
1055	1083							C_β−H bending
				1054	1051	1130, 1082	1084	C−O−C def
		1021	995			1038	1036	C_β−C_{alk} stretching
						1025, 996	1020, 994, 881	CH_2 def o.o. plan
						974	980	C_β−O stretching
			938			933	934	CH_3 rock
	830, 824					864		thiophene def
	736	721	723	755				CH_2 rocking

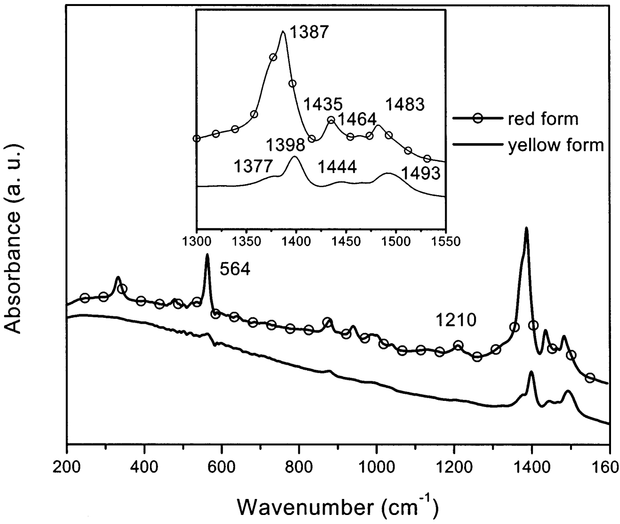

Figure 4. Raman spectra (λ_{exc} = 1064 nm) of red and yellow (after heating for 40 min at 110 °C) PMBMT.

of this polymer. By this way, all these strong resonance effects are minimized, and the evolutions of the Raman data of different polythiophenes can be assigned only to the modification of their structures. Second, to take advantage of these resonance effects, recording Raman spectra at different excitation wavelengths in the visible range should allow to unambiguously assign the bands related to the alternate C−C═C bond vibrations. Because of fluorescence effects, we only studied this polymer with the red (647 nm) and near-infrared (1064 nm) excitation lines.

After deposition and washing with acetone, we put the sample in an oven at 110 °C for 30 min. We compared the 1064 nm spectra recorded before and after heating (Figure 4); the different polymer conformations give clearly different Raman spectra. It can also be noticed that all yellow forms of this polymer, deposited from $CHCl_3$ as well as after heating, give the same spectra.

Upon heating, the main changes occur as follows: (i) the peak located at 1483 cm^{-1} increases in intensity and shifts to 1493 cm^{-1}; (ii) the peaks located at 1435 and 1387 cm^{-1} decrease in intensity and shift to 1444 and 1398 cm^{-1}, respectively; (iii) some peaks are not affected in position: 1464, 1379, and 879 cm^{-1}; (iv) the peaks pointed at 1040, 997, 987, 939, and 333 cm^{-1} disappear.

An in situ experiment was also carried out with 647 nm excitation. These measurements helped for the assignment of the C−C═C vibrations. These Raman spectra are identical up to 90 °C and are very similar to those obtained with 1064 nm excitation. Then, a thermochromic transition occurs very quickly, and it results in a different spectrum at 100 °C. Then, no change in the spectrum is noticed.

The assignment of the peaks was carried out on the basis of previous studies,[31−33] and these results are reported in Table 2. In this way, comparisons with previously assigned bands of parent polymers permit to unambiguously assign some of our bands and to help choosing between possible assignments for others. As already noticed by Pron and co-workers,[33] the presence of an alkoxy substituent induces a split of the band related to the C═C stretching.

The evolution of the spectra can be interpreted as follows:

(i) The shift toward higher frequencies, upon heating, of the out-of-phase and in-phase stretching vibrations of the C_α═C_β bond, indicates a more localized electronic density on these bonds that is associated with a decrease of the effective conjugation length along the polymer backbone. The explanation for this loss of conjugation can be related to a loss of planarity of the polymer induced by a twisting of the thiophene backbone.

(ii) The disappearance of peaks usually indicates a loss of symmetry in a molecule. For the 1064 nm line,

Table 2. Assignment of Experimental Raman Bands (λ_{exc} = 1064 nm) of PMBMT and Parent Polythiophenes

polythiophene[31]	poly(3,3′-dibutoxy-2,2′-bithiophene)[33]	poly(3-decylthiophene)[32]	poly(3,4-dihexylthiophene)	PEDOT[31]	PMBMT red	PMBMT yellow	proposed assignments
1497	1522	1512		1516	1483	1493	C═C o.o.ph stretching
		1465			1464	1464	CH_2 and CH_3 bending
1455	1451	1443	1504		1435	1444	C═C(−H or −C) in-ph stretching
	1415			1423	1387	1398	C═C(−O) in-ph stretching
1365	1290	1378	1392	1369	1379	1379	$C_\beta-C_\beta$ stretching
1220	1190	1208		1270	1210	1211	C−C inter-ring stretching
	1112			1101	1130		C−O−C def
1045							C_β−H bending
		1021			1040		$C_\beta-C_{alkyl}$ stretching
					995, 987, 939		C−O−C def
				864	879	878	CH_2 bending o.o. plan
740	754	724		750			C−S−C asym def
700	699	681		692			C−S−C sym def
		595		571	563	563	ring def
					333		skeletal def

the bands between 1040 and 939 cm^{-1} could be assigned to the "in-plane" antisymmetric and symmetric C_β substituent deformations and the 333 cm^{-1} one to skeletal C−C deformation. This is another confirmation of a loss of planarity upon heating.

All these observations are also confirmed by the intensity evolution. Indeed, the decrease of the intensity of the in-phase C═C stretching band relative to the out-of-phase stretching (at 1493 cm^{-1}) indicates an important decrease of the effective conjugation length, as already observed with thiophene oligomers.[39]

To confirm these assumptions, we compared these results with those obtained on nonplanar poly(3,4-dihexylthiophene) (PDHT) and planar poly(3,4-ethylenedioxythiophene) (PEDOT).[31] These different conformations can be explained by the different steric hindrance created by the different substituents. The Raman spectrum (1064 nm) of nonplanar PDHT only exhibits two bands, located at 1504 and 1392 cm^{-1}. These bands are assigned to the in-phase C═C stretching and C−C stretching vibrations, respectively. This spectrum is very similar to that of the "yellow" PMBMT. The Raman spectrum obtained with planar PEDOT is a bit more complex, but the main bands are assigned as follows: the out-of-phase and in-phase C═C stretching bands are located at 1516 and 1423 cm^{-1} and the C−C stretching band is at 1369 cm^{-1}. As for polythiophene and regioregular poly(3-alkylthiophene)s, which also have a planar conformation at room temperature, this spectrum is more similar to that of the "red" PMBMT, in both intensity and frequency.

The evolutions observed on PMBMT combined with the comparison to known planar and twisted polythiophenes confirm our hypothesis of a planar conformation of the "red" polymer backbone, while the "yellow" form is less planar (twisted), which results in a conjugation loss along the backbone.

Conclusion

UV−vis, FTIR, and Raman spectroscopies have been utilized to probe thermochromic transitions in polythiophene derivatives. These measurements have indicated that a twisting of the backbone, accompanied and/or triggered by side-chain disordering, is involved during the thermochromic transition. These results do not mean that interchain interactions cannot be partly responsible for these thermally induced optical changes but clearly imply a significant twisting of the polythiophene backbone. On this basis, similar combined spectroscopic measurements could be useful to investigate the relative contribution of interchain interactions and planarization in other chromic conjugated polymers.

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