Molecular Design and Characterization of Chromic Polyfluorene Derivatives

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ABSTRACT: The thermochromic and solvatochromic properties of a series of fluorene-based conjugated polymers have been investigated. Both poly(2,7-(9,9-dioctylfluorene)) and poly(2,5-(thiophene)-*alt*-2,7-(9,9-dioctylfluorene)) have revealed interesting chromic properties which, on the basis of theoretical calculations, seem to be related to a relatively flexible backbone. On the other hand, the sterically hindered, nonplanar poly(2,5-(3,4-dimethylthiophene)-*alt*-2,7-(9,9-dioctylfluorene)) does not exhibit any significant solvatochromic and thermochromic properties which could be explained by an important energy barrier against planarity. Finally, investigations on poly(2,5-(3,4-ethylenedioxythiophene)-*alt*-2,7-(9,9-dioctylfluorene)) have revealed a highly conjugated conformational structure which is not significantly modified upon temperature or solvent changes.

Introduction

Functionalization of conjugated polymers has led to the development of novel processable polymeric materials with unusual electrical, electrochemical, and optical properties.[1] Along these lines, chromic (thermochromic, solvatochromic, piezochromic, ionochromic, affinitychromic, etc.) conjugated polymers have opened new possibilities in the field of smart materials and sensors.[2] For instance, some functionalized polydiacetylenes,[2,3] polysilanes,[2,4] or polythiophenes[2,5] can show dramatic color changes in the presence of several external physical or chemical stimuli which can be described as a transduction of a physical or chemical information into an optical signal. Many different conjugated polymers have been investigated, and on the basis of these studies, it seems that such chromic phenomena can be driven by a delicate balance between the steric hindrance created by the side chains along the backbone and attractive interchain (or intrachain, through chain folding) interactions.[2,6] More precisely, it has been suggested that some functionalized conjugated polymers can form planar or nearly planar assemblies which are disrupted upon side-chain disordering, a twisting of the main chain being assumed with this diassembly. Accordingly, this conformational transition of the conjugated backbone is accompanied by a modification of the effective conjugation length and of the UV−vis absorption spectrum.[7] However, some exciton coupling effects or interchain interactions can also be involved during aggregation and can contribute to the chromic phenomena.[8]

Although most studies on chromic polymers have dealt with functionalized polydiacetylenes, polysilanes, and polythiophenes, recent studies have also revealed some interesting and intriguing chromic phenomena with poly(alkylbithiazole)s[9] and polyfluorenes.[10] In particular, recent studies on well-defined polyfluorene derivatives have revealed the presence of a new absorption peak at 437 nm upon aggregation or cooling.[10] The exact nature of this optical effect is still unknown, but it has been postulated that it could be related to an intrachain ordering which could lead to a more conjugated (presumably, coplanar) structure.[11] This effect is reminiscent of those observed in other chromic conjugated polymers, and it is the purpose of the present work to investigate the conformational structure and the chromic (thermochromic and solvatochromic) properties of several functionalized polyfluorene derivatives, namely poly(2,7-(9,9-dioctylfluorene)) (**1**), poly(2,5-(thiophene)-*alt*-2,7-(9,9-dioctylfluorene)) (**2**), poly(2,5-(3,4-dimethylthiophene)-*alt*-2,7-(9,9-dioctylfluorene)) (**3**), and poly(2,5-(3,4-ethylenedioxythiophene)-*alt*-2,7-(9,9-dioctylfluorene)) (**4**) (see Scheme 1). A careful analysis of the structure−property relationships in this class of materials should shed some light on the understanding of these optical effects and should lead to the rational design of novel chromic conjugated polymers. Moreover, polyfluorenes have recently attracted a lot of attention as highly luminescent materials,[12] and a better characterization of their structural and optical properties is also important for the efficient design of light-emitting polymeric diodes.

Experimental Section

Instrumentation. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX300 apparatus in deuterated chloroform solution at 298 K. Number-average (M_n) and weight-average (M_w) molecular weights were determined by size exclusion chromatography (SEC) with HPLC Pump using a Waters 515 differential refractometer. 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 toluene (10 mg/mL) were cast (time scale of about 5 min) on quartz plates. Heating and cooling rates for such thermochromic measurements were about 5 °C/min. Differential scanning calorimetry (DSC)

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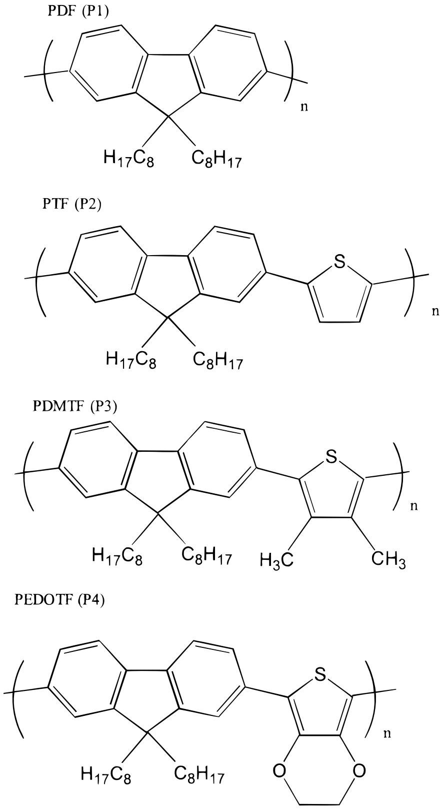
Scheme 1



analyses were performed on a Perkin-Elmer (DSC-7) instrument at 20 °C/min under an argon flow. Thermogravimetric (TGA) measurements were carried out with a TC-15 Mettler-Toledo apparatus. The heating rate was 10 °C/min under a nitrogen atmosphere.

Synthesis. Fluorene and 2,5-dibromothiophene were obtained from Aldrich Co. 2,7-Dibromo-9,9-dioctylfluorene, 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene, and tetrakis(triphenylphosphine)palladium were prepared following already published procedures.[12d,13]

2,5-Dibromo-3,4-dimethylthiophene.[14] To a solution of 3,4-dibromothiophene (Aldrich, 4.00 g, 16.5 mmol) in THF (15 mL) was added [1,3-bis(diphenylphosphino)propane]nickel(II) chloride (Aldrich, 89 mg, 0.17 mmol) and methylmagnesium bromide (Aldrich, 24.5 mL, 34.4 mmol, 1.4 M in toluene/THF 75:25). The reaction mixture was heated to 50 °C overnight and then poured into water with a few drops of 3 M hydrochloric acid to destroy the emulsion. The aqueous layer was extracted with diethyl ether, and the organic fractions were washed with brine and dried over magnesium sulfate. The solvent was removed under reduced pressure. To this crude product (1.86 g, 16.5 mmol) in $CHCl_3$ (90 mL) was added bromine (Aldrich, 1.80 mL, 34.8 mmol) at 0 °C. It is important that the reaction proceeds in the dark to avoid any bromination of the aliphatic part of the molecule. The mixture was allowed to warm to room temperature and stirred overnight. The reaction mixture was poured into water and then extracted with diethyl ether; the organic fractions were washed with brine and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the crude product was purified by flash chromatography (silica gel, hexanes) to provide 1.74 g (40%) of the title product as a colorless liquid. ^1H NMR (300 MHz, $CDCl_3$, ppm): 2.11 (s, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): 14.73, 107.30, 136.91.

2,5-Dibromo-3,4-ethylenedioxythiophene.[15] To a solution of 3,4-ethylenedioxythiophene (Bayer, 2.00 g, 14.1 mmol) in DMF (20 mL) was added NBS (Aldrich, 5.02 g, 28.2 mmol). The reaction mixture was stirred 1 h at room temperature. The resulting slurry was poured into water and then extracted with diethyl ether; the organic fractions were washed with brine and dried over magnesium sulfate. The solvent was removed under reduced pressure to afford a white solid; mp 94−95 °C (yield = 63%). ^1H NMR (300 MHz, $CDCl_3$, ppm): 4.27 (s, 4 H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): 64.98, 85.86, 139.74.

Table 1. Molecular Weights and Thermal Properties of the Polymers

polymer	M_n	M_w/M_n	T_g (°C)	T_c (°C)	T_m (°C)	T_{deg} (°C)[a]
PDF	10 000	2.1	65	105	130, 140	360
PTF	7 000	1.7			220	350
PDMTF	15 000	2.2	70	175	200	410
PEDOTF	13 000	1.4	130	190	235, 250	410

[a] Temperature for 5% weight loss.

Polymerization. All polymers were synthesized via palladium-catalyzed Suzuki couplings between dibromoaryl and diborolanylaryl compounds following already published procedures (yields: 85−90%).[12d,e,16] All polyfluorene derivatives exhibit a number-average molecular weight of about 7−15 kDa with a polydispersity index of 2.

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.[17] 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.

Results and Discussion

Following recently published procedures based on palladium-catalyzed Suzuki coupling,[12d,e,16] all polyfluorene derivatives shown in Scheme 1 have been prepared in good yields (85−90%). It is worth noting that similar well-defined polymers can also be prepared from Stille coupling.[18] All these polymers are soluble in chloroform, tetrahydrofuran, or toluene. Their molecular weights and thermal properties are reported in Table 1. In general, these aromatic polymers have a glass transition temperature above room temperature and exhibit a crystallization exothermal peak upon heating followed by one or two endothermic transitions. Moreover, all these polymers exhibit an excellent thermal stability. Similar results have been previously reported for poly(2,7-(9,9-dialkylfluorene)s.[12c,f,k]

Since the optical properties of poly(2,7-(9,9-dialkylfluorene))s have also been the subject of many recent studies,[10−12] thermochromic and solvatochromic experiments have been first carried out on poly(2,7-(9,9-dioctylfluorene)) (polymer **1**). As previously reported by Grell et al.,[11] a thin cast film (from a toluene solution) of this polymer exhibits three maxima at 386, 404, and 434 nm, at room temperature. Cast films from chloroform solutions did not show any peak at 434 nm whereas cast films from toluene solutions did not reveal any significant change when exposed to toluene vapor or upon cooling to 77 K. However, upon heating, only one broad absorption peak near 386 nm remains (Figure 1). Interestingly, the thermochromic transition occurs during a partial crystallization of the polymer, and the crystalline-to-nematic phase transition[12c,f,k] (130−140 °C) is not associated with any significant optical change in the visible range. This solid-state transition is partially reversible (at least on the time scale of these

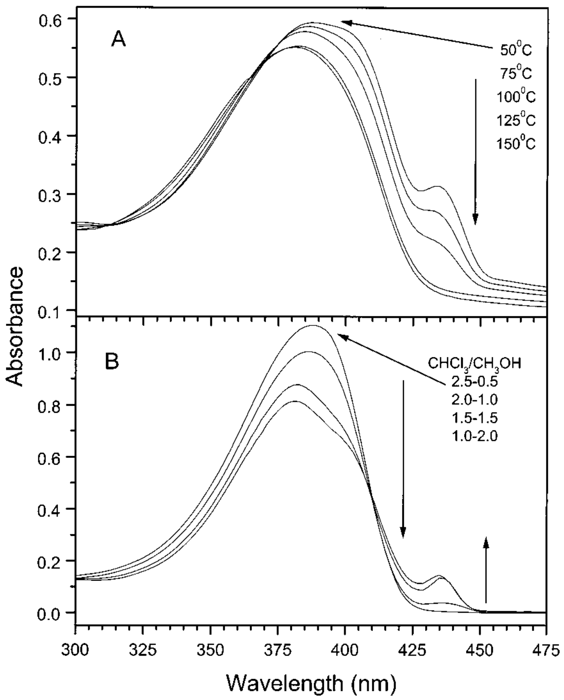


Figure 1. Solid-state temperature-dependent (a) and solvent-dependent (v/v) (b) UV−vis absorption spectra of polymer **1**.

spectroscopic measurements, i.e., 30 min), and the 434 nm band reappears upon cooling to room temperature. Similarly, solvatochromic studies in mixtures of chloroform (good solvent) and methanol (poor solvent) have revealed an increase of the 436 nm absorption band upon decreasing the quality of the solvent (Figure 1). In both cases, it can be assumed that a more conjugated (presumably, more planar) structure is appearing upon aggregation or cooling which leads to a red shift of the UV−vis absorption spectrum.

As previously reported for polythiophene derivatives,[6] the analysis of the potential energy surfaces of oligomeric compounds can be helpful to rationalize these results. Indeed, those previous studies have suggested that the extent of the blue shift observed at high temperatures in some conjugated polymers can be related to the difference in the torsional angles between a coplanar (or nearly planar) conformation (made possible through adequate interchain interactions) and the twisted structure adopted by the polymers when such assemblies are disrupted. Amid the thiophene systems examined in those previous studies, only twisted dimers having an energy barrier lower than 2.2−2.3 kcal/mol against planarity show interesting thermochromic properties in the parent polymers. The potential energy surface of 2,2′-bifluorene (BF) is displayed in Figure 2. Energies and relaxed optimized geometries for minima and maxima of BF are listed in Table 2. Two minima at 45.0° and 135.0° are obtained whereas three maxima are also observed on the potential energy surface, two for the planar conformations and one for the perpendicular one. This potential energy surface is very close to that obtained for biphenyl (BP) using the same level of calculation.[19] Indeed, two minima at 46° and 135° are observed for BP whereas the barrier against planarity is 3.3 kcal/mol. We have also observed that the presence of alkyl chains (ethyl groups) at the 9-position of BF does not significantly change its potential energy surface. This strongly suggests that the presence of octyl chains in the corresponding polymer should not intrinsically change the conformational behavior of each of the repeat units as far as they remain isolated.

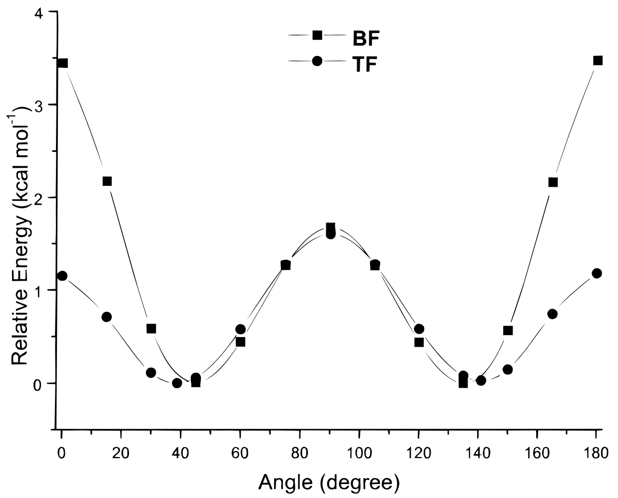


Figure 2. Ground-state potential energy surfaces of BF and TF.

Table 2. Relative Energies (in kcal mol^{-1}) and Torsional Angles (θ) Obtained by ab Initio Calculations Performed at the HF/6-31G* Level

molecule[a]	*syn*[b]	*syn-gauche*	perp[b]	*anti-gauche*	*anti*[b]
BF	3.44	0.01 (45.0°)	1.68	0.0 (135.0°)	3.47
TF	1.15	0.0 (38.7°)	1.60	0.03 (141.0°)	1.18
DMTF	5.31	0.0 (57.5°)	0.46	0.046 (123.2°)	5.39
EDOTF	1.03	0.28 (37.6°)	1.70	0.0 (144.3°)	1.00

[a] BF (2,2′-bifluorene), TF (2-thiophene-2′-fluorene), DMTF (2-(3,4-dimethylthiophene)-2′-fluorene), EDOTF (2-(3,4-ethylenedioxythiophene)-2′-fluorene). [b] *Syn*, $\theta = 0°$; *anti*, $\theta = 180°$; perpendicular, $\theta = 90°$.

It has not been yet possible to determine the exact conformation adopted by polymer **1** upon aggregation (solvatochromism) or at low temperatures (thermochromism), but these calculations do indicate that the repeat units have some conformational flexibility and that interchain interactions may modify the torsion angles between them. At the HF/3-21G* level of approximation, the energy barrier against planarity is 4.1 kcal/mol, which is above those calculated for chromic polythiophenes (i.e., 2.2−2.3 kcal/mol) but clearly below that calculated (i.e., 7.6 kcal/mol) for nonchromic poly(3,3′-dialkyl-2,2′-bithiophene)s.[6] Furthermore, the HF/6-31G* energy barrier against planarity is 3.4 kcal/mol, which is slightly lower than that obtained using the 3-21G* basis set. However, excitonic and interchain effects cannot be ruled out and must therefore be also considered in these chromic polymeric systems.

To develop novel chromic polyfluorene derivatives, various alternating copolymers have been prepared and investigated. For instance, it can be anticipated that five-membered aromatic rings should create less steric hindrance, and therefore, poly(2,5-(thiophene)-*alt*-2,7-(9,9-dioctylfluorene)) (polymer **2**) has been studied. From Figure 2 and Table 2, one can see that the torsional potential of 2-thiophene-2′-fluorene (TF) exhibits two minima which are located at 38.7° and 141.0° with an energy barrier against planarity of 1.2 kcal/mol. This shows that the most stable conformers of TF are just slightly more planar than those of BF. But the barrier

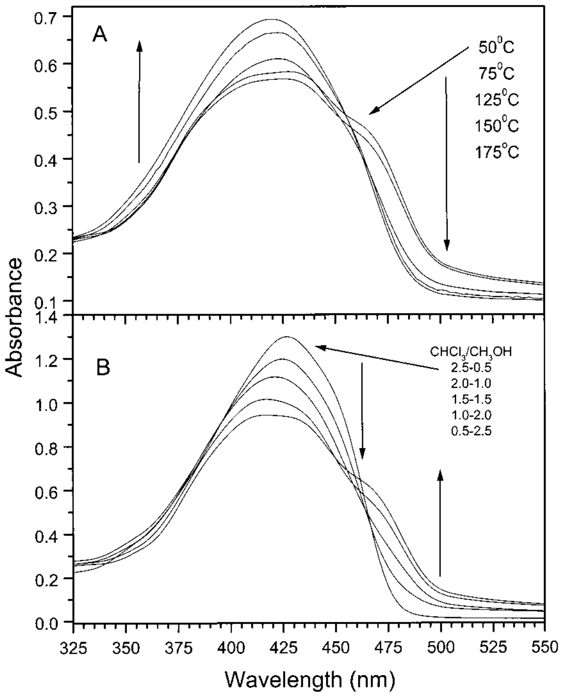


Figure 3. Solid-state temperature-dependent (a) and solvent-dependent (v/v) (b) UV−vis absorption spectra of polymer **2**.

to rotation at 180° (0°) for TF is much smaller than that obtained for BF. This clearly indicates that the steric effect between a thiophene ring and a fluorene unit is less important than that calculated between two fluorene units. Accordingly, the conformationally flexible polymer **2** exhibits well-defined thermochromic and solvatochromic effects (Figure 3). Indeed, a more highly conjugated form (characterized by an absorption band near 464 nm) is present at low temperatures or in poor solvents which disappears upon heating or improving the quality of the solvent. Once again, the endothermic transition observed near 220 °C does not induce any significant optical change, the maximum of absorption being almost constant over 175 °C. These results could be explained by a very low degree of crystallinity (or long-range organization) and by the fact that the observed optical transition would be mainly associated with the amorphous (or short-range organized) phase.

To obtain a better understanding of these chromic effects, sterically hindering side groups have been incorporated to the thiophene units. The potential energy surface of 2-(3,4-dimethylthiophene)-2′-fluorene (DMTF) shows two minima located at 57.5° and 123.2° which are very close in energy (see Figure 4). A very low rotational energy barrier at 90° is observed which allows a wide range of nonplanar conformations for this molecule. However, the rotational energy barriers against planarity (i.e., 5.3−5.4 kcal/mol) are higher than those observed for TF or BF. From previous studies performed on polythiophene derivatives,[6] these higher conformational barriers could inhibit any nonplanar to planar (chromic) conformational transition. In agreement with this assumption, poly(2,5-(3,4-dimethylthiophene)-*alt*-2,7-(9,9-dioctylfluorene)) (polymer **3**) exhibits an absorption maximum near 388 nm both in solution and in the solid state which does not vary that much upon heating (Figure 5) or by changing the quality of the solvent. Moreover, this maximum of absorption at a relatively short wavelength is in agreement with a more twisted conformation, predicted from theoretical calculations.

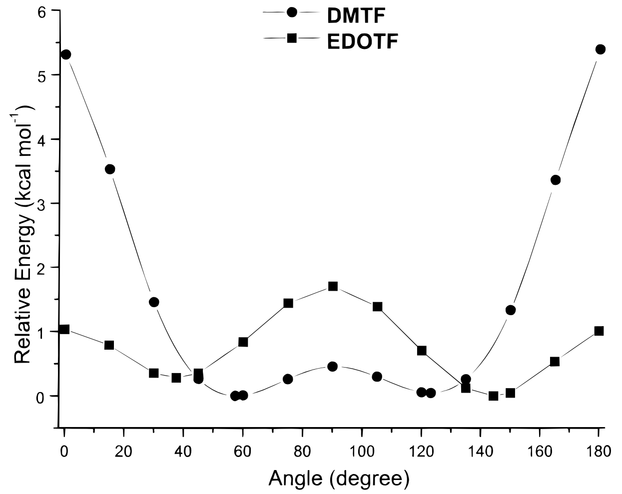


Figure 4. Ground-state potential energy surfaces of DMTF and EDOTF.

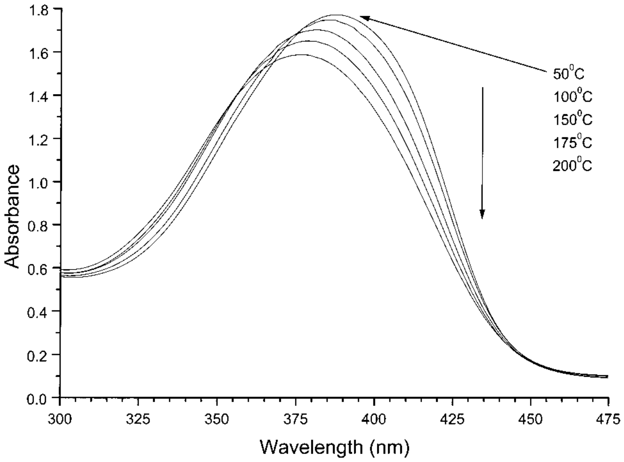


Figure 5. Temperature-dependent UV−vis absorption spectra of polymer **3** in the solid state. Heating scan.

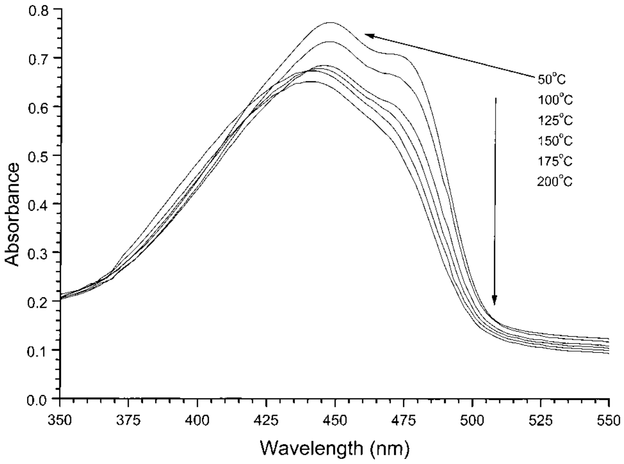


Figure 6. Temperature-dependent UV−vis absorption spectra of polymer **4** in the solid state. Heating scan.

At the other extreme, poly(2,5-(3,4-ethylenedioxythiophene)-*alt*-2,7-(9,9-dioctylfluorene)) (polymer **4**) exhibits a highly conjugated structure both in chloroform solution (two maxima at 444 and 468 nm, not shown here) and in the solid state (two maxima at 448 and 472 nm, Figure 6) which comes from the strong electron-donating properties of the alkoxy substituents and, possibly, from a highly conjugated conformational structure. Both solvatochromic and thermochromic experiments have only revealed a slight red shift of the absorption maxima upon aggregation or cooling. Figure 4 shows that the equilibrium geometry of the 2-(3,4-ethylenedioxythiophene)-2′-fluorene (EDOTF) is slightly more planar than that of TF with slightly smaller rotational barriers at 0° and 180°. The relatively small steric hindrance created by the alkoxy substituents can be related to the small van der Waals radius of the oxygen atom and to electron-donating effects.[20] For the perpendicular conformation, the rotational barrier of the EDOTF derivative is slightly higher than that obtained for TF. However, since the potential energy curves of EDOTF is similar to those calculated for BF and TF, it could be anticipated from these calculations that all these three polymers should exhibit similar chromic features. This is not exactly the case (see Figures 1, 3, and 6), and that could be explained by the fact that calculations on alkoxy-substituted thiophenes are very sensitive upon the geometry adopted by the side chains which cannot be predicted with enough accuracy.[20]

Nevertheless, all these theoretical and experimental analyses have indicated that conformationally flexible polyfluorene derivatives may exhibit interesting solvatochromic and thermochromic effects and show again that theoretical conformational analyses of dimer model compounds can be a valuable tool to understand and predict the chromic properties of various conjugated polymers. Indeed, a similar theoretical approach was successfully applied to the design of chromic polyphenylene derivatives.[21] However, some excitonic effects may also take place in these more ordered and conjugated structures, but their relative contribution has not yet be determined. This work is promising since it suggests that a thorough investigation of well-defined oligomers in different environments could determine the relative contribution of conformational versus excitonic effects.[8]

Conclusions

Poly(2,7-(9,9-dioctylfluorene)) and poly(2,5-(thiophene)-*alt*-2,7-(9,9-dioctylfluorene)) have shown interesting thermochromic and solvatochromic features. It is believed that a coexistence of a disordered structure with a more ordered (more conjugated) conformational structure occurs for each polymer. Accordingly, ab initio calculations performed on the dimers, which are the repeat units of the polymers, do indicate that these units have some conformational flexibility and that interchain interactions may modify the torsion angles between them. On the other hand, ab initio calculations performed on 2-(3,4-dimethylthiophene)-2′-fluorene (DMTF) show an energy barrier against planarity which is higher than that obtained for 2,2′-bifluorene and 2-thiophene-2′-fluorene. Therefore, the corresponding nonplanar polymer (poly(2,5-(3,4-dimethylthiophene)-*alt*-2,7-(9,9-dioctylfluorene)) exhibits an absorption spectrum which does not vary that much upon heating or by changing the quality of the solvent. Finally, the absorption spectrum of poly(2,5-(3,4-ethylenedioxythiophene)-*alt*-2,7-(9,9-dioctylfluorene)) exhibits a highly conjugated structure which has only revealed a slight blue shift upon heating. Ab initio calculations performed on the corresponding dimer (EDOTF) show that the equilibrium geometry of this dimer is slightly more planar than that of TF with a slightly smaller rotational barrier against planarity.

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References and Notes

(1) *Handbook of Conducting Polymers*, 2nd ed.; Skotheim, T. A., Elsenbaumer, R. L., Reynolds, J. R., Eds.; Marcel Dekker: New York, 1998.

(2) (a) Leclerc, M.; Faïd, K. In *Handbook of Conducting Polymers*, 2nd ed.; Marcel Dekker: New York, 1998; p 695. (b) Leclerc, M.; Faïd, K. *Adv. Mater.* **1997**, *9*, 1087. (c) McCullough, R. D. *Adv. Mater.* **1998**, *10*, 93. (d) Leclerc, M. *Adv. Mater.* **1999**, *11*, 1491.

(3) (a) Exarhos, G. J.; Risen, W. M.; Baughman R. H. *J. Am. Chem. Soc.* **1976**, *98*, 481. (b) Patel, G. N.; Chance, R. R.; Witt, J. D. *J. Chem. Phys.* **1979**, *70*, 4387. (c) Wenz, G.; Muller, M. A.; Schmidt, M.; Wegner, G. *Macromolecules* **1984**, *17*, 837. (d) Okada, S. Y.; Peng, S.; Spevak, W.; Charych, D. *Acc. Chem. Res.* **1998**, *31*, 229.

(4) (a) Trefonas, P., III; Damewood, J. R.; West, R.; Miller, R. D. *Organometallics* **1985**, *4*, 1318. (b) Harrah, L.; Zeigler, J. M. *J. Polym. Sci., Polym. Lett. Ed.* **1985**, *23*, 209. (c) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359. (d) Yuan, C. H.; West, R. *Chem. Commun.* **1997**, 1825.

(5) (a) Rughooputh, S. D. D. V.; Hotta, S.; Heeger, A. J.; Wudl, F. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *25*, 1071. (b) Inganas, O.; Salaneck, W. R.; Osterholm, J. E.; Laakso, J. *Synth. Met.* **1988**, *22*, 395. (c) Roux, C.; Leclerc, M. *Macromolecules* **1992**, *25*, 2141. (d) McCullough, R. D.; Williams, S. P. *J. Am. Chem. Soc.* **1993**, *115*, 11608. (e) Marsella, M. J.; Swager, T. M. *J. Am. Chem. Soc.* **1993**, *115*, 12214. (f) Lévesque, I.; Leclerc, M. *Chem. Mater.* **1996**, *8*, 2843. (g) Lévesque, I.; Leclerc, M. *Macromolecules* **1997**, *30*, 4347. (h) Faïd, K.; Leclerc, M. *J. Am. Chem. Soc.* **1998**, *120*, 5274.

(6) (a) Roux, C.; Bergeron, J. Y.; Leclerc, M. *Makromol. Chem.* **1993**, *194*, 869. (b) DiCesare, N.; Belletête, M.; Durocher, G.; Leclerc, M. *Chem. Phys. Lett.* **1997**, *275*, 533. (c) Raymond, F.; DiCesare, N.; Belletête, M.; Durocher, G.; Leclerc, M. *Adv. Mater.* **1998**, *10*, 599.

(7) Brédas, J. L.; Street, G. B.; Thémans, B.; André, J. M. *J. Chem. Phys.* **1985**, *83*, 1323.

(8) (a) DiCesare, N.; Belletête, M.; Marrano, C.; Leclerc, M.; Durocher, G. *J. Phys. Chem. A* **1999**, *103*, 795. (b) DiCesare, N.; Belletête, M.; Leclerc, M.; Durocher, G. *J. Phys. Chem.* **1999**, *103*, 803. (c) DiCesare, N.; Belletête, M.; Rivera Garcia, E.; Leclerc, M.; Durocher, G. *J. Phys. Chem. A* **1999**, *103*, 3864.

(9) Nanos, J. I.; Kampf, J. W.; Curtis, M. D.; Gonzalez, L.; Martin, D. C. *Chem. Mater.* **1995**, *7*, 2232.

(10) (a) Grell, M.; Bradley, D. D. C.; Long, X.; Chamberlain, T.; Inbasekaran, M.; Woo, E. P.; Soliman, M. *Acta Polym.* **1998**, *49*, 439. (b) Shkunov, M. N.; Osterbacka, R.; Fujii, A.; Yoshino, K.; Vardeny, Z. V. *Appl. Phys. Lett.* **1999**, *74*, 1648.

(11) Grell, M.; Bradley, D. D. C.; Ungar, G.; Hill, J.; Whitehead, K. S. *Macromolecules* **1999**, *32*, 5810.

(12) (a) Gu, H. B.; Morita, S.; Yin, X. H.; Kawai, T.; Yoshino, K. *Synth. Met.* **1995**, *69*, 449. (b) Pei, Q.; Yang, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7416. (c) Grell, M.; Bradley, D. D. C.; Inbasekaran, M.; Woo, E. P. *Adv. Mater.* **1997**, *9*, 798. (d) Ranger, M.; Rondeau, D.; Leclerc, M. *Macromolecules* **1997**, *30*, 7686. (e) Ranger, M.; Leclerc, M. *Can. J. Chem.* **1998**, *76*, 1571. (f) Kreyenschmidt, M.; Klaerner, G.; Fuhrer, T.; Ashenhurst, J.; Karg, S.; Chen, W. D.; Lee, V. Y.; Scott, J. C.; Miller, R. D. *Macromolecules* **1998**, *31*, 1099. (g) Grice, A. W.; Bradley, D. D. C.; Bernius, M. T.; Inbasekaran, M.; Wu, W. W.; Woo, E. P. *Appl. Phys. Lett.* **1998**, *73*, 629. (h) Bliznyuk, V. N.; Cater, S. A.; Scott, J. C.; Klaerner, G.; Miller, R. D.; Miller, D. C. *Macromolecules* **1999**, *32*, 361. (i) Cho, H. N.; Kim, J. K.; Kim, D. Y.; Kim, C. Y.; Song, N. W.; Kim, D. *Macromolecules* **1999**, *32*, 1476. (j) Uckert, F.; Setayesh, S.; Müllen, K. *Macromolecules* **1999**, *32*, 4519. (k) Teetsov, J.; Fox, M. A. *J. Mater. Chem.* **1999**, *9*, 2117. (l) Donat-Bouillud, A.; Lévesque, I.; Tao, Y.; D'Iorio, M.; Beaupré, S.; Blondin, P.; Ranger, M.; Bouchard, J.; Leclerc, M. *Chem. Mater.*, in press.

(13) Ranger, M.; Leclerc, M. *Macromolecules* **1999**, *32*, 3306.

(14) Tour, J. M.; Wu, R. *Macromolecules* **1992**, *25*, 1901.

(15) Sotzing, G. A.; Reynolds, J. R.; Steel, P. J. *Chem. Mater.* **1996**, *8*, 882.

(16) Miyaura, M.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457.
(17) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1998.
(18) Tsuie, B.; Reddinger, J. L.; Sotzing, G. A.; Soloducho, J.; Katritzky, A. R.; Reynolds, J. R. *J. Mater. Chem.* **1999**, *9*, 2189.
(19) Karpfen, A.; Choi, C. H.; Kertesz, M. *J. Phys. Chem. A* **1997**, *101*, 7426.
(20) DiCesare, N.; Belletête, M.; Leclerc, M.; Durocher, G. *J. Mol. Struct.* **1999**, *467*, 259.
(21) Dufresne, G.; Bouchard, J.; Belletête, M.; Durocher, G.; Leclerc, M. *Macromolecules*, submitted.

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