Structural Study of the Thermochromic Transition in Poly(2,5-dialkyl-*p*-phenyleneethynylene)s

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ABSTRACT: The solvatochromic and thermochromic properties of poly(2,5-di-2'-ethylhexyl-*p*-phenyleneethynylene) have been investigated. While some important changes were observed in UV-vis absorption, calorimetric, and X-ray measurements, temperature-dependent FTIR, Raman, and solid-state NMR spectra did not reveal any significant shift of the peaks associated with the polymer backbone. These results suggest that the chromic effects are not mainly governed by conformational changes of the polymer. From these data and ab initio calculations performed on model compounds, it is believed that the thermochromic transition proceeds from aggregated polymers at room temperature to "free" (weakly interacting) polymer chains at higher temperatures.

Introduction

Conjugated organic polymers¹⁻⁴ have received considerable attention in the past 25 years due to their great potential for applications in microelectronics, electrooptics, and biophotonics. For instance, the electrooptical properties of semiconducting conjugated polymers depend critically on their molecular structure, doping, and morphology.⁵ Therefore, it is of great interest to carefully study the structure/property relationships in those materials.

Some of the conjugated polymers exhibit interesting color changes (chromism) that, depending upon the stimulus involved, are called thermochromism, solvatochromism, or affinity chromism.^{6,7} These polymers can therefore detect and transduce physical or chemical information into an optical signal. Depending upon the polymer structure, this transition has been explained by a conformational change of the backbone and/or variable $\pi - \pi$ interchain interactions.⁸⁻¹³ Among these materials, poly(*p*-phenyleneethynylene)s (PPEs)^{10,14} have received particular attention. PPEs are rigid and highly fluorescent conjugated polymers.^{15–20} In the solid state, some studies have revealed that PPEs form lamellar structures, in which rotation around the triple bond is restricted. A planar arrangement of the conjugated backbone with concomitant $\pi - \pi$ stacking is therefore observed.²¹ In solution, upon the addition of a nonsolvent, aggregation of dialkyl-PPEs is accompanied by a dramatic shift of the UV-vis spectrum.^{10,22} These polymers show similar chromic transitions in the solid state.^{10,22} Interestingly, dialkoxy-substituted PPEs do not show any significant chromic feature.²³ Finally, it is interesting to note that poly(fluorenyleneethynylene) s^{24} and poly(2,5-thienyleneethynylene) s^{25} do also exhibit some thermochromic and solvatochromic transitions, whereas poly(3,6-carbazoleneethynylene)s²⁶ and poly-(2,7-carbazoleneethynylene)s²⁷ do not.

To better understand these interesting chromic effects, we report here a detailed spectroscopic investigation of a thermochromic poly(2,5-di-2'-ethylhexyl-*p*phenyleneethynylene). This polymer can be obtained in either a highly or less conjugated form depending on the temperature and will therefore be utilized as a model compound to obtain a better description of the molecular interactions involved in chromic and nonchromic PPEs and related polymers.

Experimental Section

Synthesis. Following procedures already described in the literature,^{28,29} the starting 1,4-dichlorobenzene (30.0 g, 0.204 mol) was treated with 2-ethylhexylmagnesium bromide (73.9 g, 0.449 mol) in 600 mL of anhydrous ether under reflux for 48 h to yield the 1,4-bis(2-ethyl)hexylbenzene (31.6 g, yield 51%). The latter compound (30.0 g, 0.100 mol) was iodinated via the addition of KIO_4 (27.4 g, 0.119 mol) and I_2 (30.2 g, 0.119 mol) in 300 mL of an acidic solution for 24 h at 90 °C (46.2 g, yield 84%). To obtain the acetylic compound, the 1,4-bis(2ethyl)hexyl-2,5-diiodobenzene (35.4 g, 0.064 mol) was mixed with trimethylsylilacetylene (20.0 g, 0.204 mol) in the presence of palladium tetrakis(triphenylphosphine) (4.0 mol %) and cuprous iodide (2.8 mol %) in 275 mL of triethylamine at 40 °C for 24 h (10.2 g, yield 32%), followed by a KOH (20 mol %) deprotection reaction (4.53 g, yield 77%). Poly(2,5-di-2'-ethylhexyl-p-phenyleneethynylene) was obtained through a Sonogashira coupling between the aryl acetylene moiety (0.200 g, 0.570 mmol) and the aryl halide one (0.316 g, 0.570 mmol) in a mixture of toluene and diisopropylamine (20 mL) (Scheme 1) (0.244 g, yield 73%).²⁹ Size exclusion chromatogry (SEC) measurements on poly(2,5-di-2'-ethylhexyl-p-phenyleneethynylene) gave a number-average molecular weight (M_n) of 18 000 g/mol and a polydispersity $(M_{\rm w}/M_{\rm n})$ of 3 relative to monodisperse polystyrene standards. Similar procedures were followed to synthesize poly(2,5-di-decyl-p-phenyleneethynylene).

Physical Methods. Differential scanning calorimetry (DSC) analyses were performed on a Perkin-Elmer (DSC-7) instrument at a heating rate of 20 °C/min under a nitrogen flow. Solid-state UV-vis absorption measurements were performed on polymer films deposited from CHCl₃ solutions on a quartz cell, with a Hewlett-Packard diode array spectrophotometer (model 8452) equipped with a temperature control unit. The temperature was measured with a thermocouple, with $\Delta T \sim 2$ °C.

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Scheme 1. Synthesis of Poly(2,5-di-alkyl-p-phenyleneethynylene)s



X-ray data were obtained from a X-ray diffractometer (Siemens/Bruker) using the graphite monochromatized copper radiation (K $\alpha = 1.5418$ Å). The instrument consists of a Kristalloflex 760 generator, three-circle goniometer, and Hi-Star area detector and is equipped with GADDS software. The operation power was 40 kV, 40 mA and the collimator was 0.8 mm (diameter). The samples were inserted in thin-walled (0.01 mm) glass capillary tubes (1.0 mm diameter). The sample temperature is controlled with a custom-modified HCS400 Instec hot stage equipped with a STC200D controller.

Fourier transform infrared (FTIR) experiments were performed with a Nicolet Magna 560 spectrometer on thin films coated on NaCl disks for ex situ experiments or on BaF₂ disks for in situ experiments. For in situ measurements, a calibration curve was obtained by measuring the "real" temperature in the center of a BaF₂ disk with a thermocouple vs the displayed temperature on the temperature control unit. The subsequent linear regression formula calculated was then used to obtain the real temperature around the sample.

Raman studies were performed with a multichannel Jobin-Yvon T64000 spectrophotometer connected to a CCD detector in the visible range. The excitation line was 676.4 nm. FT Raman spectra were recorded with a RFS 100 Bruker spectrometer (excitation wavelength = 1064 nm). In situ Raman experiments were carried out by increasing the temperature by 10 deg steps between 30 and 200 °C.

 $^{13}\mathrm{C}$ CPMAS NMR experiments were carried out on a BRUKER AVANCE300 (Bruker Biospin Inc, Milton, ON, Canada) spectrometer, equipped with a 4 mm CPMAS NMR probe. The $^{13}\mathrm{C}$ carrier frequency was 75 MHz, and the MAS frequency was set to 10 000 Hz. The contact time for cross-polarization was 1 ms, followed by a proton decoupling (type TPPM) of 40 ms. Typically between 7K and 12K scans were recorded at room temperature and 135 °C.

Theoretical Methods. Ab initio calculations were performed on a Pentium 4 (2.57 GHz) personal computer with 1 Gb RAM using the Gaussian 03W program, revision B.05.³⁰ The conformational analysis of the model compound was done by changing the torsional angles θ between phenylene rings and the ethynyl bond 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 0.00045 and 0.0018 au, respectively.

Results

Conformational Analyses. The ground-state energy surface obtained from theoretical HF/6-31G* ab initio calculations performed on alkyl-substituted (2-ethylphenylene-ethynyl-2-ethylphenylene) isolated model compound is shown in Figure 1. A coplanar anti structure is favored, but the rotation along the triple bond is essentially unrestricted in the gas phase. The alkoxysubstituted (2-methoxyphenylene-ethynyl-2-methoxyphenylene) model compound exhibits a very similar ground-state energy surface (results not shown). As revealed by these conformational analyses, the corresponding dialkyl-substituted (and dialkoxy-substituted) PPEs should possess more or less the same conforma-



Figure 1. Ground-state energy surface of (2-ethylphenyleneethynyl-2-ethylphenylene) model compound.



Figure 2. Solvent-dependent UV-vis absorption spectra of poly(2,5-di-2'-ethylhexyl-*p*-phenyleneethynylene).

tion. Recently, a very flexible backbone was also predicted for poly(*N*-octyl-2,7-carbazoleneethynylene).²⁷

UV-vis Absorption Measurements. As shown in Figure 2, the absorption spectrum of poly(2,5-di-2'ethylhexyl-p-phenyleneethynylene) in chloroform (good solvent) exhibits one broad feature centered around 386 nm, typical for dialkyl-substituted PPEs.²² The absorption spectrum changes dramatically if a nonsolvent (methanol) is added to the chloroform solution. Indeed, the main band is red-shifted by about 10 nm, whereas a new sharp peak appears at 428 nm, which becomes more intense with the addition of the nonsolvent. These results are in excellent agreement with those previously reported by Bunz et al. for similar PPEs.^{10,22} The absorption spectrum of poly(2,5-di-2'-ethylhexyl-p-phenyleneethynylene) in the solid state, at room temperature, shows two distinct bands at 396 and 428 nm (see Figure 3). Upon heating, the band located at 396 nm is blue-shifted by about 10 nm, whereas the peak at 428



Figure 3. Temperature-dependent UV-vis absorption spectra of a poly(2,5-di-2'-ethylhexyl-p-phenyleneethynylene) thin film.



Figure 4. DSC thermogram of poly(2,5-di-2'-ethylhexyl-*p*-phenyleneethynylene).

nm decreases in intensity and completely disappears when the temperature reaches 130 °C. Then, the resulting high-temperature solid-state spectrum is very similar to that measured in chloroform (good solvent). Upon cooling, the poly(2,5-di-2'-ethylhexyl-*p*-phenyleneethynylene) returns partially to its previous state. Indeed, both absorption bands reach their initial wavelengths, but without recovering their full intensities.

Calorimetric Measurements. In parallel to these optical measurements, DSC thermal analyses were performed on the poly(2,5-di-2'-ethylhexyl-*p*-phenyleneethynylene). The thermogram reported in Figure 4 shows two distinct transitions: a broad endotherm with a peak near 125 °C upon heating and an exothermic peak at 75 °C upon cooling. The endothermic peak corresponds to an energy of 4 J/g. When the temperature is decreased, the exothermic peak appears at a lower temperature but with a comparable energy (4 J/g). However, when the temperature exceeds 140 °C in the heating cycle, the peak upon cooling is not observed anymore, and in a second cycle, no transition is observed.

X-ray Diffraction Measurements. To obtain more information about this solid-state transition, X-ray diffraction analyses were performed at various temperatures (see Figure 5). At ambient temperature, the X-ray diagram exhibits a peak at $2\theta = 7^{\circ}$, consistent with an interlamellar distance of 12.6 Å, and two broad peaks at $2\theta > 15^{\circ}$, corresponding to *d* values of 4.9 and 4.2 Å. This diffraction pattern at room temperature is very close to the one previously reported for the same polymer by Lieser et al.,²¹ who attributed the two latter diffraction peaks to arene-arene packing distance. Upon heating, the overall peak intensities decrease and



Figure 5. X-ray diffraction data measured at various temperatures for a poly(2,5-di-2'-ethylhexyl-*p*-phenyleneethy-nylene) powder.

the peaks broaden. Above 130 °C, the material appears to be mainly amorphous. Upon cooling, a partial recrystallization is observed, the three peaks reappearing from 90 °C but without recovering their full intensities.

FTIR Spectroscopy. In situ FTIR spectra recorded on a KBr pellet do not show any significant modification upon heating (Figure 6). For instance, the intense bands at 1379, 1442, 1460, and 1500 cm⁻¹, which can be assigned to the CH₂ and CH₃ bending vibrations, remain at about the same position. Moreover, many of the weaker bands of the spectra, which are attributed to phenyl rings (like the C-H stretching band at 3021 cm^{-1} or the C=C stretching band at 1596 cm^{-1}), do not shift during the heating cycle. However, if one compares the in situ spectral position of the antisymmetric CH stretching band of the CH₂ groups, located at 2925 cm⁻¹, a slightly hypsochromic shift is observed when the temperature is increased (see Figure 7). This wellknown behavior corresponds to the transformation from a "trans" to a "gauche" conformation of these groups.⁹



Figure 6. FTIR spectra of a poly(2,5-di-2'-ethylhexyl-*p*-phenyleneethynylene) thin film at various temperatures.



Figure 7. Evolution of the position of the CH_2 antisymmetric stretching upon a heating—cooling cycle of a poly(2,5-di-2'-ethylhexyl-*p*-phenyleneethynylene) thin film.



Figure 8. Raman spectra of poly(2,5-di-2'-ethylhexyl-*p*-phe-nyleneethynylene) at various temperatures.

However, the actual shift is smaller than that observed previously for chromic polythiophenes,⁹ and it seems to precede the thermochromic transition.

Raman Spectroscopy. Figure 8 shows the in situ Raman spectra obtained at 676 nm on poly(2,5-di-2'-ethylhexyl-*p*-phenyleneethynylene) thin film. On the contrary to a previous study performed on chromic polythiophenes,⁹ we do not observe any significant change in the positions of the main bands of the spectra upon heating. Indeed, the stretching band of the ethynyl bond, located at 2196 cm⁻¹, is shifted by only 3 cm⁻¹ when the temperature is increased. Similarly, the bands located at 1595 and 1525 cm⁻¹ related to C-C(-H) and C-C(-alk) stretching vibrations, respectively, do not move, like the CH bending band (1217 cm⁻¹) that decreases in intensity without any significant spectral shift.



Figure 9. Solid-state ¹³C CP/MAS NMR spectra of poly(2,5di-2'-ethylhexyl-*p*-phenyleneethynylene) at 25 and 135 °C.



Figure 10. Expanded aliphatic regions of the $^{13}\mathrm{C}$ MAS spectra at 25 and 135 °C.

NMR Measurements. Solid-state ¹³C CP/MAS NMR spectra of the poly(2,5-di-2'-ethylhexyl-p-phenyleneethynylene) recorded at room temperature and at 135 °C are shown in Figure 9. The assignment of each resonance line was mainly made on the basis of the assignments established in solution. The peaks in the region between 120 and 150 ppm can be assigned to the aromatic mainchain carbon atoms, and the peaks in the region between 0 and 50 ppm can be assigned to the aliphatic side-chain carbon atoms. Figure 10 shows expanded ¹³C CP/MAS NMR spectra of the poly(2,5-di-2'-ethylhexyl*p*-phenyleneethynylene) in the range 0-60 ppm from room temperature to 135 °C. At room temperature, the peaks at 11.6 and 14.49 ppm correspond to the methyl groups of the side chain. The peaks from 23 to 40 ppm correspond to the methylene groups. The peak at 23.7





ppm corresponds to the α -CH₂, the one at 28.9 ppm corresponds to the β -CH₂, the one at 33.2 ppm corresponds to the internal CH₂, and the one at 40.8 ppm corresponds to the γ -CH₂ (Scheme 2). Upon heating, neither the peaks of carbon atoms associated with the main chain nor the side chains shift, but we rather observed a change in shape and line widths for the peaks of the aliphatic region and the aromatic region.

Discussion

From the optical properties and X-ray diffraction data obtained for poly(2,5-di-2'-ethylhexyl-p-phenyleneethynylene) in the solid state (thin film) at various temperatures, a relatively clear transition was observed upon heating/cooling. Indeed, from the UV-vis spectra, it is observed that the band detected at 428 nm is completely vanished upon heating at 130 °C. In agreement with these results, X-ray data show that the interlamellar organization peak at 7° almost disappears around 130 °C, indicating a disordering in the material. When cooling back the samples, they partially return to their initial state, but for both types of measurements, a total recovery of the peak intensities is not obtained. By plotting the intensity vs temperature for both UV-vis and X-ray diffraction data (figure not shown), a clear transition can be observed between 90 and 130 °C upon heating. However, in the cooling cycle, the physical transition occurs at lower temperatures, this hysteresis being probably related to the high viscosity of the system.

This physical transition between two different states of the polymer can be associated with the thermal transitions observed in the DSC measurements. This physical transition seems to proceed from an ordered state (with the presence of three main diffraction peaks) to a disordered form at temperatures higher than 130 °C. To obtain a better understanding of the nature of the molecular interactions involved in these temperature-dependent measurements, spectroscopic studies using FTIR and Raman techniques were carried out. In principle, these techniques should detect movements within the side chains and/or the backbone of the polymer during the thermal transition.⁹ As mentioned above, FTIR spectra did not show any significant change during the thermal transition. Indeed, only small spectral changes involving the alkyl chains occurred during the heating cycle and were attributed to weak modifications from "trans" to "gauche" conformations. However, the spectral shifts observed are smaller than those reported for chromic polythiophenes.⁹ Usually, Raman

spectroscopy is a very useful technique because it is complementary to infrared spectroscopy. Indeed, according to the group theory, when molecules possess a center of symmetry, the in-plane "gerade" vibration modes are only Raman-active, whereas the "ungerade" modes are only infrared-active. Thus, the combination of FTIR and Raman measurements should provide a complete assignment of the vibrational bands of the molecules investigated. As mentioned above, temperature-dependent Raman spectra did not show any significant spectral shift, in sharp contrast to chromic polythiophenes.⁹ As the temperature increases, a slight broadening and intensity decrease of all Raman peaks are observed. When comparing these results with other work on the characterization of polymers with Raman spectroscopy, one can found additional insights into two previous studies. For instance, Davidson's group³¹ used Raman spectroscopy to monitor phase transition in aliphatic ketones, and they observe broadening of the bands with a decrease of the crystallinity. They also observe a complete disappearance of some bands when the sample reaches a transition temperature pointing to a complete phase transition. A similar feature can be observed here with PPE: no shift of the Raman peaks but rather a broadening of the bands with increasing temperature. The decrease in the band intensities upon heating can also be related to a decrease of the interchain interactions as the molecular mobility within the material is activated by temperature. This loss of order correlates extremely well with the observed decrease in intensity observed by X-ray analyses which were explained by a transition from an ordered state to a disordered one upon heating. Finally, a Raman study was also carried out on another chromic conjugated polymer: polydiacetylene. This polymer is believed to show chromism through transitions from a planar to a nonplanar form of the conjugated backbone. Kiefer's group³² used Raman spectroscopy to prove that model. They did not observe any decrease in intensity in their Raman spectra but only shifts in wavenumbers, which would mean that we do not have with our PPE the same kind of behavior.

Solid-state nuclear magnetic resonance (NMR) has recently made considerable progress for the study of molecular systems that are insoluble or do not exhibit long-range structural order. In addition to the study of molecular structure, solid-state NMR also provides unique means to probe molecular dynamics. Using this technique, we aimed, for the first time, to characterize the conformational behavior of the main chain and/or the alkyl side chains of PPEs over a wide range of temperatures by ¹³C CP/MAS (cross-polarization/magic angle spinning) NMR spectroscopy and to elucidate the relation between the structure and the observed phase transition. To obtain more information concerning the conformation of the polymer chains, it is first necessary to accurately assign the peaks in the ¹³C NMR spectrum. Figure 10 shows expanded ¹³C CP/MAS NMR spectra of the poly(2,5-di-2'-ethylhexyl-p-phenyleneethynylene) in the range 0–60 ppm from room temperature to 135 °C in order to clarify the temperature changes of the side-chain conformation. The methyl signals between 11 and 15 ppm consist of two peaks, corresponding to the two different kinds of CH₃ arising one from the ethyl group of the side chain and the other from the hexyl part of the side chain. The intensity of the two peaks decreases with an increase in temperature with

Table 1. Normalized Area and Full Widths at Half-Maximum of the Different Peaks at 25 and 135 °C

25 °C		135 °C	
%	fwhm	%	fwhm
7.6	2.87	4	1.9
4.6	1.83	1.8	1.15
19.5	3.66	6.4	1.57
16	5.95	3.2	1.54
7.5	4.3	6.6	1.84
22	4.86	45.15	2.85
2.3	1.86	2	1.37
4.5	3.13	4	2.73
12.4	4.93	12.7	3.95
3.75	1.92	5.3	1.7
	$ \frac{25}{\%} 7.6 4.6 19.5 16 7.5 22 2.3 4.5 12.4 3.75 $	$\begin{tabular}{ c c c c c } \hline & 25 \ ^\circ C \\ \hline \hline & & & & & & & & & \\ \hline \hline & & & & &$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

no appearance of any other peak, which means that these side-chain methyl carbon atoms are rather in an immobile region. In the region corresponding to the methylene groups, four peaks appear at 25 °C, whereas at 135 °C at least five peaks appear in the same region. The assignments of the peaks are not shifted; only the line widths of the peaks become thinner at higher temperatures, which means these carbon atoms turn to be more mobile at higher temperatures. The chemical shifts of the respective CH₂ resonance lines at 25 and 135 °C have been found to be in good agreement with the values measured in solution, indicating that all C-C bonds of the CH₂ sequences undergo rapid transgauche exchanges in these two cases, as observed in the solution state. This is in agreement with what has been found from our analyses of infrared and Raman spectra. The increasing mobility of the molecules is also reflected by the full width at half-maximum (fwhm) of the C-Cresonance, which narrows with increasing temperature as shown in Table 1. This happens for all carbon atoms of the molecule, but it is more pronounced for the carbon atoms of the aliphatic side chains.

Moreover, as mentioned in the Introduction section, the phenyleneethynylene units can exhibit $\pi - \pi$ stacking. This phenomenon can be specifically probed in the solid state in contrast to solution state, where these effects are removed due to molecular tumbling and dilution. The resonance lines assigned to the phenylene carbon atoms at 25 and 135 °C are different in the solidstate CP/MAS spectra (141.7, 134.5, and 123.7 ppm) when compared to those obtained in solution (141.2, 133.5, and 123.3 ppm). In the solid state, the phenylene rings are located in a position not significantly deviating from the coplanar position. Such a coplanar structure may be destroyed by a rapid rotation of each phenylene ring at least at high temperatures like what happens in solution, resulting in significant changes in the chemical shifts. However, we only observed a change in the chemical shifts from the solution spectrum to the solid-state spectra but no shift between the two solidstate spectra recorded at 25 and 135 °C, indicating that the phenylene rings are not undergoing rapid rotation in the solid state, and even at high temperatures (135 °C), they seem to remain coplanar. It is also apparent from Table 1 that the half-widths of the aromatic carbon atoms are larger than those of other aliphatic carbon atoms. This difference is believed to originate from inhomogeneities in the molecular motion. These carbon atoms have therefore less mobility than the other carbon atoms. In addition to the ¹³C signals of the aromatic carbon atoms in the backbone, the first carbon atom of the side chain linked to the phenylene unit is also very intense at 135 °C compared to the aliphatic resonance peaks of the rest of the side chain. This reflects that



Figure 11. Solvent-dependent UV-vis absorption spectra of poly(2,5-didecyl-*p*-phenyleneethynylene).

the rigid components include both the backbone and the beginning of the side chain.

In previous studies, a correlation between the chromic properties of several conjugated polymers and the rotational energy barrier between adjacent moieties (based on ab initio calculations performed on dimer model compounds) has been established.³³ For instance, polymers having nonplanar structures with an energy barrier against planarity smaller than 1.3 kcal mol⁻¹ (e.g., poly[1,4-(2,5-dioctyloxyphenylene)-2,5-thiophene] and poly[1,4-(2,5-dioctylphenylene)-2,5-furan]) have revealed interesting chromic effects. On the other hand, coplanar polymers with rotational barrier close to zero (e.g., poly[1,4-(2,5-dioctyloxyphenylene)-2,5-furan) can maintain a highly conjugated conformation (coplanar or nearly coplanar), even at high temperatures, resulting in the absence of significant chromic effects. According to these results, PPEs, which are predicted to be coplanar with a very weak barrier to rotation, should not show any significant thermochromic and solvatochromic effect (or only small bandwidth changes without any significant spectral shift). Moreover, on the basis of their respective conformational analyses, dialkoxysubstituted and dialkyl-substituted PPEs should show similar chromic behaviors. However, UV-vis spectra reported above clearly show that the optical properties of dialkyl-PPEs are much affected by the presence of a bad solvent or by changing the temperature of the thin film whereas dialkoxy-substituted PPEs are not.²³ An important feature for the determination of the structural changes happening during the chromic transition is the presence of a second absorption band at 428 nm in the UV-vis absorption spectra, which appears simultaneously by addition of a nonsolvent in solution or in the solid state at room temperature. This band is included in the envelope of conformations of the main band centered at 386 nm. To determine whether this band represents the most planar conformation of the poly(2,5-di-2'-ethylhexyl-p-phenyleneethynylene), we decided to synthesize another dialkylated PPE with a different kind of substituent, the poly(2,5-di-decyl-pphenyleneethynylene). The substitution by n-decyl side chains, which are linear compared to the previous PPE with ethylhexyl side chains, should provide a better stacking of the polymer chains between themselves. The absorption spectra of this new dialkylpolyphenyleneethynylene shows the same kind of pattern as the former poly(2,5-di-2'-ethylhexyl-p-phenyleneethynylene): a large band centered near 395 nm in solution (100% chloroform) and a new band appearing at 439 nm upon the addition of a nonsolvent (Figure 11). This band at 439 nm does not belong anymore to the large envelope

of all the conformations observed in solution and seems to be related to another structure of the polymer which has its proper UV-vis signature. These results support our previous conclusions about the nature of the conformational change happening during the chromic transition. Therefore, one explanation for these chromic effects could involve interchain interactions giving rise to an excitonic effect.³⁴ Thus, the band located around 428 nm for poly(2,5-di-2'-ethylhexyl-p-phenyleneethynylene) would involve head-to-tail molecular arrangements (J-aggregates). Similar arguments were previously raised by Lieser et al. on the basis of their electron microscopy experiments.²¹ These explanations are also supported by recent results on PPEs showing a strong dependence of the UV-vis absorption features at room temperature with the bulkiness of the side chains and interchain distances.³⁵ Finally, it is worth noting again that poly(fluorenyleneethynylene)s²⁴ and poly(2,5-thienyleneethynylene)s²⁵ do show some thermochromic and solvatochromic transitions whereas poly(3,6-carbazoleneethynylene)s²⁶ and poly(2,7-carbazoleneethynylene)s²⁷ do not. On the basis of their conformational analyses, it is difficult to explain these different behaviors, and one possible explanation could be related to different interchain interactions in these polymeric systems.

Conclusion

The thermochromic transition of poly(2,5-di-2'-ethylhexyl-p-phenyleneethynylene) has been studied by using a combination of complementary techniques. From UVvis, X-ray, and calorimetric measurements, a structural change from an ordered to a disordered state of the polymer has been observed. In sharp contrast to thermochromic polythiophenes, temperature-dependent vibrational spectra (FTIR and Raman) did not show any significant spectral shift. Moreover, solid-state NMR spectra did not reveal any important modification of the peaks related to the conjugated backbone upon heating. These results strongly suggest that the chromic effects observed cannot be associated with important conformational changes of the polymer backbone. It is therefore believed that the chromic effects are mainly governed by variable intermolecular interactions between polymer chains. This assumption is in agreement with calculations performed on model compounds.

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References and Notes

- Skotheim, T. A.; Elsenbaumer, R. L.; Reynolds, J. R. Handbook of Conducting Polymers, 2nd ed.; Marcel Dekker: New York, 1998.
- (2) Shirakawa, H.; Louis, E. J.; MacDiarmid, A. G.; Chiang, C. K.; Heeger, A. J. J. Chem. Soc., Chem. Commun. 1977, 578.
- (3) Leclerc, M.; Faïd, K. Adv. Mater. 1997, 9, 1087.
 (4) (a) Leclerc, M. J. Polym. Sci., Chem. Ed. 2001, 39, 2867. (b)
- (a) Leclerc, M.; Ho, H.-A. Synlett 2004, 380. (c) Morin, J.-F.; Leclerc, M.; Adès, D.; Siove, A. Macromol. Rapid Commun. 2005, 26, 761.
- (5) Cornil, J.; Beljoune, D.; Calbert, J.-P.; Brédas, J.-L. Adv. Mater. 2001, 13, 1053.
- (6) Leclerc, M. Adv. Mater. 1999, 11, 1491.
- (7) McQuade, D. T.; Pullen, A. E.; Swager, T. M. Chem. Rev. 2000, 100, 2537.

- (8) Wenz, G.; Muller, M. A.; Schmidt, M.; Wegner, G. Macromolecules 1984, 17, 837.
- (9) Garreau, S.; Leclerc, M.; Errien, N.; Louarn, G. Macromolecules 2003, 36, 692.
- (10) Halkyard, C. E.; Rampey, M. E.; Kloppenburg, L.; Studer-Martinez, S. L.; Bunz, U. H. F. Macromolecules 1998, 31, 8655.
- (11) Rughooputh, S. D. D. V.; Hotta, S.; Heeger, A. J.; Wudl, F. J. Polym. Sci., Polym. Phys. **1987**, 25, 1071.
- (12) Politis, J. K.; Somoza, F. B.; Kampf, J. W.; Curtis, M. D.; Gonzalez Ronda, L.; Martin, D. C. Chem. Mater. 1999, 11, 2274.
- (13) Apperloo, J. J.; Janssen, R. A. J.; Malenfant, P.R. L.; Fréchet, J. M. J. Macromolecules **2000**, *33*, 7038.
- (14) (a) Ofer, D.; Swager, T. M.; Wrighton, M. S. Chem. Mater. 1995, 7, 418. (b) Zhou, Q.; Swager, T. M. J. Am. Chem. Soc. 1995, 117, 12593. (c) Mangel, T.; Eberhardt, A.; Scherf, U.; Bunz, U. H. F.; Mullen, K. Macromol. Rapid Commun. 1995, 16, 571.
- (15) Cotts, P. M.; Swager, T. M.; Zhou, Q. Macromolecules 1996, 29, 7323.
- (16) Moroni, M.; Le Moigne, J.; Pham, T. A.; Bigot, J.-Y. Macromolecules 1997, 30, 1964.
- (17) Kim, J.; Swager, T. M. Nature (London) 2001, 411, 1030.
- (18) Erdogan, B.; Wilson, J. N.; Bunz, U. H. F. *Macromolecules* 2002, *35*, 7863.
- (19) Wilson, J. N.; Wang, Y.; Lavigne, J. J.; Bunz, U. H. F. Chem. Commun. 2003, 1626.
- (20) Bunz, U. H. F. Acc. Chem. Res. 2001, 34, 998.
- (21) Bunz, U. H. F.; Enkelman, V.; Kloppenburg, L.; Jones, D.; Shimizu, K. D.; Claridge, J. B.; Loye, H.-C.; Lieser, G. Chem. Mater. 1999, 11, 1416.
- (22) (a) Miteva, T.; Palmer, L.; Kloppenburg, L.; Neher, D.; Bunz, U. H. F. *Macromolecules* **2000**, *33*, 652. (b) Fiesel, R.; Halkyard, C. E.; Rampey, M. E.; Kloppenburg, L.; Studer-Martinez, S. L.; Scherf, U.; Bunz, U. H. F. *Macromol. Rapid Commun.* **1999**, *20*, 107.
- (23) Fiesel, R.; Scherf, U. Macromol. Rapid Commun. 1998, 19, 427.
- (24) Pschirer, N. G.; Bunz, U. H. F. Macromolecules 2000, 33, 3961.
- (25) Zhang, W.; Moore, J. S. Macromolecules 2004, 37, 3973.
- (26) Brizius, G.; Kroth, S.; Bunz, U. H. F. Macromolecules 2002, 35, 5317.
- (27) Bouchard, J.; Belletête, M.; Durocher, G.; Leclerc, M. Macromolecules 2003, 36, 4624.
 (28) Huang, W. Y.; Gao, W.; Kwei, T. K.; Okamoto, Y. Macromol-
- (28) Huang, W. Y.; Gao, W.; Kwei, T. K.; Okamoto, Y. Macromolecules 2001, 34, 1570.
- (29) Lère-Porte, J. P.; Moreau, J. J. E.; Serain-Spinau, F.; Wakim, S. Chem. Commun. 2002, 3020.
- (30) Frisch, M J.; Trucks, G. W.; Schlegel, H B.; Scuseria, G. E; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, Jr., T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, B.; Rega, G. N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 2003.
- (31) Lagaron, J. M.; Powell, A. K.; Davidson, N. S. *Macromolecules* 2000, 33, 1030.
- (32) Materny, A.; Chen, T.; Vierheilig, A.; Kiefer, W. J. Raman Spectrosc. 2001, 32, 425.
- (33) Leclerc, M.; Dufresne, G.; Blondin, P.; Bouchard, J.; Belletête, M.; Durocher, G. Synth. Met. 2001, 119, 45.
- (34) Kasha, M. Radiat. Res. 1963, 20, 55.
- (35) (a) McQuade, D. T.; Kim, J.; Swager, T. M. J. Am. Chem. Soc. 2000, 122, 5885. (b) Breitenkamp, R. B.; Tew, G. N. Macromolecules 2004, 37, 1163.

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