

CHROMIC TRANSITIONS IN PHENYL-SUBSTITUTED POLYTHIOPHENES

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ABSTRACT. The solvatochromic and thermochromic behaviours of phenyl-substituted polythiophenes were studied. The pristine polymers, upon dissolution in chloroform, exhibited blue-shifted absorption. The solid films of the polymers showed significant blue-shifted as well as red-shifted absorptions when heated. While the addition of methanol to the chloroform solutions of the polymers caused dramatic chromic changes and development of red-shifted spectra for many of the polymers investigated, the symmetrically phenyl-substituted and sterically hindered polymer (polymer **1**) does not show significant changes. These chromic behaviours have been examined in terms of substituent effects and attempt has been made to explain these effects by calculating the energy barrier for rotation to a planar structure using the HF SCF method and 3-21G* basis set.

KEY WORDS: Chromic transitions, Phenyl-substituted polythiophenes

INTRODUCTION

Several groups have investigated the chromic properties of functionalized conjugated polymers in order to explain the relationship between optical properties and chemical structure [1-6]. These studies have also opened new possibilities for applications in chemical and biochemical sensors [7-10]. The chromic behaviours of substituted polythiophenes depend on conformational transitions of the polythiophene backbone caused by changes in temperature (thermochromism) or solvent (solvatochromism). The transitions are believed to be between a coplanar (highly conjugated) form and a nonplanar (less conjugated) conformational structure of the backbone [11].

In order to understand the effect of substituents on molecular conformations and subsequently on their physical properties, theoretical calculations have been of great importance. *Ab initio* calculations performed at the HF/3-21G* level on many substituted bithiophenes have provided rotational barriers that have been correlated with the thermochromism and solvatochromism observed in the parent polymers. It was reported that polymers that show chromic behaviours had a flexible backbone with relatively smaller energy barrier against planarity (for example $\leq 2.2 - 2.3$ kcal/mol per repeat unit for conjugated oligothiophenes). On the other hand, nonchromic polymers have a large energy barrier between the planar and twisted conformations. To get such barrier to rotation using *ab initio* method, the 3-21G* basis set was shown to be the minimum level of calculation that gives results in close agreement with those obtained from more elaborate basis sets [12-16].

The electrochemical activity, photovoltaic and optical properties of different kinds of 3-phenyl-substituted polythiophenes have been reported [17-18]. However, to the best of our knowledge *ab initio* calculations on phenyl-substituted polythiophenes and their correlation with

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the experimentally observed thermochromic and solvatochromic properties have not been reported in the literature.

Therefore, this paper deals with the study of the thermochromic and solvatochromic properties of different kinds of phenyl-substituted polythiophenes and correlates the results with the values of the barrier to rotation against planarity obtained using *ab initio* calculations.

EXPERIMENTAL

Ultraviolet-visible absorption spectroscopy. UV-Vis spectra were recorded from dilute solutions or films of the polymers cast on a glass substrate. The spectra were obtained with Spectronic Genesys 2PC Spectrophotometer fitted with a temperature regulating system.

Theoretical calculations. *Ab initio* calculations were performed on a personal computer using Gaussian 98W program [19]. The dimeric structures of the monomers used to synthesize the polymers were drawn using Chem Draw Ultra 7.0 of the Chem Office 2001 package. The structures were then imported to Chem3D. Gaussian 98 was used from the Chem3D interface to optimize the structures, vary the dihedral angles and calculate the energies at each dihedral angle. The conformational analyses of all the dimeric compounds were done by changing the torsional angle θ by 15° steps. The geometries were then optimised at the HF level with the 3-21G* basis set.

RESULTS AND DISCUSSION

The polymers investigated in the course of this study were phenyl-substituted polythiophenes with different side chains whose chemical structures are shown in Figure 1. These polymers were synthesized by the slow addition of a slurry of ferric chloride in chloroform in to solutions of the monomers in chloroform over an extended period of time and then by carefully dedoping with a concentrated solution of NH₄OH and 0.05 M EDTA. This method has been known to provide highly regioregular head-to-tail-coupled polythiophenes [20]. The detailed syntheses of polymers **4** [20], **6** and **7** [21] were described elsewhere. Scheme 1 outlines the syntheses of polymers **1** and **8**. The syntheses of polymers **2**, **3** and **9** are depicted in Scheme 2. Table 1 gives the molecular weights of polymers **1** – **3** and **6** – **9**.

The UV-Vis spectra of polymer **1** in chloroform solution (Table 2) at room temperature shows absorption maximum (λ_{max}) around 347 nm. When a solution of this polymer is cast on a glass substrate there is no shift in the maximum absorption wavelength indicating that there is no aggregation of the polymer film in the condensed phase. On the other hand, the other polymers studied showed red shifts by up to 37 nm (Table 2).

The symmetrically substituted polymer, polymer **1**, remains yellow when heated from room temperature up to 150°C. The UV-Vis absorption spectrum does not also reveal any significant change in the maximum absorption. On the other hand, the other polymers undergo a continuous red or blue shift solid-state thermochromic transitions. When heated, the colours of most of the polymers change from red to yellow, returning to red when cooled to room temperature. For the polymers investigated, the changes in the absorption maxima at two different temperatures are summarized in Table 3. Typical absorption spectra for the polymers that show some significant blue-shifted and red-shifted absorptions are shown in Figures 2 and 3.

Similarly, solvatochromic studies in mixtures of chloroform and methanol have revealed up to about 90 nm red shift in the maximum absorption, where the colour is changed from red to violet, as the mole fraction of methanol is increased, while there is no change in the maximum

absorption wavelength for polymer **1**. Figures 4 and 5 show some typical absorption spectra for polymer **1**, the polymer that does not show any chromic transition, while Figure 5 shows the absorption spectra for polymer **7**, the one that shows significant red shift.

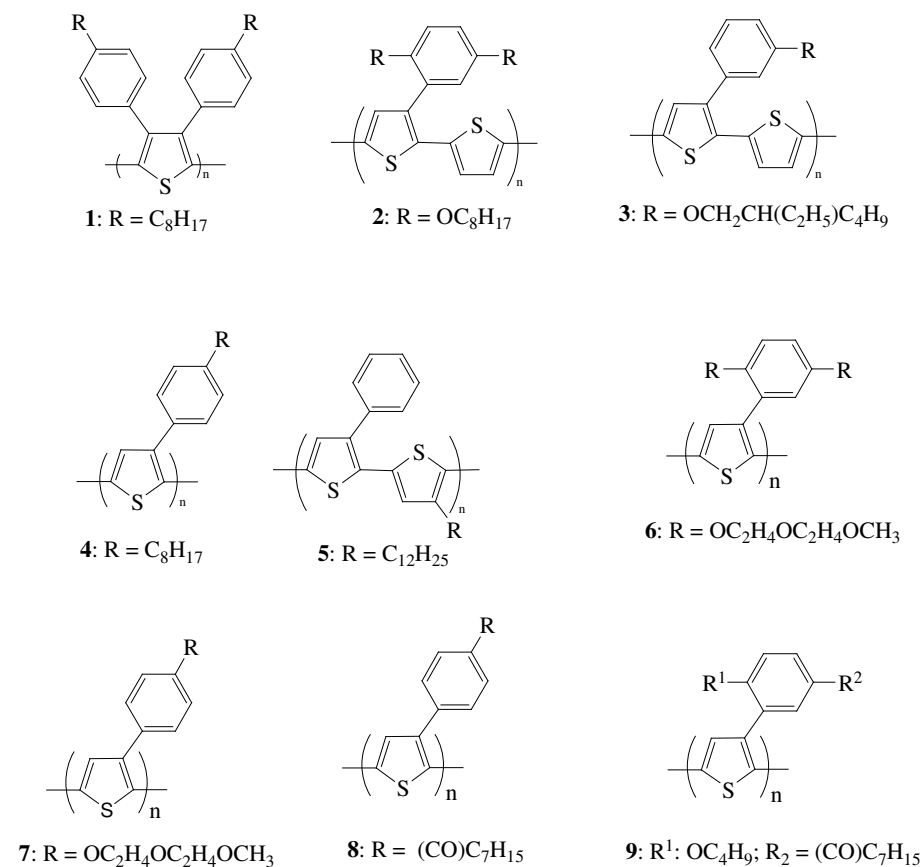
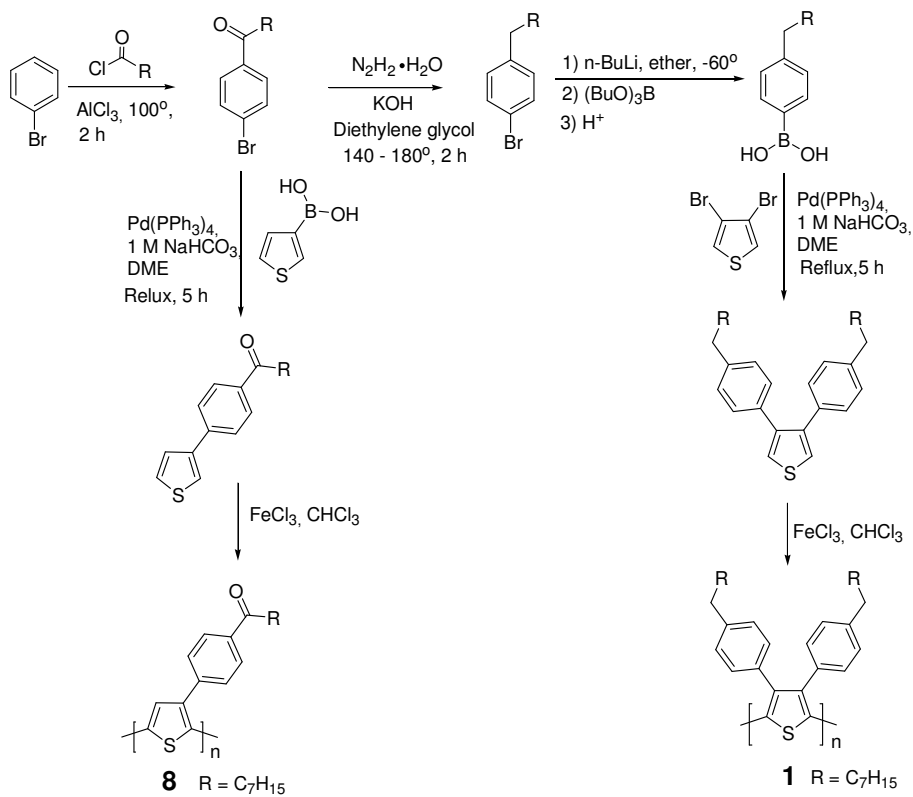


Figure 1. Chemical structures of polymers **1-9**.

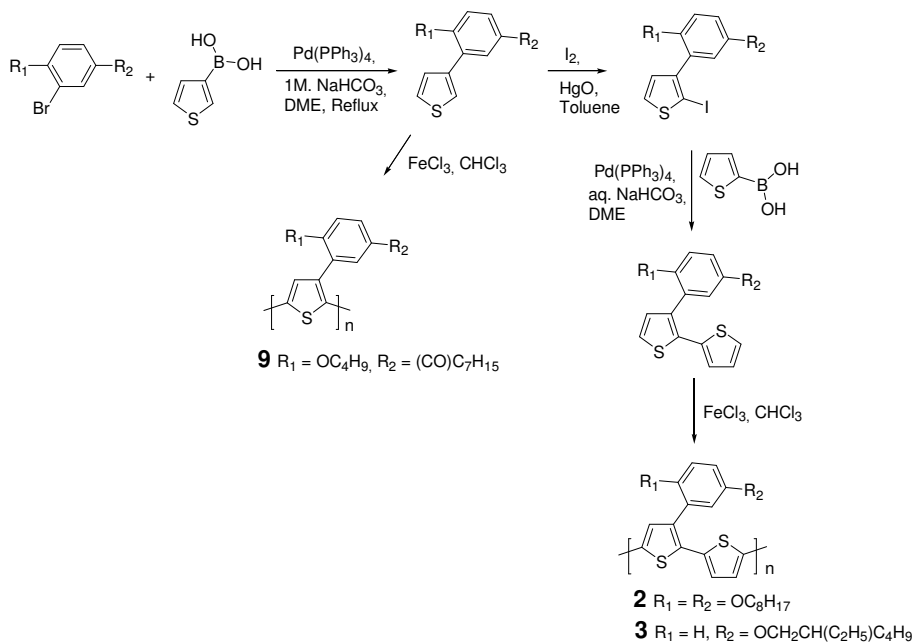
In order to understand the behaviours of these chromic transitions, theoretical quantum chemical calculations were carried out. The energy barrier for rotation of the dimeric structures of the monomers used to synthesise the polymers shown in Figure 1 are plotted as a function of the dihedral angle in Figures 6 and 7. The energy barriers for rotation to a planar structure are summarized in Table 4.

The theoretical calculation shows that (see Figure 6 and Table 4) for polymer **1** the barrier for rotation to a planar structure is much higher than the rest of the polymers investigated, which is in agreement with the nonchromic behaviour of the polymer observed experimentally. On the other hand, polymers **2** and **3**, which show some degree of chromic behaviour, still have large barrier for rotation as compared to polymers **4** and **5**, whose thermochromic and solvatochromic behaviours are reported in the literature [20, 22]. We note that the polymers reported in the

literature (polymers **4** and **5**) are regioregular polythiophenes. Therefore, as can be seen from the results of the theoretical calculations, we conclude that regioregular phenyl-substituted polythiophenes show more pronounced solvatochromic and thermochromic behaviours than the phenyl-substituted polybithiophenes. Both experimental and theoretical calculations on other similar phenyl-substituted regioregular polythiophenes further confirm this conclusion as observed in polymers **6**, **7** and **8**. For polymers **6**, **7** and **8**, the stable conformation is non planar and the barrier against planarity is relatively small as can be seen in Figure 7 and Table 4. The calculated values of the energy barriers against rotation are close in value with similar phenyl-substituted polythiophenes reported in the literature [20, 22].



Scheme 1. The syntheses of polymers **1** and **8**.

Scheme 2. The syntheses of polymers **2**, **3** and **9**.Table 1. The number average (M_n) and weight average (M_w) molecular weights of polymers **1** - **3** and **6** - **8**.

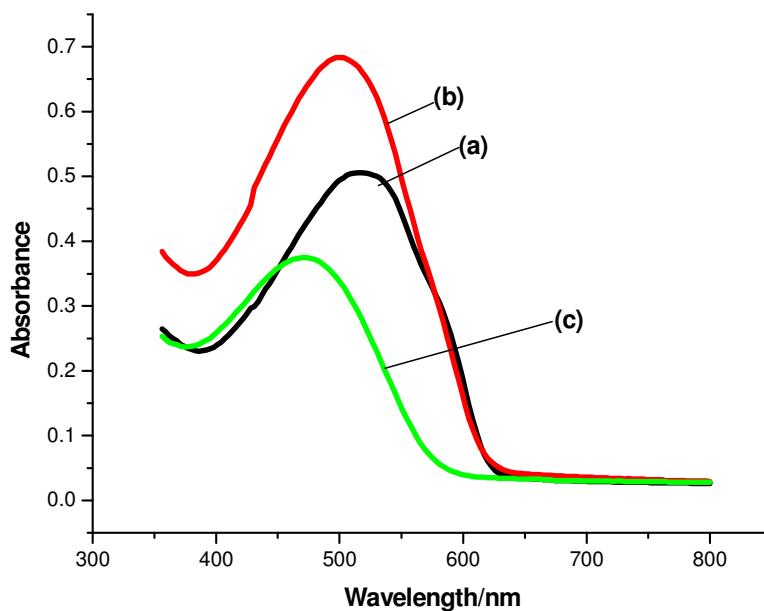
Polymer	M_n	M_w
1	21,000	63,000
2	24,500	105,000
3	3,200	9,700
6	13,600	42,000
7	7,800	25,000
8	9,400	27,000
9	76,640	140,721

Table 2. Comparison of the absorption maxima in the solution and condensed phase for the polymers investigated.

Polymer	λ_{max} (nm) in solution	λ_{max} (nm) in film	$\Delta\lambda_{\text{max}}$ (nm)
1	347	347	0
2	498	513	15
3	468	496	28
6	487	518	31
7	483	520	37
8	446	463	17
9	497	508	11

Table 3. Comparison of the absorption maxima at two different temperatures for the polymers investigated.

Polymer	λ_{\max} (nm) at 25°C	λ_{\max} (nm) at 150°C	$\Delta\lambda_{\max}$ (nm)
1	347	347	0
2	515	491	24
3	497	463	34
6	518	473	45
7	494	553	59
8	461	545	84
9	505	467	38

Figure 2. UV-Vis optical absorption spectra of polymer **6** at: (a) 18°C, (b) 85°C, and (c) 150°C.

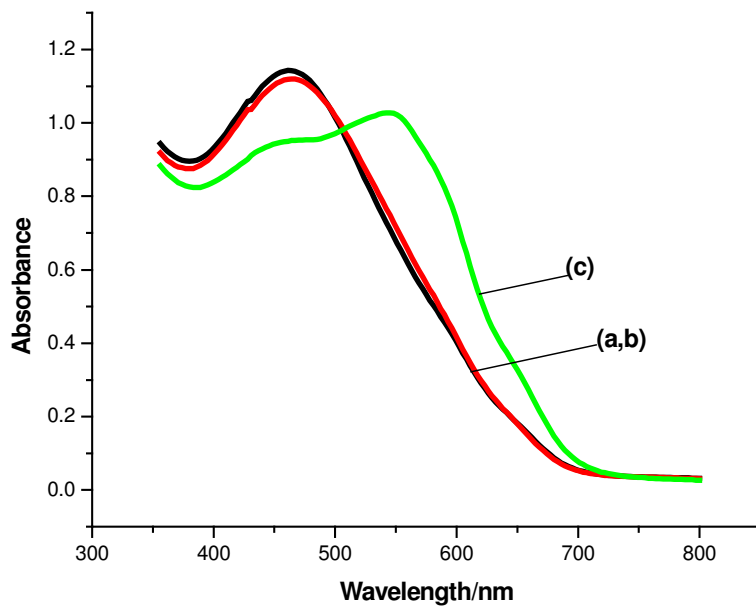


Figure 3. UV-Vis optical absorption spectra of polymer **8** at: (a) 18°C, (b) 85°C, and (c) 150°C.

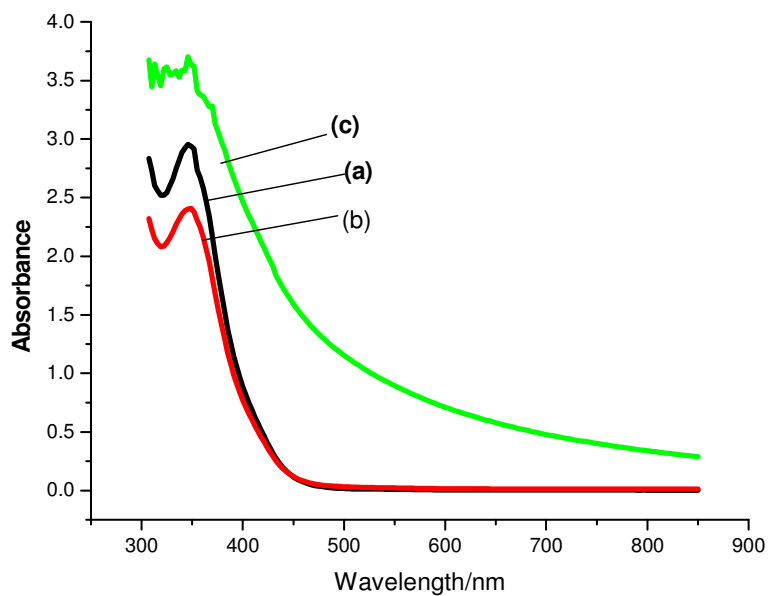


Figure 4. UV-Vis optical absorption spectra of polymer **1** in chloroform/methanol mixtures at different mole fractions of methanol: (a) 0.0, (b) 0.36, and (c) 0.64.

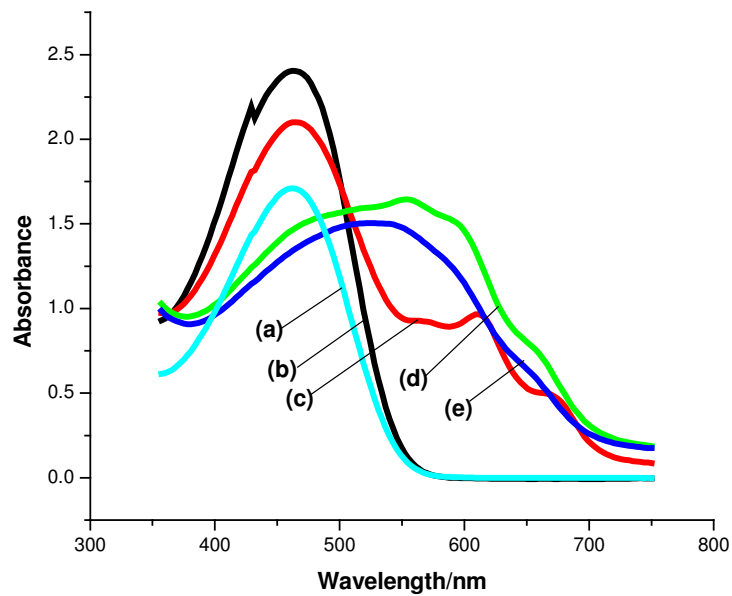


Figure 5. UV-Vis optical absorption spectra of polymer 7 in chloroform/methanol mixtures at different mole fractions of methanol: (a) 0.0, (b) 0.36, (c) 0.64, (d) 0.85, and (e) 0.96.

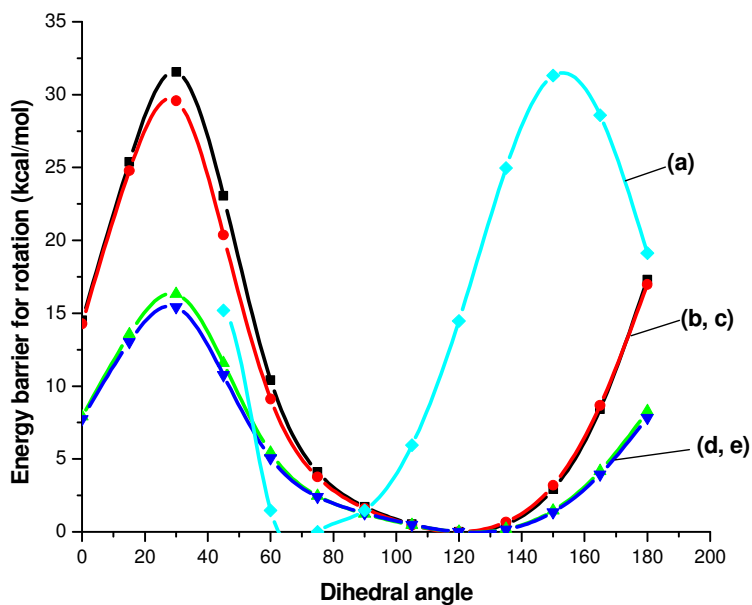


Figure 6. Potential energy curve (a) polymer 1, (b) polymer 2, (c) polymer 3, (d) polymer 4, and (e) polymer 5.

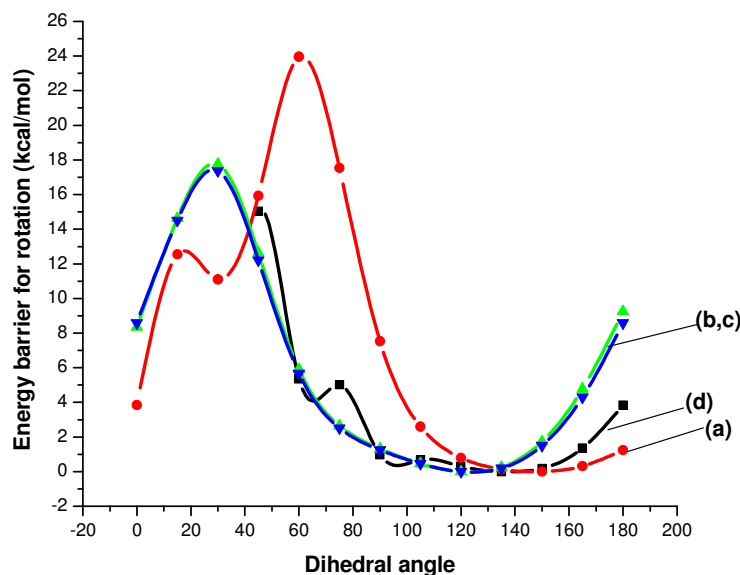


Figure 7. Potential energy curve (a) polymer 6, (b) polymer 7, (c) polymer 8, and (d) polymer 9.

Table 4. Summary of the energy barrier to rotation to a planar structure for the dimer molecules of the polymers whose structures are shown in Figure 1.

Molecule	Energy barrier against rotation (kcal/mol)	
	Syn	Anti
Polymer 1	---	19.13
Polymer 2	14.5	17.31
Polymer 3	14.28	16.97
Polymer 4	7.9	8.28
Polymer 5	7.74	7.83
Polymer 6	3.85	1.25
Polymer 7	8.59	8.59
Polymer 8	8.35	9.26
Polymer 9	---	3.85

CONCLUSIONS

In this paper we reported the thermochromic and solvatochromic properties of several phenyl-substituted polybithiophenes and polythiophenes. We observed that highly sterically hindered phenyl-substituted polythiophenes do not show chromic behaviour. We have also noted that regioregular phenyl-substituted polythiophenes show more pronounced thermochromism and solvatochromism than the phenyl-substituted polybithiophenes. Among the regioregular phenyl-substituted polythiophenes some show blue-shifted absorption band while some show red-shifted absorption band upon heating. Both show red-shifted absorption bands upon increasing the amount of the more polar solvent (methanol) whose dissolving power for the polymers decreases favouring the formation of aggregates and increased effective conjugation. This is explained by the possibility of conformational transition between less conjugated, non-planar

and more-conjugated, planar structures upon heating and changing the polarity of the solvent. Attempt has been made to explain these chromic transition by optimizing the dimers of the polymers and calculating the energy barrier for rotation from the most stable conformer to a planar structure using the HF SCF quantum chemical method and 3-21G* basis set.

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