

Ionochromic Effects in Regioregular Ether-substituted Polythiophenes

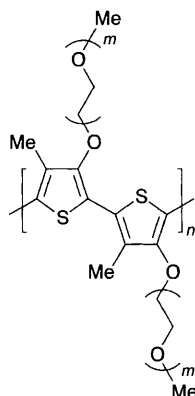
Isabelle Lévesque and Mario Leclerc*

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

Solutions of a polythiophene derivative bearing oligo(oxyethylene) side-chains show interesting chromic effects upon the addition of alkali metal ions which may lead to the development of novel ionoselective sensors.

Striking thermochromic, solvatochromic and piezochromic phenomena have been recently observed in certain polythiophene derivatives.¹⁻⁴ All these optical effects have been described in terms of a planar/non-planar conformational transition of the conjugated backbone. Indeed, in conjugated polymers, there is a strong correlation between the electronic structure and the backbone conformation. However, FTIR measurements have suggested that these colour changes are driven by order-disorder 'transitions' of the side-chains;^{4,5} side-chain disordering increasing their steric hindrance⁵⁻⁸ or disrupting co-planar lamellar assemblies,⁹ which then force the thiophene backbone to adopt a non-planar conformation. It can be thus considered that any perturbation of the side-chain organisation would induce some chromic effects. In agreement with this assumption, recent studies have indicated that non-covalent interactions between alkali metal ions and certain ether¹⁰ or crown-ether¹¹ functionalised polythiophenes induce a slight shift of their absorption maximum in solution. On the other hand, we have shown that regioregular substituted poly(3-alkoxy-4-methylthiophene)s can lead to dramatic chromic effects with the presence of a clear isosbestic point.^{4,9} This isosbestic point clearly indicates the coexistence of long sequences of non-planar and planar thiophene units. In contrast, nonregioregular polythiophene derivatives allow only the formation of weak and localised conformational defects along the polymer backbone leading to a continuous and monotonic blue shift of their absorption maximum upon heating.^{8,9} Using these properties, it is then possible to design polymers where the ratio between two conformational structures (having completely different absorption features) can lead to a colorimetric determination of various external stimuli. To verify this model and develop novel sensors, regioregular poly[3-oligo(oxyethylene)-4-methylthiophene] was synthesised and its ionochromic properties investigated.

3-Oligo(oxyethylene)-4-methylthiophene was synthesised from coupling of 3-bromo-4-methylthiophene and poly(ethyleneglycol) methyl ether (MW 350) (Aldrich), according to a procedure similar to that described by El Kassmi *et al.*¹² The oligo(oxyethylene) side-chains contain principally 3-10 oxyethylene units. The corresponding polymer was chemically polymerised, using iron trichloride as oxidising agent in chloroform.¹³ The mixture was stirred for 24 h at room temperature. The solvent was then evaporated, and the polymer was washed with water using a Soxhlet apparatus. The low



Scheme 1

molecular weight fraction was eliminated by washing with methanol at room temperature. The polymer was finally dried under reduced pressure at 40 °C. Size exclusion chromatography measurements have revealed a number-average molecular weight of 22 500 with a polydispersity index of 5.9.

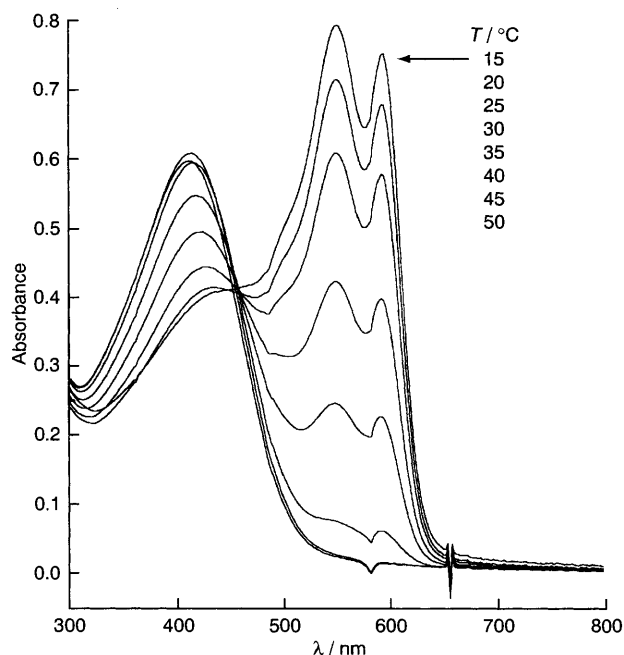


Fig. 1 Temperature-dependent UV-VIS absorption spectra of poly[3-oligo(oxyethylene)-4-methylthiophene] in methanol

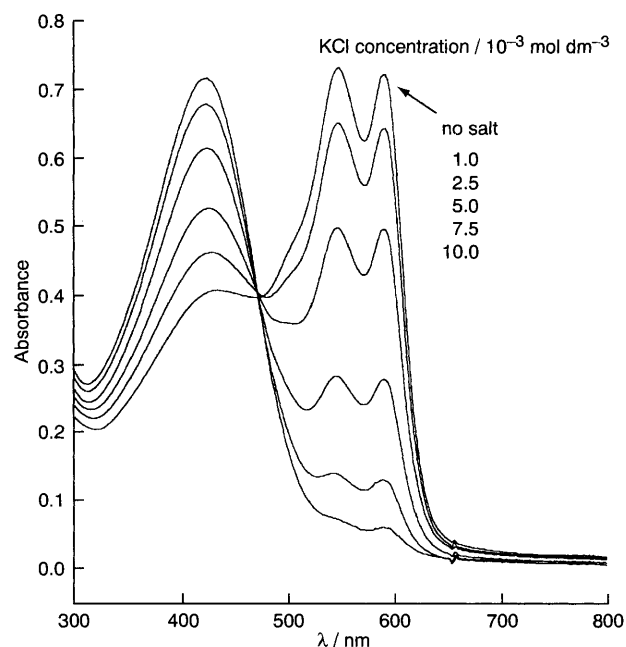


Fig. 2 UV-VIS absorption spectra of poly[3-oligo(oxyethylene)-4-methylthiophene] (10^{-4} mol dm^{-3}) in methanol with different KCl concentrations at 20 °C

NMR analyses have indicated that the resultant polymer is regioregular with a head-to-tail content higher than 95%^{4,9,13} (Scheme 1).

As observed with other regioregular poly(3-alkoxy-4-methylthiophene)s, poly[3-oligo(oxyethylene)-4-methylthiophene] is thermochromic in both the solid state and in solution (Fig. 1). For instance, at 15 °C in methanol, this polymer is highly conjugated with an absorption maximum at 550 nm, the other peak at 594 nm being related to a vibronic fine structure.¹³ Upon heating, a new absorption band appears at 426 nm while the intensity of the 550 nm band decreases. As mentioned above, this phenomenon can be explained by a thermally-induced disordering of the side-chain inducing the twisting of the main chain. Moreover, it is possible, at a fixed temperature, to modify the ratio between the highly conjugated and the less conjugated form of this polymer through the addition of KCl. As shown in Fig. 2, the absorbance at 426 nm gets higher when raising the concentration of KCl, while the absorbance at 550 nm gets lower. An isosbestic point is observed, showing the coexistence of the planar and non-planar forms. A cooperative twisting (which may lead to an amplification mechanism) of the main polymer chain then takes place upon the addition of KCl. These ionochromic effects could be explained by a disordering of the side-chains through non-covalent interactions with K⁺.

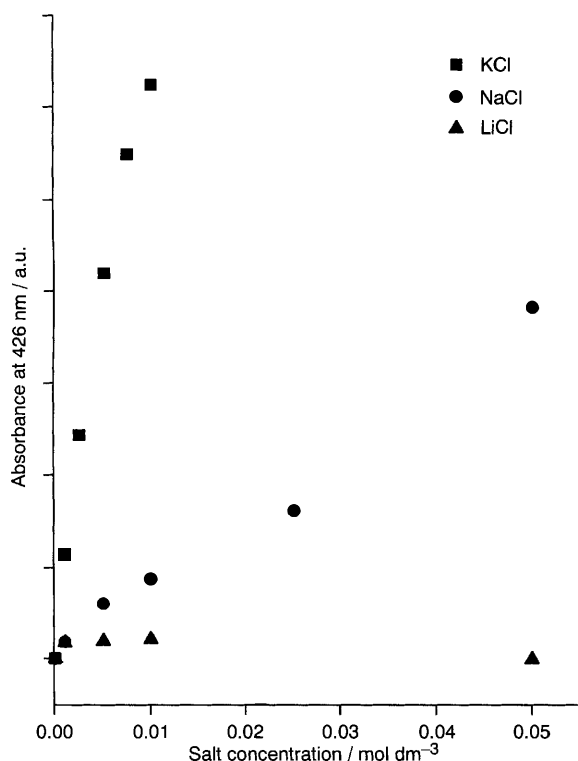


Fig. 3 Variation of the absorbance of the 426 nm band of poly[3-oligo(oxyethylene)-4-methylthiophene] (10^{-4} mol dm⁻³) in methanol as a function of the concentration of various salts at 20 °C

On the other hand, since methanol is a poor solvent, these results could be also related to solvatochromic effects, *i.e.* a better solubilisation of the polymer upon the addition of KCl. However, it is clear that noncovalent interactions between the side-chains and the ionic species are the driving force for these chromic effects. In contrast, ether-substituted polythiophenes with short side-chains [*e.g.* poly{3-[2-(2-methoxyethoxy)ethoxy]-4-methylthiophene}] exhibit a main-chain (and possibly side-chain) ordering upon the addition of K⁺.⁹ This behaviour could indicate that several oxyethylene units are necessary to allow the complexation of K⁺: involving two neighbouring repeat units in the case of poly{3-[2-(2-methoxyethoxy)ethoxy]-4-methylthiophene} and only one oligo(oxyethylene) side-chain through a possible crown-ether-like conformation.

Another interesting feature is that these chromic effects are dependent upon the nature of the cation (Fig. 3). A relatively large cation such as K⁺ produces a strong effect whereas a weaker effect is observed with Na⁺. This means that a larger quantity of NaCl is needed to induce similar optical changes than those observed with the addition of KCl. LiCl does not produce any effect in the polymer solution. Clearly, this specificity and the dependence upon the concentration of these chromic effects can be useful to develop various sensors based on non-covalent interactions between a given chemical species and some binding sites present in the side-chains. It is then believed that this planar/non-planar conformational transition of the backbone can be induced *via* a large range of external stimuli, leading to various chromic effects.

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