Thermochromic and Solvatochromic Conjugated Polymers by Design

Geneviève Dufresne,[†] Jimmy Bouchard,[†] Michel Belletête,[‡] Gilles Durocher,[‡] and Mario Leclerc*,[†]

Département de Chimie, Centre de Recherche en Sciences et Ingénierie des Macromolécules, Université Laval, Quebec City, Quebec, Canada G1K 7P4, and Département de chimie, Université de Montréal, Montréal, Quebec, Canada H3C 3J7

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ABSTRACT: The thermochromic and solvatochromic properties of a series of phenylene-based conjugated polymers have been investigated experimentally and theoretically. Poly(1,4-(2,5-dioctyloxyphenylene)-2,5-thiophene), poly(1,4-(2,5-dioctylphenylene)-2,5-furan), and poly(1,4-(2,5-didodecyloxyphenylene)-2,5-(3,4-diethylenedioxythiophene)) have revealed interesting chromic effects which, on the basis of calculations on dimer model compounds, seem to be related to a rather flexible backbone with an energy barrier against planarity <1.3 kcal/mol. However, in the absence of sterically demanding side chains (e.g., poly-(1,4-(2,5-dioctyloxyphenylene)-2,5-furan)), the conjugated polymer can maintain a highly conjugated (coplanar or nearly coplanar) conformation, even at high temperatures or in dilute solutions. Finally, as observed with poly(1,4-(2,5-dioctylphenylene)-2,5-thiophene), if the steric interactions are too strong, no coplanar conformation can be adopted upon cooling or aggregation.

Introduction

The past 20 years have witnessed the emergence of conjugated polymers as an important class of electroactive and photoactive materials.[1] This development has been sustained by the judicious utilization of a variety of synthetic tools to prepare highly pure polymers with optimized physical properties. For instance, the syntheses of well-defined polyacetylene,[2] polythiophenes,[3] polyphenylenes,[4] polyfluorenes,[5] ladder polymers,[6] and other conjugated polymers[7] have allowed a significant improvement in the performance of these polymeric materials. Many synthetic methods are therefore available to couple, in a controlled manner, various aromatic monomers to produce a large number of novel conjugated polymers. Such a combinatorial approach is one possibility to explore all features of this class of materials, but it could be more helpful to develop a rational design based on a good knowledge of the structure−property relationships in conjugated polymers. Indeed, one great challenge in polymer science is certainly the prediction of the structure and properties of synthetic polymers from the only knowledge of the structure of their monomeric units.[8]

Among the physical properties of conjugated polymers, the development of chromic (thermochromic, solvatochromic, piezochromic, ionochromic, affinitychromic) polymers has recently attracted a lot of attention, mainly because of their great potential of applications in the areas of sensors, diagnostics, and drug screening.[9−12] These intriguing optical features have been mainly observed in functionalized polydiacetylenes,[10] polysilanes,[11] or polythiophenes.[12] Extensive studies on several polythiophene derivatives have led to the conclusion that these optical effects are driven by a delicate balance between repulsive intrachain steric interactions and attractive interchain (or intrachain through chain folding) interactions.[13] More precisely, it has been postulated that chromic polythiophene derivatives can form planar or nearly planar assemblies which are disrupted upon side-chain disordering, a twisting of the backbone being involved with this diassembly. Accordingly, this conformational transition of the conjugated backbone is accompanied by a modification of the effective conjugation length which greatly affects the UV−vis absorption spectrum.[14] Recent optical studies coupled to quantum chemical calculations of the intermolecular interactions in conjugated oligothiophene model compounds have supported this model and have revealed that chromic conjugated molecules exhibit a twisted (nonplanar) conformation in the absence of interchain interactions (gas phase) but with a relatively low energy barrier against planarity (≤2.2−2.3 kcal/mol per repeat unit).[15] It seems that this energy barrier can be compensated through attractive interactions which are maximized when these conjugated molecules adopt a planar conformation. However, some exciton coupling effects may also be involved and may contribute to the observed chromic phenomena.

As mentioned above, thermochromic and solvatochromic effects are not exclusive to polythiophenes and, in principle, could be found in many aromatic polymers. In this regard, a brief mention of thermochromic effects was previously reported for poly(1,4-(2,5-dialkoxyphenylene)-2,5-thiophene)s.[16] These indications have led us to investigate in more detail the thermochromic and solvatochromic properties of these conjugated polymers. These experimental studies have also been supported by theoretical calculations on various dimer model compounds and have led to a better understanding of the optical features of poly(1,4-(2,5-dialkoxyphenylene)-2,5-thiophene)s but also to the discovery of chromic (or nonchromic) effects in other alternating conjugated copolymers derived from phenylenes. The polymers studied here are represented in Scheme 1.

Experimental Section

Materials. Poly(1,4-(2,5-dioctyloxyphenylene)-2,5-thiophene) (polymer 1), poly(1,4-(2,5-dioctylphenylene)-2,5-thiophene) (polymer 2), poly(1,4-(2,5-dioctylphenylene)-2,5-furan) (polymer 3), and poly(1,4-(2,5-dioctyloxyphenylene)-2,5-furan) (polymer 4)

[†] Université Laval.
[‡] Université de Montréal.
* To whom correspondence should be addressed.

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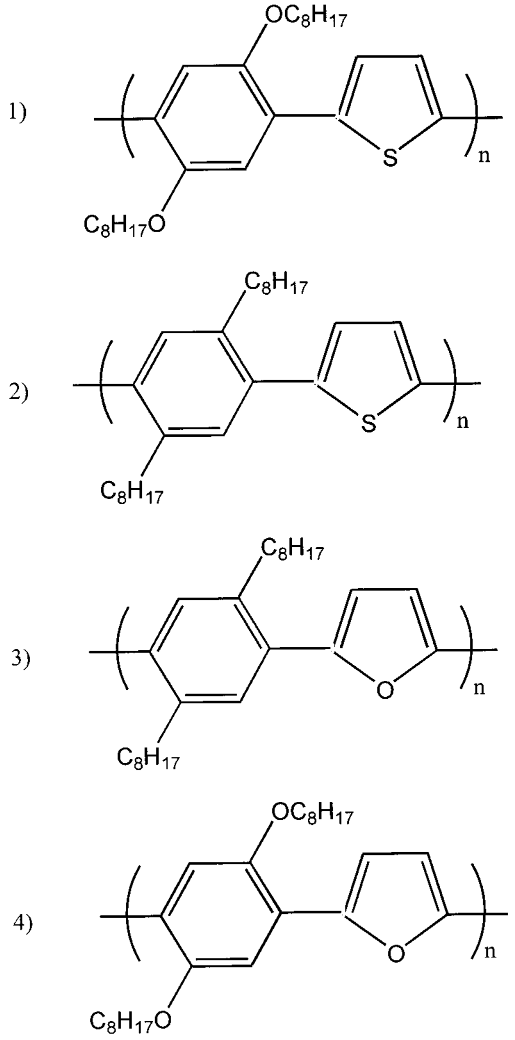
Scheme 1



have been prepared from Stille coupling between 1,4-dibromo-2,5-disubstituted phenylenes and 2,5-bis(tributylstannyl)furan or 2,5-bis(tributylstannyl)thiophene, following procedures reported in the literature.[16–19] All these polymers (see Scheme 1) are soluble in tetrahydrofuran or chloroform. Alkoxy-substituted polymers exhibit a number-average molecular weight of 5 kDa with a polydispersity index of about 1.2 whereas alkyl-substituted polymers show a number-average molecular weight of 7 kDa with a polydispersity index of about 1.6.

Instrumentation. Number-average (M_n) and weight-average (M_w) molecular weight were determined by size exclusion chromatography (SEC) with an HPLC pump using a Waters UV–vis detector. The calibration curve was made with a series of monodispersed polystyrene standards in THF (HPLC grade, Aldrich). UV–vis absorption spectra were recorded on a Hewlett-Packard diode-array spectrophotometer (model 8452A) using 1 cm path length quartz cells. The concentration of the polymer was about $(1-5) \times 10^{-5}$ M (repeat unit) in chloroform. For solid-state thermochromic measurements, polymer solutions in chloroform were cast films on quartz plates. Powder X-ray diffraction patterns were obtained with a Siemens Kristalloflex 760 generator coupled with a CCD Bruker AXS detector (sofware GADDS). The temperature of the furnace is adjusted using a standard controller (Watlow 988).

Theoretical Calculations. Ab initio calculations were performed on a Pentium III (450 Mz) personal computer with 128 Mb RAM using the Gaussian 98W program, version 5.2.[20] The conformational analysis of all dimer model compounds was done by changing the torsional angle θ by 15° steps. The geometries were optimized at the HF level with the 6-31G* basis set. The Berny analytical gradient method was used for the optimizations. The requested HF convergence on the density matrix was 10^{-8}, and the threshold values for the maximum force and the maximum displacement were 0.000 45 and 0.0018 au, respectively. To obtain the final torsional angles of the conformers in each minima, calculations of these geometries were performed without constraint on the dihedral angle.

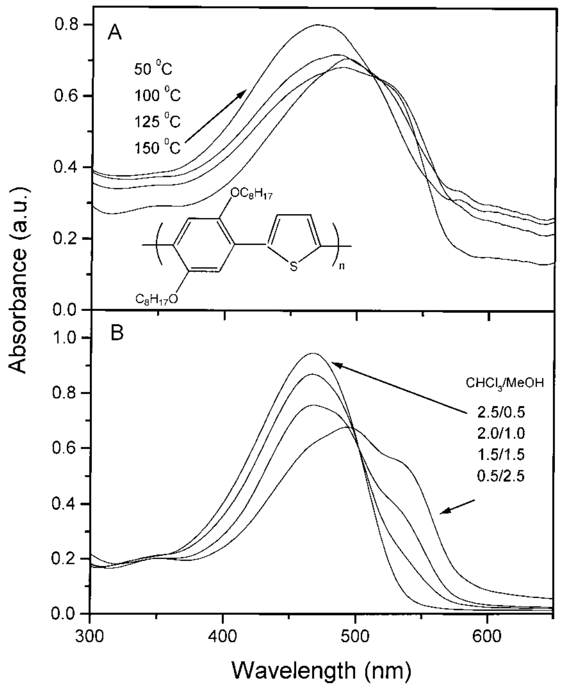


Figure 1. Temperature-dependent (A) and solvent-dependent (v/v) (B) UV–vis absorption spectra of poly(1,4-(2,5-dioctyloxyphenylene)-2,5-thiophene).

Results and Discussion

As mentioned in the Introduction, Bao et al.[16] have noted that thin films of poly(1,4-(2,5-dialkoxyphenylene)-2,5-thiophene) undergo a reversible thermochromic transition: when heated, the color of the polymer changes from red to yellow, returning to red when it is cooled to room temperature. As shown in Figure 1A, these solid-state thermochromic results have been confirmed; the maximum of absorption of poly(1,4-(2,5-dioctyloxyphenylene)-2,5-thiophene) varying from 495 nm at room temperature to 466 nm at 150 °C. Similarly, solvatochromic studies in mixtures of chloroform (good solvent) and methanol (poor solvent) have revealed a shift of the maximum of absorption from 468 to 495 nm upon decreasing the quality of the solvent (Figure 1B). In both cases, it can be assumed that a more delocalized structure is created upon aggregation or cooling which leads to a red shift of the UV–vis absorption spectrum. A vibronic fine structure is also observed at low temperatures or in a bad solvent, and this energy difference of about 0.18 eV from the main peak is consistent with a C═C stretching mode that would be expected to couple strongly to the electronic structure.[3a]

Unfortunately, very little is known about the electronic potential of the polymer backbone, but as recently reported for some polythiophene[13] and polyfluorene[21] derivatives, the analysis of the potential energy surfaces of dimer model compounds can be useful to understand these chromic effects. These previous studies have indeed suggested that planarization of twisted repeat units may occur upon stacking when the energy barrier

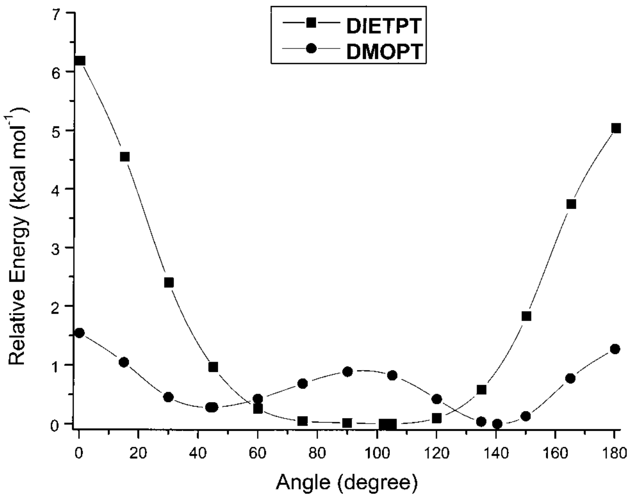


Figure 2. Ground-state potential energy surfaces of 1-(2,5-dimethoxyphenylene)-2′-thiophene (DMOPT) and 1-(2,5-diethylphenylene)-2′-thiophene (DIETPT).

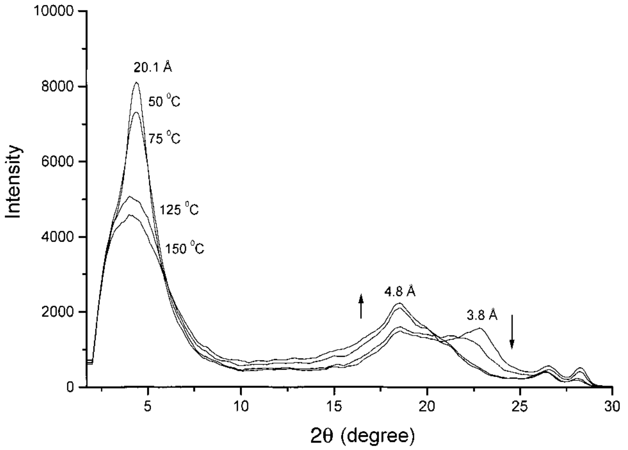


Figure 3. Temperature-dependent X-ray diffraction spectra of poly(1,4-(2,5-dioctyloxyphenylene)-2,5-thiophene).

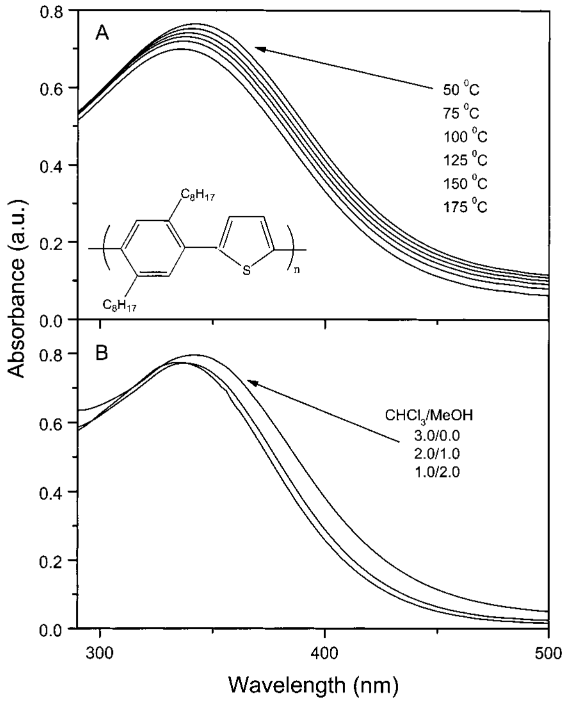


Figure 4. Temperature-dependent (A) and solvent-dependent (v/v) (B) UV–vis absorption spectra of poly(1,4-(2,5-dioctylphenylene)-2,5-thiophene).

against planarity is relatively small. In this regard, the potential energy surface of 1-(2,5-dimethoxyphenylene)-2′-thiophene (DMOPT) is reported in Figure 2. In all cases, the dimeric model compound is the repeating unit of the related polymer, an anti ($\theta = 180°$) conformation corresponding to the structure reported in Scheme 1. Moreover, to reduce the time of calculations, octyloxy side chains were replaced by methoxy side groups. Indeed, previous studies[13,21] have shown that the side chain length does not significantly influence the conformation of the backbone. Therefore, for 1-(2,5-dimethoxyphenylene)-2′-thiophene (DMOPT), the global energy minimum is located at 140° whereas a local minimum is observed near 45°. One can see that the energy barrier against planarity (180°) is only 1.3 kcal/mol. On the basis of previous calculations,[13,21] this small energy barrier should be compensated through interchain interactions, and a coplanar structure is assumed to take place in the related polymer in the solid state at low temperatures or upon aggregation in a poor solvent. A rough estimation of these attractive interchain interactions can be made from the heat of fusion of thiophene oligomers: for example, the enthalpy of fusion of terthiophene is around 1.5–2.0 kcal/mol of repeating unit.[13a] Moreover, X-ray diffraction measurements (see Figure 3) have revealed a lamellar structure for this semicrystalline polymer with an interlamellar spacing of 20.1 Å, at room temperature. Upon heating, this interchain distance increases slightly to 22.1 Å. In addition, significant structural modifications associated with either backbone or side-chain stackings (between 17° and 25°) take place. Similar temperature-dependent X-ray diffraction results were reported by Yu et al.[22] for this class of materials. All these results are consistent with both main-chain and side-chain disordering upon heating associated with chromic effects.

In Figure 2, conformational analysis of 1-(2,5-diethylphenylene)-2′-thiophene (DIETPT) is also reported, and from these results, it is predicted that this dimer (and presumably, the related polymer) would adopt a highly twisted conformation (100°) with an energy barrier against planarity (180°) of 5.0 kcal/mol. This relatively high energy barrier should inhibit the formation of a coplanar structure. Accordingly, this twisted molecule (polymer) should remain twisted upon aggregation and, therefore, should not show any significant modification of its optical absorption spectrum as a function of temperature or solvent quality. As shown in Figure 4, these assumptions have been confirmed: poly(1,4-(2,5-dioctylphenylene)-2,5-thiophene) exhibiting an absorption maximum at a relatively short wavelength (342 nm, both in the solid state and in solution) which does not significantly vary with temperature or solvent changes. X-ray diffraction measurements have revealed a rather amorphous structure with broad and weak diffraction peaks around 3° (29 Å) and 20° (4.5 Å) (figure not shown).

All these results on alternating conjugated polymers based on thiophene and 2,5-disubstituted phenylene units clearly show that minor modifications (the change of the oxygen atom next to the phenylene ring for a methylene group) in the structure of the repeat units may dramatically modify the chromic properties of the resulting polymers. Such important effects on the electrical and optical properties were already observed with various alkyl- and alkoxy-substituted conjugated

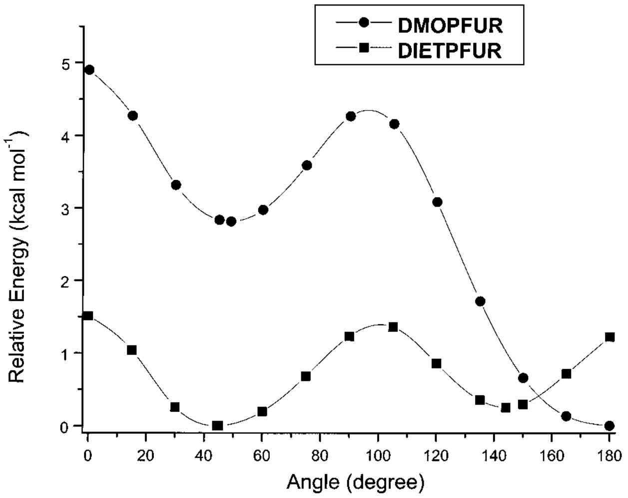


Figure 5. Ground-state potential energy surfaces of 1-(2,5-diethylphenylene)-2′-furan (DIETPFUR) and 1-(2,5-dimethoxyphenylene)-2′-furan (DMOPFUR).

polymers[3a,23−25] and were tentatively explained by the different van der Waals radius of these two chemical species and by their different electron-donating effects. Accordingly, the utilization of a furan unit instead of the thiophene ring could also give a fine-tuning of the chromic properties of the related polymers.

Such polymers have been theoretically and experimentally analyzed, and Figure 5 exhibits the potential energy curve of 1-(2,5-diethylphenylene)-2′-furan (DIETPFUR). This potential energy curve is very similar to that one reported for 1-(2,5-dimethoxyphenylene)-2′-thiophene (DMOPT): the global energy minimum is calculated at 44° with an energy barrier to a coplanar anti conformation of 1.2 kcal/mol. Once again, a coplanar structure should be possible in the solid state at low temperatures or upon aggregation in a poor solvent, and a different conformational structure should appear upon disordering (diassembly). These predictions are confirmed by results reported in Figure 6A where a highly conjugated structure (absorption maximum around 410−415 nm) is observed for poly(1,4-(2,5-dioctylphenylene)-2,5-furan) at low temperatures which is blue-shifted upon heating. As previously reported for some semicrystalline polythiophene derivatives,[26,27] the absence of a clear isosbestic point could be explained by a high degree of crystallinity. Indeed, the transition temperature of the crystallites may deviate from that of the amorphous region, and this effect can explain the absence of a clear isosbestic point during the thermochromic transition. X-ray analyses confirmed these results and revealed a relatively high degree of crystallinity at room temperature. Upon heating, the lamellar spacing distance broadens and increases from 21.0 to 21.5 Å (figure not shown). Not surprisingly, these features do not occur in the solvatochromic experiments where a near isosbestic point is observed in Figure 6B. In good solvent ($CHCl_3$), the featureless absorption maximum at 388 nm moves at 412 nm in a poor solvent, with the presence of a vibronic fine structure.

Calculations on 1-(2,5-dimethoxyphenylene)-2′-furan (DMOPFUR) have been also performed and are reported in Figure 5. These results predict a very rigid molecule with a coplanar (anti) conformation in the gas phase. On the basis of these results, the corresponding polymer should be highly coplanar and should not exhibit any

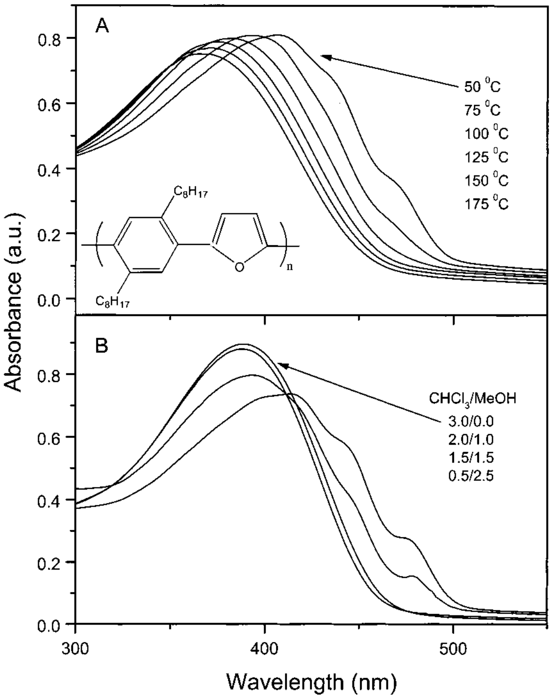


Figure 6. Temperature-dependent (A) and solvent-dependent (v/v) (B) UV−vis absorption spectra of poly(1,4-(2,5-dioctylphenylene)-2,5-furan).

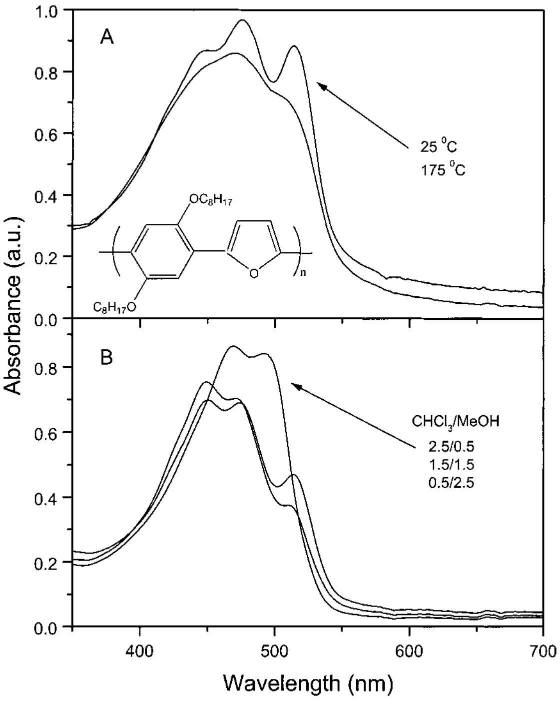


Figure 7. Temperature-dependent (A) and solvent-dependent (v/v) (B) UV−vis absorption spectra of poly(1,4-(2,5-dioctyloxyphenylene)-2,5-furan).

significant chromic features. As theoretically suggested, only weak thermochromic and solvatochromic effects have been observed for poly(1,4-(2,5-dioctyloxyphenylene)-2,5-furan) (Figure 7). In all conditions, a well-defined vibronic structure is observed which is consistent with a rigid and regular backbone. Solid-state X-ray analyses revealed a lamellar structure with a repeating distance of 21.0 Å (Figure 8). These diffraction patterns were not strongly modified upon heating (up to 175 °C). Since a coplanar structure is also assumed for this polymer in

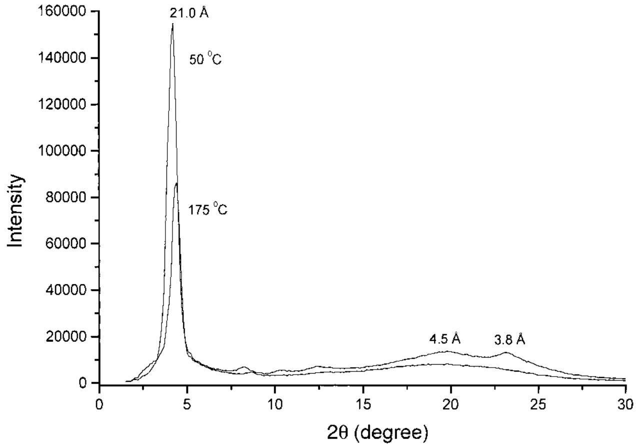


Figure 8. Temperature-dependent X-ray diffraction spectra of poly(1,4-(2,5-dioctyloxyphenylene)-2,5-furan).

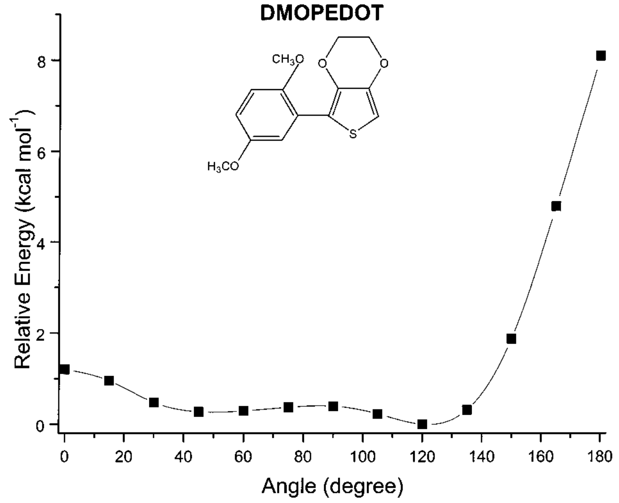


Figure 9. Ground-state potential energy surface of 1-(2,5-dimethoxyphenylene)-2′-(3,4-diethylenedioxythiophene) (DMOPEDOT). The structure shown in this figure corresponds to a torsional angle of 180°.

a good solvent, the weak solvatochromic effects can give an indication of the effect of interchain interactions (without any significant conformational change) on the UV−vis absorption spectrum. In the present case, a slight 0.05−0.10 eV red shift is observed upon (presumably) aggregation in a poor solvent. Furthermore, this rigid boardlike polymer should lead to lyotropic solutions, and the formation of liquid crystalline structures will be investigated in the near future.

Finally, during these investigations on polyphenylene derivatives, Reynolds et al.[28] have reported the synthesis and characterization of poly(1,4-(2,5-didodecyloxyphenylene)-2,5-(3,4-diethylenedioxythiophene)). Interestingly, these authors have mentioned the presence of thermochromic (from a bright red absorptive form to highly transmissive yellow) effects with this polymer. On the basis of theoretical calculations on the dimer model compound (1-(2,5-dimethoxyphenylene)-2′-(3,4-diethylenedioxythiophene), DMOPEDOT; see Figure 9), this conjugated polymer should exhibit a rather flexible backbone with an energy minimum near 120° and an energy barrier against planarity of only 1.2 kcal/mol. Following arguments developed above, this conformational curve could explain the observed thermochromic features. These theoretical and experimental studies support our assumption that flexible conjugated backbone is one of the prerequisites to obtain significant chromic properties.

Concluding Remarks

Experimental and theoretical investigations on various polyphenylene derivatives have clearly shown that thermochromic and solvatochromic phenomena in conjugated polymers can be driven by a delicate balance between steric intramolecular interactions and attractive interchain (or intrachain through a chain folding) interactions. Indeed, poly(1,4-(2,5-dioctyloxyphenylene)-2,5-thiophene), poly(1,4-(2,5-dioctylphenylene)-2,5-furan), and poly(1,4-(2,5-didodecyloxyphenylene)-2,5-(3,4-diethylenedioxythiophene)), which seem to have a rather flexible backbone with an energy barrier against planarity <1.3 kcal/mol, do show chromic effects. On the other hand, as observed with poly(1,4-(2,5-dioctylphenylene)-2,5-thiophene), when steric interactions are too large, no planar conformation is accessible, whereas in the absence of significant steric interactions, poly(1,4-(2,5-dioctyloxyphenylene)-2,5-furan) can maintain a nearly planar conformation, even at high temperatures. Consequently, with these two last classes of polyphenylene derivatives, no significant thermochromic and solvatochromic effect was observed. Finally, comparisons between all these polyphenylene derivatives and previously studied polythiophenes clearly show that subtle changes in the repeat unit of conjugated polymers can lead to completely different chromic behaviors and support the assumptions that conformational analyses on model compounds can be a highly valuable tool to make a rational design of novel smart conjugated polymers.

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