Thermochromic Properties of Polythiophenes: Oligomers vs. Polymers

Karim Faïd and Mario Leclerc*

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

The temperature dependence of the UV–VIS absorption maximum of alkyl tetrasubstituted sexithiophene and poly(dialkylterthiophene) have been investigated, and the results are consistent with a rotation of the main conjugated chain induced by an increase of disorder in the side chains upon heating.

Polythiophene derivatives exhibit interesting electrical, electrochemical and optical properties which might be useful for various applications.[1-10] For instance, it has been found that some poly(3-alkylthiophenes)[6-9] and poly[(3-alkoxy)-4-methylthiophenes][10] show important thermochromic effects. These unusual optical effects are believed to be related to an increase of disorder in the side chains upon heating which forces the twisting of the main conjugated chain.[9,10] This proposed mechanism is also supported by recent studies on poly(3-alkoxythiophenes) which have shown that, in absence of sterically demanding substituents, the polythiophene backbone can retain a highly conjugated structure even at high temperatures.[11] However, it was still unclear why these thermochromic effects occur over such a large temperature range (ca. 100–150 °C). In a first approximation, it can be supposed that this broad temperature range may be related to the irregular structure of these polymers (distribution of molecular weights, coexistence of amorphous and crystalline parts, structural and chemical defects, etc.). The study of well-defined oligomers could be very helpful to get more information about the nature of the driving force of this interesting conformational transition and, therefore, we report here the thermochromic behaviour of an alkyl tetrasubstituted sexithiophene and of the corresponding poly-(dialkylterthiophene).

3',4'-Dihexylterthiophene was synthesized from coupling of 2,5-dibromo-3,4-dihexylthiophene (1 equiv.) with of 2-thienylmagnesium bromide (2 equiv.).[12] This trimer was chemically oxidized to give the corresponding polymer A.[13a] The trimer was also treated with butyllithium and copper chloride to give 3',3'''',4',4''''-tetrahexylsexithiophene B.[12] A complete description of the synthesis and chemical characterization of all products will be published elsewhere.[14] Thermal analyses by differential scanning calorimetry (DSC) have revealed a melting temperature of −36 °C for the hexamer. A glass transition temperature of −46 °C and a melting temperature of 230 °C have been observed for the semicrystalline polymer.

Following these thermal analyses, UV–VIS absorption spectra of both compounds were recorded as a function of the temperature. As expected, the poly(3',4'-dihexylterthiophene) exhibits a highly conjugated structure at low temperatures with an absorption maximum at 494 nm (2.51 eV). This value is similar to those of other polythiophenes prepared under similar conditions.[13b] However, above 100 °C, a blue shift of the absorption maximum of the polymer is observed (Fig. 1). This behaviour is similar to that observed in

poly(3-alkoxy-3'-alkyl-2,2'-bithiophenes)[15] and can be related to the formation of a localized twisting of the backbone induced by an increase of the steric hindrance of the side chains upon heating. Moreover, the singularity observed near 200 °C in Fig. 1 may be rationalized by the coexistence of both an amorphous and crystalline phases in the polymer. Indeed, it is believed that the twisting of the main polymer chain can only take place at a temperature higher than the glass transition temperature for the amorphous phase and above the melting temperature for the crystalline phase. Therefore, the formation of such twistings occurs first in the amorphous state and, subsequently, after the melting of the crystalline phase, in the whole polymeric material.

On the other hand, as shown in Fig. 1, the corresponding sexithiophene exhibits a maximum of absorption near 446 nm (2.78 eV) at low temperatures. This wavelength, shorter than that observed for the polymer, can be related to the finite conjugation length of the oligomer.[16,17] However, similarly to the polymer, the absorption maximum of the sexithiophene is almost constant at low temperatures whereas it undergoes a linear continuous blue shift above 10 °C. It is particularly interesting to note that the melting of the hexamer, at −36 °C, does not induce any significant shift of the maximum of absorption. Indeed, it could be expected that the melting of a well-defined hexamer would induce an abrupt conformational transition of the conjugated molecule, leading to a correlated abrupt blue shift of the maximum of absorption. This is not the case and, surprisingly, it seems that twistings are created in the sexithiophene in a manner similar to that in the polymer. However, it is clear that these twistings can be created more easily (at lower temperatures) in the sexithiophene than in the polymer and this can be explained by the different viscosity of the materials.

In conclusion, on the basis of these results, it appears that the thermochromic effects observed in polythiophenes are not directly driven by the phase transitions of the molecules but rather by thermally induced steric interactions of the side chains. For these reasons the thermochromic transition takes place over a broad temperature range in this class of materials.
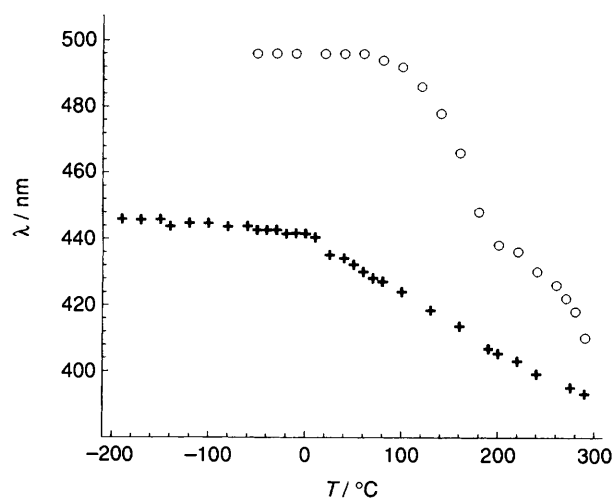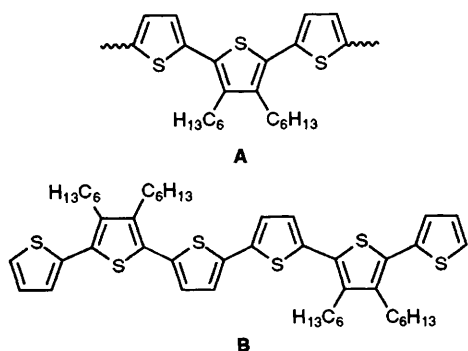

A

B

Fig. 1 Temperature dependence of the maximum of absorption in the UV–VIS range for the polymer (O) and the hexamer (+)

References

1 J. Roncali, *Chem. Rev.*, 1992, **92**, 711.
2 R. L. Elsenbaumer, K. Y. Jen and R. Oboodi, *Synth. Met.*, 1986, **15**, 169.
3 M. A. Sato, S. Tanaka and K. Kaeriyama, *J. Chem. Soc., Chem. Commun.*, 1986, 873.
4 G. Daoust and M. Leclerc, *Macromolecules*, 1991, **24**, 455.
5 R. Cloutier and M. Leclerc, *J. Chem. Soc., Chem. Commun.*, 1991, 1194.
6 O. Inganas, W. R. Salaneck, J. E. Osterholm, J. Laskso, *Synth. Met.*, 1988, **22**, 395.
7 S. D. D. V. Rughooputh, S. Hotta, A. J. Heeger and F. Wudl, *J. Polym. Sci., Polym. Phys. Ed.*, 1987, **25**, 1071.
8 K. Yoshino, S. Nakajima, M. Onada and R. Sugimoto, *Synth. Met.*, 1989, **28**, C349.
9 G. Zerbi, B. Chirichetti and O. Inganas, *J. Chem. Phys.*, 1991, **94**, 4646.
10 C. Roux and M. Leclerc, *Macromolecules*, 1992, **25**, 2141.
11 C. Roux, J. Y. Bergeron and M. Leclerc, *Makromol. Chem.*, 1993, **194**, 869.
12 D. Delabouglisse, M. Hmyene, G. Horowitz, A. Yassar and F. Garnier, *Adv. Mater.*, 1992, **4**, 107.
13 (a) M. Leclerc, F. M. Diaz and G. Wegner, *Makromol. Chem.*, 1989, **190**, 3105; (b) R. M. Eales and A. R. Hillman, *J. Mater. Sci.*, 1990, **25**, 3806.
14 K. Faïd and M. Leclerc, in preparation.
15 C. Roux, K. Faïd and M Leclerc, *Makromol. Chem., Rapid Commun.*, submitted for publication.
16 P. Bäuerle, *Adv. Mater.*, 1992, **4**, 102.
17 A. Yassar, D. Delabouglisse, M. Hmyene, B. Nessak, G. Horowitz and F. Garnier, *Adv. Mater.*, 1992, **4**, 490.