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Controlled ionochromism with polythiophenes bearing crown ether side chains

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Regioregular poly(3-alkoxy-4-methylthiophene)s bearing crown ethers of different sizes (12-crown-4), PT12C4; and (15-crown-5) PT15C5) have been synthesized and their thermochromic and ionochromic behaviors investigated. These polythiophene derivatives exhibit a highly conjugated form in the solid state at room temperature (absorption maximum around 550 nm) and a less conjugated form upon heating (absorption maximum around 425 nm). In acetone or ethyl acetate ionochromic responses have been observed upon addition of some alkali metal cations. Initially, the absorption maximum is located around 425 nm (yellow) but moves to 550 nm (violet). These results indicate the formation of planar (highly conjugated) polymeric assemblies upon the addition of alkali metal cations. PT12C4 is more sensitive to sodium salts while PT15C5 gives more intense ionochromic effects with potassium salts. These effects can be explained by a more stable 2 : 1 complexation between a given crown ether and an appropriate alkali metal cation.

Introduction

During the last twenty years, conjugated polymers (polyacetylenes, polyanilines, polypyrroles, polythiophenes, polyphenylenevinylenes, polyfluorenes, *etc.*) have attracted a lot of attention, mainly because of their interesting and unusual optical, electrochemical, and electrical properties.[1–4] These physical properties may lead to a large number of applications such as electroluminescent devices, optical signal processing, solar energy conversion, electrochemical cells, transparent antistatic coatings, biosensors, *etc.* For instance, these polymeric materials are well known for their good electrical conductivity arising upon doping (oxidation, reduction, protonation, or deprotonation).[1–5] The delocalized electronic structure of these polymers is partly responsible for the stabilization of the charge carriers created upon doping and electrical conductivities in the range of 1–100 S cm^{-1} can be reached, in most cases. Moreover, solubility and a high level of conjugation have been obtained through the incorporation of relatively long and flexible side chains, such as in monosubstituted poly(3-alkylthiophene)s[6–12] and fully substituted poly(3-alkoxy-4-methylthiophene)s.[13–15]

The introduction of various substituents along the backbone can not only enhance the processability of these aromatic polymers but can also modulate their electrical, electrochemical, and optical properties. For example, electrochemical redox processes result in important changes in the UV-visible range (electrochromism), from dark red to blue in the case of poly(3-alkylthiophene)s[16] and from dark blue to pale blue-gray for poly(3,3′-dialkoxy-2,2′-bithiophene)s[17] and poly(3,4-ethylenedioxythiophene).[18] On the other hand, the UV-visible absorption characteristics of neutral conjugated polymers can be modified by tuning their conformational structure. Indeed, it has been shown that the backbone conformation has strong effects on the electronic structure of conjugated macromolecules and, therefore, on their UV-visible absorption spectrum.[19,20] Along these lines, striking chromic effects have been reported in some polythiophene derivatives upon heating (thermochromism), both in the solid state and in solution.[21–26] These interesting optical effects have been attributed, to a first approximation, to a *transition* between a planar (highly conjugated) form and a non-planar (less conjugated) conformational structure of the backbone. It has been also found that these thermochromic properties are strongly dependent upon the nature and the position of the side chains in the repetitive units of the polymers.[27] More precisely, it has been suggested that these optical effects are driven by a delicate balance between steric repulsive interactions and attractive interchain (or intrachain, due to a chain folding) interactions.[27,28] For instance, at low temperatures, poly(3-alkylthiophene)s,[21–24] poly(3-alkoxy-4-methylthiophene)s,[25,26] poly(3-(alkylthio)thiophene)s,[29] and poly(3,3′-bis(alkylthio)-2,2′-bithiophene)s[30] can form planar assemblies, which are disrupted upon heating due to a disordering of the flexible side chains, a twisting of the main chain being assumed with this diassembly. On the other hand, as observed with poly(3,3′-dialkyl-2,2′-bithiophene)s,[27,28] when steric interactions are too large, no planar conformation is accessible whereas, in the absence of significant steric interactions, the conjugated polymer (*e.g.* poly(3,3′-dialkoxy-2,2′-bithiophene)s)[28,31] can maintain nearly planar conformations even at high temperatures. Recent calculations and experimental studies on oligomeric model compounds have supported these assumptions and have also shown that the chromic effects in substituted polythiophenes should be mainly due to conformational changes instead of excitonic effects.[32,33]

On the basis of all these studies, it was then postulated that various external stimuli could perturb the side-chain organization and, consequently, could induce some chromic effects. Along these lines, various polythiophenes, bearing appropriately designed side chains, have shown striking conformational and optical changes when exposed to pressure (piezochromism),[34] light (photochromism),[35] and chemical moieties (ionochromism and affinity chromism).[36–40] Following these studies, we report here the synthesis and chromic behaviors of polythiophenes bearing crown-ether side chains; namely, poly(3-methyl-4-(1,4,7,10-tetraoxacyclododecan-2-yl)methoxythiophene) (PT12C4) and poly(3-methyl-4-(1,4,7,10,13-pentaoxacyclopentadecan-2-yl)methoxyhexyloxythiophene) (PT15C5) (see Chart 1). Crown ethers are well known for their ability to make complexes with alkali metal cations[41,42] and using these properties combined with the chromic features

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of poly(3-alkoxy-4-methylthiophene)s new ionochromic sensors have been developed.

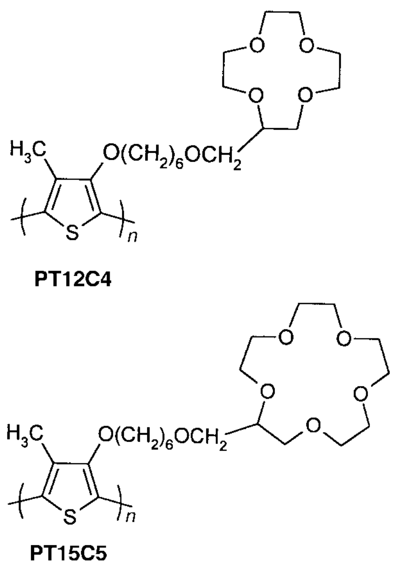

Chart 1

Experimental

Materials

From a reaction between 3-(6-bromohexyloxy)-4-methylthiophene[35,39] (1.85 g, 6.70 mmol) and 2-hydroxymethyl-1,4,7,10-tetraoxacyclododecane (1.29 g, 6.25 mmol) (Aldrich Co.), with 5.5 mL of an aqueous NaOH solution (50% w/w) in 7.0 mL of benzene in the presence of tetrabutylammonium hydrogensulfate (110 mg, 0.32 mmol) (following a procedure developed by Bäuerle and Scheib[42a]), 3-(methyl-4-(1,4,7,10-tetraoxacyclododecan-2-yl)methoxyhexyloxythiophene (T12C4) was obtained. Yield: 52%. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 1.46 (m 4 H), 1.60 (q, 2 H), 1.76 (q, 2 H), 2.09 (s, 3 H), 3.38–3.93 (m, 21 H), 6.13 (s, 1 H), 6.83 (s, 1 H). ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ 12.56, 25.74, 25.81, 29.04, 29.44, 69.71, 70.12, 70.27, 70.57, 70.58 (2C), 70.76, 70.84, 71.40, 71.70, 78.54, 95.78, 119.58, 129.05 and 156.10.

Similarly, from a reaction between 3-(6-bromohexyloxy)-4-methylthiophene and 2-hydroxymethyl-1,4,7,10,13-pentaoxacyclopentadecane (Aldrich Co.), using a coupling reaction in KOH–DMSO,[43] 3-(methyl-4-(1,4,7,10,13-cyclopentadecan-3-yl)-methoxyhexyloxy)thiophene (T15C5) was synthesized. Yield: 45%. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 1.42 (m, 4 H), 1.58 (q, 2 H), 1.77 (q, 2 H), 2.02 (s, 3 H), 3.46–4.01 (m, 25 H), 6.11 (s, 1 H) and 6.80 (s, 1 H). ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ 12.61, 25.79, 25.85, 29.09, 29.49, 69.78, 70.18, 70.47, 70.50, 70.52 (2C), 70.71, 70.86, 70.97, 70.99, 71.40, 71.52, 78.65, 95.81, 119.61, 129.12 and 156.16.

The polymers were prepared by chemical polymerization in chloroform using iron trichloride as the oxidizing agent.[15] After 12 h of stirring at room temperature, PT15C5 was precipitated in methanol, filtered off and washed with methanol in a Soxhlet apparatus for 6 h or until the washing solvent became clear. It was then dissolved in chloroform, filtered, evaporated, washed again with methanol, and dried under vacuum at room temperature for at least 24 h (30% yield). A similar procedure was used for the synthesis of PT12C4. Yield: 40%. PT12C4 and PT15C5 are completely soluble in chloroform, THF, acetone, acetonitrile and ethyl acetate at room temperature.

Physical methods

NMR spectra measurements were made on a Brüker ARX 400 or ARX 600 spectrometer. Differential scanning calorimetry (DSC) analysis was performed on a TA Instrument (Model 2910) at 10 °C min^{-1} calibrated with ultrapure indium. X-Ray diffraction patterns of polymer samples were recorded by a scintillation counter coupled with a pulse-height analyzer as detector using Ni-filtered Cu-Kα radiation from a Rigaku rotating anode generator (Rotaflex RU200). Collimation was done at wide angles with a Soller slit and a 1.0 mm pinhole. The temperature was controlled by a water-cooled copper block oven with Mylar windows.

Absorption spectra were taken with a Hewlett-Packard diode array UV-vis spectrophotometer (model 8452A) in a 1 cm quartz cell for solution measurements and on a quartz plate for solid-state measurements. A temperature control unit was used to perform the thermochromic measurements. $\mathrm{LiCF_3SO_3}$, $\mathrm{NaCF_3SO_3}$ and $\mathrm{KCF_3SO_3}$ (Aldrich) were used as received. Solutions of the salts were made in the same solvent as the polymer and equal volumes of salt and polymer solutions were mixed. Spectrograde acetone was used with PT12C4 and spectrograde ethyl acetate was used with PT15C5. In the absence of light, these solutions were stable for several days.

Results

Characterization of the polymers

It is now well established that, due to the asymmetric reactivity of the oxidized monomer,[44] chemical polymerization of 3-alkoxy-4-methylthiophenes leads to highly regioregular polymers. PT12C4 and PT15C5 belong to this class of polymers, their regioregularity being revealed by the ^{1}H and ^{13}C NMR spectra of the polymers (see Fig. 1). For instance, as shown in Fig. 1b, the aromatic region of the ^{13}C NMR spectrum of PT12C4 exhibits only four sharp peaks (between δ 115 and 155) for the four aromatic carbon atoms of one repeat unit of

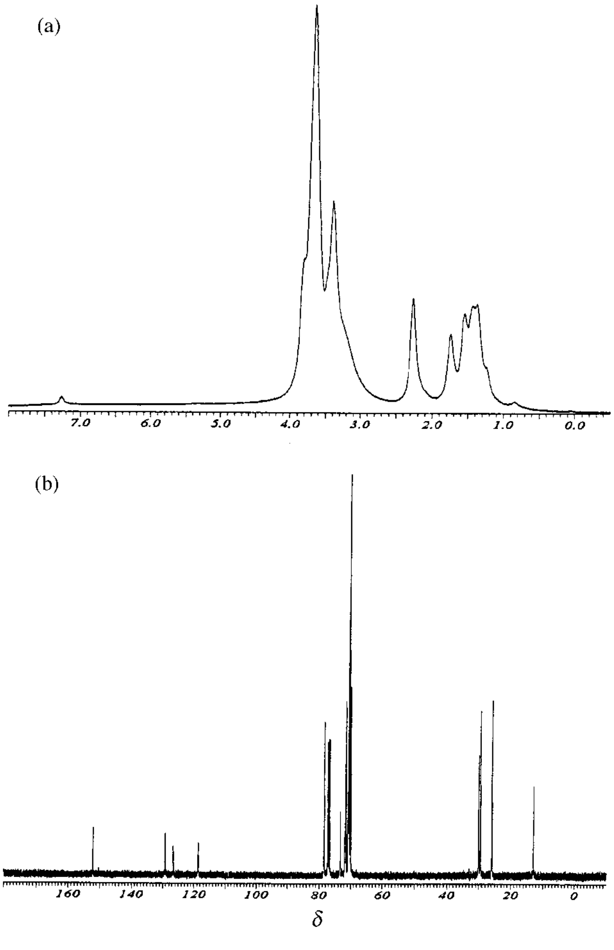

Fig. 1 NMR spectra of PT12C4 in chloroform: (a) ^{1}H and (b) ^{13}C.

the polymer. These four aromatic peaks together with the presence of one peak at δ 2.3, characteristic of the methyl group at the 4 position, in the ^{1}H NMR spectrum (Fig. 1a) confirm that PT12C4 is a highly regioregular polythiophene derivative. Similar conclusions have been drawn for PT15C5.

The molecular weight of both polymers was evaluated from the ^{1}H NMR data to be higher than 6000, the absence in the ^{1}H NMR spectra of the peaks characteristic of the end groups (δ 6.1 and 6.8) being typical of high molecular weight polymers. However, with our size-exclusion chromatographic equipment, it was impossible to determine their exact molecular weight due to a strong adsorption of the polymers within the SEC columns.

Thermochromism

The thermochromic behavior of these two polymers was investigated both in the solid state and in solution. For instance, a thin film of PT15C5, cast from a chloroform solution, shows an absorption maximum at 544 nm at room temperature which reveals a highly conjugated (planar) backbone. Upon heating, the intensity of this absorption maximum decreases and leads to a new absorption band at 434 nm, which is related to a less conjugated or twisted form of the main chain (Fig. 2). A near-isosbestic point is present which testifies to the coexistence of both forms of the polymer. The transition between these two conformations of the PT15C5 occurs at very low temperatures and this feature seems related to the presence of a highly flexible side chain in the polymer (this assumption is supported by the low glass transition temperature, see below). After the polymer has been heated it does not totally recover its initial planar form but remains, at room temperature, in a twisted form. Upon further cooling the initial absorption spectrum of the polymer film was recovered.

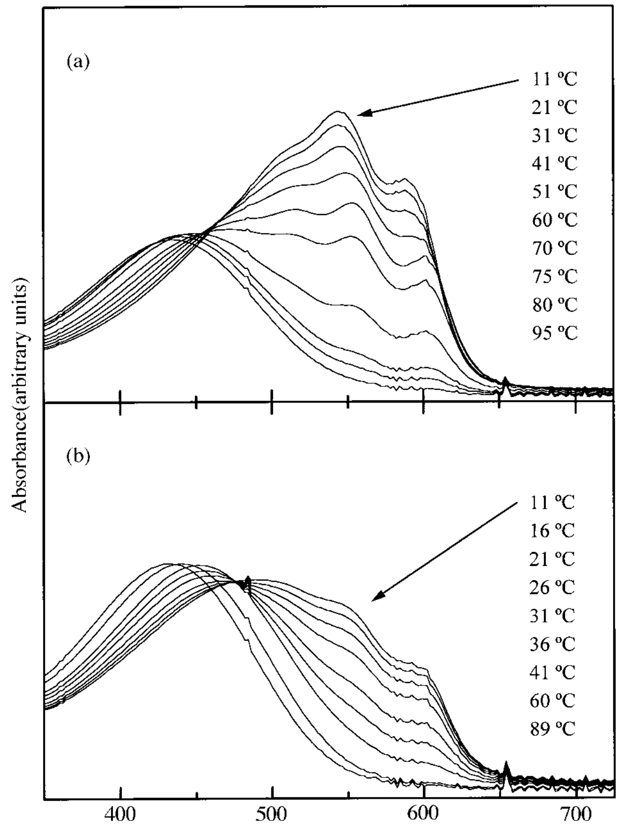

Fig. 2 Temperature-dependent UV-visible absorption spectra of PT15C5 in the solid state: (a) heating; (b) cooling.

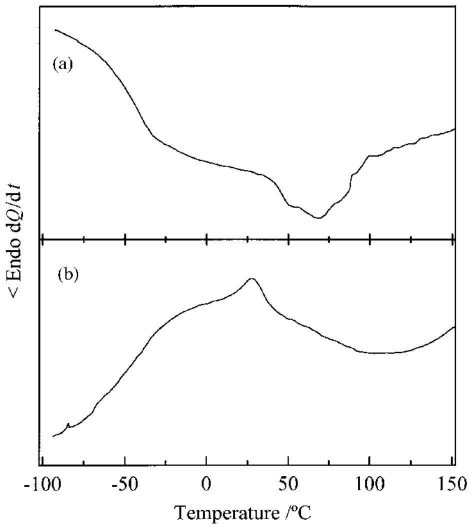

Fig. 3 Thermograms of PT15C5: (a) heating; (b) cooling.

The observations made about the thermochromic behavior of PT15C5 can also be made from the thermal analysis data (Fig. 3). The glass transition temperature of the polymer is around −40 °C and a first order thermochromic transition occurs from 40 to 90 °C. Upon subsequent cooling an exothermic transition occurs between 40 and 10 °C confirming our spectroscopic data. X-Ray diffraction patterns of the polymer were recorded before and after the chromic transition (25 and 100 °C) in order to confirm the planar to non-planar transition of the backbone upon heating (Fig. 4). At room temperature the polymer exhibits a lamellar organization, with a repeat distance of 30.6 Å ($2\theta = 2.9^0$). Distances between thiophene chains are in the range of 4.06 Å ($2\theta = 21.9^0$), allowing an efficient stacking. As the temperature increases the twisted form of the backbone prevails and the packing distance rises from 4.06 ($2\theta = 21.9^0$) to 4.19 Å ($2\theta = 21.2^0$); this form hinders a compact arrangement and the lamellar organization peak disappears as well. Although not shown here, PT12C4 exhibits very similar features. At room temperature, it has a lamellar organization with a repeat distance of 29.0 Å and a stacking distance of 4.1 Å between the polythiophene chains. This lamellar organization disappears upon heating (80 °C).

Thermochromism in solution is also observed. The transition temperature is dependent on the solvent quality since these polymers are also solvatochromic. For example, in a poor solvent, such as acetonitrile, PT15C5 exhibits a highly conjugated form at room temperature but adopts a twisted form (maximum absorption at 424 nm) upon heating (Fig. 5). An

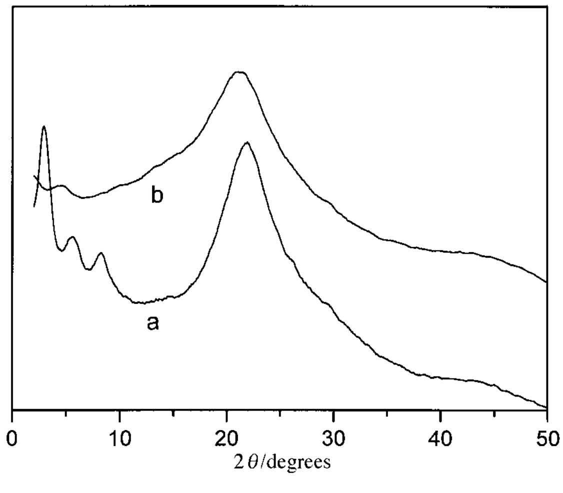

Fig. 4 X-Ray diffraction spectrum of PT15C5 at (a) 25 °C, (b) 100 °C.

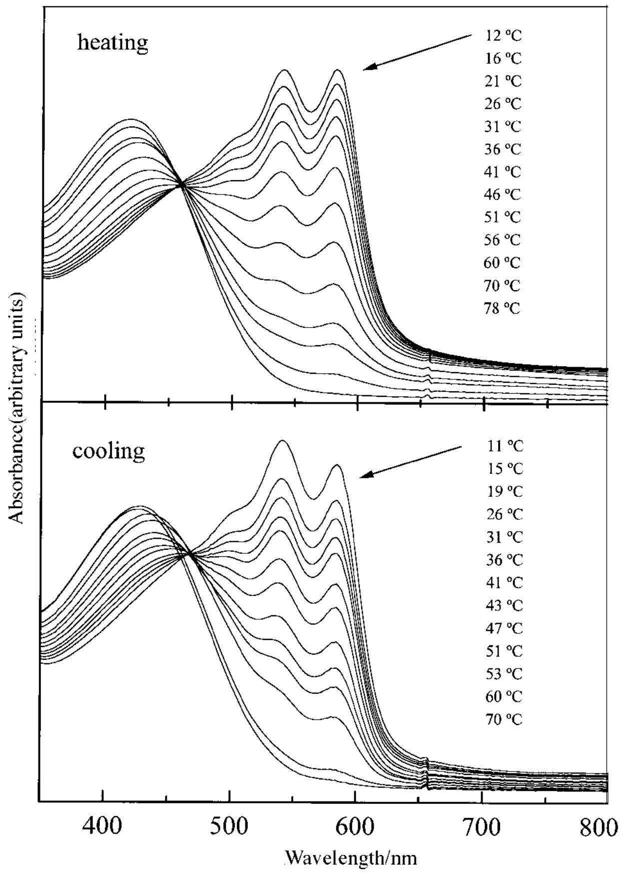

Fig. 5 Temperature-dependent UV-visible absorption spectra of PT15C5 in acetonitrile.

isosbestic point is also observed here with no significant hysteresis phenomenon. The better reversibility of the chromic transition in solution is probably due to the ease of movement of the polymer chains which cannot be recovered in the solid state. In addition, the presence of a crystalline phase in the polymer probably introduces a kinetic barrier to the reversibility of the transition in the solid state. In acetonitrile, the initially violet PT12C4 solution becomes yellow around 70 °C.

Ionochromism

Another important feature of these molecules is their chromic response to alkali metal cations in solution. Regioregular poly(3-alkoxy-4-methylthiophenes) bearing appropriate side chains are known for their ability to complex alkali metal ions and this feature has led to the development of ionochromic sensors.[26,39] The interactions between the side chains and the ions provoke a conformational modification of the backbone and a color change of the solution, either from violet (maximum of absorption around 550 nm) to yellow (maximum of absorption around 425 nm) or the opposite. One aim of this work was to synthesize tailored polymers sensing a specific alkali metal ion. For this reason, side chains bearing a crown ether, well known to complex alkali metal ions of similar radii,[41] have been introduced. Pedersen[41] showed that the most stable complex between a crown ether and an alkali metal ion was obtained when the ligand cavity was similar to the ionic radius of the guest ion such as with 12-crown-4 and Li^+ and 15-crown-5 and Na^+. Meanwhile, other stable complexes can be formed between crown ethers and alkali metal ions involving a 2:1 stoichiometry such as Na^+(12-crown-4)$_2$ and K^+(15-crown-5)$_2$, in methanol.[45–47]

The ionochromic response of PT12C4 to lithium, sodium, and potassium ions has been investigated in acetone. In this solvent the polymer is mostly in a twisted form and the maximum absorption is located at 444 nm (Fig. 6). Upon addition of any of these three ions the absorption around 544 nm increases, meaning that these ions induce a more planar conformation of the PT12C4 backbone. It could be anticipated that the polymer would best respond to lithium salts since the size of the cavity is comparable to the radius of the lithium cation. Not only this effect was not observed, but lithium cations seem to induce the least important ionochromic effect (Fig. 7). As can also be observed from Fig. 7, PT12C4 is actually more sensitive towards sodium cations. The absorption spectra at different salt concentrations (Fig. 6) show an isosbestic point, indicating the coexistence of two conformational species. Different anions were tested and, as expected, it was found that the anion did not play any major role. The same ionochromic response was found in ethyl acetate but precipitation of the polymer occurred within 30 min. Similar experiments were conducted with PT15C5 in ethyl acetate. Again, the lithium salt showed the weakest effect, but in this case potassium ions led to the strongest ionochromic effect (Fig. 8). Solid-state experiments on both polymeric materials (carried out at different temperatures) did not reveal any significant ionochromic effect. These results can be attributed to a more viscous system, where side-chain ordering (or disordering) is rendered more difficult. To the best of our knowledge, direct solid-state ionochromic effects have only been observed in some bipyridyl–phenylene–vinylene based

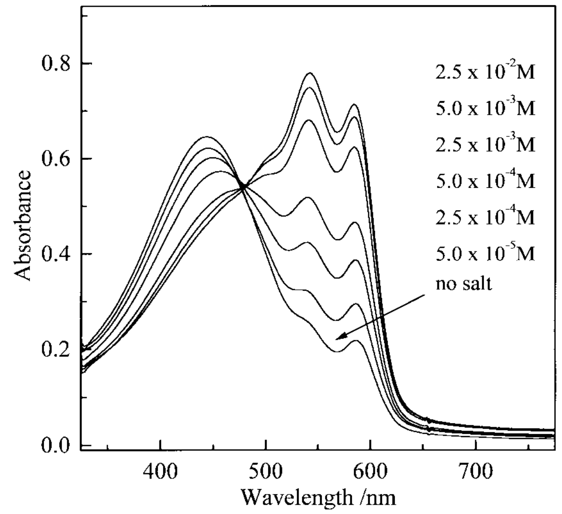

Fig. 6 UV-visible absorption spectra of PT12C4 (1×10^{-4} M) in acetone with different $NaCF_3SO_3$ concentrations.

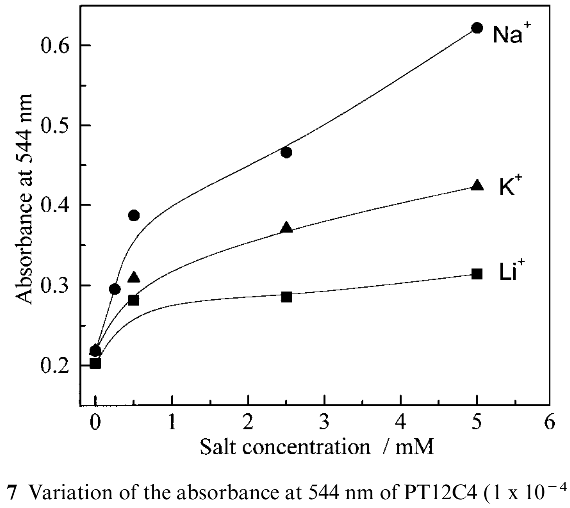

Fig. 7 Variation of the absorbance at 544 nm of PT12C4 (1×10^{-4} M) as a function of the concentration of various salts, (●) $NaCF_3SO_3$, (▲) KCF_3SO_3, and (■) $LiCF_3SO_3$, at room temperature, in acetone.

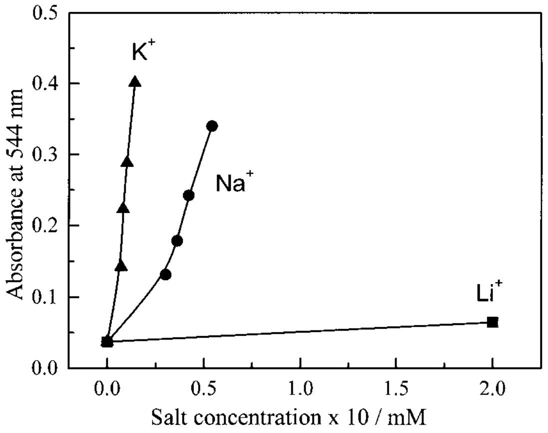

Fig. 8 Variation of the absorbance at 544 nm of PT15C5 (6 x 10^{-5} M) as a function of the concentration of various salts, (●) $NaCF_3SO_3$, (▲) KCF_3SO_3 and (■) $LiCF_3SO_3$, at room temperature, in ethyl acetate.

polymers and did not involve a significant backbone rearrangement.[48]

Discussion

The thermochromic response of both PT12C4 and PT15C5 is driven by the thermally induced side-chain disordering, forcing a mostly planar chain into a non-planar conformation. The ionochromic response of the polymers is opposite, a non-covalent interaction between the side chains and alkali metal ions driving the backbone from a mostly non-planar conformation to a planar one. Even though these two phenomena seem contradictory, they both can be explained by a co-operative conformational transition (domino effect), revealed by the presence of an isosbestic point, the twisting of one repeat unit inducing the twisting of many adjacent (intramolecular and intermolecular) units. The presence of a co-operative mechanism can be related to the formation (disruption) of supramolecular assemblies of highly regioregular polythiophene derivatives, a monotonic and ion-dependent shift of the maximum of absorption being observed with non-regioregular polythiophene derivatives.[37] On the other hand, the ion-dependent sensitivity of the present ionochromic polymers can be rationalized by considering the interactions between the crown ethers and the different ions. For instance, PT12C4 has a cavity to integrate a lithium cation but, since this ion is very small and fits well into the cavity, the change of the effective size of the side chain is small, thereby the crown ether–lithium complex is not able to induce any important modification of the side-chain organization and hence cannot induce any important effect on the backbone conformation. It is worth noting here that the presence of the counter ions in the vicinity of the polymer–lithium complexes may also induce some conformational modifications in both the side chain and main chain organizations, although this effect is difficult to assess. On the other hand, sodium and potassium cations have larger ionic radii but can form 1 : 1 complexes with 12-crown-4 with similar stability constants; however, sodium ions can form much more stable 2 : 1 complexes with 12-crown-4.[45] It is important to note that such complexes can be intramolecular or intermolecular. The difference between the ionochromic response of PT12C4 to sodium and potassium ions is then believed to be related to the formation of such stable 2 : 1 complexes which force the backbone to adopt a coplanar structure. PT15C5 has shown similar ionochromic effects which are also dependent upon the nature of the cation. The lithium cation has exhibited almost no ionochromic effect since this cation can easily be inserted within the crown ether. Moreover, 15-crown-5 can form 1 : 1 complexes of comparable stability with both sodium and potassium cations. However, the stability constant of the 2 : 1 complexes is higher with potassium ions[45] which could then explain the more intense ionochromic effects observed in PT15C5 solutions with potassium salts. Finally, comparisons between the relative limit of detection of PT12C4 and PT15C5 are not relevant since these polymers have not been studied in the same solvent. As can be anticipated, the competition for the solvation of the alkali metal ions between the crown ether and the solvent is certainly different in the two cases.

Conclusion

Regioregular poly(3-alkoxy-4-methylthiophene)s bearing crown ether moieties have easily been synthesized. Their thermochromic response is similar to that of a regioregular polythiophene bearing flexible, linear side chains. In the solid state these polymers exhibit an absorption maximum around 550 nm which upon heating moves to 425 nm and a near-isosbestic point is observed. Moreover, these polythiophene derivatives respond to ionic stimuli in solution (ionochromism). PT12C4 is more sensitive to sodium salts while PT15C5 is more sensitive to potassium salts due to the formation of stable complexes between two crown ether units and one alkali metal ion. On the basis of these studies, the ionochromic behavior of a polythiophene bearing crown ethers can now be predicted and thereby can lead to the rational design of ionochromic sensors.

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